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Mineral Cycling in Southeastern Ecosystems

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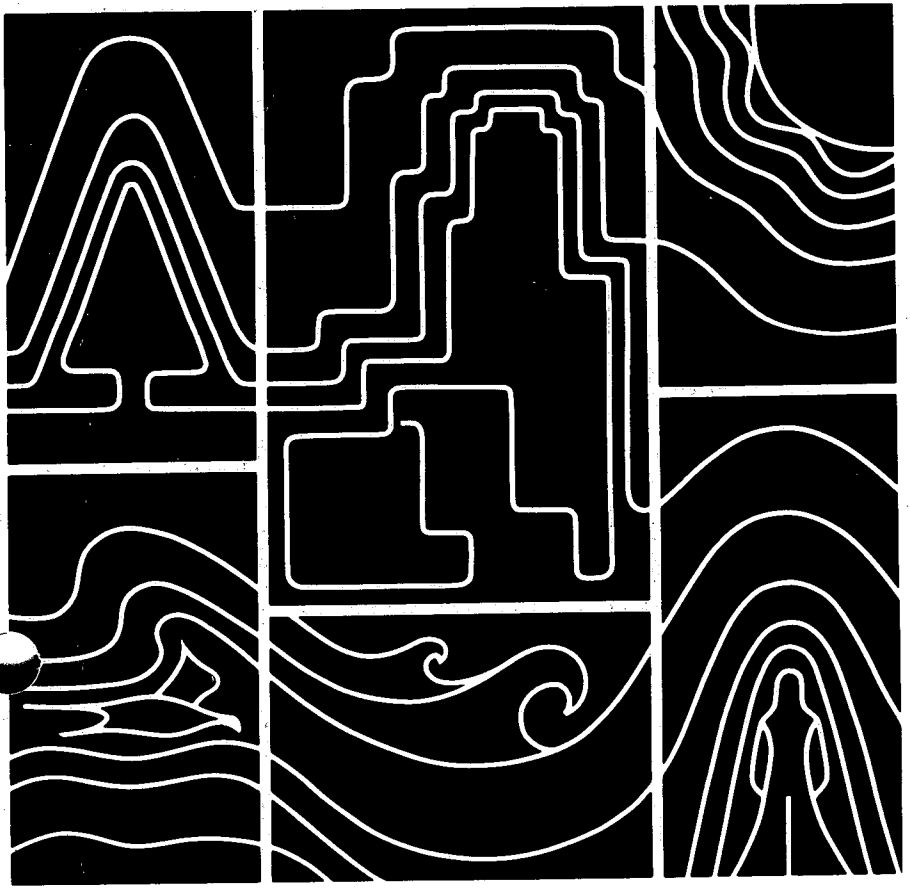

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FOREWORD

It was said of Caesar by, I believe, Mark Anthony, "We come here not to praise Caesar but to bury Caesar." My introductory comment is of two parts. I come here not to bury ecologists but to praise them, but, on the other hand, I do want to throw some dirt in their eyes to get their attention, so that future generations will honor them for their as yet undone deeds.

The title of this talk was slated to be "Energy, the Environment, and Environmentalists," but instead let us call it "Clean Energy, Ecologists, and Environmentalists," which could be equivalent to "Orderly Change vs. Emotionalism." I suspect that some may interpret this to mean that environmentalists are bad guys and ecologists good guys, but I do not believe that. Both have their time and place for action or for quiet contemplation. No one can control or dictate when or where the factions should or will meet. Their very existence leads to what I call creative tension, which must exist in a democracy where we continually justify our actions to others. We must have energy at some environmental cost, but, if the cost becomes too high in the view of some people, we debate and tension mounts. It is about these matters—energy, the environment, and environmentalists and the national research and development effort—and policy issues they affect that I want to talk. I will take the National Environmental Policy Act (NEPA) as a point of departure.

I believe history will record that the major piece of new legislation enacted in this decade—if not this generation—was the National Environmental Policy Act, passed in the closing days of 1969 and signed into law on Jan. 1, 1970. As legislation goes, this was a sleeper. At first it seemed to be a pussy cat, but it turned out to be a roaring lion. Section 102, which requires that a statement of environmental impact be presented for each federal action of any importance (and one basis for judging importance is

the degree of public interest), has become a vehicle by which concerned citizens can force the examination of all proposed actions. Environment has come to mean not only the living and physical environment but the fiscal environment as well, for the cost–benefit issue is a major summary statement of all factors. Through suits in the federal courts, the intervenors and their lawyers have been able to force compliance with NEPA, and by these actions powerful agencies once above citizen interventi[on] have been brought to heel. A ruling that I personally consid[er] landmark decision was that on Calvert Cliffs, which directed the Atomic Energy Commission to take into account all possible environmental impacts—simple certification by another agency was not judged adequate.

Since that decision, the environmental lawyers and the intervening environmentalists themselves have become sophisticated, knowledgeable, articulate, and believable. The court decisions have rolled in the direction of establishing a body of law by precedent actions favoring the preservation, protection, and enhancement of the environment. Notice that I say, "in the direction of." My own feeling is that until the courts have ruled consistently for at least a decade, and perhaps a generation, the environmental ethic will not be firmly enough established to withstand the withering fire it will encounter from time to time. What more suggestive proof does one need than the watering down of NEPA on the Alaska pipeline issue or the discussions of abridging NEPA and the Clean Air and Water Acts because of the Arab oil embargoes and the energy crisis. These attitudes arise in even the strongest congressional supporters of NEPA.

Thus, while we have made real progress in protecting our environment over the past three years, I think the battle lines are only now beginning to be drawn. We have won no major wars although for a while the enemy, bad technology, was retreating.

We must dare to ask the big question: Did the brinksmanship of our environmentalist friends get us here, or was it somethi[ng] else? We would probably all agree that the environmentalis[ts] helped, but we must also consider how often we legitimate working ecologists have got our emotions up when our facts were not adequate. If I am a bird watcher I use the defense that, if my bird is killed, the insects will take over. If I want to protect an endangered species, especially a predator, I cry out "But they protect the game by killing worthless species." My question is, Now we are pushing our environmental credibility, but what have

we been doing while our emotional environmentalist friends have been intervening?

Have we just been doing our own little thing in isolation—we who know that everything is interrelated? Let us go back to the impact statement and the information needed for decisions. Any of you who has been to the drawing board, i.e., the writing of an impact statement, realizes how limited the actual information really is. You know "intuitively" that something is awry, but intuition will not stand up in a court of law; facts are needed. In the case of the three AEC laboratories involved with the regulatory arm in writing impact statements, I have noted a marked change in the nature of the research they want supported. It is more focused, just as basic, but related to the real world. We have not used coercion to achieve this effect; I must believe it is a response to a perceived need for the scientific information required to ensure that the important ecological issues affected by changing situations are not short shrifted as we move toward self-sufficiency in energy.

The real question then is, Have we been using the resources available to us in the most effective way, or have we been singing the "environmental chant," which is supposed to automatically provide us money to do our thing, and not addressing important issues?

I am prepared to argue either side of this issue, but I believe there is at least a small amount of emotionalism in each of us which may prevent us from taking full advantage of the opportunities afforded us. I think we all agree that we need well-planned and well-designed experiments in which we contaminate a specific landscape only by deliberate choice. I would not agree that we should join our environmentalist friends to fight to the death every "progressive step," such as road building, cooling pond creation, strip mining, and brush spraying. I would argue that it is not inconceivable that these things may offer positive opportunities and we should seriously consider availing ourselves of them.

During the course of budget hearings, when the AEC Controller and I reach an impasse, he often says "Well, Jim, let me make you an offer you cannot refuse. Either accept this cut graciously or contest it mightily and get back only one-half of what you want." I do not think this kind of thinking is far removed from our taking appropriate advantage of events like the dumping of heat in a river or a swamp, placing a fossil-fuel plant

facility in a less than environmentally optimal place, or strip mining land without complete reclamation. I will argue until proven wrong that, if we would come down from our ivory towers and propose research in situations where the available facts will not support a hard line against the action, we can make far more progress toward being able to guide the development of technologies. Why? Because we become members of the team and not hard-shelled unreasonable protagonists. The point would seem to be evolution, not revolution.

Every activity having minimal impact on the environment should become a candidate for experiment. Obviously such a view must be constrained and considered, but let us not run from opportunity. It may be that taking advantage of situations will put us in the unique position of being heard and of being able to help guide technology.

My whole point is that, if we are to preserve the ground we have gained, we as ecologists must get the information needed so that the impact analysis can move from conjecture to decisions based on fact. Furthermore, we must work closely with developing technologies to make them safe to begin with rather than repairing the damage after the fact. If we do not, the environment will deteriorate at an ever increasing rate in the face of pressing demands for heat in winter, cool in summer, and a tank of gasoline. We have little time. Will we use it wisely, or will we argue?

I challenge you to consider the country's need for information and guidance and to get on with satisfying it at the same time you are "doing your own thing."

James L. Liverman
Director
Division of Biomedical and Environmental Research
U. S. Atomic Energy Commission

PREFACE

The need to understand the cycling of materials within ecosystems has been given special emphasis in recent years. Many of the basic problems associated with life in an industrialized society have become acute because of the ever-increasing human population. We are now faced with living in close association with our effluents and with other secondary products that are both intentionally and unintentionally released into the environment. Some of these substances, e.g., certain heavy metals or radioisotopes, can concentrate in the environment and become health hazards. In addition, their availability to the biota can vary regionally.

These considerations set the stage for the symposium "Mineral Cycling in Southeastern Ecosystems," which was held in Augusta, Georgia, May 1-3, 1974, under the sponsorship of the Savannah River Ecology Laboratory, the University of Georgia Institute of Ecology, and the U. S. Atomic Energy Commission. More than 300 scientists gathered to discuss cycling of natural and man-made elements. Papers presented during the three-day meeting covered mineral cycling in terrestrial, freshwater, and marine environments, as well as current ideas on modeling. A plenary session examined present knowledge of the principles governing elemental flow, and contributed-paper sessions described recent advances in mineral-cycling research. A panel discussion was devoted to radiocesium in natural environments, especially those in the southeastern United States. Not all this material is included in this volume.

The included papers reflect in many ways the "state of the art" in mineral-cycling research. Complete studies of elemental cycling frequently attempt to quantify the transfer of elements among all ecosystem compartments, but comprehensive studies of this kind are rare, perhaps nonexistent. This is undoubtedly true

in cases where turn-over times are immense. Thus most of the studies in this volume primarily document and compare elemental concentrations in various ecosystem compartments. This type of work represents only a beginning for this important discipline. Most of the papers focused on verification of techniques, documentation of data with statistically determined confidence intervals, interpretation of results, and synthesis leading to the development of concepts for this area of ecology. For this reason, although the symposium emphasized the southeastern United States as a geographic region, papers from other areas were accepted.

Ecology has flourished in the southeastern United States, and the rapid growth of interest in elemental cycling is a testimony to the efforts of many people in this region. This volume is a direct result of their efforts and should serve to stimulate and focus future research. As the field continues to expand, more emphasis should be placed on the synthesis of ideas on an intra- and interregional scale. We hope similar meetings can be held in the future.

Fred G. Howell
John B. Gentry
Michael H. Smith
Editors

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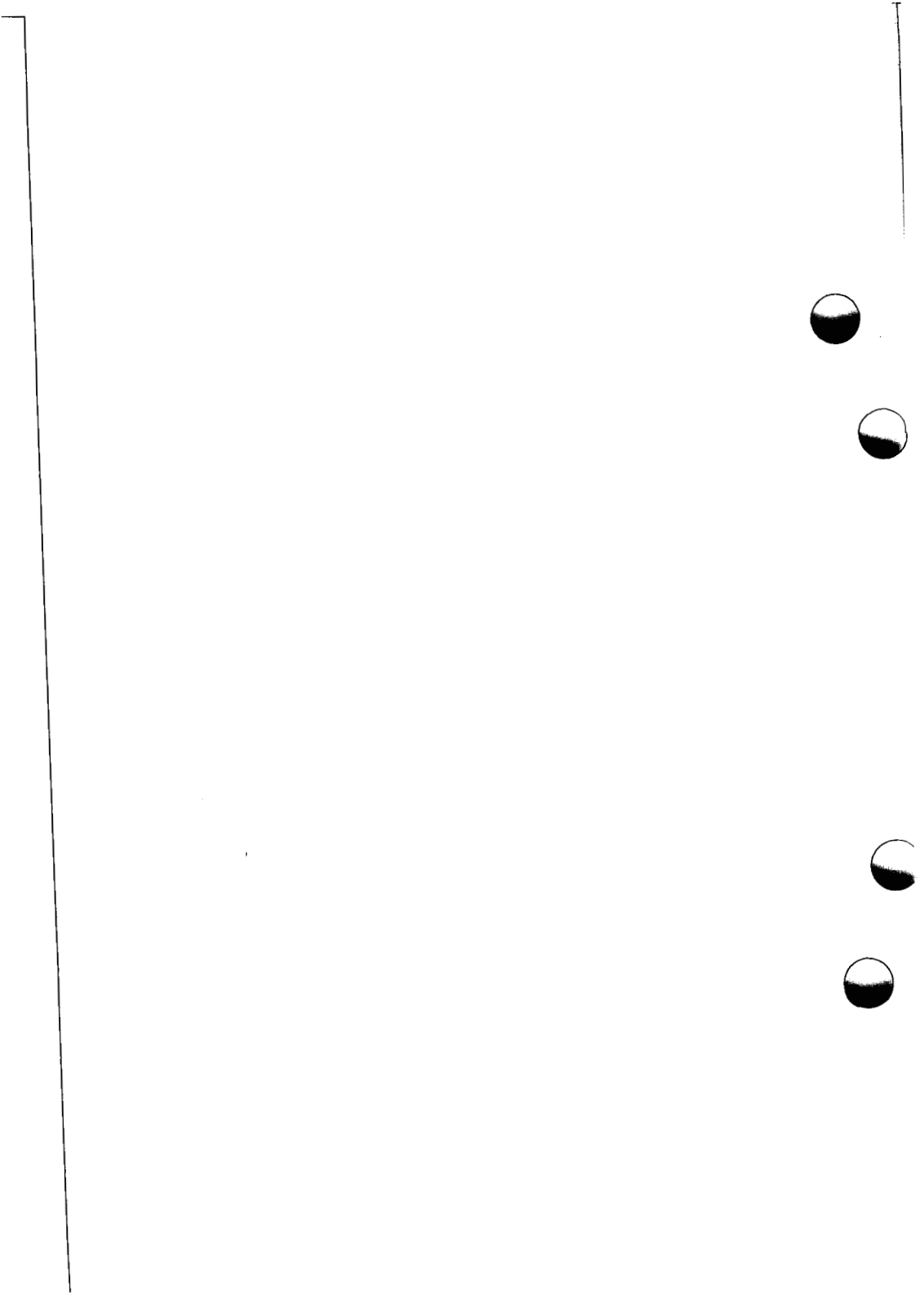

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NUTRIENT RECYCLING AND THE STABILITY OF ECOSYSTEMS

JACKSON R. WEBSTER, JACK B. WAIDE, and BERNARD C. PATTEN
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ABSTRACT

A theoretical perspective on ecosystems is elaborated which relates alternative strategies of stability to observable and measurable attributes of ecosystems. Arguments are presented for viewing nutrient cycling as positive feedback. Any resultant tendency for unlimited growth is resisted by (1) finiteness of resources, (2) kinetic limitations on resource mobilization, and (3) processes of nutrient regeneration. Ecosystem structure, a static inertia defined by the mass of biotic and abiotic components, is opposed by dynamic dissipative forces related to metabolism and erosion. Balance between these two factors (structural mass and dissipative force) guarantees the asymptotic stability of ecosystems. Attention is thus focused on two aspects of relative stability: resistance and resilience. Resistance, the ability of an ecosystem to resist displacement, results from the accumulated structure of the ecosystem. Resilience, the ability of an ecosystem to return to a reference state once displaced, reflects dissipative forces inherent in the ecosystem. A linear ecosystem model that embodies these concepts is discussed, and four relative stability indexes are derived. Random matrices, subject to mass-conservation limitations, and hypothetical ecosystem models, constructed according to a characterization of alternative properties of nutrient cycles, are analyzed to examine relationships between the relative stability indexes and specific properties of nutrient cycles.

Resistance is shown to be related to large storage, long turnover times, and large amounts of recycling. Resilience reflects rapid turnover and recycling rates. Thus resistance and resilience are inverse concepts. Factors that determine what balance between resistance and resilience an ecosystem exhibits are considered, including the degree and frequency of environmental fluctuation and the limitations placed on resource mobilization. The contribution of turnover rates of ecosystem components to the balance between resistance and resilience is also examined, involving consideration of (1) the population concepts of r and K selection, (2) the contribution of early successional species to ecosystem stability, and (3) the relation of herbivory to nutrient regeneration. The theory put forth in this paper is seen as a rigorous, operational approach to ecosystems which is testable by both observation and experimental analysis.

A dialectical point of departure for studying ecosystems is provided by the antithetical processes of biological growth and decay. At the cellular level, balance between the opposing forces of anabolism and catabolism determines both structure and reaction kinetics. Anabolic and catabolic phenomena similarly operate at the ecosystem level but are less well understood. On the one hand are the mobilization of energy and nutrient resources into organic configurations and the accretion of biomass; on the other are dissipative forces tending to erode whatever biotic structures have been realized, returning the system toward physicochemical equilibrium while regenerating assim[illegible] nutrients.

Morowitz (1966) postulated that energy dissipation is sufficient to cause associated material cycles. Such a postulate is fundamental since in the materially closed biosphere, maintenance of life requires nutrient regeneration. For most natural ecosystems, recycling rates limit primary production and so regulate, at the source, biotic energy flows. A positive-feedback loop is thus inherent in the structure of every ecosystem: energy flow produces nutrient cycles, which lead to greater energy flow. Any tendency for unlimited growth is resisted by (1) finiteness of the resource base, (2) kinetic requirements of resource mobilization, and (3) restorative processes of nutrient regeneration.

Thus biotic growth tendencies are bounded by resource availability as well as by limitations on resource assimilation. The dialectical viewpoint outlined above must account for these facts. The biotic structure of ecosystems results from the tendency of living organisms to acquire resources, as limited by the requirements of resource mobilization. Acting to erode structure are dissipative forces that tend to degrade both organic and inorganic configurations. Degradation of biotic structure is related to metabolic processes of living organisms. Decay of abiotic structure relates both to the biotic decomposition of minerals and to the purely abiotic processes of weathering and erosion. Hence, on the one hand is the structure of the ecosystem, a static inertia defined by the mass of biotic and abiotic components. On the other hand is the dissipative force tending to erode this structure, a dynamic force defined by metabolism and erosion. At the ecosystem level these two factors (structural mass and dissipative force) are not necessarily antithetical. Both contribute, in different ways, to the stability of ecosystems.

A recurrent theme in ecological literature is that ecosystem stability is related to nutrient-cycling characteristics. E. P. Odum (1969) suggested that the closing of nutrient cycles through ecosystem development contributes to increased stability. Pomeroy (1970) related the stability of several ecosystem types to elemental standing crops and turnover times, biomass, and productivity. Jordan, Kline, and Sasscer (1972) examined ecosystem stability in relation to models of forest nutrient cycles. Hutchinson (1948a, 1948b), H. T. Odum (1971), Child and Shugart (1972), and Waide et al. (1974) also suggested causal links between nutrient cycling and ecosystem stability. These arguments were

largely intuitive or heuristic, however, and did not seek the basis for causal relationships in specific properties of ecosystem nutrient cycles. In this paper we investigate relations between observable characteristics of nutrient cycles and system-level concepts of stability.

STABILITY CONCEPTS AND DEFINITIONS

Absolute Stability

Liapunov (1892) provided the basis of stability theory. Let $x(t)$ be a vector of n time-dependent state variables, with $\| x(t) \|$ a norm such as

$$\| x(t) \| = \sum_{i=1}^{n} |x_i(t)| \qquad (i = 1, 2, \ldots, n)$$

An equilibrium state x^0 ($\dot{x} = 0$ when $x = x^0$) is said to be stable in the sense of Liapunov if for every initial time t_0 and every $\epsilon > 0$ there exists $\delta > 0$ such that, if $\| x(t_0) - x^0 \| < \delta$, then $\| x(t) - x^0 \| < \epsilon$ for all $t > t_0$. In other words, a system is stable if, following displacement from equilibrium, its subsequent behavior is restricted to a bounded region of state space. A stronger stability concept involves return to equilibrium following initial displacement. An equilibrium state x^0 is said to be asymptotically stable (1) if it is stable in the sense of Liapunov and (2) if for any t_0 there exists $\alpha > 0$ such that, if $\| x(t_0) - x^0 \| < \alpha$, then $x(t) \to x^0$ as $t \to \infty$.

Holling (1973) suggested that such classical stability concepts are little more than theoretical curiosities in ecology. We suggest instead that natural ecosystems are asymptotically stable (Child and Shugart, 1972; Waide et al., 1974; Patten, 1974; Waide and Webster, 1975). A dynamic balance between the maintenance and dissipation of structure produces nonzero ecosystem states that are stable. Around this nominal (unperturbed, reference) trajectory exist basins or domains of attraction (Lewontin, 1970a; Holling, 1973) within which ecosystem displacements from nominal behavior are followed by return to the original condition. The relevant question for ecologists' attention is not "Are ecosystems stable?" but rather, "How stable?" Ecologists' concern should thus be focused on relative rather than absolute stability and on the mechanisms by which differing levels of relative stability are achieved.

Relative Stability

Attempts to measure the relative stability of ecosystems have met with limited success (e.g., MacArthur, 1955; Patten and Witkamp, 1967) because relative stability is not well defined mathematically or ecologically. Relative stability concerns the nature of an ecosystem's response to small displacement from a nominal trajectory. Two aspects of this response may be identified (Patten and Witkamp, 1967; Child and Shugart, 1972; Holling, 1973; Marks,

1974). The first aspect concerns the resistance of an ecosystem to displacement. An ecosystem that is easily displaced has low resistance, whereas one that is difficult to displace is highly resistant and is, in this sense, very stable. The second aspect of relative stability concerns return to the reference state, or resilience.* An ecosystem that returns to its original condition rapidly and directly following displacement is more resilient, more stable in this sense, than one that responds slowly or with oscillation.

Thus, given that an ecosystem is asymptotically stable, two aspects of its relative stability are (1) immovability, or resistance, which determines ext[illegible] displacement, and (2) recoverability, or resilience, which reflects rate of rec[illegible] to the original condition. This view of ecosystems identifies two alternatives for persistence. Resistance to displacement results from the formation and maintenance of large biotic and abiotic structures. Resilience following displacement reflects inherent tendencies for the dissipation of such structure, but, because i[illegible] is related to ecosystem metabolism, it also reflects rates with which structure is reformed following its destruction. In the closed biogeochemical cycles of the biosphere, the observable structural and functional attributes of ecosystems are determined by the realized balance between factors favoring resistance and resilience. Nutrient cycling, a fundamental process inherent in ecosystems, thereby becomes a central issue in the consideration of mechanisms of macroscopic relative stability.

NUTRIENT CYCLING AND FEEDBACK

The use of flow diagrams to represent conservative energy and material flows in ecosystems has partly confused the concepts of input, output, and feedback. Input is any exogenous signal† that impinges on a system. Output is any endogenous attribute of a system transmitted as signal flow to an observer. Output generation is exclusively the province of the system, while output selection is the prerogative of the observer. Often output is equated with th[illegible] state of the system, where state provides the necessary and sufficient information for a determinate mapping from input to output (Zadeh and Desoer, 1963).

Feedback exists in a system if any of its inputs are determined by its stat[illegible] the measure of state is directly related to such inputs, the feedback is positiv[illegible] the two are inversely related, the feedback is negative.

*Holling (1973) used *resilience* to denote what we term *resistance*, and *stability* for our *resilience*. Our use of resistance and resilience is consistent with common and accepted English usage (*Webster's New World Dictionary of the American Language*, Second College Edition, 1972, The World Publishing Company, New York).

†"Signal" denotes an observable and measurable flow of conserved (energy or matter) or unconserved (information) quantities.

A flow diagram of an ecosystem or ecosystem component (Fig. 1) shows inflow of material or energy which is processed by the system, resulting in outflow. Inflows and outflows are conserved. In a control diagram of this system (Fig. 1), output has been equated to state. Inflow and outflow both constitute possible inputs to the system and may be subject to feedback control. Inflow and outflow are still conserved, but no such conservation restriction applies to input and output.

It can be argued that, if feedback control of outflow exists in ecosystems, it be negative and therefore stabilizing. That is, ecosystem component losses regulated by density-dependent mechanisms. These losses of conserved

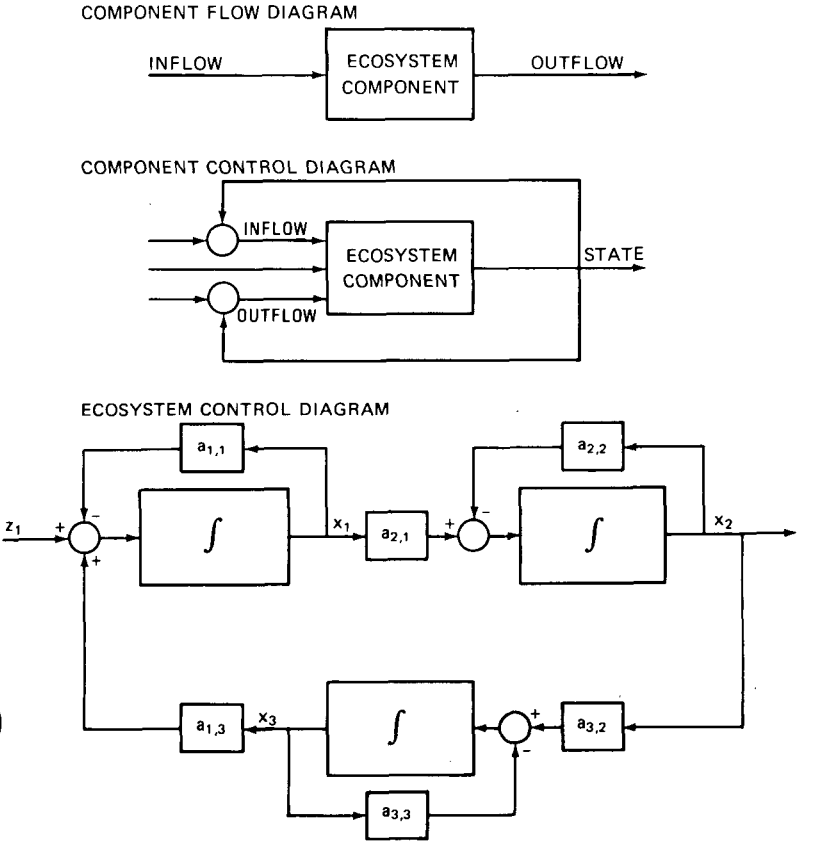

Fig. 1 Generalized flow diagram and control diagram of an ecosystem component and a control diagram of a three-component ecosystem model. Circles indicate summing junctions. Rectangles are storage (integrative) elements. z_i is an input; x_i is the state of the *i*th component; and $a_{i,j}$ is the rate coefficient for transfer from x_j to x_i.

quantities must be offset by inflows to maintain nonzero states. At the organism and population levels, positive-feedback mechanisms operate to promote inflow and are therefore potentially destabilizing (Milsum, 1968). Mobilization of resources is the essence of life processes (Smith, 1972); however, many density-dependent mechanisms exist which regulate inflow in a negative-feedback sense (Whittaker and Woodwell, 1972). Further, a macroscopic perspective leads to the conclusion that ecosystems and their components are ultimately resource limited (Hairston, Smith, and Slobodkin, 1960; Wiegert and Owen, 1971; Patten et al., 1974; Waide and Webster, 1975; Webster and W[illegible] 1975). Under unperturbed conditions ecosystems are maximally expa[illegible] within the resource hyperspace to the point of kinetic limitation of material transfers as set by the physicochemical environment (Blackburn, 1973). Thus inflow is limited by matter-recycling kinetics that ensure boundedness. Bounded inflow and negative-feedback control of outflow coupled with the first law of thermodynamics (mass conservation) form the basis of our argument for nonzero ecosystem states that are stable.

These ideas lead to a representation of ecosystems (Fig. 1) as sets of interacting components, each regulated by a negative-feedback loop related to its dissipative (i.e., turnover) character. Material recycling is displayed as feedback involving multiple system components. Because material flow is involved, recycling must be interpreted as positive feedback (H. T. Odum, 1971). This point emphasizes a fundamental difference between feedback in a control diagram and material recycling in a flow diagram. In the control diagram control is mediated by nonconservative information flows, whereas in the flow diagram control among components is exerted only through material or energy flows that must be conserved. Feedback mechanisms are not explicit in flow diagrams but must, nevertheless, be incorporated into any mathematical model of the system.

Thus a systems theoretic interpretation of nutrient cycling as feedback leads to the general conclusions already elaborated: (1) biotic tendency for unlimited growth is bounded by the first law of thermodynamics (mass conservation), a[illegible] mediated through material-recycling kinetics and (2) negative-feedback decay to abiotic physicochemical equilibrium, if material and energy inflows are removed, is assured by the dissipative character of ecosystems and the second law of thermodynamics. The first conclusion guarantees Liapunov stability. The t[illegible] conclusions together are sufficient to establish the stability of non[illegible] ecosystem trajectories (Patten, 1974).

MEASURES OF RELATIVE STABILITY

The General Linear Ecosystem Model

The dynamics of conserved quantities in an ecosystem with n components can be described mathematically as

$$\dot{x}_i = \text{inflow} - \text{outflow} \qquad (i = 1, 2, \ldots, n) \tag{1}$$

Inflow can emanate from outside the ecosystem (z_i) or from other system components ($F_{i,j}$, $j = 1, 2, \ldots, n; j \neq i$). Outflow may pass to other components ($F_{j,i}$) or out of the system ($F_{0,i}$). Hence Eq. 1 may be reformulated in compartmental form as

$$\dot{x}_i = (z_i + \sum_{\substack{j=1 \\ j\neq i}}^{n} F_{i,j}) - (F_{0,i} + \sum_{\substack{j=1 \\ j\neq i}}^{n} F_{j,i}) \qquad (i = 1, 2, \ldots, n) \tag{2}$$

Material transfers within the ecosystem represent inflows to some components and outflows from others. On the basis of the arguments given above and elsewhere (Patten et al., 1974; Webster and Waide, 1975), these internal flows, as well as outflows from the system, can be modeled as donor-based according to the equation

$$F_{i,j} = a_{i,j}x_j \tag{3}$$

If we define component turnover rates as

$$a_{i,i} = -\sum_{\substack{j=1 \\ j\neq i}}^{n} a_{j,i} - a_{0,i} \qquad (i = 1, 2, \ldots, n) \tag{4}$$

Eq. 2 becomes

$$\dot{x}_i = z_i + \sum_{j=1}^{n} a_{i,j}x_j \qquad (i = 1, 2, \ldots, n) \tag{5}$$

Because all x_i and $F_{i,j}$ represent material or energy, they must be nonnegative, which ensures that

$$a_{i,j} \geq 0 \qquad (i \neq j) \tag{6}$$

Equation 5 can be expressed in matrix form as

$$\dot{x} = Ax + z \tag{7}$$

where x is the state vector, z is the input vector, and A is a matrix of (possibly time dependent) rate coefficients defined by Eq. 3. The mathematical constraints defined in Eqs. 4 to 6 are sufficient to guarantee the asymptotic stability of this model (Hearon, 1953, 1963). In addition, the model is sufficient for simulating nominal and small displacement dynamics of ecosystems (e.g., Olson, 1963; Patten, 1972; Patten et al., 1974). Implicit within the model structure defined by Eqs. 1 to 7 are both accumulative and dissipative tendencies; thus this model is useful for examining macroscopic questions of ecosystem relative stability.

nth-Order Measures

The system defined by Eq. 7 is an *nth*-order system, being composed of n first-order equations. Relative stability indexes can be derived for this system. Specifically, the characteristic roots or eigenvalues of the system defined by Eq. 7, denoted λ_k ($k = 1, 2, \ldots, n$), can be found by solving the matrix equation

$$\det(\lambda I - A) = 0$$

where det denotes the determinant of the indicated matrix, and I is the n × n identity matrix. The solution to Eq. 7 can be expressed in terms of these characteristic roots, where each eigenvalue defines a particular mode of system behavior, as

$$x = \sum_{k=1}^{n} c_k b_k e^{\lambda_k t} + p \tag{9}$$

where c_k is a constant, b_k is the eigenvector associated with the eigenvalue λ_k, and p is a particular solution to Eq. 7 determined by z.

Clearly, if any $\lambda_k > 0$, the system will grow exponentially. According to a theorem attributed to Liapunov and Poincaré (Bellman, 1968), a system is asymptotically stable if all the characteristic roots have negative real parts.

Two relative stability measures may be derived from these n eigenvalues. The first is the critical root, defined as the characteristic root with the smallest absolute value (Funderlic and Heath, 1971). Given that the system is asymptotically stable, the critical root is the one most likely to become positive. Hence this index indicates the system's margin of stability. This critical root is the smallest turnover rate (the longest time constant) in the system. Thus the system does not recover fully from displacement until this slowest component of the transient response decays away. Second, the trace of the matrix A (the sum of the diagonal elements) relates to the response time following perturbation (Makridakis and Weintraub, 1971b). Since the sum of the main diagonal elements of A equals the sum of the eigenvalues, we have used the mean root, defined as the mean value of the n eigenvalues, as an equivalent measure of response time. The mean root reflects the time required for most of the system, or for some hypothetical mean component of the system, to recover following displacement.

Second-Order Measures

Extensive experience in control-systems engineering has demonstrated the utility of approximating higher order linear systems as second order for analytical purposes (DiStefano, Stubberud, and Williams, 1967; Shinners, 1972). Child and Shugart (1972) provided a rationale for implementing such an

approach in studying ecosystem behavior and applied it to an analysis of magnesium cycling in a tropical forest. Waide et al. (1974) used this approach in analyzing a model of calcium dynamics in a temperate forest. Hubbell (1973a, b) demonstrated the benefits of a frequency-domain analysis of second-order population models.

In this approach the behavior of an n*th*-order system of the form of Eq. 7 is approximated as second order with the equation

$$\ddot{y} + 2\zeta\omega_n\dot{y} + \omega_n{}^2 y = \omega_n{}^2 z \tag{10}$$

where ζ is the damping ratio and ω_n is the undamped natural frequency (DiStefano et al., 1967). The characteristic roots of this equation are given by

$$\lambda_1,\lambda_2 = -\zeta\omega_n \pm \omega_n (\zeta^2 - 1)^{1/2} \tag{11}$$

The roots of this second-order approximation represent the apparent roots of the original n*th*-order system. That is, these two eigenvalues, as well as the natural frequency, represent weighted mean roots of the higher order system. They capture most of the information contained in the n*th*-order trajectories. The weighting function that determines these second-order parameters from the n original eigenvalues is related to the magnitude of the eigenvector components of the n*th*-order system (Eq. 9).

From Eq. 11, if $\zeta = 1$, the system is said to be critically damped, the system responds rapidly and without oscillation following displacement, and λ_1, $\lambda_2 = -\omega_n$. If $\zeta > 1$, the system is overdamped, the response of the system is slower than that of a critically damped system, though still nonoscillatory, and the eigenvalues are real and unequal. If $\zeta < 1$, the system in underdamped, and the roots are complex and are given by

$$\lambda_1,\lambda_2 = -\zeta\omega_n \pm j\omega_n (1 - \zeta^2)^{1/2} \tag{12}$$

where $j = (-1)^{1/2}$. The response of such a system to displacement, though initially more rapid than a critically damped system, is oscillatory. If $\zeta = 0$, the roots are imaginary, and ω_n is the radian frequency of oscillation. If $\zeta < 0$, the eigenvalues have positive real parts, and the system is unstable.

Given that the system under study is asymptotically stable (i.e., $\zeta > 0$), the two parameters ω_n and ζ may be used as measures of relative stability. The natural frequency ω_n measures (inversely) the resistance of the system to displacement. A system with a large natural frequency is especially susceptible to disturbance, whereas a system with a small natural frequency strongly resists displacement. Similarly the magnitude of the damping ratio ζ indicates the rate of system response following displacement, the resilience of the system. If the system is overdamped, the return to steady state is monotonic but slow. If underdamped, the system responds in an oscillatory fashion. A critically damped

system exhibits the most rapid response possible without oscillation and thus has maximum resilience.

In this paper we investigate relationships between specific properties of ecosystem nutrient cycles and discuss the four above-mentioned relative stability indexes: critical root, mean root, natural frequency, and damping ratio. We take two approaches. The first is a stochastic approach, using Monte Carlo techniques. In the second approach we construct hypothetical ecosystem models based on a characterization of alternative properties of nutrient cycles and investigate the relative stability of these models. We also provide further ecological understanding of the four relative stability indexes and extend basis for their implementation. Attention is restricted to time-invariant systems for heuristic purposes.

STOCHASTIC APPROACH

Construction and analysis of random matrices was used successfully to further understanding of general system properties and to investigate effects of specific system characteristics (e.g., connectivity) on such system-level properties as stability (Ashby, 1952; Gardner and Ashby, 1970; Makridakis and Weintraub, 1971a, b; May, 1972, 1973; Makridakis and Faucheux, 1973; Waide and Webster, 1975; Webster and Waide, 1975). We initially followed such an approach to establish general relationships among relative stability indexes and system properties, focusing especially on the amount of recycling.

Methods

In constructing random matrices, off-diagonal elements $a_{i,j}$, $i \neq j$, of the A matrix (Eq. 7) were chosen from a specified statistical distribution (e.g., uniform on [0,1]). Rates of nutrient loss to the environment ($a_{0,i}$) were chosen from the same distribution and main diagonal elements calculated according to Eq. 4. For some analyses, off-diagonal elements were defined as nonzero according to a specified probability of connectivity. Only a single input z_1 was used for all analyses.

Following matrix construction, eigenvalues were calculated (Westley and Watts, 1970), and the critical root and mean root were determined. We calculated an index of recycling (I) as the summed flows represented by upper triangle divided by the input. That is, the ratio of nutrients recycled to nutrient input from the environment is

$$I = \frac{\left(\sum_{i=1}^{n-1} \sum_{j=i+1}^{n} F_{i,j} \right)}{z_1} \tag{13}$$

The synthetic division algorithm of Ba Hli (1971) was used to estimate the values of the natural frequency and damping ratio. A unit step input was applied

to each randomly constructed matrix to generate the required discrete input–output time series. Synthetic division yielded the coefficients of a general second-order transfer function, which were equated with coefficients of the specific transfer function of Eq. 10, allowing estimation of the natural frequency and damping ratio (Hill, 1973).

The above process was repeated 50 or 100 times for each type of matrix constructed. The resulting sets of values were subjected to linear regression analysis to determine the presence of significant relationships among calculated variables. To ensure that results were not biased by methods of matrix construction, we analyzed a variety of matrices of three sizes (n = 4, 6, 10). In various experiments, matrix elements were sampled from uniform distributions of different ranges and from normal distributions with various means and variances. We tried a wide range of upper and lower triangle connectivity, and selected several different outputs for use in the synthetic division. In some cases modifications were made to obtain a pyramid-type structure of compartmental standing crops. We also examined results of increased input and recycling.

Results

The following trends were generally observed across the range of matrices analyzed. Increases in the amount of recycling relative to input led to increases in the critical root (moved closer to zero), decreases in the mean root (moved farther from zero), and decreases in the natural frequency. Also, larger critical and mean roots were both associated with smaller natural frequencies.

Trends in the damping ratio initially appeared to be variable. In some cases ζ tended to decrease with increasing recycling, critical root, and mean root. In other cases ζ showed the opposite behavior. Closer inspection revealed that, in the first case, all systems were underdamped, whereas in the second case they were overdamped. Thus, when the quantity $|1 - \zeta|$ was considered, the results were unambiguous: $|1 - \zeta|$ increased with increasing values of recycling, critical root, and mean root.

DETERMINISTIC APPROACH

Our second approach to investigating relationships between material recycling and ecosystem stability involved construction and analysis of hypothetical ecosystem models. Two basic assumptions are inherent in these analyses: (1) ecosystems are units of selection and evolve from systems of lower selective value to ones of higher selective value (we are not invoking any superorganism concept; this evolution is accomplished through species coevolution) (Slobodkin, 1964; Darnell, 1970; Lewontin, 1970; Dunbar, 1972; Whittaker and Woodwell, 1972; Blackburn, 1973); (2) those ecosystems with highest selective value are ones which optimize utilization of essential resources. Exceptions to the

selection for ecosystems geared to efficient resource utilization would exist where resources were extremely abundant or where the system as a whole was operating under other environmental stress (Odum, 1967; Waide et al., 1974). An example might be a stream which receives large allochthonous inputs of detritus and which is strongly influenced by current action. In other ecosystems selective value involves efficient conservation and recycling of essential nutrients.

We suggest that three factors are involved in nutrient utilization in ecosystems: (1) the presence or absence of large abiotic nutrient reserves, (2) the degree of localization of nutrients within the biota, and (3) the turnover rate of the actively recycling pool of nutrients. Figure 2 schematically depicts these factors. In this figure a specific ecosystem type is associated with a given combination of factors. This conceptual scheme is clearly idealized since there exists a great range of each of these distinct types of ecosystems. However, this scheme is consistent with current ecological theory and represents a convenient method of examining relationships between nutrient cycling and stability.

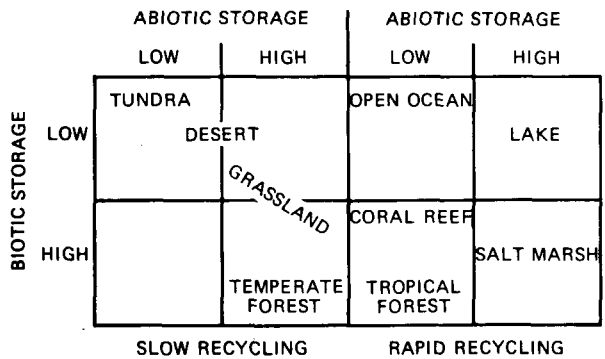

Fig. 2 Alternative properties of nutrient cycles. Shown in each box is an idealized ecosystem type that seems to exhibit the indicated combination of properties.

Methods

To facilitate quantitative comparisons among these various idealized ecosystems, we constructed a general model of nutrient cycling (Fig. 3). In this diagram the food base (x_1) may be either primary producers or detritus. Consumers (x_2) are organisms that feed directly on the food source. The $F_{3,1}$ is either death or mechanical breakdown of the food base to detritus (x_3). In an ecosystem with internal primary production, detritus is essentially dead primary producers (litter). In detritus-based systems this component is fine particulate

organic matter. Decomposers (x_4) are those organisms which feed directly or indirectly on detritus. Available nutrients (x_5) are directly available for use in primary production. Nutrients in reserve (x_6) are not available but are tied up in sediments, primary minerals, clay complexes, or other refractory materials (e.g., humics). However, they may become available through transfer to x_5. Inflows and outflows occur primarily through the available nutrient pool.

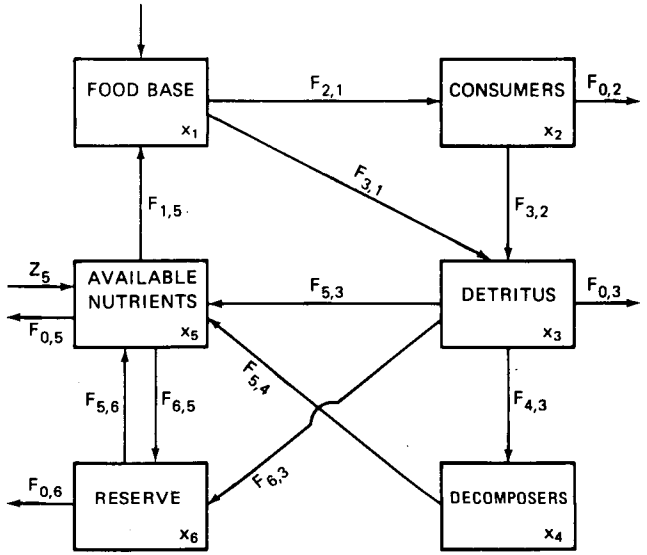

Fig. 3 General nutrient-flow model of an ecosystem. x_i is the size of the *i*th compartment; z_i is inflow to compartment x_i; $F_{i,j}$ is the flow from x_j to x_i; and $F_{o,j}$ is the outflow to the environment from x_j.

We have quantified this general model for seven of the ecosystem types shown in Fig. 2 (Table 1). We also applied this model to an idealized stream, which typifies an ecosystem without large abiotic reserves, with low biotic localization of nutrients, with little or no recycling, and with large nutrient throughflows. Standing-crop values were normalized to an available nutrient pool of 100 units. All transfers were per year. The values given in Table 1 are relative estimates that reflect differences among the idealized ecosystems, rather than exact, absolute estimates of nutrient transfers and standing crops. A variety of sources was consulted for each ecosystem type (Table 1). However, gaps and inconsistencies existed which were filled from general references or qualitative considerations. Each system was assumed to be at steady state.

From these numbers we derived several indexes which reflect structural characteristics of the eight ecosystems and which quantify the concepts of abiotic storage, biotic storage, and recycling (Table 2). Both the turnover time of the reserve ($T_6 = 1/|a_{6,6}|$) and the proportion of nutrients localized in the two abiotic pools $[(x_5 + x_6)/\Sigma x]$ are indexes of abiotic storage. Reserve turnover varies from slow in forests to fast in oceans and streams. The proportion of total nutrients in abiotic compartments is highest in temperate forests and lakes and lowest in tundra.

Biotic storage, given by the turnover time of biotic compartments $[(x_1 + x_2 + x_3 + x_4)/F_{1,5}]$, is higher in terrestrial ecosystems and lower in aquatic ecosystems.

We calculated two indexes of recycling. The turnover rate of the detritus pool ($F_{1,5}/x_3$) is higher in aquatic systems and generally lower in terrestrial ecosystems, except for tropical forests where there is a rapid turnover of detritus. The ratio of recycling to input ($F_{1,5}/\Sigma z$), as used in stochastic analyses, is approximately the inverse of the other recycling index. However, since systems with larger biotic pools typically recycle more nutrients than do systems with smaller biotic standing crops, this index partially confounds storage and recycling. This index ranges from 500 for grasslands to 0 for streams.

Two other useful indexes are the ratios of total standing crop to recycling material ($\Sigma x/F_{1,5}$) and total standing crop to total inflow ($\Sigma x/\Sigma z$). Both indexes estimate system turnover time. Longest turnover times occur in temperate forests and grasslands, whereas there is rapid turnover in stream and ocean ecosystems.

The specific values given in Table 1 have obvious deficiencies. Each idealized ecosystem represents a wide spectrum of actual ecosystems differing in many important characteristics. Similarly the kinetics of specific nutrients within a given ecosystem differ, quantitatively and qualitatively. In quantifying the general model shown in Fig. 3, we have attempted to suppress such specific details and to focus instead on the alternative properties of nutrient cycles depicted in Fig. 2. Our emphasis is thus on macroscopic properties of ecosystems rather than on specific differences between systems or nutrients. Comparison of the structural indexes (Table 2) with Fig. 2 reveals that the chosen values agree well with the idealized conceptualization.

Results

The eight models were analyzed in the same fashion as described previously, providing values for critical root, mean root, natural frequency, and damping ratio (Table 3). Both critical root and natural frequency were smallest (in absolute value) for the temperate forest and grassland models and largest for the stream model and tended to be smaller (in absolute value) for the four terrestrial ecosystem models. All values of damping were greater than 1, indicating all eight ecosystem models to be overdamped. The smallest value was obtained for the

ocean, the largest for the stream. No clear separation between terrestrial and aquatic ecosystems was obvious.

The relative stability indexes were then compared with the structural indexes given in Table 2, using least-squares regression. Correlation coefficients are shown in Table 4. Both critical and mean roots were directly related to the turnover time of the reserve nutrient pool T_6, whereas the natural frequency exhibited an inverse relationship. For longer turnover times, critical and mean roots were nearer zero, and the natural frequency was smaller.

Regressions against the proportion of nutrients in the two abiotic pools were not significant. However, when terrestrial and aquatic ecosystems were considered separately, a trend was evident. Increased abiotic storage or slower abiotic turnover produced critical and mean roots nearer zero and smaller natural frequencies.

All four stability indexes were related to recycling. A greater recycling rate ($F_{1,5}/x_3$) or a smaller ratio of recycling to input ($F_{1,5}/\Sigma z$) resulted in roots farther from zero, a larger natural frequency, and greater damping.

Both critical and mean roots, as well as natural frequency, were significantly related to system turnover ($\Sigma x/F_{1,5}$). All four indexes were correlated with turnover as related to system input ($\Sigma x/\Sigma z$). In general, the slower the system turnover rate (the greater the turnover time), the nearer the critical and mean roots were to zero, the smaller the natural frequency, and the smaller the damping ratio.

The results clearly indicate that increased storage and turnover times (abiotic, biotic, or total), as well as increased amounts of recycling, lead to critical and mean roots nearer zero and to smaller natural frequencies. Increased recycling and turnover rates (of biotic or abiotic elements, or their sum), on the other hand, lead to critical and mean roots that are farther from zero and to larger natural frequencies. Relationships involving the damping ratio are less clear. However, if we ignore the stream, which has no recycling ($F_{1,5} = 0$) and for which the second-order approximation may not be accurate owing to dominance by the extremely large nutrient inflow, other trends become apparent (Table 4). Although correlations are not as large as for the other stability indexes, damping generally tended to be directly related to storage or turnover times but inversely related to recycling or turnover rates. Thus damping and natural frequency typically showed opposite behavior relative to the structural indexes considered.

DISCUSSION

The preceding arguments were presented for the asymptotic stability of ecosystems. This stability is guaranteed by limitations on resource mobilization and by the dissipative character of ecosystems. Resistance, the ability of an

TABLE 1

SUMMARY OF RELATIVE VALUES USED IN QUANTIFYING THE GENERAL NUTRIENT CYCLING MODEL (FIG. 3) IN THE EIGHT IDEALIZED ECOSYSTEMS INVESTIGATED (FIG. 2)

Parameter*	Tundra[a]	Grassland[b]	Temperate forest[c]	Tropical forest[d]	Ocean[e]	Lake[f]	Salt marsh[g]	Str
x_1	200	500	100	500	10	10	1,000	500
x_2	15	50	0.5	2.5	10	1	25	50
x_3	200	1,000	25	5	10	25	1,000	10
x_4	20	100	1	1	0.5	25	100	20
x_5	100	100	100	100	100	100	100	100
x_6	100	1,000	5,000	1,500	50	2,000	50,000	1,000
z_1	0	0	0	0	0	0	0	1,000
z_5	1	1	1	1	110	100	75	100,000
$F_{2,1}$	20	100	1	5	500	20	100	200
$F_{3,1}$	30	400	5	46	545	180	900	800
$F_{3,2}$	20	100	1	5	500	20	100	190
$F_{4,3}$	50	480	5.5	49.9	50	180	500	300
$F_{5,3}$	0	10	0.4	1	900	10	400	600
$F_{5,4}$	50	480	5.5	49.9	50	180	500	300
$F_{5,6}$	1	10	0.6	1.1	10	20	1,000	100
$F_{6,3}$	0	10	0.1	0.1	50	10	50	0
$F_{6,5}$	1	0	0.5	1	20	10	950	100
$F_{1,5}$	50	500	6	51	1,045	200	1,000	0
$F_{0,2}$	0	0	0	0	0	0	0	10
$F_{0,3}$	0	0	0	0	45	0	50	90
$F_{0,5}$	1	1	1	1	5	100	25	100,900
$F_{0,6}$	0	0	0	0	60	0	0	0

*x_i represents the size of the *ith* compartment; z_i is the input to x_i; $F_{i,j}$ is the flow of nutrients from x_j to x_i; and $F_{0,j}$ represents nutrient loss to the environment from x_j. All values are normalized against x_5, which was set to 100 units/unit area for each system. References consulted in deriving these values are listed below.

[a]Rodin and Bazilevich, 1967; Schultz, 1969.

[b]Reuss, 1971; Rodin and Bazilevich, 1967; Sims and Singh, 1971.

[c]Bormann and Likens, 1970; Likens and Bormann, 1972; Rodin and Bazilevich, 1967.

[d]Child and Shugart, 1972; McGinnis et al., 1969; Rodin and Bazilevich, 1967.

[e]Brylinsky, 1972; E. P. Odum, 1971; Riley, 1972.

[f]Juday, 1940; Likens and Bormann, 1972; Lindeman, 1941, 1942; Williams, 1971.

[g]E. P. Odum, 1971; Pomeroy et al., 1969; Teal, 1962; Wiegert et al., 1974.

[h]Boling et al., 1974; Cummins, 1971; Woodall, 1972.

Additional general references consulted include Collier et al., 1973; Golley, 1972; Pomeroy, 1970; Wiegert and Evans, 1964.

TABLE 2

INDEXES SUMMARIZING VARIOUS STRUCTURAL CHARACTERISTICS OF THE EIGHT HYPOTHETICAL ECOSYSTEMS AND DIFFERENTIATING AMONG THE PROPERTIES OF NUTRIENT CYCLES SHOWN IN FIG. 2*

	Abiotic storage		Biotic storage	Recycling		System turnover	
System	T_6	$\frac{x_5 + x_6}{\Sigma x}$	$\frac{x_1 + x_2 + x_3 + x_4}{F_{1,5}}$	$\frac{F_{1,5}}{x_3}$	$\frac{F_{1,5}}{\Sigma z}$	$\frac{\Sigma x}{F_{1,5}}$	$\frac{\Sigma x}{\Sigma z}$
Tundra	100	0.31	8.7	0.25	50	12.7	635
Grassland	1,000	0.86	3.3	0.5	500	23.5	11,750
Temperate forest	8,333	0.97	21.1	0.24	6	870.93	5,226
Tropical forest	1,364	0.76	9.97	10.2	51	41.34	2,108
Ocean	0.714	0.83	0.029	104.5	9.5	0.173	1.64
Lake	100	0.97	0.305	8	2	10.80	21.6
Salt marsh	50	0.96	2.12	1	13.3	52.22	696
Stream	10	0.65	∞	0	0	∞	0.017
			(0.58)†	(99)†	(0.0098)†	(1.70)†	

*x_i is the size of the *ith* compartment; z_i is the input to x_i; $F_{i,j}$ is the flow of nutrients from x_j to x_i; $F_{0,j}$ is the nutrient loss to the environment from x_j; and T_6 is the time constant of x_6.

†Since $F_{1,5} = 0$ for the stream, the indicated index was recalculated using the total loss from x_3 instead of $F_{1,5}$.

TABLE 3

RESULTS OF RELATIVE STABILITY ANALYSIS OF NUTRIENT-CYCLING MODELS FOR EIGHT HYPOTHETICAL ECOSYSTEMS

System	Critical root	Mean root	Natural frequency	Damping ratio
Temperate forest	−0.0001	−1.312	0.000227	1.2174
Grassland	−0.0001	−2.218	0.000228	1.1794
Tropical forest	−0.0003	−10.456	0.001039	1.2585
Salt marsh	−0.0013	−5.128	0.003898	1.1852
Tundra	−0.0015	−0.810	0.004413	1.1840
Lake	−0.0083	−9.718	0.02924	1.2954
Stream	−0.0999	−188.350	6.2947	1.4700
Ocean	−0.7678	−61.85	1.8478	1.1404

ecosystem to resist perturbation, results from the accumulated structure of the ecosystem. Resilience, the ability of an ecosystem to return to a nominal trajectory once displaced, reflects dissipative forces inherent in the ecosystem. These concepts were shown to be implicit within the linear donor-based model formulation of Eqs. 1 to 7, from which four relative stability indexes were derived: Critical root measures the system's margin of stability. Mean root is an index of system response time. Natural frequency measures resistance to displacement, and damping ratio measures resilience following displacement. Randomly constructed matrices (subject to the restriction of mass conservation; Eqs. 4 and 6) and hypothetical ecosystem models were analyzed to examine relationships between relative stability and specific properties of nutrient cycles.

Results of the stochastic analyses indicated that an increase in the amount of recycling relative to input resulted in a decreased margin of stability, faster mean response time, greater resistance, and less resilience. Analyses of the hypothetical ecosystem models revealed similar relationships among stability measures. Greater amounts of recycling were correlated with a smaller margin of stability, slower mean response time (not consistent with stochastic results), greater resistance, and less resilience (ignoring the stream value). Deterministic results also revealed that increased storage and turnover times resulted in exactly the same relationships as described for the amount of recycling. Increases in both recycling and turnover rates produced opposite results, however, leading to a larger stability margin, faster response time, smaller resistance, and greater resilience.

The inconsistent correlations between amount of recycling and mean response time can be explained. In the stochastic analyses, increases in recycling

TABLE 4

CORRELATION COEFFICIENTS FOR RELATIONSHIPS BETWEEN RELATIVE STABILITY MEASURES AND INDEXES OF STRUCTURAL PROPERTIES*

	Structural indexes											
	Abiotic storage				Biotic storage		Recycling				System turnover	
	T_6		$\frac{x_5 + x_6}{\Sigma x}$		$\frac{x_1 + x_2 + x_3 + x_4}{F_{1,5}}$		$\frac{F_{1,5}}{x_3}$		$\frac{F_{1,5}}{\Sigma z}$		$\frac{\Sigma x}{F_{1,5}}$	$\frac{\Sigma x}{\Sigma z}$
Critical root	1	0.99	1	0.10†	4	0.89	3	−0.89	4	0.59	4 0.90	4 0.90
Mean root	4	0.70	1	0.24	4	0.72	4	−0.97	2	0.85	4 0.72	2,4 0.88
Natural frequency	4	−0.89	1	0.22†	4	−0.81	3	0.91	2	−0.85	4 −0.85	4 −0.98
Damping ratio	3	0.36	1	0.14	1	0.20	2	0.49	2	−0.85	1 −0.10	2 −0.66
	(3	0.58)‡	(1	0.25)	(4	0.26)	(3	−0.50)	(2	−0.38)	(4 0.42)	(1 −0.16)

*Each indicated variable pair was tested for (1) linear; (2) semilog, log of structural index; (3) semilog, log of stability measure; and (4) log–log relationships. The model with the largest correlation is reported and indicated to the left of the correlation coefficient. Levels of significance are 0.666 (5%) and 0.798 (1%). x_i is the size of the *ith* compartment; z_i is the input to x_i; $F_{i,j}$ is the flow of the nutrients from x_j to x_i; $F_{0,j}$ represents the nutrient loss to the environment from x_j, and T_6 is the time constant of x_6.

†These relationships were greatly improved by considering terrestrial and aquatic ecosystems separately. In each case the correlation coefficient was 0.99 (model 4). The relationship was positive for critical root and negative for natural frequency damping factor.

‡Values in parentheses represent correlations and model numbers, if the stream system is not considered (ζ only).

coefficients forced increases in turnover rates of donor compartments ($|a_{i,i}|$, Eq. 4). Since randomly constructed matrices exhibited a narrow range of coefficient values, a change in any one turnover rate was reflected in the mean response time. The deterministic models exhibited a much wider range in values of transfer coefficients (several orders of magnitude), so that larger turnover rates of x_i did not correspond to longer mean response times. The opposite relationship, in fact, existed. Those systems with large amounts of recycling also had large storage and hence mean roots near zero. Indeed, the presence of rate coefficients that range over several orders of magnitude is one important characteristic of ecosystems that differentiates them from randomly organized systems.

Table 3 shows that the eight hypothetical ecosystems, ordered from least to most resistant (largest to smallest ω_n), were stream, ocean, lake, tundra, salt marsh, tropical forest, grassland, and temperate forest. The four terrestrial ecosystem models were, on the whole, much more resistant than the four aquatic models. Analyses did not reveal such a clear separation of ecosystems with high and low resilience, nor did the eight systems differ as much with respect to the resilience aspect of relative stability as they did in relation to resistance. From least to most resilient (largest to smallest ζ), the ecosystems were stream, lake, tropical forest, temperate forest, salt marsh, tundra, grassland, and ocean. This factor is tied to system characteristics (such as recycling) which do not differ strictly between aquatic and terrestrial ecosystems. Although several of the aquatic models were more resilient than most terrestrial ones, the lake model showed one of the smallest resilience values, probably related to slow turnover of the large abiotic storage pool. These results should be interpreted cautiously, in light of the data used in this analysis. Certainly the order-of-magnitude differences in the natural frequencies would seem to reflect real differences in the idealized ecosystems. The differences in damping ratios are apparently much smaller. However, these differences actually reflect large differences in the time dynamics of the ecosystem types because ζ appears as an exponent in the time-domain solutions (Eqs. 9 and 11).

These results agree well with previous analyses. Pomeroy (1970) related ecosystem stability to the presence or absence of abiotic reserves, system turnover rate, and predictability of the physical environment. Specifically, he noted that ecosystems with low abiotic storage and rapid recycling (tropical forests and coral reefs) are slow to recover following disturbance. Consistent with this observation, Table 3 shows the tropical forest to have one of the lowest resilience values. Also, the relative rankings of ecosystems in terms of stability given by Pomeroy correspond closely to rankings depicted in Table 4. Jordan et al. (1971) also showed an inverse relationship between recovery time following displacement and the amount of nutrient recycling relative to input. Comparisons between tropical and temperate forests in this study also agree with the analyses of Child and Shugart (1972) and Waide et al. (1974).

Inverse Relationships Between Resistance and Resilience

Taken together our results indicate an inverse relationship between resistance and resilience. Those factors which tend to increase resistance decrease resilience, and those factors which increase resilience decrease resistance. In addition, those systems which are highly resistant have low resilience, and vice versa. Thus ecosystem evolution would seem to involve a compromise or balance between resistance and resilience. In some situations, selection has favored systems with large storage and a large amount of recycling, factors that contribute to ecosystem persistence by increasing resistance to displacement. Other ecosystems in other environments have low storage and rapid recycling and persist by responding rapidly following disturbance. The relationship is not an exact inverse, however. Results show, for example, the tropical forest to be both less resistant and less resilient than either the temperate forest or grassland. Also, the grassland model is next to the most stable in terms of both resistance and resilience, and the stream is least stable in both regards. Still, the notion of a functional balance between ecosystem properties favoring resistance or resilience is substantiated.

Environmental conditions that favor ecosystem resistance or resilience must be considered. In general, those environments in which resources are scarce or which place severe physicochemical limitations on resource mobilization will not favor the accumulation of large biotic stores of nutrients. Systems that recycle nutrients rapidly, and hence are highly resilient, should be favored in such environments. However, kinetic limitations on resource assimilation could be so severe as to produce systems that are neither resistant nor resilient, as streams seem to be. On the other hand, environments in which resources are available and which place less severe limitations on resource mobilization should favor the development of ecosystems that accumulate large nutrient reserves that turn over slowly and hence are relatively more resistant. Such considerations in part explain the separation between aquatic and terrestrial ecosystems in terms of resistance. With the exception of coral reefs, aquatic systems are generally limited in their ability to retain and recycle essential resources (Pomeroy, 1970; Riley, 1972). Such systems are typically more resilient, and less resistant, than terrestrial systems.

Also, as emphasized by Holling (1973), the balance between resistance and resilience is strongly influenced by the types of environmental fluctuations commonly encountered by an ecosystem. For example, results suggest that the hypothetical ocean is the least resistant ecosystem next to the stream. It is not reasonable to expect selection for maximum resistance of such an ecosystem since the environment typically encountered by oceanic ecosystems is buffered (by the surrounding water mass) compared to that impinging upon a temperate forest, the most resistant ecosystem considered. Similar buffering is attained in terrestrial ecosystems through large biotic storage.

As a corollary to these two last points, the kinds of environmental fluctuations an ecosystem "sees," and hence to which it responds, depend upon the degree of resistance or resilience it exhibits. A system will filter out or attenuate inputs with a frequency greater than its natural frequency but will pass and hence react to inputs with a lower frequency. Thus analyses indicate that terrestrial ecosystems are, on the average, currently responding to lower frequency environmental signals than are aquatic ecosystems. From the opposite perspective, we could perhaps argue that higher frequency inputs may be more damaging to terrestrial ecosystems and that selection has thus favored la slowly recycling biotic structures that attenuate such persistent, potenti destabilizing inputs. Thus the degree of resistance or resilience a given ecosystem exhibits is determined by the types and frequencies of environmental fluctuations commonly encountered by the system, as well as by the environmental limitations on resource mobilization which the system experiences.

Contribution of Component Turnover Rates to Stability

It was suggested above that one of the factors which characterizes ecosystems is the presence of a large range in values of transfer rate coefficients and turnover rates, typically over several orders of magnitude. Each component turnover rate contributes to the resultant balance between resistance and resilience for a given ecosystem.

The concept of r and K selection define alternative evolutionary strategies at the population level (Pianka, 1970, 1972). These ideas may be reformulated in an ecosystem context by considering r selected species to be ones that have rapid turnover and low storage, thereby contributing to ecosystem resilience, whereas K specialists exhibit slow turnover and high storage, and thus contribute to resistance. Hence the degree of resistance or resilience observed in a given ecosystem results from the relative proportions of K and r selected components, respectively. This treatment does not seek to destroy the original meaning of these ideas but rather to suggest their implications for behavior at the ecosystem level.

During succession, ecosystems progress from stages that are relatively mo resilient to ones that are relatively more resistant. Although differing degrees o environmental limitation and fluctuation will produce different balances between resilience and resistance, all developmental processes involve some amount of biomass accretion and nutrient storage. However, even at steady state a large variation in turnover rates of component populations is still present. It is the presence of such a variety of adaptations of component populations in steady-state ecosystems which ensures their ability to respond following disturbance and hence which confers the property of resilience on ecosystems. For example, pin cherry is an early successional woody plant common in

northeastern deciduous forests, which ensures their rapid return to steady-state function following major perturbation (Marks and Bormann, 1972; Marks, 1974). Black locust seems to play a similar role in forest ecosystems in the southern Appalachians. Yet neither species is anything more than a minor component of steady-state ecosystems in either locality. Clearly, their persistence within these ecosystems represents a system-level adaptation for resilience which is not explained by considering dominant steady-state components alone. Similar examples could be cited for other ecosystem types.

The role of component turnover rates in regulating ecosystem stability is also emphasized by a consideration of the contribution of primary consumers to ecosystem stability. Primary biophages are generally viewed as being able to regulate their rate of resource supply and hence the ability of a specific ecosystem to accumulate biomass and store nutrients (Odum, 1962; Wiegert and Owen, 1971). Where environments favor ecosystem resistance, selection would thus seem to lead to mechanisms that suppress primary consumption, allelochemically, structurally, and via predators and parasites. However, in situations where ecosystem resilience is favored, mechanisms for reducing primary consumption would not necessarily be advantageous. Indeed, in such systems herbivory would seem to be a major mechanism of nutrient regeneration and recycling (Johannes, 1968; Pomeroy, 1970). Comparison of resilience values for the eight hypothetical ecosystems investigated with estimates of the amount of primary production passing through primary biophages (Wiegert and Evans, 1967; Wiegert and Owen, 1971; Golley, 1972) reveals a direct relationship between these two parameters, with those ecosystem types in which primary consumption is higher typically being more resilient. Such a relationship between herbivory and nutrient regeneration requires further experimental verification, especially in terrestrial ecosystems.

SUMMARY

The theoretical perspective embodied in this paper represents an attempt to account for alternatives for persistence at the ecosystem level and at the same time to relate ecosystem response to specific observable and measurable attributes of ecosystems. The argument that ecosystems are asymptotically stable focuses attention on the critical area of relative stability. It clearly identifies two aspects of ecosystem relative stability, resistance and resilience. Resistance is related to the formation and maintenance of persistent ecosystem structure. Resilience results from the tendencies inherent in ecosystems for the erosion of such structures. Thus this perspective offers to integrate various areas of ecological theory into a unified picture of ecosystem structure and function. Further research should help to establish the validity of these ideas. However, at present, they seem to represent a rigorous, operational approach to ecosystem theory which is testable by both observation and experimental analysis.

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REFERENCES

Ashby, W. R., 1952, *Design for a Brain,* Chapman & Hall, Ltd., London.

Ba Hli, F., 1971, A Time Domain Approach, in *Aspects of Network and System Theory,* pp. 313-325, R. E. Kalman and N. DeClaris (Eds.), Holt, Rinehart, and Winston, Inc., New York.

Bellman, R. E., 1968, *Some Vistas of Modern Mathematics: Dynamic Programming, Invariant Imbedding, and the Mathematical Biosciences,* University of Kentucky Press, Lexington.

Blackburn, T. R., 1973, Information and the Ecology of Scholars, *Science,* **181**: 1141-1146.

Boling, R. H., Jr., R. C. Peterson, and K. W. Cummins, 1974, Ecosystem Modeling for Small Woodland Streams, in *Systems Analysis and Simulation in Ecology,* Vol. 3, pp. 183-204, B. C. Patten (Ed.), Academic Press, Inc., New York.

Bormann, F. H., and G. E. Likens, 1970, The Nutrient Cycles of an Ecosystem, *Sci. Amer.,* **220**: 92-101.

Brylinsky, M., 1972, Steady-State Sensitivity Analysis of Energy Flow in a Marine Ecosystem, in *Systems Analysis and Simulation in Ecology,* Vol. 2, pp. 81-101, B. C. Patten (Ed.), Academic Press, Inc., New York.

Child, G. I., and H. H. Shugart, Jr., 1972, Frequency Response Analysis of Magnesium Cycling in a Tropical Forest Ecosystem, in *Systems Analysis and Simulation in Ecology,* Vol. 2, pp. 103-135, B. C. Patten (Ed.), Academic Press, Inc., New York.

Collier, B. D., G. W. Cox, A. W. Johnson, and P. C. Miller, 1973, *Dynamic Ecology,* Prentice-Hall, Inc., Englewood Cliffs, N. J.

Cummins, K. W., 1971, *Predicting Variations in Energy Flow Through a Semicontrolled Lotic Ecosystem,* Michigan State University, Institute of Water Research, Technical Report 19, pp. 1–21.

Darnell, R. M., 1970, Evolution and the Ecosystem, *Amer. Zool.,* **10**: 9-16.

DiStefano, J. J., A. K. Stubberud, and I. J. Williams, 1967, *Feedback and Control Systems,* McGraw-Hill Book Company, New York.

Dunbar, M. J., 1972, The Ecosystem as a Unit of Natural Selection, *Trans. Conn. Acad. Arts Sci.,* **44**: 111-130.

Funderlic, R. F., and M. T. Heath, 1971, Linear Compartmental Analysis of Ecosystems, USAEC Report ORNL-IBP-71-4, Oak Ridge National Laboratory.

Gardner, M. R., and W. R. Ashby, 1970, Connectedness of Large Dynamic (Cybernetic) Systems: Critical Value of Stability, *Nature,* **228**: 784.

Golley, F. B., 1972, Energy Flux in Ecosystems, in *Ecosystem Structure and Function,* pp. 69-90, J. A. Wiens (Ed.), Oregon State University Press, Corvallis.

Hairston, N. G., F. E. Smith, and L. B. Slobodkin, 1960, Community Structure, Population Control, and Competition, *Amer. Natur.,* **94**: 421-425.

Hearon, J. Z., 1963, Theorems on Linear Systems, *Ann. N. Y. Acad. Sci.*, **108**: 36-68.

——, 1953, The Kinetics of Linear Systems with Special Reference to Periodic Reactions, *Bull. Math. Biophys.*, **15**: 121-141.

Hill, J., IV, 1973, Component Description and Analysis of Environmental Systems, M.S. Thesis. Utah State University, Logan.

Holling, C. S., 1973, Resilience and Stability of Ecological Systems, *Annu. Rev. Ecol. Syst.*, **4**: 1-24.

Hubbell, S. P., 1973a, Populations and Simple Food Webs as Energy Filters, I. One-Species Systems, *Amer. Natur.*, **107**: 94-121.

——, 1973b, *ibid*, II. Two-Species Systems, *Amer. Natur.*, **107**: 122-151.

Hutchinson, G. E., 1948a, Circular Causal Systems in Ecology, *Ann. N. Y. Acad. Sci.*, **50**: 221-246.

——, 1948b, On Living in the Biosphere, *Sci. Mon.*, **67**: 393-397.

Johannes, R. E., 1968, Nutrient Regeneration in Lakes and Oceans, in *Advances in Microbiology of the Sea*, pp. 203-213, M. R. Droop and E. J. F. Wood (Eds.), Academic Press, New York.

Jordan, F., J. R. Kline, and D. S. Sasscer, 1972, Relative Stability of Mineral Cycles in Forest Ecosystems, *Amer. Natur.*, **106**: 237-253.

Juday, C., 1940, The Annual Energy Budget of an Inland Lake, *Ecology*, **21**: 438-450.

Lewontin, R. C., 1970a, The Meaning of Stability, in Diversity and Stability in Ecological Systems, Symposia in Biology, No. **22**, USAEC Report BNL-50175, Brookhaven National Laboratory.

——, 1970b, The Units of Selection, *Annu. Rev. Ecol. Syst.*, **1**: 1-18.

Liapunov, M. A., 1892, *Problème Générale de la Stabilité du Mouvement*, Kharkov. Reprinted as *Annals of Mathematical Study*, No. 17, Princeton University Press, Princeton, N. J.

Likens, G. E., and F. H. Bormann, 1972, Nutrient Cycling in Ecosystems, in *Ecosystem Structure and Function*, pp. 25-67, J. A. Wiens (Ed.), Oregon State University Press, Corvallis.

Lindeman, R. L., 1942, The Trophic-Dynamic Aspect of Ecology, *Ecology*, **23**: 399-418.

——, 1941, Seasonal Food-Cycle Dynamics in a Senescent Lake, *Amer. Midland Natur.*, **26**: 636-673.

MacArthur, R. H., 1955, Fluctuations of Animal Populations, and a Measure of Community Stability, *Ecology*, **36**: 533-536.

Makridakis, S., and C. Faucheux, 1973, Stability Properties of General Systems, *Gen. Sys.*, **18**: 3-12.

——, and E. R. Weintraub, 1971a, On the Synthesis of General Systems, Part I, The Probability of Stability, *Gen. Sys.*, **16**: 43-50.

——, and E. R. Weintraub, 1971b, On the Synthesis of General Systems, Part II, Optimal System Size, *Gen. Sys.*, **16**: 51-54.

Marks, P. L., 1974, The Role of Pin Cherry (*Prunus pennsylvanica* L.) in the Maintenance of Stability in Northern Hardwood Ecosystem, *Ecol. Monogr.*, **44**: 73-88.

——, and F. H. Bormann, 1972, Revegetation Following Forest Cutting: Mechanisms for Return to Steady-State Nutrient Cycling, *Science*, **176**: 914-915.

May, R. M., 1973, *Stability and Complexity in Model Ecosystems*, Princeton University Press, Princeton, N. J.

——, 1972, Will a Large Complex System be Stable?, *Nature*, **238**: 413-414.

McGinnis, J. T., F. B. Golley, R. G. Clements, G. I. Child, and M. J. Duever, 1969, Elemental and Hydrologic Budgets of the Panamanian Tropical Moist Forest, *BioScience*, **19**: 697-702.

Milsum, J. H., 1968, Mathematical Introduction to General System Dynamics, in *Positive Feedback*, pp. 23-65, J. H. Milsum (Ed.), Pergamon Press, New York.

Morowitz, H. J., 1966, Physical Background of Cycles in Biological Systems, *J. Theor. Biol.*, 13: 60-62.

Odum, E. P., 1971, *Fundamentals of Ecology*, W. B. Saunders Co., Philadelphia.

——, 1969, The Strategy of Ecosystem Development, *Science*, 164: 262-270.

——, 1962, Relationships Between Structure and Function in the Ecosystem, *Jap. J. Ecol.*, 12: 108-118.

Odum, H. T., 1971, *Environment, Power and Society*, Wiley-Interscience, Inc., New York.

——, 1967, Work Circuits and System Stress, in *Primary Productivity and Mineral Cycling in Natural Ecosystems*, pp. 81-138, H. E. Young (Ed.), University of Maine Press, Orono, Maine.

Olson, J. S., 1963, Analog Computer Models for Movement of Nuclides Th[illegible] Ecosystems, in *Radioecology*, pp. 121-125, V. Shultz and A. W. Klements, Jr. (Eds.), Van Nostrand Reinhold Company, Cincinnati, and American Institute of Biological Sciences, Washington.

Patten, B. C., 1974, The Zero State and Ecosystem Stability, in *Proceedings of the First International Congress of Ecology*, Supplement, The Hague, Sept. 8–14, 1974, Centre for Agricultural Publishing and Documentation, Wageningen.

——, 1972, A Simulation of the Shortgrass Prairie Ecosystem, *Simulation*, 19: 177-186.

——, D. A. Egloff, T. H. Richardson, and 38 Additional Coauthors, 1974, A Total Ecosystem Model for a Cove in Lake Texoma, Texas–Oklahoma, in *Systems Analysis and Simulation in Ecology*, Vol. 3, pp. 205-421, B. C. Patten (Ed.), Academic Press, Inc., New York.

——, and M. Witkamp, 1967, Systems Analysis of ^{134}Cs Kinetics in Terrestrial Microcosms, *Ecology*, 48: 813-824.

Pianka, E. R., 1972, r and K Selection or b and d Selection? *Amer. Natur.*, 106: 581-588.

——, 1970, On r and K Selection, *Amer. Natur.*, 102: 592-597.

Pomeroy, L. R., 1970, The Strategy of Mineral Cycling, *Annu. Rev. Ecol. Syst.*, 1: 171-190.

——, R. E. Johannes, E. P. Odum, and B. Roffman, 1969, The Phosphorus and Zinc Cycles and Productivity of a Salt Marsh, in Symposium on Radioecology, pp. 412-419, Proceedings of the Second National Symposium, May 15–17, 1967, D. J. Nelson and F. C. Evans (Eds.), Ann Arbor, Mich., USAEC Report CONF-670503.

Reuss, J. O., 1971, Soils of the Grassland Biome Sites, in *Preliminary Analysis of Structure and Function in Grasslands*, pp. 35-39, N. R. French (Ed.), Colorado State University, Fort Collins.

Riley, G. A., 1972, Patterns of Production in Marine Ecosystems, in *Ecosystem Structure and Function*, pp. 91-112, J. A. Wiens (Ed.), Oregon State University Press, Corvallis.

Rodin, L. E., and M. I. Bazilevich, 1967, *Production and Mineral Cycling in Terrestrial Vegetation*, Oliver & Boyd, Edinburgh.

Schultz, A. M., 1969, A Study of an Ecosystem: The Arctic Tundra, in *The Ecosystem Concept in Natural Resource Management*, pp. 77-93, G. M. VanDyne (Ed.), Academic Press, Inc., New York.

Shinners, S. M., 1972, *Modern Control System Theory and Application*, Addison-Wes[illegible] Publishing Company, Inc., Reading, Mass.

Sims, P. L., and J. S. Singh, 1971, Herbage Dynamics and Net Primary Production in Certain Ungrazed and Grazed Grasslands in North America, in *Preliminary Analysis of Structure and Function in Grasslands*, pp. 59-124, N. R. French (Ed.), Colorado State University, Fort Collins.

Slobodkin, L. B., 1964, The Strategy of Evolution, *Amer. Sci.*, 52: 342-357.

Smith, F. E., 1972, Spatial Heterogeneity, Stability, and Diversity in Ecosystems, *Trans. Conn. Acad. Arts Sci.*, 44: 309-335.

Teal, J. M., 1962, Energy Flow in the Salt Marsh Ecosystem of Georgia, *Ecology*, 43: 614-624.

Waide, J. B., J. E. Krebs, S. P. Clarkson, and E. M. Setzler, 1974, A Linear Systems Analysis of the Calcium Cycle in a Forested Watershed Ecosystem, in *Progress in Theoretical Biology,* Vol. 3, pp. 261-345, R. Rosen and F. M. Snell (Eds.), Academic Press, Inc., New York.

——, and J. R. Webster, 1975, Engineering Systems Analysis: Applicability to Ecosystems, in *Systems Analysis and Simulation in Ecology,* Vol. 4, B. C. Patten (Ed.), Academic Press, Inc., New York (in press).

Webster, J. R., and J. B. Waide, 1975, Complexity, Resource Limitation, and the Stability of Ecosystems, in preparation.

[illegible]ley, G. W., and J. A. Watts, 1970, The Computing Technology Center Numerical [illegible]nalysis Library, Technical Report No. CTC-39, Oak Ridge National Laboratory.

[illegible]ittaker, R. H., and G. M. Woodwell, 1972, Evolution of Natural Communities, in *Ecosystem Structure and Function,* pp. 137-159, J. A. Wiens (Ed.), Oregon State University Press, Corvallis.

Wiegert, R. G., R. R. Christian, J. L. Gallagher, J. R. Hall, R. D. H. Jones, and R. L. Wetzel, 1974, A Preliminary Ecosystem Model of Coastal Georgia *Spartina* Marsh, in *Recent Advances in Estuarine Research,* J. Costlow (Ed.) (in press).

——, and F. C. Evans, 1967, Investigations of Secondary Productivity in Grasslands, in *Secondary Productivity of Terrestrial Ecosystems,* pp. 499-518, K. Petrusewicz (Ed.), Polish Academy of Science, Warsaw.

——, and F. C. Evans, 1964, Primary Production and the Disappearance of Dead Vegetation on an Old Field in S. E. Michigan, *Ecology,* **45**: 49-63.

——, and D. F. Owen, 1971, Trophic Structure, Available Resources, and Population Density in Terrestrial vs. Aquatic Ecosystems, *J. Theor. Biol.,* **30**: 69-81.

Williams, R. B., 1971, Computer Simulation of Energy Flow in Cedar Bog Lake, Minnesota, Based on the Classical Studies of Lindeman, in *Systems Analysis and Simulation in Ecology,* Vol. 1, pp. 543-582, B. C. Patten (Ed.), Academic Press, Inc., New York.

Woodall, W. R., Jr., 1972, Nutrient Pathways in Small Mountain Streams, Ph.D. Dissertation, University of Georgia, Athens.

Zadeh, L. A., and C. A. Desoer, 1963, *Linear System Theory: The State Space Approach,* McGraw-Hill Book Company, New York.

ERA

A THEORETICAL BASIS FOR ECOSYSTEM ANALYSIS WITH PARTICULAR REFERENCE TO ELEMENT CYCLING

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ABSTRACT

A conceptualization of ecosystem function is presented which considers: (1) the significance of ecosystem processes, such as element cycling, to the persistence of systems in a fluctuating environment; (2) the control mechanisms regulating these processes; and (3) the construction of a theoretical framework to synthesize available information and to suggest future investigations. The theory assumes that the central strategy of ecosystems is to maintain maximum persistent organic matter. A minimal set of state variables (an autotrophic base, a complex of heterotrophic regulators, and a detrital pool) is identified. When the complexity of the system is reduced to a set of minimal parameters, critical interactions between the components can be identified.

The role of science is to reduce the complexity of nature to some set of "sufficient parameters" (Levins, 1966) which integrates a large portion of the behavior of natural systems. In recent years analyses which seek to describe the underlying principles behind the structure and function of total ecosystems have accumulated sufficient data on diverse ecosystem types to enable us to attempt to define a set of sufficient parameters within the context of a general theory of ecosystem structure and function (Watt, 1973). Since ecologists are increasingly being asked to provide criteria for maintaining environmental quality and to forecast the consequences of man's activities, there are pragmatic as well as theoretical reasons for seeking a general interpretation of ecosystem functio and emergent properties. A theory of ecosystem function would help to integrate preliminary insights on essential ecosystem behavior and would aid in establishing the direction of future research. At this stage in the development of ecosystem science, a preliminary theory should not be expected to endure for long, but we hope that our theory and the reactions to it will form the basis for a structured approach to further study.

EMPHASES AND ASSUMPTIONS

Natural ecosystems are produced by the coevolution of their various components over a long period of time. The extremes of environmental conditions determine which populations can survive within a geographical area; the boundaries of ecosystems are determined by extreme conditions in unusual years, which cause mortality and eliminate some populations. Within the limits imposed by the extremes, seasonal, annual, or longer term environmental fluctuations may act as destabilizing influences (May, 1973a). A theory of ecosystems must account for the persistence of ecological systems in the face of such fluctuations. Holling (1973) refers to this persistence as "resilience" and argues that we must consider this factor in explaining ecosystem changes. We will emphasize the mechanisms that permit persistence of maximum biomass within limits imposed by environmental extremes. Our conceptualization assumes that populations in the system establish interactions and feedbacks to maintain the maximum biomass possible (Whittaker and Woodwell, 1971) and to minimize the effects of fluctuations in environmental factors, such as temperature and moisture.

Although we do not attempt to prove our theory, we can point out that our assumptions seem consistent with observations of other levels of biological organization. For example, proteinaceous substances are replaced, but the cell persists; cells reproduce and are replaced, but the organism persists. By analogy, populations establish and become extinct, but the ecosystem persists. Thus, at each level of organization, components are sacrificed to preserve the integrity of the system (Holling, 1973). Of course, we cannot assume that the level of integration of the ecosystem is the same type as that found in organisms since no centralized control exists (Whittaker and Woodwell, 1971). Nevertheless, this simple observation indicates that persistence in the face of fluctuation is a consistent property of living systems at all levels of organization. Since there are homeostatic mechanisms for cells, organisms, and populations, it follows that a theoretical framework for ecosystems should make a similar assumption of persistence and seek analogous feedback relationships among components which result in homeostatic persistence despite environmental fluctuations.

THE ENVIRONMENT

Like all biological entities, ecosystems function in continuous contact with their environment. In our conceptualization the environment imposes boundary conditions or limitations on the system. Environmental extremes determine the raw material of the system and thus determine which populations will be able to survive. These populations interact so that the maximum persistent biomass is maintained. Note that we emphasize maximum biomass rather than maximum

productivity (Whittaker and Woodwell, 1971). The ecosystem responds through population interactions to minimize and counteract the influence of fluctuations in the environment.

ENERGY

The first element of the environment to be considered is energy, including solar radiation. Energy imposes constraints on a system in terms of the populations that can live and reproduce within a given temperature range. In addition, available radiation may limit the photosynthetic capability that forms the energy base for the total system, but this may occur only under unusual conditions. The ecosystem is basically an energy-processing system (Lindeman, 1942; Odum, 1971; Golley, 1971).

Biological Component

An ecosystem must also be considered to be in a biological environment. Important aspects of the environment are other ecosystems in the landscape, just as important aspects of an organism's environment are other organisms (Odum, 1971; Holling, 1973). Other ecosystems in the environment influence the biological material available to a particular system (e.g., seed sources and migrating populations). The importance of the biological environment in structuring a system can be seen most vividly in recent research on island ecosystems. The studies of MacArthur and Wilson (1967) have shown the importance of area, habitat diversity, and distance between islands and source populations. Consideration of such factors is essential to understanding the nature of the biological material present in a given area.

Nutrients

Unlike energy, chemical species can be recycled in the ecosystem. An array of elements is required for growth and reproduction, replacement of structural parts, and maintenance of the energy-processing functions of the system. Because many elements are essential, mechanisms have developed at both population and species levels of organization to conserve them. If persistence in a fluctuating environment is a basic biological strategy at several levels of organization, a general theory of ecosystems must explain element turnover rates that are far slower than turnover rates of any individual population. For example, from the systems examined thus far, evolution appears to have favored ecosystems that conserve nitrogen. This is evidenced by the observation that nitrogen accumulates in the biosphere despite both the lack of a geochemical source and the high chemical mobility of some nitrogenous compounds.

BASIC ECOSYSTEM COMPONENTS

Energy Base for the System (Photosynthetic Capability)

The capture of solar radiation and the production of organic compounds are essential to the maintenance of ecosystems. Plant populations that can survive within a given range of climatic variables constitute the energy base. The populations will interact and compete, but, whatever the outcome, the system must develop an energy base for its trophic structure. A recent summary of y flow in a *Liriodendron* forest (Edwards, 1974) indicates that, of the t energy fixed annually, only 13% is accumulated as new structural material. The remainder is consumed (2%), promptly transferred to decomposers (35%), or used in maintenance respiration (50%).

Two strategies emerge as means of establishing a firm energy base.

1. A system may contain a number of plant populations, each with a slightly different spectrum of responses to the environment and each capable of rapid reproduction when conditions are optimal. As a result, there will usually be one or several populations that can rapidly expand to provide sufficient photosynthetic capability to maintain the energy base. This is the strategy employed by many aquatic ecosystems that rely heavily on phytoplankton populations to provide the energy base. The succession of phytoplankton assemblages, even during a single season, reinforces the generalization that planktonic systems employ this strategy.

2. Energy conversion can be invested in individuals of great bulk and slow reproductive rates. In this case photosynthetic capability is associated with large, extremely durable individuals that can survive unfavorable conditions by using stored resources. This strategy is exemplified, of course, by forests (Shugart et al., 1974).

It is not entirely clear at present which strategy a particular system will follow. Both are viable, and, although one or the other may predominate, an ecosystem may also have alternative capabilities. Thus lakes with rapidly expanding phytoplankton populations may also contain rooted or floating macrophytes, and, in addition to large trees, forests often have a herbaceous understory capable of reproducing rapidly (Taylor, 1974).

An analogy can be noted between the strategies adopted by these plant ulations and the "r" and "K" strategies adopted by animal populations (MacArthur and Wilson, 1967). This suggests that we investigate systems in which either the r or K strategy predominates as a key to understanding which might be adopted by a particular ecosystem to provide its energy base.

Rate Regulation (The Role of Consumers in Ecosystems)

If a system relies on rapidly reproducing populations to supply its energy base, the potential exists for dominant populations to expand exponentially, exhaust some critical resource, and then crash, since the resource cannot be

rapidly remobilized. This would cause a temporary loss of the energy base. Therefore, assuming persistence, we hypothesize that a complex food web that consumes the energy base would exert a stabilizing influence (Wiegert and Owen, 1971; May, 1973a) and would maintain a more constant energy base.

In a forest the probability of crashes in the energy base is smaller because the capability to expand rapidly and thus to stress the resources is less. In this case high biomass is maintained in the energy base, and relatively smaller consumer populations are found. Indeed, the slow response time of trees may provide negative feedback, militating against the long-term establishment of large consumer populations that may overgraze and destroy the energy base (Reichle, 1973b).

Thus it is understandable within the context of this conceptualization that planktonic ecosystems such as Long Island Sound (Riley, 1956) and the English Channel (Harvey, 1950) maintain 32 and 21 g of dry matter per square meter, respectively, in consumer populations as regulators of planktonic populations. Deciduous forest systems in England (Satchell, 1971) and in the southeastern United States (Reichle et al., 1973a) maintain 0.31 and 0.25g/m^2 in consumer populations. Nevertheless, herbivority by these small populations of consumers appears to exert greater control over primary production than the small amount of organic matter consumed would indicate. Reichle et al. (1973b) reported herbivorous insect consumption, in the absence of insect epidemics, in a *Liriodendron tulipifera* forest to be 2.6% (3-year average) of net primary production of foliage biomass. Because of leaf expansion, however, the "hole" area initiated by insect consumption represented an annual loss of 7.7% in photosynthetic surface area.

It is generally accepted that it is difficult to isolate decomposition processes from faunal activities without disturbing the microbial processes (Mignolet, 1972). One of the effects of faunal populations on detrital processing is comminution, which exposes greater surface area to microbial attack (Van der Drift and Witkamp, 1960; Nef, 1957; McBrayer, Reichle, and Witkamp, 1974). Macfadyen (1964) suggested four activities of fauna that could influence microbial processes: (1) spore transport; (2) production of toxic secretions (e.g., allelopathic substances); (3) excretion of material with high surface-to-volume ratio and moisture content; and (4) harvest of senescing microbial colonies. These observations reinforce the concept that a basic role of heterotrophs in ecosystem is one of rate regulation. The magnitude of the role of regulators energy–mineral processing is apparent from results of experiments that selectively disturbed the forest-floor food web. Witkamp and Crossley (1966) measured a 25% reduction in breakdown rates of white oak (*Quercus alba*) litter following napthalene treatment to eliminate forest-floor arthropods.

The Big–Slow Component (The Role of Dead Organic Matter in the Ecosystem)

Regardless of the strategy adopted to provide the energy base for an ecosystem, extreme environmental conditions still occur at some level of

probability and may seriously damage the plant populations. Similarly, since certain elements are essential for reestablishment of the autotrophic energy base, element conservation is required over time spans that exceed those of any individual population in the ecosystem. Therefore an alternative energy base, even though suboptimal, could provide an important alternate source for regulator heterotrophs that control release of essential elements during establishment of autotroph populations. Characteristics of such an alternative energy base would be large size (partially compensating for the suboptimal availability), [illegible]y to retain elements without maintenance energy input, and slow response t[illegible]s, so that short-term alterations in environmental conditions would have little effect.

A wide variety of ecosystems possesses a component with these characteristics, the large pool of organic matter (Table 1). In terrestrial systems this component is found in the litter and soil organic matter and the structural biomass of autotrophs (Edwards, Harris, and Shugart, 1974). In aquatic systems the particulate and dissolved organic matter plays a similar role. We hypothesize that a component of this type contributes significantly to the persistence of an ecosystem.

The spring ecosystem is the one exception to the general rule that the turnover time of the vegetation component is at least an order of magnitude faster than the large organic pool (Table 1). The spring ecosystem has an alternative energy base that is only four times slower than the photosynthesizers. Our theory predicts that this system would be substantially less able to persist in the face of environmental changes. Indeed, we can speculate that the spring system is likely to be highly sensitive to changes in the environment, e.g., changes in leaf litter input, and that its lack of capability to maintain a persistent maximum biomass in a fluctuating environment might well follow from the lack of an adequate energy base. Another system that seems to lack a big, slow pool of organic matter is the open ocean. Here we might hypothesize that the water mass itself provides a sufficient buffer from environmental fluctuations and permits persistence (Waide, 1974).

Organic matter also plays a key role in the recycling of nutrients through an ecosystem, preventing excessive amounts of nutrients from being lost from the [illegible]em. The big–slow component provides the system with a large capability to [illegible]in nutrients; the slow turnover time of the organic pool ensures that nutrients will be kept within the system. The organic pool holds large quantities of nutrients, which are bound tightly in its structure and are not readily available. Nevertheless, decomposer activity can activate this reserve. Given the strategy of persistence, this capability to retard element loss is an important conservation mechanism.

We can hypothesize that, given adequate energy and water for the system, the maximum persistent organic matter in an ecosystem will be determined by the supply of nutrients and the mechanisms for recycling them. If energy or

TABLE 1

SLOWEST COMPONENT AND TURNOVER TIME FOR A VARIETY OF ECOSYSTEMS

	Slowest component	Turnover time, years	Slowest component vs. autotroph biomass*
Terrestrial ecosystems			
Tundra (Whitfield, 1972)	Soil organic	340.6	20
Deciduous forests			
Calcium (Duvigneaud and Denaeyer-DeSmet, 1970)	Soil	108	225
Radiocesium (Olson, 1965)	Soil	25	92
Energy (Satchell, 1971)	Soil organic	76	16
Carbon (Harris et al., 1974)	Structural organic matter	155	163
Nitrogen (Henderson and Harris, 1974)	Soil organic	109	56
Tropical rain forests			
Elements (McGinnis et al., 1969)	Soil	41	29
Energy (Odum and Pigeon, 1970)	Soil	26	56
Peat Bog			
Biomass (Gore and Olson, 1967)	Anaerobic peat	526	35
Aquatic ecosystems			
Aquarium microcosms			
Radiophosphorus (Whittaker, 1961)	Sediment	0.03	11
Spring			
Energy (Tilly, 1968)	Detritus	0.037	4
Marine			
Carbon (Bolin, 1970)	Sediment	4×10^6	5202

*Turnover time of the slowest component divided by the turnover time of autotrophic biomass.

water are limited, the recycling problem is minimal, since a standing crop large enough to exhaust the nutrient resource cannot be maintained. We hypothesize, then, that in terrestrial systems, nutrient-conserving mechanisms should be best developed in mesic conditions (Shugart et al., 1974).

Some evidence substantiates this hypothesis. Table 2 summarizes the turnover times for soil-organic and structural-wood components for a Puerto Rican rain forest. In the tropics the woody structural components of vegetation

TABLE 2

TURNOVER TIMES (IN YEARS) FOR SOIL AND WOOD COMPONENTS OF A TROPICAL FOREST*†

Element	Soil	Wood
Calcium	1.7	*6.4*
Potassium	0.2	*1.0*
Magnesium	5.1	*6.1*
Sodium	1.8	*10.5*
Iron	*12.5*	4.4
Manganese	*9.1*	6.2
Copper	0.2	*5.9*
Strontium	*16.7*	10.0

*Based on data from C. F. Jordan, J. R. Kline, and D. S. Sasscer, Relative Stability of Mineral Cycles in Forest Ecosystems, *American Naturalist*, **106**: 237-253(1972).

†Values in italics are those for the component having the longer turnover time for a specific element.

seem to play an active role in the big–slow component of the system. Note that the generalization of inactive or nonmetabolizing organic matter still holds and the generalization of slow still holds, but, instead of relying on a single component (i.e., soil), some tropical ecosystems appear to rely on a more complex system of soil and structural wood to supply the big–slow component of the system. Note, too, that sometimes the soil is slower and sometimes the wood is slower, depending on the element being considered. The importance of the soil–wood recycling systems in the tropics has been investigated by Child and Shugart (1972) and by Jordan, Kline, and Sasscer (1972). It is evident from their studies that tropical systems have, indeed, developed elaborate feedback mechanisms for recycling nutrients; this is consistent with our hypothesis and therefore consistent with a major premise of our theory.

We can also expect that mesic temperate forests will develop elaborate cycling mechanisms. The discovery of the role that root sloughing appears to play in the recycling process (Harris, Kinerson, and Edwards, 1974) suggests a complex mechanism consistent with our theory. The investigators discovered that, if carbohydrate reserves are allocated to root tissue, bacterial attack and decomposition are encouraged and the roots die. The nutrients are retained in the decomposing tissue or microbial biomass, however, and are not lost by the system. Subsequent root growth permits resorption of the nutrients, but the metabolic cost of maintaining active root tissue is avoided during periods of the year when the roots are not required for absorbing water and nutrients from the soil.

DISCUSSION

Ecosystem carbon (Reichle et al., 1973a; Harris et al., 1974) and nitrogen (Henderson and Harris, 1974) cycles have been examined in the context of our theory (Table 3). Although other chemical species are conserved and cycled in the system, nitrogen is of particular interest since it exists naturally in gaseous form and ordinarily must be bound in organic form to be utilized by the system. In addition, since there are no large nitrogen reservoirs in soil minerals, we can expect that conservation mechanisms will be well developed.

Carbon residence times of 50 to 150 years in woody structure and soil organic matter are consistent with the potential role of accumulated organic matter as an alternate energy base to support element release essential to establishing new populations after a catastrophe. The residence times of carbon and nitrogen vary five orders of magnitude among components of the system. The small but rapid fluxes of nitrogen through the heterotrophs (regulators) are sufficient to maintain autotroph processes. Furthermore, the rapid activity of regulators, which results in a small pool of soluble nitrogen at any instant, serves to minimize leaching losses from the system. Because of the accumulation of organic matter in the ecosystem, the 1800-year mean residence time of nitrogen in the system is an order of magnitude greater than the residence time within any component (Table 3). No single component or population of the system appears to have a residence time sufficient to provide for nitrogen conservation.

TABLE 3

COMPARISON OF TURNOVER TIMES FOR CARBON AND NITROGEN IN TEMPERATE DECIDUOUS FORESTS IN TENNESSEE

Component	Turnover time, years	
	Carbon*	Nitrogen†
Soil	107	109
Forest biomass‡	155	88
Litter (01 + 02)	1.12	<5
Total	54	1815
Regulators	0.01	0.02

*Data based on carbon metabolism of yellow poplar forest (Harris et al., 1974, Reichle et al., 1973a).

†Data based on nitrogen budget for mixed deciduous forest (Henderson and Harris, 1974).

‡Considers aboveground biomass pool. Cyclic renewal of structural roots (Kolesnikov, 1968) would lower turnover time. Tree mortality is estimated from permanent-plot resurvey (3-year interval) and likely underestimates the mortality rate over the duration of a forest generation.

One obvious omission from this discussion is the role of the chemical-exchange capacity of secondary minerals, but our objective is to define a sufficient set of ecosystem variables. Along gradients of climate and soil development, excluding arid regions, from 30 to 100% of the cation (element) exchange capacity is determined by soil organic matter (Black, 1957). Decay and weathering of soil organic matter also influence chemical reactions of secondary mineral formation. Therefore, accumulation of organic matter in the system, both as an alternate energy base and as an element conservation mechanism, [illegible]rs to influence other biogeochemical processes.

[illegible]here elemental material is chemically fixed or otherwise tightly bound (e.g., entrapment of potassium in the clay lattice structure), we hypothesize that such retention is external to the system and that biological control of transport is minimal; physicochemical processes dominate element accumulations in the soil [illegible]s geologic processes affect further transport among ecosystems.

SUMMARY

The conceptualization of ecosystem function which we have outlined attempts to:

1. Identify a central strategy for the system: we hypothesize that this strategy is to attain maximum persistent biomass.
2. Identify the minimum number of essential state variables: we hypothesize that these variables are an energy base, regulator organisms, and an organic pool.
3. Identify the minimal set of necessary interactions among and between these components and the environment.

This theory is preliminary; data on total ecosystems which will permit critical evaluation of our generalizations are just beginning to emerge. We fervently hope that, in presenting these ideas, we will stimulate an active dialogue that will further advance the theoretical base for ecosystem science. In the interim, each stage in the evolution of a general theory will provide a framework within which to examine progress and suggest future research.

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REFERENCES

Black, C. A., 1957, *Soil-Plant Relationships,* John Wiley & Sons, Inc., New York.

Bolin, B., 1970, The Carbon Cycle, *Sci. Amer.,* **223**(3): 124-146.

Child, G. I., and H. H. Shugart, 1972, Frequency Response Analysis of Magnesium Cycling in Tropical Ecosystems, in *Systems Analysis and Simulation in Ecology,* B. C. Patten (Ed.), Vol. 2, pp. 103-134, Academic Press, Inc., New York.

Duvigneaud, P., and S. Denaeyer-DeSmet, 1970, Biological Cycling of Minerals in Temperate Deciduous Forests, in *Analysis of Temperate Forest Ecosystems,* pp. 199-225, D. E. Reichle (Ed.), Springer-Verlag, New York.

Edwards, N. T., 1974, Oak Ridge National Laboratory, personal communication.

——, W. F. Harris, and H. H. Shugart, 1974, Carbon Cycling in Deciduous Forest, in *The Belowground Ecosystem: A Synthesis of Plant-Associated Processes,* U. S. International Biological Program Interbiome Symposium, Ft. Collins, Colorado, September 1973, in press.

Golley, F. B., 1971, Energy Flux in Ecosystems, in *Ecosystem Structure and Function,* Biology Colloquium, Oregon State University, 1970, pp. 69-90, J. A. Wiens (Ed.), Oregon State University Press, Corvallis.

Gore, A. J. P., and J. S. Olson, 1967, Preliminary Models for Accumulation of Organic Matter in a *Eriophorum/Calluna* Ecosystem, *Aquilo. Ser. Botanica,* 6: 297-313.

Harris, W. F., R. S. Kinerson, Jr., and N. T. Edwards, 1974, Comparison of Belowground Biomass of Natural Deciduous and Loblolly Pine Plantations, in *The Belowground Ecosystem: A Synthesis of Plant-Associated Processes,* U. S. International Biological Program Interbiome Symposium, Ft. Collins, Colo., September 1973, J. K. Marshall (Ed.), in press.

——, P. Sollins, N. T. Edwards, B. E. Dinger, and H. H. Shugart, 1974, Analysis of Carbon Flow and Productivity in a Temperate Deciduous Forest Ecosystem, in *Productivity of World Ecosystems,* International Biological Program Fifth General Assembly, Seattle, September 1972, D. E. Reichle, D. Goodall, and P. T. Baker (Eds.), National Academy of Science, in press.

Harvey, H. W., 1950, On the Production of Living Matter in the Sea off Plymouth, *J. Mar. Biol. Ass. U.K.,* **29**: 97-137.

Henderson, G. S., and W. F. Harris, 1974, An Ecosystem Approach to Characterization of the Nitrogen Cycle in a Deciduous Forest Watershed, in *Forest Soils and Forest Land Management,* B. Bernier and C. H. Winget (Eds.), Laval University Press, Quebec, Canada, in press.

Holling, C. S., 1973, Resilience and Stability of Ecological Systems, *Annu. Rev. Ecol. Syst.,* 4: 1-23.

Jordan, C. F., J. R. Kline, and D. S. Sasscer, 1972, Relative Stability of Mineral Cycles in Forest Ecosystems, *Amer. Natur.,* **106**: 237-253.

Kolesnikov, V. A., 1968, Cyclic Renewal of Roots in Fruit Plants, in Methods of Productivity Studies in Root Systems and Rhizosphere Organisms, International Symposium, USSR, pp. 102-106, reprinted for the International Biological Program by Biddles, Ltd., Guildford, U.K.

Levins, R., 1966, The Strategy of Model Building in Population Biology, *Amer. Sci.*, **54**: 421-431.

Lindeman, R. L., 1942, The Trophic-Dynamic Aspect of Ecology, *Ecology*, **23**: 399-418.

MacArthur, R., and E. O. Wilson, 1967, *The Theory of Island Biogeography*, Princeton University Press, Princeton, N. J.

McBrayer, J. F., D. E. Reichle, and M. Witkamp, 1974, Energy Flow and Nutrient Cycling in a Cryptozoan Foodweb, USAEC Report EDFB-IBP-73-8, Oak Ridge National Laboratory.

Macfadyen, A., 1964, Relation Between Mites and Microorganisms and Their Significance in Soil Biology, *Acarology*, pp. 147-149.

[illegible]nis, J. T., F. B. Golley, R. G. Clements, G. I. Child, and M. J. Duever, 1969, [illegible]lemental and Hydrologic Budgets of the Panamanian Tropical Moist Forest, *Bioscience*, **19**: 697-700.

May, R. M., 1973a, *Stability and Complexity in Model Ecosystems*, Princeton University Press, Princeton, N. J.

——, 1973b, Time-Delay Versus Stability in Population Models with Two and Three Trophic Levels, *Ecology*, **54**: 315-325.

Mignolet, R., 1972, Etat Actuel des Connaissances sur les Relations Entre la Microfaune et la Microflori Edaphiques, *Rev. Ecol. Biol. Sol.*, **9**: 655-670.

Nef, L., 1957, Etat Actuel des Connaissances sur le Rôle des Animaux dans la Decomposition des Litières de Forets, *Agricultura*, **5**: 245-316.

Odum, H. T., 1971, *Environment, Power and Society*, John Wiley & Sons, Inc., New York.

——, and R. F. Pigeon (Eds.), 1970, A Tropical Rain Forest: A Study of Irradiation and Ecology at El Verde, Puerto Rico, USAEC Report TID-24270, U. S. Atomic Energy Commission.

Olson, J. S., 1965, Equations for Cesium Transfer in a *Liriodendron* Forest, *Health Phys.*, **11**: 1385-1392.

Reichle, D. E., B. E. Dinger, N. T. Edwards, W. F. Harris, and P. Sollins, 1973a, Carbon Flow and Storage in a Woodland Ecosystem, in Carbon and the Biosphere, pp. 345-365, G. M. Woodwell and E. V. Pecan (Eds.), Proceedings of the 24th Brookhaven Symposium in Biology, Upton, N. Y., May 16–18, 1972, USAEC Report CONF-720510, Brookhaven National Laboratory.

——, R. A. Goldstein, R. I. Van Hook, and G. J. Dodson, 1973b, Analysis of Insect Consumption in a Forest Canopy, *Ecology*, **54**: 1076-1084.

Riley, G. A., 1956, Oceanography of Long Island Sound, 1952-54. IX. Production and Utilization of Organic Matter, *Bull. Bingham Oceanogr. Coll.*, **15**: 324-344.

Satchell, J. E., 1971, Feasibility Study of an Energy Budget for Meathop Wood, in *Productivity of Forest Ecosystems*, pp. 619-630, P. Duvigneaud (Ed.), UNESCO, Paris.

Shugart, H. H., W. F. Harris, N. T. Edwards, and B. S. Ausmus, 1974, Modeling of the Belowground Processes Associated with Roots in Deciduous Forest Ecosystems, in *The Belowground Ecosystem: A Synthesis of Plant-Associated Processes*, U. S. International Biological Program Interbiome Symposium, Ft. Collins, Colo., September 1973, in press.

Taylor, F. G., Jr., 1974, Phenodynamics of Production in a Mesic Deciduous Forest, in *Phenological and Seasonality Modeling*, H. Leith and F. Stearns (Ed.), Springer-Verlag, New York, in press.

Tilly, L. J., 1968, The Structure and Dynamics of Cone Spring, *Ecol. Monogr.*, **38**: 169-197.

Van der Drift, J., and M. Witkamp, 1960, The Significance of the Breakdown of Oak Litter by *Enoicylla pusilla* Burm, *Archs. Néerl. Zool.*, **13**: 486-492.

Waide, J. B., 1974, University of Georgia, personal communication.

Watt, K. E. F., 1973, *Principles of Environmental Science*, McGraw-Hill Book Company, New York.

Whitfield, D. W. A., 1972, Systems Analysis, in Devon Island Project, International Biological Program, High Arctic Ecosystem, pp. 392-409, L. C. Bliss (Ed.), Department of Botany, University of Alberta, Edmonton, Alberta, Canada.

Whittaker, R. H., 1961, Experiments with Radiophosphorus Tracer in Aquarium Microcosms, *Ecol. Monogr.*, **31**: 157-188.

——, and G. M. Woodwell, 1971, Evolution of Natural Communities, in *Ecosystem Structure and Function,* Biology Colloquium, Oregon State University, 1970, pp. 137-159, J. A. Wiens (Ed.), Oregon State University Press, Corvallis.

Wiegert, R. G., and D. F. Owen, 1971, Trophic Structure, Available Resources and Population Density in Terrestrial Versus Aquatic Ecosystems, *J. Theor. Biol.*, **30**: 69-81.

Witkamp, M., and D. A. Crossley, 1966, The Role of Arthropods and Microf[illegible] Breakdown of White Oak Litter, *Pedobiologia,* 6: 293-303.

ERA

A PRELIMINARY COMPARTMENT MODEL OF THE NITROGEN CYCLE IN A DECIDUOUS FOREST ECOSYSTEM

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ABSTRACT

A compartment model of nitrogen storage and transfer in a mature hardwood forest at Coweeta Hydrologic Laboratory is described and discussed. Most of the nitrogen in this ecosystem is localized in large storage compartments that turn over slowly. Over 80% of the total nitrogen is in soil organic matter, with about 11% in vegetation, 3% in litter, 4% in microbes, and 2% in free soil pools. Uptake of nitrogen is estimated to be 141.6 kg ha^{-1} $year^{-1}$, of which about 10% is retained within the vegetation. A quantitatively large pool of nitrogen is shown to recycle annually within plants, a strategy which contributes to nitrogen conservation. Calculations suggest that litter inputs to soil organic pools are dominated by belowground material, especially small roots and mycorrhizae. In the soil available nitrogen seems to be rapidly immobilized by soil biota or taken up by the root–mycorrhizae complex, with very little nitrogen being lost from the system in stream water or via denitrification. The picture that emerges from this study is that of a dynamic cycle in which nitrogen is efficiently retained and recycled within the ecosystem. The importance of obtaining additional information on belowground processes, as well as of employing qualitative or theoretical considerations to fill gaps in current knowledge, is stressed.

The productivity of any natural ecosystem depends to a large extent on the system's ability to conserve and recycle its nutrient resources. Although multiple abiotic processes ensure that essential resources are retained and recirculated within ecosystems, the depletion or shortage of a given nutrient often retards or limits the progress of ecosystem development. Nitrogen especially seems to limit the productivity of diverse ecosystems.

Most research into nitrogen dynamics has been conducted on agronomic systems, which tend to be both simpler and more completely understood than natural systems. In recent years, however, several investigators have attempted to

trace the pathways of nitrogen movement in natural terrestrial ecosystems, including deserts (West, 1974); grasslands (Reuss and Cole, 1973; Reuss, 1974); Douglas fir forests (Cole, Gessel, and Dice, 1967); spruce and beech forests (Tamm, 1968; Ulrich, 1971); temperate deciduous forests (Denaeyer-DeSmet, 1971; Duvigneaud and Denaeyer-DeSmet, 1970; 1971; Henderson and Harris, 1974); tropical forests (Edmisten, 1970); and several forest types in Japan and Thailand (Tsutsumi, 1971). Ellenberg (1971) summarized data from several ecosystem types, and Rodin and Bazilevich (1967) presented extensive data on numerous ecosystems.

With few exceptions, previous studies of nitrogen dynamics in terrestrial ecosystems have ignored fundamental pathways in the total cycle. The magnitude of these poorly understood transfers must be estimated and evaluated in relation to the more well-known processes if an accurate picture of the nitrogen cycle is to emerge. In this paper we describe functionally and quantitatively the distribution of nitrogen in a temperate deciduous-forest ecosystem, estimate the rates of important internal nitrogen transfers, and describe the various system inputs and outputs.

EXPERIMENTAL SITE

Research was conducted on watershed 18 (WS18) at the Coweeta Hydrologic Laboratory, Franklin, N. C. Since 1969 the natural and manipulated watersheds at Coweeta have served as a study area for cooperative research into nutrient circulation in forested ecosystems between the Institute of Ecology, University of Georgia, and the Forest Service, U. S. Department of Agriculture. The advantages of using small watersheds as experimental units and for the study of nutrient cycles is well established (Hewlett, Lull, and Reinhart, 1969; Bormann and Likens, 1967). A well-documented history of hydrologic and climatological monitoring exists for Coweeta watersheds.

The model described is of a control hardwood watershed (WS18) vegetated by a mature oak–hickory forest. Johnson and Swank (1973) described both the Coweeta basin and WS18.

THE MODEL

The data on the nitrogen cycle of WS18 have been synthesized in the form of a compartment model of nitrogen storage and transfer. In this section we discuss the model compartmentalization and consider the data sources consulted in its quantification. In later sections we will discuss the actual quantification.

Inputs and Outputs

The mass transfers of nitrogen into and out of WS18 result from the combined activity of biological and physical processes. Total inputs of nitrogen

(14.3 kg N ha^{-1} $year^{-1}$) are composed of meteorological inputs from precipitation and dryfall (3.4 kg N ha^{-1} $year^{-1}$) and biotic gaseous inputs as nitrogen fixation (10.9 kg N ha^{-1} $year^{-1}$). Total nitrogen losses from WS18 (18.51 kg N ha^{-1} $year^{-1}$) can be partitioned into dissolved losses in stream water (0.08 kg N ha^{-1} $year^{-1}$), losses in sediments (0.23 kg N ha^{-1} $year^{-1}$), and biotic gaseous losses as denitrification (18.20 kg N ha^{-1} $year^{-1}$).

These data show that both input and output of nitrogen are dominated by biotic gaseous transformations (Todd, Waide, and Cornaby, this volume). Comparing cumulative inputs and outputs, we see that this ecosystem is apparently losing nitrogen to the surrounding environment. Nitrogen inputs are being monitored incompletely, however. For example, nitrogen fixation by canopy epiphytes contributes significantly to the nitrogen budgets of forest ecosystems (Edmisten and Kline, 1968; Jones, 1970). This source of nitrogen has not yet been quantified for WS18. Another possible cause for the discrepancy between nitrogen input and output relates to the fact that meteorological inputs have been determined only in terms of water-soluble nitrogen; organic nitrogen in dryfall was not detected in the analyses performed (Swank and Henderson, 1974). Closing these two data gaps may reveal a closer agreement between inputs and outputs of nitrogen or may show that the system is slowly accumulating rather than losing nitrogen. Other aspects of these input–output data are discussed by Todd, Waide, and Cornaby (this volume).

Compartments and Flows

The model is defined as a 15-compartment system (Table 1). These compartments can be divided into five plant components—reproductive parts, leaves, branches, stems, and roots; three litter components—woody litter, O1 litter, and O2 litter; three soil pools—soil organic matter, NO_3–N, and NH_4–N; two faunal components—aboveground consumers and litter–soil fauna; and two microbial components—litter–soil microflora and mycorrhizal fungi. For the purposes of the model, "stem" is the entire stump, including that belowground. Transfers of nitrogen among these compartments are depicted in Fig. 1.

Data Sources

Table 2 lists the major sources for data synthesized in the model by the compartment for which the indicated source is appropriate. These same references also apply to nitrogen flows among the indicated compartments.

In quantifying this model we attempted to use data collected on WS18 whenever possible. For many compartments and transfers, especially aboveground, this was possible. For other compartments and flows, however, especially belowground, no data or only preliminary data exist. In such cases we did not hesitate to use preliminary values, numbers derived from literature

TABLE 1

ESTIMATED STANDING CROPS OF NITROGEN AND ESTIMATED TURNOVER RATES AND TIMES OF NITROGEN POOLS IN A MATURE HARDWOOD FOREST (WS18) AT COWEETA

Compartment	Standing crop		Turnover rate per year*	Turnover time,* years
	Kg N/ha	% of total		
Reproductive parts	2.738	0.06	1.084	0.923
Leaves	94.98	1.97	0.884	1.131
Branches	115.6	2.39	0.037	26.75
Stems	194.2	4.02	0.002	653.9
Roots	150.7	3.12	0.280	3.572
Herbivores	0.388	0.01	17.08	0.058
Woody litter	40.27	0.83	0.308	3.242
O1 litter	34.58	0.72	0.682	1.467
O2 litter	62.41	1.29	0.192	5.197
Soil organic matter	3873	80.19	0.007	149.6
Soil fauna	2.033	0.04	11.25	0.089
Microflora	77.56	1.61	6.451	0.155
Mycorrhizae	94.95	1.97	0.955	1.047
NO_3–N	33.60	0.70	5.335	0.187
NH_4–N	52.92	1.10	5.336	0.187
Total system	4830	100.0		

*Estimates for branches and stems include only mortality losses rather than total losses. The value for soil organic matter does not include inputs to this pool from roots, mycorrhizae, consumers, and soil fauna, which are subsequently metabolized by soil microflora.

sources, or theoretical considerations. Given our incomplete knowledge of nitrogen cycling in terrestrial ecosystems, it seems that we may get a potentially more-distorted view of the total cycle by ignoring critical but unmeasured pathways than by including preliminary but reasonable estimates of the unknown values. Critical evaluation of the estimated values in relation data-based numbers, as well as in a modeling framework, should reveal information about the processes which could not have been obtained if the unmeasured transfer had been ignored.

Nitrogen Distribution

Table 1 estimates the standing crops of nitrogen in the 15 model compartments and the turnover of these nitrogen pools. These data reflect standing crops found on WS18 before leaf drop in late fall. Nearly all the values

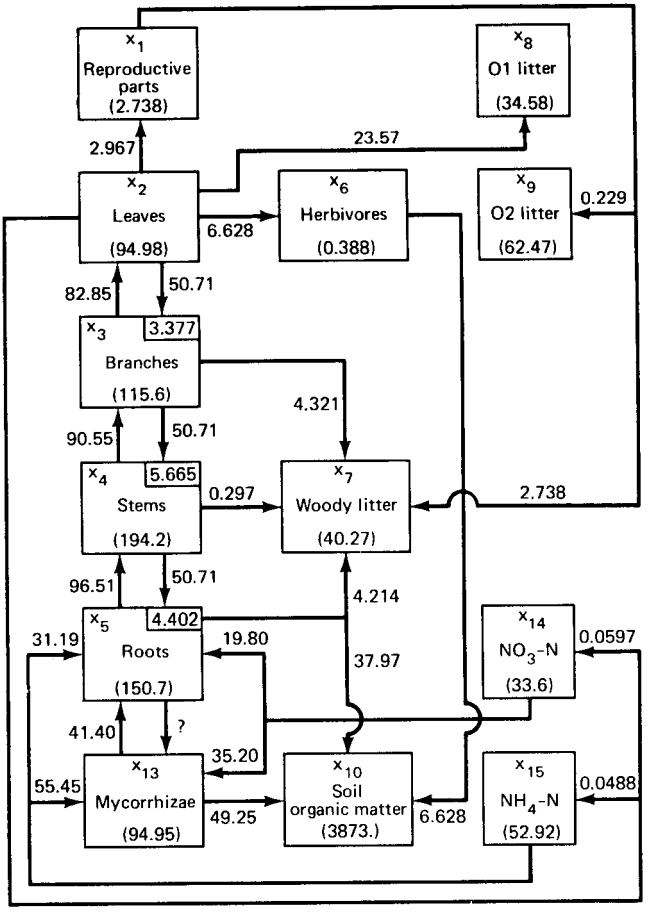
TABLE 2

SOURCES OF DATA SYNTHESIZED IN THE CURRENT MODEL

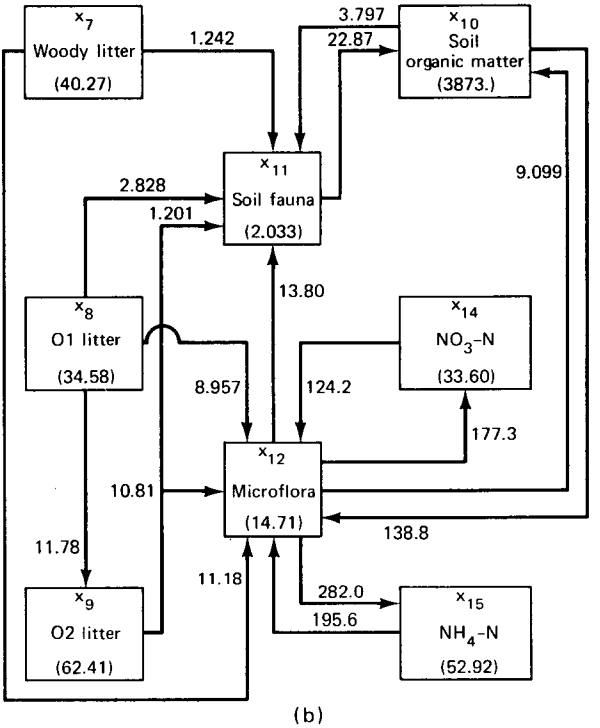
Compartment	Nitrogen standing crop	Biomass	Nitrogen concentration
Reproductive parts	Cromack (1973) Day (1974) McGinty (1972)		
Leaves	Day (1974)		
anches		Day and Monk (1974)	Cromack (1973)
ems		Day and Monk (1974) McGinty (1974)	Henderson (1971)
Roots		McGinty (1974) Harris, Kinerson, and Edwards (1974)	Duvigneaud and Denaeyer-DeSmet (1970)
Herbivores		Crossley (1974) Nabholz (1973)	King (1957)
Woody litter	Cromack (1973)		
O1 litter	Todd (1974b)		
O2 litter	Todd (1974b)		
Soil organic matter	Todd (1974b)		
Soil fauna		Gist (1972) Bornebusch (1930)	McBrayer, Reichle, and Witkamp (1973)
Soil microflora		Todd (1974)	
Mycorrhizae		McGinty (1974) Todd (1974b) Harris, Kinerson, and Edwards (1974)	
NO_3–N	Todd (1974b)		
NH_4–N	Todd (1974b)		

in Table 1 are data based, at least with respect to biomass if not to nitrogen pool size. Several nitrogen concentrations were taken from literature sources (Table 2). The value shown for microflora is based on biomass measurements given by Todd (1974a), assuming a nitrogen concentration of 5% of dry weight. he biomass of soil fauna was taken from Gist (1972) and incremented to ccount for unmeasured groups. Very little data on mycorrhizal biomass exist for any ecosystem. We estimated a biomass of 1900 kg/ha dry weight on the basis of preliminary electron microscope and microprobe analysis by Todd (1974b) and of root studies of McGinty (1974). The nitrogen pool size was again estimated assuming a nitrogen concentration of 5%.

The standing-crop data show that over 80% of the total nitrogen in this forest ecosystem is localized in soil organic matter. The rest is split among vegetation (11.4%). litter pools (2.8%), soil biota (3.6%), and free soil pools (1.8%). Turnover times of these nitrogen pools range from very fast for soil biota


x1
Reproductive parts
(2.738)
x8
O1 litter
(34.58)
2.967
23.57
x2
Leaves
(94.98)
6.628
x6
Herbivores
(0.388)
x9
O2 litter
(62.47)
0.229
82.85
50.71
x3
3.377
Branches
(115.6)
4.321
90.55
50.71
x4
5.665
Stems
(194.2)
0.297
x7
Woody litter
(40.27)
2.738
96.51
50.71
4.214
x5
4.402
Roots
(150.7)
31.19
19.80
37.97
x14
NO3-N
(33.6)
0.0597
41.40
?
35.20
55.45
x13
Mycorrhizae
(94.95)
49.25
x10
Soil organic matter
(3873.)
6.628
x15
NH4-N
(52.92)
0.0488

(a)



1 Compartment model of the nitrogen cycle in a mature hardwood forest (WS18) at Coweeta Hydrologic Laboratory. Values in parentheses inside boxes are standing crops of nitrogen (kg N/ha); values in the small rectangles in x_3, x_4 and x_5 are net increments of nitrogen in new biomass (kg N ha^{-1} $year^{-1}$). Numbers on arrows are intercompartmental transfers of nitrogen (kg N ha^{-1} $year^{-1}$). The total compartment diagram is split into two parts for ease of understanding (several compartments are sh[illegible] both parts). Part a summarizes nitrogen transfers within plant compartments, from plants to litt[illegible]pools, and from soil pools to plants. Part b summarizes transfers associated with litter decomposition and nitrogen regeneration.

and free nitrogen pools to extremely slow for soil organic matter and stems. The value given for stems is probably a large overestimate because of the lack of a good estimate of tree mortality (Cromack, 1973). Thus it is obvious that most of the nitrogen in this ecosystem is tied up in long-term storage, with only a small fraction in pools that turn over rapidly.

Annual Nitrogen Transfers

Figure 1 depicts the annual transfers of nitrogen among the model compartments, in units of kilograms of nitrogen per hectare per year. In this section we indicate which flows represent actual field measurements and how other transfers were calculated. In this discussion the symbolism A_{ij} represents the transfer of nitrogen from compartment x_j to x_i ($i, j = 1, 2, \ldots, 15$).

In the model gaseous inputs and outputs of nitrogen enter and leave the microbial pool (x_{12}). Meteorological inputs were divided between leaves (33%) and free nitrogen pools (67%). Nitrogen outputs in stream water and sediments occur from NO_3 and NH_4 pools.

Data for all nitrogen transfers from aboveground vegetation to litter pools (woody litter, O1 litter, and O2 litter) were taken from Cromack (1973) and McGinty (1972). Best (1974) provided data on leaching losses to soil pools ($A_{14,2}$ and $A_{15,2}$). Data for annual increments of branches (x_3) and stems (x_4) follow Day and Monk (1974). Percentage root increment was set equal to the percent increment of branches.

The total transfer of nitrogen from branches to leaves (A_{23}) was measured by Day (1974) as 82.85 kg N ha^{-1} $year^{-1}$. Herbivorous consumption of leaves (A_{62}) was estimated as 8% of this value (i.e., 8% of leaf net primary production). Under a mass balance assumption, output from consumers to soil organic matter ($A_{10,6}$) was set equal to consumption. Similarly, transfer of nitrogen from leaves to reproductive parts (A_{12}) was set equal to total losses from x_1.

Mortality of roots and mycorrhizae was estimated from literature sources. Following Harris, Kinerson, and Edwards (1974), we assumed that small roots (<0.5 cm in diameter) turn over annually ($A_{10,5}$). These investigators measured this root fraction as 21% of total root biomass. We set the proportional mortality of large roots (>0.5 cm) equal to that of branches (A_{75}). In addition we assumed that 50% of mycorrhizae turn over annually with the small roots and the remaining 50% follow the large-root mortality rate. These two values were summed as a single transfer from mycorrhizae to soil organic matter ($A_{10,13}$).

Comparing the summed losses of nitrogen from leaves (litterfall, consumption, and transfer to reproductive parts) with the measured inputs (about 84 kg N ha^{-1} $year^{-1}$, including precipitation) reveals that about 51 kg N ha^{-1} $year^{-1}$ is not accounted for in these losses We assumed that this amount of nitrogen was translocated to branches (A_{32}) before leaf abscission. Since we had

no information about the site where this nitrogen is stored until the following spring, when it is again mobilized for new growth, we set the flows from branches to stems (A_{43}) and from stems to roots (A_{54}) equal to this same value, thus assuming that this internally recycled pool of nitrogen is stored entirely in roots during the dormant season.

These assumptions allow total nitrogen uptake to be estimated as the sum of vegetation increments plus vegetation losses to litter and soil pools and to consumers minus precipitation inputs to leaves. These calculations yield an estimate of nitrogen uptake of 141.6 kg N ha^{-1} $year^{-1}$. To partition total uptake between roots and mycorrhizae, we assumed that 80% of uptake occurs via the small root component (80% of which is mediated by mycorrhizal fungi) and that uptake of NO_3 and NH_4 is proportional to the respective relative pool sizes. These assumptions allowed us to estimate the transfers $A_{5,14}$, $A_{5,15}$, $A_{13,14}$, and $A_{13,15}$. Although these calculations allowed us to quantify unmeasured transfers and hence to complete the model for simulation purposes, undue significance should not be attached to the resultant values. We are currently initiating research in these areas in an attempt to improve estimates of these transfers.

The transfer of nitrogen from mycorrhizae to roots ($A_{5,13}$) was calculated as uptake less mycorrhizal mortality. This value represents a net one-way flow. We have no information on any possible backflow of nitrogen from roots to mycorrhizae ($A_{13,5}$). Nitrogen flow from roots to stems (A_{45}) was estimated as input to roots from mycorrhizae ($A_{5,13}$) plus direct uptake by roots from soil minus root increment and mortality plus the amount of nitrogen recycling within the vegetation (A_{32}). The remaining transfer involving vegetation pools, that from stems to branches (A_{34}), was set equal to input to stems from roots (A_{45}) less stem increment and mortality.

Several interesting trends emerge from these calculations. Table 3 compares the estimates of nitrogen taken up by the vegetation, retained in plant increments, and returned to litter pools with the pools of nitrogen in the vegetation and soil. These values show that only about 10% of the nitrogen taken up by the vegetation is retained; the rest is returned to the soil as litter. An amount of nitrogen equal to 164 and 25% of the soil and vegetation pools, respectively, is estimated to be taken up annually, but only 16 and 2%, respectively, are actually retained within the plant compartments.

The demonstration that a large pool of nitrogen is recycled annually within the vegetation compartments reveals the existence of an important mechanism for nutrient conservation within this forest ecosystem. The cycling of nitrogen internally, by translocating nitrogen out of leaves before leaf fall, decreases the need for newly acquired nitrogen each spring. Although the estimate of the magnitude of this nitrogen transfer may be slightly in error, the existence of the transfer is firmly established by measurements both of the nitrogen content of leaves through time (Day, 1974) and of litterfall (Cromack, 1973) and

TABLE 3

MACROSCOPIC PROPERTIES OF THE NITROGEN CYCLE IN A MATURE HARDWOOD FOREST (WS18) AT COWEETA

	Uptake*	Retained*	Returned*
Amount, kg N/ha			
Aboveground	45.80	9.04	37.89
Belowground	95.84	4.40	91.43
Total	141.6	13.44	129.3
Percent of available nutrient pools†	163.7	15.5	149.4
Percent of vegetation‡	25.4	2.4	23.2
Percent of uptake §		9.5	91.3

*Uptake = retained + returned nitrogen minus precipitation inputs to canopy. "Retained" is nitrogen in the vegetation increments; "returned" refers to total nitrogen returned to soil pools.

†"Available nutrient pools" refers to the NO_3 and NH_4 pools. The values are the percentages of nitrogen contained in the available nutrient pools which are taken up, retained, and returned.

‡These values are the percentages of the total nitrogen contained in vegetation pools which are taken up, retained, and returned.

§These values are the percentages of the total nitrogen uptake which are retained and returned.

throughfall (Best, 1974). Quantitatively this internal recycling in plants accounts for over half the total transfer of nitrogen from roots to stems. This transfer also represents over 200% of the nitrogen contained in annual litterfall. A similar pattern has been demonstrated for potassium in this ecosystem but not for calcium, which is relatively immobile in the phloem (Waide and Swank, 1974).

Table 4 presents estimates of transfers of nitrogen from vegetation to litter pools. Of the total amount, over 70% is estimated to emanate from belowground sources. Turnover of mycorrhizae and small roots seems to be especially important in this regard. These values are based on numerous assumptions, and collectively they emphasize the need to obtain improved information on the functional roles of these two compartments in forest nutrient cycles.

The remainder of the internal transfers, namely, those associated with decomposition and nutrient regeneration, are also shown in Fig. 1. The woody litter compartment on WS18 is dominated by decaying logs of American chestnut (*Castanea dentata*), which probably fell in the 1930s after arrival of the chestnut blight at Coweeta. The current model must account for the decay of

this material. To quantify this process, we proceeded as follows: Kovner (1955) estimated the chestnut basal area on WS18 to be 8.44 m^2/ha in 1934. Using diameter at breast height and biomass regression equations (Sollins and Anderson, 1971), we estimated a biomass of chestnut stems of 40,480 kg/ha in 1934. Assuming exponential decay of chestnut logs in the subsequent 40 years and given a current estimate of 11,844 kg/ha for the standing crop of chestnut logs (Cromack, 1973), we calculated a decay rate of 0.03072 per year for this material. Multiplying this value by the current standing crop of chestnut logs and

TABLE 4

ESTIMATED INPUTS OF NITROGEN TO LITTER POOLS IN A MATURE HARDWOOD FOREST (WS18) AT COWEETA

Source	Nitrogen transfer	
	kg N/ha	% of total
Aboveground		
O1 litter	23.57	18.24
Reproductive parts	2.967	2.30
Woody litter	4.618	3.57
Frass	6.628	4.50
Subtotal	37.78	29.24
Belowground		
Large roots	4.214	3.26
Small roots	37.97	29.38
Mycorrhizae	49.25	38.11
Subtotal	91.43	70.76
Total	129.2	100.0

then multiplying the resulting number by the nitrogen concentration of chestnut logs (Cornaby and Waide, 1973), we estimated a current chestnut decay of 0.848 g N ha^{-1} $year^{-1}$.

Assuming mass balance of the nonchestnut woody litter, we calculated total output of nitrogen from woody litter as the sum of the chestnut loss plus total inputs to the compartment from vegetation. We further assumed that 10% of this sum is consumed by soil fauna ($A_{11,7}$) and 90% is metabolized by microflora ($A_{12,7}$).

Total output of nitrogen from O1 litter was set equal to total input. This output was then partitioned among several flows based on litter-bag studies,

especially on differences between first-year loss rates of nitrogen and dry weight, and on faunal exclusion studies employing naphthalene (Cromack, 1973). These calculations yielded relative transfers of 12% O1 litter to fauna ($A_{11,8}$), 38% to microflora ($A_{12,8}$), and 50% directly to O2 litter (A_{98}).

Flows of nitrogen out of O2 litter were again equated with inputs. This total loss was broken down as 10% to fauna ($A_{11,9}$) and 90% to microflora ($A_{12,9}$).

Inputs to soil organic matter include frass from aboveground consumers, dead roots (<0.5 cm), and mycorrhizae. We assumed that all the frass and mycorrhizal inputs and 90% of roots are metabolized by microflora and remaining 10% of roots are consumed by fauna ($A_{11,10}$).

All flows into soil fauna have been discussed except that from microflora ($A_{11,12}$). We assumed that this faunal compartment is composed of decomposing reducers, fungivores, and bacterial feeders in the proportions 0.5 : 0.25 : 0.25. On the basis of assumed turnover rates of these three fractions, we calculated an output from soil fauna ($A_{10,11}$) of 22.87 kg N ha^{-1} $year^{-1}$. Consumption of microflora was thus set equal to 13.8 kg N ha^{-1} $year^{-1}$ to balance total inputs with output.

The assumption of steady state for the microflora, NO_3, and NH_4 compartments leads to the calculation of the following net one-way flows: from microflora to NO_3, 53.13 kg N ha^{-1} $year^{-1}$; from microflora to NH_4, 86.42 kg N ha^{-1} $year^{-1}$; and from soil organic matter to microflora, 129.7 kg N ha^{-1} $year^{-1}$. Equations derived from mass flows of carbon and nitrogen and from the following assumed carbon-to-nitrogen ratios of decaying materials were used to calculate the individual flows of these three two-way transfers: average plant litter, 50 : 1; mycorrhizae and microflora, 10 : 1; consumer frass and soil fauna excreta, 25 : 1; and soil organic matter, 20 : 1. These calculations complete the quantification of the nitrogen model.

Several interesting trends are suggested by these decomposition-related transfers. Table 5 compares the various outputs from the microbial pool. Although based on many assumptions, these values suggest that the transfers of nitrogen which occur in the soil may be much more dynamic than we would expect if only net flows were considered. Over six times more nitrogen is estimated to flow through this compartment annually than is contained within it. Losses of nitrogen from the microflora are dominated by mineralization to NO_3 and NH_4. Only a small fraction of the total output is lost from the system through denitrification.

Table 5 also presents estimates of total annual transfers from the NH_4 pool to other compartments in this watershed ecosystem. These values again suggest a dynamic, rapidly turning over pool of nitrogen in the soil. Nearly 70% of total outputs from NH_4 is estimated to be taken up by microflora, and about 30% is taken up by the root–mycorrhiza complex. Only an extremely small proportion of the total output of NH_4 is lost from the ecosystem in stream water and sediments.

Comparing inputs to and outputs from soil organic matter shows this compartment to be losing nitrogen at a current rate of 16.8 kg N ha^{-1} $year^{-1}$. All other model compartments, except those for which increments were measured or calculated, are balanced. It is not clear at present what the significance of this net loss is or even whether it is real. However, the large input of organic material to the litter–soil subsystem of this forested watershed after the chestnut blight may be involved. This compartment may now be decaying to a new steady-state level following the metabolism of this chestnut input over the last 40 years.

TABLE 5

ESTIMATED TRANSFERS OF NITROGEN FROM THE MICROBIAL AND AMMONIUM POOLS TO SELECTED COMPARTMENTS IN A MATURE HARDWOOD FOREST (WS18) AT COWEETA

Donor compartment	Recipient compartment	Nitrogen transfer		Transfer rate per year
		Kg N/ha	% of total	
Microflora	Soil organic matter	9.10	1.82	0.117
	NO_3–N	177.3	35.43	2.286
	NH_4–N	282.0	56.35	3.636
	Soil fauna	13.8	2.76	0.180
	Denitrification	18.2	3.64	0.235
	Total	500.4	100.0	6.454
NH_4–N	Microflora	195.6	69.26	3.696
	Mycorrhizae	55.45	19.63	1.048
	Roots	31.19	11.04	0.589
	Stream water	0.040	0.01	0.0008
	Sediments	0.141	0.05	0.0027
	Total	282.4	99.99	5.336

DISCUSSION AND CONCLUSIONS

The dominant picture of the nitrogen cycle in the oak–hickory forest on WS18 which emerges from this study is one of a dynamic cycle in which nitrogen is efficiently conserved and recycled within the system. Most of the nitrogen contained within the ecosystem is localized in soil organic matter and vegetation pools, which turn over slowly. Thus only a small amount of the total nitrogen in the system is recycling at any one time and, therefore, is susceptible to loss from the system. A mobile pool of nitrogen recycles annually within the vegetation, thereby providing sufficient nitrogen for physiological processes while decreasing the dependence of plants on nitrogen recycled through soil pools. This is certainly a strategy geared to nitrogen conservation.

Decomposition processes and synergistic interactions among soil biota within the soil also foster nutrient retention and recirculation. Only small pools of free nitrogen are present at any given time. Most of the NO_3 or NH_4 that becomes available seems to be rapidly immobilized by microflora or taken up by the root–mycorrhizae complex. These belowground processes are poorly understood at present. The role of mycorrhizal fungi in ecosystem nutrient cycles is an especially critical area where research is needed. The large predominance of belowground over aboveground inputs to pools of decaying organic matter may be another factor contributing to efficient cycling of nitrogen. Belowground litter inputs may decay more rapidly than aboveground sources, yielding their contained nutrients to soil biota for recycling. Interactions between root sloughing, mycorrhizal death, and belowground decomposer organisms and the implications of these interactions for ecosystem nutrient cycles are other areas where data are lacking.

The purposes of this modeling effort were twofold. The primary task was to synthesize available information on nitrogen dynamics in a hardwood watershed at Coweeta and to examine the implications of this initial synthesis. Second, the model was undertaken to identify gaps in our knowledge and to assist in planning future research in these areas. Although many of the results presented in this paper rely on assumptions concerning nitrogen standing crops and transfers, much of the discussion relies on actual field measurements. The trends suggested by our assumptions are probably qualitatively accurate if not quantitatively so. We must emphasize, however, that the compartment model described herein is preliminary and, hence, should be viewed as an initial effort, to be refined and corrected as better information becomes available.

Further work on the model is following three lines. First, ongoing research at Coweeta is attempting to improve our understanding of the processes involved. Second, simulations involving the model described will help us to understand the consequences of the assumptions made and to improve them where possible. Finally, the nitrogen model will eventually be coupled to a model of cation dynamics to provide a unified model of the transfers of cations and nitrogen in this ecosystem as influenced by various abiotic parameters. Since a complete understanding of the nitrogen cycle for any terrestrial ecosystem may be far away, it is important that we fill holes in our knowledge with qualitative or theoretical considerations. This is one of the major roles that modeling can play in ecosystem analysis.

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REFERENCES

Best, G. R., 1974, University of Georgia, unpublished data.

Bormann, F. H., and G. E. Likens, 1967, Nutrient Cycling, *Science,* **155**: 424-429.

Bornebusch, C. H., 1930, The Fauna of Forest Soil, *Forsögswaesen Copenhagen,* **11**: 1-224.

Cole, D. W., S. P. Gessel, and S. F. Dice, 1967, Distribution and Cycling of Nitrogen, Phosphorus, Potassium, and Calcium in a Second-Growth Douglas Fir Ecosystem, in *Symposium on Primary Productivity and Mineral Cycling in Natural Ecosystems,* H. E. Young (Ed.), pp. 197-232, University of Maine Press, Orono.

Cornaby, B. W., and J. B. Waide, 1973, Nitrogen Fixation in Decaying Chestnut Logs, *Plant and Soil,* **39**: 445-448.

Cromack, K., Jr., 1973, Litter Production and Decomposition in a Mixed Hardwood Watershed and a White Pine Watershed at Coweeta Hydrologic Station, North Carolina, Ph. D. Thesis, University of Georgia, Athens.

Crossley, D. A., Jr., 1974, University of Georgia, unpublished data.

Day, F. P., Jr., 1974, Primary Production and Nutrient Pools in the Vegetation on a Southern Appalachian Watershed, Ph. D. Thesis, University of Georgia, Athens.

——, and C. D. Monk, 1974, Vegetation Patterns on a Southern Appalachian Watershed, *Ecology,* **55**: 1064-1074.

Denaeyer-DeSmet, S., 1971, Teneurs en Eléments Biogènes des Tapis Végétaux dans les Forêts Caducifoliées d'Europe, in *Productivity of Forest Ecosystems,* Proceedings of the UNESCO Brussels Symposium, P. Duvigneaud (Ed.), pp. 515-525, Unipub, Inc., New York.

Duvigneaud, P., and S. Denaeyer-DeSmet, 1971, Cycle des Eléments Biogènes dans les Ecosystèmes Forestiers d'Europe (Principalement Forêts Caducifoliées), in *Productivity of Forest Ecosystems,* Proceedings of the UNESCO Brussels Symposium, P. Duvigneaud (Ed.), pp. 527-542, Unipub, Inc., New York.

——, and S. Denaeyer-DeSmet, 1970, Biological Cycling of Minerals in Temperate Deciduous Forests, in *Analysis of Temperate Forest Ecosystems,* D. E. Reichle (Ed.), pp. 199-225, Springer-Verlag, New York.

misten, J. A., 1970, Preliminary Studies of the Nitrogen Budget of a Tropical Rain Forest, in *A Tropical Rain Forest: A Study of Irradiation and Ecology at El Verde, Puerto Rico,* H. T. Odum and R. F. Pigeon (Eds.), USAEC Report TID-27270, pp. H-211–H-215, U. S. Atomic Energy Commission.

——, and J. R. Kline, 1968, Nitrogen Fixation by Epiphyllae, in The Rain Forest Project Annual Report, USAEC Report PRNC-119, pp. 141-143, Puerto Rico Nuclear Center.

Ellenberg, H., 1971, Nitrogen Content and Mineral Cycling, in *Productivity of Forest Ecosystems,* Proceedings of the UNESCO Brussels Symposium, P. Duvigneaud (Ed.), pp. 509-514, Unipub, Inc., New York.

Gist, C. S., 1972, Analysis of Mineral Pathways in a Cryptozoan Foodweb, Ph. D. Thesis, University of Georgia, Athens.

Harris, W. F., R. S. Kinerson, and N. T. Edwards, 1974, Comparison of Belowground Biomass of Natural Deciduous Forests and Loblolly Pine Plantations, in *The Belowground Ecosystem: A Synthesis of Plant Associated Processes,* U. S. International Biological Program Interbiome Symposium Fort Collins, Colo., September 1973, J. K. Marshall (Ed.), in press.

Henderson, G. S., 1971, Nutrient Concentrations in Woody Components of Sixteen Tree Species, Eastern Deciduous Forest Biome Memo Report 71-90, U. S. International Biological Program, Oak Ridge National Laboratory.

——, and W. F. Harris, 1974, An Ecosystem Approach to Characterization of the Nitrogen Cycle in a Deciduous Forest Watershed, in Proceedings of Fourth North Amer[illegible] Forest Soils Conference, Quebec, August 1974, in press.

Hewlett, J. D., H. W. Lull, and K. G. Reinhart, 1969, In Defense of Experimental Watersheds, *Water Resour. Res.,* 5: 306-316.

Johnson, P. L., and W. T. Swank, 1973, Studies of Cation Budgets in the Southern Appalachians on Four Experimental Watersheds with Contrasting Vegetation, *Ecology,* 54: 70-80.

Jones, K., 1970, Nitrogen Fixation in the Phyllosphere of Douglas Fir, *Ann. Bot.,* 34: 239-244.

King, R. C., 1957, The Major Inorganic Constituents of Adult *Drosophila Melanogaster, Amer. Natur.,* 91: 319.

Kovner, J. L., 1955, Changes in Streamflow and Vegetation Characteristics of a Southern Appalachian Mountain Watershed, Ph. D. Thesis, State University of New York, Syracuse.

McBrayer, J. F., D. E. Reichle, and M. Witkamp, 1973, Energy Flow and Nutrient Cycling in a Cryptozoan Food Web, Eastern Deciduous Forest Biome Report 73-8, U. S. International Biological Program, Oak Ridge National Laboratory.

McGinty, D. T., 1974, unpublished data.

——, 1972, The Ecological Roles of *Kalmia latifolia* L. and *Rhododendron maximum* L. in the Hardwood Forest at Coweeta, M. S. Thesis, University of Georgia, Athens.

Nabholz, J. V., 1973, Small Mammals and Mineral Cycling on Three Coweeta Watersheds, M. S. Thesis, University of Georgia, Athens.

Reuss, J. O., 1974, Nitrogen Cycling in Grasslands, paper presented at the Symposium on Metabolism of Terrestrial and Freshwater Ecosystems, 25th Annual American Institute of Biological Sciences Meeting, Tempe, Ariz., June 16-21, 1974.

——, and V. C. Cole, 1973, Simulation of Nitrogen Flow in a Grassland Ecosystem, in *Proceedings of the 1973 Summer Computer Simulation Conference,* Montreal, July 17-19, Vol. II, pp. 762-768, Simulations Councils, Inc., La Jolla, Calif.

Rodin, L. E., and N. I. Bazilevich, 1967, *Production and Mineral Cycling in Terrestrial Vegetation,* Oliver and Boyd, Edinburgh.

Sollins, P., and R. M. Anderson (Eds.), 1971, Dry-Weight and Other Data for Trees and Woody Shrubs of the Southeastern United States, Eastern Deciduous Forest Biom[illegible] Report 71-6, U. S. International Biological Program, Oak Ridge National Laboratory.

Swank, W. T., and G. S. Henderson, 1974, Atmospheric Input of Some Cations and Anions to Forest Ecosystems in North Carolina and Tennessee, paper presented at the Symposium on Chemistry of Atmospheric Precipitation, 55th Annual Meeting, American Geophysical Union, Washington, D. C., April 8-12, 1974.

Tamm, C. O., 1968, An Attempt to Assess the Optimum Nitrogen Level in Norway Spruce under Field Conditions, *Stud. Forest. Suec.,* 61: 1-67.

Todd, R. L., 1974a, Microbial Dynamics in Forest Ecosystems, paper presented at the Symposium on Decomposition and Mineral Cycling Processes in Forests, 25th Annual American Institute of Biological Sciences Meeting, Tempe, Ariz., June 16-21, 1974.

——, 1974b, University of Georgia, unpublished data.

Tsutsumi, T., 1971, Accumulation and Circulation of Nutrient Elements in Forest Ecosystems, in *Productivity of Forest Ecosystems*, Proceedings of UNESCO Brussels Symposium, P. Duvigneaud (Ed.), pp. 543-552, Unipub, Inc., New York.

Ulrich, B., 1971, Investigations on Cycling of Bioelements in Forests of Central Europe (Preliminary Results of the Solling Project), in *Productivity of Forest Ecosystems*, Proceedings of the UNESCO Brussels Symposium, P. Duvigneaud, (Ed.), pp. 501-507, Unipub, Inc., New York.

Waide, J. B., and W. T. Swank, 1974, Comparative Studies on Nutrient Cycling in Watershed Ecosystems in the Southern Appalachians, paper presented at the Symposium on Metabolism of Terrestrial and Freshwater Ecosystems, 25th Annual American Institute of Biological Sciences Meeting, Tempe, Ariz., June 16-21, 1974.

West, N. E., 1974, Nitrogen Cycling in Deserts, paper presented at the Symposium on Metabolism of Terrestrial and Freshwater Ecosystems, 25th Annual American Institute of Biological Sciences Meeting, Tempe, Ariz., June 16-21, 1974.

A MODEL OF WATER CONTENT AND EVAPORATION FOR HARDWOOD LEAF LITTER

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ABSTRACT

A predictive model of water content and evaporative losses in the litter of a mixed deciduous forest is being developed. The model uses readily obtainable data on total daily incoming solar radiation, rainfall, mean daytime temperature, and mean daytime relative humidity. The model also requires data on site latitude, slope, and aspect; initial litter accumulation; annual quantity and timing of leaf fall; and transmission of solar radiation through the canopy. Evaporation rates are calculated from a modified Penman formula but are limited by the vapor conductivity of the litter. The model incorporates throughfall and litter-decay functions. Model performance was tested against independent data collected at the Coweeta Hydrologic Laboratory. The simulated evaporation over 8- and 12-day periods in summer and winter seasons agreed with measured evaporation to within 13%. Daily values of litter water content were usually within the error limits of experimental data. Simulated evaporation and litter water content over an 80-day period also showed good agreement with experimental data.

The litter layer is an important and distinguishing component of forest ecosystems which is generally lacking in other terrestrial systems. Forest litter plays an important role in maintaining the infiltration capacity of soils (Kittredge, 1938; Johnson, 1940) and in reducing erosion (Munns, 1947; Trimble, Hale, and Potter, 1951). Litter also provides the habitat for abundance of flora and fauna (Crossley, 1970) and is a major compartment for the transfer of nutrients in forest ecosystems (Bray and Gorham. 1964).

Information on the flux of water in the litter layer is central to understanding biotic and abiotic processes in litter. A few studies have been concerned with the moisture-holding capacity, drying time, or rainfall interception characteristics of litter (Blow, 1955; Metz, 1958; Helvey, 1964). But, in

view of the importance of litter moisture, it is surprising that more effort has not been devoted to research on the hydrologic properties of forest litter.

This paper describes the development and performance of a predictive model (LEM) of daily water content, evaporation, and drainage from litter of a mixed deciduous forest. Our objective in developing this model is to provide a representation of litter hydrology that can be used as a submodel in simulations of water flux on forested watersheds (Swift et al., 1973). The LEM could be linked to models of other ecosystem processes, such as mineral cycling and mposition, and it also has potential practical application for assessing fuel ture in fire-danger rating systems.

MODEL DEVELOPMENT AND IMPLEMENTATION

Extensive work has been done (Penman, 1956; McIlroy, 1957; Geiger, 1961; Van Bavel, 1966; Ritchie, 1972) on evaporation from water and soils. Most of these techniques depend on solving the energy balance. We adopted this technique in developing the LEM, using primarily the method of Penman.

Choices had to be made early as to how much detail to include in data input and output. Penman (1956) indicated that minute-by-minute fluctuations in such parameters as sunlight and temperature should be included for most accurate results in calculating evaporation with his formula. We decided against using such detailed data and in favor of using daily totals for sunlight and rain and daytime means for temperature and humidity primarily for two reasons:

1. Although such detailed data is available to us at Coweeta Hydrologic Laboratory, it would probably not be available at other sites where the model may be used, and its inclusion would greatly increase the work of data preparation. Thus a simpler model would have wider application.

2. The available data on litter moisture, with which the output of the LEM was to be compared for validation, is not highly detailed and has great variability because of the inherent heterogeneity of the litter layer. Although a detailed model might be intellectually satisfying, its validity would be largely conjectural. We felt that a simpler, cruder model would be more useful and that sophistication could be added later if the model proved inadequate.

The model defines three hydrologic compartments—atmosphere, litter, and —and one biomass compartment—the litter dry weight. For simplicity only two of the intercompartmental flows are modelled—evaporation from litter to atmosphere and drainage from litter to soil. Soil and atmosphere are treated as sinks for these flows, although cumulative evaporation and drainage are recorded during a model run and atmospheric moisture is included in the model as a data input (relative humidity). Moisture input to the litter (throughfall) is a forcing function. The litter accumulates moisture until it reaches field capacity, 215% of dry weight according to Helvey (1964); additional throughfall and all stemflow pass directly to the soil. Condensation from the atmosphere and upward

diffusion of moisture from the soil, although they undoubtedly occur and may at times be important, are not modelled. We treated the litter itself as a single, homogeneous hydrologic entity; other investigators (e.g., Plamondon, Black, and Goodell, 1972) have found it convenient to subdivide it.

A list of the parameters used in the model is given in Table 1. Fixed parameters, such as the relationship of vapor pressure to temperature, defined by HULIST, are read in initially and are followed by site parameters (e.g., the litter decay rate, LOSSRT; the slope and aspect parameters, DEGINC and AZIM; the canopy solar-radiation-transmission function, CANTRN; and the leaf-fall parameters, JFALL and FALMAX). Initial conditions for a run are set by biomass (LITDRY) and litter moisture content (LRTH20). Parameters that change daily are Julian date (JDATE), temperature (TEMPF), humidity (RELHUM), solar radiation (R2), and precipitation (RAIN). In accordance with the decision to keep input parameters simple, for the solar-radiation parameter R2, we used the daily total measured on a level, open site and modified by a seasonally varying slope function (Swift and Luxmoore, 1973) and a canopy transmission function for a similar site (Swift, 1972). Rainfall (RAIN) is also input as a daily total. Temperature and relative humidity (TEMPF and RELHUM) are read in as means of daytime maxima and minima.

A flow chart for the LEM is shown in Fig. 1. The initial litter moisture is converted to millimeters of equivalent depth and then recalculated at hourly intervals as evaporation takes place. Hourly integration steps provide output that may be chosen to correspond with the time of day at which comparison data were collected and are short enough to prevent erratic changes in litter moisture. No special significance is attached to other hourly values. An hourly integration step does not, of course, imply that meaningful hourly values can be calculated from daily totals and means.

Evaporation is determined by a slightly modified version of Penman's (1956) formula and by a vapor conductivity function based on information in Plamondon, Black, and Goodell (1972), with the use of empirical constants from earlier model runs. Penman's formula was used in much the form that he presented it. The influence of wind was neglected, however, since wind velocities near the forest floor were not measured and cannot be calculated from other data. (The wind-speed term was set at a value of 1, which is equivalent to a wind speed of 50 cm/sec.) Evaporation is considered to occur only during the day when incoming radiation is positive, because, when there is no energy input, potential evaporation is quite small. Since the energy balance is always positive, dewfall does not occur in the model.

Vapor conductivity decreases with litter moisture and is recalculated hourly and compared with potential evaporation to determine which process is controlling. It has been a difficult function to model. Plamondon, Black, and Goodell (1972) provides curves of matric potential at several levels in coniferous forest litter vs. litter moisture content and of hydraulic conductivity vs. matric potential. We were unable to relate their hydraulic-conductivity data to our

TABLE 1

LITTER EVAPORATION MODEL (LEM) PARAMETERS

Symbol	Description	Range of values
	Initial parameters*	
CANLST (I) JCAN (I)	Canopy light transmission, table of values, and Julian dates. Used to calculate CANTRN, the canopy transmission, corresponding to the date JDATE.	0.1 to 0.5
DELLST (I)	Psychrometer function table, values at 10°C temperature intervals. Used to calculate DELGAM, Δ/γ, in Penman's formula.	0.67 at 0°C 8.77 at 50°C
HULIST (I)	Vapor pressure table of values (mm Hg) at 10°C temperature intervals. Used to calculate HUMAX, the saturation vapor pressure at temperature TEMP, used in Penman's formula.	2.46 at −10°C 149.38 at 60°C
LOSSRT	Exponential decay rate of litter (annual).	−0.7
MIDFAL FALMAX	Julian date of middle of leaf-fall period (date on which half of total annual accumulation has fallen), and total annual leaf fall. Used to calculate FALL, the daily increment in leaf-litter dry weight calculated on JDATE, only for MIDFAL − 30 MIDFAL + 30.	264 3600
DEGINC	Average slope of study area, degrees from horizontal. Used in slope function to determine incoming solar radiation hours of sunlight.	23
AZIM	Aspect of study area, degrees clockwise from North.	135
DEGLAT	Latitude of study area, degrees.	35
KTIME	Time of day in hours past midnight at which daily output parameters are printed (must be between sunrise and sunset). Chosen to match sample time for experimental data.	15
	Variable parameters	
JDATE	Combined year and Julian date, days past January 1. Input daily.	61001 to 62365
LITDRY	Dry weight of litter at beginning of run (lb/acre).†	8031 3900
LRTH20	Litter moisture ratio (grams of water per gram of litter dry mass) at beginning of run. A new value must be given if JDATE is not consecutive.	2.15 to 0.40
TEMPF	Temperature (°F.) daytime average. Input daily.†	‡
RELHUM	Relative humidity (%) daytime average.	‡
R2	Incoming solar radiation measured on the level in the open (langleys/day).	‡
RAIN	Rainfall in previous 24 hr (in.).†	‡

*Initial parameters are constant during a run.

†These values are input in English units to conform to units used in the data sets provided by the U. S. Forest Service. They are converted into metric equivalents internally and for output.

‡The ranges of these parameters are environmentally determined.

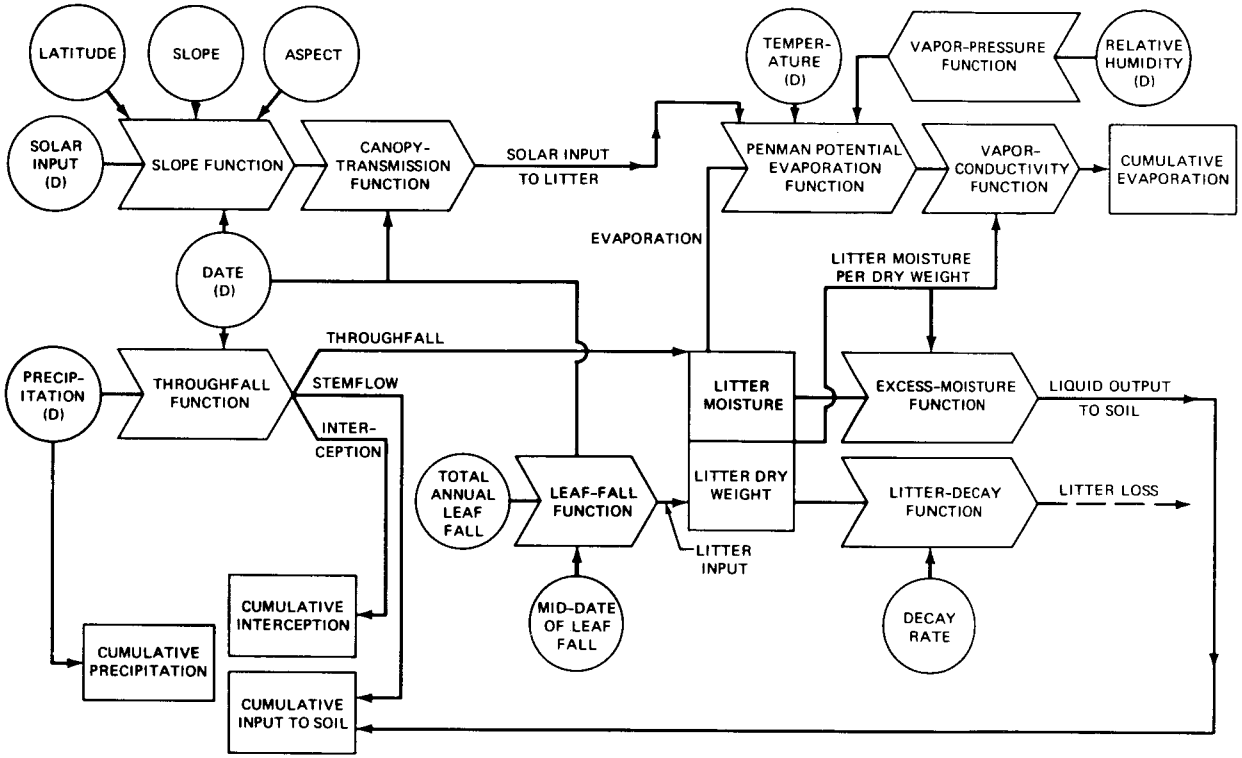

Fig. 1 Flow chart of litter evaporation model (LEM). Circles represent input parameters; (D) indicates that new values are input for each day of a model run. Arrow-shaped blocks indicate functions by which a main flow is modified by other parameters (input from side). Rectan[illegible]blocks ind[illegible]output parameters.

drying curves, but we have used their curves to derive a function to calculate matric potential. We used this function as a parameter in an empirical formula for vapor conductivity which gives the rate of water loss from the litter as a function of water content. When vapor conductivity falls below potential evaporation, it assumes control of the evaporation rate.

At the end of each day's run, moisture input to the litter from throughfall was calculated from interception equations for hardwood forests given by Helvey and Patric (1965). Both growing- and dormant-season equations are used; [redacted]odel chooses the appropriate season based on a canopy light-transmission [redacted]meter.

Leaf-litter dry weight is also recalculated at the end of the day. The decay decrement is a pure exponential function (Cromack, 1973), and the annual-rate exponent is divided by 365 to give a daily rate. Leaf fall is added if the date is ±30 days from the mid-date of the leaf-fall period (MIDFAL). A sigmoid function is used which depends on a total annual leaf fall (FALMAX).

After these calculations are made, the model reads a new day's data and repeats the calculations. If the new date is not in sequence, new values for litter dry weight and litter moisture must be provided.

Cumulative values for precipitation, evaporation, canopy interception, and drainage to the soil are printed out at 10-day intervals (on Julian dates ending in zero) and on the last day of a sequential run. A break in the date sequence sets these cumulative registers to zero, and a new accumulation is begun.

The model's output consists of the initial values of litter dry weight (grams per square meter) and of the litter moisture ratio (grams of moisture per gram of dry litter), and the date and daily calculated values of litter mass (grams per square meter), litter moisture (millimeters of equivalent depth), potential evaporation (millimeters per hour), vapor conductivity (millimeters per hour), matric potential (bars), hours from sunrise to sunset, maximum sunlight on the level for the date (langleys per day), measured sunlight recalculated for the slope (langleys per day), temperature (degrees Centigrade), relative humidity (percent), and canopy transmission (ratio of transmitted to incoming sunlight). Calculated leaf fall and precipitation, if any, are also printed. Litter moisture and vapor conductivity are printed out at hourly intervals, along with the [redacted]esponding time of day. Although potential evaporation does not change [redacted]rly, it is printed hourly to facilitate comparison with vapor conductivity. Hourly output for these few variables is printed only to permit us to follow the computation process; the values do not correspond to actual evaporation at these times. Hourly output terminates at sunset. The hours containing sunrise and sunset are determined from the slope function and the date and are used to control the number of hourly integration steps. At the end of each day, evaporation and litter moisture are corrected for the difference between the number of hourly steps and the actual day length. The daily summary values are printed out at a time of day specified by the user (KTIME).

COMPARISON OF SIMULATED AND EXPERIMENTAL DATA

Data for simulation and experimental comparison were taken from a watershed at the Coweeta Hydrologic Laboratory in western North Carolina. The 2.8-ha watershed is covered with a cove hardwood stand composed chiefly of yellow poplar (*Liriodendron tulipifera* L.), hickory (Carya sp.), and scarlet oak (*Quercus coccinea* Muenchh.) in the overstory and dogwood (*Cornus florida* L.) in the understory. The study by Helvey (1964) of rainfall interception by hardwood litter on this watershed provides data on maximum field w content, moisture-depletion rates, and the effect of rainfall on litter mois Since the forest occupies a cove site, litter production is high, in the upper range of values for stands in the Coweeta basin.

Annual precipitation in the study area averages about 203 cm. Air temperatures and relative humidity were measured with a recording hygrothermograph located beneath the forest canopy at 1.5 m above the ground. Data on total incoming solar radiation were obtained from a permanent climatic station located 1.5 km from the stand. Initial litter accumulation, needed at the beginning of each date sequence, was taken from Helvey (1964), and timing of leaf fall was determined from studies in the experimental basin.

Two short-term comparisons of simulated and measured evaporation were made, one with summer data (June 28 to July 5, 1961) and one with data from late winter (Mar. 12 to 23, 1962). Total simulated litter evaporation for the 8-day summer period was 1.37 mm, 1% below the measured evaporation of 1.39 mm. Simulated evaporation for the 12-day winter period was 2.48 mm, 13% above the actual evaporation, which measured 2.19 mm. Estimates from experimental data included errors in sampling litter weights and moisture content, giving a standard error of estimate of about 20% of the mean. Therefore total simulated evaporation for both periods is considered to be in good agreement with experimental values. Simulations were further tested against experimental data by comparing individual simulated values of litter water content with values estimated at 1400 hr each day (Fig. 2). The daily results show reasonable agreement between simulated and measured values, particularly for the first two days after a rain, when evaporation rates depend primarily on potential evaporation. At lower litter moisture contents, the model gives poor agreement; simulated values usually fall outside the confidence interval of standard error but within the interval of 2 standard errors.

Model performance was also examined throughout an 80-day period in the fall of 1961 (Fig. 3). During this period interception and leaf-fall subroutines were used, and the simulated moisture content once again shows reasonable agreement with the experimental data; there is a tendency for simulated values to be larger than measured values, however. Simulation shows greatest evaporation following rainfall and rewetting of litter. The maximum simulated daily evaporation was 0.70 mm on November 22 after a large rain. Total rainfall

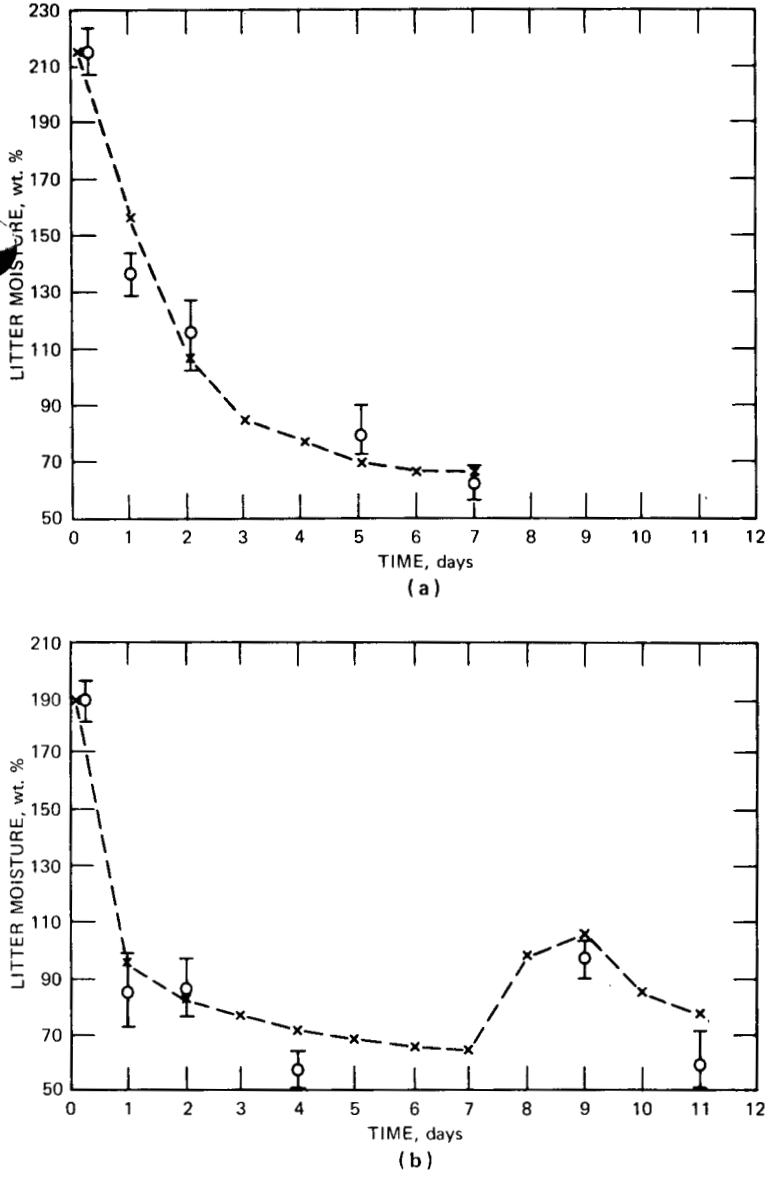

Fig. 2 Comparison of simulated (x- - -x) and experimental (o) daily litter water content for winter and summer periods. Vertical bars denote the standard errors of the means. (a) June 28 to July 5, 1961. (b) March 12 to 23, 1962.

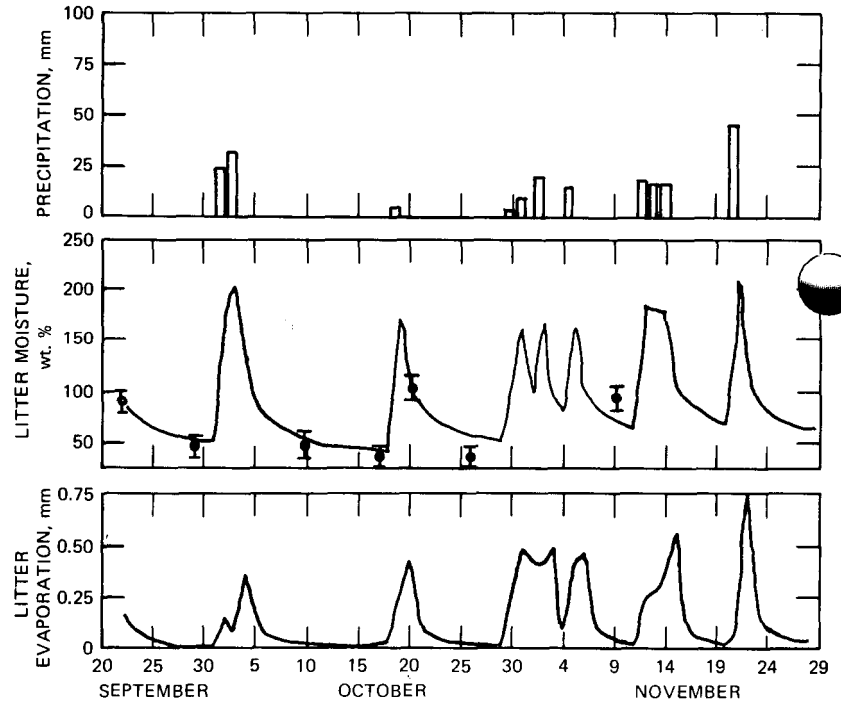

Fig. 3 Measured precipitation, simulated litter moisture content, and litter evaporation over an 80-day period in 1961. Experimental estimates of water content, with vertical bars denoting standard errors of means, are shown at intervals throughout the period.

for the 80-day period was 227 mm, and simulated litter evaporation was 8.3 mm, or 3.6% of rainfall. These results were well within the range of long-term experimental totals reported for hardwood litter in the southern Appalachians (Helvey, 1964).

A formal sensitivity analysis of the model has not been attempted. Such analysis is, of course, an important aspect of evaluating the model's performa and is valuable in determining the appropriate degree of precision for the vari parameters. The problem of sensitivity will be addressed during the next phase of model development.

DISCUSSION

On the basis of the comparison of simulated and experimental values, it appears that LEM describes daily litter hydrology adequately for many purposes.

On the other hand, the comparison we have presented must be interpreted with caution because of limited experimental data; the model may contain some deficiencies not uncovered in these applications. Clearly the model is only for leaf litter and could not be used to predict the moisture relations of woody material on the forest floor.

Model results show best agreement in the first 2 to 3 days after wetting of the litter, when evaporation is high. This is to be expected because evaporation during this period is high and is limited primarily by energy input, which we can [illegible]ate quite accurately. The function that describes evaporation during this p[illegible]d, the Penman formula, has a long history of successful application. Although we excluded the wind-speed term of the formula, results indicate that this may not be a serious omission when we are dealing with the surface beneath [illegible] forest stand.

The accuracy of our energy-input estimate depends on direct measurement of incident solar radiation from a level, open site near the study area, a slope function, and a canopy-transmission function. The slope function is a subroutine developed by Swift and Luxmoore (1973) which calculates day length on a given date and latitude and total incoming radiation on a given slope from total incoming radiation on the level. We have modified this further with a canopy-transmission function derived from the data of Swift (1972) and from unpublished data collected in his study. Our slope function is based on a comparison of incoming short-wave radiation above the forest canopy with radiation near the soil surface. Totals for entire days are used; so the effects of changing angles of incident radiation are included in the transmission ratio. Swift's study was done at Coweeta on forests similar to those in Helvey's litter-drying study. Canopy transmission varied from about 50% during the dormant season to 10% during the growing season. The canopy transmission function is simply a set of values and dates; the program interpolates between these values. Different values can be supplied as input data; our values should [illegible]ot be used uncritically in applications of the LEM to different sites.

As the litter dries and moisture is no longer supplied as rapidly as the energy input can evaporate it, the Penman formula ceases to apply. At this point, our understanding of the controlling processes becomes sketchy and our formula [illegible]mes empirical. Plamondon, Black, and Goodell (1972) provide curves of the [illegible]c potential vs. moisture content at several levels in coniferous forest litter and of hydraulic conductivity vs. matric potential. We began by considering hydraulic conductivity to be the rate at which water could be conducted to the litter surface to be exposed to evaporation, a process that would limit the evaporation rate as it fell below potential evaporation. But when we wrote equations that fit Plamondon's curves (at lower values of moisture content), the resulting evaporation rate fell off too sharply as litter moisture decreased. In fact, simulated evaporation effectively ceased at values of litter moisture where actual evaporation was still rapid. It became apparent that the hydraulic

conductivity of Plamondon, Black, and Goodell was not the function that limited the evaporation rate. This is not surprising since their primary interest was in the drainage process, where liquid water is conducted through a plane defining the boundary of a layer. Evaporation can take place from internal surfaces, however, with moisture diffusing through the pore spaces of the litter. We are currently using an empirical function based on the fourth power of matric potential, which is derived from Plamondon, Black, and Goodell's curve for matric potential vs. litter moisture. The constants in the function were chosen to bring vapor conductivity into the range of values for potential evaporation at litter moisture values of 100 to 120% of dry weight and to permit moisture to approach an asymptote of 40% during a 10-day drying period. The test of an empirical curve is whether it fits the data. This one is a reasonable first approximation but could stand some refinement. We remain open to more theoretically defensible approaches.

Plamondon, Black, and Goodell considered their litter layer to be divisible into three parts with distinct hydrologic properties. Zonation into at least two distinct layers is apparent at Coweeta, but we did not feel that treating these layers as separate compartments and modelling their moisture exchanges would provide verifiable benefits since data on drying rates in different layers are not available. Likewise we have no information on upward diffusion of moisture to the litter from the soil. Although it may occur, it is probably a minor process compared with evaporation rates, except when the litter is very dry.

The litter-decay function also oversimplifies a complex process. A negative exponential with an appropriate constant will give reasonable values for remaining leaf-litter mass and is theoretically defensible as a first approximation (Olson, 1963), but short-term decay rates are greatly affected by temperature and moisture. Because the overall rate of change of litter mass is slow, the errors in calculated litter mass caused by decay-rate fluctuations are probably unimportant for our purposes. For other purposes, e.g., for mineral-cycling studies in which the decay rate itself is the important variable, the effects of temperature and moisture would be critical. The LEM provides a detailed picture of litter moisture which should facilitate a more detailed study of litter decay.

REFERENCES

Blow, F. E., 1955, Quantity and Hydrologic Characteristics of Litter Under Upland Oak Forests in Eastern Tennessee, *J. Forest,* 53: 190-195.

Bray, J. R., and E. Gorham, 1964, Litter Production in Forests of the World, in *Advances in Ecological Research,* J. B. Cragg (Ed.), Vol. 2, pp. 101-157, Academic Press, Inc., New York.

Cromack, K., Jr., 1973, Litter Production and Decomposition in a Mixed Hardwood Watershed and a White Pine Watershed at Coweeta Hydrologic Station, North Carolina, Ph.D. Thesis, University of Georgia, Athens.

Crossley, D. A., Jr., 1970, Roles of Microflora and Fauna in Soil Systems, in *Pesticides in the Soil: Ecology, Degradation and Movement,* International Symposium on Pesticides in the Soil, pp. 30-35, Michigan State University Press, East Lansing, Mich.

Geiger, R., 1961, *Das Klima der bodennahen Luftschicht,* Fr. Vieweg u Sohn, Braunschweig, West Germany.

Helvey, J. D., 1964, Rainfall Interception by Hardwood Forest Litter in the Southern Appalachians, Research Paper SE-8, Southeastern Forest Experiment Station, Forest Service, U. S. Department of Agriculture.

——, and J. H. Patric, 1965, Canopy and Litter Interception of Rainfall by Hardwoods of Eastern United States, *Water Resour. Res.,* **1**: 193-206.

[illegible]on, W. M., 1940, Infiltration Capacity of Forest Soil as Influenced by Litter, *J. [illegible]rest.,* **38**: 520.

Kittredge, J., Jr., 1938, Comparative Filtration in Forest and Open, *J. Forest.,* **36**: 1156-1157.

McIlroy, I. C., 1957, The Measurement of Natural Evaporation, *J. Aust. Inst. Agr. Sci.,* **23**: 4-17.

[illegible]etz, L. J., 1958, Moisture Held in Pine Litter, *J. Forest.,* **56**: 36.

Munns, E. N., 1947, Forests in Soil and Water Conservation, *J. Soil Water Conserv.,* **2**: 28-30, 56-58.

Olson, J. S., 1963, Energy Storage and the Balance of Producers and Decomposers in Ecological Systems, *Ecology,* **44**: 322-331.

Penman, H. L., 1956, Evaporation: An Introductory Survey, *Neth. J. Agr. Sci.,* **4**: 9-29.

Plamondon, P. A., T. A. Black, and B. C. Goodell, 1972, The Role of Hydrologic Properties of the Forest Floor in Watershed Hydrology, in *National Symposium on Watersheds in Transition,* S. C. Csallany, T. G. McLaughlin, and W. D. Striffler (Eds.), Proceedings Series 14, pp. 341-348, American Water Resources Association, Urbana, Ill.

Ritchie, J. T., 1972, A Model for Predicting Evaporation from a Row Crop with Incomplete Cover, *Water Resour. Res.,* **8**: 1204-1213.

Swift, L. W., Jr., 1972, Effect of Forest Cover and Mountain Physiography on the Radiant Energy Balance, D. For. Thesis, Duke University, Durham, N. C.

——, and R. J. Luxmoore, 1973, Computational Algorithm for Solar Radiation on Mountain Slopes, Eastern Deciduous Forest Biome, Memo Report 73-10, U. S. International Biological Program.

——, W. T. Swank, J. B. Mankin, R. J. Luxmoore, and R. A. Goldstein, 1973, Simulation of Evapotranspiration for Mature, Cut, and Regrowing Forest Vegetation, Eastern Deciduous Forest Biome, Memo Report 73-79, U. S. International Biological Program.

Trimble, G. R., Jr., C. E. Hale, and H. S. Potter, 1951, Effect of Soil and Cover Conditions on Soil–Water Relationships, Paper 39, Northeast Forest Experiment Station, Forest Service, U. S. Department of Agriculture.

Van Bavel, C. H. M., 1966, Potential Evaporation: The Combination Concept and Its Experimental Verification, *Water Resour. Res.,* **2**: 455-467.

SIMULATION OF NITROGEN DISTRIBUTION AND ITS EFFECT ON PRODUCTIVITY IN EVEN-AGED LOBLOLLY PINE PLANTATIONS

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ABSTRACT

Nitrogen often limits the productivity of loblolly pine in the southeastern United States. The amount of nitrogen available to roots depends on organic-matter decomposition on the forest floor and in the soil, on influx by rain and fertilization, and on uptake by roots. Nutrient concentrations have been observed in tree parts, forest floor, and mineral soil, and growth rates of stems, branches, needles, and roots are well known. Synthesis of this information has led to a simulation model, which integrates rates of nitrogen transfer between and changes within several compartments in the nitrogen cycle. The model calculates growth of trees from basic processes where nitrogen limits assimilation. Critical areas for further research in relation to plantation productivity are indicated.

One problem impeding the improvement of forestry practices is the long time delay before the effects of certain management practices can be measured by changes in yield. Except for young stands, yearly weight increments seldom exceed 10% of the standing crop, and the natural variation in tree size severely limits the detectability of small, but nevertheless important, changes in growth rates and yield. The interrelations of physiological, microbiological, and silvicultural aspects of productivity of plantations add another dimension to the problem. Therefore, little of the knowledge concerning the physiology and the nutrient requirement of forests has been of use in forest-productivity predictions.

Simulation techniques provide a tool to integrate the knowledge of basic processes in a system, such as a plantation, and to study growth and productivity as a function of cultural measures. Simulation methods, which have been applied

successfully in many fields of scientific research, have been used to describe the behavior of the total system from knowledge of individual basic processes which could not be derived otherwise (De Wit and Goudriaan, 1974).

To summarize the many individual processes and point out how they may affect productivity over many decades, we have made a simulation model of even-aged pure loblolly pine (*Pinus taeda*) plantations. Loblolly pine is a major source of timber and pulp in the southeastern United States. In significant areas loblolly pine production is limited by the availability of nitrogen in the soil (), 1970). Such production systems are suitable for simulation because the e aged stands have a relatively simple growth pattern. Annual nitrogen input by rain is well known. The amount of basic information available for loblolly pine should allow the model to more precisely predict the behavior of this system in response to cultural practices. Another important function of the model is that it indicates more clearly than any other method the most relevant areas for future research.

With our model we try to describe growth in even-aged loblolly pine plantations from seedlings to mature trees on sites where nitrogen availability is limiting. Such sites are characterized by a site index of 50 to 90 (height of dominant trees in feet at 25 years of age) where rotation occurs every 25 to 40 years. Although nitrogen is the growth-limiting factor over a 2- to 3-year period, severe droughts can also limit growth in some years. We define growth as the increase in dry matter in aboveground and belowground parts of the vegetation.

Nitrogen is present in the soil, forest floor, and trees, and a variety of processes are responsible for its flux in the system. Dropping of needles, branches, and stem bark carries nitrogen to the forest floor, as does thinning and harvesting. Decomposition returns nitrogen to the soil, and artificial fertilization may also be used. The annual influx of nitrogen by rain amounts to 6 to 10 kg ha^{-1} $year^{-1}$ in the Piedmont area of North Carolina, while efflux by drainage is 0 to 50 times less. Rates of fixation of gaseous nitrogen and denitrification are mall (Wells and Jorgensen, 1973), while burning causes about 7% of the nitrogen in the biomass to move out of the forest.

Only those plantations will be considered in which the number of trees and shrubs in the understory is kept low. In such forests normal practices include ing and prescribed burning; artificial fertilization is currently under consideration. Duration of a rotation and the intensity and frequency of the above-mentioned measures can be manipulated by the forester in accordance with various production policies.

Two standard situations will be used in the modeling effort. These include plantations managed as described above with a 25- or 40-year rotation. Trees 25 years old are harvested mainly for pulpwood, and trees 40 years old, for timber. The growth rate of a forest with a stocking density that is optimized for timber production and the density of trees (Fig. 1) was taken from Wahlenberg (1960).

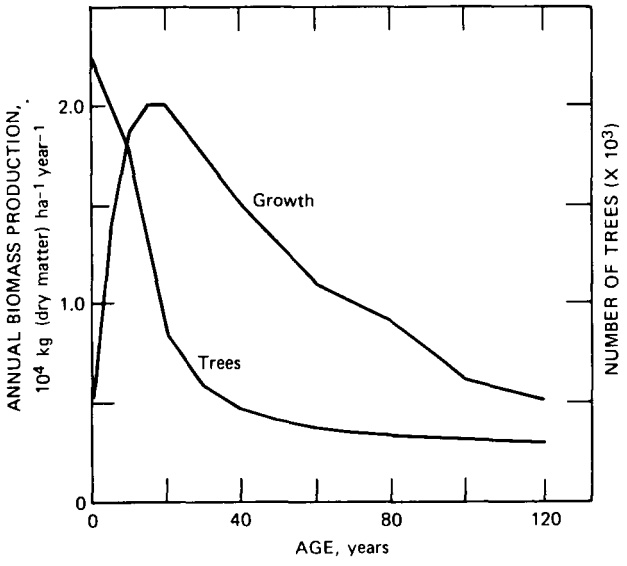

Fig. 1 The annual biomass production and the number of surviving trees at different ages in an optimally stocked plantation. (Adapted from Wahlenberg, 1960.)

THE MODEL

Mineral soil, forest floor, and the loblolly pine trees are the major components of the system. The rooted layer of the mineral soils of pine forests is often shallow (0.5 to 1 m) and contains 40 to 100% of the nitrogen in the forest (800 to 3000 kg/ha). Most of the nitrogen is in organic compounds, which need decomposition before becoming available to the root system (roots plus mycorrhiza). About 4% of the total nitrogen annually becomes available to the trees (Wells and Jorgensen, 1973). The amount of this fraction is affected by the physical structure and the water content of the soil, probably via its aeration. In areas with well-distributed rainfall, as in the Piedmont, this fraction is relatively constant. Rapid root turnover (Harris, Kinerson, and Edwards, 1973) and chemical absorption to lignin (Beek and Frissel, 1973) annually fix 30% of the available nitrogen into dead roots and humus.

Nitrogen in rain and fertilizer is predominantly in the form of NO_3 and NH_3 and should be available for uptake within 1 year. Nitrogen moving from the forest floor into the soil is predominantly unavailable to the trees and requires alteration before uptake occurs. Little nitrogen is present in stemflow and throughfall. Unlike nitrogen in rain, stemflow and throughfall cause only a redistribution of nitrogen in the system.

Beek and Frissel (1973) constructed a model from basic principles to simulate decomposition processes in soils. This model simulates decomposition processes over periods of months, but its authors already indicate that the knowledge is still lacking for extrapolation to longer periods or greatly different soil or climatic conditions.

The forest floor consists of dead needles, branches, and stem bark normally less than 15 years old. The forest floor contains 0 to 15% of the total nitrogen in the plantation. Its decomposition results largely from microbial activity. Conifer litter has a very low nitrogen content (a carbon/nitrogen ratio up to 100), which supposedly limits microbial activity. The rate of decomposition of total biomass is greater than the nitrogen release; so its carbon/nitrogen ratio decreases. The carbon/nitrogen ratio is assumed to be the key factor that controls the rate of decomposition and nitrogen release. In addition to what is expected on the basis of its carbon/nitrogen ratio, 5 to 15% of the freshly fallen litter decomposes in the first year on the forest floor. This is probably due to degradation of easily accessible material, such as protoplasm.

Wells and Jorgensen (1973) observed forest-floor decomposition and nitrogen contents of soil and tree fractions in experiments carried out over more than a decade in Duke Forest and more recently in the Eastern Deciduous Forest Biome–International Biological Program at the forest stand at Saxapahaw (Murphy et al., 1973); both sites are in the Piedmont region of North Carolina. Our study draws heavily from their results, most of which are annual observations. The rate of decomposition and nitrogen release of the forest floor is simulated by treating 20-year classes of litter separately. In each class the amount of biomass and nitrogen is simulated. Decomposition rates are calculated from the ratio of total carbon and nitrogen per layer, rather than treating needles and branches separately. To avoid the detailed calculation of the water status of the litter, we ignored the effect on decomposition of increasing humidity in lower layers. In a stable climate, errors resulting from this simplification are small over the time scale used. With these simplifications, decomposition and forest-floor buildup are simulated quite well in the Piedmont area, but the model eventually needs to include effects of temperature and humidity on decomposition for application in other climatic regions.

Trees were subdivided into roots, stem wood, stem bark, branches, and first- and second-year needles. Total dry weight and nitrogen content are simulated for each of these fractions. Needles have a life span of 1½ years. Before needles fall, 30 to 50% of the nitrogen of second-year needles is stored in the tree for next spring's growth. Branches in the bottom of the crown grow only a few needles and soon die. It was assumed that 50% of the branches older than 5 years are removed by self-pruning. The self-pruning rate of branches decreases somewhat if the individual tree grows faster than the average. It is assumed that, once the bark for 1 year is laid down, it begins to slough off at a rate that results in a 25% loss of the bark at age 10, 50% by age 20, 75% by age 30, and the loss of the remainder of the 1-year bark increment by age 40.

We obtained the growth rate of the simulated plantation by subtracting the respiration for maintenance of cell integrity from the total-stand assimilation. Annual forest assimilation is thought to be dependent on the total amount of nitrogen in the needles, thus accounting for changes in assimilation by changes in biomass and nitrogen content of the needles. A simple description of annual maintenance respiration relates its rate to the nitrogen content of the living tree parts. The biochemical composition of the biomass produced annually changes little with age or site so that growth respiration is a constant fraction of growth rate (Penning de Vries, 1974). At the present stage of knowledge of the assimilation and dissimilation and the general level of detail in this model it is not appropriate to make more refined calculations of tree growth.

In our model the limiting effect of nitrogen is on assimilation, rather than on growth as such. Some observations support this assumption (Kozlowski and Keller, 1966), but this very important relationship requires further investigation. The rate of photosynthesis per unit of surface of loblolly pine needles is low. However, photosynthesis per gram of nitrogen in needles is high (Higginbotham, 1974), which also suggests that nitrogen limits photosynthesis.

Observations by Wahlenberg (1960), Ralston (1974), and others provide an estimate of the distribution of the total biomass increment over the tree fractions (Fig. 2). In young trees most of the annual growth goes to branches and needles, whereas in mature trees stem wood gets the largest share of growth.

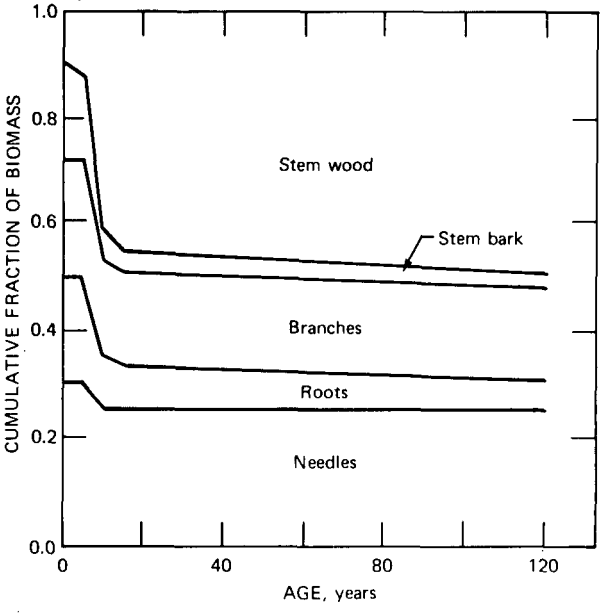

Fig. 2 Distribution of annual biomass production to the various tree fractions for the standard case as a function of age.

The difference in the distribution of biomass among tree organs and the relationship of this distribution to tree density suggest that growth per tree is an important variable. Tree growth pattern can be simulated by dividing actual tree growth by the growth per tree in the optimally stocked situation. If the resulting ratio is greater than 1, stem and branch growth are stimulated more than other factors, but, if the ratio is less than 1, these fractions are reduced the most (Fig. 3). For the calculated growth rate to be met in conditions where the relative growth per tree is not equal to unity, the growth of needles and roots is given first priority, and the remainder of tree growth is distributed over stem wood, stem bark, and branches. Because a larger share of the assimilates in young trees is used for needle formation than in older ones, the relationships between relative growth of stem wood, stem bark, and branches depend on the age of the trees.

The concentration of nitrogen in the annual increment of each of the tree fractions is related to the relative availability of nitrogen in the soil (Fig. 4). The relative availability of nitrogen is expressed as the amount of soil nitrogen available for uptake divided by the amount taken up in a well-stocked stand of the same age. It is assumed that the effect of nitrogen availability on nitrogen content does not change with age. Data to construct Figs. 3 and 4 come mainly from careful, but subjective, observations of forest growth since existing data

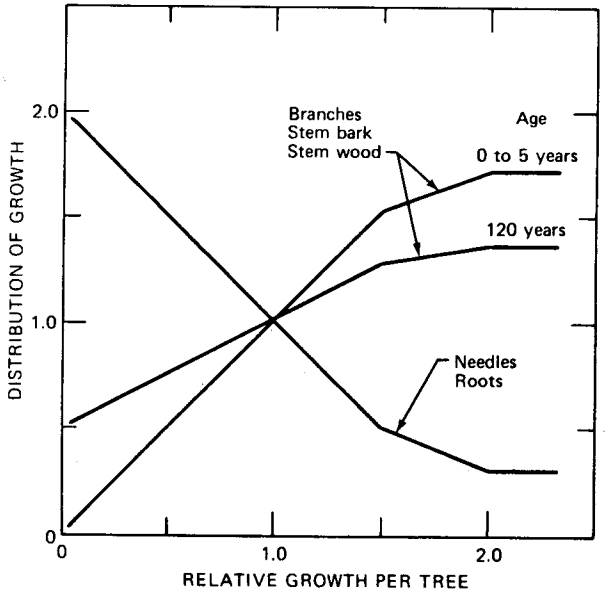

Fig. 3 The relationships for distributing growth over tree fractions for nonstandard cases as a function of available assimilates, expressed as relative growth per tree. Both axes are normalized with respect to the standard case.

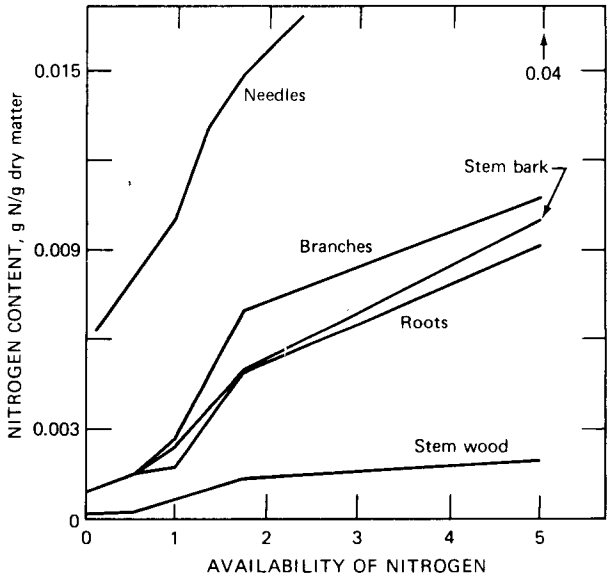

Fig. 4 The relationships between the relative availability of soil nitrogen with respect to the standard case and the nitrogen concentration of the tree fractions.

usually concern growth alterations due to change of these factors simultaneously.

Simulation of the number of trees per hectare includes removal by thinning; a natural death rate of 2% per year for the first 10 years and 0.8% thereafter.

The present model can be adapted easily to simulate distribution of other nutrients and growth when these nutrients limit tree assimilation. Also, simulation of these processes on plantations containing other tree species will change little of the model's basic structure. For these changes, however, we must have adequate knowledge about the species and nutrients.

SIMULATION PROGRAM

The model describes the physiological, microbiological, and mechanical processes relevant to nitrogen distribution and forest growth. Its computer program is formulated in the simulation language Continuous Simulations Modeling Program (CSMP; IBM, 1972). This user-oriented language provides many input and output facilities and allows a deductive style of program writing which improves its readability. A preprocessor is used, which expands a shorthand notation of repetitive features into CSMP (De Wit and Goudriaan, 1974). This program integrates the rates of change over 1 year and reports

resulting amounts of nitrogen and biomass in the various parts of the system. Further integration occurs from the recalculation of the rates of processes resulting from the amounts of biomass and nitrogen in the various parts of the system. The cycle is repeated until the required time span has elapsed. Sudden modifications of distribution caused by cultural practices are taken into account. Rates are calculated on an annual basis to avoid more detail in input and output than is useful. A listing of the program is available on request.

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When the parameters of the model are set to simulate growth in the standard situation, the predicted values correspond well with observed rates (Wahlenberg, 1960), and the distribution of biomass over tree organs agrees well with reality (Ralston, 1974). Since many of the basic inputs were taken from the standard situation, agreement is to be expected. Thus the consistency of the model is emphasized. Weights of the tree fractions change over time in the standard situation, where growth was permitted to continue for 100 years (Fig. 5). Few observations are reported on growth rates of needles, branches, and roots in plantations; so even in the standard situation a thorough evaluation of model behavior is impossible. Decomposition of litter and buildup of the forest floor

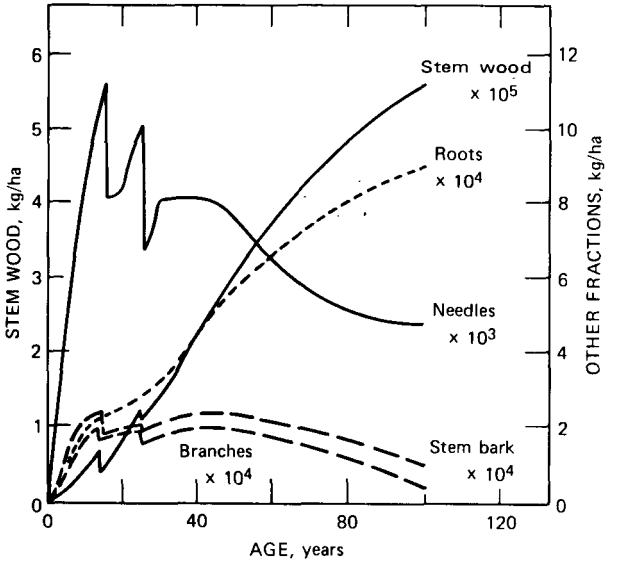

Fig. 5 Simulated growth of biomass of tree fractions in a standard situation with thinnings at age 15 and 25 years.

corresponds closely to that reported by Wells and Jorgensen (1973). Nitrogen content of needles increases significantly after thinning (Boggess, 1959), and the simulation program calculates a similar pattern in response to the smaller number of trees that take up nitrogen.

The model was tested under more extreme conditions. The tests included growth in rotations as short as 10 years with whole-tree harvests and as long as 100 years; plantations on soils with two and one-half times as much nitrogen as the standard plantations and with five times less; and four times as many trees per hectare initially as in the standard case and four times less. Vari[illegible] short-term perturbations, for example, heavy thinning, heavy fertilization, a[illegible] hot fire each 5*th* year in plantations older than 15 years were imposed to check model stability. The constancy of the total amount of nitrogen in the system, corrected for the nitrogen added by rain and fertilization or lost by fire and harvesting, was checked after each integration. Many of the results of such tests cannot be validated objectively because of the lack of observations. In such situations the experience of a forester is very valuable in judging the simulated results. The behavior of the model in these situations seemed realistic, although growth after age 60 was often too high. At soil-nitrogen contents of 600 kg/ha or less, the calculated annual nitrogen uptake can approach or even exceed the amount of available nitrogen present. Thus the assumption that rates can be calculated for one growing season using data from the last growing season is not correct. A time interval of about a month should be used to account for feedback of nitrogen on growth rates within 1 year. The present version of the simulation program is not adaptable to change in the time-step interval.

Assuming that the structure of the model is a legitimate simplification of the real world, we made sensitivity analyses of those parameters for which numeric values were estimated. These analyses indicate that parameters of major importance are:

(1) The amount of energy consumed in biochemical maintenance processes. A consumption rate of 50 kg of carbohydrates for maintenance for 1 year of 0.5 kg of nitrogen in needles, 1 kg of nitrogen in bark and branches, 1.7 kg of nitrogen in roots, or 3 kg of nitrogen in stem wood has been used in most simulations. The resulting maintenance respiration rate resembles that in actual plantations. Predicted forest growth is sensitive to this parameter, and t[illegible] partitioning, which has little fundamental basis, is important. Only physiologi[illegible] and biochemical research will result in better estimates and improved model structure.

(2) The fractions of soil nitrogen that are transferred between the available and unavailable pool. The numeric value used is an educated guess, but it is an important number to relate absolute soil-nitrogen contents to nitrogen uptake and growth rates. Its constancy at all nitrogen contents may be questioned. Microbiological and physiological research can provide better data for the description of these processes.

(3) The fraction of the nitrogen in biomass lost by burning. Its value is about 0.7. When burning of the forest floor is included in the management practices, hundreds of kilograms of nitrogen are lost from a plantation per rotation, which makes it a very important parameter in the long run. A better knowledge of its variability should prove rewarding in terms of this simulation model.

(4) The fraction of nitrogen in second-year needles that is transferred back into the tree before needles fall. This fraction is set to the constant 0.3, but it may vary between years. If stems drop green needles, very little is recycled into the tree. This parameter determines largely the carbon/nitrogen ratio of forest-floor layers and thus litter decomposition and forest-floor buildup. Productivity of harvestable wood is calculated to be 5% larger than that in the standard simulation run if the fraction transferred amounts to 0.6; it drops by 6% if this fraction is 0. In both cases the nitrogen from old needles is recycled to the tree, but the fastest recycling gives the best growth response. However, if the forest floor is burned, much of the nitrogen is not recycled. Making further observations about this fraction seems relatively simple and useful, particularly for situations where forest-floor burning is intensive.

(5) The amount of nitrogen added by rain. Numerically this amount is similar to the net influx of nitrogen when rain and drainage are important. Varying this number over a twofold range affects stem-wood formation little for one or two decades but becomes of major importance when accumulated over one or two rotations. Predictive values for the annual amount of nitrogen added by rain or lost by drainages are therefore important numbers for long-term forest-productivity predictions.

Results of simulation of growth at sites with different soil-nitrogen contents are plotted in Fig. 6 and show a positive response in productivity up to a soil-nitrogen content of about 3000 kg/ha, followed by a slight decrease, if any, above this number. The productivity is calculated as the weight of stem wood and harvestable roots (supposedly 50% of root weight) obtained in thinning and final harvest divided by the duration of the rotation and amounts of 4000 to 7400 kg dry matter ha^{-1} $year^{-1}$ (about 110 to 205 ft^3 $acre^{-1}$ $year^{-1}$) in a 25-year rotation. Wahlenberg's volume table (1960) at age 40 was converted from a site index of 50 years to a site index of 25 years and added to the ordinate of Fig. 6. The productivity is about 500 kg ha^{-1} $year^{-1}$ (14 ft^3/acre) higher in a 40-year rotation where wood formation is emphasized (Fig. 2) during a larger fraction of the rotation. The productivities at soil-nitrogen levels below 2200 kg/ha were obtained by keeping the pool of unavailable nitrogen constant to prevent soil exhaustion.

The highest rate of productivity in Fig. 6 is about 7800 kg ha^{-1} $year^{-1}$ (218 ft^3 $acre^{-1}$ $year^{-1}$) and slightly exceeds Wahlenberg's maximum. In the model the maximum results from the assimilation and dissimilation rates for which numeric values are not well established may have been too high and too low, respectively. Recent observed rates of CO_2 exchange in plantations (Higginbotham, 1974)

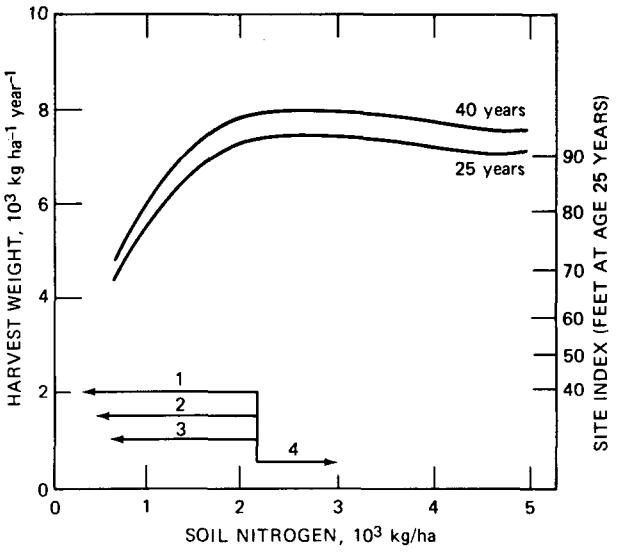

Fig. 6 **The effect of soil nitrogen on the mean annual harvest for rotations of 25 and 40 years. The arrows indicate the effect on soil nitrogen of three treatments carried out during four rotations of 25 years: (1) complete removal of trees from thinnings and harvests (−1860 kg/ha); (2) removal of stems with harvests followed by slash burning (−1770 kg/ha); (3) removal of stems only at thinnings and harvests (−1610 kg/ha); (4) represents nitrogen influx by rain (+800 kg/ha).**

will provide a basis for improvement of this part of the model. The small decrease in stand productivity at the highest soil-nitrogen levels in Fig. 6 results from high maintenance cost of the biomass, which is a response to the nitrogen concentrations in these situations (Fig. 3). A plantation with a site index of about 70 has a nitrogen level of about 1400 kg/ha in a 0- to 60-cm layer of the forest floor. This point is below the curve in Fig. 6, suggesting that more nitrogen per year becomes available from the unavailable pool than was assumed. The response of simulated productivity to fertilization, however, agrees very well with observed stem growth (volume inside bark) in loblolly pine plantations a[t] poor sites. The growth in a 5-year period was increased up to 10,000 kg dr[y] matter at a fertilization rate of 400 lb of nitrogen per acre and decreasing beyond this rate (Wells et al., 1974). In Wells' model less than 0.3 of the nitrogen added to the soil ends up in stem wood within 5 years, but in our model the effect of fertilization persists for 6 to 10 years. A small backlash in productivity was calculated after heavy fertilization owing to the increased load of maintenance respiration and diminishing assimilation.

In Fig. 6 the amount of nitrogen removed in four rotations of 25 years is shown with three alternative management practices: the standard situation

where slash is left at the forest floor to decompose, burning of the slash at the plantation, and removal of whole trees from the plantations. In each case the nitrogen influx by rain is smaller than that of nitrogen removal, and the soil-nitrogen content drops significantly.

Figure 6 could have been constructed without a computer program. However, accounting for effects of a multitude of factors in a dynamic situation is possible only with the use of a predictive computer model. Some examples of productivity and the amount of nitrogen removed from plantations with various harvesting procedures or stocking densities are summarized in Table 1. Burning in particular causes large amounts of nitrogen to be lost. Frequent burning of the forest floor removes only slightly more nitrogen than burning once before a new rotation (standard case). Although burning removes much nitrogen in the long run, its effects are small in terms of the change of productivity within one rotation. The increased rate of cycling of a part of the nitrogen opposes the decrease of the total nitrogen in the system, leading to a small and temporary productivity increase. Frequent burning of the forest floor in actual loblolly pine plantations for 10 or 20 years has not shown any clear effect on tree growth (Ralston, 1974). Slash burning or whole-tree harvests remove slightly more nitrogen from a plantation than forest-floor burning. Fertilization increases the nitrogen content of the biomass, thus increasing nitrogen losses at harvest. Productivity (in kilograms per hectare) at high stocking densities without thinning is almost equal to that in the standard case, and the rates of nitrogen removal are similar. Although the weight of the standing crop is larger just before the final harvest in these stands, no intermediate yields have been obtained by thinning. This makes plantations less productive at lower stocking densities without thinning.

Woodmansee and Innis (1973) simulated growth of a lodgepole pine forest for sites where productivity is limited by potassium. Their study has much in common with the present model. They describe the growth rate of the forest as a function of age and potassium availability. Less attention is paid to the distribution of biomass of tree organs. Their conclusions about the rate of removal of nutrients from a plantation are numerically smaller but essentially similar to the ones reported here.

ACKNOWLEDGMENTS

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TABLE 1

PRODUCTIVITY AND RATE OF NITROGEN REMOVAL IN LOBLOLLY PINE PLANTATIONS RESULTING FROM VARIOUS TREATMENTS

	25-year rotation			40-year rotation		
	Nitrogen removal,* kg/ha	Productivity,† kg/ha	Density,‡ trees/ha	Nitrogen removal, kg/ha	Productivity, kg/ha	Density,‡ trees/ha
Standard treatment	21.0	6960	850	15.6	7550	550
Burning slash	25.0	6960	850	18.0	7550	550
Whole-tree harvests	26.7	6960	850	19.1	7550	550
No forest-floor burning before next planting	8.4	6960	850	8.0	7550	550
Moderate forest-floor burning§	22.8	7040	850	21.8	7575	550
Fertilization,¶ kg N ha^{-1} $year^{-1}$						
200	22.9	7150	850	16.6	7675	550
400	24.6	7240	850	17.5	7750	550
600				18.1	7800	550
Planting density,** trees/ha						
2250	23.2	7080	1700	15.6	7625	1580
1500	19.6	6400	1150	15.8	7400	1050
1000	19.5	5320	860	15.3	6625	700

*Total nitrogen lost (kg N ha^{-1} $year^{-1}$) by harvesting and burning from a plantation in one rotation divided by the duration.

†Calculated (kg dry matter ha^{-1} $year^{-1}$) as total stem- and stump-wood weight harvested at the end of a rotation divided by the duration of the rotation.

‡Productivity divided by the number of trees per hectare at the end of the rotation indicates size of individual trees.

§At ages 15, 20, 30, 35, 40 years.

¶Two years after thinning.

**No thi

REFERENCES

Beek, H., and M. J. Frissel, 1973, *Simulation of Nitrogen Behavior in Soils,* Simulation Monographs, Pudoc, Wageningen, The Netherlands.

Boggess, W. R., 1959, Foliar Nitrogen Content of Shortleaf Pine as Influenced by Thinning, Agricultural Experiment Station Forestry Note No. 80, Department of Forestry, University of Illinois, Urbana.

De Wit, C. T., and J. Goudriaan, 1974, *Simulation of Ecological Processes,* Simulation Monographs, Pudoc, Wageningen, The Netherlands.

Harris, W. F., R. S. Kinerson, and N. T. Edwards, 1973, Comparison of Belowground Biomass in Natural Deciduous and Loblolly Pine Plantations, in The Belowground Ecosystem: A Synthesis of Plant-Associated Processes, U. S. International Biological Program Interbiome Symposium (in press).

Higginbotham, K. O., 1974, The Influence of Canopy Position and Tissue Age on Growth and Photosynthesis in Loblolly Pine, personal communication.

IBM, 1972, System/360 Continuous System Modeling Program, User's Manual, International Business Machine Corporation, White Plains, New York.

Kozlowski, T. T., and T. Keller, 1966, Food Relations in Woody Plants, *Bot. Rev.,* **32:** 293-383.

Murphy, C. E., T. R. Sinclair, R. S. Kinerson, K. O. Higginbotham, K. R. Knoerr, and B. R. Strain, 1973, Modeling the Primary Productivity Process—a Coordinated Effort at an Intensive Research Site, in *Summer Computer Simulation Conference,* pp. 684-690, Simulation Councils Inc., La Jolla, Calif.

Penning de Vries, F. W. T., 1974, Substrate Utilization and Respiration in Relation to Growth and Maintenance in Higher Plants, *Neth. J. Agr. Sci.* (in press).

Ralston, C. W., 1974, Annual Primary Productivity in a Loblolly Pine Plantation, in *Biomass Studies,* H. E. Young (Ed.), pp. 106-117, International Union of Forest Research Organizations, Working Party on the Mensuration of the Forest Biome, College of Life Sciences and Agriculture, University of Maine, Orono.

Wahlenberg, W. G., 1960, *Loblolly Pine; Its Use, Ecology, Regeneration, Protection, Growth, and Management,* School of Forestry, Duke University, Durham, N. C.

Wells, C. G., 1970, Nitrogen and Potassium Fertilization of Loblolly Pine on a South Carolina Piedmont Soil, *Forest Sci.,* **16:** 172-176.

——, D. M. Crutchfield, and I. H. Trew, 1974, Five-Year Volume Increment of Pole Size Loblolly Pine from Nitrogen Fertilization, Southeastern Forestry Experiment Station, U. S. Department of Agriculture Research Paper, personal communication.

——, and J. R. Jorgensen, 1973, Nutrient Cycling in Loblolly Pine Plantations, Eastern Deciduous Forest Biome, Memo Report No. 73-81, U. S. International Biological Program, Oak Ridge National Laboratory.

Woodmansee, R. G., and G. S. Innis, 1973, A Simulation Model of Forest Growth and Nutrient Cycling, in *Summer Computer Simulation Conference,* pp. 697-721, Simulation Councils Inc., La Jolla, Calif.

A MODEL OF MINERAL-ELEMENT CYCLING FOR AN INVERTEBRATE FOOD WEB IN A SOUTHEASTERN HARDWOOD FOREST LITTER COMMUNITY

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ABSTRACT

A 10-compartment model of the movement of calcium and potassium through a selected cryptozoan food web was constructed. The compartments were litter and microflora, Diplopoda, Cryptostigmata, Orthoptera, Pulmonata, Collembola, medium Araneida, Coleoptera, small Araneida, and Mesostigmata. The densities of these compartments were estimated using standard population-estimation techniques. The fluxes of potassium and calcium between the compartments were estimated using radioactive tracers. Two sets of models for each element were constructed: time-varying-coefficient models based on the state of the systems in the summer and constant-coefficient models that use the annual integrated fluxes from the first set of models. After the nutrient models were made, two biomass models based on the annual potassium and calcium fluxes were constructed. Results indicated that the models based on the summer states of the systems overemphasized the contribution of mesofauna to litter decomposition. On the basis of the annual nutrient models, Cryptostigmata and Collembola were the most important saprovores and small Araneida and Mesostigmata were the most important predators. The biomass model based on calcium fluxes showed that saprovores accounted for 20% of the total annual input; this agrees with the literature. The models may have underestimated the impact of saprovores on litter decomposition for two reasons. First, animal feeding rates may have been underestimated because of inflated uptake values, and, second, the fauna may control litter decomposition either directly or indirectly, but feeding-rate studies measure only the direct controls, which may be of lesser importance to litter decomposition.

Current ecological theory holds that soil–litter invertebrates operate either directly or indirectly to control plant- and animal-litter decomposition and nutrient release. Digestion and assimilation of the litter, which can be considered direct controls, may be of lesser importance. The more important indirect control may include dissemination of fungal spores, inoculation of litter with

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microflora as it passes through the animal gut, mixing of substrates, tunneling and other activities, and increasing the litter surface area by fragmentation through feeding activities. Increased surface area presumably increases leachability, and leaching is an important activity affecting nutrient loss from decomposing litter (Crossley, 1970).

This study is an attempt to describe the dynamics of potassium and calcium in an invertebrate-litter system from a hardwood forest floor. A box-and-arrow compartment model was constructed as a conceptual framework for invertebrates on substrates (Fig. 1). Measurements of elemental concentrations on feeding crops in these compartments are reported elsewhere (Gist and Crossley, 1974a). The application of radioactive tracers to estimate some of the rates for the conceptual model is reported elsewhere also (Crossley and Gist, 1973; Gist and Crossley, 1974b). This paper describes a digital-computer simulation of the general model as a means of interpreting the direct importance of invertebrates for mineral-element (potassium and calcium) loss from decomposing litter.

Generally, litter decomposition is a process resulting from the interactions of many different types of biota. Most cellulose breakdown is accomplished by microflora, either in the litter or as symbionts in animal guts. Fungi are also important in mycorrhizal associations with plant roots and affect reconcentration and assimilation of nutrients by plants. The animal community associated with the decomposition process is taxonomically and ecologically diverse. In many cases the feeding habits of animals are known only generally, and rates are only approximated (Kowal and Crossley, 1971). The value of our modeling efforts and of other similar efforts (MacBrayer and Reichle, 1971) lies in the attempt to resolve the generalized concept into a quantifiable overview, which we hope will lead to refinements in understanding of the function of the system.

The conceptual model (Fig. 1) is essentially taxonomic and is based primarily on arthropod mesofauna. Some important groups (earthworms, nematodes, and protozoa) were omitted because of sampling limitations. Some compartments include groups with different ecologies. We have defined compartment boundaries and their contents, together with the current status of knowledge of feeding habits, susceptibility to predation, and responses to temperature and moisture.

TTER (X_1)

As organic materials reach the forest floor, they are attacked by the microflora and fauna and release nutrient substances; 40 to 90% of the initial weight may be lost during the first year. The actual amount varies with species and locality (Edwards, Reichle, and Crossley, 1970). Witkamp and Olson (1963) showed a nonlinear rate of weight loss, possibly because of leaching of soluble materials. The initial loss is followed by a slower loss rate during the winter months and an accelerated rate during spring and summer (Crossley, 1970).

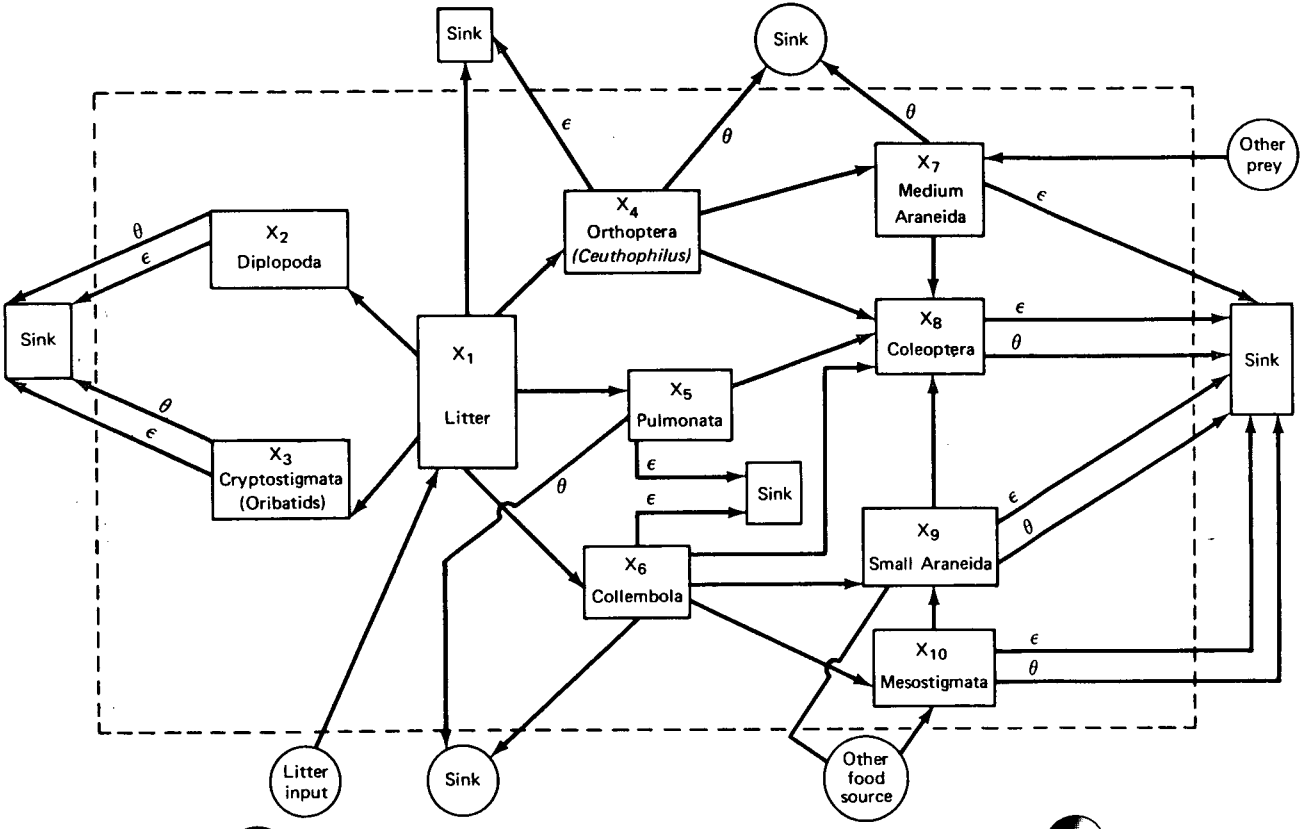

Fig. 1 Conceptual diagram of the cryptozoan food web under study.

Since fresh leaf litter may remain unpalatable to soil fauna until the polyphenols in the stem and leaf material are removed (Edwards and Heath, 1963; Satchell and Lowe, 1966), faunal attack on the litter may be delayed for some time.

Physical factors in the soil–litter complex were used as driving variables for the models. The temperature on the forest floor is more constant than that above the floor in the forest. This allows animals that are fully active at only a few degrees centigrade (e.g., mites and Collembola) to continue their activities under a blanket of snow, provided the snow has not fallen on frozen ground (Kuhnelt, 1955). If the soil freezes, the animals cease to function; when the soil thaws, however, they continue their activity unperturbed (Kuhnelt, 1955). Some soil animals (e.g., millipedes, earthworms, and isopods) burrow into the soil to escape the freezing temperatures. Conversely, exposure to intensive solar radiation may cause the fauna to undergo a vertical migration to escape high temperatures. Many small arthropods disappear during the daylight hours and reappear after sundown (Kuhnelt, 1955).

Thamdrup (1939) ascertained that, in a Danish heathland, a humus moisture content of 10 to 20% (dry matter + water = 100%) corresponds to ambient relative humidity of 75 to 90% in the litter. He considered that even under very severe drought conditions (moisture content of ~30%) the ambient relative humidity does not fall below 90%. This evidence corroborates the view that low humidity is rarely a limiting factor to populations in the F and H layers of the forest floor. Gasdorf and Goodnight (1963) found no definite correlation between mite populations and soil moisture. They concluded that temperature had a greater effect on mite populations than the moisture content of the litter.

DIPLOPODA (X_2)

Habitat

Diplopods (millipedes) are part of the litter and cryptozoic fauna over much of the world (Cole, 1946). Generally, however, they are restricted to forests with moderate temperatures and high ambient humidity (O'Neill, 1968). Soil type, as well as temperature and moisture, is important for the millipedes. Many prefer a mull type of soil (Bornebusch, 1930) with high calcium content (Blower, 1955).

Feeding Habits

The diplopods are generally viewed as primary decomposers, converting litter into a state suitable for further breakdown by microorganisms (Elliot, 1970; Jacot, 1940; O'Neill, 1968), but *Apheloria* may prefer fungal mycelia (Birch and Clark, 1953; Blower, 1955). The millipedes are exclusive saprovores and are known to be poor food assimilators, defecating a large portion of their intake as fecal matter. Bocock (1963) showed that *Glomeris marginata* utilized from 6 to 10% of the dry matter consumed, and Gere (1956) stated that maximum feeding

efficiency for the millipedes he studied was about 7%. However, the *Glomeris* may consume as much as 120 g of deciduous litter per square meter in a year (Bocock, 1963) and may be quite important in litter decomposition (Van der Drift, 1950). Jacot (1940) states that millipedes are instrumental in mixing the organic material with the mineral substrate.

Van der Drift (1950) showed a rapid increase in the feeding rate of millipedes with a rise in temperature and found an optimum temperature for the species he examined to be between 17.5 and 22.5°C. Gere (1956) concluded that *Glomeris* may have an optimum feeding temperature greater than 22°C.

Predation

Cloudsley–Thompson (1949) stated that millipedes are seldom preyed upon. Cole (1946) observed two laboratory cases in which millipedes were attacked and killed by carabid beetles, but in both cases the millipede was immediately dropped and not eaten.

Temperature and Moisture

Lyford (1943) found that in the northeastern United States millipede activity started as soon as the frost was out of the soil and ceased when the soil froze. O'Neill (1968) found that *Narceus americanus* hibernated at temperatures below 19°C and that temperatures above 25°C may be detrimental to the animal. Shaw (1968) found that in New York the millipede *Narceus annularis* moved into the litter from its winter locations by April 15, most of the population being active by early June. The number of millipedes decreased in autumn until none were found in late October. Presumably they penetrated directly into the soil to overwinter since no migrations in or out of the study area were observed. Millipedes on the forest floor are very susceptible to desiccation and are found only in humid and moist conditions (Blower, 1955).

CRYPTOSTIGMATA (Oribatids) (X_3)

Habitat

Cryptostigmata (mites) generally are most dense in the litter layers of the forest floor (Van der Drift, 1950). Crossley and Bohnsack (1960) found that mites were the most abundant arthropods in short-leaf pine litter, comprising 83% of the total animal count; adult cryptostigmata numbered 26% of this total.

Feeding Habits

Beginning with the work of Michael (1883), cryptostigmatid mites as a group have been considered to be general saprovores.

Luxton (1972) reviewed the use of the terms "microphytophage" and "macrophytophage" to separate cryptostigmatids feeding on microflora from those feeding on the remains of higher plants. We have avoided such a separation because of conflicting reports on feeding habits for various species, inability to specify feeding habits for many forms, possible differences in immature and adult feeding habits, and evidence for other types of feeding (e.g., coprophagy) (Wallwork, 1967). Little is known about rates of feeding for cryptostigmatids, but current experimental work is yielding suggestive values (Luxton, 1972, and others). Assimilation efficiencies and respiration rates are also being reported (Good and Lawton, 1973).

Predation

There are few studies, if any, dealing with predators on adult oribatids. Immature stages may be subject to predation, but little concrete information exists.

Temperature and Moisture

The activities of cryptostigmatids are closely linked to soil temperature. Van der Drift (1950) suggested that cryptostigmatid mortality is linked to frost, and yet in the same work he states that the microarthropod fauna does not suffer seriously from frost. Hartenstien (1962a) found *Belba kingi* as an adult or a deutonymph in the upper 3 in. of soil when the ground water was frozen. It appeared that only the adult of *Metabelba montanna* overwintered, however (Hartenstien, 1962b). The population density fluctuated with time; the population peaks in an oak–hickory forest in Indiana occurred in May and November, and the lows occurred in August and January.

ORTHOPTERA (Ceuthophilus) (X_4)

Habitat

The camel cricket, *Ceuthophilus*, is generally uncommon on the forest floor (Cantrall, 1943) and, except for very local areas, is usually not an important contributor to litter decomposition (Cole, 1946; Bornebusch, 1930). During the day crickets are inactive and retreat under rocks or in logs. Cantrall (1943) suggested that the prevalence of suitable retreats in which to hide may be one limiting factor for camel cricket populations. He found that adult crickets live for only one summer; the small nymphs and eggs are the forms that overwinter.

Feeding Habits

Very little is known about the feeding habits of the *Ceuthophilus*. They are generally assumed to be nocturnal saprovores (Blatchley, 1920). Reichle and

Crossley (1965) estimated that *Ceuthophilus* consumed 2.4% of its body weight per day in an east Tennessee forest.

Predation

As with the other aspects of the natural history of this animal, very little is known about its predators. However, the Carabidae (Balduf, 1969) and spiders (Moulder, Reichle, and Auerbach, 1970) are considered predators of the litter Orthoptera.

PULMONATA (X_5)

Habitat

Pulmonata (land snails) are most numerous in moist deciduous forests with a high calcium content. Bornebusch (1930) found that snails were numerous in deciduous forests, both on mull and raw humus, but were scarce in coniferous forests. They were found in all hardwood forests that had not been heavily grazed, trampled, or burned (Jacot, 1940). Oughton (1948) found that the food of land snails included fungal hyphae of decaying litter and, to a lesser extent, the larger fleshy fungi, litter, and living plant tissue.

Since snails contain proportionally large quantities of calcium, their demand for this element is high. Oughton (1948) stated that there are three sources from which they may obtain calcium: plant foods, the skeletons of other animals, and calciferous soil or rocks. Skeletons and plant-food sources appeared to be the most important.

Temperature and Moisture

The life of snails is intimately linked to water. Kunkel (1916) believed that water was the most important factor in the life of terrestrial mollusks. Van Cleave (1931) estimated that 99% of a population of land snails may be eliminated by severe drought. Blake (1931) found that fluctuations in snail populations were more closely correlated with changes in humidity than with changes in temperature in an Illinois woodland.

There is some disagreement on the reaction of the land snail to temperature. Cole (1946) and Blake (1931) suggested that snails burrow into the soil to escape freezing temperatures, but Cole also observed that these animals are resistant to cold temperatures and continue to breed in near-freezing temperatures.

Predation

Terrestrial snails appear to have several predators. Cole (1946) listed birds, moles, toads, shrews, staphylinids, and carabid beetles as predators of land snails.

COLLEMBOLA (X_6)

Habitat

Collembola abound in all moist soils throughout the world and are numerous in the humus litter zone in moist forests (Cole, 1946; Jacot, 1940; Birch and Clark, 1953). Mites generally outnumber them (Bornebusch, 1930), but Naglitsch (1962) found Collembola more numerous than mites in selected German forests.

Food Habits

Collembola are considered general feeders. They will consume fungi, algae, microorganisms, humus, leaf litter, and living vegetation. There is some general agreement on the main food source. Englemann (1968) stated that Collembola feed mainly on fungi. Singh (1969) found that many Collembola preferred fungi and that they may select for specific fungal species. He also found that certain Collembola feed on humus only if microorganisms are present in the material.

Temperature and Moisture

Moisture appears to be a more important environmental variable to Collembola than temperature. Davies (1928) found that the optimum relative humidity for the species tested was about 100%. Cole (1946) noted that soil Collembola populations increased conspicuously with an increase in soil moisture. Blake (1931) felt that population fluctuations were correlated with both temperature and humidity, but moisture seemed to be the most important factor as the forest floor became dry. Collembola have a definite tolerance for low temperatures (Kuhnelt, 1955; Blake, 1931). Cole (1946) found vertical migration in response to frost, but the animals may survive freezing. Hale (1967) contended that, although many soil animals living under subarctic conditions are active at low temperatures, this is particularly noticeable in Collembola, which are fully active just above the freezing point.

Population

Since Collembola are a stable food source for mites, Coleoptera, nematodes, dipterous larvae, chilopods, and spiders (Hale, 1967), they have a high mortality rate. This is compensated for by a very high reproductive potential. Gist, Merchant, and Crossley (1974) found *Sinella curviseta* to have a biotic potential (r) of 11.5 per day, i.e., a replacement rate of about 428 individuals per female in 37 days under ideal laboratory conditions.

The life span of Collembola varies from slightly less than to more than 1 year (Joose, 1969).

ARANEIDA (X_7 AND X_9)

Habitat

Very few studies of the forest floor discuss Araneida (spiders) to any extent. Moulder, Reichle, and Auerbach (1970) conducted an energetics study on the spiders in a *Liriodendron* forest in Tennessee. Clark and Grant (1968) and Gasdorf and Goodnight (1963) also made some observations on spiders. Blake (1931), in his study of an Illinois woodland, found that spiders were present but were not very common. Both Van der Drift (1950) and Bornebusch (1930), their excellent works on the forest floor, mention spiders only in passing.

The paucity of information on forest-floor spiders seems somewhat surprising since there is general agreement that they are a conspicuous part of the leaf-litter community of a climax forest (Clark and Grant, 1968; Moulder, Reichle, and Auerbach, 1970; Van der Drift, 1950; Bornebusch, 1930; Gasdorf and Goodnight, 1963). Moulder, Reichle, and Auerbach found that spiders were the most important predator group in the *Liriodendron* litter population in terms of biomass and numbers. The mean annual population density exceeded that of the next two most numerous predator groups, Chilopoda and Coleoptera. Within the litter–mineral-soil complex the spiders appear to be restricted to the litter layer. Jacot (1940) stated that spiders, although common in litter, are not known to enter the mineral soil of woodlands to any extent.

Although it is generally agreed that spiders do appear in the forest floor in significant numbers, there is disagreement on their relative importance. Moulder, Reichle, and Auerbach (1970) stated that little is known about the impact of these animals on lower trophic levels. Van der Drift (1950) implied that spiders have a great influence on the community, and Clark and Grant (1968) conducted a study that partially substantiated this. Clark and Grant postulated that, since spiders are highly mobile and strictly carnivorous, they might be expected to exert considerable influence on their coexisting prey populations. Their experimental results support this hypothesis to a limited extent. In contrast, Bornebusch (1930) felt that spiders have little direct influence on the leaf-litter community.

Feeding Habits

There is general agreement that spiders are exclusively predatory (Moulder, Reichle, and Auerbach, 1970; Clark and Grant, 1968; Jacot, 1940). Clark and Grant showed that Collembola formed the largest numerical part of the potential prey populations for small spiders.

Temperature and Moisture

Populations of spiders seem to vary widely with season; the high peaks depend on the locality of the study. Cole (1946) found that in Illinois spiders

attained maximum numbers in the fall. Gasdorf and Goodnight (1963) found an early spring peak. The population decreased in summer, began to increase in September, and then leveled off until February, when it once again rose, culminating in a spring high. Moulder, Reichle, and Auerbach (1970) found that small spiders remained active throughout the year in Tennessee.

Gasdorf and Goodnight (1963) found little correlation between the seasonal population fluctuations and temperature and humidity. Lowrie (1942) stated that substrate and humidity are very important factors in controlling the distribution of spiders. Moulder, Reichle, and Auerbach (1970) demonstrated that temperature is quite important to spiders also. Below 5°C spiders were observed to become very sluggish, ceasing movement and feeding. It was assumed that energy assimilated equaled energy lost through respiration at this temperature. Small spiders had an optimum efficiency at 10 to 15°C, and temperatures greater than 25°C were detrimental to them.

COLEOPTERA (CARABIDAE) (X_8)

Habitat

As on spiders, ecological information on forest-floor carabids is scattered. The information available generally indicates that these beetles are numerous. Carabids may form a predominant part of the litter fauna (Cole, 1946).

Feeding Habits

The Carabidae are generally considered nocturnal predators (Balduf, 1969); they attack and consume Annelida, mollusks, arthropods, and small chordates. The bulk of the prey taken, however, consists of insects. Bornebusch (1930) and Cole (1946) also found this group to consume vegetable material. Cole found the carabids to be cannibalistic.

Temperature and Moisture

Little is known of the carabid's response to temperature or moisture. Balduf (1969) stated that some carabid species are killed by winter frost. Jacot (1940) found that *Clivina* migrated through the soil from near the surface to as deep as 6 ft when the soil surface became dry. Cole (1946) stated that the carabids showed no apparent discrimination between wet and dry substrate, but in a humidity gradient they moved fairly rapidly to the moist end and remained motionless there. Access to free water seems to be necessary for the well-being of this animal group (Balduf, 1969).

Predation

Balduf (1969) recorded several predators on carabids. Most of them are vertebrates, e.g., skinks, shrews, raccoons, and foxes. Other predators include

toads and birds. The carabid's nocturnal activity, obscure habits, and rapid locomotion probably afford them some protection from predators.

MESOSTIGMATA (X_{10})

Habitat

In general there is a paucity of ecological information on the litter-dwelling mesostigmatid mites. Wallwork (1967) and Bornebusch (1930) found that *Veigaia* and *Pergamasus* are among the most numerous mesostigmatid mites in the litter layer.

Feeding Habits

The mesostigmatid mites are large active mites feeding on thin-skinned mites, proturans, Collembola, paurapods, nematodes, and Diptera larvae (Wallwork, 1967). Collembola evidently are preyed upon by the Mesostigmata in great numbers, and, because the predators are large and gluttonous, they may have an important impact on the prey species.

Temperature and Moisture

There is very little information on the temperature and moisture responses of mesostigmatid mites. Wallwork (1967) indicated that low temperature and low moisture are unfavorable for this group. Mollin and Hunter (1964) found that *Cosmolaelaps passali,* which lives in passalid beetle tunnels, will not reproduce in the laboratory at temperatures of 70°F but will reproduce between temperatures of 75 and 85°C only.

MATERIALS AND METHODS

Study Area

We sampled the biota at Coweeta Hydrologic Laboratory, Macon County, N. C., to derive elemental contents for the compartments shown in Fig. 2. Features of the particular watershed sampled (No. 18) and a general description of the study area are given by Johnson and Swank (1973). Samples were taken four times a year so that models could be constructed on seasonal as well as annual bases. Details of the sampling program and estimates of elemental standing crops have been reported separately (Gist and Crossley, 1974a).

Model

The cryptozoan food-web model in this study was linear and donor controlled with time-varying and temperature-varying coefficients. Since the

temperature function actually depended on time also, the only true independent variable in the model was time. All the time functions were sinusoids with a frequency of 2π radians per year and a summer peak equal to 19°C. The 19°C temperature was the average daytime temperature measured in the litter during the summer. The temperature function was used to control the feeding rates of the litter animals in the model and was based on a Q_{10} of 2 (Kowal and Crossley, 1971). This function ranged between 0 and 1, equaling 1 when the temperature was at 19°C since this was the temperature at which the isotopic [illegible]nation of the fluxes was conducted (Gist and Crossley, 1974b).

It was assumed that moisture was not a controlling factor for the invertebrates in this study since Cromack (1972) stated that the minimum water content in the leaves was approximately 30% of dry weight, which would correspond to an ambient relative humidity of greater than 90% (Thamdrup, 1939).

Field observations indicated several inputs to and outputs from the system. The inputs included animals migrating to the soil to overwinter or to pupate and some which fell out of the canopy to the forest floor through their own activities or through leaf fall and/or wind. The outputs were mainly predators that entered the system, fed, and left, e.g., birds, robber flies (Asilidae), and small mammals. We attempted to account for inputs and outputs by use of outside forcings and sinks.

Generalized systems were mostly equations of the general linear form:

$$x_i = (\text{total gain fluxes to i}) - (\text{total loss fluxes from i})$$

These were simple ordinary differential equations with time-varying coefficients. Generalized systems equations and time-varying coefficients developed for potassium and calcium models were listed by Crossley and Gist (1973).

The time-varying-coefficient model was used to simulate the dynamics of potassium and calcium in this litter food web. To simulate the system, we used the CSMP language on the IBM 360/65 digital computer. Fourth-order Runge–Kutta fixed step was the integration technique used, with 10 iterations per day and a simulation time of 2 years. A total annual flux to each of the animal groups was calculated by summing the daily fluxes to each compartment,

$$\text{Total } f_{ij} = \sum_{t=1}^{365} a_{ij}(t)\, X_i(t) \tag{1}$$

This total annual flux was later used to construct a constant-coefficient model holding all the parameters constant,

$$a_{ij} = \frac{\text{total } f_{ij}}{\bar{\bar{X}}_i} \tag{2}$$

where $\bar{\bar{X}}_i$ is the annual mean compartment size.

RESULTS

Quantification of the conceptual model was accomplished for both potassium and calcium by deriving values for components and rates. Results are presented separately for the summer season alone (Figs. 2 and 3) and for the annual fluxes (Figs. 4 and 5). The discussion here pertains to feeding activities by fauna, but it is clear that the major flux of each element is from litter to soil via leaching ($\lambda 10$).

Summer Fluxes (Figs. 2 and 3)

Three of the saprovore compartments dominated summer flux of calcium and potassium from leaf litter. Millipedes (Diplopoda) had the greatest summer flux for both calcium and potassium. Cryptostigmata were second to millipedes in calcium flux but ranked behind Orthoptera in potassium flux. Pulmonata and Collembola were unimportant. Coleoptera lead the predator compartments in both calcium and potassium fluxes.

These fluxes represent the system of definition under summer conditions and tend to underemphasize the importance of the microarthropods. The microarthropods are active all year and are actually at population lows during the summer (Gist and Crossley, 1974b). On the other hand, the macroarthropods may have a greater importance attributed to them than they actually possess. It has been previously pointed out that the macroarthropods are at their maximum during the summer and are not abundant for much of the rest of the year. Therefore they make a large contribution in mineral movement for a short period of time, but, over the course of the year, they may make a less important contribution to mineral movement in the litter than the microarthropods.

Annual Fluxes (Figs. 4 and 5)

The annual fluxes were calculated by integrating the daily fluxes of potassium and calcium based on a 1-year simulation.

On an annual basis, the Cryptostigmata emerges as the most important saprovore group for calcium flux and the second most important for potassium flux; both fluxes exceed those for millipedes by nearly an order of magnitude. Collembolans exceeded the cryptostigmatid mites in the flux of potassium and were second to them in the flux of calcium. Thus microarthropods emerge as fauna of primary importance in the elemental flux from litter in models considering annual fluxes.

Among predators, small spiders and mesostigmatid mites emerged as the more important groups for elemental flux on an annual basis.

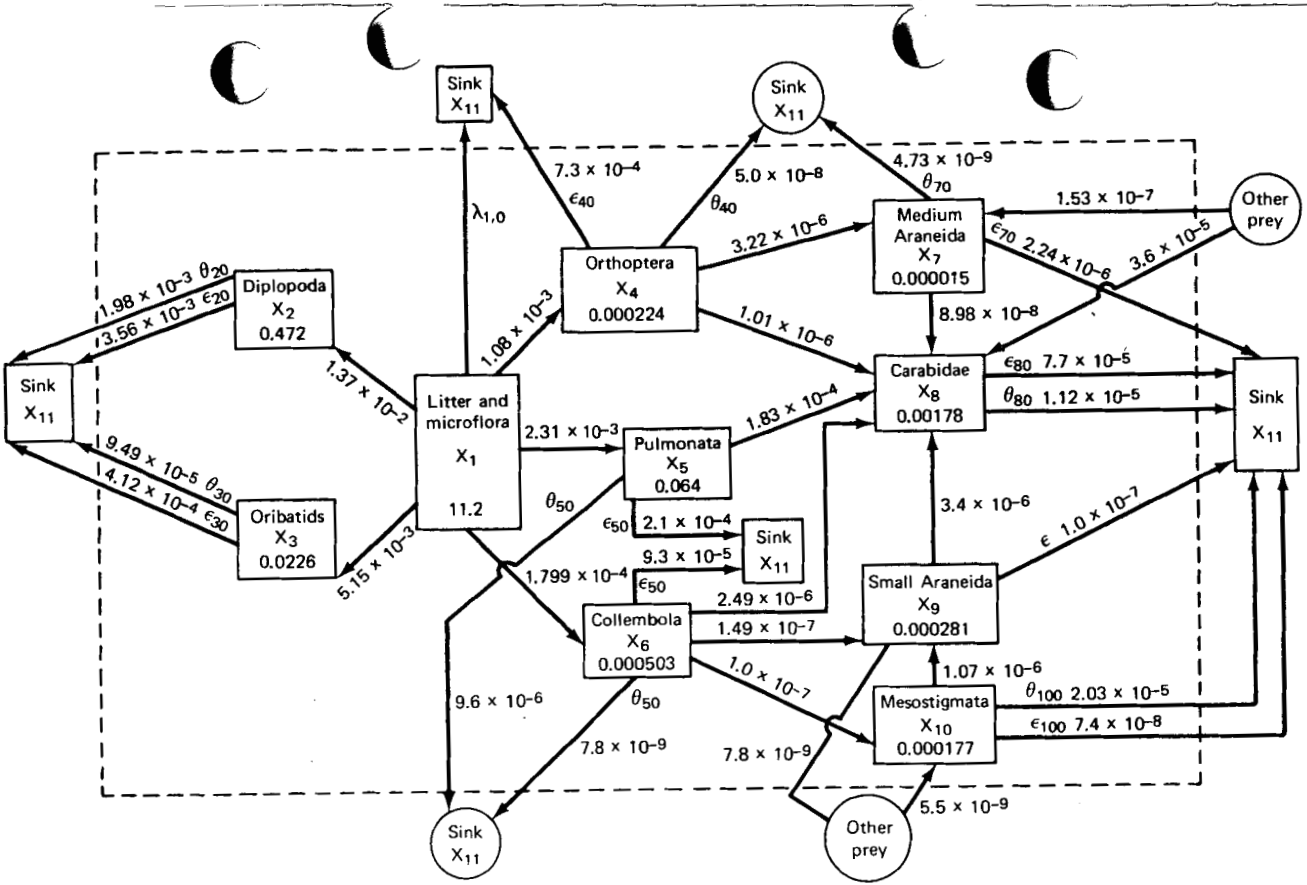

Fig. 2 Control diagram for calcium summer flux. Fluxes are given in grams per square meter per day, and compartment sizes are given in grams per square meter.

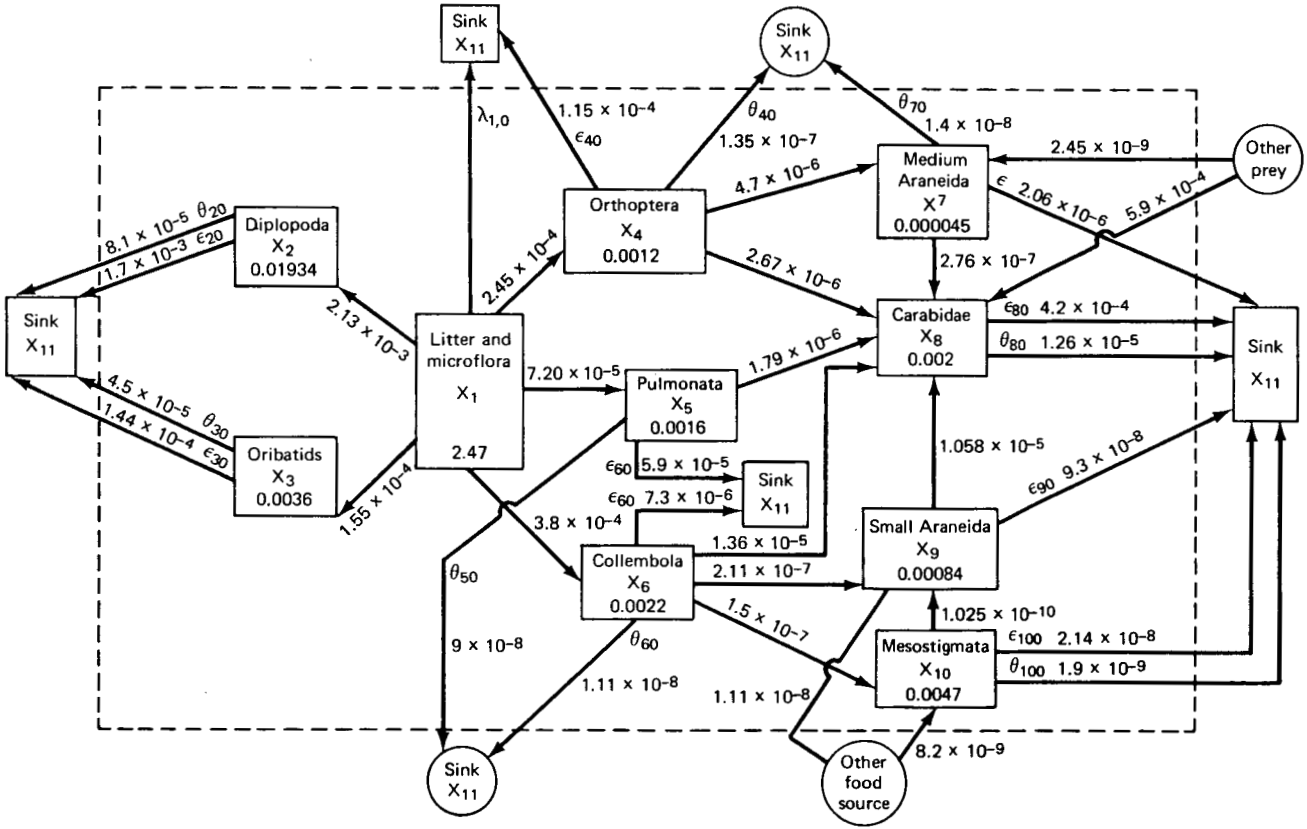

Fig. 3 Control diagram for potassium summer flux. Fluxes are given in grams per square meter per day; compartment sizes are given in grams per square meter.

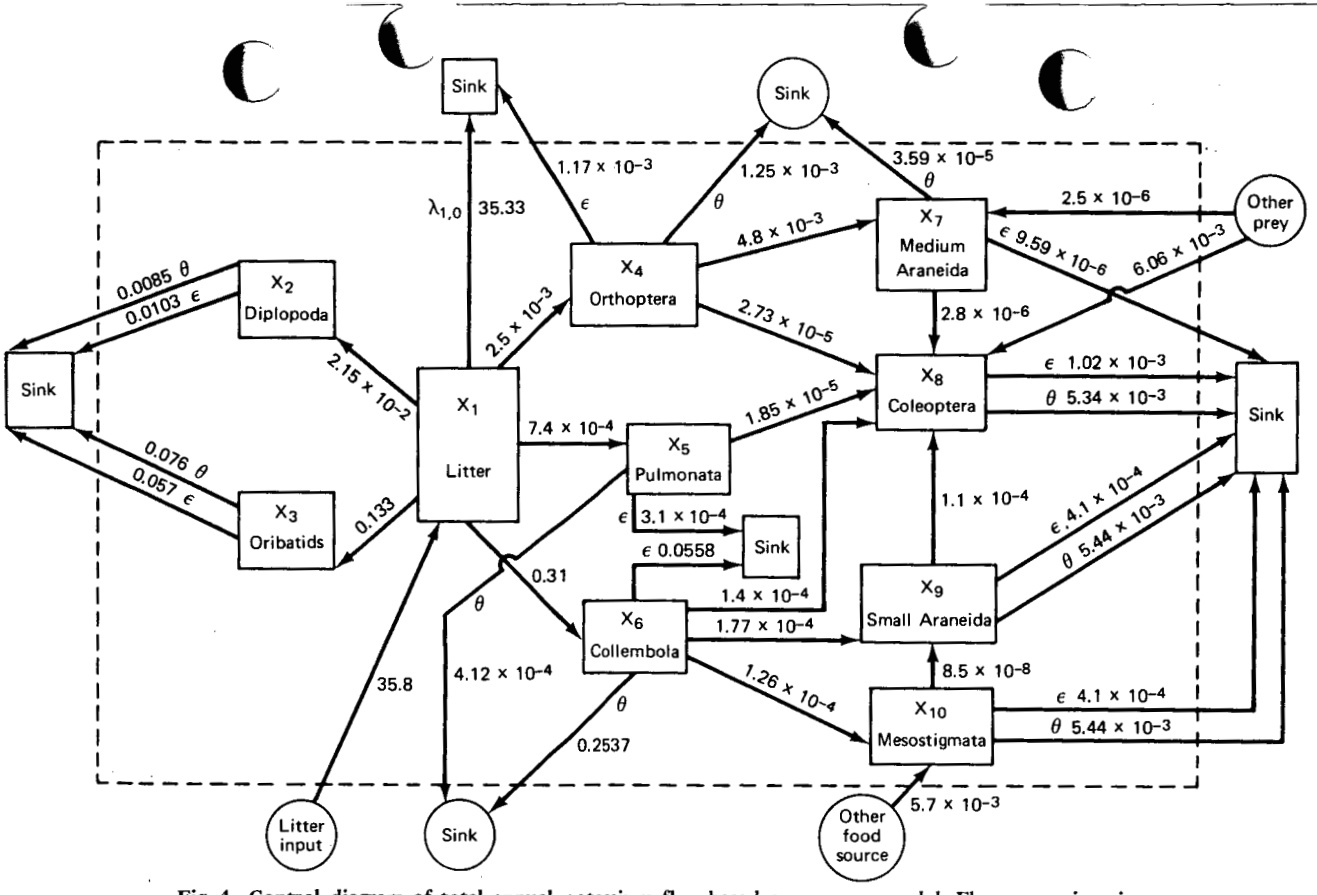

Fig. 4 Control diagram of total annual potassium flux based on summer model. Fluxes are given in grams per square meter per year, and the compartment size is given in grams per square meter.

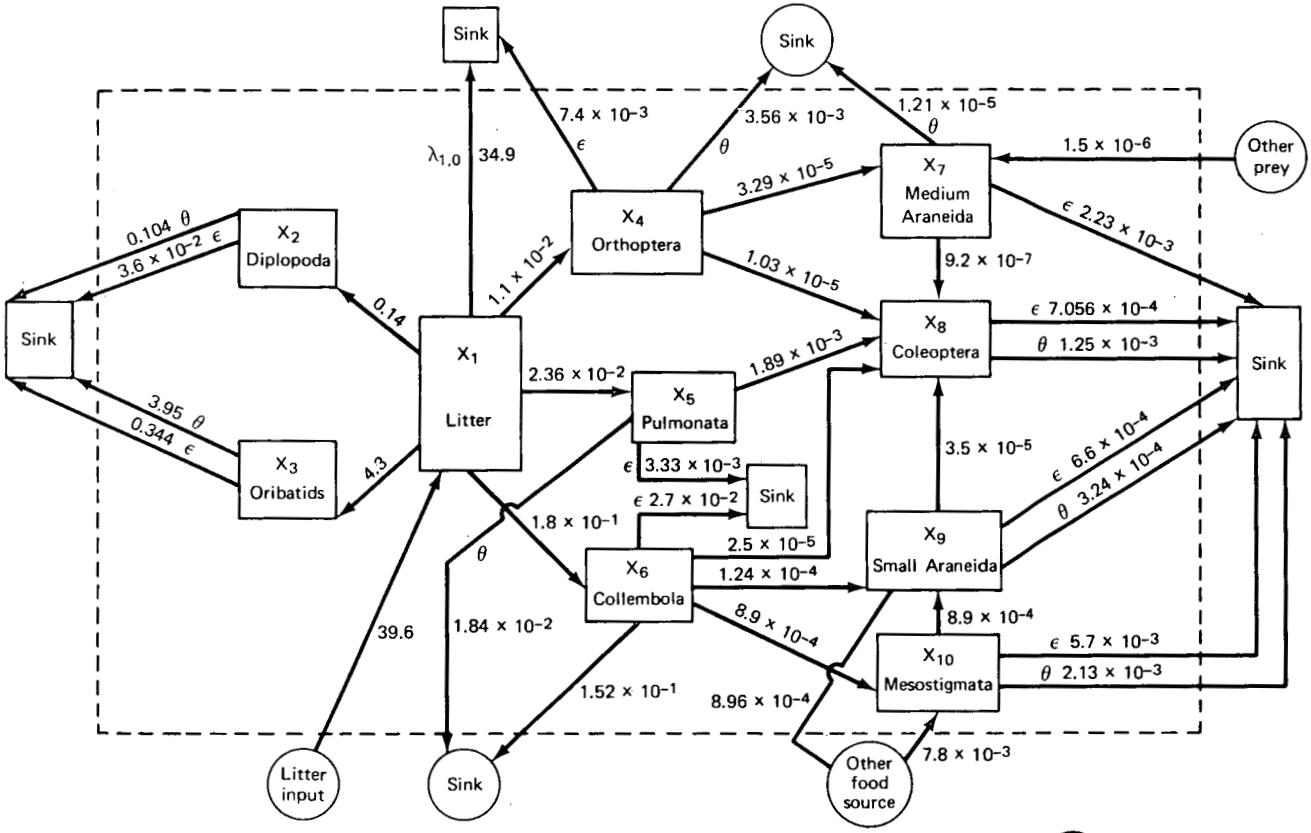

Fig. 5. Control diagram of total annual calcium based on summer model. Fluxes are given in [illegible] per square [illegible] per year, and compartment sizes are given in grams per square meter.

Biomass Model

The preceding models were of calcium and potassium only, and a model with greater generality based on the data gathered for the elemental models may be desired. The generality of a model can be increased if the values of the model can be expressed in terms of biomass. An elemental model has all the necessary pathways for a biomass model, with the exception of rate constants from the compartments representing respiration. The biomass intake fluxes (grams of [illegible] per square meter per unit of time) for each animal compartment can be [illegible]ated from mineral intake fluxes since the mineral concentrations are known.

The annual biomass flux from the litter compartment to saprovores was estimated independently from calcium and potassium concentrations and movements. On the basis of calcium, data consumption by saprovores amounted to 81 g/m^2 (20.3% of annual input). For potassium, consumption by saprovores was estimated to be 30 g/m^2 (7.5% of annual input). These estimates assume an annual input of 400 g/m^2 (Cromack, 1972).

It is interesting to note that the biomass annual flux from the litter compartment to the saprovores in this model accounts for 7.5% (potassium) or 20% (calcium) of the total annual input into the litter compartment. On the other hand, the saprovores in the mineral models account for only 1% (potassium) or 12% (calcium) of the total annual elemental inputs to the litter compartment. This discrepancy between the biomass fluxes and the mineral fluxes shows that, although a significant portion of the biomass is being processed through the saprovores, a smaller portion of the mineral nutrients is processed by them.

The two estimates for the biomass flux from the litter compartment to the saprovores straddle the 15% minimum effect on the litter by litter arthropods reported by Crossley and Witkamp (1964). These investigators found that excluding most of the arthropods resulted in a reduction of litter decomposition in terms of biomass of over 15% and a reduction in the loss rate of ^{137}Cs (the potassium analog) of over 50%. Based on this information, we can postulate that fauna has a greater impact on the decomposition of litter and nutrient movement than just the removal of a given quantity of biomass. In other words, indirect controls on litter decomposition mentioned in the introduction may indeed be more important in litter breakdown than the direct effects of feeding. Thus the saprovores can be looked at as processors in that they break up and inoculate the litter material with microflora, which do the actual breakdown. Little of the litter is actually absorbed in the process.

This study supports the idea that the fauna may regulate the breakdown of litter on the forest floor without making any great demands on the content of the material itself, as postulated in the introduction and the literature review. This would be analogous to a thermostat regulating a large heating unit; the

thermostat demands very little energy but at the same time controls vast amounts of energy.

DISCUSSION

The saprovores in the potassium model accounted for only 1% of the total potassium flux from the litter compartment. Since potassium is not tightly bound by such structures as cell walls, it is considered very mobile and highly leachable. Best (1971) found that as much as 60% of the total potassium was in the form of leaching. Thus the high loss from the litter compartment by leaching and other decomposers might have been expected.

In the calcium model, 12% of the annual calcium input was accounted for by the saprovores. Since calcium is bound in the structure of the cell wall, it is less mobile than potassium. Consequently, the resistant cellulose and lignins of the wall must be at least partially broken down before the calcium is released. The decrease in calcium flow through leaching and other decomposers ($\lambda_{1,0}$ in Figs. 4 and 5) as compared with potassium probably reflects a decrease in leaching rather than a decrease in the flow through other decomposers.

The biomass model based on calcium fluxes showed a biomass flux of 20% of the annual input through the saprovores. This value is only slightly lower than the values of 28% reported by Ulrich (1933) and 20 to 25% by Bornebusch (1930). The fluxes may be low in this study because of high uptake estimates in the feeding experiments (Gist and Crossley, 1974a) or possibly because some of the saprovores were not included in the model.

We have made some obvious omissions in this model, e.g., the Diptera, Nematoda, and Protozoa. Van der Drift (1950) stated that the dipteran families Bibionidae, Sciaridae, and Tipulidae were saprovores associated with litter decomposition. He also listed Leptidae and Dolichopodidae as predators in the litter. The Nematoda seem to be mainly bacteriovores or plant feeders and are not very closely associated with litter decomposition directly. In an earlier work Bornebusch (1930) considered the nematodes one of the major contributors to litter decomposition. At any rate, Fenton (1947) felt that the nematodes are suppressed in deciduous forest litter and reach their peak on the coniferous forest floor; therefore omitting the nematodes in this model probably caused no great error. Fenton also felt that the Protozoa made less contribution to litter decomposition than did the nematodes.

The model can be simplified by lumping compartments that are functionally the same or by eliminating compartments that do not contribute significantly to the dynamics of the model. In the annual models of potassium and calcium, some lumping appears to be warranted. Since Orthoptera and Pulmonata, for example, contribute very little to the dynamics of the mesofaunal saprovores, they could quite easily be included in the diplopod compartment or even eliminated from the model. The seasonal dynamics of these three mesofaunal

saprovores were the same; however, the Orthoptera and Pulmonata had fluxes to the medium Araneida and Coleoptera which the Diplopoda compartment lacked. If a compartment of mesofaunal saprovores were constructed, a portion of the total flux from it could be partitioned to the predator compartments.

The mesofaunal predator compartments may be lumped also since the medium Araneida do not make a significant contribution to the models in terms of the annual flux of nutrients or biomass. The microarthropod predators both make significant contributions to the dynamics of the annual models. Based on the contribution of the microarthropod predators and the fact that their ...lation dynamics were different, it seems justified to maintain them as separate compartments.

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REFERENCES

Balduf, W. V., 1969, *The Bionomics of Entomophagus Coleoptera,* E. W. Classey, Ltd., Faringdon, Berkshire, England.

Best, G. R., 1971, Potassium, Sodium, Calcium and Magnesium Flux in a Mature Hardwood Forested Watershed and an Eastern White Pine Forested Watershed at Coweeta, M.S. Thesis, University of Georgia, Athens.

Birch, L. C., and D. P. Clark, 1953, Forest Soil as an Ecological Community with Special Reference to the Fauna, *Quart. Rev. Biol.,* **28**: 13-36.

Blake, I. H., 1931, Further Studies on Deciduous Forest Animal Communities, *Ecology,* **12**: 508-527.

Blatchley, W. S., 1920, *Orthoptera of Northeastern America,* The Nature Publishing Co., ...ndianapolis, Indiana.

...er, J. G., 1955, Millipeds and Centipeds as Soil Animals, in *Soil Zoology,* pp. 138-151, D. K. McE. Kevan (Ed.), Academic Press, Inc., New York.

Bocock, K. L., 1963, The Digestion and Assimilation of Food by *Glomeris,* in *Soil Organisms,* pp. 85-91, J. Doeksen and J. Van der Drift (Eds.), North-Holland Publishing Co., Amsterdam.

Bornebusch, C. H., 1930, The Fauna of the Forest Soil, *Forstl. Forsogav. Danmark,* **11**: 1-224.

Cantrall, I. J., 1943, The Ecology of the Orthoptera and Dermaptera of the George Reserve, Michigan, Miscellaneous Publication, Museum of Zoology, University of Michigan, No. 54, University of Michigan Press, Ann Arbor.

Clark, R. D., and P. R. Grant, 1968, An Experimental Study of the Role of Spiders in a Forest Litter Community, *Ecology,* **49**: 1152-1154.

Cloudsley-Thompson, J., 1949, Enemies of Myriapods, *Naturalist,* **1949**: 137-401.

Cole, L. C., 1946, A Study of the Cryptozoa of an Illinois Woodland, *Ecol. Monogr.,* **16**: 50-86.

Cromack, K., 1972, Oregon State University, personal communication.

Crossley, D. A., Jr., 1970, Roles of Microflora and Fauna in Soil Systems, in *Pesticides in the Soil: Ecology, Degradation and Movement,* International Symposium on Pesticides in the Soil, Feb. 25-27, 1970, pp. 30-35, Michigan State University Press, East Lansing.

——, and K. K. Bohnsack, 1960, Long-Term Ecological Study in the Oak Ridge Area. III. The Oribatid Mite Fauna in Pine Litter, *Ecology,* **41**: 628-638.

——, and C. S. Gist, 1973, Use of Radioisotopes in Modeling Soil Microcommunities, Proceedings of the First Soil Microcommunities Conference, Oct. 18-20, 1971, D. L. Dindal (Ed.), USAEC Report CONF-711076, pp. 258-278.

——, and M. Witkamp, 1964, Effects of Pesticides on Biota and Breakdown of Forest Litter, in *Eighth International Congress of Soil Science,* Aug. 30—Sept. 9, 1964, Vol. III, pp. 87-91, Bucharest, Romania.

Davies, W. M., 1928, The Effect of Variation in Relative Humidity on Certain Species of Collembola, *J. Exp. Biol.,* **6**: 79-86.

Edwards, C. A., and J. W. Heath, 1963, The Role of Soil Animals in Breakdown of Leaf Litter, in *Soil Organisms,* pp. 76-84, J. Doeksen and J. Van der Drift (Eds.), North-Holland Publishing Co., Amsterdam.

——, D. E. Reichle, and D. A. Crossley, Jr., 1970, The Role of Invertebrates in Turnover of Organic Matter and Nutrients, in *Analysis of Temperate Forest Ecosystems,* D. E. Reichle (Ed.), Springer-Verlag, New York.

Elliot, H. J., 1970, The Role of Millipedes in Decomposition of *Pinus Radiata* Litter in the Australian Capital Territory, *Aus. For. Res.,* **4**: 3-10.

Englemann, M. D., 1968, The Role of Arthropods in Community Energetics, *Amer. Zool.,* **8**: 61-69.

Fenton, G. R., 1947, The Soil Fauna: With Special Reference to the Ecosystem of Forest Soil, *J. Anim. Ecol.,* **16**: 76-93.

Gasdorf, E., and C. J. Goodnight, 1963, Studies on the Ecology of Soil Arachnids, *Ecology,* **44**: 261-268.

Gere, G., 1956, The Examination of the Feeding Biology and Humificative Function of Diplopoda and Isopods, *Acta Biol. Acad. Sci. Hung.,* **6**: 257-271.

Gist, C. S., and D. A. Crossley, Jr., 1974a, Ecology Center, Utah State University, unpublished data.

——, and D. A. Crossley, Jr., 1974b, The Litter Arthropod Community in a Southern Appalachian Forest: Numbers, Biomass, and Element Content, in *Amer. Midland Natur.,* **93**: 107-122.

——, V. A. Merchant, and D. H. Crossley, 1974, Analysis of Life Tables for the Collembola *Sinella Curviseta, Environ. Entomol.,* **3**: 840-844.

Hale, W. G., 1967, Collembola, in *Soil Biology,* pp. 397-411, A. Burges and F. Raw (Eds.), Academic Press, Inc., New York.

Hartenstien, R., 1962a, Soil Oribatei. II. *Belba kingi,* New Species (Acarina, Belbidae), and a Study of Its Life History, *Ann. Entomol. Soc. Amer.,* **55**: 357-361.

——, 1962b, Soil Oribatei. III. Studies on the Development Biology and Ecology of *Metabelba nervosa* n. sp. (Acarina, Eremaeidae), *Ann. Entomol. Soc. Amer.,* **55**: 361-367.

Jacot, A. P., 1940, The Fauna of the Soil, *Quart. Rev. Biol.,* **15**: 28-57.

Johnson, P. L., and W. T. Swank, 1973, Studies of Cation Budgets in the Southern Appalachians on Four Experimental Watersheds with Contrasting Vegetation, *Ecology*, **54**: 70-80.

Joose, E. N. G., 1969, Population Structure of Some Surface Dwelling Collembola in a Coniferous Forest Soil, *Neth. J. Zool.*, **19**: 621-634.

Kowal, N. E., and D. A. Crossley, Jr., 1971, The Ingestion Rates of Microarthropods in Pine Mor Estimated with Radioactive Calcium, *Ecology*, **52**: 444-452.

Kuhnelt, W., 1955, An Introduction to the Study of Soil Animals, in *Soil Zoology*, pp. 3-19, D. K. McE. Kevan (Ed.), Academic Press, Inc., New York.

Kunkel, K., 1961, *Zur Biolgie der Lungenschnecken*, Ergebnisse Vieljahr Zuchtgr. V. [illegible]perimente veroffentilicht im Unterstutz. d. Heidelberg Akademie d. Wissenschl.

[illegible]e, D. C., 1942, The Ecology of Spiders of Xeric Dune Lands in the Chicago Area, *Bull. Chicago Acad. Sci.*, **6**: 161-189.

Luxton, M., 1972, Studies on the Oribatid Mites of a Danish Beech Wood Soil. I. Nutritional Biology, *Pedobiologia*, **12**: 434-463.

[illegible]yford, W. H., 1943, The Palatability of Freshly Fallen Forest Tree Leaves to Millipedes, *Ecology*, **24**: 252-261.

McBrayer, J. F., and D. E. Reichle, 1971, Trophic Structure and Feeding Rates of Forest Soil Invertebrate Populations, *Oikos*, **22**: 281-288.

Michael, A. D., 1883, The Hypopus Question of Certain Acarina, *J. Linn. Soc.*, **27**: 371-394.

Mollin, K., and P. E. Hunter, 1964, Mites Associated with the *Passalus* Beetle. II. Biological Studies of *Cosmolaelaps passali*, *Acarologia*, **6**: 421-431.

Moulder, B. C., D. E. Reichle, and S. I. Auerbach, 1970, Significance of Spider Predation in the Dynamics of Forest Floor Arthropod Communities, USAEC Report ORNL-4452, Oak Ridge National Laboratory.

Naglitsch, F., 1962, Untersuchungen Uber Individuen-und Artenzahl der Collembolem auf Leichten und Schweren Boden, in *Soil Organisms*, pp. 395-405, J. Doeksen and J. Van der Drift (Eds.), North-Holland Publishing Co., Amsterdam.

O'Neill, R. V., 1968, Population Energetics of the Millipede *Narceus americanus* (Beuvois), *Ecology*, **49**: 803-809.

Oughton, J., 1948, *A Zoogeographical Study of the Land Snails of Ontario*, University Toronto Press, Toronto, Canada.

Reichle, D. E., and D. A. Crossley, Jr., 1965, Radiocesium Dispersion in a Cryptozoan Food Web, *Health Phys.*, **11**: 1375-1384.

Satchell, J. E., and D. G. Lowe, 1966, Selection of Leaf Litter by *Lumbrieus terrestris*, in *Progress in Soil Biology*, pp. 102-119, O. Graff and J. E. Satchell (Eds.), North-Holland Publishing Co., Amsterdam.

Shaw, G. G., 1968, Population Size, Ecology and Mineral Reservoir of the Millipede, *Narceus annularis* (Raf.), *Ecology*, **49**: 1163-1166.

Singh, S. B., 1969, Preliminary Observations on the Food Preference of Certain Collembola (Insecta), *Rev. Ecol. Biol. Sol*, **6**: 461-467.

[illegible]drup, H. M., 1939, Studier over Jydsky Heders Okologi. I. Hede budens Fugtighedsforhold, *Acta Jutland Suppl.*, **11**: 1-82.

Ulrich, A. T., 1933, Die Macrofauna der Waldstreu, *Mitt. Forst., Forstwiss.*, **4**: 283-323.

Van Cleave, H. J., 1931, Some Biological Effects of Drought, *Sci. Mon.*, **33**: 301-306.

Van der Drift, J., 1950, Analysis of the Animal Community in a Beech Forest Floor, *Wageningen. Ponsen and Looijen*: 1-168.

Wallwork, J. A., 1967, Acari, in *Soil Biology*, pp 363-395, A. Burges and F. Raw (Eds.), Academic Press, Inc., New York.

Witkamp, M., and J. S. Olson, 1963, Breakdown of Confined and Nonconfined Oak Litter, *Oikos*, **14**: 138-147.

Wood, T. G. and J. H. Lawton, 1973, Experimental Studies on Respiration Rates of Mites (Acari) from Beech-Woodland Leaf Litter, *Oecologia (Berlin)*, **12**: 169-191.

FREQUENCY DISTRIBUTIONS OF RADIOCESIUM CONCENTRATIONS IN SOIL AND BIOTA

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ABSTRACT

Frequency distributions of radiocesium (primarily ^{137}Cs) concentrations in 33 samples of soils, plants, and animals from contaminated environments of the U. S. Atomic Energy Commission's Savannah River Plant were compared to normal, log-normal, exponential, and Weibull distributions. The log-normal and Weibull distributions showed close agreement to many of the samples, but the normal and exponential distributions showed close agreement to relatively few of the samples. None of the distributions were appropriate for all the samples. Radiocesium distributions were highly skewed in plants but tended to be less skewed in animals.

Considerable evidence demonstrating that the frequency distributions of radionuclide concentrations in living organisms are often positively skewed has been accumulated (Schubert, Brodsky, and Tyler, 1967; Remmenga and Whicker, 1967; Turner, 1965; Rustagi, 1964; Federal Radiation Council, 1961). Understanding and describing this skewness is important since it affects (1) determination of health physics standards, (2) design of monitoring programs, and (3) estimation of contamination levels by sampling procedures. It is also important to understand the skewness because the form of the frequency distribution can provide information about the processes controlling contamination levels (Hahn and Shapiro, 1967; Koch, 1966).

One of the objectives of nutrient-cycling studies at the Savannah River Ecology Laboratory has been to analyze and compare frequency distributions of radionuclide concentrations in various components of ecosystems. This paper reports the results of the studies for radiocesium (primarily ^{137}Cs, although a small fraction of the total is ^{134}Cs). The approach used in the studies was to evaluate four simple distributions, normal, log normal, exponential, and Weibull,

as possible models of observed frequency distributions of radiocesium concentrations. Descriptions of the model distributions are presented later.

It is impossible to prove a posteriori that any given set of data follows any specific distribution, but distributions showing close agreement to the data can be used as models of its distribution. If any of the distributions considered show close agreement to observed radiocesium distributions, it can be concluded that the model represents a close approximation to the true distribution of radiocesium concentrations. Moreover, this model distribution can be used to summarize radiocesium data and to make predictions about the relative frequency of various contamination levels. A priori analyses of radionuclide frequency distributions (i.e., deducing the probable distribution from a consideration of the factors affecting the nuclide's concentration) (Turner, 1965; Eberhardt et al., 1974) suggest distributions with positive skewness but do not show that the data follow any specific distribution.

DESCRIPTION OF MODEL DISTRIBUTIONS

This discussion of frequency distributions is by no means exhaustive. It emphasizes some basic properties of the distributions and some properties that might make them suitable models of radiocesium distributions. Where appropriate, additional comments concerning similarities and differences between the distributions are made. These distributions are described in detail by Johnson and Kotz (1970) and Hahn and Shapiro (1967).

Before proceeding, we will briefly review distribution statistics. Distributions of a continuous random variable (x) are uniquely described by their probability density function (pdf):

$$f(x) = \theta(x,\alpha,\beta,\gamma) \tag{1}$$

The pdf expresses the relative probability of observing a value of size x as a function (θ) of one or more parameters, which are generally referred to as scale (α), shape (β), and location (γ) parameters. Shape parameters usually determine the skewness (s_3) and kurtosis (k_4) of the distribution but may also determine the mean (μ) and variance (σ^2). Scale and location parameters usually determine μ and σ^2; however, the relationships between α, β, and γ and μ, σ^2, s_3, and k_4 are controlled by θ and depend on the specific distribution under consideration. Several distributions require more than three parameters, but none of these will be considered here.

The cumulative distribution function (cdf), symbolized by F(x), expresses the probability of observing a value equal to or less than x. The cdf and pdf have the relationship

$$F(x) = \int_t^x f(x)\,dx \tag{2}$$

where t is some lower bound on the distribution which may be $-\infty$, 0, or a specific location parameter. The integral is not always solvable, however, and F(x) may exist only in tables or as approximations. F(x) is of particular importance in radionuclide contamination studies since it can be used to predict the proportion of individuals with body burdens less than a specific limit or food items below a maximum acceptable contamination level.

The normal distribution has the pdf

$$f_N(x) = \frac{1}{\alpha_N (2\pi)^{1/2}} \exp\left[-\frac{1}{2}\left(\frac{x - \gamma_N}{\alpha_N}\right)^2\right] \quad (\text{for } \alpha_N > 0) \tag{3}$$

where α_N is a scale parameter and γ_N is a location parameter. The normal distribution has $\mu = \gamma_N$ and $\sigma^2 = \alpha_N^2$. Thus, if the normal is an adequate representation of the data, calculating $\hat{\mu}$ ($\hat{\mu} = n^{-1} \sum x_i$) and $\hat{\sigma}$ ($\hat{\sigma}^2 = n^{-1}\{\sum x_i^2 - [(\sum x_i)^2/n]\}$) provides a relatively complete summary of the data.

The normal distribution lacks a shape parameter and is always symmetrical. Since it has a constant shape, its skewness and kurtosis have fixed values ($s_3 = 0$ and $k_4 = 3$). The cdf of the normal distribution is unobtainable, but F(x) has been tabulated (Beyers, 1973), and computer algorithms approximating F(x) have been developed (Bargmann and Ghosh, 1963). The normal distribution is the basis of most parametric statistics (e.g., analysis of variance, correlation, regression, and construction of confidence intervals) and is one of the simplest and most studied distributions. For these reasons, the normal distribution is often a useful model of data distributions.

In the following analyses $\hat{\mu}$ is used to estimate γ_N and $\hat{\sigma}$ is used to estimate α_N.

The log-normal distribution has the pdf

$$f_L(x) = \begin{cases} \dfrac{1}{\beta_L (x - \gamma_L)\sqrt{2\pi}} \exp\left\{-\left[\dfrac{(\ln(x - \gamma_L) - \alpha_L)^2}{2\beta_L^2}\right]\right\} & (\text{for } x > \gamma_L \text{ and } \beta_L > 0) \\ 0 \quad (\text{for } x \leqslant \gamma_L) \end{cases} \tag{4}$$

where β_L, α_L, and γ_L are shape, scale, and location parameters, respectively. Equation 4 is the three-parameter form of the log normal; the two-parameter log normal, with $\gamma_L = 0$, is more commonly used. The two-parameter log normal has

$$\mu = \exp\left(\alpha_L + \frac{1}{2}\beta_L^2\right)$$

and

$$\sigma^2 = \exp(2\alpha_L + \beta_L^2)\,[\exp(\beta_L^2) - 1]$$

For $z = \ln x$, the variable z has $\mu_z = \alpha_L$ and $\sigma_z = \beta_L$, and z has a normal distribution. The log-normal distribution has positive skew ($s_3 > 0$), and

skewness and kurtosis are functions of β_L (Hahn and Shapiro, 1967). In the following analyses α_L and β_L were estimated by $\hat{\mu}_z$ and $\hat{\sigma}_z$, respectively.

The log-normal distribution has been used as a model of radionuclide concentration by several investigators (Walton, Kologrivov, and Kulp, 1959; Yamagata, 1962; Rustagi, 1964; Turner, 1965; Schubert, Brodsky, and Tyler, 1967; Martin, 1969; and others). Koch (1966) studied the first-order kinetics equation

$$C_t = C_o \exp(-kt)$$

where C_t is the concentration of a substance in an organism at time t, C_o is the initial concentration, and k is the first-order rate constant for the elimination of the substance. Koch showed that the distribution of C_t is asymptotically log normal if either k or t, but not both, have a normal distribution. Since Eq. 5 is often an adequate model of radionuclide elimination, we can expect the log-normal distribution to be an appropriate model of radiocesium concentrations. Koch (1969) also showed that the log normal approximates several other common distributions. Thus the log normal is supported as a possible model of radiocesium distributions by (1) empirical results, (2) its relationship to first-order kinetics, and (3) its similarity to other distributions.

The third model, the exponential distribution, is considered because it is both simple and highly skewed. The exponential distribution has the pdf

$$f_E(x) = \begin{cases} \alpha_E^{-1} \exp\left(-\dfrac{(x-\gamma_E)}{\alpha_E}\right) & (\text{for } x > \gamma_E \text{ and } \alpha_E > 0) \\ 0 \quad (\text{for } x < \gamma_E) \end{cases} \tag{6}$$

with scale parameter α_E and location parameter γ_E. However, γ_E is usually defined as zero, and the resulting single-parameter exponential distribution has $\mu = \alpha_E$ and $\sigma^2 = \alpha_E^2$. Since the exponential distribution lacks a shape parameter, the skewness and kurtosis are fixed at 2 and 9, respectively. F(x) for the exponential is obtainable and has the form

$$F_E(x) = 1 - \exp\left(-\frac{x}{\alpha_E}\right) \quad (\text{for } x > 0)$$

In the following analyses α_E was estimated by $\hat{\mu}$.

The last model distribution is the Weibull distribution, with pdf

$$f_W(x) = \begin{cases} \left(\dfrac{\beta_W}{\alpha_W}\right)\left(\dfrac{x-\gamma_W}{\alpha_W}\right)^{\beta_W - 1} \exp\left[-\left(\dfrac{x-\gamma_W}{\alpha_W}\right)^{\beta_W}\right] & \begin{array}{l}(\text{for } x > \gamma_W, \\ \beta_W > 0, \text{ and} \\ \alpha_W > 0)\end{array} \\ 0 \quad (\text{for } x < \gamma w) \end{cases} \tag{7}$$

where α_W, β_W, and γ_W are scale, shape, and location parameters, respectively. The Weibull is an extremely flexible distribution that can resemble both normal and log normal. Weibull distributions with different shape and scale parameters are shown in Fig. 1. For β_W near 3.6, the Weibull distribution is symmetrical and resembles the normal distribution. For β_W from 1.2 to 3, the Weibull resembles the log normal. For $\beta_W > 3.6$, the Weibull distribution is negatively skewed. The exponential distribution is a special case of the Weibull which occurs when $\beta_W = 1$. Equation 7 describes the three-parameter Weibull; the two-parameter Weibull

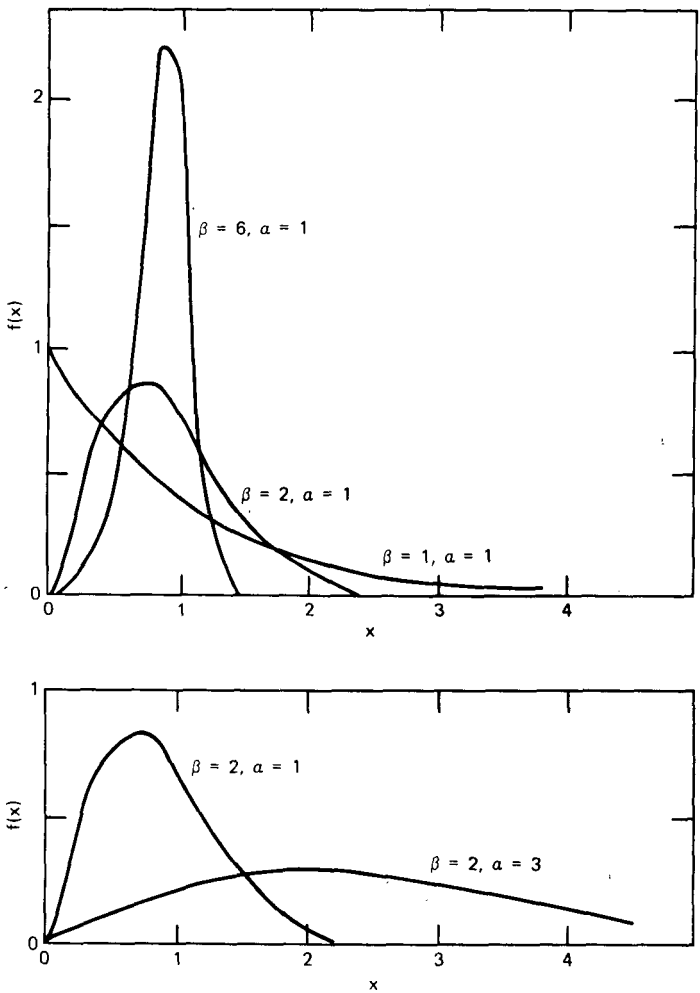

Fig. 1 Weibull distributions with various shape (β) and scale (α) parameters.

with $\gamma_W = 0$ is more frequently employed, however. The two-parameter Weibull has

$$\mu = \alpha_W \, \Phi(1)$$

and

$$\sigma^2 = \alpha_W^2 \, [\Phi(2) - \Phi(1)^2]$$

where

$$\Phi(m) = \Gamma\left(\frac{m}{\beta_W} + 1\right)$$

Skewness and kurtosis are functions of β_W (Hahn and Shapiro, 1967; Whitten and Cohen, 1972; Rousu, 1973). The cdf of the two-parameter Weibull distribution has the form

$$F(x) = 1 - \exp\left[-\left(\frac{x}{\alpha_W}\right)^{3W}\right]$$

The Weibull is potentially a useful model of radionuclide concentrations because (1) it is flexible and can assume a wide variety of shapes; (2) it resembles several other common distributions; and (3) the cdf is known, thus eliminating the need for tabulated cdf values. The Weibull has been used extensively in engineering as a time-to-failure model (Hahn and Shapiro, 1967) and has also been employed as a model of the distribution of particle sizes and tensile strengths (Steiger, 1971). Mikolaj (1972) used the Weibull to model oil-spill size and duration in California.

Many methods exist for estimating β_W and α_W (see Johnson and Kotz, 1970; Harter, 1971; Whitten and Cohen, 1972), and the development of new estimators is currently an area of considerable statistical research. The method used here is the unbiased maximum-likelihood method of Thoman, Bain, and Antle (1969). The advantage of this method is that confidence intervals on the estimates can be easily constructed (Thoman, Bain, and Antle, 1969; Thoman and Bain, 1969).

METHODS

The model distributions were compared to the frequency distributions of radiocesium concentrations of soil, plant, and animal samples from the U. S. Atomic Energy Commission's Savannah River Plant near Aiken, S. C. This facility encompasses 300 sq miles and contains several nuclear production reactors (Bebbington, 1973). In the operation of these reactors, releases of radiocesium (primarily ^{137}Cs) have occurred which have resulted in the

contamination of several ecosystems, notably the floodplain and delta of Steel Creek and an artificial impoundment, Par Pond. Another stream, Four Mile Creek, and several other small impoundments associated with Par Pond have also been contaminated. The history of releases into Steel Creek has been documented by Marter (1970), and the history of releases into the ponds are discussed by Brisbin, Geiger, and Smith (1973). The data from the creeks include samples of soils, plants, arthopods, fishes, amphibians, and mammals. The data from the ponds include samples of plants, fishes, and birds. In addition samples from particular locations, data were also available on a free-ranging population of crows (Straney et al., 1975). A complete description of the data sets is presented in Appendix A.

Radiocesium concentrations were determined using either a whole-body counter or a pulse-height analyzer. Methodological differences among investigators were minimal, and specific counting procedures are described in the references cited in Appendix A. Radiocesium concentrations were usually expressed as picocuries per gram of dry weight. For some fish samples concentrations were expressed as picocuries per gram of wet weight.

The data were restricted to clearly homogeneous samples, i.e., data on single species populations collected over a relatively short time interval. Where location or time differences were possible, the data were tested for internal consistency using analysis-of-variance procedures to test for differences among means and either Bartlett's test or the F_{max} test to test for differences in variances (Kirk, 1968). Where differences in means or variances were observed, the data were either divided into separate samples and analyzed independently or eliminated from further consideration.

A total of 33 sets of sample data were analyzed. Sample sizes ranged from 20 to 235; median sample size was 38. The majority of samples (73%) were composed of 30 or more individuals. Many studies of plants from Steel Creek include determinations of radiocesium concentrations of roots, stems, leaves, and/or fruits from the same individuals. Only the leaf data are reported in this paper since preliminary analyses demonstrated only minor differences in the types of frequency distributions found in different plant components.

Parameters of the four model distributions were estimated for each sample according to the methods previously described. In addition, skewness was estimated by

$$\hat{s}_3 = \frac{M_3}{(\hat{\sigma})^{3/2}}$$

and kurtosis was estimated by

$$\hat{k}_4 = \frac{M_4}{(\hat{\sigma})^4}$$

where

$$M_q = \frac{\sum_{i=1}^{n} (x_i - \bar{x})^q}{n}$$

In a few cases, particularly where mean concentrations were low, counting procedures indicated radiocesium concentrations less than 0 pCi/g. The occurrence of negative concentrations is due to sampling error associated with the counting procedures, but ignoring these results biases the estimates of mean radionuclide concentration. When negative values occurred, the location parameter in the exponential, log-normal, and Weibull distributions was defined as $\gamma = |(\text{minimum pCi/g}) - 1|$. The data were then transformed by the relationship $x = x + \gamma$ and analyzed as a single-parameter exponential and two-parameter log-normal and Weibull distributions. Soil radiocesium concentrations showed a bimodal distribution of clay content in the soil (Brisbin et al., 1974; Sharitz et al., 1975). For this reason, soil samples were divided into high- and low-level samples. Low-level samples ranged from 0 to about 85 pCi/g, and high-level samples ranged from approximately 115 to over 1000 pCi/g. To simplify the analyses, we assumed that for high-level samples $\gamma = 110$ pCi/g for exponential, log-normal, and Weibull distributions.

The suitability of each model was judged using Lillifors' test (Lillifors, 1967; 1969):

$$D = \max_x |F(x) - S(x)|$$

where D is the test statistic, F(x) is the cdf of the model distribution, and S(x) is the sample cdf. The null hypothesis, H_0: $F(x) = S(x)$, is rejected for large values of D. The values of D required to reject the normal and exponential models have been tabulated (Lillifors, 1967; 1969), but the values of D required to reject the log-normal and Weibull distributions have not. For the log normal we used $D = \max |F(\ln x) - S(\ln x)|$ and the tabulated values for the normal distribution to reject H_0. For the Weibull distribution the levels tabulated for the exponential distribution were used for $\hat{\beta}_W \leq 1.6$ because of the similarity of the Weibull and the exponential in this region. For $\hat{\beta}_W > 1.6$, the values of D tabulated for the normal distribution were used to reject H_0. These approximate tests for the log-normal and Weibull should be accurate.

RESULTS

The range of D values shown in Table 1 indicates that each model was appropriate for some sample distributions and inappropriate for others. The log normal demonstrated the closest fit (measured as the smallest D of the four models) to 18 of the 33 samples. The normal and exponential distributions showed closest agreement to relatively few sample distributions. Because of its

TABLE 1

SUITABILITY OF THE FOUR MODEL DISTRIBUTIONS*

Distribution	Best fit	Lillifors' test†		
		Mean D	Minimum D	Maximum D
Normal	3	0.150	0.052	0.257
Log normal	18	0.105	0.035	0.198
Exponential	0	0.254	0.062	0.485
Weibull	12	0.109	0.055	0.199

*As expressed by best fits, measured as the number of sample distributions to which each model showed closest agreement, and D, the Lillifors' test statistic.

†See the text for a description of Lillifors' test.

flexibility, the Weibull might have been expected to show the closest agreement to more samples than the other models, but this was not the case. Moreover, when the Weibull showed the closest agreement to a sample, it was usually only slightly better than one of the other models. If the Weibull is ignored, the normal shows the closest agreement to 7 samples, the log normal to 22 samples, and the exponential to 4 samples. A complete listing of the results of the Lillifors' tests is presented in Appendix B.

When F(x) was the normal distribution, the null hypotheses, H_0: F(x) = S(x), was rejected for 66.7% of the samples at the 0.1 significance level. If all radiocesium distributions were truly normal, then rejection should have occurred in only 10% of the cases. In a similar manner the log normal was rejected in 24.2% of the samples, the exponential in 69.7%, and the Weibull in 33.3%. All these represent significantly more rejections than expected (chi-square tests; $P < 0.05$). The high incidences of rejection indicate that none of these models can be used as a general model of radiocesium concentration distributions. This result is not surprising since radiocesium concentrations are affected by numerous factors and might be expected to have complex distributions that can only be approximated by simple models. Moreover, even if the radiocesium distributions did follow one of these models, a higher than expected incidence of rejection might have occurred because of methodological errors in determining radiocesium concentrations. A difference between the true concentration (expressed as x) and the measured concentration (expressed as x′) always occurs, and, if it is large enough, it can obscure the true distribution of x. Even the effects of small differences between x and x′ become apparent if the sample size is large. Errors in measurement usually cause the distribution of x′ to be different from that of x, with the variance, skewness, and kurtosis of x′ being greater than that of x (Eadie et al., 1971). For the analyses performed in this study, we assumed that the differences between x′ and x were negligible and that the high incidences of rejection were caused by discrepancies between the

models and the distributions of x. Since all the models were rejected for 20% or more of the samples, this assumption seems reasonable.

The mean D tabulations in Table 1 are means of the maximum differences between F(x) and S(x) for each of the models. These means represent the maximum error expected when we use F(x) to predict S(x). Since D is partially dependent on sample size (i.e., large D values are more likely to occur when sample sizes are small), the actual magnitudes of the mean D values are of little importance, but their relative magnitudes can be used to compare the ability of each model to predict the sample cdf. The normal and exponential distributions had larger D values than the log-normal and Weibull distributions. This was probably because of the flexibility in shape of the log normal and Weibull. Because of this flexibility these distributions had relatively few large values of D. The maximum observed D values for the log normal and Weibull were 0.198 and 0.199, respectively. By comparison, the distributions with fixed shapes, the normal and exponential, had maximum D values of 0.257 and 0.485, respectively. Whether the log-normal and Weibull distributions are satisfactory predictions of S(x) depends on the degree of precision required and on the range of S(x) to be predicted. The values of D in Table 1 and Appendix B are calculations for the entire range of S(x) and are not necessarily appropriate for judging suitability within a restricted portion of S(x). Predicting the upper regions of S(x) (e.g., $S(x) > 0.80$) is of particular interest in radionuclide contamination work. A separate comparison of F(x) and S(x) within this range would be required to evaluate the predictability of each model. The data in Table 1 suggest that the normal and exponential might be eliminated from this further comparison.

Distributions of radiocesium concentrations in producer organisms were generally highly skewed with large kurtosis (Fig. 2), and most (9 of 11) showed closest agreement to the log-normal model. The normal was rejected for all the producer distributions. Distributions in consumer organisms were generally less skewed and had lower $\hat{s}_3$ than producers. Several consumer distributions showed closest agreement to the normal distribution, and the normal was not rejected for 50% of the samples. These results suggest that frequency distributions of radiocesium concentrations may differ between trophic levels and that the distributions may approximate the normal distribution at higher trophic levels. The differences in $\hat{s}_3$ and $\hat{k}_4$ between producers and consumers must be analyzed with care, however. For a distribution with $s_3 \neq 0$, $\hat{s}_3$ is an asymptotically unbiased estimator of s_3, with the expected value of $\hat{s}_3$ [symbolized $E(\hat{s}_3)$] being a function of s_3, n, and the form of the distribution. The expected value, $E(\hat{s}_3)$, is equal to s_3 only when n equals ∞, and $E(\hat{s}_3)$ may be greater or less than s_3. Since sample sizes for consumers were generally less than those for producers, it is possible that producer and consumer distributions had similar s_3 and that the differences observed in $\hat{s}_3$ were caused by differences in n. Similar statements can be made about $\hat{k}_4$.

Although differences in n could have affected $\hat{s}_3$ and $\hat{k}_4$, the conclusion of reduced skewness and kurtosis among consumer distributions is supported by data on $\hat{\beta}_L$ and $\hat{\beta}_W$. Values of $\hat{\beta}_L$ were higher among producers (range = 0.356 to 1.137, median = 0.742) than among consumers (range = 0.142 to 1.340, median = 0.399), and s_3 of the log-normal distribution is proportional to β_L. Furthermore, the log-normal distribution approaches the normal as β_L approaches zero. Values of $\hat{\beta}_W$ were lower for producers (range = 1.04 to 2.07, median = 1.37) than for consumers (range = 0.97 to 7.09, median = 2.66). Values of $\hat{\beta}_W$ obtained by the method of Thoman, Bain, and Antle (1969) are unbiased, and the increase in the median values indicates reduced skewness among consumers. Thus the results from $\hat{s}_3$, $\hat{\beta}_L$, and $\hat{\beta}_W$ indicate that radiocesium distributions in consumers are less skewed and more similar to normal distributions than those in producers.

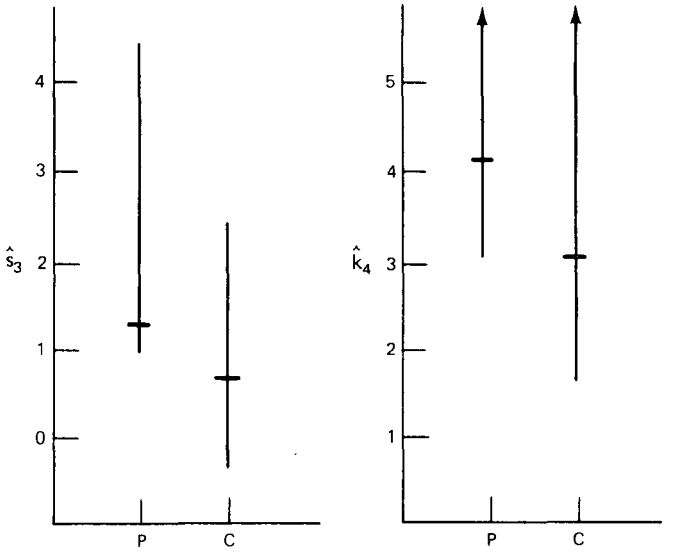

Fig. 2 Comparisons of skewness ($\hat{s}_3$) and kurtosis ($\hat{k}_4$) in radiocesium distributions from producers (P) and consumers (C). Vertical bars denote ranges, and horizontal bars denote medians. The maximum $\hat{k}_4$ observed was 76.4 for producers and 11.1 for consumers.

The reduction in skewness and kurtosis explains why none of the models showed good agreement to all the data. As skewness and kurtosis decrease, the distributions change from approximately log normal and exponential to approximately normal. Thus, each of these models approximated some but not all the sample distributions.

DISCUSSION

The data indicate that a simple general model applicable to all the frequency distributions of radiocesium concentrations may not exist. The frequent rejection of the hypothesis $F(x) = S(x)$ for all models, the occurrence of at least some large values of D for each model, and the reduction in skewness and kurtosis from producers to consumers indicate that the distributions are too complex and varied to be accurately modeled by any one of the four distributions. The two-parameter gamma distribution (Johnson and Kotz, 197[illegible] used as a model of radiocesium frequency distributions by Ellett and Brown[illegible] (1964) is similar to the models employed in this analysis. Thus it is unlikely that it would provide a significant improvement over either the log-normal or the Weibull distribution. More complicated distributions, such as the four-parameter generalized gamma distribution (Johnson and Kotz, 1970; Whitten and Cohen, 1972), may prove to be better models, but their usefulness is offset by difficulties in estimating their parameters. That each model evaluated in this study was applicable in at least a few cases may explain why other investigators have sometimes found various simple distributions to be applicable to radiocesium distributions.

Most commonly employed statistical procedures, such as confidence intervals, analysis of variance, correlation, and regression, are based on the assumption that the data follow a normal distribution. Violation of this assumption can greatly affect and even invalidate these procedures. Deviations in skewness from $s_3 = 0$ affect the construction of confidence intervals, and deviations from $k_4 = 3$ affect the variance of $\hat{\sigma}$ (Cochran, 1963; Scheffe, 1959).

The data in Fig. 2 show that most radiocesium distributions have positive skewness. Positive skewness in radiocesium distributions has also been reported by Onstead, Oberhausen, and Keary (1960), Yamagata (1962), Ellett and Brownell (1964), Schubert, Brodsky, and Tyler (1967), and others. Positive skewness causes underestimation of both the lower and upper bounds of the confidence interval about $\hat{\mu}$. Thus $\hat{\mu}$ and its confidence interval are an underestimate of μ, the true mean concentration, and the actual contamination level is probably greater than that indicated by the sample. The underestimation resulting from positive skewness decreases as the sample size increases (Cochra[illegible] 1963; Scheffe, 1959), and Cochran suggests that $n = 25(s_3)^2$ is sufficient t[illegible] make the effects of positive skewness negligible. For $n = 25(s_3)^2$, μ will occur outside the 95% confidence interval (defined as $\hat{\mu} \pm t\hat{\sigma}$, where t = Student's t statistic for P = 0.025 and df = n−1) 6% of the time. However, μ will exceed the upper bound of the confidence interval ($\hat{\mu} + t\hat{\sigma}$) more than 3% of the time. Since it is more important to accurately estimate the upper bound of the confidence interval in radionuclide studies, $n = 25(s_3)^2$ should be considered the minimum acceptable sample size. The $\hat{s}_3$ is usually used to estimate s_3. Since $E(\hat{s}_3)$ may be less than s_3, the required sample size computed from $\hat{s}_3$ may be less than that

computed from s_3. Thus, in studies where the mean concentration is to be accurately estimated, the sample size should probably be greater than $25(\hat{s}_3)^2$.

Another problem to be considered in calculating $\hat{\mu}$ and its confidence interval is the effect of excess kurtosis ($k_4 > 3$) on $\hat{\sigma}$. For $k_4 > 3$, the variance of $\hat{\sigma}$ is greater than that expected when sampling from a normal distribution (Scheffe, 1959; Cochran, 1963). Thus values of $\hat{\sigma}$ will occur which are much larger or smaller than expected for estimates of σ. In radionuclide contamination studies, underestimating σ is a greater problem than overestimating. Overmating σ causes overestimation of the upper bound of the confidence rval. This indicates a higher level of contamination than actually exists and thus is conservative. Underestimating σ indicates a lower level of contamination than actually occurs. For a single sample with large $\hat{k}_4$, it is impossible to determine whether $\hat{\sigma}$ is an under or overestimate. The effects of excess kurtosis are not eliminated by large n; but, as is generally the case, a large n provides a better estimate of σ.

An important aspect of radioecology and radiation monitoring is estimating the probability that an individual in a population will have a radionuclide concentration exceeding a given maximum permissible level (MPL). This may involve predicting the number of people with body concentrations exceeding the MPL or predicting the percentage of food items with dangerously high concentrations. The probability that an individual will exceed the MPL may be expressed as

$$P(x \geqslant \text{MPL}) = \int_{\text{MPL}}^{\infty} f(x)\, dx \qquad (8)$$

where x is the concentration and f(x) is the pdf of x. If the form of f(x) is constant (e.g., if x always has a log-normal distribution), then parameters of f(x), and consequently $P(x \geqslant \text{MPL})$, could be estimated from even relatively small samples. Schubert, Brodsky, and Tyler (1967) recommended such a procedure for estimating fallout ^{90}Sr in humans using the log-normal distribution. They also concluded that ^{90}Sr, ^{226}Ra, and ^{137}Cs concentrations are always distributed log normally in humans, but the results of our study indicate the log normal is not universally applicable. These results are easily reconciled, however. In our study each model was found to be applicable in at least a few cases. ubert, Brodsky, and Tyler found the log normal applicable in humans, and ir results were collaborated by Liebscher and Smith (1968), who reported log-normal distributions for the concentrations of most nonessential elements in humans. Our results indicate that, unless previous sampling has shown x to follow a specific frequency distribution, it is unreasonable to assume any specific distribution.

To use Eq. 8, where the form of f(x) is unknown or varies, we must have sample sizes large enough to determine the type of distribution as well as to estimate its parameters. If the form of f(x) is unknown, it may be preferable to estimate $P(x \geqslant \text{MPL})$ from the frequency of observations in the sample $\geqslant$ MPL.

Whichever method of estimation is used, the sample sizes must be large. The required sample size would depend on the degree of precision required and would increase with $|MPL - \mu|$.

Usually an estimate of $P(x \geqslant MPL)$ is desired for $MPL > \mu$ and $s_3 > 0$. In these cases it is preferable to increase n and accept a larger measurement error, i.e., the difference $x' - x$. The measurement error will cause the distribution of x' to be more skewed and have a greater variance than that of x. Thus $P(x' \geqslant MPL) > P(x \geqslant MPL)$, and the estimated probability will be conservative.

The tendency to normality at higher trophic levels is intriguing. That consumer distributions should be less skewed than plant distributions is clear. Koch's (1966) analysis of Eq. 5 predicts approximately log-normal distributions, but his analysis concerns only elimination processes and ignores intake processes. If concentrations depend more on intake than on elimination processes, it could be expected that distributions for consumer species would be less skewed and more normal than distributions for food sources. This follows from the central-limit theorem of statistics (Kendall and Stuart, 1969), which states that sums of a random variable y are asymptotically normal regardless of the distribution of y (provided y has a finite σ^2). The degree of approach to normality depends on the number of observations summed and the distribution of y. The occurrence of both normal and highly skewed distributions suggests that neither Koch's work nor the central-limit theorem are sufficient explanations of the concentration distributions. The distributions are a result of both intake and elimination processes, and more research relating these processes to the variability of elemental concentrations is required before the patterns can be explained. Rustagi (1964) commented on the difficulty of determining the frequency distribution of body burdens even when the frequency distributions in food, feces, and urine are known.

All elements may not show distributions and changes across trophic levels similar to those observed here for radiocesium. Liebscher and Smith (1968) report normal distributions for concentrations of required elements in humans and skewed distributions for such nonessential elements as Cu, Zn, As, Sb, and Hg. This observation is supported by the distributions of elemental concentrations in *Sagittaria latifolia* Willd. (R. R. Sharitz, 1974). In *Sagittaria* nitrogen and potassium have near normal distributions, but aluminum and radiocesium have distributions with positive skewness.

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REFERENCES

mann, R. E., and S. P. Ghosh, 1963, Statistical Distribution Programs for a Computer Language, Research Report RC-1094, International Business Machines.

Bebbington, W. P., 1973, Nuclear Operations and the Environment: Savannah River Plant, USAEC Report DPSPU 72-30-9, E. I. Du Pont de Nemours and Co., Aiken, S. C., Savannah River Plant.

Beyers, R. J., and E. B. Davidson, 1974, Savannah River Ecology Laboratory, personal communication.

Beyers, W. H. (Ed.), 1973, *Handbook of Tables for Probability and Statistics,* 2nd ed., The Chemical Rubber Company, Cleveland, Ohio.

Brisbin, I. L., Jr., et al., 1974, Patterns of Radiocesium in the Sediments of a Stream Channel Contaminated by Production Reactor Effluents, *Health Phys.,* **27**: 19-27.

——, R. A. Geiger, and M. H. Smith, 1973, Accumulation and Redistribution of Radiocesium by Migratory Waterfowl Inhabiting a Reactor Cooling Reservoir, in *Environmental Behaviour of Radionuclides Released in the Nuclear Industry,* Proceedings Series, Aix-en-Provence, 1973, pp. 373-384, International Atomic Energy Agency, Vienna (STI/PUB/345).

Cochran, W. G., 1963, *Sampling Techniques,* 2nd ed., John Wiley & Sons, Inc., New York.

Dapson, R. W., and L. Kaplan, 1975, Biological Half-life and Distribution of Radiocesium in a Naturally Contaminated Population of Green Treefrogs (*Hyla cinerea*), *Oikos,* **26**: 39-42.

Eadie, W. T., D. Dryard, F. E. James, M. Roos, and B. Sadoulet, 1971, *Statistical Methods in Experimental Physics,* American Elsevier Publishing Company, Inc., New York.

Eberhardt, L. L., R. O. Gilbert, H. L. Hollister, and J. M. Thomas, 1974, Sampling for Contaminants in Ecological Systems, unpublished manuscript.

Ellett, W. H., and G. L. Brownell, 1964, Caesium-137 Fall-Out Body-Burdens, Time Variation and Frequency Distribution, *Nature,* **203**: 53-55.

Federal Radiation Council, 1961, *Background Material for the Development of Radiation Protection Standards,* Report No. 2, Superintendent of Documents, U. S. Government Printing Office, Washington.

Gentry, J. B., 1974, Savannah River Ecology Laboratory, personal communication.

Hahn, G. J., and S. S. Shapiro, 1967, *Statistical Models in Engineering,* John Wiley & Sons, Inc., New York.

ter, H. L., 1971, Some Optimization Problems in Parameter Estimation, in *Optimizing Methods in Statistics,* J. S. Rustagi (Ed.), Academic Press, Inc., New York.

Howell, F. G., 1974, University of Southern Mississippi, personal communication.

Johnson, N. L., and S. Kotz, 1970, *Distributions in Statistics: Continuous Univariate Distributions,* Vol. 1, John Wiley & Sons, Inc., New York.

Kendall, M. G., and A. Stuart, 1969, *Advanced Theory of Statistics,* Vol. 1. *Distribution Theory,* 3rd ed., Charles Griffin & Company, Ltd., London.

Kirk, R. E., 1968, *Experimental Design: Procedures for the Behavioral Sciences,* Brooks/Cole Publishing Company, Monterey, Calif.

Koch, A. L., 1969, The Logarithm in Biology. II. Distributions Simulating the Lognormal, *J. Theor. Biol.,* **23**: 251-268.

——, 1966, The Logarithm in Biology. I. Mechanisms Generating the Lognormal Exactly, *J. Theor. Biol.*, **12**: 276-290.

Liebscher, K., and H. Smith, 1968, Essential and Nonessential Trace Elements, *Arch. Environ. Health*, **17**: 881-890.

Lillifors, H. W., 1969, On the Kolmogorov–Smirnov Test for the Exponential Distribution with Mean Unknown, *J. Amer. Statist. Ass.*, **64**: 387-389.

——, 1967, On the Kolmogorov–Smirnov Test for Normality with Mean and Variance Unknown, *J. Amer. Statist. Ass.*, **62**: 399-402.

Marter, W. L., 1970, Radioactivity in the Environs of Steel Creek, USAEC Report DPST-70-435, E. I. Du Pont de Nemours and Co., Aiken, S. C., Savannah River Laboratory.

Martin, A., 1969, Content and Distribution of Stable Strontium and ^{226}Ra in Hu Skeletons from Wisconsin Decedents, *Brit. J. Radiol.*, **42**: 295-298.

Mikolaj, P. G., 1972, Environmental Applications of the Weibull Distribution Function: Oil Pollution, *Science*, **176**: 1019-1021.

Mondecar, M. C., 1974, University of Georgia, personal communication.

Onstead, C. O., E. Oberhausen, and F. V. Keary, 1960, Messun des Kalium und Casium-137-Gehaltes der deutschen Vevolkerung, *Atompraxis*, **9**: 337-341.

Remmenga, E. E., and F. W. Whicker, 1967, Sampling Variability in Radionuclide Concentrations in Plants Native to the Colorado Front Range, *Health Phys.*, **13**: 977-983.

Rousu, D. A., 1973, Weibull Skewness and Kurtosis as a Function of the Shape Parameter, *Technometrics*, **15**: 927-930.

Rustagi, J. S., 1964, Stochastic Behavior of Trace Substances, *Arch. Environ. Health*, **8**: 68-76.

Scheffe, H., 1959, *The Analysis of Variance*, John Wiley & Sons, Inc., New York.

Schubert, J., A. Brodsky, and S. Tyler, 1967, The Log-Normal Function of the Distribution of Strontium-90 and Other Fission Products in Humans, *Health Phys.*, **13**: 1187-1204.

Sharitz, R. R., S. L. Scott, J. E. Pinder III, and S. K. Woods, 1975, Uptake of Radiocesium from Contaminated Floodplain Sediments by Herbaceous Plants, *Health Phys.*, **28**: 23-28.

——, 1974, Savannah River Ecology Laboratory, personal communication.

Steiger, F. H., 1971, Practical Applications of the Weibull Distribution Function, *Chem. Technol.*, **1**: 225-231.

Straney, D. O., B. Beaman, I. L. Brisbin, Jr., and M. H. Smith, 1975, Radiocesium in Birds of the Savannah River Plant, *Health Phys.*, **28**: 341-345.

Thoman, D. R., and L. J. Bain, 1969, Two Sample Tests in the Weibull Distribution, *Technometrics*, **11**: 805-815.

——, L. J. Bain, and C. E. Antle, 1969, Inferences on the Parameters of the Weibull Distribution, *Technometrics*, **11**: 445-460.

Turner, F. B., 1965, Uptake of Fallout Radionuclides by Mammals and a Stochastic Simulation of the Processes, in *Radioactive Fallout from Nuclear Weapons Tests*, A. Klement (Ed.), pp. 800-820, AEC Symposium Series (CONF-765), Germantown, M 1965.

Walton, A., R. Kologrivov, and J. L. Kulp, 1959, The Concentration and Distribution of Radium in the Normal Human Skeleton, *Health Phys.*, **1**: 409-416.

Whitten, B. J., and A. C. Cohen, 1972, *Estimation of Parameters of Skewed Distributions*, Technical Report No. 86, Department of Statistics and Computer Science, University of Georgia, Athens.

Yamagata, N., 1962, The Concentration of Common Cesium and Rubidium in the Human Body, *J. Radiat. Res.*, **3**: 9-30.

APPENDIX A

DESCRIPTION OF THE 33 DATA SETS USED IN THE ANALYSIS DESCRIBED IN THIS PAPER

Sample number	Material sampled	Number of observations	Sample time	Sample location	Reference
			Soils		
1	Soils, coarse textured	86	October 1971	Delta of Steel Creek	Brisbin et al., 1974
2	Soils, fine textured	78	October 1971	Delta of Steel Creek	Brisbin et al., 1974
3	Soils, low level	28	Summer 1972	Delta of Steel Creek	Sharitz et al., 1975
4	Soils, high level	69	Summer 1972	Delta of Steel Creek	Sharitz et al., 1975
			Producers		
5	*Andropogon virginicus* L., leaves	76	October 1971	Steel Creek floodplain, transect A	Garten et al., this volume, pp. 489-497
6	*A. virginicus* L., leaves	26	October 1971	Steel Creek floodplain, transect B	Garten et al., this volume, pp. 489-497
7	*S. latifolia* Willd., leaves	98	October 1971	Steel Creek floodplain, transect A	Garten et al., this volume, pp. 489-497
8	*S. latifolia* Willd., leaves	32	October 1971	Steel Creek floodplain, transect B	Garten et al., this volume, pp. 489-497
9	*S. latifolia* Willd., leaves	56	Summer 1972	Delta of Steel Creek from low-level soils	Sharitz et al., 1975
10	*S. latifolia* Willd., leaves	138	Summer 1972	Delta of Steel Creek from high-level soils	Sharitz et al., 1975
11	*Polygonum punctatum* Ell., leaves	235	Summer 1972	Delta of Steel Creek	Sharitz et al., 1975
12	*Scirpus cyperinus* (L.) Kunth, leaves	70	November 1973	Pond B	Sharitz, 1974
13	*Erianthus* sp., leaves	24	November 1973	Pond B	Sharitz, 1974
14	*Salix nigra* Marshall, leaves	20	November 1973	Pond B	Garten et al., this volume, pp. 498-508
15	*Typha latifolia* L., leaves	25	November 1973	Pond B	Sharitz, 1974
			Consumers		
16	*Argiope aurantia*, females	25	September 1972	Delta of Steel Creek	Howell, 1974
17	Grasshoppers, unidentified species	118	Summer 1972	Delta of Steel Creek	Howell, 1974
18	*Macromia illinoiensis*, aquatic larva	55	Summer 1972	Delta of Steel Creek	Gentry, 1974

APPENDIX A (Continued)

Sample number	Material sampled	Number of observations	Sample time	Sample location	Reference
19	*Ictalurus nebulosa*	24	Summer 1972	Four Mile Creek	Beyers and Davidson, 1974
20	*Lepomis auritus*	23	Summer 1972	Four Mile Creek	Beyers and Davidson, 1974
21	*Micropterus salmoides*	206	Summer 1972	Par Pond	Beyers and Davidson, 1974
22	*M. salmoides*	30	Summer 1972	Pond B	Beyers and Davidson, 1974
23	*M. salmoides*	40	Summer 1972	Pond C	Beyers and Davidson, 1974
24	*Lepomis macrochirus*	24	Summer 1972	Par Pond	Beyers and Davidson, 1974
25	*Hyla cinerea*	36	July 1972	Delta of Steel Creek	Dapson and Kaplan, 1975
26	*H. cinerea*	38	Late July 1972	Delta of Steel Creek	Dapson and Kaplan, 1975
27	*H. cinerea*	65	August 1972	Delta of Steel Creek	Dapson and Kaplan, 1975
28	*Fulica americana*	30	December to February 1972	Par Pond, North Arm	Brisbin, Geiger, and Smith, 1973
29	*F. americana*	30	December to February 1972	Par Pond, Hot Arm	Brisbin, Geiger, and Smith, 1973
30	*F. americana*	30	December to February 1972	Par Pond, West Arm	Brisbin, Geiger, and Smith, 1973
31	*Corvus brachyrhynchos*	35	Summer 1972 and summer 1973	All areas of Savannah River Plant	Straney et al., 1975
32	*Oryzomys palustris*	42	Summer 1972	Delta of Steel Creek	Mondecar, 1974
33	*Sigmodon hispidus*	80	Summer 1972	Delta of Steel Creek	Mondecar, 1974

APPENDIX B

COMPARISON OF EACH SAMPLE DISTRIBUTION TO THE FOUR MODEL DISTRIBUTIONS ACCORDING TO THE MODIFIED LILLIFORS' TESTS DISCUSSED IN THE TEXT

Sample† number	Number of observations	Lillifors' D‡§			
		Normal	Log normal	Exponential	Weibull
1	86	0.106*	0.120*	0.137*	0.091*
2	78	0.133*	0.114*	0.062	0.059
3	28	0.137	0.096	0.189*	0.078
4	69	0.127*	0.097	0.105	0.055
5	76	0.136*	0.059	0.240*	0.100*
6	26	0.172*	0.106	0.136	0.110*
7	98	0.114*	0.103*	0.208*	0.068
8	32	0.160*	0.112	0.074	0.060
9	56	0.169*	0.059	0.239*	0.118*
10	138	0.110*	0.053	0.256*	0.073*
11	235	0.257*	0.051	0.127*	0.113*
12	70	0.205*	0.056	0.126*	0.108
13	24	0.236*	0.144	0.165	0.165
14	20	0.179*	0.098	0.157	0.102
15	25	0.205*	0.148	0.354*	0.183*
16	25	0.132	0.073	0.198	0.108
17	118	0.100*	0.121*	0.288*	0.079
18	55	0.138*	0.138*	0.102	0.099
19	24	0.255*	0.136	0.193	0.189*
20	23	0.158	0.168	0.237*	0.101
21	206	0.052	0.035	0.480*	0.083*
22	30	0.084	0.089	0.485*	0.100
23	40	0.086	0.083	0.472*	0.096
24	24	0.139	0.133	0.264*	0.097
25	36	0.168*	0.102	0.347*	0.148
26	38	0.112	0.051	0.292*	0.081
27	65	0.070	0.093	0.339*	0.080
28	30	0.136	0.085	0.400*	0.134
29	30	0.110	0.151*	0.420	0.103
30	30	0.196*	0.132	0.437*	0.199*
31	35	0.167*	0.198*	0.459*	0.167*
32	42	0.156*	0.062	0.246*	0.115
33	80	0.251*	0.183*	0.146*	0.130*
$\bar{x}$		0.150	0.105	0.254	0.109

†Sample numbers correspond to those in Appendix A.

‡Values marked with an asterisk are those for which the null hypothesis, F(x) = S(x), is rejected at the 0.1 significance level.

§Underlined values denote the model showing closest agreement to the sample distribution.

FACTOR ANALYSIS: AN EXPLORATORY TECHNIQUE APPLIED TO MINERAL CYCLING

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ABSTRACT

Factor analysis and its definition and historical roots are discussed. This statistical technique is contrasted with pseudo factor analysis, i.e., principal-components analysis. Factor extraction and factor rotation as they apply in factor analysis are clarified and interpreted. Advantages and disadvantages of the statistical method are enumerated. Applications of factor analysis in mineral-cycling studies and their usefulness in ecology are presented.

Factor analysis is a multivariate statistical method that constructs artificial (unobservable) variables to explain the dependence structure found in a correlation matrix. These artificial variables are called common factors. A vector of correlations is generated between the observable attributes and such common factors. Those attributes, highly correlated with a common factor, form a group the members of which share some common property over and beyond that which they share with the other observed attributes. It is an exploratory technique to classify attributes (Bargmann, 1967). The exploratory approach is used to gain a better understanding of complex and poorly defined interrelationships among a large set of imprecisely measured attributes (Comrey, 1973).

Factor analysis is a way of generating hypotheses of what we measure about nature. If an investigator is uncertain about the structure of his attribute set, factor analysis will permit him to formalize biological hypotheses about the nature of the processes (common factors) generating the structure. If he has some prior knowledge of the processes present in the attribute set, he can build a structural hypothesis and either confirm or reject that hypothesis with factor analysis.

Although common factors are useful in understanding and describing relationships within a scientific field, interpretation of these factors must be

confirmed by evidence outside the factor analysis itself. Factor analysis should be developed over a series of related studies rather than a single investigation (Comrey, 1973).

Spearman (1904, 1927) developed the technique to investigate his hypothesis that the correlations among a set of intelligence-test scores could be generated by a single unknown common factor of general intellective ability (Morrison, 1967). Since one common factor might not represent all the causes of correlation in a set of attributes, Thurstone formulated an extension of Spearman's model to include many common factors. The divergent schools that developed around other models and their computational problems are discussed by Harman (1967) and Solomon and Rosner (1954). Lawley (1940) approached the extraction of factors as a statistical problem in maximum-likelihood estimation. This accomplished two things. It reduced factor extraction to a well-defined procedure of statistical estimation, and the generalized likelihood-ratio principle could rigorously test the goodness-of-fit of a solution (Morrison, 1967).

Thurstone's multiple-factor model is:

$$y_{ij} = f_{i1} z_{1j} + f_{i2} z_{2j} + \ldots + f_{ik} z_{kj} + u_{ij} \tag{1}$$

where y_{ij} is the j*th* response on the i*th* observable attribute, z_{kj} is the j*th* response on the k*th* artificial variable, and f_{ik} is a factor loading. With proper normalization techniques, we can report the factor loadings (f_{ik}) as correlations between the observable attributes (y_{ij}) and the common factors (z_{kj}). The u_{ij} is the unique contribution to the variation of each observable attribute which is not a part of the common-factor space. The matrix model can be written as

$$\mathbf{y} = \mathbf{F}\,\mathbf{z} + \mathbf{u} \tag{2}$$

where $\mathbf{y}$ is a vector of observable random attributes (p), $\mathbf{z}$ is a vector of common factors (k), $\mathbf{F}$ is a matrix (p × k) of factor loadings, and $\mathbf{u}$ is a vector of unique factors (p). It is assumed that var($\mathbf{u}$) = diagonal and cov($\mathbf{z}$, $\mathbf{u}'$) = 0. This model is statistically equivalent to the null hypothesis:

There may exist k common factors ($z_1, z_2, \ldots, z_k$) such that the partial correlations between the observable attributes ($\mathbf{y}$) are zero after this set of common factors ($\mathbf{z}$) has been partialed out (Bargmann, 1957).

This model is based on the assumption of a multivariate normal distribution for each population sampled. The inference tests for the null hypothesis depend on this assumption (Cooley and Lohnes, 1971). Some investigators believe it is advantageous for the common factors ($\mathbf{z}$) to be orthogonal, but the model does not require independent factors (Kendall and Stuart, 1963). Thurstone preferred to let the question of factor independence be a matter of convenience (Wolfle,

1940). In maximum-likelihood factor analysis, the estimation equations are less complicated when the factors are assumed to be orthogonal (Press, 1972). The assumptions that underlie factor-analysis models are discussed in detail by Anderson and Ruben (1956) and Armstrong (1967).

Factor analysis should not be confused with principal-component analysis (Pearson, 1901; Hotelling, 1933). Confusion does exist in the literature and in available computer programs; e.g., BMD (see Appendix A). Factor analysis makes inferences from the sample to a population, and principal-component analysis is a data analytical technique that describes the data at hand but m[illegible] no inference to the population. The first principal component is a selecti[illegible] weights ($a^{(i)}$) in a linear combination (z) of the observed attributes (p) for each experimental unit

$$z = a^{(1)}y^{(1)} + a^{(2)}y^{(2)} + \ldots + a^{(p)}y^{(p)} \qquad (3)$$

in such a way that, in terms of z, there is maximum distance between individuals. Additional principal components are meaningful constructs in the attempt to approximate the data at hand by other data exhibiting lower complexity. Principal-component analysis has nothing to do with the hierarchy of dependence implicit in factor analysis. A common factor is not a linear combination of the attributes. In the factor-analysis model (Eq. 1), the factor loadings (f_{ik}) are not weights to be applied to the attribute to produce each factor (Tatsuoka, 1971). The common factors (z_k) and a factor unique to that attribute (u_i) are linearly combined to express each attribute (y_i) (Kendall and Stuart, 1963). This is the opposite of principal-component analysis (Eq. 3) where the component (z) or factor is a linear combination of the observed attributes ($y^{(p)}$).

Factor analysis consists of two separate procedures, factor extraction followed by factor rotation. The analysis is always started from a correlation matrix computed from a sample variance–covariance matrix or a multiple thereof, e.g., the matrix of sums of squares and products for error. The sample variance–covariance matrix estimates the variation present within the population of interest. When that population has been sampled randomly, the sample variance–covariance matrix represents the estimated error found within th[illegible] population. When the population has been sampled selectively, the sam[illegible] variance–covariance matrix may not adequately represent the population variance. Introduced variation resulting from selective sampling (i.e., time, location, etc.) may bias any sample variance–covariance matrix of the population. Southwood (1966) states that the investigator on a priori grounds must test for differences that might result from selective sampling. Multivariate analysis of variance can interpret whether this introduced bias is significant. When the effects of time and location are determined to be significant, the variation due to these effects is removed from the sample variance–covariance

TABLE 1

NOTATION FOR MATRICES* IN ESTIMATING THE CORRELATION MATRIX (R)

Matrix	Type	Definition
Σ	Population	Variance–covariance
E	Sample	Estimated corrected sums of squares and cross products due to error
$S = E/\eta_e = \hat{\Sigma}$	Sample	Unbiased estimate of variance–covariance
H	Sample	Estimated corrected sums of squares and cross products due to the hypothesis
R = E	Selective sampling	When the selective effect results in a significant difference
R = H + E	a. Nonsignificant selective sampling b. Random sampling	When the selective effect in non-significant or random sampling has occurred

*The order of all matrices is p x p. η_e is degrees of freedom due to error.

matrix. Factor analysis is then performed on the adjusted or within-error variance–covariance (E) matrix representing the population of interest. If selective sampling is determined to have no effect on the study, then the factor analysis is performed on the total or sample variance–covariance (H + E) matrix of the population (Table 1).

Some effects, such as species, will not always presuppose that selective sampling has occurred. If an investigator has specifically sampled two designated species, his sampling procedure would be interpreted as being selective. That is, he has focused his attention on two species and will confine interpretation of conclusions to the attribute relationships existing between and within these species. He may analyze each species separately to determine attribute-dependence patterns for each group or, alternatively, may employ multivariate analysis of variance to determine whether there is a significant difference between the species. He would then factor analyze either the E, if the between-species effect is significant, or the H + E, if the difference between species is not significant. In either case he has randomly sampled individuals within the two species.

The investigator whose objective is to sample a composite population, i.e., a small-mammal component, would randomly sample individuals from the component representing different species of mice, shrews, rats, etc. He would not designate his sampling method as being selective for species, but the sample may be selective in regard to the component. That is, the investigator has not selected a species; he has sampled individuals of the small-mammal component,

even though those individuals may represent different species. He is interested in analyzing the behavior of the small-mammal component, not in analyzing the behavior unique to an individual species. Therefore, the species effect would not be removed from the sample variance–covariance matrix of the population, a random selection of individuals of small mammals. It is evident that an accurate definition of the population of interest becomes very important in interpreting the underlying dependence structure in that population.

The first step of the analysis is to perform a test of internal independence on the correlation matrix. The null hypothesis is:

H_0: The correlation matrix is an identity matrix (I) indicating no relationship between the attributes.

If we accept this hypothesis, the analysis is stopped, and we conclude that independence is plausible; i.e., no dependence structure is indicated. If we reject this hypothesis, we state a new model or null hypothesis:

H_1: Whatever independence then exists between the observable attributes can be explained in terms of one common factor (z_k, k = 1), or there may exist a single common factor such that all partial correlations between the attributes are zero after this common factor has been partialed out.

An ideal common factor is found that accounts for the greatest amount of dependence existing among the observable attributes. Therefore a vector of correlations between the observable attributes and this single common factor is estimated and partialed out from the correlation matrix. If we accept the hypothesis, we conclude that the model of one factor was plausible to explain the dependence, and the analysis is stopped. If we reject the hypothesis, a new model is formulated:

H_2: There exist two common factors (z_k, k = 2) such that the partial correlations between the attributes are zero after these common factors have been partialed out.

A second ideal common factor is found which explains a maximum amount of the remaining dependence. A vector of correlations between the observed variables and this second factor is again estimated and partialed out from the matrix of partial correlations. If this hypothesis is rejected, we can test the plausibility of three common factors explaining all the dependence. This sequence is continued until the model of k factors is plausible. A generalized flow diagram of this process is presented in Fig. 1.

At each step the probability (p_k) that the observed correlation matrix or a correlation matrix with larger off-diagonal elements could have occurred if the model H_k had been true is obtained. If p_k is large enough (e.g., $p > 0.50$), the model is certainly plausible, and the hypothesis H_k is accepted. We stop the sequence and say that independence (R = I) is plausible. If p_k is very small

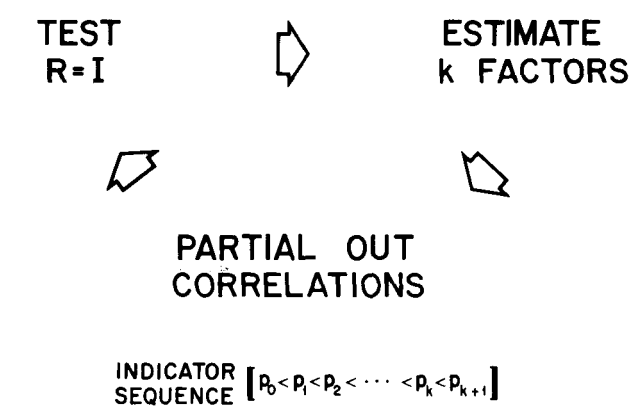

Fig. 1 Generalized flow diagram of the sequential method of factor extraction using an indicator sequence as a feedback control. When a large jump in the indicator probability occurs, the model of k factors is termed plausible, and the process terminates.

($p < 0.01$), the H_k model is not plausible, and a new model, H_{k+1}, is stated. This procedure is called the goodness-of-fit approach (Bargmann, 1957). These probabilities ($p_0 < p_1 < p_2 < \ldots < p_k < p_{k+1}$) are called an indicator sequence. If at any stage this sequence turns from implausible ($p < 0.01$) to plausible ($p > 0.50$) values, the indicator is unambiguous in meaning. The "correct" number of factors has clearly been determined (Bargmann, 1974). Accepting the hypothesis H_k does not prove that k is the true number of common factors present (Lawley and Maxwell, 1971). All it means is that there would be no need to fit additional factors to the data since they probably would not be distinguishable from experimental error. The number of factors can be specified in advance in most available computer programs, and this is prefectly acceptable in exploratory factor studies. Like other models (e.g., curve fitting), the basic factor model is useful only as an approximation to reality.

Associated with each extracted factor (z_k) is a vector of factor loadings (f). These vectors can be normalized to correlations between the attributes (y) and the common factor (z_k). The observable attributes having high correlations with the factor are considered to be "like" the factor in some sense, and those with zero or near-zero correlations are considered "not like" the common factor. The related attributes must be examined by the investigator to determine what they share in common that would cause the factor to appear in the data. Attributes that correlate perfectly with a factor are considered to be identical with it. Guilford (1965) defined a reliability coefficient that indicates the degree of overlap of an attribute with its factor. It is the square of the correlation between the attribute and the factor. A high reliability coefficient (0.81 or greater) indicates strong overlap. Attributes with low reliability coefficients ($<4/n$, where n is the sample size) share nothing with this factor. The sum of squares of the loadings for an

attribute (i) over k factors, called the estimated communality (h_i^2), indicates the extent of overlap between that attribute and the set of k extracted factors of the square of the multiple correlation of the *ith* observable attribute and the entire set of k factors. For all i attributes, $0 < h_i^2 < 1$. If h_i^2 is equal to 1.0, the *ith* attribute overlaps totally with the set of factors, and the *ith* attribute contains no specific component unrelated with the other attributes in the set. This would indicate that the uniqueness (u_i^2) of the *ith* attribute is zero, since $u_i^2 = 1 - h_i^2$. Communality estimates are inflated when small sample sizes characterize the study. Guertin and Bailey (1970) state that with small sample sizes the rand[illegible] errors of the less reliable correlation coefficients increase the absolute size of correlations in the matrix. This results in greater communalities and a larger amount of common-factor variance because of spurious common-factor variance.

Sample size also affects factor loadings (f_{ik}) and the number of extractable factors. Reliable factor loadings result from improvements of the reliability of the sample correlations (r). The sample correlations are improved by increasing sample size, but improvement will occur with diminishing returns (Comrey, 1973). The number of extracted factors obtained by maximum-likelihood factor analysis increases as sample size increases because a higher degree of dependence appears more plausible in studies having large sample sizes (Bargmann, 1966). This situation is not unique to factor analysis but also occurs in the process of statistical curve fitting. For example, a straight line is the only possible fit to any two points, but a higher order polynomial may be plausible where many points are present.

The matrix of loadings (F) obtained after extraction is an arbitrary representation of the common-factor space and is useless for interpretation. Different numerical factor-analysis techniques yield different initial representations of the same result. Therefore the extracted F matrix is rotated or transformed in such a way that most of the factor loadings produced are near zero, leaving only a few near 1. Thurstone (1935) called the rotated matrix a simple structure. It is the representation of a mathematically identical result in a different coordinate system. There is no best or optimal representation. Rotation indicates which attributes have the most in common with each factor.

Attributes with loadings below 0.30 are usually disregarded in interpreting common factors (Comrey, 1973). The 0.05 level of the correlation between attributes and common factors is unknown but is approximately $2/\sqrt{n}$, where n is sample size. Statistical tests do exist to test the significance of a simple structure (Bargmann, 1955).

A doublet factor consists of two attributes with high loadings. It represents alternate ways of asking the same question. The two attributes could be considered analogous variables. Doublet factors are produced by including two like attributes in the same analysis. These factors can usually be avoided when all observable attributes having simple correlations greater than 0.80 in the original correlation matrix are combined or analyzed separately (Bargmann, 1974). In

factor analysis, as in all multivariate analyses, grossly misleading results can occur if the number of determinations made for the study is less than the number of attribute measures included in the analysis. When a linear combination and the attributes comprising the combination are included in the same analysis, strong but misleading factors must result. The only way to learn something about these common factors is to study the attributes. Investigating these attributes should lead to hypotheses about the nature of the common factors. Further pursuit of such hypotheses requires confirmatory analysis, usually multiple regression.

Multiple-regression analysis selects a subset of predictor variables that best predict the criterion variable and determines the relative weights for making that prediction. Applied in conjunction with factor analysis, predictor variables are attributes, and the criterion variable is the common factor. The investigator selects or creates a new attribute that he believes is a relatively pure measure of this common factor. Multiple-regression analysis will indicate how well he has interpreted the nature of the common factor and the level of prediction for criteria. A lengthier discussion can be found in Comrey (1973).

Relatively new disciplines or sciences, such as ecology, should consider the factor-analysis technique to help synthesize the wealth of available data (see Appendix B: Recommended Literature). Often data has been collected with a greater depth of detail than is relevant or necessary to answer the questions posed by the investigator. Extracting common factors from the collection of observed attributes can focus attention on relationships that might not be obvious. This avoids duplication of material and wasted time searching for patterns and structures inherent in the attributes.

The advantage of the factor-analysis technique is its ability to reduce a large set of attributes to a few common factors; this permits the attributes to be defined more precisely and helps the investigator to decide which attributes should be studied further and how to relate them to each other.

The difficulty with the technique is that the very process of selecting attributes to be included in a factor analysis determines its outcome. If the included attributes are not the important ones, we will have extracted common factors that do not in fact indicate the desired underlying interrelationships. Factor analysis will reflect cruelly the experimenter's ability or inability to choose attributes from a homogeneous collection (Bargmann, 1966). A second disadvantage results from a limitation of the sample size. Comrey (1973) argues that sample sizes of 1000 give excellent results, but samples of 200 give only fair results. Guertin and Bailey (1970) recommended sample sizes as large as possible (500 being ideal). Although large sample sizes are always desirable, many researchers have difficulty obtaining large samples. Adequate sample size depends on the accuracy and precision of the collection methods used to measure the attributes and on the number of attributes in the study. In general, the greater the number of attributes, the larger the sample size required. On the

basis of our own experience, we determine the minimum sample size (N) for a study by multiplying the number of attributes (p) by 10 and adding 30; e.g., the minimum sample for a study containing 19 attributes would be 220. If Pearson product–moment correlations are not used, Comrey (1973) indicates that a larger sample size is needed to achieve the same level of stability of the correlation coefficient. But Kendall and Stuart (1963) warn that factor analysis of matrices (R) obtained by methods other than product–moment correlations are not always valid. Such matrices are not necessarily positive definite and in certain cases may result in some latent roots being negative. When the sample size is minimum and the accuracy and precision of measurement are less reliable, the investigator must be conservative in his interpretation of the common factors.

There also exists a difference of opinion about whether the common factors should be arbitrary descriptive variables or real entities in nature awaiting discovery (Comrey, 1973). Some investigators (Allport, 1937; Kelley, 1940) believe that factor analysis is simply a problem of description in several dimensions, the factors being only statistical coefficients without any more reality than a mean or a correlation coefficient. Others argue that each factor corresponds to some influence that is a functional unity in nature (Cattell, 1952; Guilford, 1964). Wolfle (1940) explained that factor analysis does not create common factors; the factors result from the structure of the available data. If we recognize that the presence of some process that generates a systematic set of correlations will also produce a factor, then it becomes absurd and naive to suppose that every factor will necessarily represent an ultimate and unitary natural event. Thurstone (1947; 1938; 1940), Thomson (1951), and Tryon (1939) never supported such an assumption. Factors attributed to causes peculiar to a particular study are of relatively little interest, but common factors appearing repeatedly in different studies are of great interest, both in naming them and in inquiring about their basic natures. The name given to a factor is merely the investigator's hypothesis regarding the nature of the factor.

Factor analysis is applied to four sets of mineral data to show how this technique may assist mineral-cycling studies. A distinct population of interest and slightly different sets of attributes characterize each study. The first study presented applies factor analysis to whole-body elemental-composition data for the small-mammal component of an oak–hickory forest in the eastern deciduous forest (Nabholz, 1973). The data set consists of 14 chemical elements and body measurements of 188 individuals. Temporal and spatial effects were removed from the sample variance–covariance matrix. Three pairs of highly correlated variables [wet weight and dry weight ($r = 0.99$), total length and tail length ($r = 0.88$), and phosphorous and calcium content ($r = 0.85$)] were segregated and analyzed separately with the remaining 13 attributes. An initial factor analysis of 16 attributes including dry weight, tail length, and calcium concentration resulted in the extraction of five common factors (Table 2).

TABLE 2

ROTATED FACTOR LOADINGS FOR FIVE EXTRACTED FACTORS FROM A STUDY OF THE WHOLE-BODY ELEMENTAL COMPOSITION OF A SMALL-MAMMAL COMPONENT*†

I		II		III		IV		V	
TAL	0.89	K	0.55	Sr	0.52	Al	0.81	B	0.83
HFL	0.74	Na	0.53	Ba	0.49	Fe	0.70	Mo	0.44
Ba	0.32	N	0.39	Ca	0.47	Mo	0.38	Cu	0.36
Na	−0.34	Ca	0.30						
		Mg	0.25‡						

*Nabholz, 1973.

†The correlation matrix consisted of 13 chemical elements and 3 body measurements (N = 188). TAL is tail length; HFT is hind-foot length.

‡*Usually disregarded, reported here because magnesium is an* electrolyte.

Factors II, III, and V represent groups of essential minerals involved in the major metabolic functions [electrochemical and structural (II), supporting structure (III), and enzymatic (V)] occurring in the mammal body.

The cations that maintain the electrical neutrality of the body and nitrogen, a major component of soft tissue, are present in factor II. The earth alkalies represented by factor III provide strong supporting structures in bony animals. Two metalloenzymes and an element with no known function, boron, comprise factor V. Similar groupings of essential elements based on qualitative criteria are discussed by Bowen (1966) and Frieden (1972). The first factor appears to be a size factor indicating the progression from small to large small mammals in the study. Factor IV (Table 2) represents the presence of ingested soil in the intestinal tract. After silicon, aluminum and iron are the most abundant constituents of soil (Buckman and Brady, 1974) and correlate strongly (Jones, 1974). The presence of ingested soil probably results from the investigator's not removing the intestinal tracts of the small mammals. A subsequent analysis with wet weight, total length, and phosphorous concentration extracted the factors of the previous analysis except the electrolyte factor (Table 2). Total length replaced tail length in factor I, and phosphorous was substituted for calcium in the third factor. Both pairs of attributes can be considered analogous attributes. Failure of the second analysis to identify the electrolyte factor was the result of high correlations of total length with wet weight and hind-foot length. The variable total length should have been separated from wet weight and hind-foot length in this analysis.

A second study by Briese (1973) investigated the factor structure in whole-body elemental-composition data for *Sigmodon hispidus*, a small mammal

TABLE 3

ROTATED FACTOR LOADINGS FOR FIVE EXTRACTED FACTORS FROM A STUDY OF THE ELEMENTAL COMPOSITION OF THE STOMACH CONTENTS OF *Sigmodon Hispidus**†

I		II		III		IV		V	
Sr	0.96	Fe	0.90	Zn	0.73	K	0.80	Ash	0.81
Ba	0.89	Al	0.88	P	0.72	Na	−0.75	N	0.58
Mg	−0.89	Mo	0.76	N	0.70				
Ash	−0.80			Cu	0.62				
Mn	0.77								
Ca	−0.74								
B	0.72								

*Briese, 1973.

†The correlation matrix consisted of 14 chemical elements and per cent ash. Sample size was not reported.

found in broom-sedge fields. Correlations between 14 chemical elements and 4 body components for 295 individuals were analyzed after stratification effects for age, sex, season, and their interactions were removed from a sample variance–covariance matrix. No variation due to reproductive condition or location was present since embryos had been removed and all individuals were sampled from one location. This study represented the analysis of an idealized individual of *Sigmodon hispidus.* Of the three factors extracted, the first and third appeared to be very complex and not easily interpretable. The second factor consisted of five attributes representing major body components: fat, 0.68; water, 0.52; nitrogen, 0.44; iron, 0.38; and ash, 0.35. Briese (1973) reported that this factor was related to fat storage since it was eliminated when concentrations based on lean dry weight rather than on dry weight were analyzed. Comparing this study with the Nabholz (1973) study suggests that the processes operating in a small-mammal component are different from those in an idealized individual of a small-mammal species.

An additional analysis by Briese (1973) of the elemental composition of the stomach contents of *S. hispidus* (Table 3) produced five factors. The correlation matrix consisted of 14 chemical elements and per cent ash; sample size was not reported. Briese concluded that the factors may be related to changes in elemental composition of the diet. Elemental composition varies with the percentage of available grasses, seeds, and insects and with seasonal and/or locational changes in plant mineral concentrations.

The first factor, which is the strongest (Table 3), represents a bipolar factor and indicates that, when strontium, barium, manganese, and boron concentrations are high, ash, magnesium, and calcium concentrations are low. Such factors usually require additional investigation before a hypothesis can be made about

TABLE 4

ROTATED FACTOR LOADINGS FOR FOUR EXTRACTED FACTORS FROM A STUDY OF THE ELEMENTAL COMPOSITION OF THE LEAF COMPARTMENT OF A TROPICAL FOREST*†

I		II		III		IV	
P	0.62	Ca	0.77	K	0.36	Na	0.90
K	0.60	Sr	0.68	Na	−0.33	Zn	0.47
Cu	0.45	Ba	0.46			Mn	0.44
Zn	0.41	B	0.43				
Mg	0.33						

*Golley et al., 1975.

†The correlation matrix consisted of 14 chemical elements (N = 168).

their natures. Factor II represents the presence of ingested soil in the stomach contents of *S. hispidus*. A similar factor (Table 2, factor IV) was identified in the whole-body elemental-concentration study by Nabholz (1973). Like factors extracted from different studies suggest that the same process is occurring in both populations. Such results are mutually supportive and lend greater creditability to the nature of the process (Press, 1972).

The third factor grouped four elements strongly associated in the photosynthetic process (Bowen, 1966). This interpretation is not surprising since herbacious plants form an important part of the diet of this mammal. Doubleton factors like IV and V (Table 3) generally are not reported since they are analogous attributes usually highly correlated in the input matrix.

The final study presented here analyzes the elemental composition of a tropical rain forest (Golley et al., 1975). The data matrix consisted of concentrations of 14 elements from 168 samples. Initial application of the technique sought to find factor structures in sample variance–covariance matrices from which effects of location (forests) and compartmentalization (leaves, stems, fruits and flowers, roots, and litter components) were removed. In instances, whether the effects were removed individually or together, the or analysis indicated no significant patterns. When the forest was viewed as components instead of as a complete entity, factor structures began to emerge. Analysis of the leaf component with location effects removed resulted in extraction of four factors (Table 4). Factor I grouped five elements associated with the photosynthetic process (Bowen, 1966). Factor III is a doubleton and would have been ignored except that this factor and factor I were identified previously in Briese's analysis of the elemental composition of the stomach contents of *S. hispidus* (Table 3, factors III and IV, respectively). The common factors found in the leaf compartment of the tropical forest appear to be the

same as those extracted in the stomach contents of *S. hispidus.* This correspondence is possible since both studies contain measures of elemental concentrations in leaves. Elements that contribute to leaf structure are correlated with factor II. These elements, except boron, perform a similar function in small mammals (Table 2, factor III), with one major difference. In mammals calcium and phosphorous are analogous, but in leaves phosphorous has no apparent structural function (Bowen, 1966). A similarity can be seen between this second factor (Table 4) and the first factor of Briese's stomach contents study (Table 3), but the polarity in factor I (specifically calci[illegible] makes a correspondence between these factors rather tenuous. A com[illegible] denominator among the attributes of factor IV has not been found. Hence we could not interpret this factor at the present time.

Can factor analysis provide information about the processes present in mineral data and aid in the generalization of mineral-cycling models? Consider for a moment the current analytical approach to modeling mineral cycles. For each element a unique model is being built. If in fact elements are related in the ecosystem (which some researchers believe) and if it can be shown that groups of elements behave or function alike in concentrations, standing crops, and flux rates, then it would be possible to take a first step toward generalizing mineral models. Mineral-cycling models can be generalized in two directions—within ecosystems and between ecosystems. First, factor analysis of components within an ecosystem will indicate how closely a model for one element could apply to other elements correlated with a common factor. Second, if like factors can be found in the same components of diverse biomes, then these factors might suggest a basis for formulating a common model between ecosystems. For example, we suggest that the photosynthetic, structural, and potassium–sodium associations of the forest leaf compartment are the same associations formed in the leaves of old-field vegetation. Although this supposition is relatively tenuous, we agree with Holliday and Pugh (1975) that it seems justifiable to suggest a speculative hypothesis that may lead to a meaningful experimental approach, particularly when this hypothesis is based on a portion of the known data. Additional confirmatory studies are needed to either substantiate or repudiate these hypotheses about the formulation of general mineral-cycling models.

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REFERENCES

Allport, G. W., 1937, *Personality, a Psychological Interpretation,* Henry Holt & Co., New York.

Anderson, T. W., and H. Ruben, 1956, Statistical Inference in Factor Analysis, in *Proceedings of the Third Berkeley Symposium on Mathematical Statistics and Probability,* J. Neyman (Ed.), Vol. 5, pp. 111-150, University of California Press, Berkeley.

Armstrong, J. S., 1967, Derivation of Theory by Means of Factor Analysis, or Tom Swift and His Electric Factor Analysis Machine, *Amer. Statistn.,* **21**: 17-21.

Bargmann, R. E., 1974, University of Georgia, personal communication.

——, 1967, Exploratory Techniques Involving Artificial Variables, in *Multivariate Analysis:* Proceedings of an International Symposium, P. R. Krishnaiah (Ed.), Vol. 2, pp. 567-580, Academic Press, Inc., New York.

——, 1966, Factor Analysis, address presented at the Second Annual Goddard Computer Science Symposium, Dallas, Texas.

——, 1957, A Study of Independence and Dependence in Multivariate Normal Analysis, Institute of Statistics, Publication No. 186, University of North Carolina, Durham.

——, 1955, Signifikanzuntersudrungar der einfachen in der faktorenanalyse, *Mitt. f.d. Math. Statistik (Metrika),* **1**: 1-24.

Bowen, H. J. M., 1966, *Trace Elements in Biochemistry,* Academic Press, Inc., New York.

Briese, L. A., 1973, Variations in Elemental Composition and Cycling in the Cotton Rat, *Sigmodon hispidus,* M.S. Thesis, University of Georgia, Athens.

Buckman, H., and N. C. Brady, 1974, *The Nature and Properties of Soils,* 8th ed., Macmillan Publishing Co., Inc., New York.

Cattell, R. B., 1952, *Factor Analysis,* Harper & Brothers, New York.

Comrey, A. L., 1973, *A First Course in Factor Analysis,* Academic Press, Inc., New York.

Cooley, W. W., and P. R. Lohnes, 1971, *Multivariate Data Analysis,* John Wiley & Sons, Inc., New York.

Frieden, E., 1972, The Chemical Elements of Life, *Sci. Amer.,* **227**: 52-60.

Golley, F. B., J. T. McGinnis, R. G. Clements, G. I. Child, and M. J. Duever, 1975, *Mineral Cycling in a Tropical Moist Forest Ecosystem,* University of Georgia Press, Athens.

Guertin, W. H., and J. P. Bailey, 1970, *Introduction to Modern Factor Analysis,* J. W. Edwards, Publisher, Inc., Ann Arbor, Mich.

Guilford, J. P., 1965, *Fundamental Statistics in Psychology and Education,* 4th ed., McGraw-Hill Book Company, New York.

——, 1964, Some New Looks at the Nature of Creative Processes, in *Contributions to Mathematical Psychology,* N. Frederiksen and H. Gulliksen (Eds.), pp. 161-182, Holt, Rinehart & Winston, Inc., New York.

Harman, H. H., 1967, *Modern Factor Analysis,* 2nd ed., The University of Chicago Press, Chicago.

Holliday, R., and J. E. Pugh, 1975, DNA Modification Mechanisms and Gene Activity During Development, *Science.* **187**: 226-232.

Hotelling, H., 1933, Analysis of a Complex of Statistical Variables into Principal Components, *J. Educ. Psycol.,* **24**: 417-441, 498-520.

[illegible]es, J. B., 1974, University of Georgia, personal communication.

[illegible]elley, T. L., 1940, Comment on Wilson and Worcester's "Note on Factor Analysis," *Psychometrika,* **5**: 117-120.

Kendall, M. G., and A. Stuart, 1963, *The Advanced Theory of Statistics,* Vol. 3, Hafner Service Agency, New York.

Lawley, D. N., 1940, The Estimation of Factor Loadings by the Method of Maximum Likelihood, *Proc. Roy. Soc. Edinburgh, Sect. A,* **60**: 64-82.

——, and A. E. Maxwell, 1971, *Factor Analysis as a Statistical Method,* Butterworth & Co. (Publishers) Ltd., London.

Morrison, D. F., 1967, *Multivariate Statistical Methods,* McGraw-Hill Book Company, New York.

Nabholz, J. V., 1973, Small Mammals and Mineral Cycling on Three Coweeta Watersheds, M.S. Thesis, University of Georgia, Athens.

Pearson, K., 1901, On Lines and Planes of Closest Fit to a System of Points in Space, *Phil. Mag.*, **2**: 557-572.

Press, S. J., 1972, *Applied Multivariate Analysis Including Bayesian Techniques*, Holt, Rinehart & Winston, Inc., New York.

Solomon, H., and B. Rosner, 1954, Factor Analysis, *Rev. Educ. Res.*, **24**: 421-438.

Southwood, T. R. E., 1966, *Ecological Methods*, Chatman and Hall, London.

Spearman, C., 1927, *The Abilities of Man*, The Macmillan Company, New York.

——, 1904, General Intelligence Objectively Determined and Measured, *Amer. J. Psychol.*, **15**: 201-293.

Tatsuoka, M. M., 1971, *Multivariate Analysis: Techniques for Educational and Psychological Research*, John Wiley & Sons, Inc., New York.

Thomson, G. H., 1951, *The Factorial Analysis of Human Ability*, University of London Press, London.

Thurstone, L. L., 1947, *Multiple Factor Analysis*, The University of Chicago Press, Chicago.

——, 1940, Current Issues in Factor Analysis, *Psychol. Bull.*, **37**: 189-236.

——, 1938, Shifty and Mathematical Components: A Critique on Anastasi's Monograph on the Influence of Specific Experience upon Mental Organization, *Psychol. Bull.*, **35**: 223-236.

——, 1935, *The Vectors of Mind*, The University of Chicago Press, Chicago.

Tryon, R. C., 1939, *Cluster Analysis*, Edwards Bros., Ann Arbor, Mich.

Wolfle, D., 1940, *Factor Analysis to 1940*, The University of Chicago Press, Chicago.

APPENDIX A: COMPUTER PROGRAMS

Recommended computer programs for factor analysis:

FCAN Maximum-likelihood factor extraction and rotation to simple structure. Available from Nabholz and Richardson, Institute of Ecology, University of Georgia, Athens.

UMLFA Unrestricted maximum-likelihood factor analysis. Goodness-of-fit is tested by Lawley's chi square test based on the likelihood-ratio technique (Press, 1972). Available from K. G. Jöreskog, Educational Testing Service, Princeton, N. J., or The University of Chicago Computer Center, Chicago.

BMD03M (revised) Iteration of principal-factor axis; arrives at the same solution obtained by maximum-likelihood factor analysis but tends to overfactor. Available in the BMD Biomedical Package, University of California, Berkeley.

We recommend programs utilizing maximum likelihood to estimate communalities and factor loadings and rotating to simple structure.

APPENDIX B: RECOMMENDED LITERATURE

Suggested literature for introduction to factor analysis. We recommend the following order:

1. Wolfle (1940), a review of the fundamental and historical development of factor analysis with emphasis on general logic, chief results, use, and limitations.
2. Guertin and Bailey (1970), Chaps. 10 and 11 discuss what constitutes [illegible]equate sampling in factor analysis.
3. [illegible]derson and Ruben (1956) and/or Armstrong (1967), discuss the assumptions underlying the factor-analysis model and how their violation affects results.
4. Horst, P., 1965, *Factor Analysis of Data Matrices,* Holt, Rinehart & Winston, Inc., New York, establishes factor analysis from a matrix-algebra viewpoint.
5. Harman (1967), emphasizes the mathematical techniques and formulas of factor analysis.
6. Lawley and Maxwell (1971), develop maximum-likelihood factor analysis.
7. Guilford, J. P., 1952, When Not to Factor Analyze, *Psychol. Bull.,* **49**: 26-37, and/or Hotelling, H., 1957, The Relation of the Newer Multivariate Statistical Methods to Factor Analysis, *Brit. J. Stat. Psychol.,* **10**: 69-79, discusses situations in which factor analysis is inappropriate.

Additional sources of information:

Thurstone (1947) and Thomson (1951), classic texts in factor analysis.

Cattell (1952), emphasizes advanced topics of experimental design employing factor analysis.

Fruchter, B., 1954, *Introduction to Factor Analysis,* D. Van Nostrand Co., Inc., New York, an elementary nonmathematical introduction to factor analysis.

Comrey (1973), an introductory approach emphasizing psychological applications.

Rummel, R. J., 1970, *Applied Factor Analysis,* Northwestern University Press, Evanston, Ill., a factor-analysis text emphasizing applications in the social sciences.

A SPECIFIC-ACTIVITY AND CONCENTRATION MODEL APPLIED TO CESIUM MOVEMENT IN AN OLIGOTROPHIC LAKE

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ABSTRACT

A linear systems-analysis model was derived to simulate the time-dependent dynamics of specific activity and concentration of radionuclides in aquatic systems. Transfer coefficients were determined for movement of ^{137}Cs in the components of an oligotrophic lake. These coefficients were defined in terms of basic environmental and ecological data so that the model can be applied to a wide variety of sites. Simulations with a model that ignored sediment–water interactions predicted much higher ^{137}Cs specific activities in the lake water and biota than did those with the complete model. Comparing ^{137}Cs concentrations predicted by the model with concentrations reported for the biota of an experimentally contaminated oligotrophic lake indicated that the transfer coefficients derived for the biota are adequate.

Our purpose is to present a linear systems-analysis model to simulate the time-dependent dynamics of ^{137}Cs specific activity and concentration in components of an oligotrophic lake. This has necessitated the derivation of general equations for change of specific activity and radionuclide concentration in a compartment and the determination of transfer coefficients for the different compartments. In aquatic systems transfer coefficients, especially those of abiotic components, are highly site specific. For this reason we were careful to define the transfer coefficients in terms of basic environmental data so that the model could be realistically applied to a wide variety of sites. This model is meant to be a first step in the development of a general model for radionuclide dynamics in aquatic systems. When completed, the general model will be incorporated as a submodel of the larger Cumulative Exposure Index (CUEX)

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model of the Environmental Sciences Division at Oak Ridge National Laboratory.

Of particular concern was the amount of detail and realism required to simulate radionuclide dynamics in aquatic systems realistically. The necessary data for deriving transfer coefficients are available for cesium, but this is not true for most radionuclides. To gain insight into the required detail and realism, we first constructed as complete a model for cesium as allowed by the available data and compared its predictions with those of simpler models that assumed ilability of a less extensive data base. In this study we built a constant-fficient model for ^{137}Cs with as much detail and realism as allowed by the available data base and simulated the dynamics of specific activity in components of a hypothetical oligotrophic lake after a pulse input of ^{137}Cs. Since we were particularly concerned about the importance of sediment–water interactions, for which relatively few data are available, we compared the simulation of the full model with that of a model that neglected sediment–water interactions.

A model should represent the state-of-the-art knowledge of a system to the extent necessary for the desired resolution. In this regard, an important part of modeling is verification since verification may reveal areas requiring further research. Therefore we tried to locate data that could be compared with our predictions. Data for a pulse input of ^{137}Cs were desired because realistic simulation of the pulse release, which simulates an accidental release, requires adequate transfer coefficients for fast as well as slow compartments. Time histories of ^{137}Cs concentration in water and biota of an oligotrophic lake after a pulse input were available from the ^{137}Cs pollution experiments of Kolehmainen et al. (1968) on Finnish lakes. Using their time history of ^{137}Cs concentration in the water as a forcing function, we made a preliminary evaluation of the biotic transfer coefficients by comparing model predictions with measured ^{137}Cs concentrations.

THE MODEL

Specific-Activity Equation

The basic dynamic viewpoint is that stable-element and radionuclide flow be treated by first-order coupled linear differential equations and that the dynamics of specific activity follow along naturally. Let

Z_i = mass of the stable element in compartment i (g)

$a_{ij}Z_j$ = rate at which the stable element moves from compartment j to compartment i (g/day)

$\gamma_i Z_i$ = rate at which the stable element moves from compartment i to surroundings external to the system (g/day)

R_i = rate at which the stable element enters compartment i from the surroundings external to the system (g/day)

Then

$$\dot{Z}_i = \sum_j^{i\prime} a_{ij} Z_j - (\gamma_i + \sum_j^{i\prime} a_{ji})\, Z_i + R_i \tag{1}$$

where the primed summation symbol, $\sum_j^{i\prime}$, is taken to mean the sum over all j except i.

The radionuclide is presumed to move between compartments following the same laws as the corresponding stable element; i.e., X_i, the amount radionuclide in compartment i, changes according to the relation

$$\dot{X}_i = \sum_j^{i\prime} a_{ij} X_j - (\gamma_i + \lambda + \sum_j^{i\prime} a_{ji})\, X_i + K_i \tag{2}$$

where λ is the physical decay constant of radionuclide (day^{-1}) and K_i is the rate at which the radionuclide enters compartment i from the surroundings external to the system (μCi/day).

Specific activity, S_i, is defined as

$$S_i = \frac{X_i}{Z_i} \tag{3}$$

Hence

$$\dot{S}_i = \frac{\dot{X}_i}{Z_i} - \dot{Z}_i \left(\frac{X_i}{Z_i^2}\right) \tag{4}$$

Combining Eqs. 1 to 4 gives

$$\dot{S}_i = \sum_j^{i\prime} a_{ij} \frac{Z_j}{Z_i} S_j - \left(\lambda + \frac{R_i}{Z_i} + \sum_j^{i\prime} a_{ji} \frac{Z_j}{Z_i}\right) S_i + \frac{K_i}{Z_i} \tag{5}$$

Defining

$$\alpha_{ij} = a_{ij} \frac{Z_j}{Z_i} \tag{6}$$

we obtain the desired specific-activity relation:

$$\dot{S}_i = \sum_j^{i\prime} \alpha_{ij}(S_j - S_i) - \lambda S_i + \left(\frac{K_i}{Z_i} - \frac{R_i}{Z_i} S_i\right) \tag{7}$$

In words, α_{ij} is the flow of stable element (g/day) into compartment i from compartment j divided by the amount of stable element in compartment i; thus α_{ij} is in units of day^{-1}. If the compartment is composed of animals, it includes whole animals minus their gut contents; thus α_{ij} for animals applies to the rate of uptake of the element by the body, i.e., the absorbed portion of total intake of the element.

Equation 7 does not assume constant Z_i. The equation would apply, for example, to a compartment composed of a cohort of fish in which the amount of stable element in the compartment is increasing because of growth. In this case, and for other biological compartments, the terms in the second parentheses of Eq. 7 would not appear unless there was immigration of individuals into the population comprising the compartment. More usually, however, Z_i of both abiotic and biotic compartments is treated as constant; for the biotic compartments this implies constant biomass and stable element concentration.

Conversion of Specific Activities to Concentrations

Comparing model predictions with the concentration measurements of Kolehmainen et al. (1968) required conversion of specific-activity prediction, S_i, to prediction of radionuclide concentration, (X_i/W_i), where W_i is the mass of compartment i and X_i is defined in Eq. 2. This conversion has additional importance because radionuclide concentrations in some components, e.g., sediment and water, are necessary for calculating radiological dose from external exposure. From Eq. 3

$$\frac{X_i}{W_i} = \frac{S_i Z_i}{W_i} \tag{8}$$

and, therefore, the required conversion could have been accomplished by use of Z_i/W_i, the stable-element concentration (grams of stable element per gram of mass) of compartment i, for each component where comparisons were desired. Although the parameter Z_i/W_i was not available from the experiment and is quite variable from one environment to another, Eq. 8 can be rewritten in terms of known ratios.

Taking Z_1/W_1 as the radionuclide concentration in the water, we can write

$$\frac{X_i}{W_i} = \frac{S_i Z_i}{W_i} \frac{Z_1/W_1}{Z_1/W_1} = S_i \frac{Z_i/W_i}{Z_1/W_1} \frac{X_1/S_1}{W_1} = \frac{S_i}{S_1} B_i \frac{X_1}{W_1} \tag{9}$$

where $B_i = (Z_i/W_i)/(Z_1/W_1)$ is the ratio of the elemental concentration in compartment i to the elemental concentration in compartment 1, the water. The values of B_i and of X_i/W_i for various compartments are available from the measurements of Kolehmainen et al. (1968). The ratios of S_i to S_1 determined by our model can therefore be compared to the equivalent ratios $(X_i/W_i)/[B_i(X_1/W_1)]$, all of whose terms are available. Obviously concentrations can be obtained from the specific-activity model by the relation

$$\frac{X_i}{W_i} = B_i \frac{S_i}{S_1} \left(\frac{X_1}{W_1}\right) \tag{10}$$

Structure of Lake-Ecosystem Model

Figure 1 shows a control diagram for simulating the flow of specific activity in a hypothetical oligotrophic lake. (Note that this diagram must be interpreted differently from radionuclide and other mass-flow diagrams.) Specific activity in a compartment is controlled only by the flows entering the compartment and by loss of specific activity because of radioactive decay. In contrast, the amount of radionuclide in a compartment is regulated by both inflow and outflow arrows.

The compartments in the lake can be classified as biotic or abiotic. The abiotic compartments include sediment, interstitial water, and water. Cesium is found in suspended and soluble phases in water. In the soluble phase it exists

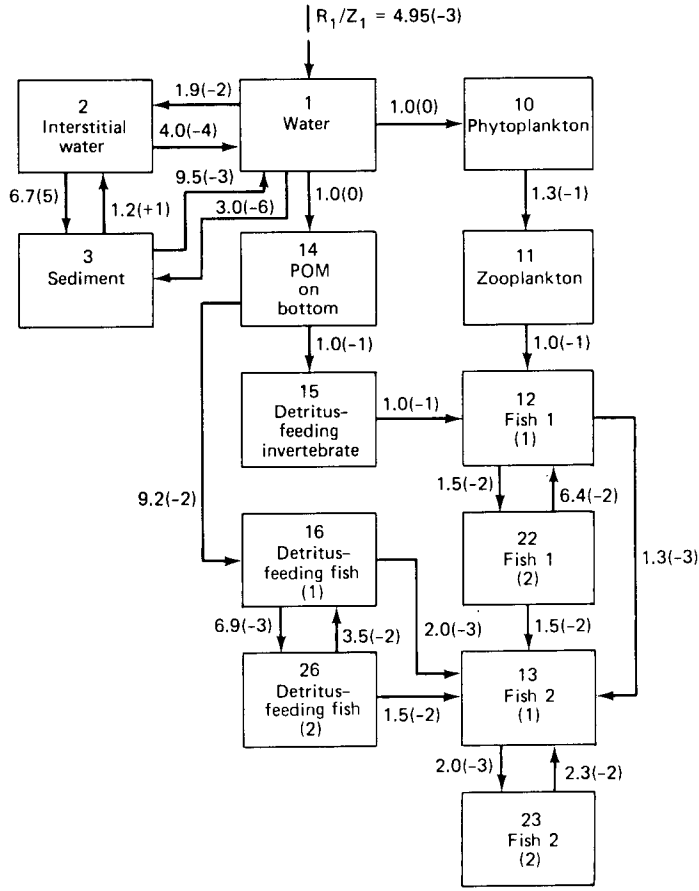

Fig. 1 Control diagram and transfer coefficients for simulation of specific-activity flow in a hypothetical oligotrophic lake. Values of α_{ij} are indicated on arrows. Numbers are given in a form such that 1.9(−2) is read as 1.9×10^{-2}. (See Eq. 7 for clarification of the ratio R_1/Z_1.)

primarily as free ions. Soluble cesium has a strong tendency to sorb to suspended clay particles. For this reason the fraction of cesium in the suspended phase increases with increased concentration of suspended solids (Vanderploeg et al., 1974). Implicit in our treatment of water as a single compartment (Fig. 1) is that the specific activity of radiocesium in the particulate phase of water is equal to that in the soluble phase. Clearly this is reasonable for cesium exchangeably bound but not for cesium nonexchangeably bound to suspended sediments. For this reason the quantities R_1, Z_1, and X_1 refer to amounts of cesium isotopes in soluble plus exchangeable particulate forms, and S_1 is the specific activity of radiocesium in both soluble and exchangeable particulate forms.

Soluble cesium enters the food web via sorbtion to phytoplankton and particulate organic matter (POM). Cesium accumulation by organisms other than phytoplankton is from the food web. The mass balance of cesium in the water is assumed to be controlled entirely by the dynamics of the abiotic compartments. This control is indicated by feedback, or return, arrows from compartments 2 and 3. The assumption is justified by the dominance of sediment–water interactions and the small amount of cesium in biotic components relative to the sediment. Natural clays and silts have cesium concentrations of the same order as or greater than the biota but have masses in aquatic systems that are orders of magnitude greater than the biota.

Our sediment compartment is composed of typical temperate-region clays and silts (Booth et al., 1975). The detritus-feeding invertebrates and fish are assumed to derive all food and cesium from a thin layer of particulate organic matter which overlies the sediment.

Transfer coefficients for the model are shown next to the arrows in Fig. 1. Derivation of the coefficients is discussed in the following section.

DERIVATION OF TRANSFER COEFFICIENTS

Sediment–Water Interactions

Transfer coefficients of sediment–water interactions, shown in Fig. 1, were calculated from the model of Booth et al. (1974). This model expressed the net transfer of dissolved species across the interface between the interstitial water and lake water as equal to an effective transfer velocity times the concentration difference across this interface (Lerman and Brunskill, 1971). Radionuclide transfers caused by sedimentation of suspended sediments were derived from representative values of the sedimentation rate [depth of new sediment added to the lake bottom each year (meters/year)], K_d [(micrograms of stable element on sediment per gram of sediment)/(microgram of stable element in water per milliliter of water)], and porosity of the sediment.

The transfer coefficients were adjusted to account for space dependence of the radioactivity within the sediment compartment. To accomplish this, Booth

TABLE 1

ENVIRONMENTAL PARAMETERS REQUIRED TO CALCULATE TRANSFER COEFFICIENTS BETWEEN LAKE WATER, INTERSTITIAL WATER, AND SEDIMENTS

Parameter	Value
Average depth of water above the sediments, m	10
Depth of sediments, m	0.1
Sedimentation rate, m/year	5.0×10^{-4}
Porosity of sediment	0.88
Effective transfer velocity between lake water and interstitial water, m/year	0.6
Diffusion coefficient of interstitial water, m^2/year	1.1×10^{-2}
K_d value for cesium, ml/g	2.7×10^{4}
Cesium concentration in lake water, ppm	2.0×10^{-5}
Cesium concentration in sediments, ppm	6.0

et al. (1975) solved a diffusion equation with convection for the radionuclide concentration in the interstitial water as a function of depth below the bottom of the lake. The diffusion equation included interdiffusion while in solution, sorption–desorption reactions, apparent translation due to sedimentation, and radioactive decay.

The environmental parameters that characterized our hypothetical lake are given in Table 1. To facilitate comparison of the predictions of our concentration model with the data of Kolehmainen et al. (1968), we assigned a value of 0.00495 day^{-1} to R_1/Z_1; this corresponds to the 140-day half-time observed for ^{137}Cs in the water of the experimental lake. The initial condition on specific activity in the water was set equal to 1.0 μCi/g.

Single-Compartment Organisms

Theory

Radiocesium-retention experiments indicate that all organisms in the model except fishes, can be treated as single compartments. In single-compartment organisms the change in body burden, Z, of the stable element is given by

$$\dot{Z} = \alpha_i Z - \beta_i Z \tag{11}$$

where α_i is the uptake coefficient, i.e., the rate of stable-element uptake per body burden of the element, and β_i is the elimination coefficient, i.e., the rate of stable-element loss per body burden of the element. The basic principle behind

the derivation of α_{ij} is that α_i, a quantity that can be estimated by experiment, can be partitioned into values of α_{ij} by

$$\alpha_{ij} = f_{ij}\alpha_i \tag{12}$$

where f_{ij} is the proportion of total stable-element uptake of compartment i derived from compartment j. Since our model structure assumes only one source of cesium to these compartments, α_{ij} is equal to α_i.

Values for α_i were estimated from the turnover coefficients (TC) derived from studies of radionuclide retention. As indicated in Appendix A, the TC derived from analysis of time series of radionuclide content is β_i, the TC derived from analysis of time series of specific activity is α_i, and the TC derived from time series of radionuclide concentration is $\beta_i + \dot{W}/W$, where W is the weight of the organism. Since most values of TC were derived from retention patterns of ^{137}Cs content in organisms, β_i was the TC usually available. By Eq. 11

$$\alpha_i = \beta_i + \frac{\dot{Z}}{Z} \tag{13}$$

If we assume that stable cesium concentration in organisms remains constant with weight, as it does in fishes (Tong et al., 1974), then $\dot{Z}/Z = \dot{W}/W$, and Eq. 13 becomes

$$\alpha_i = \beta_i + \frac{\dot{W}}{W} \tag{14}$$

Use of a constant-coefficient model implicitly assumes that α_i is constant. If α_i is greater than β_i, Eq. 11 predicts that Z will increase exponentially. This cannot be true for the entire life-span of an organism because both rate of growth and rate of increase in Z diminish with age. If we are modeling a cohort or individual organism, Eq. 14 forces us to assume $\alpha_i \rightarrow \beta_i$ as age increases because $\dot{W}/W \rightarrow 0$ with age. Thus Eq. 7 is strictly applicable to an individual organism or cohort only over time intervals in which α_i can be treated as constant. Actually, $\dot{W}/W$ is significant relative to β_i for only young, rapidly growing organisms (Vanderploeg, 1973a; 1973b; 1975), and for mature organisms α_i can be approximated by β_i. Thus difficulties with time-varying α_i arise only when we are simulating a cohort from young to old stages. Practically speaking, however, before this becomes a significant problem, the feeding habits of the organism would probably change, necessitating a change in model structure. For all single-compartment components where the TC available was β_i, we approximated α_i by

$$\alpha_i \approx \beta_i \tag{15}$$

The β_i values vary with temperature according to Q_{10} law. The Q_{10} of β_i in arthropods (Reichle, 1968) and fishes (Kevern, Griffith, and Grizzard, 1964; Häsänen, Kolehmainen, and Miettinen, 1968; Ulrikson, Nelson, and Griffith, 1971; Kolehmainen, 1972) is about 2. For the sake of uniformity, we applied a

Q_{10} of 2.15, the Q_{10} of the long-component β_i of carp (Kevern, Griffith, and Grizzard, 1964) to single-compartment organisms and long components of fishes to convert β_i determined at various experimental temperatures to β_i at 15°C, the average temperature of the hypothetical lake. Derivation of α_{ij} for specific compartments is given in later discussion.

Coefficients for Single-Compartment Organisms

The retention pattern of ^{137}Cs concentration in phytoplankton (Williams and Pickering, 1961) is consistent with an α_i of about 1. This result is expected from the short generation time (on the order of days) of phytoplankton and the rapidity of the sorption process. The α_i of POM (derived from phytoplankton) is likewise assumed to be fast (Fig. 1).

The turnover rate of zooplankton was estimated from that of *Aedes* larvae (Guthrie and Burzynski, 1972). Note that the excretion coefficient of *Aedes* is very close to that of *Chironomus* (Fig. 2), another small insect larva.

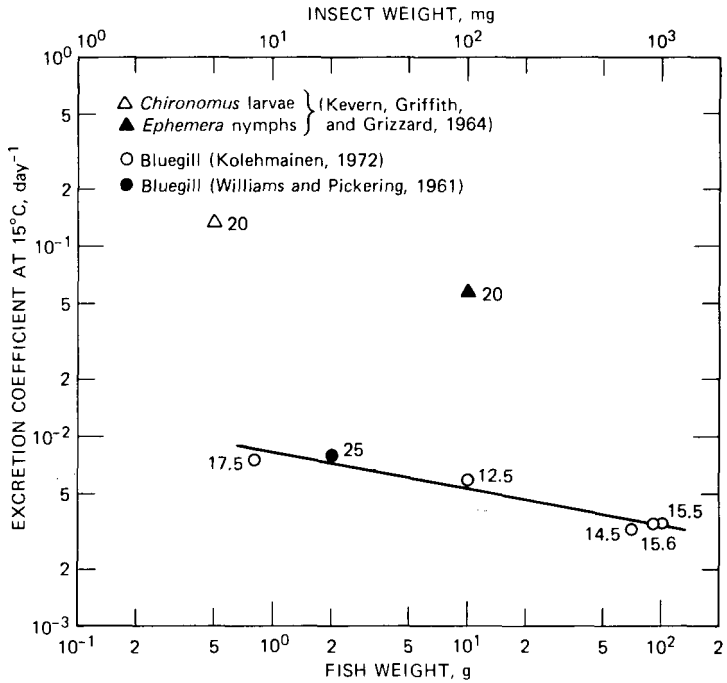

Fig. 2 Elimination coefficients of two insect larvae and the long-component elimination coefficient of bluegills as a function of weight. To convert excretion coefficients determined at the various temperatures, which are indicated next to the data points, to excretion coefficients at 15°C, we used a Q_{10} of 2.15. Bluegill data were fit by the relationship ln Y = ln a + b ln X, where a = −4.80 ± 0.0829 and b = −0.188 ± 0.0251.

The excretion coefficients of the midge larva *Chironomus* and the mayfly nymph *Ephemera* (Kevern, Griffith, and Grizzard, 1964) are plotted as a function of weight in Fig. 2. *Chironomus* and *Ephemera*, respectively, represent examples of small and large insect-larvae detritovores likely to be commonly available to fishes. An average β_i of these two detritovores was taken to characterize β_{15}.

Fishes

Theory

The treatment of cesium kinetics in fishes is different from that in the other organisms discussed because fishes must be treated as the sum of two compartments. Each fish is composed of a fast compartment (1) and a slow compartment (2), with specific activities of S_i and S_{i+10}, respectively (Fig. 1). Each fish is characterized by its α_i, $\alpha_{i,i+10}$, and $\alpha_{i+10,i}$, which we collectively call rate coefficients. The α_{ij} ($j \neq i$ or $i + 10$) is derived by partitioning α_i as

$$\alpha_{ij} = f_{ij}\,\alpha_i \qquad (\text{for } j \neq i \text{ or } i + 10) \tag{16}$$

where f_{ij} is the proportion of i (i, the fast-turnover compartment, denotes the whole fish) cesium uptake derived from j. The specific activity, $(S_i)_T$, and radionuclide concentration, $(X_i/W_i)_T$, of the whole fish are given by

$$(S_i)_T = S_i f_i + S_{i+10}\, f_{i+10} \tag{17}$$

and

$$\left(\frac{X_i}{W_i}\right)_T = B_i \frac{(S_i)_T}{S_1}\left(\frac{X_1}{W_1}\right) \tag{18}$$

where f_i and f_{i+10} are the fractions of the total mass of stable element in the fast and slow compartments, respectively, and B_i is understood to be the bioaccumulation factor of the whole fish.

Since fishes obtain nearly all their cesium from food (Kevern, 1966; Kolehmainen, 1972), α_{ij} represents uptake of cesium from food. The rate of stable-element flow, r_{ij}, into i from j is

$$r_{ij} = a_{ij}\left(\frac{Z_j}{W_j}\right)R_{ij} \tag{19}$$

where R_{ij} is the amount of j eaten by i per day (g/day) and a_{ij} is the absorption efficiency of cesium from j in i's gut. Since

$$f_{ij} = \frac{r_{ij}}{\sum_j{}' r_{ij}} \tag{20}$$

then

$$f_{ij} = \frac{a_{ij}(Z_j/W_j)R_{ij}}{\sum_j' a_{ij}(Z_j/W_j)R_{ij}} = \frac{a_{ij}B_jR_{ij}}{\sum_j' a_{ij}B_jR_{ij}} \tag{21}$$

If we assume that all the quantities $a_{ij}(Z_j/W_j)$ (or all $a_{ij}B_j$) are equal, then f_{ij} is the proportion, p_{ij}, of i's diet derived from j, i.e.,

$$f_{ij} = p_{ij} = \frac{R_{ij}}{\sum_j' R_{ij}} \tag{22}$$

Practically speaking Eq. 22 assumes that all values of B_j are equal and all values of a_{ij} are equal. To estimate the f_{ij} of fish 1 and the detritus-feeding fish, we used Eq. 22. For the piscivorous fish (fish 2), f_{ij} (i.e., $f_{13,j}$) was given by

$$f_{13,j} = p^*_{13,j}f_j \tag{23}$$

where $p^*_{13,j}$ is the proportion of fish 2's diet derived from the whole fish composed of compartments j and j + 10 and f_j is the proportion of body burden of stable cesium in compartment j of the prey fish.

In contrast to our model of the fish, the standard methodology (Kolehmainen, 1972; 1974a) treats a fish as the sum of two uncoupled compartments. Intuitively the coupled model is more reasonable than the uncoupled model. Since parameters were available for the uncoupled model only, we established relations between the coupled and uncoupled model parameters. A brief description of the uncoupled model, which is given in the following paragraph, is necessary for understanding the origin of the parameters used for the coupled model. Appendix B gives the algebraic equations that relate the parameters of the coupled to the uncoupled model.

In the uncoupled model each fish is characterized by two uptake parameters, α_i' and α_{i+10}', the uptake rates of 1 and 2, respectively. As for single-compartment organisms, α_i' and α_{i+10}' are given by

$$\alpha_i' = \beta_i + \frac{\dot{W}}{W} \tag{24}$$

$$\alpha_{i+10}' = \beta_{i+10} + \frac{\dot{W}}{W} \tag{25}$$

where β_i and β_{i+10} are the excretion coefficients of 1 and 2, respectively. Implicit in Eqs. 24 and 25 is that the specific growth rates of 1 and 2 are equal to the specific growth rate, $\dot{W}/W$, of the whole organism. Further, specific activity, $(S_i)_T'$, and radionuclide concentration, $(X_i/W_i)_T'$, are

$$(S_i)'_T = f'_i S'_i + f'_{i+10} S'_{i+10} \tag{26}$$

and

$$\left(\frac{X_i}{W_i}\right)_T = B_i \frac{(S_i)'_T}{S_1}\left(\frac{X_1}{W_1}\right) \tag{27}$$

where f'_i and f'_{i+10} are fractions of the total mass of stable element in 1 and 2, respectively, estimated according to the standard methodology from radiosium-retention patterns.

Coefficients for Fishes

The fishes chosen to populate our lake represent a broad spectrum of species, both in terms of feeding habits and rate coefficients. The weights of the fishes and the values of $\dot{W}/W$ and β_i from which the values of α'_i were derived are given in Table 2. The values of f_i, α_i, $\alpha_{i,i+10}$ and $\alpha_{i+10,i}$ were derived from the parameters in Table 2 by use of equations in Appendix B.

The rate constants were derived from studies on bluegills (*Lepomis macrochirus*) (fish 1) (Kolehmainen, 1972) and carp (*Cyprinus carpio*) (detritus-feeding fish) (Kevern, 1966) from White Oak Lake, Tennessee (Table 2). Fish 1 exhibits a high specific growth rate, and the detritus-feeding fish exhibits a moderate specific growth rate. Linear interpolation of the excretion coefficient vs. weight plot in Fig. 2 was used to estimate the excretion coefficient of fish 1, β_{22}. Fish 1's diet was presumed to be 50% zooplankton and 50% detritus-feeding invertebrates.

Fish 2 is of particular interest because it represents the top carnivore in the lake, a highly desirable game species likely to be eaten by man. Because of the practical difficulties encountered in doing radionuclide-retention experiments with large fishes, no excretion coefficients are available for fishes weighing 2 kg, the weight of fish 2. To estimate β_{23}, we extrapolated the excretion coefficient–weight relationship for bluegill shown in Fig. 2 to 2000 g. The slope (exponent) of this relation was also applied to β_{12} to estimate β_{13}. Because fish 2 was presumed to be a mature individual, $\dot{W}/W$ was set equal to zero. Fish 2's diet was presumed to be 50% fish 1 and 50% detritus-feeding fish.

SIMULATIONS AND DISCUSSION

Specific Activities in Hypothetical Lake

The time histories of specific activity in water and fishes in the hypothetical lake (Fig. 3) are contrasted with time histories that would be obtained if sediment–water interactions were not included (Fig. 4). Without the interstitial water and sediment compartments (Fig. 4), the specific activity decreases more

TABLE 2

RATE COEFFICIENTS FOR UNCOUPLED MODEL OF FISHES*

Fish	Compartment No.	Weight, g	$\dot{W}/W$, day^{-1}	β_i,† day^{-1}	f_i'	α_i', day^{-1}
Fish 1		1.0(1)	9.3(-3)‡			
1	12			9.0(-2)¶	2(-2)¶	9.1(-2)
2	22			5.3(-3)§	9.8(-1)¶	1.5(-2)
Detritus-feeding fish**		1.5(2)	2.1(-3)			
1	16			7.4(-2)	6(-2)	7.6(-2)
2	26			4.8(-3)	9.4(-1)	6.9(-3)
Fish 2		2.0(3)	0			
1	13			3.3(-2)††	2(-2)‡‡	3.3(-2)
2	23			2.0(-3)††	9.8(-1)‡‡	2.0(-3)
Perch		~ 5(1)	–			
1¶¶				5.8(-2)	2.5(-3)	5.8(-2)
2¶¶				3.5(-3)	9.97(-1)	3.5(-3)

*Numbers in parentheses are exponents of 10; e.g., 9.3(-3) is read 9.3×10^{-3}.

†To correct for temperature, we applied Q_{10} values of 2.15 and 2.0 to β_i of 1 and 2, respectively (Kevern, Griffith, and Grizzard, 1964).

‡Specific growth rate of 10-g bluegill in White Oak Lake, Tennessee (Kolehmainen and Nelson, 1969).

¶Mean of values for 0.8-g and 100-g bluegills (Kolehmainen, 1972).

§Interpolation of Fig. 2.

**Calculated from data of Kevern (1966) and Kevern, Griffith, and Grizzard (1964) for carp in White Oak Lake.

††Extrapolated from 10-g bluegill using slope of β_i–weight relation shown in Fig. 2.

‡‡Assumed same as in bluegill.

¶¶Data from Häsänen, Kolehmainen, and Miettinen (1968).

slowly than in the full model (Fig. 3), the decrease in the former being entirely due to stable cesium inflow, R_1/Z_1, to the lake. After about 600 days the specific activity in the hypothetical lake (full model) decreases more slowly than before because of feedback from interstitial water and sediment compartments. After 2000 days the full model, because of this feedback from the sediment, predicts higher specific activities in the water than does the incomplete model.

The importance of including sediment–water interactions increases as the mass of sediment relative to water increases; therefore including sediment–water interactions is more important for small shallow lakes than for large deep lakes. Sedimentation rate is another important factor.

As we expected, much higher specific activities in fishes are seen in Fig. 4, where loss of specific activity to the sediment is not included. In both Figs. 3 and 4, the specific-activity maximums of fish 1, detritus-feeding fish, and fish 2, are highest, intermediate, and lowest as well as occurring first, second, and third,

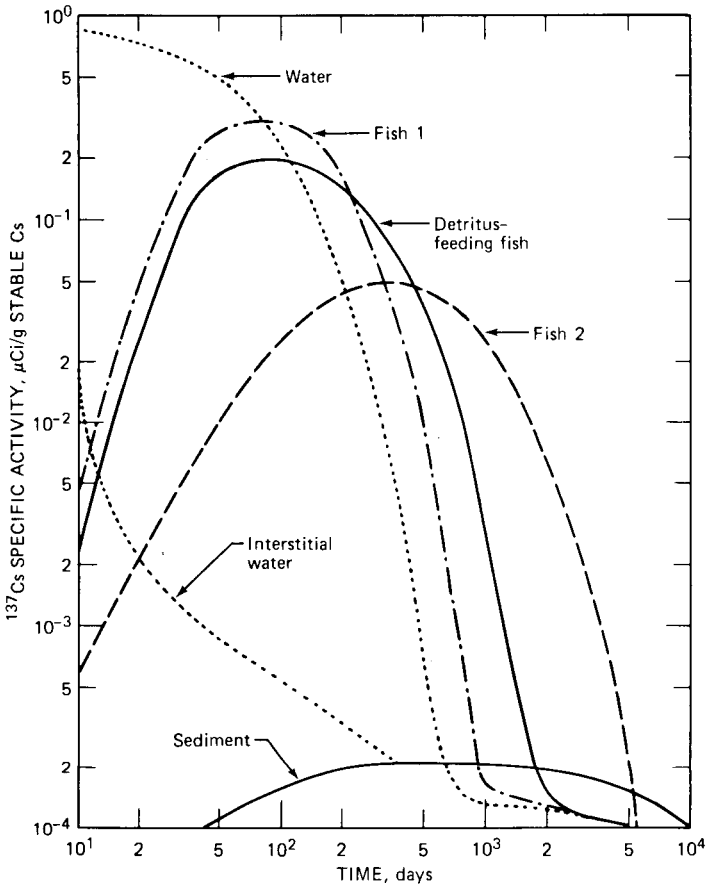

Fig. 3 Specific activity in water, interstitial water, sediment, and fishes of the hypothetical oligotrophic lake after the pulse input of ^{137}Cs. The terminal-operated computer code MODSOV (Clark, Booth, and Vanderploeg, 1974) was used for this and all other simulations.

respectively. The much lower and later specific-activity maximum of fish 2 follows from its preying on the other fishes and its very slow rate coefficients.

An important feature of a specific-activity model that can be seen in the simulations in Figs. 3 and 4 is that the specific activity of the initial condition of the water is the highest possible specific activity observed in any compartment. For radionuclides like ^{137}Cs, for which the critical pathway in aquatic systems is consumption of aquatic organisms, calculating specific activities in the various compartments would be unnecessary if the specific activity of water in the initial condition were less than that of the maximum permissible specific activity of a critical organ in man (National Academy of Sciences–National Research Council, 1962). For a constant input of the radionuclide, the maximum specific

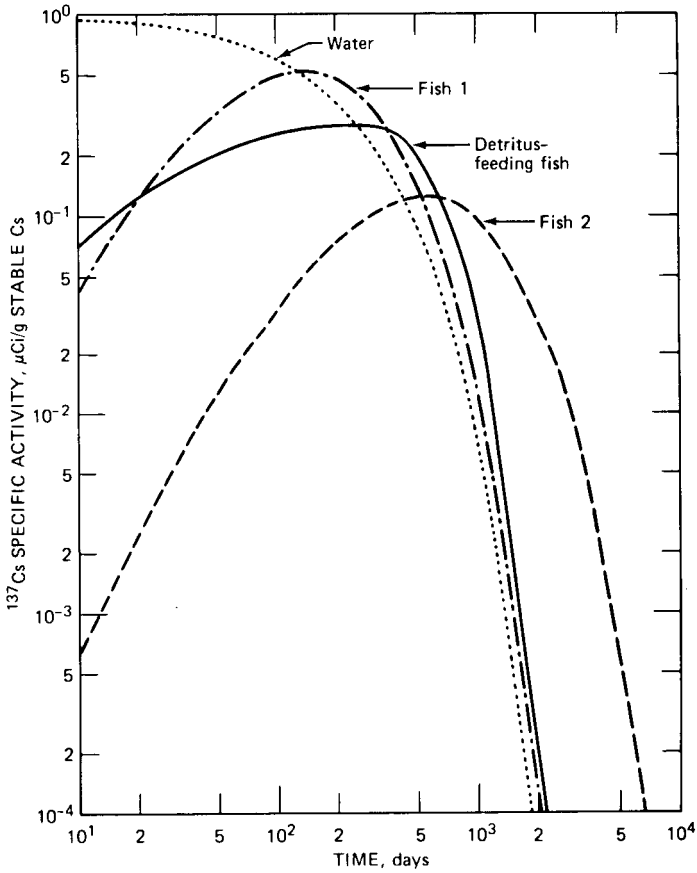

Fig. 4 Specific activity in water and fishes of the hypothetical oligotrophic lake which would result if values of α_{ij} of sediment–water interactions were set equal to zero.

activity possible in any compartment would be the specific activity of the source, i.e., K_1/R_1.

Concentrations in Experimental Lake

The turnover time of ^{137}Cs specific activity in the water predicted by the incomplete model for the hypothetical lake was chosen to be the same as that observed for ^{137}Cs concentration in the experimental lake. The incomplete model was used for these comparisons because ^{137}Cs was not concentrated to any measurable level by the sediments. Both temperatures in the hypothetical and the experimental lake were taken to be 15°C. Temperatures available for another Finnish lake (Kolehmainen, 1974b) indicate this is a reasonable approximation for the experimental period, summer through fall. Thus predicted

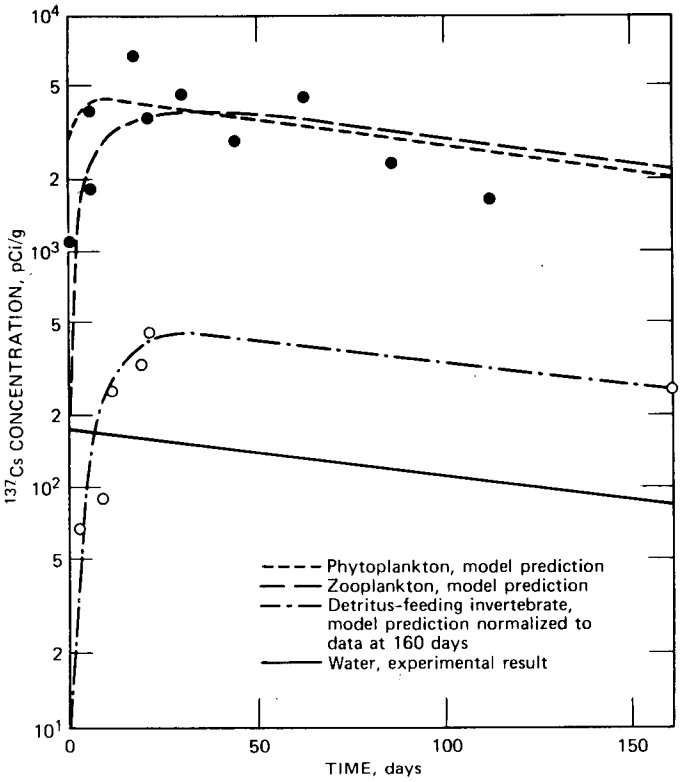

Fig. 5 Comparison of predicted ^{137}Cs concentrations in single-compartment organisms with field data of Kolehmainen et al. (1968). •, zooplankton. ○, benthic organisms, mostly *Trichoptera* larvae.

specific activities of biota for the incomplete model (Fig. 4) of the hypothetical lake were converted to predicted concentrations in the experimental lake by use of Eqs. 10, 17, and 18.

Predictions of the model for single-compartment components agree well with the corresponding field data (Fig. 5). Bioaccumulation factors for zooplankton and phytoplankton were taken from those given by Kolehmainen et al. (1968). Since concentrations of ^{137}Cs were expressed per dry weight of the organism, bioaccumulation factors expressed in terms of dry weight were used. For the detritus-feeding invertebrate, the model prediction was normalized to the last data point since no bioaccumulation factors were available. These results suggest that the values of α_{ij} of these components are correct and that the model structure is appropriate at least for the period of simulation.

To compare the predicted ^{137}Cs concentrations in the hypothetical fishes with those in perch captured in the experimental lake (Fig. 6), we selected a

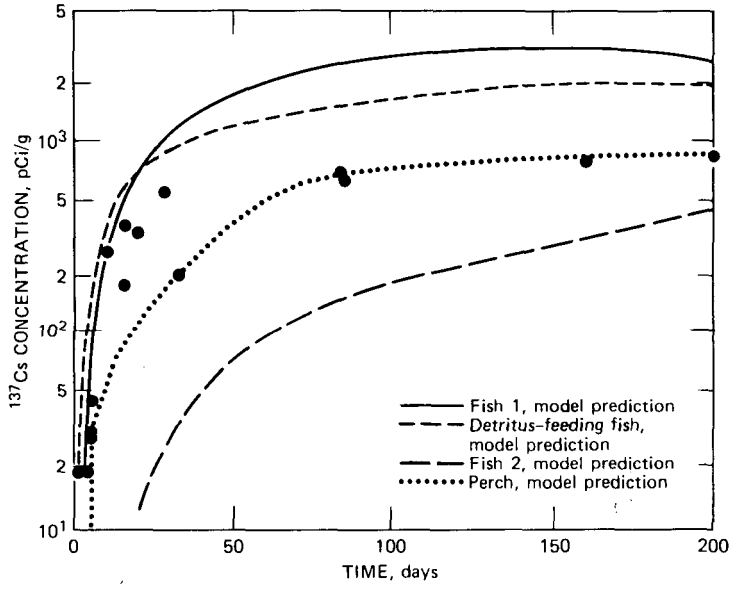

Fig. 6 Predictions of ^{137}Cs concentration in the hypothetical fishes and perch compared with the field data obtained for perch by Kolehmainen et al. (1968). To make conversions from specific activities to concentrations, use $f_{12} = 7.7 \times 10^{-2}$ $f_{13} = 7.9 \times 10^{-2}$ $f_{16} = 1.2 \times 10^{-1}$ $f_{22} = 9.2 \times 10^{-1}$ $f_{23} = 9.2 \times 10^{-1}$ $f_{26} = 8.8 \times 10^{-1}$ and f_i and f_{i+10} of perch equal to 6.3×10^{-2} and 9.4×10^{-1}, respectively.

priori a bioaccumulation factor of perch (*Perca fluviatilis*) from the review of Vanderploeg et al. (1974). The bioaccumulation factors of cesium are strongly diminished by increasing concentrations of potassium and suspended solids (Vanderploeg et al., 1974). Therefore a B_i of perch from an environment having similar concentrations of potassium and suspended solids was selected. The bioaccumulation factor used was that for perch in Lake Trawsfynydd, England (Preston, Jefferies, and Dutton, 1967); that lake has a potassium concentration of 0.36 ppm, which compares well with the 0.34-ppm concentration in the experimental lake. Concentrations of suspended solids in both lakes were presumed to be low. The value of B_i was 6000 (rounded from 5800), expressed in terms of wet weight. This was converted to a dry-weight B_i of 30,000 by multiplying 6000 by 5, the wet- to dry-weight ratio of a fish.

The predicted concentrations in the fishes (Fig. 6) form an envelope around the perch data because of the perch's feeding habits and rate coefficients. The perch, a predator of benthic invertebrates in the oligotrophic lake, has feeding habits that are, in terms of specific-activity flow, nearly equivalent to those of fish 1, a predator of zooplankton and benthic invertebrates ($\alpha_{14,1} = \alpha_{10,1}$ and $\alpha_{15,14} \approx \alpha_{11,10}$). The estimates of $\alpha_i(5.8 \times 10^{-2})$, $\alpha_{i,i+10}(5.2 \times 10^{-2})$, and

$\alpha_{i+10,i}(3.5 \times 10^{-3})$ of perch are intermediate to those for the detritus-feeding fish and fish 2 (Fig. 1). Thus the measured concentrations in perch fall within the envelope of concentrations predicted by the specific-activity kinetics of the other fishes and the perch's bioaccumulation factor.

As a further comparison, we simulated the concentrations in perch using the appropriate values of α_{ij} for its accumulation pathway:

Water → POM → detritus-feeding invertebrate → perch

simulation agrees well with the experimental results (Fig. 6), considering the rtainty of our estimate of the rate coefficients of the perch. The model may have underestimated concentrations between days 15 and 30 because the temperature of the water was probably higher than 15°C at this time (summer) and because the specific growth rate of perch may not have been zero, as we had assumed. Another source of uncertainty is the estimate of the compartment sizes and β_i of 1 and 2, which were derived from the experimental data of cesium retention in perch.

The close agreement between model predictions and ^{137}Cs concentrations in biota lends strong support to the adequacy of model structure and our estimates of biotic transfer coefficients. For this reason we will identify the more hypothetical aspects of the model that these results support. Estimates of the α_i of invertebrates—especially that of zooplankton, from data on *Aedes*—and the assumption that invertebrates obtain all their cesium from food might be criticized by some. Perhaps the most debatable assumptions are that POM can be neatly separated from the abiotic sediments beneath it and that it is the only source of cesium to the detritus-feeding invertebrates and fish. Clearly, both the detritus-feeding invertebrates and the fish may ingest some clay particles. Since fishes (Eyman and Kitchings, 1974) and presumably invertebrates can absorb cesium sorbed to ingested clays, the sediment in our model may be a source of cesium to the detritus-feeding invertebrates and fish, as well as their predators.

With regard to the invertebrates, the question of the fraction of cesium uptake from water and food is not important because of the fast uptake from either pathway. Also, accurate estimates of α_{ij} are not required because the predictions of ^{137}Cs concentrations over the time scale of interest, weeks or ths, are not very sensitive to uncertainties in the large values of α_{ij} of the le-compartment components.

The question of how to handle the sediment is more difficult. Obviously it would be naive to make the slowly responding (Figs. 1 and 3) 10-cm-deep sediment compartment the major source of cesium to the detritovores, especially in view of the excellent agreement we obtained with our model for bottom invertebrates and fishes. We note that this agreement does not preclude the possibility of superficial sediment's being an important source of ^{137}Cs to the detritovores since sorption uptake of cesium by clay is rapid.

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REFERENCES

Booth, R. S., S. V. Kaye, M. J. Kelly, and P. S. Rohwer, 1975, A Compendium of Radionuclides Found in Liquid Effluents of Nuclear Power Stations, USAEC Report ORNL-TM-3801, Oak Ridge National Laboratory.

Clark, F. H., R. S. Booth, and H. A. Vanderploeg, 1974, User's Manual for MODSOV, a Terminal Operated Program Solving the Linear Matrix Equation $\dot{x} = Ax + k$, USAEC Report ORNL-TM-4404, Oak Ridge National Laboratory.

Eyman, L. D., and J. T. Kitchings, 1974, Availability of ^{137}Cs to Fishes from Ingested Clays, in Proceedings of the XIX Congress of the International Association of Limnology, Winnipeg, Manitoba, Canada, Aug. 22-29, 1974, *Verh. Int. Verein. Limnol.*, in press.

Guthrie, J. E., and A. Z. Burzynski, 1972, Accumulation of ^{137}Cs by *Aedes aegypti* Larvae and the Effect of Potassium Concentration, *Can. Entomol.*, **104**: 411-416.

Häsänen, E., S. Kolehmainen, and J. K. Miettinen, 1968, Biological Half-Times of ^{137}Cs and ^{22}Na in Different Species of Fish and Their Temperature Dependence, in *Proceedings of the First International Congress on Radiation Protection,* W. J. Snyder (Ed.), Vol. 1, pp. 401-406, Pergamon Press, Inc., New York.

Kevern, N. R., 1966, Feeding Rate of Carp Estimated by a Radioisotopic Method, *Trans. Amer. Fish. Soc.*, **95**(4): 363-371.

——, N. A. Griffith, and T. Grizzard, 1964, Biological Half-Life of ^{134}Cs in Carp and Two Aquatic Insects, in Health Physics Division Annual Progress Report for Period Ending July 31, 1964, USAEC Report ORNL-3697, pp. 101-102, Oak Ridge National Laboratory.

Kolehmainen, S. E., 1974a, Daily Feeding Rates of Bluegill (*Lepomis macrochirus*) Determined by a Refined Radioisotopic Method, *J. Fish. Res. Board Can.*, **31**: 67-74.

——, 1974b, Puerto Rico Nuclear Center, personal communication.

——, 1972, The Balances of ^{137}Cs, Stable Cesium and Potassium of Bluegill (*Lepomis macrochirus* Raf.) and Other Fish in White Oak Lake, *Health Phys.*, **29**: 301-315.

——, and D. J. Nelson, 1969, The Balances of ^{137}Cs, Stable Cesium, and the Feeding Rates of Bluegill (*Lepomis macrochirus* Raf.) in White Oak Lake, USAEC Report ORNL-4445, Oak Ridge National Laboratory.

——, H. Romantschuk, S. Takatalo, and J. K. Miettinen, 1968, Pollution Experiments Cs-137 in Lakes of Two Limnologically Different Types, in Congrès international sur la radioprotection du milieu devant le développement des utilisations pacifiques de l'énergie nucléaire, Tulouse, Mar. 14-16, 1967, pp. 181-200, Societé Française de Radioprotection, Paris.

Lerman, A., and G. J. Brunskill, 1971, Migration of Major Constituents from Lake Sediments into Lake Water and Its Bearing on Lake Water Composition, *Limnol. Oceanogr.*, **16**(6): 880-890.

National Academy of Sciences—National Research Council, 1962, Disposal of Radioactive Waste into Pacific Coastal Waters, NAS—NRC Publication No. 985.

Preston, A., D. F. Jefferies, and J. W. R. Dutton, 1967, The Concentration of Cesium-137 and Strontium-90 in the Flesh of Brown Trout Taken from Rivers and Lakes in the British Isles Between 1961 and 1966: The Variable Determining the Concentrations and Their Use in Radiological Assessments, *Water Res.*, **1**: 475-496.

Reichle, D. E., 1968, Relation of Body Size to Food Intake, Oxygen Consumption, and Trace Element Metabolism in Forest Floor Arthropods, *Ecology*, **49**(3): 538-542.

Tong, S. S. C., W. D. Youngs, W. H. Gutemann, and D. J. Lisk, 1974, Trace Metals in Lake Cayuga Lake Trout (*Salvelinus namaycush*) in Relation to Age, *J. Fish. Res. Board Can.*, **31**: 238-239.

Ulrikson, G. U., D. J. Nelson, and N. A. Griffith, 1971, The Effect of Temperature on Elimination Rates of ^{137}Cs in Bluegill (*Lepomis macrochirus*), in Ecological Sciences Division Annual Progress Report for Period Ending July 31, 1970, USAEC Report ORNL-4634, pp. 106-107, Oak Ridge National Laboratory.

Vanderploeg, H. A., 1975, Dynamics of ^{65}Zn Specific Activity in Benthic Fishes on the Outer Continental Shelf off Central Oregon, *J. Fish. Res. Board Can.*, in preparation.

——, 1973a, Rate of Zinc Uptake by Dover Sole in the Northeast Pacific Ocean: Preliminary Model and Analysis, in *Radionuclides in Ecosystems*, Proceedings of the Third National Symposium on Radioecology, May 10-12, 1971, Oak Ridge, Tenn., D. J. Nelson (Ed.), USAEC Report CONF-710501-P2, pp. 840-848.

——, 1973b, The Dynamics of ^{65}Zn in Benthic Fishes and Their Prey off Oregon, Ph. D. Thesis, Oregon State University, Corvallis.

——, W. H. Wilcox, J. R. Kercher, D. C. Parzyck, and S. V. Kaye, 1974, Bioaccumulation Factors for Radionuclides in Freshwater Biota, USAEC Report ORNL-5002, Oak Ridge National Laboratory.

Williams, L. G., and Q. Pickering, 1961, Direct and Food-Chain Uptake of Cesium-137 and Strontium-85 in Bluegill Fingerlings, *Ecology*, **42**: 205-206.

APPENDIX A

It is not always appreciated that biological turnover coefficients (TC) derived from analysis of kinetics of radionuclide content, specific activity, and radionuclide concentration are mathematically different and often numerically different quantities. Moreover, we must realize that the turnover coefficient derived from an experiment of radionuclide uptake is the same as that derived from a study of radionuclide retention. This appendix defines precisely the turnover coefficients derived from tracer studies and relates them to α_i, the quantity used in our model.

Let us consider the differential equation for radionuclide content, X, in an organism deriving its stable element and radionuclide from a single source:

$$\dot{X} = rF - r'\left(\frac{X}{Z}\right) - X\lambda \qquad (A.1)$$

where r = uptake rate of stable element (μg/day)
F = specific activity of source (μCi/g)
r′ = loss rate of stable element (μg/day)
Z = stable-element content of organism (μg)
λ = physical decay constant of radionuclide (day^{-1})

The elimination coefficient β and the uptake coefficient α (where the subscript notation has been dropped) are

$$\beta \equiv \frac{r'}{Z} \qquad \alpha \equiv \frac{r}{Z} \tag{A.2}$$

Thus Eq. A.1 becomes

$$\dot{X} = \alpha ZF - (\beta + \lambda)\, X \tag{A.3}$$

For the classic retention experiment, the solution to Eq. A.3 is

$$X = X(0)\, e^{-(\beta+\lambda)t} \tag{A.4}$$

where X(0) is the initial condition. For the uptake experiment

$$X = \frac{\alpha FZ}{\beta + \lambda}\,(1 - e^{-(\beta+\lambda)t}) \tag{A.5}$$

where F is a constant and X(0) is 0. Thus it is obvious that the turnover coefficient determined from uptake and loss experiments of radionuclide content or from any time series of radionuclide content in an organism or cohort is β.

The equation for change in specific activity, S, in an organism obtaining the radionuclide and stable element from one source is by Eq. 7:

$$\frac{dS}{dt} = \alpha(F - S) - S\lambda \tag{A.6}$$

Obviously the TC derived from analyses of time series of S is α.

The equation for change in concentration, C, of the radionuclide may be derived as follows: Since $C \equiv X/W$, where W is weight of the organism,

$$\dot{C} = \frac{\dot{X}}{W} - \frac{X}{W^2}\dot{W} \tag{A.7}$$

From Eqs. A.3 and A.7,

$$\frac{dC}{dt} = \frac{\alpha FZ}{W} - \frac{X}{W}\left(\beta + \lambda + \frac{\dot{W}}{W}\right) \tag{A.8}$$

Thus the TC derived from time series of radionuclide concentration in an organism or cohort is $\beta + \dot{W}/W$, which equals α if stable-element concentration is constant over weight, as it is for cesium.

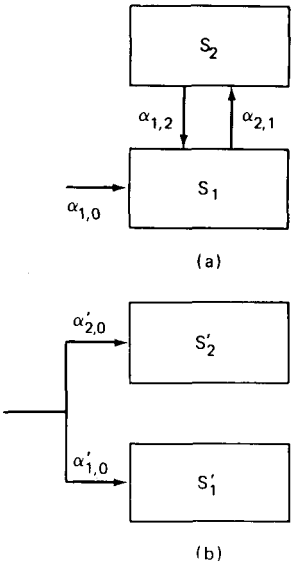

Fig. B.1 Block diagrams of the (a) coupled and (b) uncoupled models for cesium transfer through a fish.

APPENDIX B

Parameters required for our coupled model of cesium movement through fish (Fig. B.1a) were obtained from parameters determined by Kolehmainen (1972; 1974), who fit an uncoupled model (Fig. B.1b) to his measurements. We judged that both models could mimic his measurements within their statistical accuracy and that the coupled model was more realistic. This does not imply that the two models are interchangeable in general. In the derivation that follows, we will show that the two models have similar dynamic responses only for certain ranges of parameter values.

All parameters that apply to the uncoupled model, the primed symbols, were assumed known, and expressions were derived for the unprimed parameters of the coupled model. These expressions and the constraints associated with them are discussed separately for each of the three parameters required by the coupled model.

Derivation of Expressions for $\alpha_{1,0}$

We required that both models have the same total inputs and outputs:

$$\alpha'_{1,0} Z'_1 + \alpha'_{2,0} Z'_2 = \alpha_{1,0} Z_1 \tag{B.1}$$

$$\beta_1 Z'_1 + \beta_2 Z'_2 = \beta_1 Z_1 \tag{B.2}$$

where the symbols have the definitions given in the text and the known parameters of the uncoupled model are indicated by a superscript prime. Substituting the relationships $Z_i' = f_i' Z_T$ and $Z_i = f_i Z_T$ (Z_T is the total cesium content of the fish and f_i is the fractional content in compartment i) into Eqs. B.1 and B.2 and solving the resulting expressions for $\alpha_{1,0}$ and f_1 yields

$$\alpha_{1,0} = \alpha'_{1,0}\left(\frac{f_1'}{f_1}\right) + \alpha'_{2,0}\left(\frac{f_2'}{f_1}\right) \tag{B.3}$$

and

$$f_1 = f_1' + \left(\frac{\beta_2}{\beta_1}\right) f_2' \tag{B.4}$$

These two expressions define $\alpha_{1,0}$ in terms of only primed parameters.

Derivation of Expressions for $\alpha_{2,1}$

The dynamic responses of the two models will be similar only if the roots of their characteristic equations are similar. The roots of the uncoupled model are $-(\alpha'_{1,0} + \lambda)$ and $-(\alpha'_{2,0} + \lambda)$, and those of the coupled model are derived from the quadratic equation

$$(p + \alpha_{1,2} + \alpha_{1,0})(p + \alpha_{2,1}) - \alpha_{2,1}\alpha_{1,2} = 0 \tag{B.5}$$

where $p = r + \lambda$ (r represents the characteristic roots for the coupled system). If $\alpha_{1,2} \ll \alpha_{1,0}$, then

$$r_1 = -(\alpha_{2,1} + \lambda) \tag{B.6}$$

and

$$r_2 = -(\alpha_{1,0} + \lambda) \tag{B.7}$$

The characteristic roots of the two models are nearly equal if $\alpha_{2,1} \approx \alpha'_{2,0}$ and $\alpha_{1,0} \approx \alpha'_{1,0}$. The constraint $\alpha_{1,2} \ll \alpha_{1,0}$ requires that only a small fraction of the cesium uptake of compartment 1 come from compartment 2. The constraint $\alpha_{1,0} \approx \alpha'_{1,0}$ will be satisfied only if $\alpha'_{2,0} \ll \alpha'_{1,0}$ and $f_2' \approx f_2$ (see Eq. B.3, and note that $f_1' = 1 - f_2'$). Equation B.6 was used to determine $\alpha_{2,1}$ by requiring that $r_1 = -(\alpha'_{2,0} + \lambda)$. Thus

$$\alpha_{2,1} = \alpha'_{2,0} \tag{B.8}$$

Derivation of Expressions for $\alpha_{1,2}$

Conservation of cesium in compartment 2 requires that

$$\alpha_{2,1} = \alpha_{1,2}\left(\frac{Z_1}{Z_2}\right) + \frac{\dot{Z}_2}{Z_2} \tag{B.9}$$

where $\dot{Z}_2$ represents the time rate of change of cesium in compartment 2. From the definition of $\alpha_{2,1}$ we have

$$\alpha_{2,1} = \beta_2 + \frac{\dot{Z}_2}{Z_2} \tag{B.10}$$

Equating like terms in Eqs. B.9 and B.10 yields

$$\alpha_{1,2} = \beta_2\left(\frac{Z_2}{Z_1}\right) = \beta_2\left(\frac{f_2}{f_1}\right)$$

where f_1 is determined from Eq. B.4 and $f_2 = 1 - f_1$.

THE ROLE OF PHYSICAL MODELING IN MARSH-ESTUARINE MINERAL CYCLING RESEARCH

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ABSTRACT

Predictive models are needed to evaluate the impact of coastal perturbations on mineral cycling in marsh–estuarine ecosystems. Adequate mathematical models for simulating the hydraulics and mineral cycling of these systems presently are not available. Physical hydraulic models are useful for studying circulation patterns and quantifying mass flows, and physical simulations of ecosystem functions appear feasible for evaluating the impact of engineering and management alternatives on mineral cycling and for developing and verifying mathematical models. Scaled simulations are forced mechanically to create mass, momentum, and energy-transport regimes similar to those of prototype systems, with approximately real-time water residence and biochemical rates. Simulations designed to study the effects of the disposal of dredged material on cycling of heavy metals and nutrients indicate that further research is warranted.

The National Environmental Policy Act (NEPA) of 1969 requires a priori evaluation of engineering and resource management alternatives that may significantly alter the environment. Predictive models and research techniques incorporating ecosystem complexity and allowing comparison of treatment–control alternatives are essential for evaluating impacts on basic ecosystem functions. Efforts to meet the requirements of NEPA have exposed major gaps in our understanding of marsh–estuarine mineral cycling and have emphasized the need to accelerate the development of predictive research tools. This paper discusses the role of physical modeling of marsh–estuarine ecosystems as a supplement to more-traditional field, laboratory, and mathematical modeling research. More-specific objectives are (1) to point out the potentials that existing physical hydraulic models of southeastern estuaries offer in designing and interpreting field studies and in developing and verifying mathematical models

and (2) to describe the design of a physical simulation for studying mineral cycling in marsh–estuarine ecosystems.

THE NEED FOR PHYSICAL MODELING

Much of the biological and economic importance of coastal ecosystems is attributable to interactions between tidal marshes and estuaries (Shaw and Fredine, 1971; Douglas and Stroud, 1971; Gosselink, Odum, and Pope, 1973). Functional interactions, driven by hydrodynamic energy subsidies, involve material cycling and energy flow (Teal, 1962; Odum, 1971; Pomeroy et al., 1972). Choosing the appropriate area in which to evaluate ecological effects is essential in making environmental-impact assessments and formulating management strategies. Because of the mutualistic nature of marsh–estuarine interactions, both the estuary and the surrounding marsh must be considered relevant ecosystem units for evaluating impacts of most coastal alterations. Environmental perturbations to an estuary may significantly affect the ecology of the surrounding marsh, and vice versa.

Predictive models embodying the biological, chemical, and physical complexities of both tidal marsh and estuarine systems are needed to enable us to consider adequately the diversity of interactions influencing mineral cycling. Adequately verified mathematical models to fulfill this need are not presently available. A number of one- and two-dimensional hydrodynamic models for steady and unsteady flow conditions in stratified and completely mixed estuaries are available (Tracor, Inc., 1971; Huval, 1973), but specifying proper dispersion coefficients and considering partially mixed and braided channel situations remain difficult problems (Huval, 1973). Mathematical models of the hydrodynamics of tidal marshes are just beginning to be developed (Hacker, Pike, and Wilkins, 1971). Furthermore, the state of the art of mathematical modeling of biological and chemical aspects of marsh–estuarine systems can best be described as rapidly developing but in its infancy in comparison with hydraulic modeling.

Synecological field studies, supplemented by laboratory experiments to define specific processes, have provided some basic understanding of the structure and function of marsh–estuarine ecosystems. Without models that consider the diversity of system interactions, however, existing knowledge of various ecosystem processes is of limited value in evaluating the consequences of environmental alterations. Conceptualization of detailed compartment models, as a first step toward mathematical model development, has made significant contributions in organizing field and laboratory investigations and in formulating pertinent research questions. Several problems that are inherent to traditional laboratory and field studies (Beyers, 1964; McIntire, 1969; Cooper and Copeland, 1973) continue to hamper the development and verification of mathematical models and the evaluation of ecological effects of engineering

alternatives. In traditional laboratory research approaches, hydrodynamic and biological realism have often been sacrificed for experimental control and replication. Field studies traditionally have been limited by logistics; by limitations in the use of research techniques, such as radioactive tracers; by the inability to define boundary conditions; and by the inherent variability of nature. Various approaches have been used to avoid some of these problems in studying marsh–estuarine systems. Laboratory approaches include the application of chemostat methodology (Margalef, 1967) and the use of continuous-flow laboratory microecosystems (McIntire, 1969; Cooper and Copeland, 19[illegible] Some investigators have used large outdoor concrete tanks (Odum et al., 1[illegible] and ponds (Odum and Chestnut, 1970) to simulate natural systems. Short-lived radioactive tracers have been applied in the field (Reimold, 1972), and barriers have been used to partially isolate experimental areas in the field (University of Georgia, 1971).

Relatively large physical simulations of the hydrodynamic and ecological aspects of marsh–estuarine systems have significant potential as much-needed linkage between mathematical modeling and more-traditional laboratory and field studies of mineral cycling. Physical hydraulic models have played a significant role in developing and verifying mathematical models of estuarine hydrodynamics, and use of these models is presently the only practical technique for three-dimensional studies of estuarine hydrodynamics (Herrmann, 1973). Development and application of physical simulations to ecological problems have lagged far behind their application to hydraulic problems, despite the fact that both techniques were introduced in the mid-1800s (Beyers, 1964; Harleman, 1971).

The potential usefulness of physical simulations in ecological research has been demonstrated by Odum et al. (1963), Beyers (1964), McIntire (1969), Cooper and Copeland (1973), and others. A variety of simulation techniques, ranging from gnotobiotic cultures (Taub, 1969) to transplanted portions of natural systems (Copeland and Wohlschlag, 1968), has been used with varying success. Most of these simulations are limited to consideration of a specific portion of an ecosystem, however. Only a few have been designed to consider one-dimensional spatial gradients (Cooper and Copeland, 1973; Falco and Sanders, 1973). Two-dimensional spatial gradients and interactions among adjoining ecosystems have been simulated less frequently (Keeley, 1971). A major weakness of most microecosystem studies has been lack of adequate simulation of physical phenomena, such as turbulence, residence time, area-to-volume and depth-to-volume ratios, and density gradients.

PHYSICAL HYDRAULIC MODELS

Physical hydraulic models constructed for engineering purposes, e.g., navigation and coastal construction projects, can provide significant assistance in

mineral-cycling research. Phenomena that can be simulated with varying resolution in hydraulic models include tides, tidal currents, density currents, littoral currents, currents generated by river flows, salinity distributions, heat dispersion, shoaling, hurricane surges, tsunami surges, and the effects of wave and ship action on sediment resuspension (Herrmann, 1973).

Reproduction of hydrodynamic phenomena in a physically scaled model is based on the theory of similitude. Conditions necessary to achieve similarity between model and prototype usually are developed by concepts of dimensional sis (Harleman, 1971). A series of dimensionless numbers for relationships o mportance are calculated from prototype data. Hydraulic similitude is achieved by designing and adjusting the geometry, surface roughness, and inflow–outflow of the scaled model so that model and prototype have similar dimensionless numbers. Some similarity usually is sacrificed because of the need to distort model geometry in the vertical scale.

The boundaries and scales of most existing hydraulic models make them more useful as aids for studying mass flows within main channels of estuaries and between estuaries and the ocean than for studying marsh–estuarine interactions. Models could be constructed specifically for the latter purpose, but it would be too expensive to obtain sufficiently detailed similarity of flows through marsh grasses, braided channels, and potholes to be of significant value. When physical hydraulic models are available, however, their benefits to estuarine mineral-cycling research easily justify operating costs.

Physical hydraulic models of southeastern estuaries that are operational or are under construction at the Waterways Experiment Station include Mobile Bay, Savannah River, Charleston Harbor, Georgetown Harbor, Masonboro Inlet, St. Johns River, Beaufort Inlet, Orgeon Inlet, Murrells Inlet, and Little River Inlet. These models can be used in mineral-cycling studies to aid in designing and interpreting field studies, provide hydraulic flow data for calculating mass balances, and provide an understanding of water circulation patterns needed in mathematical modeling.

PHYSICAL SIMULATION OF MARSH–ESTUARINE MINERAL CYCLING

gn Concepts

Concepts for designing physical simulations to study ecosystem functions are significantly different from concepts of physical hydraulic modeling. The objective of ecosystem simulations is to provide a suitably controlled physical environment so that biological and chemical processes can interact similarly to those occurring in natural systems. In hydraulic modeling, where hydrodynamic similitude is the design objective, water residence times are speeded up inversely with model size. For example, in a typical scaled model of an estuary, a tidal cycle may be simulated every 15 min. Obviously biological interactions and

some chemical reactions cannot keep up with hydraulic model time, and physical simulations probably will remain restricted essentially to real time.

Since organisms cannot be scaled, the usefulness of physical ecosystem simulations is restricted to processes dominated by organisms whose functions are not significantly affected by behavioral responses to spatial boundaries. Although areas and volumes are scaled, physical simulations seem to be valid for studying ecosystem functions that are dominated by small or relatively immobile organisms, as long as their densities remain similar in both model and prototype. These restrictions prevent realistic consideration of many organisms occu higher trophic levels. It seems feasible to simulate their function, howeve controlled harvesting and subsequent detrital input to maintain balanced populations at lower trophic levels.

Design criteria for physical simulations of a variety of ecosystems are being evaluated at the Waterways Experiment Station for use by the Corps of Engineers in developing mathematical models and for evaluating effects of engineering alternatives on ecosystem functions. General concepts for model design are:

1. Compartmentalize the prototype system on the basis of field data to obtain the desired degree of resolution of spatial gradients.

2. Scale surface areas and volumes of each compartment proportionally to a feasible experimental unit size, maintaining real depths whenever possible.

3. Transplant appropriate materials from the prototype system into scaled containers housed in environmental chambers or greenhouses.

4. Connect compartments by tubes and force simulations mechanically to create mass, momentum, and energy-transport regimes similar to those of the prototype system; this is done by use of a combination of pumps, stirrers, and heat exchangers.

5. Allow biological and chemical processes to occur at essentially real-time rates by mechanically adjusting flow through and mixing to maintain natural water residence times and turbulence levels within compartments.

6. Maintain a dynamic system by providing proportionally scaled inputs and losses appropriate for the system.

In this paper, we describe attempts to design a simulator suitable for studying mineral cycling between a shallow estuary and the surrounding marsh. The simulator was designed for use in treatment–control experimen study differences between nutrient and heavy-metal cycling in natural marsh–estuarine ecosystems and those in ecosystems artificially created with dredged material.

Materials and Methods

The design was based on results of a pilot simulation of a prototype system in Barataria Bay, Louisiana. Data for the Barataria Bay ecosystem were obtained

from Ho (1971), Stowe et al. (1971), Perret et al. (1971), Hacker, Pike, and Wilkins (1971), and Brannon (1973).

The experiment consisted in transplanting salt-marsh substrate with grass, estuarine sediment, and water from the Barataria ecosystem into Plexiglas tanks housed in an environmental chamber. The chamber was equipped with fluorescent lights providing an average light intensity of 17,000 lux at a distance of 46 cm from the light source for a 12-hr photoperiod. Relative humidity was maintained at 60 ± 10% over a temperature range of 20 to 25°C. Three tanks connected in series were used to simulate estuarine, streamside, and salt-marsh portions of the Barataria ecosystem (Fig. 1).

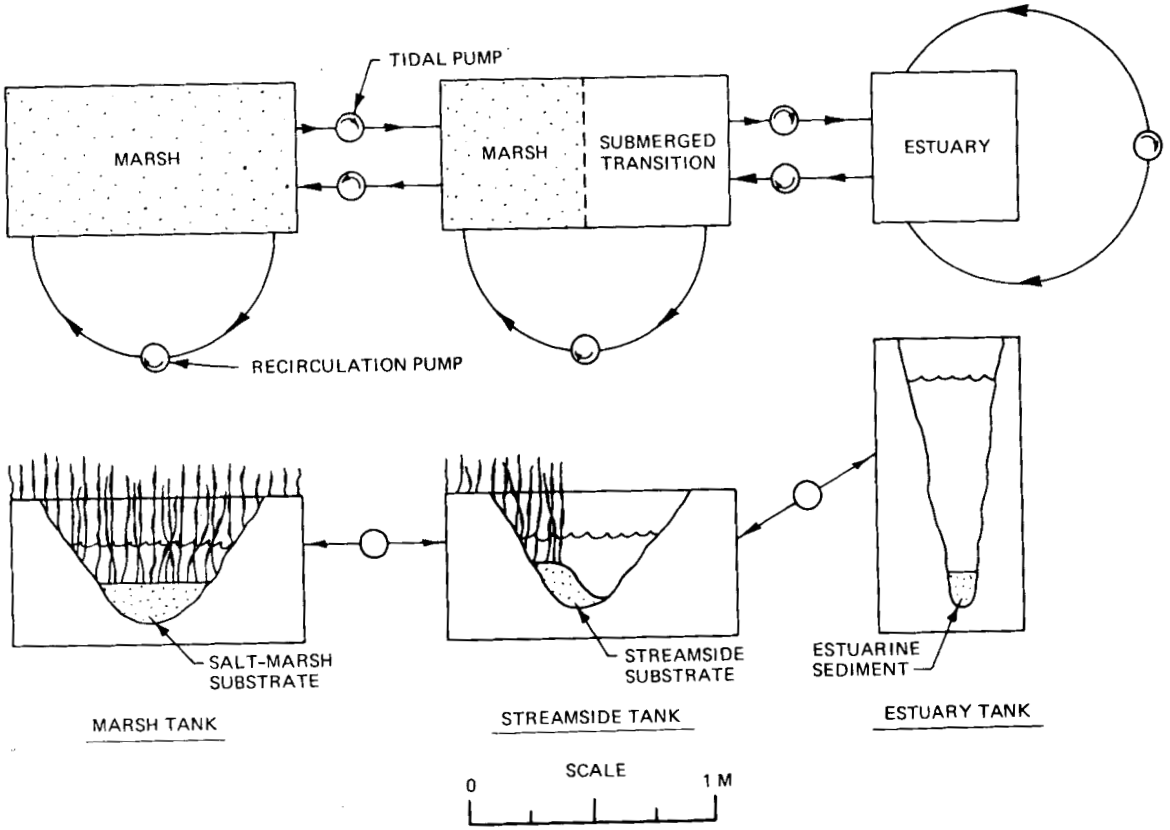
About 350 liters of flood-tide water were distributed in marsh, streamside, and estuarine tanks in quantities to simulate average depth characteristics of the Barataria Bay system. Tidal cycles among tanks and circulation within tanks were achieved by use of plastic tubing and peristaltic pumps operated by timers. A 12-hr flood tide and 12-hr ebb tide, with a tidal amplitude on the marsh of about 10 cm, were maintained. Internal circulation provided an average horizontal planar velocity within tanks of about 2.4 cm/sec.

The simulation was operated as a closed system except that distilled water was sprinkled over the salt marsh to make up for evaporation and to wash salt residues from the grass. In the natural system there are freshwater inflows and exchanges between the estuary and the Gulf of Mexico, but these fluxes were not simulated in the pilot experiment. Also, no provision was made for allowing marsh substrate to drain to the mean low water table during ebb tide.

The simulation was established in October 1973 and operated continuously for 7 months. The flora and fauna were observed, and water temperature, dissolved oxygen, pH, salinity, and water currents were measured periodically throughout the experiment. A 48-hr intensive sampling of the simulation was conducted in March 1974 to measure diel and tidal cycles of carbon, nitrogen, and phosphorus and community metabolism. Chemical analyses were conducted according to methods recommended by the U. S. Environmental Protection Agency (1971). Community metabolism was estimated by the diurnal oxygen curve method of Odum and Hoskin (1958). Atmospheric reaeration coefficients were estimated by sparging circulating tanks of water with argon to remove dissolved oxygen and measuring the rate of dissolved oxygen recovery. Redox potential (Eh) profiles were measured with platinum electrodes.

Results and Discussion

A representative fauna and flora of the Barataria Bay ecosystem existed in the pilot simulation. At least 8 genera of algae and 30 genera of animals representing major phyla from Protozoa to Chordata were maintained in the simulation; these included snails, crabs, shrimp, small fin fishes, and marsh-grass insects. The marsh was dominated by *Spartina alterniflora* with some *Distichlis spicata.*



Fi[illegible] Experimental units used to simulate salt-marsh, streamside, and estuarine po[illegible]s of the Ba[illegible]a Bay ecosy[illegible] Louisiana.

Although marsh grasses in the field had begun to die in October when materials were collected, in the environmental chamber the grass remained green and numerous new shoots appeared through December. Almost all mature grass died during January and February, and only a few new shoots had appeared when the experiment was terminated in April. The normal cycle of the marsh grass may have been modified by warmer temperatures and lower light intensities in the chamber. A large insect population, consisting primarily of aphids and leafhoppers, which developed on the marsh grass in December and January, possibly could have promoted die-off. When the experiment was terminated, we observed that grass roots were extremely pot-bound. A substrate depth of about 30 cm was used in the marsh tanks, and recent studies have shown that some marsh grasses have active root penetration to a depth of at least 55 cm in some substrates. Thus pot-bound roots, combined with the fact that no provision was made for substrate drainage during ebb tide, may have contributed to die-off.

During February and March, mats of benthic algae developed along the edge of the marsh and on the sediment in the streamside tank. Filamentous algae developed along the walls of the estuary tank. Algal growths in the streamside tank were typical of those found in similar Barataria Bay habitats. No attempt was made to control the growth of filamentous algae on the estuary tank walls during the experiment.

Sediment Eh profiles were similar to those measured by Brannon (1973) in Barataria Bay (Table 1). Concentrations of all aqueous chemical constituents were highest in the marsh and lowest in the estuary tank (Table 1). This indicates a net transport of all nutrients from the marsh to the estuary. Ammonia nitrogen declined from a high concentration in the marsh to below the level of detection in the estuary tank, suggesting that the system was nitrogen-limited, as would be expected from other studies (Teal and Valiela, 1973).

Data taken at 2- to 4-hr intervals for a 48-hr period indicate that fluxes of several chemical parameters were influenced by diel and tidal cycles. Typical diurnal variations in dissolved oxygen and metabolism were observed (Fig. 2). Metabolic data available for the Barataria estuary (Table 1) are not comparable with simulation data because the light–dark bottle method used by Stowe et al. (1971) did not measure benthic metabolism. Metabolic values for the simulation were within the range of values reported for coastal ecosystems by Odum et al. (1963), Copeland and Wohlschlag (1968), Cooper and Copeland (1973), and Pomeroy et al. (1972).

From the results of this experiment, we found that desirable modifications and additions to the design of a marsh–estuarine simulator are:

1. Increase the depth of marsh substrate used in simulations to exceed the depth of grass root penetration to prevent pot-bound distortions.

TABLE 1

COMPARISON OF ELECTROCHEMICAL AND METABOLIC DATA FROM THE BARATARIA BAY SALT MARSH–ESTUARY WITH A SIX-MONTH-OLD LABORATORY SIMULATION OF THE ECOSYSTEM

Parameter	Estuary tank*	Streamside tank*	Marsh tank*	Barataria estuary	Barataria streamside	Barataria marsh
Sediment Eh, mV						
0 cm	+35	−30	+155			
1 cm	−35	−45	+100		−150 to +90†	−400 to +80†
5 cm	−105	−140	−140		−250 to +50†	−225 to +50†
10 cm	−140	−145	−175		−280 to −40†	−350 to −100†
TKN, μg/liter	106	157	210			
NH_3–N, μg/liter	<10	11	184	30‡		
NO_3–N, μg/liter	<10	<10	<10	<10‡		
PO_4–P, μg/liter	9	9	21	10‡		
Total P, μg/liter	28	42	56	110‡		
Total organic C, mg/liter	15.0	16.6	17.8			
Dissolved organic C, mg/liter	14.9	15.9	16.8			
Gross primary productivity, g O_2 m^{-2} day^{-1}	3.5§	5.4§			2.2¶	1.4¶
Total community respiration, g O_2 m^{-2} day^{-1}	3.1§	8.2§				

*Averages based on sampling at 2- to 4-hr intervals for 48 hr, Apr. 10-11, 1974.

†Ranges for 1972 from Brannon (1973).

‡Data for April 1969 (nitrogen) and April 1970 (phosphorus) from Ho (1971).

§Metabolic values for submerged community only.

¶Calculated from light–dark bottle data for epiphytic and phytoplankton communities, June to October 1970 (Sto[illegible]l., 1971).

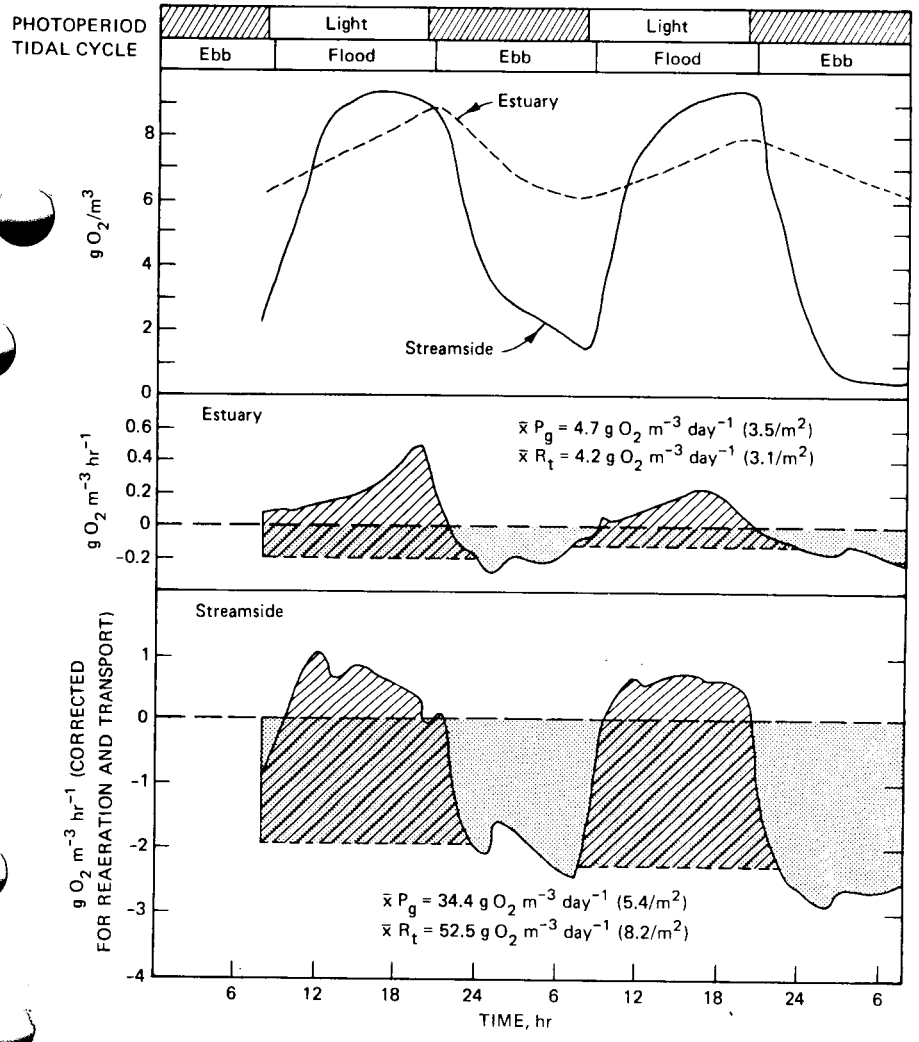


Fig. 2 Diurnal variations in dissolved oxygen and metabolism in simulations of Barataria estuary and streamside ecosystems. P_g is gross primary productivity, and R_t is total community respiration.

2. Install a drainage system in the bottom of marsh tanks; this could be a perforated plastic pipe covered by washed sand sized to promote substrate drainage during ebb tide. The outlet of the drainage system could be connected to a flexible pipe whose height can be adjusted to control the elevation of the low water table.

3. Use multiple marsh tanks connected in series by tubes, valves, pumps, and timers to control residence time of tidal flows within each tank, and sequence the flooding and draining to simulate spatial gradients in the natural marsh.

4. Use a spray-bar distribution system constructed of perforated pipe and connected to intakes and discharges of internal circulation pumps to achieve a more uniform spatial distribution of water velocities.

5. Scrape sides of estuarine tank walls and exchange and clean circulation systems frequently to prevent accumulation of attached biological growths.

6. Simulate exchange rates between estuary and ocean by scaled withdrawals and additions to the estuarine tank using flood-tide water collected from the field or artificial media prepared with commercial ocean salts.

We conclude that physical simulations such as the one described here offer significant potential in assessing the effects of many coastal perturbations on marsh–estuarine mineral cycling. Furthermore, physical simulations of marsh–estuarine ecosystems and physical hydraulic models offer significant potential for supplementing more-traditional field and laboratory studies in environmental-impact assessment and mathematical model development.

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REFERENCES

Beyers, R. J., 1964, The Microcosm Approach to Ecosystem Biology, *Amer. Biol. Teacher*, **26**(7): 449-498.

Brannon, J. M., 1973, Seasonal Variation of Nutrients and Physicochemical Properties in the Salt Marsh Soils of Barataria Bay, Louisiana, M.S. Thesis, Louisiana State University, Baton Rouge.

Cooper, D. C., and B. J. Copeland, 1973, Responses of Continuous-Series Estuarine Microecosystems to Point-Source Input Variations, *Ecol. Monogr.*, **43**: 213-236.

Copeland, B. J., and D. E. Wohlschlag, 1968, Biological Responses to Nutrients–Eutrophication: Saline Water Considerations, in *Advances in Water Quality Improvement*, Water Resources Symposium, No. 1, 1967, E. F. Gloyna and W. W. Eckenfelder (Eds.), pp. 65-82, University of Texas Press, Austin.

Douglas, P. A., and R. H. Stroud, 1971, *A Symposium on the Biological Significance of Estuaries,* Sport Fishing Institute, Washington, D. C.

Falco, J. W., and W. M. Sanders III, 1973, A Physical Model for Simulation of Aquatic Ecosystems, in *Modeling the Eutrophication Process,* E. J. Middlebrooks, D. H. Falkenborg, and T. E. Maloney (Eds.), Workshop Proceedings, Logan, Utah, U. S. Environmental Protection Agency, PRWG136-1.

Gosselink, J. G., E. P. Odum, and R. M. Pope, 1973, The Value of the Tidal Marsh, Work Paper No. 3, Urban and Regional Development Center, University of Florida, Gainesville.

Hacker, S., R. W. Pike, and B. Wilkins, Jr., 1971, *Analysis of the Energy, Mass, and Momentum Transfer in the Louisiana Coastal Marsh Region,* Coastal Studies Bulletin No. 6, pp. 109-153, Louisiana State University, Baton Rouge.

Harleman, D. R. F., 1971, Physical Hydraulic Models, in *Estuarine Modeling: An Assessment,* Water Pollution Control Research Series, U. S. Environmental Protection Agency Project No. 16070 DZV, pp. 215-263, Superintendent of Documents, U. S. Government Printing Office, Washington, D. C.

Herrmann, F. A., Jr., 1973, Physical Models of Estuaries, in *Estuarine Processes Short Course Manual,* U. S. Army Engineer Waterways Experiment Station, Vicksburg, Miss.

Ho, C., 1971, *Seasonal Changes in Sediment and Water Chemistry in Barataria Bay,* Coastal Studies Bulletin No. 6, pp. 67-84, Louisiana State University, Baton Rouge.

Huval, C. J., 1973, Mathematical Modeling for Estuarine Hydrodynamic and Transport Phenomena, in *Estuarine Processes Short Course Manual,* U. S. Army Engineer Waterways Experiment Station, Vicksburg, Miss.

Keeley, J. W., 1971, A Feasibility Study of a Laboratory Model as a Research Tool for Impoundment Water Quality Investigations, Ph. D. Thesis, University of Oklahoma, Norman.

Margalef, R., 1967, Laboratory Analyses of Estuarine Plankton Systems, in *Estuaries,* G. H. Lauff (Ed.), pp. 515-524, American Association for the Advancement of Science, Washington, D. C.

McIntire, C. D., 1969, A Laboratory Approach to the Study of the Physiological Ecology of Benthic Algal Communities, in *Proceedings of the Eutrophication–Biostimulation Assessment Workshop,* E. J. Middlebrooks, T. E. Maloney, C. F. Powers, and L. M. Koack (Eds.), pp. 146-157, U. S. Environmental Protection Agency.

Odum, E. P., 1971, *Fundamentals of Ecology,* 3rd ed., W. B. Saunders Company, Philadelphia.

Odum, H. T., and A. Z. Chestnut, 1970, *Studies of Marine Estuarine Ecosystems Developing with Treated Sewage Wastes,* North Carolina State University, Annual Report 1969-1970, Sea Grant Publication No. GS-18.

——, and C. M. Hoskin, 1958, *Comparative Studies on the Metabolism of Marine Waters,* Institute of Marine Science Publication No. 5, pp. 16-46, University of Texas, Austin.

——, W. L. Siler, R. J. Beyers, and N. Armstrong, 1963, *Experiments with Engineering of Marine Ecosystems,* Institute of Marine Science Publication No. 9, pp. 373-403, University of Texas, Austin.

Perret, W. S., et al., 1971, *Cooperative Gulf of Mexico Estuarine Inventory and Study, Louisiana, Phases I-IV,* Louisiana Wildlife and Fisheries Commission, New Orleans.

Pomeroy, L. R., L. R. Shenton, R. D. H. Jones, and R. J. Reimold, 1972, Nutrient Flux in Estuaries, in *Nutrients and Eutrophication,* Special Symposium, Vol. 1, pp. 274-291, American Society of Limnology and Oceanography.

Reimold, R. J., 1972, The Movement of Phosphorus Through the Salt Marsh Cord Grass, *Spartina alterniflora* Loisel, *Limnol. Oceanogr.,* **17**(4): 606-611.

Shaw, S. P., and C. G. Fredine, 1971, *Wetlands of the United States: Their Extent and Their Value to Waterfowl and Other Wildlife,* U. S. Fish and Wildlife Service, Circular 39.

Stowe, W., C. Kirby, S. Brkich, and J. G. Gosselink, 1971, *Primary Production in a Small Saline Lake in Barataria Bay, Louisiana,* Coastal Studies Bulletin No. 6, pp. 27-37, Louisiana State University, Baton Rouge.

Taub, F. B., 1969, A Biological Model of a Freshwater Community: A Gnotobiotic System, *Limnol. Oceanogr.,* **14**: 136-142.

Teal, J. M., 1962, Energy Flow in the Salt Marsh Ecosystem of Georgia, *Ecology,* **43**(4): 614-624.

——, and I. Valiela, 1973, The Salt Marsh as a Living Filter, *J. Marine Tech. Soc.,* **7**(8): 19-21.

Tracor, Inc., 1971, *Estuarine Modeling: An Assessment,* Water Pollution Control Research Series, U. S. Environmental Protection Agency Project No. 16070 DZV, Superintendent of Documents, U. S. Government Printing Office, Washington, D. C.

U. S. Environmental Protection Agency, 1971, *Methods for Chemical Analysis of Water and Wastes,* Water Pollution Control Research Series, U. S. Environmental Protection Agency Project No. 16020, Superintendent of Documents, U. S. Government Printing Office, Washington, D. C.

University of Georgia, 1971, Flux of Radionuclides Through a Salt Marsh Ecosystem, Progress Report, Jan. 1, 1971, to Dec. 30, 1971, USAEC Report SR-639-11.

SYSTEMS MODELS FOR PHOSPHORUS MANAGEMENT IN FLORDIA

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ABSTRACT

Systems models of phosphorus flux were developed for the state of Florida and for the Peace River Estuary. The percent effect on the overall geochemical cycle of the present phosphorus flows in peninsular Florida was determined by evaluating an overall phosphorus-budget model for Florida. Through mining, Florida is draining its phosphorus supply 125 times as fast as it is replaced. Phosphorus mobilized by mining was three orders of magnitude higher than the phosphorus cycling through Florida's waterways, and 50% of the total input of phosphorus to inland waters was from man's activities, including sewage effluent (6%), agricultural runoff (34%), urban runoff (3%), and mining effluent (7%). Digital computer simulation of the phosphorus flux in the Peace River Estuary showed the relative importance of projected changes in mining and population. Total phosphorus (all forms) in the system was high, ranging from 0.3 to 1.0 mg/liter. Simulations indicated that daily mining-water discharges had little effect on total phosphorus concentrations and that the periodic spills from slime ponds in the mining district, caused by tidal turbulence reworking the settled slime, elevated phosphorus levels for many years. Analog computer simulations of a productivity model for the Peace River mouth indicated that high phosphorus levels keep nitrogen levels low (less than 0.1 mg/liter), and this limits productivity.

Phosphorus moves through the land, air, and sea, concentrating in some rock deposits, e.g., the phosphate deposits of Florida. The natural cycles of phosphorus have been much changed by the activities of man in mining, applying fertilizer, and releasing wastes. Recently Stumm (1972) presented a global phosphorus circulation model that indicated the abundance of phosphorus in terrestrial and marine plants, in soils, sediment and water, and in the

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earth's crust. From examination of transfer rates, he concluded that man, through mining, is restoring marine phosphorus to the land at higher rates than it washes to the sea, causing pollution in inland and coastal waters.

Phosphorus is one of the major nutrient elements affecting eutrophication in lakes, rivers, and estuaries and is a critical factor in the agricultural and industrial economics of Florida. An understanding of the phosphorus cycle is required in making any sensible plans for resource management and pollution control. Florida offers a unique opportunity to examine the phosphorus cycle since we find here examples of the benefits and the problems associated with man's use of phosphorus. What are the effects of man's activities on the state's original phosphorus cycle? What happens under intensive agriculture and population growth?

Two systems in Florida were selected and defined for modeling, calculations, and simulation. The first systems model examines phosphorus flux in peninsular Florida, quantifying the rates of flow and present storages so that flows can be examined in terms of their percent effect on the overall geochemical cycle. The second examines phosphorus-flux and nutrient-productivity relationships in the Peace River–Charlotte Harbor estuarine complex, which drains Florida's phosphate mining district. Phosphorus enrichment of this river–estuarine complex is a result of the natural rich geochemical cycle of phosphorus in the area and of the urban expansion of man. Regulation of waste discharge in the Peace River Basin requires understanding of the present state of phosphorus and factors affecting its flows. The effect of population growth and the alternatives of water and waste management are tested with calculations and simulations.

STUDY AREAS

Peninsular Florida

Florida produces three-fourths of the nation's and one-third of the world's marketable phosphate rock (Florida Phosphate Council, 1973). A sophisticated agricultural system using superphosphate fertilizer exists in the state. Florida's highly urbanized areas have the usual associated nutrient waste-disposal problems, and its many lakes and estuaries, acting as the nutrient traps, are subject to enrichment and associated depleted oxygen supplies.

The Environmental Protection Agency and Florida's State Pollution Control Board are currently attempting to fix waste-water effluent standards for phosphorus. For example, the Wilson–Grizzle Bill passed in the Florida state legislative session of 1972 requires the city of Tampa to use advanced waste-treatment processes for phosphorus removal to 1 mg of phosphorus per liter of water. Although higher standards for phosphorus control in domestic waste-water and mining waste-water effluent are being met, Florida's population continues to grow exponentially; so the net gain in water quality may be

negligible. To evaluate this, we must calculate a percent effect for specific water bodies.

The facts indicate that setting effluent standards based on concentrations may be less useful than setting limits on percent effects on existing flows. The approach demonstrated here for evaluating phosphorus cycling in Florida allows the percent effect of each flux on the overall chemical cycle to be determined. The systems model, which defines peninsular Florida by the Suwannee River on the northwest and by state boundaries elsewhere, shows the magnitude of the outside sources of phosphorus to the state, of the storages and recycling pathways within the state, and of the phosphorus losses from the state.

Peace River Estuary

Since the Peace River district, which is uniquely rich in phosphorus, is the projected site of the largest future population growth in Florida, management of phosphorus wastes becomes an important part of the total ecological engineering concerns of this area. The Peace River begins 1 mile east of Bartow and extends 98 miles southward, emptying into Charlotte Harbor at the town of Punta Gorda. Average depth of the river is 0.9 to 2.4 m, with a maximum depth at Arcadia of 6.1 m (Lanquist, 1953). The width of the river varies from 18.3 to 61 m. Charlotte Harbor is one of the largest and least contaminated (Alberts et al., 1970) estuarine complexes in Florida. Its geochemistry has been examined by Alberts et al. (1970). Water temperature in August averages 30°C, in December 16°C, and in March 19°C. The salinity structure is one of decreasing salinity from Boca Grande Pass, where it meets the Gulf of Mexico, to Punta Gorda at the Peace River mouth. Just inside Boca Grande Pass at high tide, the salinity was 30 ppt and at low tide 15 ppt. At Punta Gorda at high tide, the salinity was 12 ppt and at low tide 1 ppt.

Sewage from 200,000 people is presently discharged into the Peace River. The phosphate-mining industry in Polk County exerts the greatest influence on the entire Peace River–Charlotte Harbor system. Commercial-grade phosphate rock occurs as pebble-size nodules (> 1 mm) in a fine clay. Obtaining the high-grade rock involves strip-mining and slurrying the phosphate-rich material into a pit by hydraulic guns. This slurry of phosphate, quartz, and clay is pumped to washer and flotation plants, where useable phosphate pebbles are separated from a clay slime. The slime, which is stored in settling ponds, is 9 to 16% solids by weight and takes as long as 30 years to settle (Specht, 1950). Since the major constituents of the slime wastes are clay minerals whose retention of water increases their volume 6 to 10 times, the volume of wastes exceeds the original volume of rock removed by 1.25 to 1.5 times. As a result, all the waste will not fit into the mined-out pits, and diking above grade is required. This is hazardous because of potential spillage, and, in fact, dozens of slime spills have occurred in the past 25 years (Dequine, 1974). Major slime spills containing 7540 ppm of phosphorus kill river fish and cause heavy mortality of

the benthic invertebrates. The short- and long-range effects of this large phosphorus release are examined here with simulations.

METHODS

From a review of the literature and from conferences with many individuals concerned with the problem, we developed preliminary models using the energy-circuit language developed by H. T. Odum (1971, 1972). Figure 1 [illegible] summary of the symbols used. The energy-circuit language is an easy way [illegible] portray complex relationships in a readily visualized unity. Differential equations are a precise translation of the language. The energy diagram includes mass–balance relationships and the driving functions, multiplier effects, and other energy-driven controlling processes affecting the mass flows. Energy diagrams keep track of the potential energy inflows and often reveal hidden driving forces. The circle represents a source; the tank symbol is a passive energy-storage module; and the pathways are flows of energy from sources and storages to other compartments. These energy transfers are always accompanied by a loss that flows through the heat-sink symbol, representing ultimate energy dispersal. All the symbols used have mathematical properties that, when combined in a system diagram, can be written as a set of equations.

The model-building process led to the identification of major pathways and state variables. Numerical data on magnitudes were obtained from the literature. When observed data from the area were unavailable, numbers for the same process in a similar area were used. Missing values in some instances were calculated by difference, as if the system were in steady state, assuming only conservation of water mass. The numbers were calculated from the sources given in the tables. These detailed calculations are not included here because of space limitations but may be found in Gilliland (1973). After each pathway was identified and estimated numerically, we were able to calculate an overall budget for the whole system and for unit models within the system as well as residence times and turnover times for each storage. This made possible identification of the relative importance of each pathway and yielded insight and perspective into times involved for change and stability.

Computer simulation of the entire model could not be easily done and w[illegible] not useful, but at this stage the relative importance of each pathway was estimated and a simplified model was developed. The model included the pathways and compartments which play a major role in model behavior and which are important for variations to be simulated. We tested the simplified model to identify unexpected model behavior.

The set of differential equations associated with each system was written directly from the energy-language diagram of the system. The Peace River estuarine system model was simulated on an IBM 1800 digital computer. The

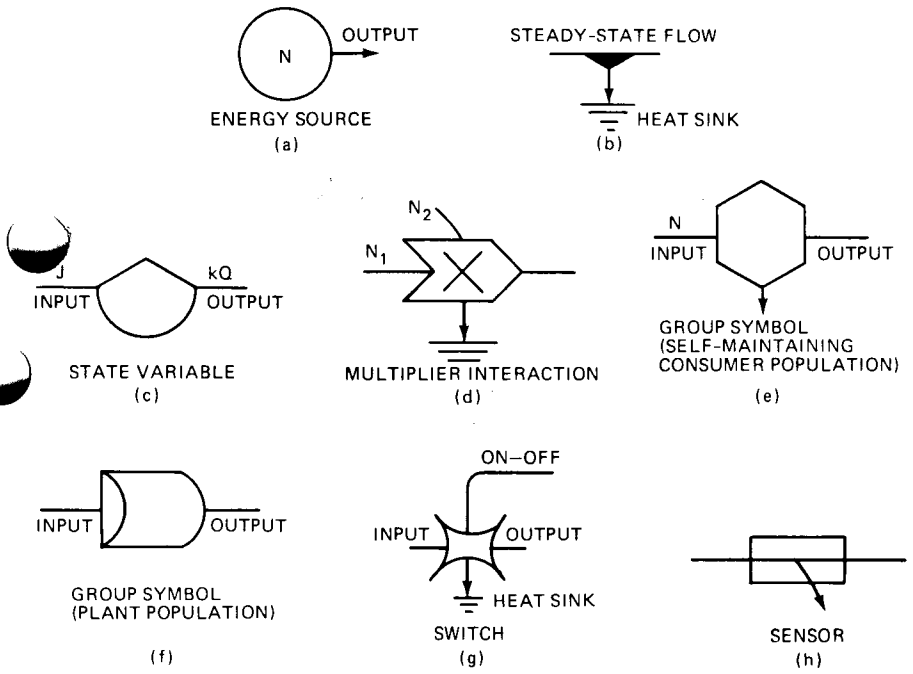


Fig. 1 Symbols of the energy-circuit language used in this paper (H. T. Odum, 1971). (a) Outside source of energy delivering forces according to a program controlled from outside, a forcing function (N). (b) A pathway whose flow is proportional to the quantity in the storage or source upstream (J = kN). The heat sink represents the energy losses associated with friction and back forces along pathways of energy flow. (c) A compartment of energy storage within the system storing a quantity as the balance of inflows and outflows ($\dot{Q} = J - kQ$). (d) Multiplicative intersection of two pathways coupled to produce an outflow in proportion to the product of both; control action of one flow on another; limiting factor action; work gate (kN_1N_2). (e) A combination of "active storage" and a "multiplier" by which potential energy stored in one or more sites in a subsystem is fed back to do work on the successful processing and work of that unit; autocatalytic $\{\dot{Q} = kQ\,[N - (Q/C)]\}$ and many variations. (f) Production and regeneration module (P–R) formed by combining a cycling receptor module, a self-maintaining module that it feeds, and a feedback loop that controls the inflow process by multiplicative and limiting actions. The green plant is one example. On a large scale the module may represent plants and consumers of ecosystems, or it may represent agriculture and cities. (g) Logic switch used for flows, which have only on and off states, controlling other flows by switching actions. (h) Sensor delivering a force to a diverging pathway which is proportional to the flow sensed and deriving its energy from it.

differential equations were programmed in Digital Simulation Language using centralized and fourth-order Runge–Kutta integration.

The set of differential equations for the submodel of the Peace River system, showing nitrogen and phosphorus interactions, was written and programmed on an Electronic Associates, Inc., MiniAc analog computer. The state variables are the storages, and the potentiometer settings on the computer are the pathway coefficients. These were calculated for a particular set of initial conditions; the equations were magnitude and time scaled according to standard computation practices; and simulations were run under various conditions. The models were used as though controlled experiments had been performed for one factor at a time.

RESULTS

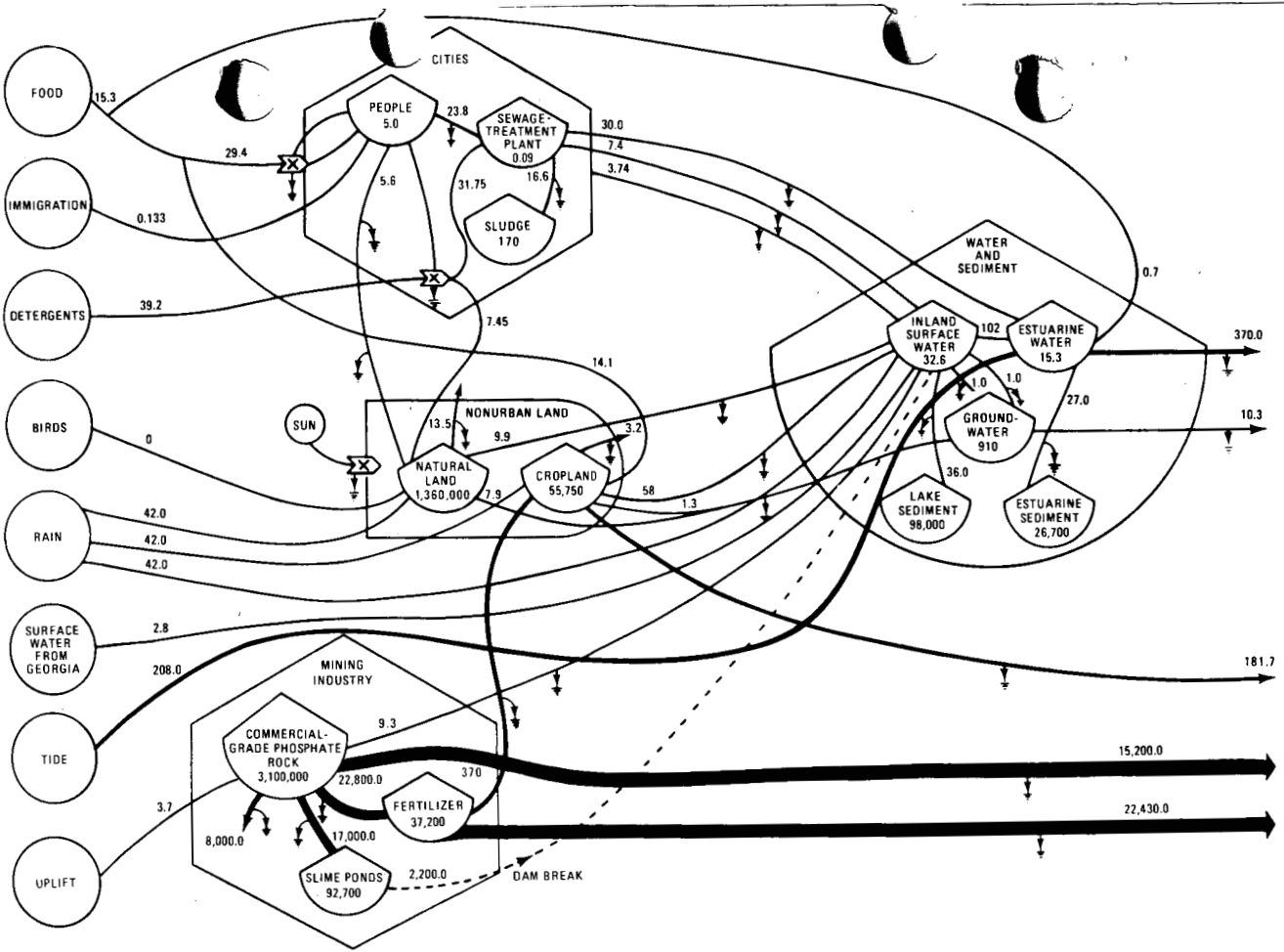
Phosphorus in Peninsular Florida

Figure 2 shows the major phosphorus storages and flows in peninsular Florida. Data are uneven, some being correct only to orders of magnitude. All data are given in grams per square meter of peninsular Florida. Total land area is 10^{11} m^2; thus total quantities can be found by multiplying by 10^{11} m^2.

Only the active portion of sediment or soil (the uppermost 1.5 m) was included in the phosphorus storages for natural lands, croplands, lake sediment, and estuarine sediment. Pastureland was included as part of natural lands because it does not receive the heavy energy subsidies (e.g., fertilizers) received by cropland. Groundwater (Q_8) was defined as only the main Florida aquifer; the small shallow aquifers around the state were neglected. Commercial-grade phosphate rock includes only that which is of the grade presently considered economical to mine (6.2% phosphorus).

Because of lack of data, some numbers are more reliable than others. Three numbers in particular are questionable. The phosphorus in runoff from cropland to lakes and rivers (58 mg m^{-2} year^{-1}, Fig. 2) is quite variable. Brezonik and Shannon (1971) gave values that, when converted to the units of Fig. 2, ranged from 2.1 to 15.7 mg m^{-2} year^{-1}, and Heaney, Perez, and Fox (1971) gave a value for the truck-farming district of Florida of 2134.4 mg m^{-2} year^{-1}. Biggar and Cory (1969) gave national averages of 65.0 to 267 mg m^{-2} year^{-1} for agricultur

Fig. 2 A quantitative model of the phosphorus cycle in peninsular Florida, which is defined on the northwest by the Suwannee River and incorporates an area of 10^{11} m^2. The model shows sources of phosphorus to the state on the left (circles), exports of phosphorus out of the state on the right, and internal phosphorus cycling pathways, center. Numerical values in the storages (tank-shaped symbols) are in milligrams of total phosphorus per square meter of peninsular Florida; values on the lines (rates) are in milligrams of total phosphorus per square meter per year.


CITIES
FOOD
15.3
PEOPLE
5.0
23.8
SEWAGE-TREATMENT PLANT
0.09
30.0
7.4
3.74
29.4
5.6
31.75
16.6
SLUDGE
170
IMMIGRATION
0.133
DETERGENTS
39.2
7.45
14.1
WATER AND SEDIMENT
0.7
INLAND SURFACE WATER
32.6
102
ESTUARINE WATER
15.3
370.0
1.0
1.0
27.0
GROUND-WATER
910
10.3
BIRDS
0
SUN
NONURBAN LAND
13.5
9.9
3.2
NATURAL LAND
1,360,000
7.9
CROPLAND
55,750
58
1.3
36.0
LAKE SEDIMENT
98,000
ESTUARINE SEDIMENT
26,700
RAIN
42.0
42.0
42.0
SURFACE WATER FROM GEORGIA
2.8
208.0
MINING INDUSTRY
181.7
TIDE
9.3
COMMERCIAL-GRADE PHOSPHATE ROCK
3,100,000
22,800.0
370
15,200.0
FERTILIZER
37,200
3.7
8,000.0
17,000.0
22,430.0
UPLIFT
SLIME PONDS
92,700
2,200.0
DAM BREAK

land fertilized in a manner similar to Florida's cropland. The often-quoted value for phosphorus concentration in runoff from fertilized cropland is 1 mg/liter or 47 mg m^{-2} $year^{-1}$ for Florida. The value used here (58 mg m^{-2} $year^{-1}$, is a weighted average since runoff from the peat in the truck-farming district is quite high, but runoff in other areas is much lower (Brezonik and Shannon, 1971; Heaney, Perez, and Fox, 1971).

Losses of phosphorus to the air from natural land and cropland are also uncertain. The Southeastern Forest Fire Laboratory in Macon, Ga., is making some measurements on the phosphorus in smoke from forest fires to determin[illegible] in particular, the quantity in smoke which does not fall back immediately bu[illegible] later rained out. The value for phosphorus calculated here (13 mg m^{-2} $year^{-1}$) is based on the amount of biomass burned multiplied by its phosphorus content. Since all the phosphorus in burned biomass probably does not go into the air, this number may be high. In cropland phosphorus may be blown up into the air in dust after heavy fertilization.

Florida is losing phosphorus through mining 125 times as fast as it is gaining phosphorus. Neglecting the mining industry and the crops exported, we find that the input of phosphorus is about the same as the output: 307 mg m^{-2} $year^{-1}$ input vs. 380 mg m^{-2} $year^{-1}$ output.

Note that input and output from the tide dominate the natural flows. Inputs from rain and from detergents are presently the same. Florida exports six times more phosphorus in food than it consumes (181 mg m^{-2} $year^{-1}$ in food exported and 29.4 mg m^{-2} $year^{-1}$ in food consumed).

A great many of the phosphorus flows are in the range of 10 to 40 mg m^{-2} $year^{-1}$. These include flows generally considered natural (e.g., land drainage and rain) and flows generally considered man induced (e.g., detergents and sewage effluent). River runoff, tidal input and output, and flows associated with agriculture are higher (100 to 300 mg m^{-2} $year^{-1}$), and the exports of the mining industry are two orders of magnitude higher still than these. The impact of a slime spill on the receiving stream is readily observable from the dashed line (**Fig. 2**) showing a spill equal in magnitude to one that occurred in December 1971 into the Peace River (Harriss, Hanke, and Mattraw, 1972). Although the slime does not affect all waters of the peninsula, it is shown for magnitude comparison. Of the enormous amount of phosphorus mobilized by mining, 0.9% of that marketed is used in agriculture in Florida (60% is used in the Uni[illegible] States); this increases the flux between land and waterways in Florida by [illegible] times. Forty percent of the phosphorus mined stays in Florida in the form of slime and other waste products.

Total input to inland waters is 133 mg m^{-2} $year^{-1}$, of which 78 mg m^{-2} $year^{-1}$ (58.6%) is a result of man's activities. This amount includes urban runoff, sewage effluent, agricultural runoff, and mining effluent. Mining effluent does not affect all waters, but principally the Alafia and Peace rivers. Of these contributors, the largest is agriculture, with 58 mg m^{-2} $year^{-1}$ in runoff (43.6%

of the total input to inland waters). Since agricultural runoff is highly variable, however, the value could range from 15 mg m^{-2} $year^{-1}$ (15% of total inland water input) to virtually 100% of input. Indications are that for Florida agricultural runoff contributes at least one-third of the input.

Since a large proportion of Florida's population resides in coastal cities, a large proportion of the total sewage is discharged into estuaries. Sewage effluent contributes 30 mg m^{-2} $year^{-1}$ phosphorus to the estuaries (8.8% of all contributions).

Phosphorus in the Peace River–Charlotte Harbor Estuarine System

Data Evaluation

The simplified model for the Peace River system is given in Fig. 3. Included are the mathematical terms for each source, storage, and flow. Table 1 describes the mathematical terms defined and gives numerical values and sources for the numbers.

The relative magnitude of the flows of water and phosphorus into the river mouth (i.e., into Q_4 and Q_5) are shown in summary diagrammatic form in Fig. 4 for easy conceptualization. Note that the river flow, mining water, and tidal input are all the same order of magnitude [Fig. 4(a)]. Sewage effluent is less by two orders of magnitude, and water from a slime spill is higher by one order of magnitude. Mining water is a significant percentage of the river flow (26% when the river is at intermediate flow).

The total phosphorus contribution of each source [Fig. 4(b)] to the river depends not only on the phosphorus concentration but also on the amount of water from the source. Except during the dry season, the river proper, whose phosphorus comes from the natural drainage of the Peace River system [~3625 km^2 (Lanquist, 1953)], is the major phosphorus contributor. Phosphorus in mining water, in the drainage water proper, and in the flood-tide input is the same order of magnitude. Contributions from sewage and sediments are one order of magnitude smaller, but, if a dam breaks and a slime spill occurs, the contribution of phosphorus is five orders of magnitude larger than all other contributors.

As calculated, the model is in steady state so that no net erosion or deposition in or out of the sediment occurs.

Simulation Evaluation

Differential equations needed for a simulation of the system were written directly from Fig. 3. Abbreviations for variables used in the differential equations, where H is the mean tidal range as defined in Table 1 and D is the mean depth of Q_8 (2.87 m), are:

$$x = Q_4/(A_4 + Z) \qquad a = Q_5/Q_4$$
$$y = Q_6/A_6 \qquad b = Q_7/Q_6$$
$$z = Q_8/A_8 \qquad c = Q_9/Q_8$$
$$w = H + D$$

Differential equations written from Fig. 3 are

$$\dot{Q}_1 = -k_1 Q_1 J_{3B} - k_2 Q_1 J_{3A}$$

$$\dot{Q}_2 = J_{3B} - \overbrace{k_3 Q_2}^{(\text{if } Q_2 > R_1;\ J_4 > 7)}$$

$$\dot{Q}_3 = k_1 Q_1 J_{3B} - \overbrace{k_3 Q_3}^{(\text{if } Q_2 > R_1;\ J_4 > 7)}$$

$$\dot{Q}_4 = J_1 + J_{3A} + J_5 - k_5 (x - y) + \overbrace{k_3 Q_2}^{(\text{if } Q_2 > R_1;\ J_4 > 7)}$$

$$\dot{Q}_5 = J_1 J_2 + J_5 J_6 + k_2 Q_1 J_{3A} - k_7 J_9 Q_5 + k_8 J_{10} Q_{10} - \overbrace{k_9 a(x - y)}^{(\text{if } y < x)} - \overbrace{k_{10} b(x - y)}^{(\text{if } y > x)} + \overbrace{k_3 Q_3}^{(\text{if } Q_2 > R_1;\ J_4 < 7)} - \overbrace{k_6 Q_5}^{(\text{if } a > R_2)}$$

$$\dot{Q}_6 = J_7 + k_5 (x - y) - k_{11} (y - z)$$

$$\dot{Q}_7 = J_7 J_8 + \overbrace{k_9 a(x - y)}^{(\text{if } y < x)} + \overbrace{k_{10} b(x - y)}^{(\text{if } y > x)} - \overbrace{k_{12} b(y - z)}^{(\text{if } z < y)} - \overbrace{k_{15} c(y - z)}^{(\text{if } z > y)} - k_{13} J_{11} Q_7 + k_{14} J_{12} Q_{11}$$

$$\dot{Q}_8 = k_{11} (y - z) - k_{16} (z - w)$$

$$\dot{Q}_9 = \overbrace{k_{12} b(y - z)}^{(\text{if } z < y)} + \overbrace{k_{15} c(y - z)}^{(\text{if } z > y)} - \overbrace{k_{17} J_{16} (z - w)}^{(\text{if } w > z)} - \overbrace{k_{18} c(z - w)}^{(\text{if } w < z)} - k_{19} J_{13} Q_9 + k_{20} J_{14} Q_{12}$$

$$\dot{Q}_{10} = k_7 J_9 Q_5 - k_8 J_{10} Q_{10} + \overbrace{k_6 Q_5}^{(\text{if } a > R_2)}$$

$$\dot{Q}_{11} = k_{13} J_{11} Q_7 - k_{14} J_{12} Q_{11}$$

$$\dot{Q}_{12} = k_{19} Q_9 J_{13} - k_{20} J_{14} Q_{12}$$

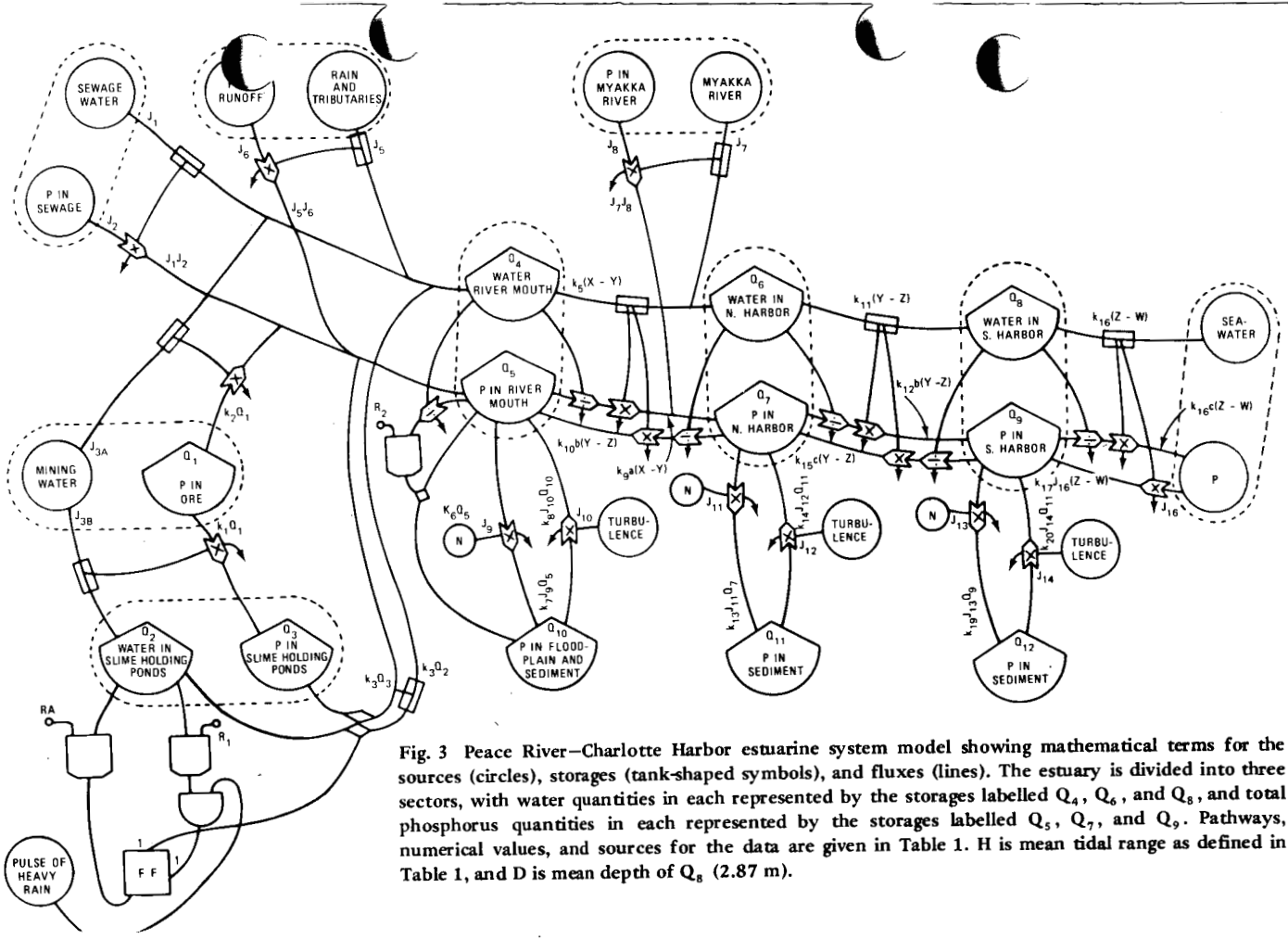


Fig. 3 Peace River–Charlotte Harbor estuarine system model showing mathematical terms for the sources (circles), storages (tank-shaped symbols), and fluxes (lines). The estuary is divided into three sectors, with water quantities in each represented by the storages labelled Q_4, Q_6, and Q_8, and total phosphorus quantities in each represented by the storages labelled Q_5, Q_7, and Q_9. Pathways, numerical values, and sources for the data are given in Table 1. H is mean tidal range as defined in Table 1, and D is mean depth of Q_8 (2.87 m).

TABLE 1

NUMERICAL VALUES, PATHWAY DESCRIPTIONS, AND DATA SOURCES FOR SOURCES, STORAGES, AND RATES FOR THE PEACE RIVER–CHARLOTTE HARBOR ESTUARINE SYSTEM MODEL* (FIG. 3)

Mathematical term	Description	Numerical value	Source
λ_1	Phosphorus remaining in the ore in Florida	3.10×10^{14} g	Eilersten (1969) Fullam and Faulkner (1971)
$(Q_2 = R_1)$	Water stored in the slime holding pond	3.0×10^{7} m^3	Harriss, Hanke, and Mattraw (1972) Specht (1950)
Q_3	Phosphorus stored in slime holding pond	7540 g/m^3	Toler (1967)
Q_4	Water in Peace River mouth	2.66×10^{7} m^3	U. S. Coast and Geodetic Survey (1971)
Q_5	Phosphorus in Peace River mouth	1.597×10^{7} g (0.6 mg/liter)	Alberts et al. (1970)
Q_6	Water in northern section of Charlotte Harbor	4.67×10^{8} m^3	U. S. Coast and Geodetic Survey (1971)
Q_7	Phosphorus in northern section of Charlotte Harbor	1.63×10^{8} (0.35 mg/liter)	Alberts et al. (1970)
Q_8	Water in southern section of Charlotte Harbor	5.38×10^{8} m^3	U. S. Coast and Geodetic Survey (1971)
Q_9	Phosphorus in southern section of Charlotte Harbor	1.34×10^{8} g (0.25 mg/liter)	Alberts et al. (1970)
Q_{10}	Phosphorus in sediments and floodplain of Peace River mouth	1.57×10^{10} g (15 cm deep)	Huang and Goodell (1967)
Q_{11}	Phosphorus in sediments of northern section of Charlotte Harbor	4.3×10^{11} g (15 cm deep)	Huang and Goodell (1967)
Q_{12}	Phosphorus in sediments of southern section of Charlotte Harbor	5.5×10^{11} g (15 cm deep)	Huang and Goodell (1967)

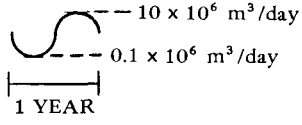
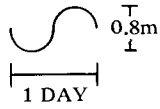
J_1	[illegible]e water entering the Peace River	7.54×10^4 m^3/day	In[illegible]y of Public S[illegible]age Systems in Florida (1966)
J_2	Phosphorus in sewage entering the river	5.0 g/m^3	Cook (1969)
J_{3A}	Water from mining operations entering river	1.3×10^6 m^3/day	Lanquist (1953) Specht (1950)
J_{3B}	Water from mining operations entering an average slime pond	41.7×10^3 m^3/day	Specht (1950)
J_4	Pulse of heavy rain required for a slime spill	17.8 cm/day	Specht (1950)
J_5	Primary river flow resulting from rain and tributaries		Dragovich, Kelly, and Goodell (1968) USGS (1961-1968)
J_6	Phosphorus content of primary river flow	1.5 g/m^3	U. S. Geological Survey (1968)
J_7	Myakka River discharge	5.0×10^5 m^3/day	Dragovich, Kelly, and Goodell (1968)
J_8	Phosphorus content of Myakka River	0.35 g/m^3	Dragovich, Kelly, and Goodell (1968)
J_9	Factors affecting precipitation of phosphorus in the river mouth	0.152 g/m^3	U. S. Geological Survey (1968)
J_{10}	Turbulence causing phosphorus to redissolve into surface waters from sediment	56.16×10^9 kcal/day	Estimate of potential energy of tide
J_{11}	Factors affecting precipitation of phosphorus in the northern harbor	0.018 g/m^3	Alberts et al. (1970)
J_{12}	Turbulence in northern section of Charlotte Harbor	95.76×10^{10} kcal/day	Estimate of potential energy of tide

Table 1 (Continued)

Mathematical term	Description	Numerical value	Source
J_{13}	Factors affecting precipitation of phosphorus in the southern harbor	0.018 g/m^3	Alberts et al. (1970)
J_{14}	Turbulence in southern section of Charlotte Harbor	166.5×10^{10} kcal/day	Estimate of potential energy of tide
J_{15}	H = mean tidal range		U. S. Department of Commerce (1972)
J_{16}	Phosphorus in seawater	0.031 mg/l	Graham, Amison, and Marvin (1954)
$k_1 Q_1 J_3 B$	= $J_3 C$, flux of phosphorus in ore to phosphorus in the slime holding ponds	7540 g/m^3	Toler (1967) Specht (1950)
$k_2 Q_1 J_3 A$	= $J_3 D$, flux of phosphorus to river from mining operations	1.0 g/m^3	Lanquist (1953)
$k_3 Q_2$	Water released to Peace River when dam breaks	2.88×10^7 m^3/day	Specht (1950) Harriss, Hanke, and Mattraw (1970)
$k_3 Q_3$	Phosphorus released to river when dam breaks	$2.1715 \times 10^{1.1}$ g/day	Toler (1967)
$k_5\left[\left(\frac{Q_4}{A_4} + Z\right) - \frac{Q_6}{A_6}\right]$	Flux of water in and out of river mouth. Z = base level	5.76×10^6 m^3/day	U. S. Coast and Geodetic Survey (1971)
$k_6 Q_5$	Flux of phosphorus to sediment when the river load exceeds its capacity (usually when a lime spill o[illegible]	2.10×10^{11} g/day	Harriss, Hanke, and [illegible]ttraw (1972)

$k_7 J_9 Q_5$	Flux of phosphorus from surface water to sediments in river mouth	1.33×10^5 g/day	Harriss, Hanke, and Mattraw (1972) Pomeroy et al. (1972)
$k_8 J_{10} Q_{10}$	Flux of phosphorus from sediments to surface water in river mouth	1.33×10^5 g/day	Harriss, Hanke, and Mattraw (1972) Pomeroy et al. (1972)
$k_9 \frac{Q_5}{Q_4}\left[\left(\frac{Q_4}{A_4} + Z\right) - \frac{Q_6}{A_6}\right]$	Flux of phosphorus out of the river mouth	3.456×10^6 g/day	Alberts et al. (1970)
$k_{10} \frac{Q_7}{Q_6}\left[\left(\frac{Q_4}{A_4} + Z\right) - \frac{Q_6}{A_6}\right]$	Flux of phosphorus into the river mouth	1.98×10^6 g/day	Alberts et al. (1970)
$k_{11}\left(\frac{Q_6}{A_6} - \frac{Q_8}{A_8}\right)$	Flux of water in and out of northern section of Charlotte Harbor with tides	85.0×10^6 m^3/day	U. S. Department of Commerce (1972) U. S. Coast and Geodetic Survey (1971)
$k_{12} \frac{Q_7}{A_6}\left(\frac{Q_6}{A_6} - \frac{Q_8}{A_8}\right)$	Flux of phosphorus out of northern section of Charlotte Harbor	2.975×10^7 g/day	Alberts et al. (1970)
$k_{13} J_{11} Q_7$	Flux of phosphorus from surface water to sediments in northern section of harbor	2.4×10^6 g/day	Alberts et al. (1970)
$k_{14} J_{12} Q_{11}$	Flux of phosphorus from sediment to surface water	2.4×10^6 g/day	Alberts et al. (1970)
$k_{15} \frac{Q_9}{Q_8}\left(\frac{Q_6}{A_6} - \frac{Q_8}{A_8}\right)$	Flux of phosphorus into northern section of Charlotte Harbor	2.12×10^7 g/day	Alberts et al. (1970)
$k_{16}\left[\frac{Q_8}{A_8} - (H + D)\right]$	Flux of water in and out of the southern harbor through Boca Grande Pass	1.13×10^8 m^3/day	O'Brien (1969)
$k_{17} J_{16} \cdot \left[\frac{Q_8}{A_8} - (H + D)\right]$	Flux of phosphorus into the lower harbor through Boca Grande Pass	3.50×10^6 g/day	Graham, Amison, and Marvin (1954)

Table 1 (Continued)

Mathematical term	Description	Numerical value	Source
$k_{18}\frac{Q_9}{Q_8}\left[\frac{Q_8}{A_8} - (H + D)\right]$	Flux of phosphorus out of the lower harbor through Boca Grande Pass	2.825×10^7 g/day	Alberts et al. (1970)
$k_{19}J_{13}Q_9$	Flux of phosphorus from surface water to sediment in southern section of harbor	2.78×10^6 g/day	Alberts et al. (1970)
$k_{20}J_{14}Q_{12}$	Flux of phosphorus from sediments to surface water	2.78×10^6 g/day	Alberts et al. (1970)

*Pathways on Fig. 3 may be referenced to this table by the mathematical terms given on both.

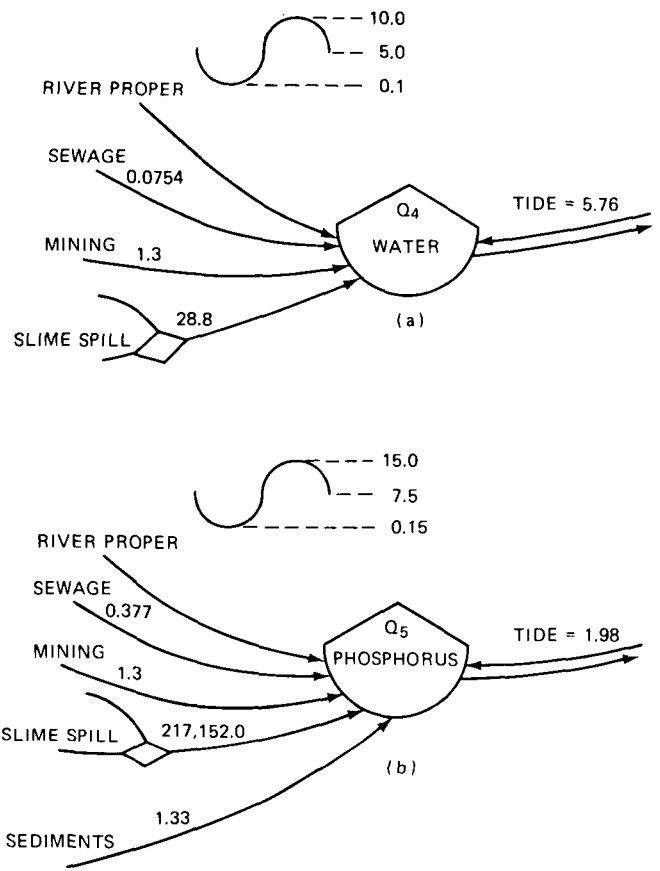


Fig. 4 Summary models of water and phosphorus flux showing numerical values for the Peace River mouth (Q_4 and Q_5 of Fig. 3). Surface area is 1.78×10^7 m^2. (a) Flux of water into the Peace River mouth (Q_4) (units are 10^6 m^3/day). (b) Flux of phosphorus into the Peace River mouth (Q_5) (units are 10^6 g/day).

Results of the digital simulation for 5 years are shown in graphic form in Fig. 5. Salient results were:

1. Maximum water discharge occurred in August.

2. The total quantity of phosphorus depended largely on the total volume of water present.

3. The phosphorus concentration curve for the river mouth [Fig. 5(b)] was almost flat, reflecting a situation in which input concentrations were relatively constant but water volume varied.

4. The lowest phosphorus concentration occurred in the dry season when natural drainage, which is high in phosphorus concentration, was lowest.

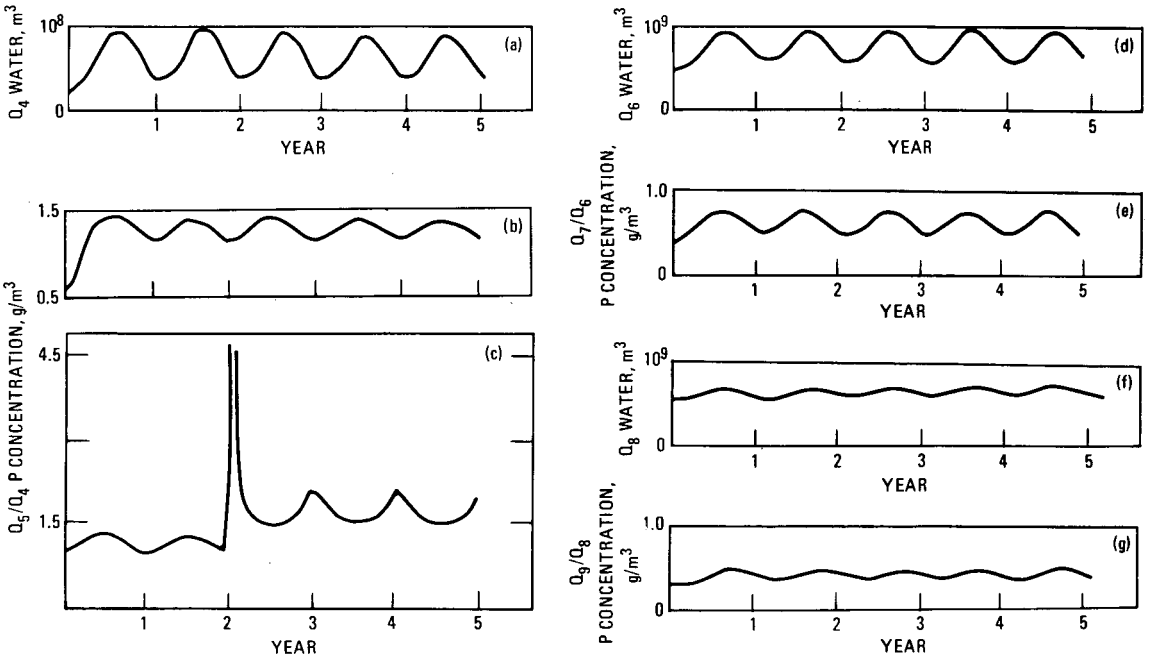


Fig. 5 Simulation results of the model in Fig. 3. Phosphorus concentration is total P. (a) and (b) Water and phosphorus concentration in the Peace River mouth. Surface area is 1.78×10^7 m^2. (c) Effect of a slime spill on phosphorus concentration in the Peace River mouth (Q_5). (d) and (e) Water and phosphorus concentration in northern Charlotte Harbor. Surface area is 1.468×10^8 m^2. (f) and (g) Water and phosphorus concentration in southern Charlotte Harbor. Surface area is 1.87×10^8 m^2.

5. The amplitude of seasonal fluctuations was lowest in the southern-most downstream portion of the estuary because of the dampening effect of the tide and the larger area over which the river discharge was spread.

6. Time lags between minimum and maximum points for the downriver portions relative to the upriver portion were 7 days for the river-mouth sector to the northern harbor sector and 7 days for the northern harbor sector to the southern harbor sector.

The simulation predicted total phosphorus concentrations of 1.13 to 1.39 g/m^3 in the river-mouth sector [Fig. 5(b)], 0.45 to 0.75 g/m^3 for the northern sector of Charlotte Harbor [Fig. 5(e)], and 0.3 to 0.41 g/m^3 for the southern sector of Charlotte Harbor [Fig. 5(g)].

The frequency and amplitude of fluctuations predicted by the simulations agreed well with measured data. Water and phosphorus fluctuations may be more frequent if examined on a daily basis (Huang and Goodell, 1967; Dragovich, Kelly, and Goodell, 1968; U. S. Geological Survey, 1961–1968), but the simulations represented an accurate smoothed effect of fluctuations. Dragovich, Kelly, and Goodell (1968) also found that the quantity of nutrients contributed by the river to the sea was determined by the volume of river flow. Concentrations measured in the river mouth ranged from 0.6 g/m^3 average dissolved phosphorus (Alberts et al., 1970)—total phosphorus was not measured—to 0.93 g/m^3 average total phosphorus (Dragovich, Kelly, and Goodell, 1968) to 1.9 g/m^3 (Dequine, 1974) average total phosphorus. Dissolved phosphorus measured in the northern sector of Charlotte Harbor averaged 0.35 g/m^3 and in the southern sector, 0.25 g/m^3 (Alberts et al., 1970). Total phosphorus was not measured.

To gain insight into the effects of increased pollution pressures that may arise with population increases in South Florida, we examined three variations of the simulation: reducing mining effluent, increasing sewage, and following a surge from a slime-pond dam break.

Part of the clear effluent from the slime ponds is not reused but is wasted to the river (Boyle, 1969). Simulation of the model for the case in which no mining water was discharged to the river resulted in a decrease of 25% in water volume in the river mouth and a decrease of 4% in the northern sector of Charlotte Harbor during the dry season and an overall decrease of 10% during periods of maximum flow. The dry-season minimum in phosphorus concentration in the river mouth [Fig. 5(b)] was negated. Thus we see that the mining water contributed significantly to river flow but diluted the phosphorus concentration slightly.

Results of a simulation in which the phosphorus from sewage effluent was increased by estimating a population of 500,000 people with secondary treatment (the population is presently 200,000 people) indicated that during periods of maximum flow no measurable phosphorus concentration change

occurred but during the dry season the river-mouth phosphorus concentration increased 16%.

Effects of slime spills into the Peace River are readily observable; the white, turbid water can be seen all along the river immediately after a spill. Results of simulating a surge of slime moving down the river are presented in Fig. 5(c). Phosphorus concentrations in the river mouth increased initially to 18.0 g/m^3 and then dropped to 1.6 g/m^3 as the slime settled out [Fig. 5(c)]. The new steady state was higher, and the shape of the curve changed. Maximum concentration in the river mouth occurred during the dry season rather than during periods of maximum flow, as was the case before a spill. Harriss, Hanke, and Mattraw (1972) measured a fourfold increase in phosphorus in the river mouth after a slime spill; the high value was 1.6 g/m^3. The fact that concentration now peaked during the dry season indicated that the flux of phosphorus from sediment to surface waters was a larger fraction of the total flux of phosphorus to surface waters during the dry season than during periods of maximum river flow.

After a dam break most of the slime settles into the sediment of the river mouth, which in the Peace River is the portion of the river that is sluggish (the river becomes braided) and is affected by flood tides. Harriss, Hanke, and Mattraw (1972) stated that the slime settled into the river-mouth sediment because of rapid reduction in river-current velocity and because of flocculation of the fine-grained phosphate waste by the intrusion of brackish water. The simulation suggested that turbulence associated with boat traffic or high winds could bring phosphate from the sediment into the surface waters for many years after a slime spill. For the December 1971 spill, Harriss, Hanke, and Mattraw (1972) found that the phosphate slime was reactive, having 375 ppm soluble phosphorus; thus the slime in the sediment continues to contribute to surface-water phosphorus concentrations and eventually is partially flushed into Charlotte Harbor and finally into the Gulf of Mexico.

Nitrogen, Phosphorus, and Productivity in the Peace River Mouth

Phytoplankton populations in Charlotte Harbor were smaller than populations measured in other Florida estuaries (Harriss, Hanke, and Mattraw, 1972; Spence, 1971). Since both phosphorus and nitrogen are critical nutrients for algal growth and since high values of phosphate are present in the river mouth and harbor, there is a possibility that low nitrogen concentrations are limiting the phytoplankton populations. Results of a nutrient bioassay experiment in the Peace River estuary (Harriss, Hanke, and Mattraw, 1972) indicated that increased quantities of dissolved nitrogen, as well as silicon, stimulated productivity.

A model depicting some interactions of phosphorus, nitrogen, and light is shown in Fig. 6. Figure 6(b) shows the model simulated, which is a simplifica-

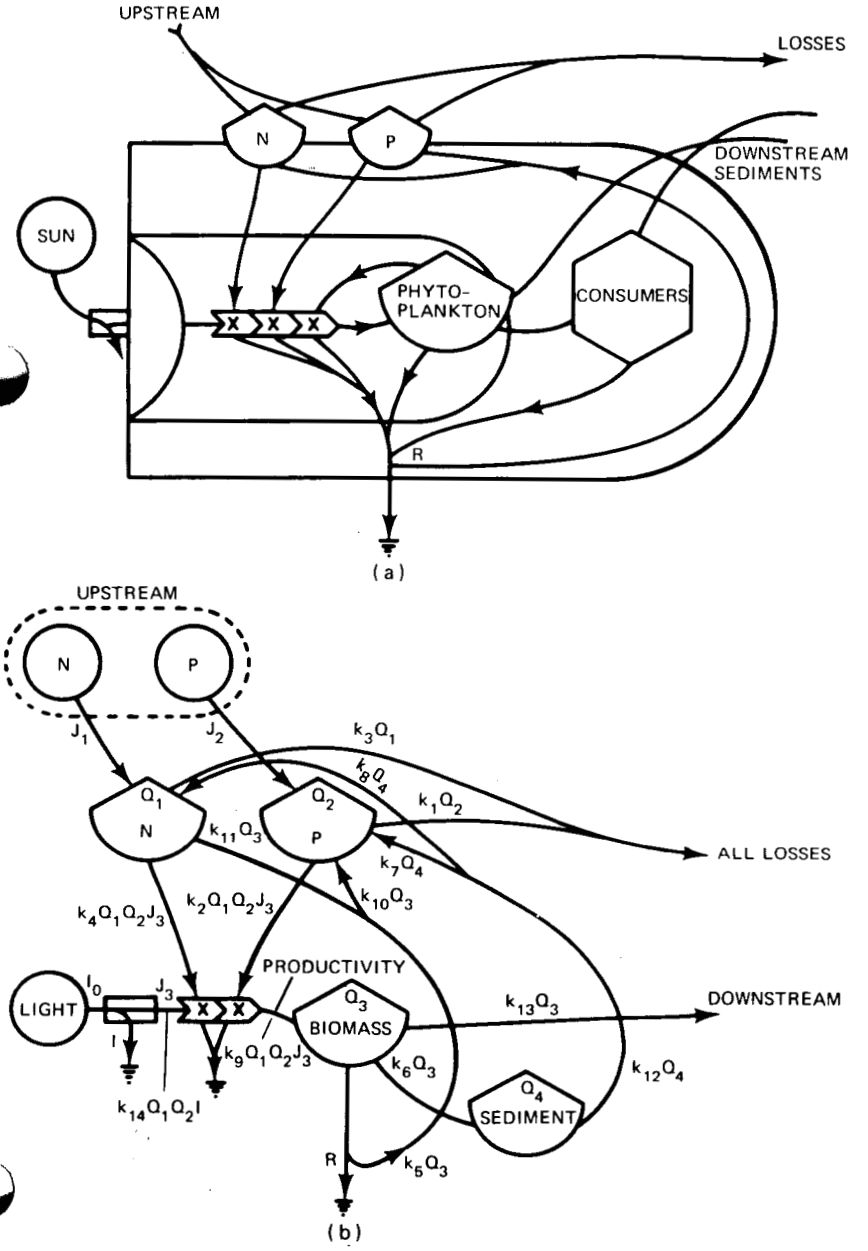


Fig. 6 (a) General ecosystem representation of the Peace River mouth sector of the Charlotte Harbor estuary showing upstream sources, downstream losses, producers, consumers, and the main internal nutrient-cycling pathways. (b) Simplified ecosystem model of the mouth estuary giving the mathematical terms associated with each pathway. Pathways, numerical values, sources for the data, and the differential equations written from this diagram are given in Table 2.

tion of the more comprehensive system shown in Fig. 6(a). Some interactions are not included in the simplified version; e.g., productivity is also a function of phytoplankton population and other elements. The mathematical terms for each pathway are shown in Fig. 6(b), and Table 2 gives the numerical values and differential equations.

Simulation of the model [Fig. 6(b)] using the numbers given for state variables and pathways resulted in small change from the initial conditions in Table 2. At steady state total phosphorus concentration increased from 1.0 to 1.8 g/m^3, total nitrogen concentration decreased from 0.15 to 0.08 g/m^3, standing crop decreased from 0.85 to 0.64 g/m^3, and gross primary productivity decreased from 0.57 to 0.3 g m^{-3} day^{-1}. The indication was that the steady-state condition depleted total nitrogen even more than the low starting value.

To test the sensitivity of the system to an increase in available nitrogen, we increased the input from the upstream source (J_3) of nitrogen from 0.06 g m^{-3} day^{-1} (which corresponds to an upstream nitrogen concentration of 0.47 g/m^3) successively to fluxes of 0.126, 0.2, and 0.3 g m^{-3} day^{-1} (which correspond to upstream concentrations of 1.1, 1.6, and 2.4 g/m^3, respectively). Results of this increased nitrogen input are given in Fig. 7 (a and b), along with a graph of steady-state nitrogen concentrations vs. phytoplankton standing crop and gross primary productivity [Fig. 7(c)]. Both standing crop and productivity steadily increased as available nitrogen increased. The nitrogen levels were within the expected range as the population pressures expected in the area increased sewage and urban runoff. Increasing the population by about 300,000 people and assuming secondary treatment for all sewage would result in a nitrogen input from sewage alone of 1.1 g/m^3 in the upstream source [shown in Fig. 7(a)]. This simulation yielded a total nitrogen concentration in the estuarine water of 0.13 g/m^3, a standing crop of 1.38 g/m^3, and a gross productivity of 0.8 g organic matter m^{-3} day^{-1}. A total population of one million people would result in an upstream nitrogen input from sewage alone of 1.6 g/m^3. This simulation yielded an estuarine water nitrogen concentration of 0.16 g/m^3, a standing crop of 2.2 g/m^3, and a gross productivity of 1.4 g organic matter m^{-3} day^{-1}. If nitrogen from runoff from increased urban areas were added, standing crop and productivity might be higher still. Nitrogen from urban runoff is in the range of 0.88 g per square meter of land-use area per year (Brezonik and Shannon, 1971, from Weibel, 1969). For an urban land area the size of Tampa and St. Petersburg, 0.88 g m^{-2} year^{-1} converts to an additional input of 2 X 10^6 g of nitrogen per day. Figure 7(b) shows the results of a simulation in which the input of total nitrogen from upstream was 2.4 g/m^3, a value that could reflect the sum of agricultural input, sewage, urban runoff, and natural drainage.

In all cases where nitrogen availability was increased, the actual estuarine concentration remained low [maximum of 0.2 g/m^3 in Fig. 7(b)], and standing crop and productivity increased (maximum of 3.27 g/m^3 and 2.2 g organic matter m^{-3} day^{-1}, respectively). The nutrients stored in the sediment also

increased as production increased; the flux of phosphorus to sediment increased from 0.003 g P m^{-3} day^{-1} for initial conditions to 0.012 g P m^{-3} day^{-1} at the highest nitrogen level simulated.

Sediment–water exchange rates given by Pomeroy et al. (1972) give additional perspective to those obtained here. Their values range from 8 to 14 mg P m^{-2} day^{-1} (0.003 to 0.005 g P m^{-3} day^{-1}). This is well within the range predicted here for various nitrogen levels.

Production values measured by the Federal Water Pollution Control Administration (1969) in Hillsborough Bay, which is one of Florida's waste-recovery estuaries, also give additional perspective. Total dissolved nitrogen there ranged from 0.1 to 1.0 g/m^3, and the average gross photosynthesis measured averaged 3.8 g O_2 m^{-3} day^{-1}.

DISCUSSION

Mobilization of phosphorus through mining affects not only the area where phosphorus is mined but also the entire earth. As pointed out by Stumm (1972), the rate of mining of phosphorus exceeds the rate of transport to the sea, and thus high levels of phosphorus are being accumulated in a small part of the earth's total land surface. For example, agriculture results in a continual drain of phosphorus from the soil; this deficit is made up by the addition of phosphate fertilizers. Eventually the phosphorus from agricultural crops is found in sewage, which in turn is discharged to inland waters and estuaries. These changing rates of phosphorus cycling are evaluated for Peninsular Florida and for the Peace River Estuary draining Florida's mining district.

Peninsular Florida

The data for the peninsular Florida model indicated that the phosphorus extracted and mobilized by mining is higher by three orders of magnitude than the phosphorus cycling through Florida's waterways and than that brought in by rain. New phosphorus sources created are dilute in comparison with the concentrated source of phosphate rock. Forty percent of the phosphorus mined stays in Florida in the form of slime and other waste products.

Agricultural runoff may contribute to an increase of phosphorus in Florida's land waters; at least half of all inputs are due to man's activities, with agricultural runoff contributing at least one-third of the total. Sewage effluent to inland water is a minor contributor since a large proportion of Florida's population resides in coastal cities and thus a large proportion of the total sewage is discharged into estuaries. But even this is a small amount of phosphorus compared to the large quantities brought in by the tides (this involves enormous quantities of water at low phosphorus concentrations). Where estuarine conditions are such that tidal flushing occurs readily, phosphorus from

TABLE 2

NUMERICAL VALUES, PATHWAY DESCRIPTIONS, AND DATA SOURCES FOR SOURCES, STORAGES, AND RATES FOR THE SIMPLIFIED ESTUARINE ECOSYSTEM MODEL* [FIG. 6(b)]

Mathematical terms†	Description	Numerical value	Source
Q_1	Total nitrogen stored	0.15 g/m^3	Finucane and Dragovich (1959) Connell and Associates (1972)
Q_2	Total phosphorus stored	1.0 g/m^3	Alberts et al. (1970)
Q_3	Phytoplankton stored	0.85 g/m^3	Spence (1971)
Q_4	Sediment storages (top 1 cm)	39 g/m^3 phosphorus 6.5 g/m^3 nitrogen	Huang and Goodell (1967)
I	Sun	3800 kcal m^{-2} day^{-1}	Odum, E. P. (1971)
$k_4 I = J_3$	Light available	760 kcal m^{-2} day^{-1}	Estimate
J_1	Total nitrogen from upstream	0.068 g m^{-3} day^{-1}	U. S. Geological Survey (1961-1968) Odum et al. (1955) and velocity data from Fig. 3
J_2	Total phosphorus from upstream	0.15 g m^{-3} day^{-1}	Previous simulation (Fig. 3)
$k_1 Q_2$	Phosphorus losses downstream	0.13 g m^{-3} day^{-1}	Previous simulation (Fig. 3)
$k_2 Q_1 Q_2 J_3$	Phosphorus incorporated into biomass	0.01 g m^{-3} day^{-1}	Based on productivity and ratios from Sverdrup, Johnson, and Fleming (1947) and velocity data from Fig. 3
$k_3 Q_1$	Nitrogen losses downstream	0.02 g m^{-3} day^{-1}	Harriss, Hanke, and Mattraw (1972) Finucane and Dragovich (1959) and velocity data from Fig. 3
$k_4 Q_1 Q_2 J_3$	Nitrogen incorporated into bio	0.075 g m^{-3} day^{-1}	Based on productivity and r om Sverdrup, Jo n, and Fleming (1947)

$k_5 Q_3$	Res[illegible]on	$0.29\ g\ m^{-3}\ day^{-1}$	S[illegible]-state calculation
$k_6 Q_3$	Org[illegible]natter flux to sediment	$0.164\ g\ m^{-3}\ day^{-1}$	
$k_7 Q_4$	Phosphorus recycled from sediment	$0.003\ g\ m^{-3}\ day^{-1}$	Steady-state calculation
$k_8 Q_4$	Nitrogen recycled from sediment	$0.021\ g\ m^{-3}\ day^{-1}$	Steady-state calculation
$k_9 Q_1 Q_2 J_3$	Gross primary production	$0.57\ g\ m^{-3}\ day^{-1}$	Estimated from Spence (1971)
$k_{10} Q_3$	Phosphorus regenerated from respiration	$0.0053\ g\ m^{-3}\ day^{-1}$	Based on respiration of organic matter and ratios by Sverdrup, Johnson, and Fleming (1947)
$k_{11} Q_3$	Nitrogen regenerated from respiration	$0.038\ g\ m^{-3}\ day^{-1}$	Based on respiration of organic matter and ratios by Sverdrup, Johnson, and Fleming (1947)
$k_{12} Q_4$	Nutrients recycled from sediment		Sum of $k_7 Q_4$ and $k_8 Q_4$
$k_{13} Q_3$	Biomass loss downstream	$0.11\ g\ m^{-3}\ day^{-1}$	Steady-state calculation and velocity data from Fig. 3

*Pathways on Fig. 6(b) may be referenced to this table by the mathematical terms given on both.

†Differential equations:

$$\dot{Q}_1 = J_1 + k_{11} Q_3 + k_8 Q_4 - k_3 Q_1 - k_4 J_3 Q_2 Q_1$$
$$\dot{Q}_2 = J_2 + k_{10} Q_3 + k_7 Q_4 - k_1 Q_2 - k_2 Q_2 J_3 Q_1$$
$$\dot{Q}_3 = k_9 J_3 Q_1 Q_2 - k_5 Q_3 - k_6 Q_3 - k_{13} Q_3$$
$$\dot{Q}_4 = k_6 Q_3 - k_{12} Q_4$$
$$I = I_0 - k_{14} Q_1 Q_2 I$$

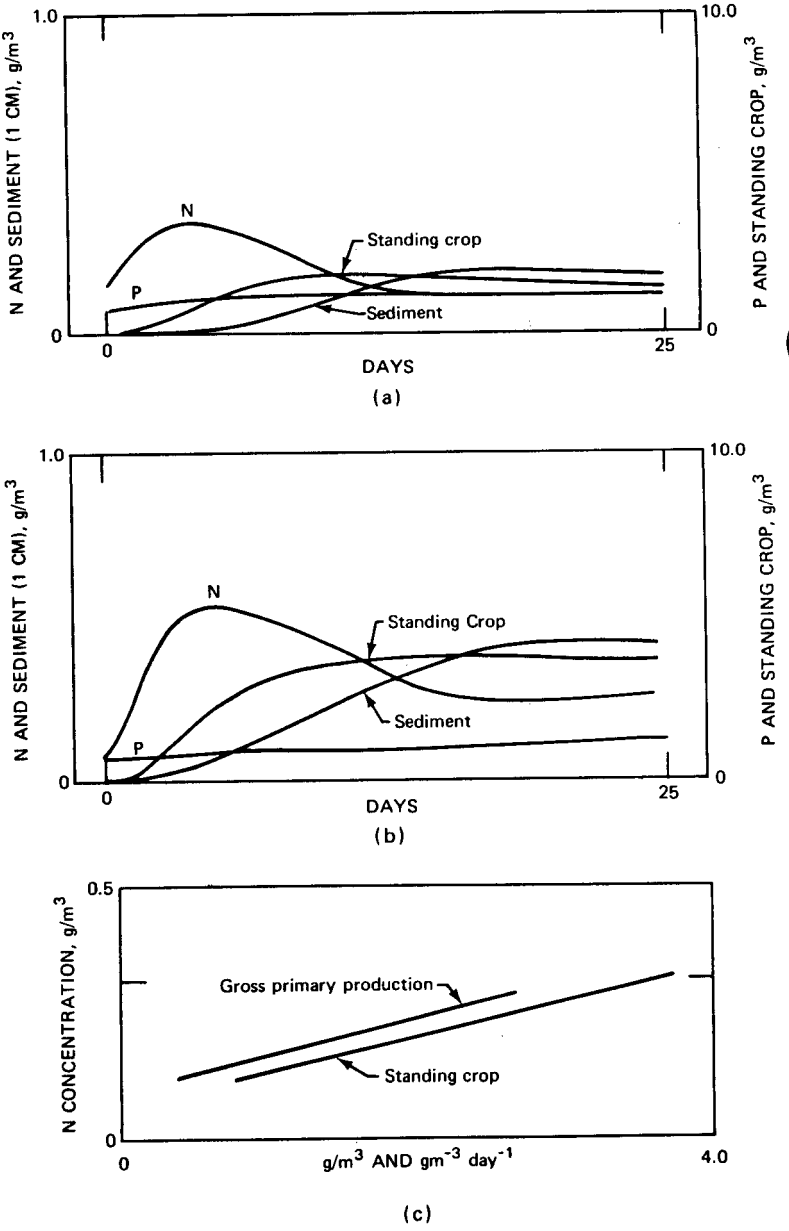


Fig. 7 Simulation of the model in Fig. 6(b) showing changes in stocks for levels of available nitrogen. (a) Results of nitrogen input (J_1) increase to 0.13 g m^{-3} day^{-1} (input concentration 1.1 g/m^3), yielding a steady-state stock of nitrogen of 0.12 g/m^3 (Q_1). (b) Results of nitrogen input (J_1) increase to 0.3 g m^{-3} day^{-1} (input concentration 2.4 g/m^3), yielding a steady-state stock of nitrogen of 0.2 g/m^3 (Q_1). (c) Steady-state nitrogen concentration vs. steady-state phytoplankton standing crop and steady-state productivity.

land sources may not be significant. On the other hand, in enclosed or protected estuaries where little tidal input occurs, sewage effluent may be an important contributor of phosphorus.

Peace River Estuary

On the basis of observations and of the simulation of the model in Fig. 3, we determined that the entire Peace River Estuary is high in total phosphorus, ranging from 0.3 to 1.0 g/m^3, with the lower values occurring in the southern sector of Charlotte Harbor. Since the river drains a basin with a soil and rock content uniquely high in phosphorus, natural runoff is the major phosphorus contributor. In the simulations neither daily mining-water discharges nor sewage from present populations increased the phosphorus levels significantly.

Simulation of a slime spill indicated that both short- and long-term changes were significant. Phosphorus concentrations increased drastically for several days and then leveled off higher than before the spill. Dry-season levels were higher than levels during periods of maximum flow after a slime spill, whereas the inverse was true before a slime spill. Phosphorus levels in the river mouth remained elevated for many years after a slime spill. High turbulence from a hurricane or greatly increased boat traffic caused erosion of the slime and resulted in above normal turbidity in Charlotte Harbor.

The model simulated in Fig. 6(b) shows the effect of the high phosphorus levels on primary production in the estuary. The results are preliminary since a simplified version of the model was used, but the presence of high phosphorus appears to keep nitrogen levels low, possibly limiting productivity. At present, primary production in this estuary is low relative to that in other Florida estuaries. The simulations indicated that productivity was sensitive to small increases in total dissolved nitrogen (Fig. 7); production did not increase to levels common in other Florida estuaries, however, even when nitrogen inputs were high. This may be caused by the flushing rate of the estuary, the sediment uptake, or other factors. The mechanism is not known. Based on the findings of Barrett (1952) for fertilized trout lakes in Michigan and of Copeland and Hobbie (1972) and Hobbie (1970) for the Pamlico River Estuary of North Carolina, which also receives high phosphorus, sediment uptake is a possibility. Barrett found that, when phosphorus was added to trout lakes in Michigan, the extremely high calcium levels in the lakes caused the added phosphorus to disappear from epilimnial waters with no increase in productivity. In the Pamlico River Estuary, phosphorus added by mining operations is entering an estuary naturally rich in phosphorus. In that study, phosphorus additions did not cause increased carbon uptake, and mud removed significant amounts of dissolved reactive phosphorus from the water column.

The research generated several principles that may have general scientific value. First, the presence of high phosphorus levels in Charlotte Harbor kept nitrogen levels low, and primary productivity was low. The question then arises,

could the extreme excess of one nutrient make an aquatic system more oligotrophic? If so, this is somewhat countercurrent to intuition. Second, water-quality-control programs based on the percent effect of a given flow on the overall chemical cycle may be more meaningful and efficient than the current practice of setting effluent standards based on concentrations.

IMPLICATIONS FOR PHOSPHORUS MANAGEMENT IN FLORIDA

The system models used to measure the impact of man on phosphorus flo indicated:

1. Since phosphorus levels are naturally high in the Peace River and in Charlotte Harbor, requiring advanced waste treatment for phosphorus removal from domestic sewage or from the daily mining effluent discharged to the river may not have any advantages for the Charlotte Harbor system.

2. Since slime spills were deleterious to the Peace River and Charlotte Harbor both in short- and long-term effects, the strict control and monitoring of the earthen dams recently begun by the state of Florida is warranted.

3. The simulation indicated that increased urbanization of the area, with associated increased nitrogen discharges to the system (from sewage, urban runoff, finger canal construction, and agriculture), may increase primary productivity in Charlotte Harbor, but productivity will not reach levels common in other normal Florida estuaries. If sewage discharges to the estuary increase to five times the present level, discharge to terrestrial systems or nitrogen removal should be considered.

4. Since in Florida agricultural runoff from fertilized cropland is the highest man-dominated phosphorus flow to inland waters, more judicious and efficient use of phosphate fertilizers is warranted.

5. Phosphorus in domestic sewage from detergents and food may not be implicated on a statewide basis as a large contributor to inland waters. Analyses on a percent-effect basis for specific lakes and estuaries are needed to determine the magnitude of local effects.

6. When United States phosphorus reserves become depleted, the enormous quantities of phosphate stored in the mine tailings and slime ponds in Florida may be looked to as a phosphorus source. In preparation for this, we shou consider a cost–benefit study of the energy cost of obtaining the phosphorus the energy benefits the phosphorus produced at its point of use (e.g., the value of fertilized crops).

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REFERENCES

Alberts, J., H. Mattraw, R. Harriss, and A. Hanke, 1970, Charlotte Harbor Estuarine Studies. Progress Report II. *Studies on the Geochemistry and Hydrography of the Charlotte Harbor Estuary, Florida,* Department of Oceanography, Florida State University, Tallahassee.

Barrett, P. H., 1952, Relationships Between Alkalinity and Absorption and Regeneration of Added Phosphorus in Fertilized Trout Lakes, *Trans. Amer. Fish. Soc.,* **82**: 78-90.

Biggar, J. W., and R. B. Cory, 1969, Agricultural Drainage and Eutrophication, in *Eutrophication: Causes, Consequences, Correctives,* pp. 404-445, Division of Biology and Agriculture, National Academy of Sciences, Washington, D. C.

Boyle, J. R., 1969, *Waste Disposal Costs of Florida Phosphate Operation,* Bureau of Mines Information Circular No. 8404.

Brezonik, P. L., and E. E. Shannon, 1971, *Trophic State of Lakes in North Central Florida,* Florida Water Resources Research Center, Publication 13, University of Florida, Gainesville.

Connell and Associates, 1972, Environmental Assessment Study, Punta Gorda Area, mimeographed, Miami, Fla.

Cook, L. M. (Ed.), 1969, *Cleaning Our Environment, the Chemical Basis for Action,* American Chemical Society, Washington, D. C.

Copeland, B. J., and J. E. Hobbie, 1972, *Phosphorus and Eutrophication in the Pamlico River Estuary, N. C., 1966-1969—A Summary,* Water Resources Research Institute of the University of North Carolina, Chapel Hill.

Dequine, J. F., 1974, Florida Game and Fresh Water Commission, Lakeland, personal communication.

Dragovich, A., J. Kelly, and H. G. Goodell, 1968, Hydrological and Biological Characteristics of Florida's West Coast Tributaries, *U. S. Fish Wildl. Serv. Fish. Bull.,* **66**: 463-477.

Eilersten, D. E., 1969, Phosphate Rock, preprint from *Minerals Yearbook, 1968,* Bureau of Mines, U. S. Department of the Interior.

Federal Water Pollution Control Administration, 1969, *Problems and Management of Water Quality in Hillsborough Bay,* Superintendent of Documents, U. S. Government Printing Office.

Finucane, J. H., and A. Dragovich, 1959, Counts of Red Tide *Gymnodinium breve* and Associated Oceanographic Data from Florida West Coast, 1954-1957, U. S. Fish and Wildlife Service, Special Scientific Publication, Fisheries, No. 289, pp. 1-220.

Florida Phosphate Council, 1973, Economics Fact Sheet, Lakeland, Fla.

Fullam, H. T., and B. P. Faulkner, 1971, *Inorganic Fertilizer and Phosphate Mining Industries—Water Pollution and Control,* Water Pollution Control Research Series 12020 FPD 09/71, Environmental Protection Agency.

Gilliland, M. W., 1973, Man's Impact on the Phosphorus Cycle in Florida. Ph.D. thesis, University of Florida, Gainesville.

Graham, H. W., J. M. Amison, and K. T. Marvin, 1954, Phosphorus Content of Waters Along the West Coast of Florida, U. S. Fish and Wildlife Service, Special Scientific Report, Fisheries, No. 122, pp. 1-43.

Harriss, R., A. Hanke, and H. Mattraw, 1972, Impact of the Phosphate Slime Spill (December, 1971) on Sediments and Water Quality in the Charlotte Harbor Estuary, mimeographed, Florida State University, Tallahassee.

Heaney, J. P., A. Perez, and J. Fox, 1971, Nutrient Budget Within the Organic Soils Area North of Lake Apopka, Oklawaha Comprehensive River Basin Study, mimeographed, University of Florida, Gainesville.

Hobbie, John E., 1970, Phosphorus Concentrations in the Pamlico River Estuary of North Carolina, Water Resources Research Institute of the University of North Carolina, Report No. 33, Chapel Hill.

Huang, Tei-Chen, and H. G. Goodell, 1967, Sediments of Charlotte Harbor, Southwestern Florida, *J. Sediment. Petrol.*, 37: 449-474.

Inventory of Public Sewerage Systems in Florida, 1966, Florida State Board of Health, Bureau of Sanitary Engineering, Jacksonville.

Lanquist, Ellis, 1953, A Biological Survey of the Peace River, M.S. Thesis, University of Florida, Gainesville.

O'Brien, M., 1969, Equilibrium Flow Areas of Inlets on Sandy Coasts, *J. Waterways Harbors Div., Amer. Soc. Civil Eng.*, 6405: 43-52.

Odum, E. P., 1971, *Fundamentals of Ecology*, 3rd ed., W. B. Saunders Company, Philadelphia.

Odum, H. T., 1972, An Energy Circuit Language for Ecological and Social Systems: Its Physical Basis, in B. C. Patten (Ed.), *Systems Analysis and Simulation in Ecology*, Vol. II, pp. 140-210, Academic Press, Inc., New York.

___, 1971, *Environment, Power, and Society*, John Wiley & Sons, Inc., New York.

___, J. B. Lackey, J. Hynes, and N. Marshall, 1955, Some Red Tide Characteristics During 1952-1954, *Bull. Mar. Sci. Gulf Carib.*, 5: 247-258.

Pomeroy, L., L. Shenton, R. Jones, and R. Reimold, 1972, Nutrient Flux in Estuaries, *Limnol. Oceanog.*, Special Symposium, 1: 274-291.

Specht, R. C., 1950, *Phosphate Waste Studies*, Bulletin 32, pp. 1-28, University of Florida Engineering and Industrial Experiment Station.

Spence, L., 1971, *Cyclotella* Taxonomic and Ecological Relations of the Diatom Genus in South Florida Waters, M.S. thesis, Florida State University, Tallahassee.

Stumm, Werner, 1972, The Acceleration of the Hydrogeochemical Cycling of Phosphorus, in David Dyrssen and Daniel Jagner (Eds.), *The Changing Chemistry of the Oceans*, pp. 223-259, John Wiley & Sons, Inc., New York.

Sverdrup, H. U., M. W. Johnson, R. H. Fleming, 1947, *The Oceans, Their Physics, Chemistry, and General Biology*, Prentice-Hall, Inc., Englewood Cliffs, N. J.

Toler, L. G., 1967, Fluoride in Water in the Alafai and Peace River Basins, *Florida Geological Survey R.I.*, 46: 1-46.

U. S. Coast and Geodetic Survey, 1971, Map of Estero Bay to Lemon Bay, National Oceanic and Atmospheric Administration.

U. S. Department of Commerce, 1972, Tide Tables, National Ocean Survey.

U. S. Geological Survey (USGS), 1961-1968, Water Resources Data for Florida, Parts 1 and 2.

Weibel, S. R., 1969, Urban Drainage as a Factor in Eutrophication, in *Eutrophication: Causes, Consequences, and Correctives*, pp. 383-403, National Academy of Sciences, Washington, D. C.

MINERAL CYCLING IN MARINE ECOSYSTEMS

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ABSTRACT

Synthesis of recent work on marine grass communities, coral reefs, and oceanic plankton leads to a reexamination of some concepts of the flux of essential elements through marine communities. Where they occur, storage compartments and inputs from outside the system have a marked effect on stability. In planktonic communities, which have minimal storage and input, nutrient demand must be met largely from recycling and successional shifts of dominant species in response to changing nutrient limitations. Diversity in the plankton results in part from the successional mosaic created by local changes in nutrient limitations and by the presence of biochemical niches. Coral reefs also develop successional mosaics, but the forces at work here include storm and predator damage as well as interspecies competition. Marine grass meadows, on the other hand, show less spatial and temporal diversity, little succession, and high stability. In the marine communities considered, stability appears to be more strongly related to availability of nutrients than to diversity. The most stable communities are the least diverse.

Populations and communities are self-reproducing configurations of chemical elements that maintain their integrity and continuity through continuous reconstruction of tissues and reproduction of individuals. These processes require a constant flux of elements and energy through both individual organisms and communities. Although individual organisms may sometimes concentrate one or more essential elements and recycle them internally, populations and communities cannot do this because loss of elements is inevitable through the death and degradation of individuals. A source of essential elements is necessary, and communities may be shaped in part by their availability. The interaction between communities and the elements moving through them can influence species composition, diversity, and stability. Concepts of limiting nutrients must now take into account a number of complexities that did not concern Liebig (1840).

Much of the conceptualization of diversity and stability of communities has been related to food-web structure and particularly to interspecies interactions. Moreover, there has been a dichotomy between results with mathematical and laboratory model systems, on the one hand, and observations of natural communities, on the other. Up to the present time, most theoretical models consider one or two factors at a time, eliminating by definition all others. Modulations of nutrient supply are usually among the factors eliminated from models for the sake of simplicity. Recent studies of real-world communities permit us to consider specifically the influence of essential elements on community structure and stability and to compare this knowledge with the output from theoretical models. The synthesis presented in this paper will focus on four contrasting marine communities. Although they do not include all the possibilities to be found in the biosphere, they represent some extremes of community development quite well, and all of them are well described by recent research reports.

MARINE GRASS COMMUNITIES

Mineral cycling in two contrasting estuarine communities has been studied in some detail: the subtidal eelgrass (*Zostera marina*) meadows and the intertidal cordgrass (*Spartina alterniflora*) meadows. In the *Zostera* meadows of Izembek Lagoon in Alaska, phosphorus and nitrogen move from the sediments into roots and then into leaves. Nutrients fixed in protoplasm are remineralized into the water when the leaves are eaten by consumers or die and decay. However, nearly half the phosphate, ammonia, and nitrate that reaches the leaves from the roots washes out into the water before being utilized by the leaf tissue (McRoy and Barsdate, 1970; McRoy, Barsdate, and Nebert, 1972; McRoy and Goering, 1974). Some of the lost nutrients are utilized immediately by layers of specialized periphytic algae which tightly cover the leaves (Harlin, 1973; Sieburth and Thomas, 1973; McRoy and Goering, 1974). Epiphytes on eelgrass, and probably on other sea grasses, recover dissolved materials that are lost from the leaves in much the same manner that epiphytes and understory plants in a rain forest recover materials washed from trees of the canopy (Tukey, 1970).

In the *Spartina* marshes of the Georgia coast, half the phosphate brought into the leaves from the sediments is fixed in plant tissues and half is lost at high tide or during rains. Epiphytes appear to be less well developed on the intertidal *Spartina* than on the subtidal sea grasses. Phosphate is lost from healthy growing leaves throughout the growing season (Reimold, 1972). This is net loss of reactive phosphate, measured chemically, and not a result of a tracer study, which might misrepresent net flux.

Both McRoy, Barsdate, and Nebert (1972) and Reimold (1972) estimated the loss of molybdate-reactive phosphate from individual plants cleaned of epiphytes and then extrapolated from these measurements to estimate the loss

of phosphate from the meadows. The estimate for *Zostera* in Alaska was a flux of 2 mg atoms P m^{-2} day^{-1}, while the estimate for *Spartina* in Georgia was 20 mg atoms P m^{-2} day^{-1}. Izembek Lagoon has about twice the area of the Duplin River in Georgia, which was studied by Reimold, but the two watersheds have about the same high-tide volume. In spite of the difference in estimated loss from the two grass populations, the mean phosphate concentration in the water of both Izembek Lagoon and the Duplin River is 1 mg atom P m^{-3}, and the maximum observed values are between 5 and 10. This suggests that phosphate is being recycled more actively in the Duplin River despite the better development of epiphytes on *Zostera*. Most likely the phosphate is being more actively sorbed by sediments since the sediments of the Duplin River are fine clays (kaolinite and montmorillonite) and the sediments of Izembek Lagoon are volcanic sands. Since much of the sediment of the Duplin River is intertidal, there is good contact of water with sediments. The sorptive equilibrium concentration of phosphate in the water has been shown experimentally to be 1 mg atom P m^{-3} (Pomeroy, Smith, and Grant, 1965).

McRoy, Barsdate, and Nebert (1972) postulated a continuous loss of phosphate from Izembek Lagoon and resupplying by degradation of the volcanic sands. On the basis of the experimentally observed sorptive capacity of the clays, Pomeroy et al. (1972) and Reimold (1972) postulated concentration in the sediments of the Duplin River. Neither group has produced good evidence in the field to support their suppositions, however. High concentrations of phosphate extend out to sea from the inlets of both systems. Whatever the long-term geochemical processes may be, both sea-grass systems are clearly endowed with a nutrient reserve in their sediments. The principal limits to growth probably are crowding and shading.

CORAL REEF COMMUNITIES

In contrast to the grass communities, coral reefs, like planktonic communities and some tropical rain forests, have very small abiotic storage compartments for nutrients. There is storage in the tissue of living organisms, and there is continuous input of low concentrations of essential elements as seawater, propelled by wind, surf, and tides, passes over the reef. Recent work has markedly changed our concept of both the food web and the mechanisms of mineral cycling on coral reefs.

The first detailed examination of the food web of coral reefs was by Yonge and his colleagues on the Great Barrier Reef Expedition (Yonge, 1930). The presence of symbiotic algae in the tissues of reef corals, tridacnid clams, and other organisms raised questions about the nature of the trophic relationships of these organisms and the impact of the symbiosis on the food web and nutrient flux. Yonge concluded that corals are basically carnivores, feeding on zooplankton that are washed over the reef.

A reconsideration of the food web of coral reefs began when Sargent and Austin (1949) measured the change in oxygen in the water as it passed across a reef of Rongelap Atoll in the Marshall Islands. Diurnal changes in dissolved oxygen in the water flowing across the reef indicated that the reef was autotrophic. Sargent and Austin suggested that algae on the reef were major primary producers. Odum and Odum (1955), in a detailed study of Japtan Reef at Eniwetok, found that the reef was autotrophic. They also showed that individual coral heads were net producers of oxygen. While these field studies were going on, laboratory work with corals revealed that soluble orga materials of low molecular weight, such as glycerol, were lost by the symbi dinoflagellates and assimilated by coral tissue (Muscatine, 1967). A quantitative field study in Bermuda (Johannes, Coles, and Kuenzel, 1970) showed that the supply of zooplankton was not sufficient to sustain metabolism and growth in the absence of some other food source. All these studies led to the erroneous assumption that most primary production in coral reefs is accomplished by dinoflagellates living symbiotically within coral tissues. Pomeroy and Kuenzler (1969) showed that corals conserve phosphorus much more efficiently than do other heterotrophic organisms of similar body size. This suggested that the mineral cycles of coral reefs were specialized and partly internal. What was not clear was how corals were related to the food web of the dense and diverse consumer populations of the reef. Release of mucus by corals was suggested as a possible energy link to the consumers (Marshall, 1965; 1968; Johannes, 1967). Such a link would be analogous to a detrital system, with bacterial degradation of mucus a probable intermediate step.

New insight into the food web and mineral cycling of the Eniwetok reefs was provided recently by the Symbios Expedition. An important discovery was that photosynthesis is more intense on bare reef rock and rubble than in areas populated by corals (Johannes et al., 1972). Algal mats on the rocks are grazed so intensively by fishes and invertebrates that they are hardly evident, but their photosynthetic rate is impressive. Although this finding does not negate any previously established pathways of energy and materials, it adds a new pathway of substantial magnitude.

In an ecosystem as complex as a coral reef, the flux of materials takes many pathways through highly specialized populations although there may be fe major primary and secondary pathways. Delineation of major pathways rema difficult. The state of our ignorance is summarized in Fig. 1. An evident pathway is filamentous algae to grazing fishes and invertebrates to feces to deposit feeders. The density of holothurians on many reefs is impressive, but other deposit feeders are also abundant though nocturnal and less conspicuous. The quantitative significance of this pathway is in doubt since reef fishes account for only a small part of total reef respiration and, therefore, can hardly be major movers of essential elements (Johannes, 1974). This being the case, invertebrates are probably the major grazers.

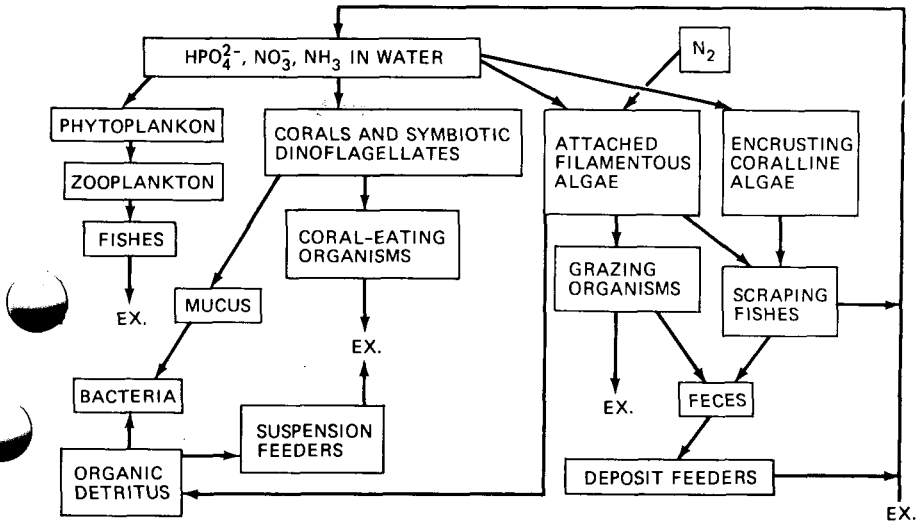

Fig. 1 A compartmental model of the flux of nitrogen and phosphorus through a coral-reef community which combines three postulates about the food web. EX. is the excretory flux of nitrogen and phosphorus. See text for discussion.

Another generally accepted pathway of materials is coral to mucus to bacteria to filter feeders. But, since there is little loss of phosphorus and probably a relatively small loss of nitrogen from the corals along this pathway, bacterial requirements for these two elements must come from phosphate and nitrate in reef water.

When we consider both these pathways, plus that through the symbiotic dinoflagellates in reef corals and other invertebrates, we are still unable to account quantitatively for the recycling of all the phosphorus and nitrogen known to be assimilated in primary production on the reef. Since many reefs are highly autotrophic, there may be a significant export of particulate materials that escape the many mouths and tentacles. Circumstantial evidence does not suggest this, however. Pilson and Betzer (1973) found no change in the concentration of molybdate-reactive phosphate in water as it passed over the windward reef of Eniwetok Atoll, and nitrate in the water actually increased as it crossed the reef (Johannes et al., 1972). These findings suggest a balanced uptake and release of nutrients by the community, with some nitrogen fixation by algal mats. Support for that view was found in the tracer studies of the Eniwetok reef community by Pomeroy, Pilson, and Wiebe (1974), which showed that, with the exception of the coral–dinoflagellate symbiosis, none of the reef populations showed any unusual retention of phosphate. Reef communities may

be adjusted to various steady-state rates of nutrient supply, competing successfully for space with faster growing algae (Roy and Smith, 1971; Connell, 1974). Of course, if nutrient concentrations in the water change, other populations may replace the typical coral-reef community, as seen in Kaneohe Bay, Hawaii (Smith, Chave, and Kam, 1973).

PLANKTONIC COMMUNITIES

Planktonic communities have small abiotic storage compartments for essential elements and little living biomass in which elements can reside. Moreover, the lifetime of individuals in the community is short. These constraints make all planktonic communities somewhat nutrient limited. Even in upwellings, half the flux of nitrogen must come from recycled ammonia (Dugdale and Goering, 1967). Since the flux of essential elements in planktonic communities is coupled closely to the food web, our understanding of nutrient flux in the open sea depends on our knowledge of the food web.

Our concept of the planktonic food web is undergoing a radical change. The classical view of the food web in the open sea was a relatively simple chain from diatoms to copepods and other net plankton to fishes (compartments X_9 to X_{11} in Fig. 2). All theoretical constructs and models up to this time have been made on the basis of this food chain or fragments of it. Evidence that diatoms do not always dominate primary production in the sea began to appear long ago. Atkins (1945) pointed out that, since the depletion of silicate in the English Channel during the summer was not proportional to the depletion of phosphate, diatoms could be the major producers only if silicate were recycled more rapidly than phosphate. That seemed unlikely then, and we now know that it is not the case. Atkins was among the first to suggest that the nannoplankton (<60 μm) were significant primary producers. Recently it was suggested that the nannoplankton dominate the open sea and that large diatoms dominate the nutrient-rich regions, such as upwellings, the Antarctic Ocean, coastal waters, and estuaries (Ryther, 1969; Dugdale, 1972; Parsons and Takahashi, 1973). Ryther suggested that differences in the size of the primary producers led to a fundamentally different food web in the open sea, where nannoplankton must be consumed by other microorganisms, which results in an inefficient tertiary production of nekton. Most of the important fisheries were said to be in upwellings and coastal waters because the food chain from producers to nekton was shorter there. However, a number of studies of the relative rate of photosynthesis by net plankton and nannoplankton have shown that nannoplankton are responsible for over 90% of the photosynthesis in most marine waters most of the time, including upwellings, coastal waters, and estuaries (Pomeroy, 1974). Moreover, Semina (1972) reports that the mean size of phytoplankton is in fact smaller in the Peru Current than elsewhere in the Pacific Ocean.

If primary production is dominated by nannoplankton, the implication is that many of the primary consumers may also be very small. Empirical evidence suggests that this is so. Comparative studies of the respiratory rate of net plankton and microorganisms in the sea show that over 90% of the respiration is usually microbial (Pomeroy and Johannes, 1966). It is by no means certain, however, that the food web is a simple one of protozoans consuming small green flagellates. Andrews and Williams (1971) present evidence that a substantial fraction of the energy flux in the sea moves through a shunt of soluble organic compounds of low molecular weight which escape from the phytoplankton and are consumed by bacteria. Under the nutrient-deficient conditions of the open sea, the ratio of photosynthesis to respiration in the phytoplankton themselves is quite low and nearly half the carbon fixed by them is lost almost immediately as dissolved materials. In contrast, the photosynthesis-to-respiration ratio of phytoplankton in nutrient-rich upwellings is less than 10% of the carbon fixed (Thomas, 1971). Therefore, in nutrient-rich waters there are substantial numbers of phytoplankton of various sizes to be consumed directly, but, in the nutrient-depleted open sea, half or more of the flow of energy may be through the shunt of dissolved organic matter to heterotrophic microorganisms (Andrews and Williams, 1971; Pomeroy, 1974). This emerging view of the planktonic food web is far from clear and probably is still a minority view. Recent work on phytoplankton nutrition, however, tends to support the contention that the classical concept of the planktonic food web is oversimplified. Some of the alternate pathways are shown in Fig. 2, which is a highly simplistic representation of current speculation about the ocean's food web. The many roles of bacteria, for example, in the cycle of nitrogen, have not been delineated. We

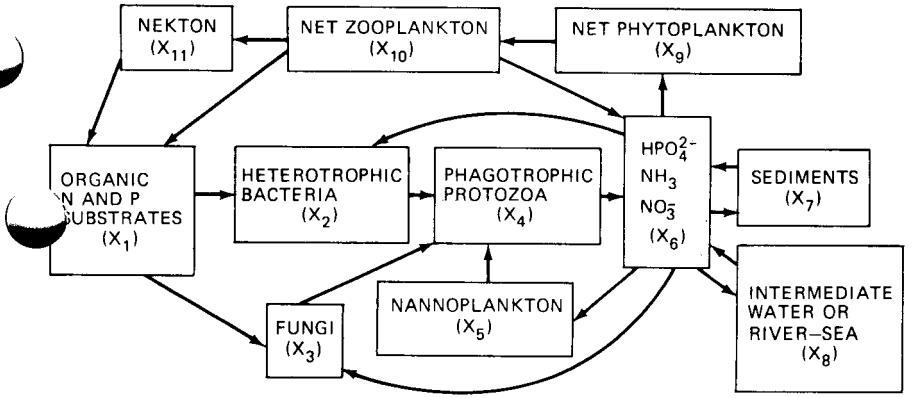

Fig. 2 A compartmental model of the flux of nitrogen and phosphorus through marine planktonic communities.

have long realized the complexity of the roles played by microorganisms, but we are just now beginning to appreciate the quantitative importance of total microbial metabolism.

BIOCHEMICAL NICHES

There is a long literature documenting experimentation and speculation on the factors permitting a diverse assemblage of phytoplankton species to persist, all presumably sharing one niche. One variable operating to preserve diversity is the periodic shift of nutrient limitation from one element to another. Nitrogen is now thought to be the most usual limiting nutrient in the sea although phosphorus is in nearly limiting supply. Even with a single limiting element, such as nitrogen, changes in nitrate and ammonia concentration shift the optimal growth rate from one phytoplankton species to another. There is experimental evidence that the half-saturation constants, K_s, and the growth constants, μ, of phytoplankters vary and are adapted to different regimes of each of several nutrients (Dugdale, 1967; Guillard, Kilhan, and Jackson, 1973). Moreover, since phytoplankton species have different daily regimes of nutrient uptake, some species are accumulating nutrients while others are not (Eppley et al., 1971). Induction of nutrient-specific enzymes or uptake sites may be inhibited either by the absence of a specific nutrient (NO_3^-) or by the presence of another (NH_3), depending on the algal species (Eppley and Rogers, 1970). Our understanding of these subtle interactions is imperfect, however, because it is based on batch-culture laboratory experiments at rather high nutrient concentrations. Metabolic activity or dormancy of populations can also be induced by changing temperature regimes (Wall and Dale, 1970).

Diatoms have a substantial requirement for silicon, in addition to the usual essential elements. When conditions otherwise favor the growth of diatoms over smaller organisms, they may be limited by available silicon. This has been demonstrated for species from upwellings (Dugdale, 1972; Davis, Harrison, and Dugdale, 1973) and even for species from the Sargasso Sea (Guillard, Kilhan, and Jackson, 1973). Silicon limitation may explain why the results of a model that assumes nitrogen limitation (Parsons and Takahashi, 1973) do not agree with empirical observations of planktonic populations (Semina, 1972).

Shifts from one nutritional limiting condition to another, whether through change from one limiting nutrient to another or in nutrient concentration, will give the advantage first to one set of species of phytoplankters and then to another. Such activity introduces into the phytoplankton community an almost kaleidoscopic kind of succession that will assort itself differently with each successive turn of the nutrient limitations. This succession may be quite uniform over large areas of the ocean, but often it probably is not. Only occasionally are we able to recognize the time sequence of events, all parts of which usually appear at once as part of a spatial mosaic of species distribution. Margalef (1956)

described a linear sequence of succession in the Ría de Vigo. The experimental production of a succession in phytoplankton has been demonstrated by Menzel, Hulbert, and Ryther (1963) and by Barber et al. (1971).

The relatively large diversity that is typical of oceanic plankton results at least in part from the presence of a mosaic of various stages of successional responses to nutrient limitation within a small distance, small, that is, in terms of the dimensions of the ocean. The complexity of the mosaic is enhanced by the differences in response of a set of phytoplankton species to constantly shifting concentrations of a set of limiting nutrients. Each species has evolved a distinct set of uptake constants and growth rates for the set of limiting nutrients, thereby finding for itself a biochemical niche in a nearly homogeneous environment.

RECYCLING

Nutrient sources for phytoplankton probably are somewhat more varied than we had realized. In the ocean two sources generally recognized are advection and recycling. Each appears to include a range of processes with varying rates. Advection operates especially well in upwellings, but the significance of such mechanisms as salt fingers in the permanently stratified tropical seas is not well understood. In coastal waters and estuaries, advection includes input from the bottom and from the land. Recycling, however, is a significant component of nutrient flux everywhere. In upwellings it supplies half the nitrogen (Dugdale and Goering, 1967), and some estuaries and coastal waters appear to function almost entirely on recycled nutrients (Pomeroy et al., 1972; Haines, 1974).

Recycling usually is attributed to bacterial metabolism, although experimental proof of this in natural waters is lacking. Many alleged experimental demonstrations of bacterial recycling of phosphate and ammonia do not discriminate between the activities of bacteria and other protists, and even zooplankton in some cases (Pomeroy, 1970). Attempts to isolate phosphatizing bacteria in seawater have been unsuccessful (Lear, 1965). Ammonifying bacteria do exist, but their quantitative significance in recycling has not been established in natural waters (Wiebe, 1974). An alternate pathway of recycling is excretion of metabolites and defecation of incompletely digested food by heterotrophic consumers of all kinds except bacteria.

Although there are a number of estimates of the roles of various consumer groups in excretory recycling, we still do not have enough information to evaluate fully its magnitude. The few existing estimates of the rate of recycling of nitrogen and phosphorus by zooplankton tend to suggest that it rarely supplies a significant fraction of photosynthetic demand (Pomeroy, 1970). In most marine ecosystems it is easy to calculate that nekton and other macrofauna cannot possibly be important in recycling (see Pomeroy and Bush, 1959;

Holdgate, 1967). Dugdale (1972) suggested that nekton are major recyclers in upwellings. Whitledge and Packard (1971), comparing the recycling rates of net zooplankton with those of anchovetas in the eastern tropical Pacific, concluded that anchovetas were the principal recyclers where they were abundant. The role of protists was not considered, however. A careful quantitative evaluation of all excretory processes seems desirable.

On the basis of relative respiratory rates, Pomeroy (1970) suggested that most recycling of phosphorus is accomplished by heterotrophic protists other than bacteria. Because of their relatively high concentration of phosphorus and their tendency to store polyphosphate, bacteria usually are net consumers of phosphorus, competing with phytoplankton for the available supply. Because of the difficulty of measuring both excretory and respiratory rates of specific kinds of marine protists, there is no experimental proof that they are in fact the major pathway of recycling in the sea. Microbial respiration exceeds that of net zooplankton and nekton by at least an order of magnitude (Pomeroy and Johannes, 1966; 1968). If excretion is correlated with respiration, microorganisms may be major agents in recycling. So far, however, no one has determined the relative rates of excretion of the various kinds of protists in the sea.

STABILITY, DIVERSITY, AND ESSENTIAL ELEMENTS

The response to limitation by essential elements at the population level was described in a general way by Liebig (1840). Populations may be limited absolutely by the availability of essential elements. At the community level the response to nutrient limitation is succession. The term "succession" is used here to mean a change in species composition of a community. The change usually represents a shift that serves to maintain community stability, but there is no implication here that it is part of an orderly or predictable sequence of events. The stimulus for succession may originate within the population structure, from the abiotic environment, from the impact of human activities, or from any combination of these factors. The organisms that will dominate a community at any given time are those with K_s and μ appropriate to the rate of supply of essential elements. To understand how mineral cycling affects communities, we must remember that community response to limitation is not the same as that of single-species populations.

Stability at the community or ecosystem level can be defined in various ways (Holling, 1973), but, in general terms, stability is the tendency of a community to persist and to return to an equilibrium state after being perturbed. The concept of Webster, Waide, and Patten (this volume) of two distinct components to relative stability, resistance and resilience, fits the observed responses of the four communities discussed here. The most stable of the four is the intertidal salt marsh. With a large reserve of nutrients in the sediment and a tidal energy subsidy to circulate them, the salt marsh is highly resistant to perturbation. It is

also resilient when perturbed. Destruction of a salt marsh usually results in rapid leveling of the sediments by water currents and seeding in of new stands of *Spartina*. There is little succession other than microbial succession. Nearly as stable are the subtidal grass communities. They, too, have nutrient reserves and energy subsidies, they recover from mechanical damage by grazers or storms more slowly than do *Spartina* meadows.

Although coral reefs give the superficial impression of stability, they are rather easily damaged by mechanical insults from storms, predators, and man and are slow to recover. With a constant nutrient and energy input, coral reefs go through a complex and variable succession after disturbance (Connell, 1974). Their resistance is low, and their resilience is slow.

Least stable of the four are planktonic communities. They do not even have a substratum to support and conserve biomass. Nutrient reserves are severely limited, and there is constantly shifting species composition as the community, having little resistance, tracks the shifting nutrient regime. Even in upwellings, deficiencies develop and succession goes on. Stability in planktonic communities is achieved largely by the resilience provided by succession. In this case stability is survival—continuity of the community—and little more. In this sense all extant communities have absolute stability (Webster, Waide, and Patten, this volume) because they have not become extinct. In terms of relative stability, planktonic communities are unstable.

It follows that naturally enriched systems are least sensitive to pollution by nutrients. Enriched communities already have species with K_s and μ appropriate for high concentrations of nutrients, and there may be abiotic sinks to take up excess nutrients. Most sensitive to pollution will be the nutrient-impoverished systems with low K_s and μ and limited storage capacity. Their only recourse in the presence of pollution is succession, sometimes to an almost entirely different kind of community, as, for example, in the coral reefs in Kaneohe Bay (Smith, Chave, and Kam, 1973).

In theoretical ecology, stability of a community is usually related to its species diversity rather than to its supply of essential elements or the way it utilizes them. MacArthur (1955) developed a simple model in which energy flow was constant, nutrient limitation was not considered, and stability was defined as analogous to entropy. This model predicted that stability would always be a function of diversity. May (1971) showed, however, that other models may behave in the opposite way. Elton (1958) postulated that the stability of a community in the face of invasions by new species would be related to the number of branches in a food web. Population interaction theory was made more tractable and applicable to the real world by the treatise of MacArthur and Wilson (1967). They were concerned mostly with higher animals and with population interactions, however. Interactions between populations, communities, and their abiotic environment (except for its insularity) were not considered. Moreover, the effects of abiotic parameters, such as nutrients, light,

and temperature, first show their influence on the lower trophic levels. These, in turn, set the stage for population interactions at the higher levels.

It has also been widely accepted in ecological theory that diversity increases as succession proceeds; this theory is based principally on the orderly, predictable successional sequences described for terrestrial plant communities. In the broader sense of the term, succession is not always orderly or predictable, as, for example, in the changes in phytoplankton communities. When we examine a broad spectrum of communities, it is evident that various factors may influence community diversity. These include population interactions of both the r and K types of MacArthur and Wilson (1967). Underlying these interactions are not only the effects of the populations on each other but also the effects of nutrient availability on the adaptive success of species populations. Also important in many communities is the effect of physical damage from storms, grazers and predators, and human impact, all of which tend to set the successional sequence back to its starting point. By their nature, however, these insults to communities affect only parts or patches at any time, thereby tending to increase diversity by the creation of a successional mosaic.

Both Hutchinson (1959) and Holling (1973) have drawn attention to the presence of an environmental mosaic underlying living communities. They point out that the abiotic environment is different enough from place to place to produce a mosaic of community response. In deciduous forests diversity is in part the result of disturbance and tends to diminish under the most protective management practices (Loucks, 1970). Probably disturbance is a significant cause of diversity in coral reefs, and, as with forests, the successional response is slow in the terms in which we measure time. Therefore, the coral reef we see is a successional mosaic. In planktonic communities adjacent patches of water in different nutrient-limitation states may also produce a successional mosaic that is particularly difficult to visualize since it is seen imperfectly by our sampling techniques. The net diversity of a community, therefore, is the result of population interactions taking place under temporally and spatially varying nutrient regimes and constantly interrupted by physical destruction of portions of the community which will have varying degrees of insularity with respect to repopulation. When seen in this light, the most diverse communities are not necessarily the most stable ones. Rather, diversified communities have moderate resistance and resilience.

Of the four communities we have considered, the intertidal *Spartina* meadows are the most stable and the least diverse. They can hardly be described as an early successional stage; in many cases they have persisted for thousands of years, giving way only to geological changes. Coral reefs are the most diverse of the four, and they seem to have intermediate stability. The planktonic communities are the most unstable, having moderate to high diversity. When we look across this spectrum of communities, it appears that, where essential elements are present in excess of needs, populations of high stability develop. Where nutrients are available, though not in great excess, communities of

intermediate stability develop. Where nutrients are in short supply and where the specific limiting elements may change with time and space, communities are unstable. The relation between stability and species diversity in these communities seems less clear-cut than the relation between stability and the availability of essential elements.

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REFERENCES

Andrews, P., and P. J. leB. Williams, 1971, Heterotrophic Utilization of Dissolved Organic Compounds in the Sea. III. Measurement of the Oxidation Rates and Concentrations of Glucose and Amino Acids in Sea Water, *J. Mar. Biol. Ass. U. K.*, **51**: 111-124.

Atkins, W. R. G., 1945, Autotrophic Flagellates as the Major Constituent of the Oceanic Phytoplankton, *Nature*, **156**: 446-447.

Barber, R. T., R. C. Dugdale, J. MacIsaac, and R. Smith, 1971, Variations in Phytoplankton Growth Associated with the Source and Conditioning of Upwelling Water, *Invest. Pesq.*, **35**: 171-193.

Connell, J. H., 1974, Population Ecology of Coral Reefs, in *The Geology and Biology of Coral Reefs.* O. A. Jones and R. Endean (Eds.), Academic Press, Inc., New York, in preparation.

Davis, C. O., P. J. Harrison, and R. C. Dugdale, 1973, Continuous Culture of Marine Diatoms Under Silicate Limitation. I. Synchronized Life Cycle of *Skeletonema costatum*, *J. Phycol.*, **9**: 175-180.

Dugdale, R. C., 1972, Chemical Oceanography and Primary Productivity in Upwelling Regions, *Geoforum*, **1972**(11): 47-61.

——, 1967, Nutrient Limitation in the Sea: Identification and Significance, *Limnol. Oceanogr.*, **12**: 685-695.

——, and J. J. Goering, 1967, Uptake of New and Regenerated Forms of Nitrogen in Primary Productivity, *Limnol. Oceanogr.*, **12**: 196-206.

Elton, C. S., 1958, *The Ecology of Invasions by Plants and Animals*, Methuen & Co. Ltd., London.

pley, R. W., and J. N. Rogers, 1970, Inorganic Nitrogen Assimilation of *Dilylum brightwellii*, a Marine Plankton Diatom, *J. Phycol.*, **6**: 344-351.

——, J. N. Rogers, J. J. McCarthy, and A. Sournia, 1971, Light/Dark Periodicity in Nitrogen Assimilation of the Marine Phytoplankters *Skeletonema costatum* and *Coccolithus huxleyi* in N-Limited Chemostat Culture, *J. Phycol.*, **7**: 150-154.

Guillard, R. R. L., P. Kilhan, and T. A. Jackson, 1973, Kinetics of Silicon-Limited Growth in the Marine Diatom *Thalassiosira pseudonana* Hasle and Heimdal (=*Cyclotella nana* Hustedt), *J. Phycol.*, **9**: 233-237.

Haines, E. B., 1974, Processes Affecting Production in Georgia Coastal Waters, Ph.D. Thesis, Duke University, Durham, N. C.

Harlin, M. M., 1973, Transfer of Products Between Epiphytic Marine Algae and Host Plants, *J. Phycol.*, **9**: 243-248.

Holdgate, M. W., 1967, The Antarctic Ecosystem, *Phil. Trans. Roy. Soc. London, Ser. B*, **252**: 363-383.

Holling, C. S., 1973, Resilience and Stability of Ecological Systems, *Ann. Rev. Ecol. Systemat.*, **4**: 1-23.

Hutchinson, G. E., 1959, Homage to Santa Rosalia or Why Are There so Many Kinds of Animals? *Amer. Natur.*, **93**: 145-159.

Johannes, R. E., 1974, Department of Zoology, University of Georgia, personal communication.

——, 1967, Ecology of Organic Aggregates in the Vicinity of a Coral Reef, *Limnol. Oceanogr.*, **12**: 189-195,

——, S. L. Coles, and N. T. Kuenzel, 1970, The Role of Zooplankton in the Nutrition of Some Scleractinian Corals, *Limnol. Oceanogr.*, **15**: 579-586.

——, et al., 1972, The Metabolism of Some Coral Reef Communities: A Team Study of Nutrient and Energy Flux at Eniwetok, *Bioscience*, **22**: 541-543.

Lear, D. W., 1965, Bacterial Participation in Phosphate Regeneration in Marine Ecosystems, Ph.D. Thesis, University of Rhode Island, Kingston.

Liebig, J., 1840, *Organic Chemistry and Its Applications to Agriculture and Physiology*, Taylor and Walton, London.

Loucks, O. L., 1970, Evolution of Diversity, Efficiency, and Community Stability, *Amer. Zool.*, **10**: 17-25.

MacArthur, R. H., 1955, Fluctuations of Animal Populations, and a Measure of Community Stability, *Ecology*, **36**: 533-536.

——, and E. O. Wilson, 1967, *The Theory of Island Biogeography*, Princeton University Press, Princeton, N. J.

McRoy, C. P., and R. J. Barsdate, 1970, Phosphate Absorption in Eel Grass, *Limnol. Oceanogr.*, **15**: 6-13.

——, R. J. Barsdate, and M. Nebert, 1972, Phosphorus Cycling in an Eelgrass (*Zostera marina* L.) Ecosystem, *Limnol. Oceanogr.*, **17**: 58-67.

——, and J. J. Goering, 1974, Nutrient Transfer Between the Seagrass *Zostera marina* and Its Epiphytes, *Nature*, **248**: 173-174.

Margalef, R., 1956, Estructura y dinámica de la "purga de mar" en la Ría de Vigo, *Invest. Pesq.*, **5**: 113-114.

Marshall, N., 1968, Observations on Organic Aggregates in the Vicinity of Coral Reefs, *Mar. Biol.*, **2**: 52-53.

——, 1965, Detritus over the Reef and Its Potential Contribution to Adjacent Waters of Eniwetok Atoll, *Ecology*, **46**: 343-344.

May, R. M., 1971, Stability in Multi-Species Community Models, *Math. Biosci.*, **12**: 59-79.

Menzel, D. W., E. M. Hulbert, and J. H. Ryther, 1963, The Effects of Enriching Sargasso Sea Water on the Production and Species Composition of the Phytoplankton, *Deep-Sea Res.*, **10**: 209-219.

Muscatine, L., 1967, Glycerol Excretion by Symbiotic Algae from Corals and *Tridacna* and Its Control by the Host, *Science*, **156**: 516-519.

Odum, H. T., and E. P. Odum, 1955, Trophic Structure and Productivity of a Windward Coral Reef Community on Eniwetok Atoll, *Ecol. Monogr.*, **25**: 291-320.

Parsons, T. R., and M. Takahashi, 1973, Environmental Control of Phytoplankton Cell Size, *Limnol. Oceanogr.*, **18**: 511-515.

Pilson, M. E. Q., and S. B. Betzer, 1973, Phosphorus Flux Across a Coral Reef, *Ecology*, **54**: 581-588.

Pomeroy, L. R., 1974, The Ocean's Food Web, a Changing Paradigm, *Bioscience*, **24**: 499-504.

——, 1970, The Strategy of Mineral Cycling, *Ann. Rev. Ecol. Systemat.*, **1**: 171-190.

——, and F. M. Bush, 1959, Regeneration of Phosphate by Marine Animals, International Oceanography Congress, Preprints, pp. 893-895, American Association for the Advancement of Science, Washington, D. C.

——, and R. E. Johannes, 1968, Occurrence and Respiration of Ultraplankton in the Upper 500 Meters of the Ocean, *Deep-Sea Res.*, **15**: 381-391.

——, and R. E. Johannes, 1966, Total Plankton Respiration, *Deep-Sea Res.*, **13**: 971-973.

——, and E. J. Kuenzler, 1969, Phosphorus Turnover by Coral Reef Animals, in *Symposium on Radioecology*, D. J. Nelson and F. C. Evans (Eds.), Proceedings of the Second National Symposium, Ann Arbor, Mich., May 15-17, 1967, USAEC Report CONF-670503, pp. 474-482, U. S. Atomic Energy Commission, The Ecological Society of America, and The University of Michigan.

——, M. E. Q. Pilson, and W. J. Wiebe, 1974, Tracer Studies of the Exchange of Phosphorus Between Reef Water and Organisms on the Windward Reef of Eniwetok Atoll. Proceedings of the Second International Symposium on Coral Reefs, in preparation.

——, L. R Shenton, R. D. H. Jones, and R. J. Reimold, 1972, Nutrient Flux in Estuaries, in *Nutrients and Eutrophication*, G. E. Likens (Ed.), American Society of Limnology and Oceanography, Special Symposium No. 1, pp. 274-291.

——, E. E. Smith, and C. M. Grant, 1965, The Exchange of Phosphate Between Estuarine Water and Sediment, *Limnol. Oceanogr.*, **10**: 167-172.

Reimold, R. J., 1972, The Movement of Phosphorus Through the Salt Marsh Cord Grass, *Spartina alterniflora* Loisel., *Limnol. Oceanogr.*, **17**: 606-611.

Roy, J. K., and S. V. Smith, 1971, Sedimentation and Coral Reef Development in Turbid Water: Fanning Lagoon, *Pac. Sci.*, **25**: 234-248.

Ryther, J. H., 1969, Photosynthesis and Fish Production in the Sea, *Science*, **166**: 72-76.

Sargent, M. C., and T. S. Austin, 1949, Organic Productivity of an Atoll, *Trans. Amer. Geophys. Union*, **30**: 245-249.

Semina, H. J., 1972, The Size of Phytoplankton Cells in the Pacific Ocean, *Int. Rev. Gesam. Hydrobiol.*, **57**: 177-205.

Sieburth, J. McN., and C. D. Thomas, 1973, Fouling on Eelgrass, *J. Phycol.*, **9**: 46-49.

Smith, S. V., K. E. Chave, and D. T. O. Kam, 1973, *Atlas of Kaneohe Bay: A Reef Ecosystem Under Stress*, Sea Grant Technical Report, TR-72-01, University of Hawaii Sea Grant Program.

Thomas, J. P., 1971, Release of Dissolved Organic Matter from Natural Populations of Marine Phytoplankton, *Mar. Biol.*, **11**: 311-323.

Tukey, H. B., 1970, Leaching of Metabolites from Foliage and Its Implication in the Tropical Rain Forest, in *A Tropical Rain Forest: A Study of Irradiation and Ecology at El Verde, Puerto Rico*, H. T. Odum and R. F. Pigeon (Eds.), USAEC Report TID-24270, pp. H-155—H-160, U. S. Atomic Energy Commission.

Wall, D., and B. Dale, 1970, Living Hystrichosphaerid Dinoflagellate Spores from Bermuda and Puerto Rico, *Micropaleontology*, **16**: 47-58.

Whitledge, T. E., and T. T. Packard, 1971, Nutrient Excretion by Anchovies and Zooplankton in Pacific Upwelling Regions, *Invest. Pesq.*, **35**: 243-250.

Wiebe, W. J., 1974, Department of Microbiology, University of Georgia, personal communication.

Yonge, C. M., 1930, Studies on the Physiology of Corals. I. Feeding Mechanisms and Food, *Sci. Rept. Great Barrier Reef Exped.*, **1**: 14-57.

ERA

DISTRIBUTION OF COPPER AND ZINC IN OYSTERS AND SEDIMENTS FROM THREE COASTAL-PLAIN ESTUARIES

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ABSTRACT

Copper and zinc were analyzed in oysters (*Crassostrea virginica*) from the Newport River estuary, North Carolina, and the Rappahannock River estuary, Virginia. Results indicated that a concentration gradient existed, higher concentrations of metals being found in animals living in fresher waters as was shown previously for oysters in the James, York, and Rappahannock estuaries in Virginia. Absorbed, precipitated–coprecipitated, and organic fractions of copper and zinc in the <63-μm portion of the sediments from the Rappahannock and York rivers and estuaries were estimated from collections made in January 1972 and June 1973. These sediment data are discussed for both estuarine systems and are compared with metal concentrations in oysters. These comparisons indicated that the concentration gradient found in oysters does not appear to be related to the distribution of copper and zinc in the sediments. Alternative explanations for the inverse relationships between concentrations of copper and zinc in oysters and salinity are given.

The transport of trace metals from fresh waters through estuaries and eventually to the oceans has been studied by many investigators over the past several decades. The relative importance of the various mechanisms postulated has changed as hypotheses and analytical techniques have improved. Originally, calculations were mainly based on the solubility products of the metal sulfides or hydroxides. While such calculations are valid for a pure inorganic system, they may not always apply to conditions encountered in nature. Goldberg (1957), for instance, noted the importance of the biosphere in the budgets of metals; subsequently its role in the concentration, transport, and storage of these elements was shown. Turekian and Scott (1967) have shown that the role of inorganic suspended matter cannot be ignored in the metal budget of streams,

and they suggest that simple ion-exchange mechanisms for removing metals from solution to suspended sediments are not sufficient to explain their data but that coprecipitation may be. From the work of these men and others, we conclude that not only the solution chemistries but also the biological and surface chemistries must be considered in the routes and rates of metal transport in estuarine systems.

Scientists concerned with trace metals as environmental contaminants must take into account not only the total natural budgets of the elements but also, and most important, the biologically available fractions due to either natural or man-made inputs. This requires that analytical schemes be developed which will selectively identify the elements in question from individual phases in which they exist. Gibbs (1973) has recently developed a procedure that differentiates between metals in adsorbed, precipitated, and coprecipitated organic solids and crystalline phases. Huggett and Bender (1972) have reported another method yielding metals from inorganic-noncrystalline and organic sediment phases.

Even though the cation-exchange metal concentration for suspended matter is low (Turekian and Scott, 1967; Gibbs, 1973), metals in this form are easily mobilized by low pH. Such filter-feeding organisms as oysters eat suspended particles and pass them through their gut, which has a pH as low as 4 (Wilbur and Yonge, 1966). A portion of the adsorbed metal fraction of the sediment could be mobilized in the gut and made available to the animal. In the upper estuarine portion of the Rappahannock River in Virginia, oysters (*Crassostrea virginica*) have zinc concentrations of about 600 ppm (whole body, wet weight) (Huggett, Bender, and Slone, 1973). A calculation based on a 20-g animal, a pumping rate of up to 575 liters/day (Haven, 1973), a suspended-particle concentration of 30 mg/liter (Turekian and Scott, 1967) with an adsorbed zinc concentration of 2 ppm (this paper), and a 100% stripping efficiency by the animal shows that the animal could have reached its present body burden in about 1 year. Obviously the efficiency of stripping and assimilation by the animal is not 100%. However, it does serve to show that, if the adsorbed fraction is biologically available and even though the adsorbed concentration is small compared to the total concentration on the particle, it cannot be ignored and may be an important factor in bioconcentration by these animals since they may live for 10 years or more.

Characterized in this report are copper and zinc in sediments and oysters from two adjacent rivers and estuaries entering the Chesapeake Bay. One system, the Rappahannock River, is pristine in nature; the other, the York, receives acid mine drainage. The relationships between concentrations of metals in the sediments and those in the animals were investigated in an effort to define the biologically available fractions. Also reported here is research to confirm a previously demonstrated natural metal concentration gradient for oysters living in waters of different salinity.

METHODS AND PROCEDURES

Oysters

Samples of oysters, *Crassostrea virginica*, were collected by various standard methods (dredge, rake, tongs), depending on water depth and bottom type from the Rappahannock and the York river estuaries in Virginia and from the Newport River estuary and Bogue Sound in North Carolina. All samples were analyzed by atomic absorption spectrophotometry; however samples analyzed by the Virginia Institute of Marine Science (VIMS) were oxidized by digestion with concentrated acid and those prepared at the Atlantic Estuarine Fisheries Center (AEFC) were oxidized in a high-temperature oven. Specific preparative methods at each institution is given by Huggett and Bender (1973) and Cross and Brooks (1973).

Sediments

Bottom sediments were collected from the channels of the Rappahannock River in 1972 and 1973 and from the York River in 1972. The samples were obtained with a Ponar grab sampler. The top 1 cm of undisturbed sediments was extracted from each sampler. The samples were stored in plastic bags on ice until returned to the laboratory (<8 hr), where the samples were immediately wet sieved (U. S. standard sieve, No. 230, 63-μm openings). Subsequent resieving through the stainless-steel sieve resulted in no discernable increase of metal concentrations; therefore contamination from this source was negligible. The <63-μm portion of each sample was air dried and saved for analysis. Since the concentration of the precipitated–coprecipitated and adsorbed fractions of the metals must be a function of the surface area per unit mass of the sediment grains and since the bottom sediments are not uniform in size distribution, this procedure was necessary to help normalize the samples.

Most samples were extracted in three ways to differentiate among the various biologically available fractions: adsorbed metals, precipitated–coprecipitated metals, and organic metals. Metals bound within the crystalline matrixes of minerals were considered unavailable to the biological community and were not measured. The adsorbed metals were obtained by extracting the sediments with 1.0*N* $MgCl_2$ (Gibbs, 1973). The precipitated–coprecipitated and adsorbed metals were extracted with 0.1*N* HCl, and the total noncrystalline metals were extracted with concentrated HNO_3 (Huggett and Bender, 1972). Analyses of replicate samples showed the nitric acid extraction to have a precision of ±7% for copper and ±5% for zinc; that of the hydrochloric acid procedure was ±4% for both copper and zinc. These three extraction procedures allow a quantitative estimate of those metals adsorbed, coated (precipitated or coprecipitated), and organically bound in the bottom sediments. Obviously the reagents mobilize some metals from nonintended phases, but these are

considered to be negligible on the basis of replicate analyses and extraction efficiencies that are in turn based on reextractions of the same sample.

RESULTS

Oysters

In 1971 a survey of metal levels in oysters from the southern Chesapeake Bay ...cated that a natural concentration gradient exists which is a function of, or is ...sured by, salinity (Huggett, Bender, and Slone, 1973). Animals living in fresher waters consistently contained more copper and zinc than those from a more saline environment (Fig. 1). This finding had not been shown previously and has not been tested since. It is extremely important, however, in light of environmental problems associated with anthropogenic additions of metals to the environment that effects of environmental variables on concentrations of metals in marine organisms be understood.

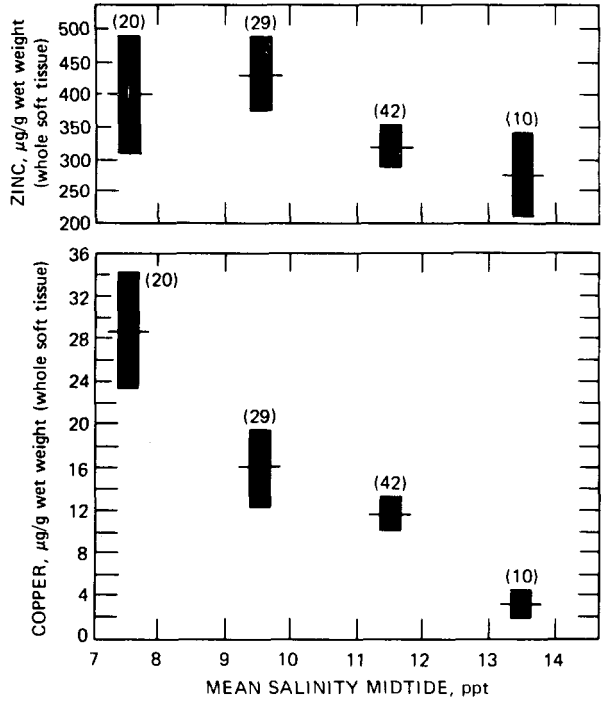

Fig. 1 Mean concentrations ∓2 standard errors of copper and zinc in oysters collected from the Rappahannock River estuary. The numbers in parentheses represent the individuals analyzed at each station.

To confirm earlier findings of Huggett, Bender, and Slone (1973) and Huggett and Bender (1973) that concentrations of copper and zinc decrease in oysters with increasing salinity and to compare analytical techniques between our two laboratories, we collected 50 oysters in January 1974 from each of two oyster beds in the Newport River estuary and one in Bogue Sound, N. C. One-half of the oysters from each of the three beds was sent to VIMS, and the remaining oysters were retained at AEFC and held in the same manner as the samples that were sent to VIMS. On the same day the oysters were opened by identical methods at each laboratory and then analyzed for concentrations of copper and zinc.

Results of these analyses (Fig. 2) show that concentrations of both copper and zinc decrease with increasing salinity in the Newport River estuarine system as described previously for the Rappahannock River estuary (Fig. 1), although absolute values are considerably lower in the Newport River estuarine system than in the Rappahannock. Similar relationships between concentrations of copper and zinc and salinity have been reported for the James and York river estuaries (Huggett, Bender, and Slone, 1973). In addition, statistical comparisons between concentrations of copper and zinc obtained at each laboratory were not significantly different at the 99.9% confidence level; thus the data from both laboratories are polled in Fig. 2.

Sediments

The intent of this study was to delineate any trends in the sediment-metals concentrations which could be explained by natural estuarine variables, such as salinity and pH. Once these trends were established, they could be compared to the concentration trends found in the biota. The sediment results are given as moving averages between three adjacent stations in Figs. 3 to 7. This method was used because replicate sediment samples were not taken at each site, and no estimate of variability of a single station could be obtained. By averaging adjacent stations (moving averages), a better approximation is gained. This type of presentation does not change the trends but rather smooths out the data (Lewis, 1963).

Rappahannock River and Estuary

Copper

The precipitated–coprecipitated metal concentrations in sediments (Fig. 3) from both sampling periods are almost identical from the mouth of the estuary up to the salt water–freshwater interface (normally between 55 and 70 km). The levels vary between 10 and 15 ppm from the mouth to 55 km. From 55 to 100 km from the mouth, the 1972 samples show an increase of approximately 100% over downstream samples. The 1973 samples show such an increase

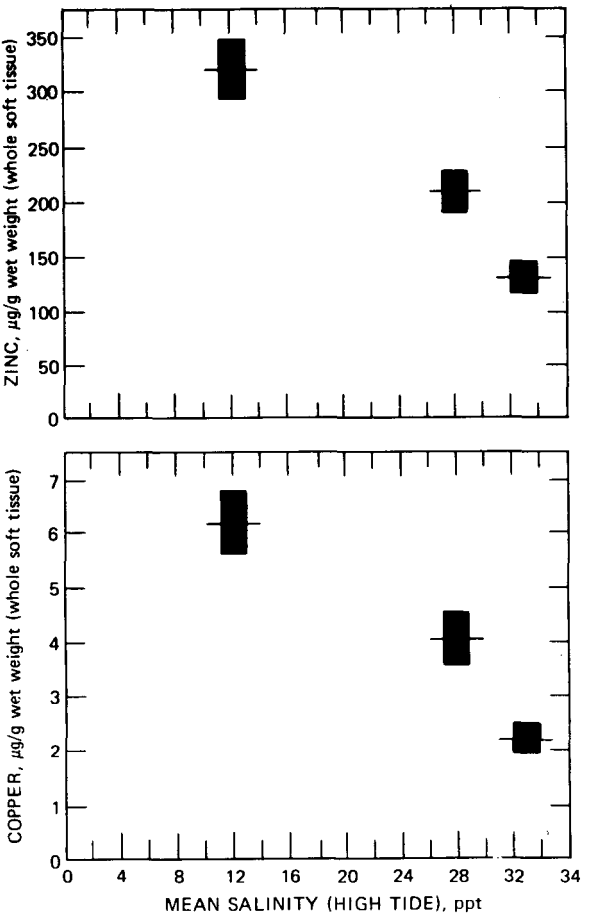

Fig. 2 Mean concentrations ∓2 standard errors of copper and zinc in oysters collected from Newport River estuary (12 and 28‰) and Bogue Sound (33‰). Each set of values represents the analysis of 50 individuals.

tween 70 and 88 km from the mouth. The reason for these increases is unclear, but two possibilities arise:

1. The sorption reactions are controlled by salinity.

2. They result from sedimentation due to the flocculation at the turbidity maximum which occurs in this segment of the river (Nichols, 1974).

In addition, the organic copper concentrations (Fig. 3) are nearly constant (10 ppm) throughout the entire river and estuary sampled.

The adsorbed phase, as indicated by magnesium chloride extraction, shows that in the estuary the adsorbed fraction of copper is low compared to the other

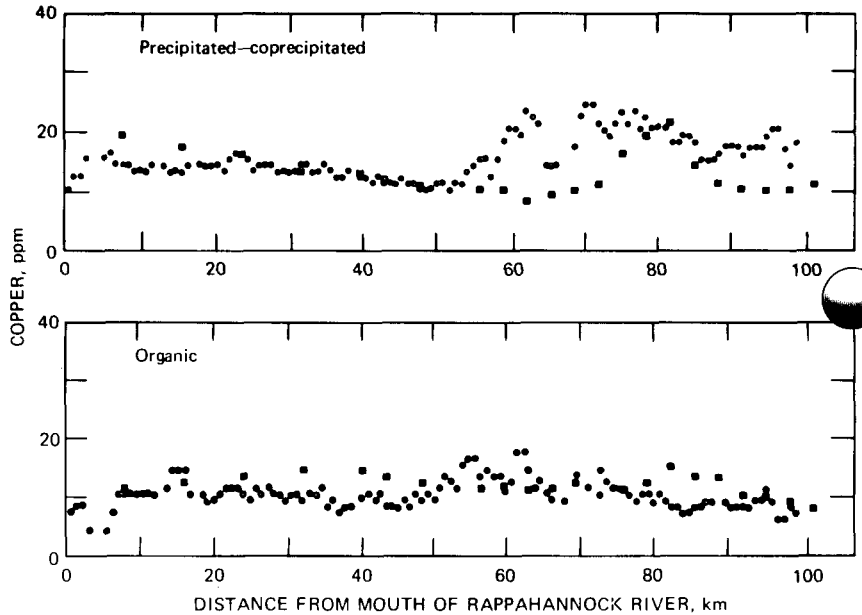

Fig. 3 Moving averages (3) of concentrations of precipitated–coprecipitated and organic copper in the ≤63-μm fraction of sediments from the Rappahannock River and estuary collected in January 1972 (•) and June 1973 (▪). Zero kilometers represents the mouth of the estuary.

two fractions (Fig. 4). Because magnesium is an abundant element in seawater, estuarine sediments have already been "stripped" of some absorbed metallic ions. The variations in adsorbed concentrations in the freshwater portions (55 km upstream) are probably due to either surface area or mineralogical changes in the sediments as a result of sedimentation parameters (particle density, flocculation, current velocity, etc.). This is somewhat confirmed by the lower concentrations found in samples taken in areas of scour in the river. The increase in copper toward the mouth of the estuary is probably due to particle-size differences, smaller particles being deposited downstream.

Zinc

The precipitated–coprecipitated zinc concentrations increased toward the mouth of the estuary while the organic phases decreased (Fig. 5). The range of concentrations was approximately the same for both sampling periods.

To our knowledge there are no man-made sources of zinc in the Rappahannock River. The three-fold increase in precipitated–coprecipitated zinc from freshwater to the estuary mouth may be explained, in part, by the particle sizes of the bottom sediments. Under normal conditions the carrying

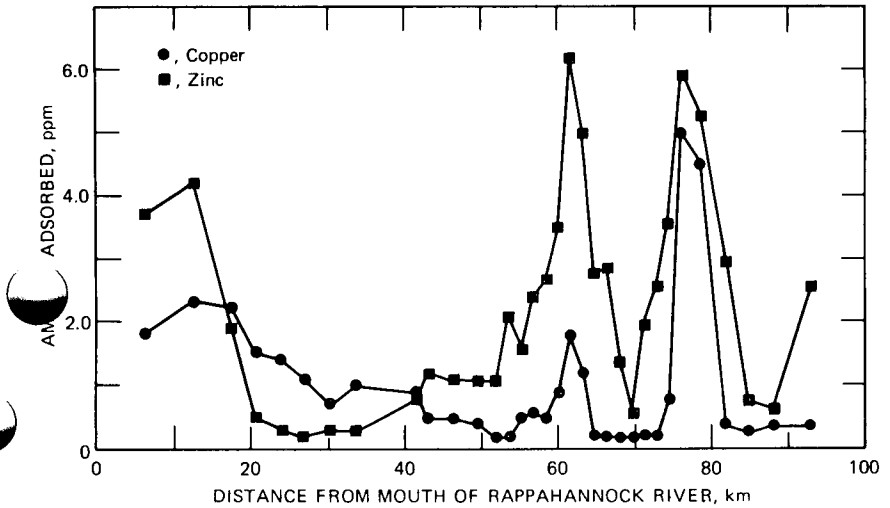

Fig. 4 Moving averages (3) of concentrations of adsorbed copper and zinc in the ≤63-μm fraction of sediments from the Rappahannock River and estuary collected in January 1972. Zero kilometers represents the mouth of the estuary.

capacity of an estuary for suspended sediments decreases with increasing salinity. This should result in the downstream deposition of finer grained sediments. If the concentrating mechanism for inorganic zinc is dependent on sediment surface area, then the increase may be expected.

The decrease in organic zinc may be a result of one or more of the following:

1. Zinc's being bound inorganically and hence made unavailable to be bound organically.
2. A decreasing concentration of organic material toward the mouth of the estuary.

The decreasing trend follows that found for zinc in oysters from this stream (Huggett, Bender, and Slone, 1973).

The adsorbed fraction follows the same trend as that of copper and is generally slightly higher in concentration, suggesting this element to be more favored in adsorption reactions or more abundant in the incoming waters. (Fig. 4).

York River

The York River is situated between the James and Rappahannock rivers and is unique in that it bifurcates approximately 45 km upstream from its mouth, the Pamunkey River being the southern tributary and the Mattaponi River the

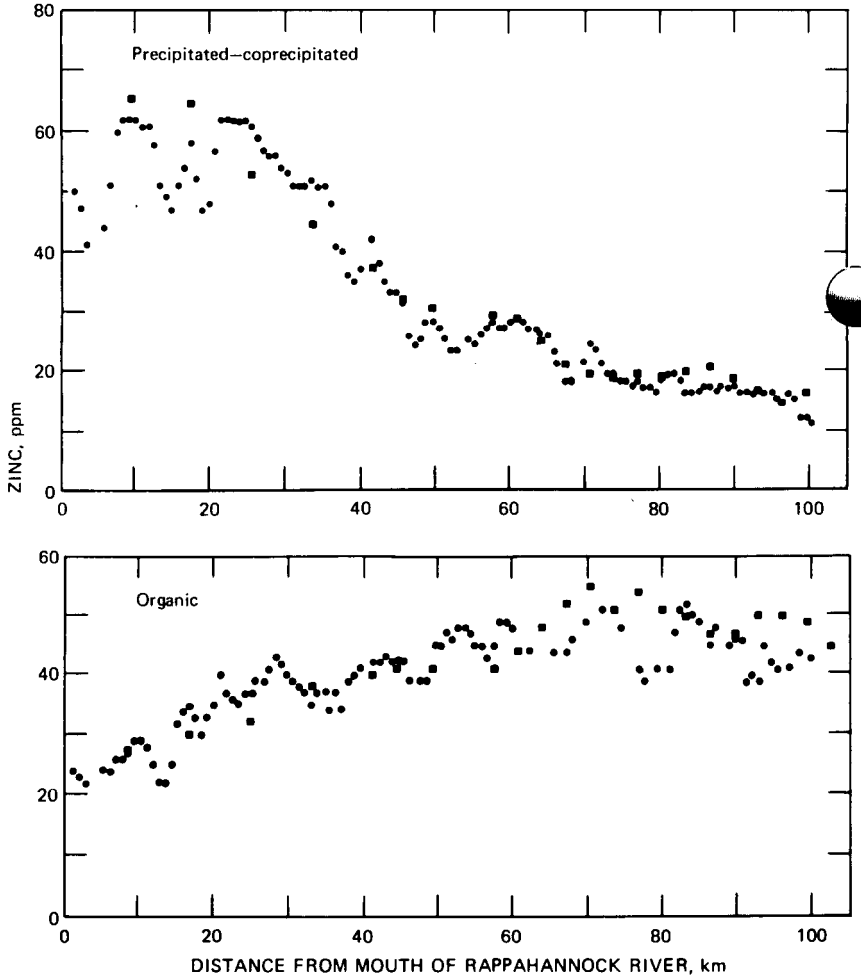

Fig. 5 Moving averages (3) of concentrations of precipitated–coprecipitated and organic zinc in the ≤63-μm fraction of sediments from the Rappahannock River and estuary collected in January 1973 (•) and June 1973 (▪). Zero kilometers represents the mouth of the estuary.

northern tributary. Under normal conditions the freshwater–salt water interface is located approximately 7.5 km above the bifurcation point. The two tributaries are almost identical in size, drainage basin, and bordering vegetation. One exception, however, is that the Pamunkey River receives mine drainage from abandoned pyrite mines that were operated from the middle of the last century up until the early 1900s. This drainage enters the stream approximately 130 km

above the bifurcation point. As will be shown, this abandoned mine has affected the metals budgets of the stream and that of the parent river.

Copper

The distribution of precipitated–coprecipitated copper in the York riverine and estuarine sediments does not resemble that in the Rappahannock River (Fig. 6). There appears to be an unnatural source of copper between 7.5 and

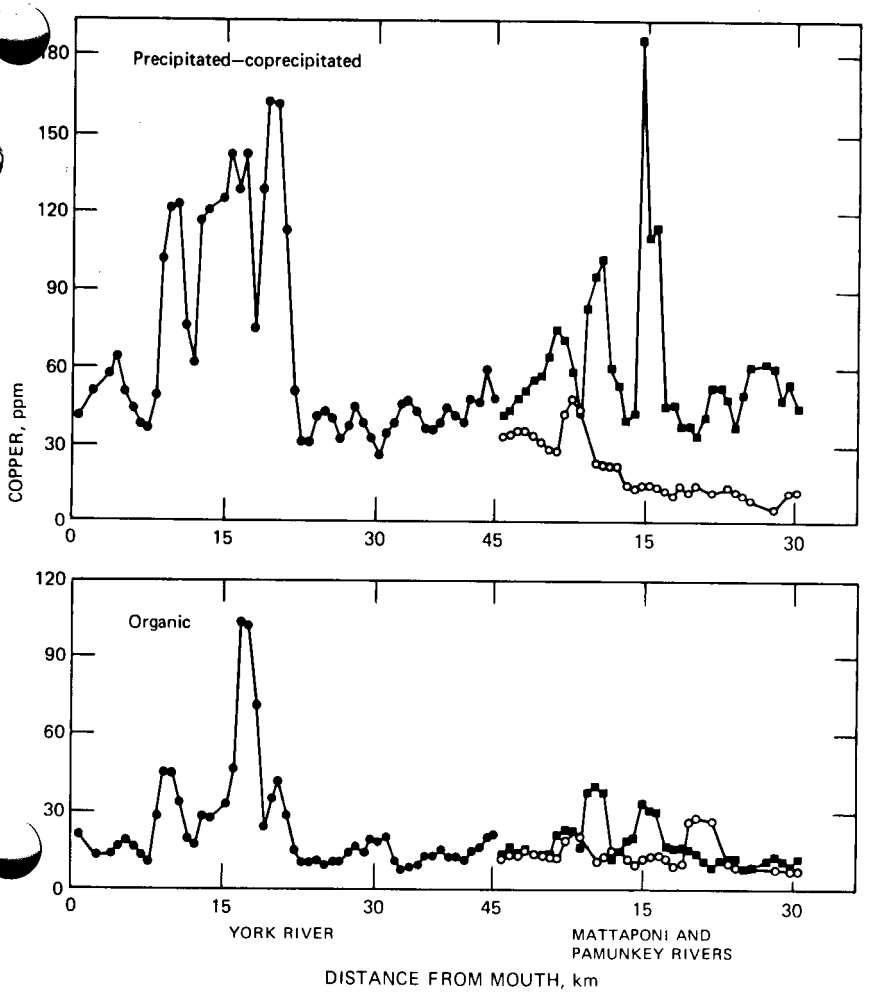

Fig. 6 Moving averages (3) of concentrations of precipitated–coprecipitated and organic copper in the ⩽63-μm fraction of sediments from the York River and estuary collected in June 1973: •, York River. ○, Mattaponi River. ▪, Pamunkey River.

22 km from the mouth. At this segment of the river, the concentrations are three to four times higher than those on either side. Within this area there are at least two possible sources for this metal. One source is a primary sewage outfall located approximately 6 km upstream, and the other is the Naval Weapons Station located approximately 16 km upstream. In addition, the effect of the abandoned mines draining into the Pamunkey River is evident. The concentrations are 100 to 200% higher in this stream relative to its counterpart, the Mattaponi River.

The organic copper concentrations reflect the unnatural input into the lower river but otherwise do not appear greatly different than the Rappahannock River sediments (Fig. 6). The levels in the Mattaponi and Pamunkey rivers are similar, indicating that the inorganic copper from mine drainage is not greatly manifested in the organic phases.

Zinc

The precipitated–coprecipitated zinc levels in this system are greatly elevated over those of the Rappahannock (Fig. 7). This is apparently due to the input from the previously mentioned abandoned mines. The concentrations decrease in a linear manner from the most upstream station on the Pamunkey River to the mouth of the York River. The lower stations on the York River have nearly the same concentrations as do those at the mouth of the Rappahannock (40 to 60 ppm). The levels in the Mattaponi River increase downstream as did those in the unpolluted Rappahannock.

The organic zinc concentrations are similar to those found in the Rappahannock except that the Pamunkey levels are apparently being affected by the mine drainage (Fig. 7). The general trend is a decrease in organic zinc with increasing salinity to about 10 ppt (32 km upstream) and then steady to the mouth of the York River.

Discussion

A concentration gradient exists in the oyster samples from the Newport River estuarine system, with progressively higher concentrations of either copper or zinc being found in progressively fresher waters. This gradient, which also has been shown in the Rappahannock and York estuaries, suggests that a natural phenomenon is responsible. One explanation might be that those animals in fresher waters are closer to the source, if the metals are supplied from the natural weathering of rocks. Thus a gradient should exist for concentrations of copper and zinc in solution in the river waters similar to that found in oysters. The efforts at VIMS to analyze the copper and zinc content of Rappahannock River water, passed through 0.45-μm membrane filters, have not been satisfying. Two methods were tried, each with limited success: aniodic stripping voltametry and organic chelation and extraction. Each has the limitation of matrix

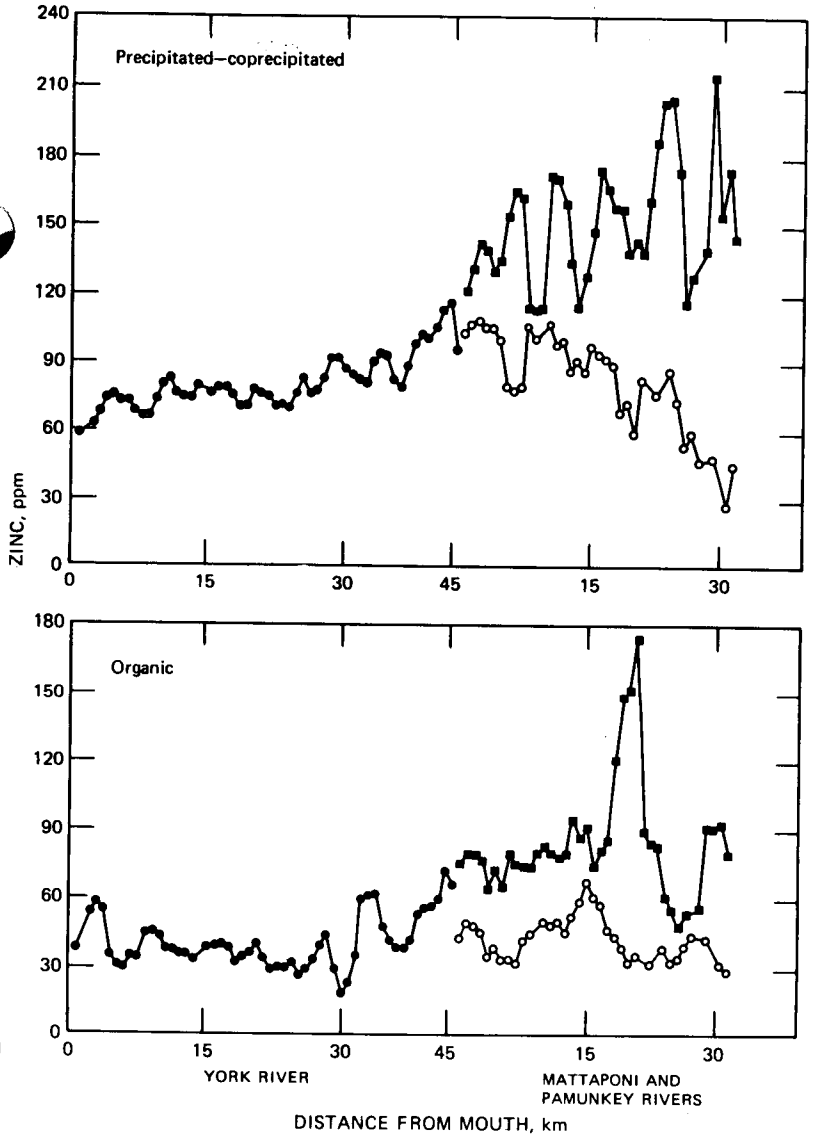

Fig. 7 Moving averages (3) of concentrations of precipitated–coprecipitated and organic zinc in the ⩽63-μm fraction of sediments from the York River and estuary collected in June 1973: ●, York River. ○, Mattaponi River. ■, Pamunkey River.

interferences as salinities change. Even so the limited data obtained do not show a concentration gradient for copper, cadmium, or zinc. Recently Cronin et al. (1974) reported on metal–water data from samples collected in the upper Chesapeake Bay. As in the case of the Rappahannock River samples, no consistent metal trends were shown in these samples as a function of salinity. Similarly, Cross, Duke, and Willis (1970) report that concentrations of zinc in unfiltered water samples were constant throughout the Newport estuary, North Carolina. These data imply that the concentration gradients found in the oysters are not a result of a similar gradient in the water.

Another possible explanation is that sediments serve as a source of copper and zinc to oysters, and thus sediments may control directly the levels of metals found in these filter-feeding organisms. The sediment data presented in this paper, however, tend to dispute this hypothesis. Even though the sediments were extracted by several techniques and concentration trends were noted, they were not similar to those found in the oysters except for organic zinc in sediments from the Rappahannock estuary. Concentrations of copper in this fraction, however, remained constant throughout the estuary. If this fraction was controlling directly the availability of copper and zinc to the oysters, we would expect both metals to decrease in sediments with salinity, as is shown for oysters.

The precipitated–coprecipitated zinc concentrations in the Rappahannock River sediments decreased with decreasing salinity, and the same phase of copper remained relatively constant in the estuarine portion of the river. But the copper and zinc concentration in oysters from the same river increased with decreasing salinity. Comparison of all the various sediment metal fractions with the metals in oysters in this manner showed no consistent relationships. Cronin et al. (1974) conclude that trace-metal concentrations in oysters do not depend on the concentration of the metals on suspended material. This confirms our findings if the assumption is made that suspended material is similar in nature and composition to the fine surface sediments at any point in an estuarine system.

If gradients in concentrations of dissolved and particulate copper and zinc are eliminated as possible factors controlling the inverse relationship between salinity and concentrations of copper and zinc in oysters, we are left with the following explanations:

1. In his attempt to explain the high concentrations of zinc found in oysters relative to other marine organisms, Wolfe (1970) postulated that zinc may be assimilated from the environment along with calcium by a relatively nonspecific ion-transport mechanism to satisfy the organisms' large calcium requirements for shell deposition. Because concentrations of calcium in seawater are dependent on salinity, oysters may have to extract calcium from seawater more efficiently at lower salinities and may also concentrate greater quantities of other inorganic cations such as copper and zinc during this process of maintaining adequate calcium reserves for shell deposition (Wolfe and Stillings, 1975).

2. At higher salinities the more abundant cations in seawater (magnesium, calcium, etc.) may be outcompeting the less abundant metals such as copper or zinc for binding sites in the soft tissues. Although copper and zinc form more stable chelates with proteins than do magnesium, manganese, or calcium (Pringle et al., 1968), the greater concentrations of these less abundant ions at higher salinities may overwhelm this relationship. Romeril (1971) showed, for example, that the uptake of ^{65}Zn in the oyster, *Ostrea edulis,* was decreased by the addition of iron and cobalt.

3. Another explanation for the observed metal concentration gradients in oysters could be that chelation or complexation of the metals in solution by natural organics, such as fulvic acids, make the elements more available to oysters. These humic substances are believed to be derived from decaying plant materials on land and are leached and washed away by surface or subsurface waters, eventually reaching the estuaries (Swanson and Palacas, 1965). This means that the concentrations of fulvic acids should decrease with increasing salinity (because of dilution) as do the levels of zinc and copper in the oysters. Metal complexes and chelates of humic substances have been found and studied by many investigators (Jenne, 1968; Shapiro, 1964), and an excellent review on the subject was written by Schnitzer and Khan (1972). One logical mode of uptake of the organometals by the oysters would be by direct partitioning of the substances from solution into the body mucus and then into the tissues. Without further research, however, none of these three hypotheses can be proved.

This discussion illustrates our lack of knowledge of the environmental processes controlling the availability of trace metals to estuarine biota. Yet this aspect of estuarine biogeochemistry is receiving very little effort at the present time. This is an unfortunate situation because our estuarine systems are being subjected to environmental modifications (dredging, filling, etc.) and anthropogenic inputs of contaminants.

Without adequate basic information on bioavailability of metals to organisms, the consequences of increased releases of metals into estuarine systems cannot be predicted by management agencies, and hence the proper management of estuarine ecosystems is impossible.

ACKNOWLEDGMENTS

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REFERENCES

Cronin, L. E., D. W. Pritchard, J. R. Schubel, and J. A. Sherk, 1974, Metals in Baltimore Harbor and Upper Chesapeake Bay and Their Accumulation by Oysters, Joint Report by Chesapeake Bay Institute, The Johns Hopkins University, and Chesapeake Biological Laboratory, University of Maryland.

Cross, F. A., and J. H. Brooks, 1973, Concentrations of Manganese, Iron, and Zinc in Juveniles of Five Estuarine-Dependent Fishes, in *Radionuclides in Ecosystems,* Proceedings of the Third National Symposium on Radioecology, May 10–12, 1971, D. J. Nelson (Ed.), USAEC Report CONF-710501-P2, pp. 769-775, Oak Ridge National Laboratory.

——, T. W. Duke, and J. N. Willis, 1970, Biogeochemistry of Trace Elements in a Coa Plain Estuary: Distribution of Manganese, Iron, and Zinc in Sediments, Water, and Polychaetous Worms, *Chesapeake Sci.,* **11**(4): 221-234.

Gibbs, R. J., 1973, Mechanisms of Trace-Metal Transport in Rivers, *Science,* **180**: 71.

Goldberg, E. D., 1957, Biochemistry of Trace Metals, *Geol. Soc. Amer. Mem.,* **67**(1): 345-358.

Haven, D. S., 1973, Virgina Institute of Marine Science, personal communication.

Huggett, R. J., and M. E. Bender, 1973, Effects of Tropical Storm Agnes on the Trace Metals, Cadmium, Copper, and Zinc in the Eastern Oyster, Final Report to the Shellfish Sanitation Group of the Food and Drug Administration, Washington, D. C.

——, and M. E. Bender, 1972, Sediment–Heavy Metal Relationships in Rappahannock River Sediments, Annual Report, 1971–1972, Chesapeake Research Consortium, Inc., The Johns Hopkins University, Baltimore, Md.

——, M. E. Bender, and H. D. Slone, 1973, Utilizing Metal Concentration Relationships in the Eastern Oyster (*Crassostrea virginica*) to Detect Heavy-Metal Pollution, *Water Res.,* 7: 451-460.

Jenne, E. A., 1968, Controls on Mn, Fe, Ni, Cu, and Zn Concentrations in Soils and Water: The Significant Role of Hydrous Magnesium on Iron Oxides, in *Trace Inorganics in Water,* American Chemical Society, Advances in Chemistry Series 73.

Lewis, E. E., 1963, *Methods of Statistical Analysis in Economics and Business,* Houghton-Mifflin Company, Boston.

Nichols, M., 1974, personal communication.

Pringle, B. H., D. E. Hissong, E. L. Katz, and S. T. Mulawka, 1968, Trace-Metal Accumulation by Estuarine Mollusks, *J. Sanit. Eng. Div., Amer. Soc. Civil Eng.,* 94(SA3): 455-475.

Romeril, M. G., 1971, The Uptake and Distribution of ^{65}Zn in Oysters, *Mar. Biol.,* 9: 347-354.

Schnitzer, M., and S. U. Khan, 1972, *Humic Substances in the Environment,* Marcel Dekker, Inc., New York.

Shapiro, J., 1964, Effects of Yellow Organic Acids on Iron and Other Metals in Water, *J. Amer. Water Works Ass.,* **56**: 1062-1082.

Swanson, V. E., and J. G. Palacas, 1965, *Humate in Coastal Sands of Northwest Flori* U. S. Geological Survey, Bulletin No. 12 H-B, pp. B1-B27.

Turekian, K. K., and M. R. Scott, 1967, Concentrations of Cr, Ag, Mo, Ni, Co, and Mn in Suspended Material in Streams, *Environ. Sci. Technol.,* **1**: 940.

Wilbur, K. M., and C. M. Yonge, 1966, *Physiology of Mollusks,* Academic Press, Inc., New York.

Wolfe, D. A., 1970, Zinc Enzymes in *Crassostrea virginica, J. Fish. Res. Board Can.,* **27**(1): 59-69.

——, and B. R. Stillings, 1975, Zinc in Aquatic Organisms, in National Academy of Science Report on Zinc (in press).

EFFECTS OF ENVIRONMENTAL LEVELS OF MERCURY AND CADMIUM ON RATES OF METAL UPTAKE AND GROWTH PHYSIOLOGY OF SELECTED GENERA OF MARINE PHYTOPLANKTON

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ABSTRACT

Rates of ^{203}Hg and ^{109}Cd uptake by algae were found to be dependent on concentrations of the metals in growth media, length of exposure to the metals, and algal genus. Concentrations of ^{203}Hg above 40 ng/liter did not significantly increase rates of uptake. Rates of ^{109}Cd uptake were one to two orders of magnitude lower than ^{203}Hg and were directly proportional to the concentration of metal added between 20 to 80 ng/liter. Populations of *Nitzschia closterium* had higher rates of uptake for both metals than either *Carteria* sp. or *Dunaliella tertiolecta*. Concentrations of mercuric ion between 30 and 350 ng/liter significantly depressed algal growth. Lowered cell-division rates were accompanied by decreases in total cellular nitrogen and lipid and increases in carbon and mercury concentrations.

Phytoplankton represent a critical component within an ecosystem in governing the transfer of energy and materials, such as heavy metals. Specifically, phytoplankton are known to concentrate metals in amounts that can be toxic and, with certain metals, in excess of their physiological requirements [e.g., copper (Mandelli, 1969)]. As a result of such uptake by phytoplankton, some metals are increasingly concentrated at higher trophic levels and may eventually be returned to man. If physiological processes are altered, metal uptake may also serve to decrease general productivity.

The toxicity of relatively high concentrations of mercury and cadmium complexed with various organic and inorganic compounds was studied among several genera of phytoplankton. Harriss, White, and Macfarlane (1970) determined that, compared with phenylmercuric acetate, methylmercury dicyandiamide, and N-methylmercuric tetrahydromethanohexachlorophthalimide, diphenylmercury was least toxic. Furthermore, at 1 ppb or less, productivity and

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growth were reduced by exposure to any of these compounds, while a 50-ppb addition totally inhibited carbon assimilation. Mercury was reported to inhibit the rate of cellular division significantly more than exposure to the same concentrations of copper, lead, cadmium, or DDT (Hannan and Patouillet, 1972). Hannan and Patouillet (1972) also found that recovery from exposure to mercury was slower than recovery from exposure to the other noxious metals. Although relatively high levels of mercury or mercury compounds have been used in most investigations, Nuzzi (1972) found that phenylmercuric acetate inhibited phytoplankton growth at 60 ng/liter. Furthermore, Knauer and Martin (1972) reported enhancement in photosynthetic activity up to concentrations of 1 ng/liter by inorganic Hg ($HgCl_2$) but a reduction in activity when cells were exposed to organic Hg (CH_3Hg^+) at a concentration of 0.05 ng/liter.

This study was performed to determine the rates of mercury and cadmium uptake by selected unicellular algae, amounts of metal concentrated per unit algal biomass, and the effects of such metal uptake on general algal physiology. The work was conducted specifically to relate both uptake rates and biological effects of mercury and cadmium to the levels presently occurring in the estuarine and coastal waters of Georgia (Windom, 1972; Windom and Smith, 1972).

MATERIALS AND METHODS

Populations of the same age, having the same biomass, and of generally similar physiological condition were used in all experiments involving uptake rates and biological effects. Primary stocks were created by transferring from laboratory cultures, inoculating at a cellular biomass of 1.06×10^{-3} mg/ml, and growing under standard conditions (described below) for 96 hr. Cultures to be used for either isotope inoculation or growth study were then subcultured from these stocks. Media was prepared by adding nutrients to a seawater base (Rice, 1953) drawn from the same seawater stock. Algal dry weights were determined according to the formula of Strickland (1966), with cell volumes of 1.017, 0.407, and 0.115 $mm^3 \times 10^{-6}$ for *Carteria*, *Dunaliella*, and *Nitzschia*, respectively, based on cell counts taken at each subsampling period.

All cultures of primary stocks were freed of bacteria and grown axenically as previously described by Sick (1975). Tests for bacterial contamination were periodically made using nutrient agar plates incubated at 20°C for 48 hr.

Isotope uptake rates were determined by inoculating cultures with ^{203}Hg (added as $^{203}HgCl_2$ with a specific activity of 4.85 mCi/mg) or ^{109}Cd (added as $^{109}CdCl_2$ with a specific activity of 2600 mCi/mg), filtering the cells onto a Millipore membrane filter pad, and assaying radioactivity of filters and filtrate using a sodium iodide well crystal and scaler. The ^{203}Hg and ^{109}Cd were added to respective culture flasks at concentrations of 20, 40, 60, and 80 ng/liter. Subsamples of 2 ml each were withdrawn and filtered onto 25-mm Millipore

membrane filter pads. Adsorption of both isotopes was not significantly higher on membrane compared to glass-fiber filter pads.

To compare the effects of mercury additions on phytoplankton growth and associated changes in fundamental cellular chemistry, including mercury content, we grew representative populations of each genera of algae at mercury concentrations (added as $HgCl_2$) of 20, 40, 60, 100, 150, 200, 250, 300, and 350 ng Hg/liter. These concentrations are representative of the range in Georgia coastal waters (Windom, 1972). In addition, the cellular biomass at initial inoculation was approximately 4×10^{-1} mg/liter for each species, a level typical of environmental concentrations. Cultures were grown for 5 days in 1-liter flasks that contained 1 liter of culture medium and were placed in a culture chamber with a temperature-controlled water bath.

Population growth at each concentration of metal was compared to cell growth in a culture medium having ambient environmental levels of mercury (20 ng/liter). An algal growth constant (k) for this control was calculated from

$$C_2 = C_1 e^{k(t_2 - t_1)}$$

where C_1 and C_2 are cell concentrations (cells/milliliter) at times t_1 and t_2. An algal–metal effect coefficient (a) for given metal concentrations was then calculated:

$$C_2 = C_1 e^{(k-a)(t_2 - t_1)}$$

Therefore, using appropriate values of k and a, we calculated average cell concentrations at any mercury concentration at the given time interval $t_2 - t_1$:

$$C = \frac{C_1 e^{(k-a)(t_2 - t_1)}}{(t_2 - t_1)(k - a)}$$

(see Fig. 3). All population counts were determined with a Coulter counter, model ZBI, fitted with a 75-μ aperture tube.

For analyses of cellular constituents, the cultures were centrifuged in a Sorvall continuous-flow centrifuge. The algae were freeze-dried and divided into subsamples for respective chemical analyses.

Concentrations of mercuric ion were determined by the chemical reduction method using a double-beam cold-vapor mercury analyzer (Windom, Taylor, and Stickney, 1973). This technique has a precision of ±15% of the stated value. Total carbon and nitrogen values were determined with an F and M, CHN analyzer, model 185. Total lipid fractions were ascertained by a dry-weight difference following an ether–chloroform extraction (Sick, 1974).

RESULTS

In general, ^{203}Hg uptake was dependent on concentration of metal in growth media, genus of algae concerned, and the time of exposure to given metal concentrations (Figs. 1 and 2). During the first hour, ^{203}Hg uptake decreased rapidly among all three genera and over all concentrations of metals. Increases in the rate of ^{203}Hg uptake were greatest between metal additions of 20 and 40 ng/liter. *Nitzschia closterium* had the highest average ^{203}Hg uptake rate over time (Fig. 2). *Carteria* sp. also had relatively high average rates of uptake, bu 80 ng/liter there was no significant difference in rates between *Nitzschia* a *Carteria*. Rates of uptake by *Dunaliella* were significantly lower than those for

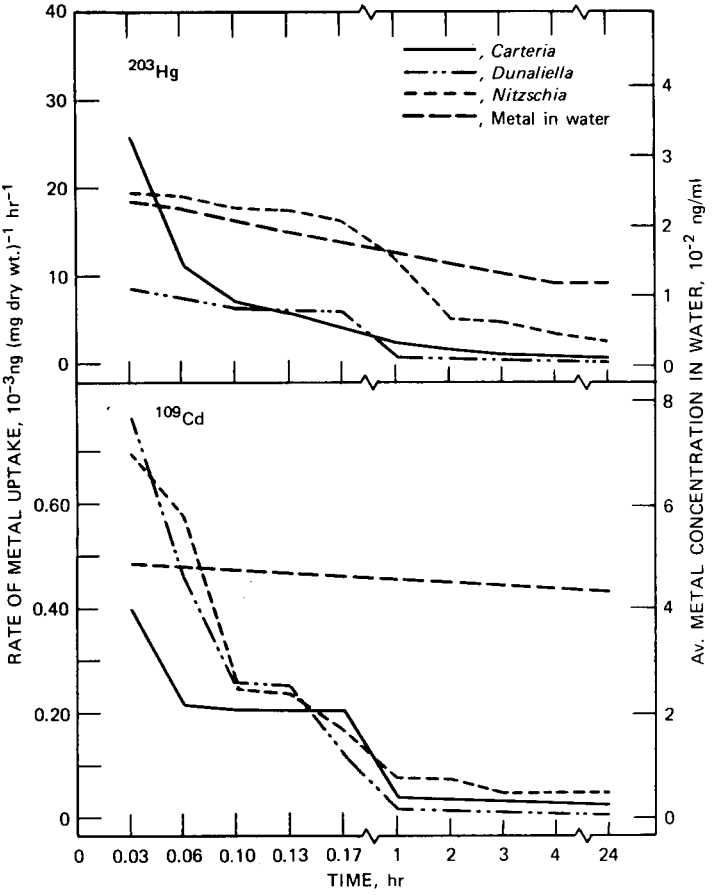

Fig. 1 Uptake rates and metal concentrations in growth media for algal cultures inoculated with metal concentrations at 40 ng/liter. Values are means for three replications.

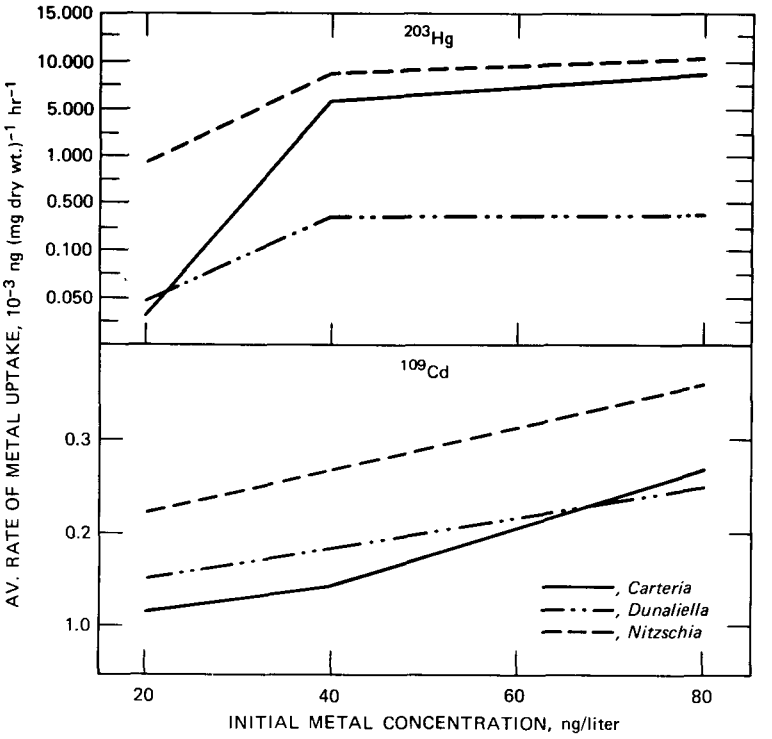

Fig. 2 Average rate of metal uptake over a 24-hr period. Values are means for three replications.

Nitzschia at all metal concentrations and were significantly lower than *Carteria* at 40 and 80 ng/liter. Analysis of variance, using a factorial design, revealed that differences among species and time after inoculation were significant at the 1% level but that differences among concentrations of ^{203}Hg added were only significant at 10% (F tests).

The uptake of ^{109}Cd was more constant but at lower rates than ^{203}Hg (Figs. 1 and 2). Unlike ^{203}Hg, ^{109}Cd uptake increased significantly over all concentrations tested ($P < 1\%$), and average uptake rates were one to two orders of magnitude less than mercury. Among the three genera, *Nitzschia* had the highest average rate of uptake, but *Dunaliella* had higher rates than *Carteria* cells at concentrations of 20 and 40 ng/liter (Fig. 2). Similar to mercury, cadmium uptake by *Dunaliella* decreased more rapidly with time than either *Carteria* or *Nitzschia*. Differences among time of inoculation and metal concentration were significant at 1% and among species at 5% (F tests).

A general loss of ^{203}Hg from the phytoplankton–water system was observed in all cultures, but total ^{109}Cd levels remained constant (Table 1; Fig. 1). This loss of ^{203}Hg was apparently due to adsorption to glassware and perhaps some volatilization during the experiments.

TABLE 1

RELATIVE PERCENTAGES* OF TOTAL ^{203}Hg AND ^{109}Cd REMAINING IN SYSTEM (CELLS PLUS CULTURE MEDIUM) OVER TIME

Metal isotope	Genus	Sampling time, hr			
		0.03	0.10	1.00	24.00
^{203}Hg	*Carteria*	91	75	61	12
	Dunaliella	88	70	52	14
	Nitzschia	94	87	72	20
^{109}Cd	*Carteria*	96	88	87	87
	Dunaliella	98	89	81	75
	Nitzschia	94	91	89	84

*Percentages are means obtained by three replications.

The growth of all phytoplankton tested decreased with successively higher concentrations of elemental mercury (Fig. 3). At levels typical of unpolluted environments [20 ng/liter (Windom, 1972)], *Nitzschia* had a higher rate of growth over 96-hr period than *Dunaliella* and *Carteria*. After exposure to increasing concentrations of mercury (20 to 350 ng/liter), *Nitzschia* suffered the greatest decline in growth. A severe depression in all genera occurred at 350 ng/liter [concentrations found for the Savannah River during the summer (Windom, 1972)]. The rate of cell division of *Carteria* and *Dunaliella* exposed to this level were at or only slightly higher than that necessary to sustain population numbers.

In general, total cellular nitrogen and lipid decreased while total cellular carbon content increased with successively higher additions of mercury (Table 2). *Nitzschia* had highest total carbon and lipid and lowest total nitrogen concentrations. The cellular content of elemental mercury increased in all genera with successively higher additions (Table 2). Correlation coefficients between cellular mercury content and nitrogen, carbon, and lipid, respectively, were relatively high for each species (approximately 0.9) except in the cases of nitrogen in *Carteria* (−0.63), carbon in *Carteria* (0.31), and lipid in *Dunaliella* (−0.15) (Table 2).

DISCUSSION

The more rapid decline in ^{203}Hg uptake rate compared to that of ^{109}Cd (Fig. 1) may have been due to losses of ^{203}Hg from the residual pool of isotope available for adsorption by phytoplankton. Since the rate of ^{203}Hg uptake was one to two orders of magnitude greater than that of ^{203}Cd (Fig. 2) and loss

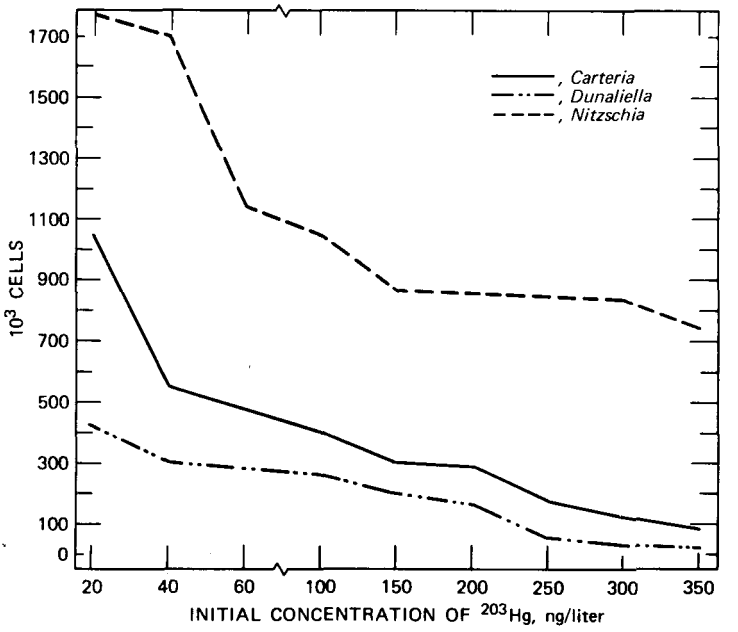

Fig. 3 Effect of mercury concentration on algal population size. All cultures were inoculated at an initial biomass of 4×10^{-1} mg/liter. Values are means for three replications.

from the water–algal cell system exceeded 80 to 88% (Table 1) after 24 hr, the equilibrium ratios between isotope concentrations in cells and water may have been significantly lower for ^{203}Hg cultures than ^{109}Cd. Therefore kinetic processes involved in adsorption of metal onto or into algal cells were probably inhibited in cells exposed to ^{203}Hg.

As was the case for mercury and cadmium (Fig. 1), high rates of uptake in the first hour of study for other metals were reported. *Nitzschia closterium* and several other species of green algae and diatoms concentrate cerium 300 to 3000 times over amounts in the media within a period of 0.5 hr (Rice and Willis, 1959). *Thalassiosira fluviatilis* and *Dunaliella tertiolecta* concentrate the highest percentage of copper ions in 0.5 hr (Mandelli, 1969).

Differences in rates of metal uptake in the three genera of algae studied may be attributed to enzyme kinetics, relative surface area to weight ratio of respective algal populations, and/or general physiological adaptations of each genus to specific culture conditions. Such electronegative metals as mercury are highly reactive with macromolecular groups associated with such enzymes as carboxyl, amino, and sulfhydryl. If metals are taken up by reaction with such groups, uptake rates will depend on the specific enzyme systems of the given algae.

Passive adsorption of metals onto cell walls is a function of surface area. Since *Nitzschia* had the highest surface area among the three genera, this may explain higher uptake rates of ^{109}Cd and ^{203}Hg by *Nitzschia* (Fig. 2). The relatively large loss of ^{203}Hg from batch systems (Table 1) may explain the

TABLE 2

EFFECT OF ELEMENTAL MERCURY ON CELLULAR CONTENT OF NITROGEN, CARBON, LIPID, AND CELLULAR MERCURY FOR POPULATIONS OF *CARTERIA* SP., *DUNALIELLA TERTIOLECTA* AND *NITZSCHIA CLOSTERIUM**

Genus	Hg, ng/liter	N, %	C, %	Lipid, %	Hg, μg/g dry weight
Carteria	20	12.90 ± 0.1	17.66 ± 1.6	21.90 ± 0.1	
	40	13.30 ± 0.3	18.05 ± 1.4	22.00 ± 0.2	
	60	12.41 ± 0.2	19.89 ± 1.5	23.10 ± 0.1	0.80 ± 0.1
	150	8.40 ± 0.1	20.93 ± 1.7	23.50 ± 0.4	0.91 ± 0.1
	250	6.30 ± 0.1	22.30 ± 0.8	12.20 ± 0.1	2.84 ± 0.3
	300	2.04 ± 0.1	33.07 ± 2.0	11.85 ± 0.2	2.05 ± 0.5
	350	2.03 ± 0.1	46.65 ± 2.9	11.63 ± 0.2	1.90 ± 0.2
Correlation coefficient		−0.63†	0.31†	−0.89‡	
Dunaliella	20	14.90 ± 0.9	26.11 ± 1.1	20.71 ± 1.7	
	40	13.71 ± 0.1	27.10 ± 1.8	22.00 ± 1.5	
	60	12.10 ± 0.3	29.21 ± 0.9	21.00 ± 1.9	0.72 ± 0.04
	150	11.10 ± 0.2	28.00 ± 1.3	16.71 ± 2.1	0.61 ± 0.08
	250	8.21 ± 0.4	31.21 ± 2.1	19.21 ± 1.1	0.80 ± 0.09
	300	5.60 ± 0.5	37.81 ± 1.1	18.40 ± 1.0	1.70 ± 0.1
	350	2.11 ± 0.2	39.70 ± 2.3	18.21 ± 2.2	1.65 ± 0.2
Correlation coefficient		−0.90‡	−0.98§	−0.15†	
Nitzschia	20	7.21 ± 0.2	25.71 ± 1.2	33.89 ± 1.5	
	40	6.71 ± 0.4	27.22 ± 1.7	31.77 ± 1.8	
	60	5.42 ± 0.1	37.22 ± 0.9	28.22 ± 2.1	0.81 ± 0.21
	150	3.11 ± 0.1	34.18 ± 1.2	27.22 ± 1.9	
	250	2.01 ± 0.2	37.21 ± 2.2	29.18 ± 1.8	
	300	1.97 ± 0.1	48.99 ± 0.8	21.22 ± 1.3	1.91 ± 0.
	350	1.51 ± 0.1	49.01 ± 2.2	20.01 ± 1.8	2.48 ± 0.2
Correlation coefficient		−0.97§	0.94‡	0.98§	

*Values are means and standard errors based on three replications, and correlation coefficients are given for cellular content of mercury regressed against total nitrogen, carbon, and lipid, respectively.

†N. S., not significant at the 0.05 level.

‡Significant at the 0.05 level.

§Significant at the 0.01 level.

relative differences in uptake rates of ^{109}Cd and ^{203}Hg for cultures of *Dunaliella* to *Carteria* (Fig. 2).

The depression in cellular division rate on exposure to mercury may result from enzyme inhibition and/or toxic effects caused by external adsorption to cell walls or direct incorporation of metal. Copper and mercury can inactivate respiratory-related enzymes (Mandelli, 1969). It is conceivable that absorption of essential nutrients and oxygen and the excretion of metabolites could be partially or critically blocked by physical adsorption of metals to the algal cell wall.

Depression in phytoplankton growth has been reported for metals other than mercury. Selective toxicity of copper above naturally occurring levels was reported in selected marine algae (Mandelli, 1969). In a comparative study of several metals, mercury more severely inhibited algal growth and photosynthesis than copper, lead, or cadmium (Hannan and Patouillet, 1971). Considering the relative magnitude of metal uptake and concentration (Fig. 2), cadmium at concentrations used in this study would not be expected to inhibit algal growth as severely as did mercury.

If results from this study are extrapolated from the laboratory to the field, the levels of mercury found in the Savannah River (350 ng/liter, Windom, 1972) may inhibit primary productivity. However, before such an extrapolation can be made, several factors need to be considered. The species composition of a field population will be important. A diatom (*Nitzschia*), for example, is more tolerant to high metal concentrations than green algae (*Carteria* and *Dunaliella*) (Fig. 3). In addition, temperature, salinity, light intensity, and nutrient content and chemical form of metal all synergistically affect the tolerance of algae to metals (Mandelli, 1969).

Alteration in cellular content of total carbon, nitrogen, and lipids (Table 2) may have been due to inhibition by mercury of enzyme systems regulating assimilation of nutrients. Matsen, Mustoe, and Chang (1972) reported that both mercuric chloride and methyl mercuric chloride inhibited the biosynthesis of lipids (specifically galactolipids) in algae. Furthermore, deficiencies in critical nutrients, which would functionally result in deficiencies in assimilated material and therefore result in metabolic inhibition similar to enzyme inhibition, have been associated with change in cellular chemistry among phytoplankton. For example, relatively low concentrations of phosphorus and nitrogen in growth media have resulted in decreases in total carbohydrate fraction (Pearsall and Loose, 1937; Myers and Cramer, 1948). Nitrogen deficiency has also been related to decrease in total cellular nitrogen and specifically protein synthesis (Pearsall and Loose, 1937; Spoehr and Milner, 1949; and Thomas and Krauss, 1955).

Changes in the chemical composition of algal cells and decreased productivity caused by exposure to naturally occurring levels of mercury could conceivably affect growth and productivity at higher trophic levels. Differences

in the age and nutritional value of some phytoplankton affected growth and sexual development in oysters (Loosanoff and Davis, 1963). Similarly changes in total protein, carbohydrate, and lipid significantly affected the growth and survival of filter-feeding crustaceans (Sick, 1974). Therefore the ability of phytoplankton to concentrate mercury (Table 2) could conceivably affect growth and productivity of filter-feeding organisms.

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REFERENCES

Hannan, P., and C. Patouillet, 1972, Effects of Pollutants on Growth of Algae, Report of Naval Research Laboratory Progress, pp. 1-8.

Harriss, R. C., D. B. White, and R. B. Macfarlane, 1970, Mercury Compounds Reduce Phytosynthesis by Plankton, *Science*, **170**: 736-737.

Knauer, George A., and John H. Martin, 1972, Mercury in a Marine Pelagic Food Chain, *Limnol. Oceanogr.*, **17**(6): 868-876.

Loosanoff, V. L., and H. C. Davis, 1963, Rearing of Bivalve Mollusks, in *Advances in Marine Biology*, F. S. Russell (Ed.), Vol. 1, pp. 1-136, Academic Press, Inc., New York.

Mandelli, E. F., 1969, The Inhibitory Effects of Copper on Marine Phytoplankton, *Mar. Sci.*, **14**: 38-41.

Matson, R. S., G. E. Mustoe, and S. B. Chang, 1972, Mercury Inhibition of Lipid Biosynthesis in Freshwater Algae, *Environ. Sci. Technol.*, **6**: 158-160.

Myers, J., and M. Cramer, 1948, Metabolic Conditions in *Chlorella.*, *J. Gen. Physiol.*, **32**: 103.

Nuzzi, R., 1972, Toxicity of Mercury to Phytoplankton, *Nature*, **237**: 38-40.

Pearsall, W. H., and L. Loose, 1937, The Growth of *Chlorella vulgaris* in Pure Culture, *Proc. Roy. Soc. (London) Ser. B*, **121**: 451.

Rice, Theodore R., 1953, Phosphorus Exchange in Marine Phytoplankton, *Fish. Bull.*, 54(80): 77-89.

—, and Virginia M. Willis, 1959, Uptake, Accumulation, and Loss of Radioactive Cerium-144 by Marine Planktonic Algae, *Limnol. Oceanogr.*, 4(3): 277-290.

Sick, Lowell V., 1975, The Nutritional Value of Five Species of Marine Phytoplankton Growth and Survival of the Brine Shrimp, *Artemia salina*, in press.

Spoehr, H. A., and H. W. Milner, 1949, The Chemical Composition of *Chlorella*, Effect of Environmental Conditions, *Plant Physiol.*, **24**: 120.

Strickland, J. H., 1966, *Measuring the Production of Marine Phytoplankton*, Fisheries Research Board of Canada, Bulletin No. 122.

Thomas, W. H., and R. W. Krauss, 1955, Nitrogen Metabolism in *Scenedesmus* as Affected by Environmental Changes, *Plant Physiol.*, **30**: 113.

Windom, H. L., 1972, Mercury Distribution in Estuarine–Nearshore Environment, in American Society of Civil Engineers National Water Resources Engineering Meeting, Jan. 24–28, 1972, Atlanta, Ga.

, and R. G. Smith, 1972, Distribution of Cadmium, Cobalt, Nickel, and Zinc in Southeastern U. S. Continental Shelf Waters, *Deep-Sea Res.*, **19**: 727-730.
, F. Taylor, and R. Stickney, 1973, Mercury in North Atlantic Plankton, *J. Cons., Cons. Int. Explor. Mer.*, **35**: 18-21.

THE ROLE OF *Spartina alterniflora* IN THE FLOW OF LEAD, CADMIUM, AND COPPER THROUGH THE SALT-MARSH ECOSYSTEM

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ABSTRACT

The heavy metals cadmium, lead, and copper are important by-products of industrialization, and we can expect increased concentrations of these potentially toxic substances in estuarine environments. Lead and cadmium have no reported significance for the normal metabolism of the major marsh plant *Spartina alterniflora,* but small concentrations of copper are required for the proper functioning of enzymes. Our measurements indicate that this plant plays only a minor role in the cycle of these toxic heavy metals in the estuary. Laboratory plants responded differently to high concentrations of each of these metals: complete mortality to copper; inhibition and growth modification to lead; and no growth modification due to cadmium. Measurements of the input of these metals from southeastern river systems and the concentrations of these metals in the sediment and *Spartina* are used to construct a rough budget for these elements. The budget is discussed in light of the laboratory data, and an estimate is made of the role of *Spartina* now and in the future in the cycle of these important heavy-metal by-products of industrial society.

Cadmium, lead, and copper are important by-products of a mechanized society, and we can expect elevated concentrations of these heavy metals in the estuarine environments receiving industrial discharges. The toxic characteristics of these and other heavy metals have received particular attention in recent years because of their potential effect on man and because of their largely unknown fate in marine food chains. Copper in small concentrations is required for the proper functioning of plant enzymes, as a component of cytochrome oxidase electron transport, but no biological role for lead or cadmium has been defined for plants.

In this paper we will examine the significance of these metals for *Spartina* production and assess the importance of *Spartina* in controlling their flux within the marsh system and subsequently to the coastal marine environment. Halophytic plants like *Spartina* can survive the rigors of a saline environment

because they possess unique systems that allow cellular metabolism under changing osmotic pressures. The uptake, toxicity, and concentration of heavy metals therefore may be influenced by *Spartina's* halophytic mode of existence.

METHODS

Cores (40 cm deep) and whole *Spartina* plants (including roots) were sampled for metal analysis at the end of the growing season from marshes adjacent to six important southeastern rivers (Santee, Cooper, Savannah, Altamaha, Satilla, and St. Johns). At each river system two core sites in marshes on each side of the river were sampled. Ten *Spartina* plants were sampled at each site and mixed, and three subsamples from each site were analyzed for metals. Thus data points for metal concentrations represent the mean of 6 measurements for *Spartina* and 10 measurements for the sediment.

Samples were prepared for trace-metal analysis by a modification of the wet-ashing procedure of Middleton and Stuckey (1954), which is described in detail by Smith and Windom (1972). Samples, dried at 80°C, were digested in fuming nitric acid under 300°C until the acid evaporated. Nitric acid is added and evaporation is repeated until a white residue remains. The residue is dissolved in hydrochloric acid and analyzed by atomic absorption spectrophotometry. Vycor vessels were used in the cadmium and copper analysis, and fused quartz was used for the lead. Analytical precision, based on replicate analysis, is ±15% for cadmium, ±10% for copper, and ±17% for lead of the values stated. In addition to total metal concentrations, a measure of the more available metals (carbonates, oxides, and nonlattice crystal sites) in the sediment was made by analysis of a leachable fraction [hydroxalmine–hydrochloride–acetic acid digestion (Chester and Hughes, 1967)].

Laboratory plants were grown from seed collected in marshes at Skidaway Island, Ga. Germination was induced by subjecting the seeds to a diurnal thermal period, using temperatures of 32 to 15°C. Experimental plants were grown in acid-washed pure quartz sand (Hewett, 1952) using Hoagland's medium (Hoagland and Arnon, 1950). Growth experiments using 4-week-old seedlings were run for 8 weeks in high metal concentrations of 100 ppm which were renewed weekly together with the growth medium.

RESULTS AND DISCUSSION

Concentrations of Cadmium, Copper, and Lead in the Estuary

Cadmium, copper, and lead occur in the various fractions of the natural system at about the same general range of concentrations: 1 to 5 ppb in the water, 10 to 100 ppm in the suspended sediment, and 0.5 to 20 ppm in the marsh sediment and *Spartina.* These levels are an order of magnitude higher than mercury, an order of magnitude less than manganese, and 1000-fold less than

iron. The level of these three metals dissolved in estuarine water (1.13 cadmium, 3.3 copper, and 2.2 lead) are about the same as that in river water (0.84 cadmium, 4.5 copper, 2.3 lead), indicating that their concentrations are not greatly influenced by the transition from fresh to brackish water. This situation is different from soluble iron, for example, which is almost completely precipitated out at the river–estuary boundary and trapped in the salt marsh ecosystem (Windom, 1974). The accumulation of cadmium, copper, and lead in the marsh substrate is mainly the result of the sedimentation of particulate matter from river water and is apparently not due to chemical precipitation of dissolved compounds as is iron. Regionally, concentration of these metals in southeastern salt marshes does not vary greatly except in the Santee estuary, which is higher in cadmium and copper (Fig. 1). Concentrations of iron and manganese in marsh sediments do not correlate with the concentrations of these metals in *Spartina* from the same site (Dunstan and Windom, 1974). It appears that in nature *Spartina* accumulates iron and manganese until saturated, and beyond that no further increases occur. An alternate explanation could be that chemical measurements in the environment do not reflect the availability of these metals to the plants. There were no significant differences between the concentrations of cadmium, copper, or lead in *Spartina* among the six river systems. There were significant differences in the sediment concentrations of cadmium and copper in the Santee estuary, and the *Spartina* did not show any concomitant increase. Apparently the concentrations of cadmium and copper in *Spartina* are not directly related to concentrations measured in the sediment, which is similar to the response reported for iron and manganese.

Laboratory Plants Exposed to High Metal Concentrations

Spartina seedlings exposed over an 8-week period to 100-ppm concentrations of cadmium, copper, and lead showed three different responses. Growth was inhibited by copper for 2 weeks, after which the plants died. Lead inhibited growth (Fig. 2) and caused high mortalities; over 50% of the plants were dead after 8 weeks. Those plants which survived in the high-lead media grew at a slower rate, were 70% shorter, and weighed 80% less than the controls. In plants surviving high-lead media, less lead was accumulated than in nature, reflecting the aberrant physiological conditions of these stunted plants. The response of *Spartina* to lead is in contrast to the response of *Spartina* to methyl mercury. With methyl mercury 50% of the plants rapidly died, but the plants that did survive grew at rates that were not significantly different from the controls. Mercury levels in the surviving plants were five times control levels (Windom, 1974).

In the laboratory plants exposed to 100 ppm cadmium, there was no significant difference from control plants in growth rate, length, or dry weight. Concentrations as high as 94 ppm cadmium were observed in healthy plants. This is about 150 times the amount measured in natural samples of *Spartina*.

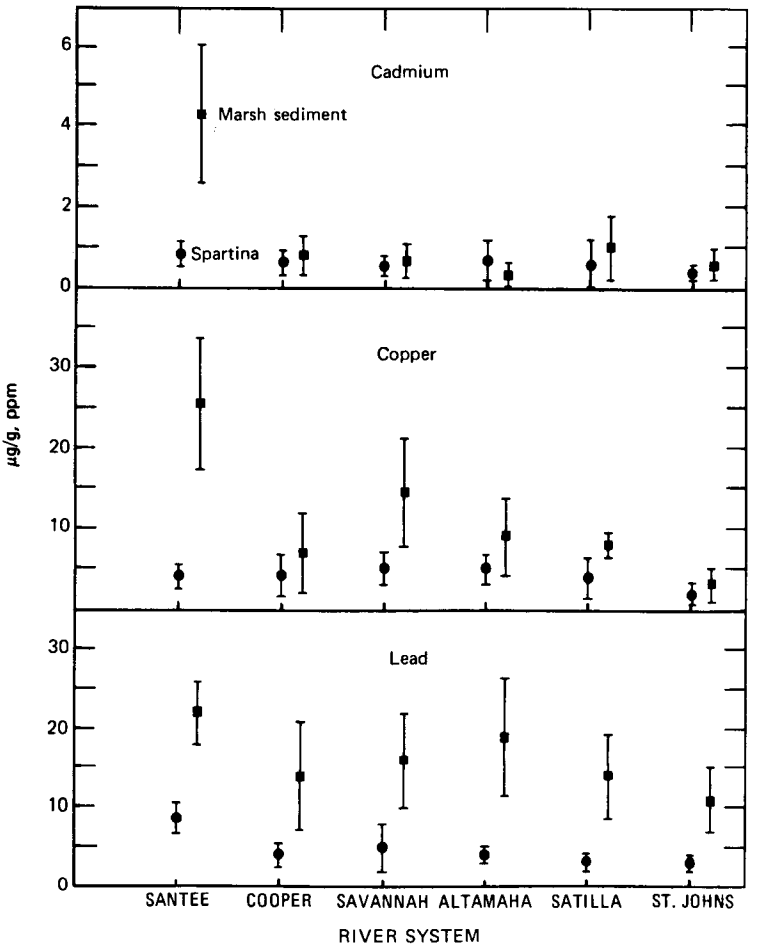

Fig. 1 Mean metal concentrations in *Spartina* and marsh sediment from six southeastern rivers. Each point represents the mean of at least 6 measurements for *Spartina* and 10 measurements for the sediment. The standard deviation about each mean is indicated by the vertical lines.

Since the highest cadmium measurements were in the belowground portions of the plant, it appears that cadmium is not transported within the plant but is concentrated through adsorption and absorption.

The high levels of the metals used in our initial laboratory work are useful in bracketing the potential problem. Although we are continuing our work using more realistic levels, we can say that cadmium has little potential as an inhibiting agent or toxicant for *Spartina*. The plant can safely accumulate high levels that are pooled or trapped in the belowground portions of the plant. An analogous

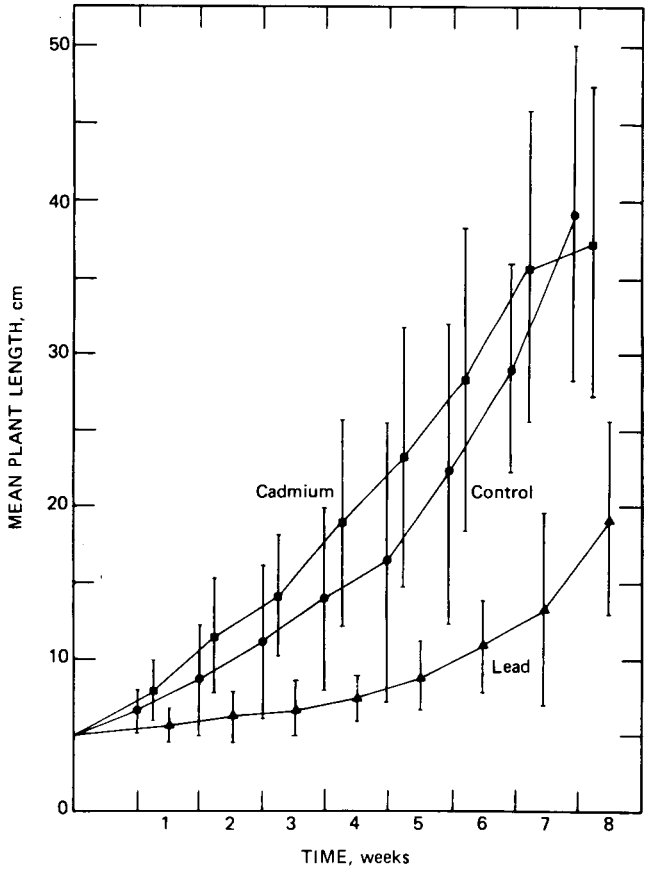

Fig. 2 Weekly height measurement of *Spartina* seedlings exposed to high concentrations of cadmium and lead over 8 weeks. Each point is the mean of measurements on 12 plants. The standard deviation about each mean is indicated by the vertical lines.

response was reported by Wyn-Jones, Sutcliffe, and Marshall (1971) for zinc-tolerant clones of *Agrostis tenuis*. Cellular fractionation of the tolerant clones indicated that most of the zinc was in the cell wall, whereas in nontolerant clones the cell wall did not act as a barrier.

Lead and copper are potentially more harmful to *Spartina*, and marshes proximate to point sources of these metals might be affected. Toxic levels, however, are an order of magnitude or more higher than levels now occurring in the environment.

Spartina in the Flux of Cadmium and Copper

In addition to the effects of metals on *Spartina,* the role of *Spartina* in controlling the flux of metals through natural systems is also of interest. The annual flux and concentrations of cadmium and copper through estuaries are shown in Table 1. Actually a very small portion of the metals discharged by the river systems of the southeastern Atlantic coast is trapped in the marsh mud or in *Spartina.* In the case of cadmium only, above 17% is deposited in the sediment and about 3% occurs in the *Spartina* crop (Table 1). Eighty percent of cadmium bypasses the marsh system and enters coastal waters. For copper picture is much the same, with about 3% in *Spartina,* 22% in the sediment, and 75% flowing through the marsh system.

The mean concentration of the cadmium in sediments surrounding *Spartina* is 1.19 ppm, whereas the leached fraction (see Methods section) contains 0.45 ppm, which is close to the mean of 0.61 ppm found in the plant. The amount available to *Spartina* represents a very small portion of the cadmium and copper in the total system.

Excluding point sources of the metals studied, increased levels of cadmium, lead, and copper have little effect on *Spartina.* Furthermore, *Spartina* is

TABLE 1

ANNUAL FLUX OF CADMIUM AND COPPER IN NINE SOUTHEASTERN RIVER ESTUARIES

River input*	*Spartina* uptake†	Sediment accumulation‡	Into and through estuaries
	Cadmium		
52×10^3 kg/year	$\longrightarrow 1.4 \times 10^3$ kg/year (2.7%)		
	$\longrightarrow$	9×10^3 kg/year (17.3%)	
	$\longrightarrow$		80%
	Copper		
4×10^3 kg/year	$\longrightarrow 10.4 \times 10^3$ kg/year (3.4%)		
	$\longrightarrow$	66×10^3 kg/year (21.7%)	
	$\longrightarrow$		74.9%

*Based on concentrations measured in particulate and dissolved fractions and annual river flow; see Windom, 1974.

†Based on mean concentration of all *Spartina* samples taken; a yearly average crop in the southeast of 700 g/m^2 and areal extent of southeastern marshes of 400,000 ha.

‡Sedimentation rate based on mean concentration measured at 10-cm intervals in 25 cores and an average rate of 1 mm/year and average specific gravity of 1.5 g/cm^3; see Windom, 1974.

well-buffered against increasing levels of these metals since only a small portion of the annual input of each accumulates in the plant-available fraction of the sediment. For example, to increase the leached fraction of copper from 1.9 to 3.8 ppm, the level of copper discharged by the nine southeastern rivers studied would have to increase by 300×10^3 kg/year, assuming that the distribution of the metal between different forms remained constant.

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REFERENCES

Chester, R., and M. Hughes, 1967, A Chemical Technique for the Separation of Ferro-Manganese Minerals, Carbonate Minerals, and Adsorbed Trace Elements from Pelagic Sediments, *Chem. Geol.*, 2: 249-262.

Dunstan, W. M., and H. Windom, 1974, The Influence of Environmental Changes in Heavy Metal Concentrations on *Spartina alterniflora,* Proceedings of the International Estuarine Research Conference, Myrtle Beach, S. C., in press.

Hewett, E. J., 1952, *Sand and Water Culture Methods used in the Study of Plant Nutrition,* Commonwealth Bureau of Horticulture Plantation Crops, Technical Communication, No. 22.

Hoagland, D. R., and D. I. Arnon, 1950, The Water-Culture Method for Growing Plants Without Soil, California Agricultural Experiment Station, Circular 347.

Middleton, G., and R. E. Stuckey, 1954, The Preparation of Biological Material for the Determination of Trace Metals, *Analyst,* 79: 138-142.

Smith, R. G., and H. L. Windom, 1972, *Analytical Handbook for the Determination of Arsenic, Cadmium, Cobalt, Copper, Iron, Lead, Manganese, Mercury, Nickel, Silver, and Zinc in the Marine and Estuarine Environments,* Technical Report Series No. 72-6, Georgia Marine Science Center, Skidaway Island, Ga.

Windom, H., 1974, Heavy Metal Fluxes Through Salt Marsh Estuaries, Proceedings of the Second International Estuarine Research Conference, Myrtle Beach, S. C., in press.

Wyn-Jones, R. G., M. Sutcliffe, and C. Marshall, 1971, Physiological and Biochemical Basis for Heavy Metal Tolerance in Clones of *Agrostis tenuis,* in *Recent Advances in Plant Nutrition,* Vol. 2, R. M. Savish (Ed.), Gordon & Breach, Science Publishers, Inc., New York.

HEAVY-METAL CONCENTRATIONS IN SELECTED GEORGIA ESTUARINE ORGANISMS WITH COMPARATIVE FOOD-HABIT DATA

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ABSTRACT

Tissue levels of cadmium, copper, lead, mercury, and zinc were determined for 11 species of southeastern United States estuarine fishes: *Opsanus tau, Bairdiella chrysura, Cynoscion regalis, Leiostomus xanthurus, Micropogon undulatus, Stellifer lanceolatus, Ancylopsetta quadrocellata, Citharichthys spilopterus, Etropus crossotus, Scophthalmus aquosus,* and *Symphurus plagiusa.* Analyses for the same metals were run on selected invertebrates that are important food organisms to the fishes studied. Comparison between heavy-metal levels and food habits of the fishes generally indicated no positive correlation, although high levels of mercury in *O. tau* appeared to be associated with elevated levels of mercury in crabs, its major food source. Copper and zinc were commonly higher in the tissues of invertebrates than in the fish that fed upon them. The level of trace metals in organisms from different trophic levels apparently depends more on physiological processes within each organism than on the metal concentration in the food. This relationship probably will not apply in cases where pollution leads to heavy-metal concentrations high enough to overcome homeostatic mechanisms.

Considerable information regarding the biogeochemical cycling of heavy metals in estuaries and the effect of elevated levels of heavy metals on various types of estuarine organisms has appeared in the literature within the past decade, but our basic understanding of the cycling of trace metals at ambient levels in estuaries is incomplete. Preliminary investigations into various compartments of estuaries of the southeastern United States have provided information from which further field and laboratory studies can be designed (Windom, Beck, and Smith, 1971; Windom and Smith, 1972; Stickney et al., 1972; Windom, 1973; Windom et al., 1973; Rahn, 1973). Other data on the cycling of heavy metals

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and radioisotopes in estuaries (with special emphasis on western North Atlantic estuaries) are also available (e.g., Duke, 1963; Duke, Willis, and Price, 1966; Cross, Duke, and Willis, 1970; Cross, Willis, and Baptist, 1971; Wolfe and Rice, 1972). Many other investigations relating to the uptake of various stable and radioisotopes of heavy metals in water have appeared in recent years. No attempt will be made to review this extensive literature.

Our study concentrated on an examination of cadmium, copper, lead, mercury, and zinc in the muscle tissue of selected species of southeastern United States estuarine fishes and a comparison of heavy-metal levels with the food habits of those fish. Trace-metal levels in the fish under study and in several types of common estuarine invertebrates were also compared. Our studies have centered on the estuarine area of the southeastern Atlantic coast of the United States between Georgetown, S. C., and Jacksonville, Fla. (Fig. 1). This region is characterized by a complex of barrier islands separated by sounds. Behind the barrier islands is a network of rivers and tidal creeks dissecting vast expanses of salt marsh dominated by *Spartina alterniflora*. The areal extent of the marshes is enhanced by the low relief of the coastal plain in conjunction with the relatively high tide range (up to 3 m during spring tides near the center of the study area). Higher trophic-level productivity appears to be largely based on a detritus food web (Odum and de la Cruz, 1963, 1967), with *S. alterniflora* providing the bulk of the autochthonous detritus.

MATERIALS AND METHODS

Fish and invertebrates were obtained with otter trawls and plankton nets during all seasons of the year in the estuarine zone between Georgetown, S. C., and Jacksonville, Fla. (Fig. 1). Organisms to be analyzed for heavy metals were frozen immediately after capture. In the laboratory the animals were thawed and dissected. Muscle tissue from the fish was removed from just below the dorsal fin. Care was taken to avoid contaminating the selected muscle tissue with outer mucosal material. With small fish it was often necessary to pool samples from two or more individuals to obtain enough material for analysis.

Edible muscle tissue from the shrimp *Penaeus aztecus, P. setiferus,* and *Xiphopeneus kroyeri* and claw meat from the crabs *Hexapanopeus augustifrons, Menippe mercenaria,* and *Callinectes sapidus* was analyzed. In no case were exoskeletal material included in the tissue samples. Additional samples of gills and egg masses were obtained from several blue crabs (*C. sapidus*). Because of their small sizes, the remaining decapod, amphipod, copepod, and mysid crustaceans were analyzed by pooling whole animals. Several thousand individual copepods were required. They were obtained by centrifuging zooplankton samples.

Samples for cadmium, copper, lead, and zinc analyses were wet ashed in fuming HNO_3 at 60°C and dissolved in quartz-distilled nitric acid. The matrix of

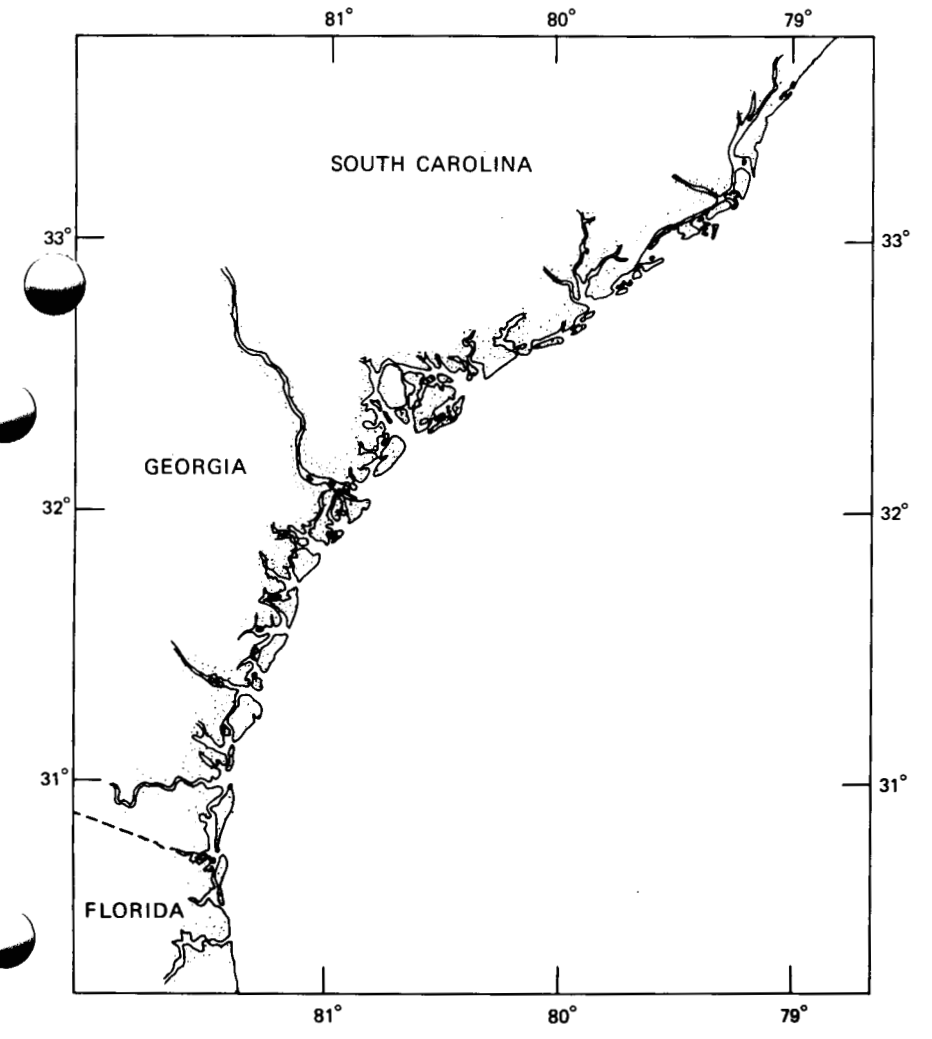

Fig. 1 Map of the study region.

each sample was established by sodium, potassium, calcium, and magnesium analyses. Copper and zinc concentrations were determined by flame atomic absorption, and cadmium and lead were analyzed by a heated graphite furnace. Calibration curves for standards made up in matrixes similar to those of the samples were used for all analyses.

Tissue samples for mercury analysis were wet digested overnight in concentrated sulfuric and nitric acids in a water bath at 60°C. After digestion

the samples were diluted and further oxidized with potassium permanganate and potassium disulfate; then the mercury was reduced to zero valence state with stannous sulfate. The samples were then aerated by a peristaltic pump into a cold-vapor atomic-absorption system for analysis. The resulting absorption was compared with standards.

Replicate analyses of a single sample established the standard deviation of each analysis as ±10% for copper, zinc, and mercury and ±15% for cadmium and lead. Where there were four or more individual analyses available for a particular type of tissue from one species, the mean and standard deviation of concentration of each metal were determined. If less than four analyses were available, only the average values for each metal were calculated.

Fishes to be used for food-habit analysis were preserved immediately after capture in 10% Formalin. In the laboratory the stomachs were removed and the contents inspected under a dissecting microscope. The food organisms were classified as completely as possible and ennumerated. Food-habit data were condensed under major groups of organisms; however, more detailed information on each species is available (Stickney, Taylor, and Heard, 1974; Stickney, Taylor, and White, 1975).

RESULTS AND DISCUSSION

Eleven common species of southeastern United States estuarine fishes were selected for this study because of their abundance and because their food habits have been elaborated in our laboratory and not because of their economic importance. Fishes of the families Sciaenidae and Bothidae are the most commonly occurring benthic species in the estuaries of the study area. Among the many sciaenids that occur in the region, *Bairdiella chrysura* (silver perch), *Cynoscion regalis* (weakfish), *Leistomus xanthurus* (spot), *Micropogon undulatus* (Atlantic croaker), and *Stellifer lanceolatus* (star drum) were selected for study. Representatives from the family Bothidae were *Ancylopsetta quadrocellata* (oscellated flounder), *Citharichthys spilopterus* (bay whiff), *Etropus crossotus* (fringed flounder), and *Scophthalmus aquosus* (windowpane). In addition, *Opsanus tau* (oyster toadfish) and *Smyphurus plagiusa* (blackcheek tonguefish) were included from the families Batrachoididae and Cynoglossidae respectively.

The food habits of each fish species are shown in Table 1. Values represent the percentage of total number of food organisms recovered attributed to each taxonomic group. Since copepods are smaller than fish, polychaetes, decapods, etc., the values do not necessarily hold on a volumetric basis. However, the fact that in most cases the preponderance of the food material for any individual species of fish was from only two or three taxonomic categories indicates that the numerical tendencies shown are also commonly valid volumetrically.

TABLE 1

PERCENTAGE OF TOTAL NUMBER OF FOOD ORGANISMS CONTRIBUTED BY VARIOUS TAXA OF ANIMALS AS DETERMINED BY ANALYSIS OF STOMACHS FROM THE FISH SPECIES INDICATED

Fish species examined	No. stomachs examined	Percentage of total number of food organisms contributed by each taxon								
		Polychaeta	Decapoda	Amphipoda	Copepoda	Cumacea	Mysidacea	Isopoda	Teleostei	Others
Batrachoididae										
Opsanus tau	260	3.4	58.7	6.9	0.0	0.0	0.9	0.5	2.2	27.4*
Sciaenidae										
Bairdiella chrysura	183	2.7	8.1	6.8	27.5	0.0	51.3	0.4	2.1	1.2
Cynoscion regalis	120	2.8	1.9	0.4	4.8	0.0	86.8	0.4	2.7	0.2
Leiostomus xanthurus	126	0.1	0.1†	0.2	97.6	0.1	0.1	0.0	0.0	1.8
Micropogon undulatus	202	7.8	2.6	6.8	67.5	4.4	8.1	0.4	0.7	1.7
Stellifer lanceolatus	205	0.2	0.4	8.8	81.6	0.5	7.2	0.7	0.3	0.3
Bothidae‡										
Ancylopsetta quadrocellata	217	0.4	9.8	5.4	0.9	0.1	81.0	0.1	0.5	1.8
Citharichthys spilopterus	210	0.3	18.3	0.3	1.0	0.1	72.1	0.0	3.6	4.3
Etropus crossotus	421	6.8	1.0	1.9	84.7	2.1	3.1	0.4	0.0	0.0
Scophthalmus aquosus	105	0.3	0.2	1.0	1.5	0.5	96.3	0.0	0.0	0.2
Cynoglossidae										
Symphurus plagiusa	124	1.8	7.3	10.8	37.3	2.3	2.3	0.3	1.2	36.7§

*The high percentage of animals in this category is mainly attributed to crustacean remains (87.7% of the organisms tabulated under "Others"). If these unidentified crustacean remains are assumed to be Decapoda, the values for "Decapoda" and "Amphipoda" become 82.8 and 3.4%, respectively.

†Virtually all the Decapoda found in *L. xanthurus* stomachs consisted of megalops and zoea larval stages.

‡Bothidae data were taken from: Stickney, R. R., G. L. Taylor, and R. W. Heard III, 1974.

§Organisms contributing to this value were approximately equally divided between unidentified crustaceans and mollusks.

Careful examination of the sciaenid and bothid data in terms of where in the estuary the fish were captured (sounds as opposed to rivers), seasons of the year, and size of the fish indicate that location and season had virtually no effect on food habits (Stickney, Taylor, and Heard, 1974; Stickney, Taylor, and White, 1975). Size was important in a few instances. In general, *B. chrysura, C. regalis, M. undulatus,* and *C. spilopterus* became increasingly piscivorous with increased size. The maximum size of the fish examined was less than 200 mm standard length in all cases for fish from the families Bothidae and Sciaenidae.

Each species examined feeds primarily on crustaceans. The bulk of the diet of *O. tau* is composed of decapods (mainly crabs of various species), and the remaining species feed to a large extent on copepod and/or mysid crustaceans. *Symphurus plagiusa* seems less discriminating in its food preferences.

The levels of cadmium, copper, lead, mercury, and zinc in dorsal muscle tissues of each species of fish are shown in Table 2. Cadmium was generally present at levels less than 0.10 parts per million (ppm) on a dry-weight basis. Exceptions were *B. chrysura* and *A. quadrocellata.* The high values obtained from these two species may not be reliable since for *A. quadrocellata* only one was analyzed and for *B. chrysura,* a high standard deviation was found. Comparison of heavy-metal and food-habit data (Table 1) gives no indication of a food-related basis for the higher cadmium levels in these two species.

Virtually all the values obtained for copper in fish muscle tissue lay within the same order of magnitude (Table 2). Consistent data were also obtained for lead among the 11 fish species analyzed. Average values above 0.10 ppm showed high standard deviations.

Opsanus tau, B. chrysura, and *S. aquosus* muscle averaged more than 1.0 ppm mercury, and the mean value for *S. plagiusa* exceeded 0.5 ppm. All others averaged less than 0.5 ppm. Zinc, like cadmium, copper, and lead, was relatively constant among the fish species analyzed.

Many values in Table 2 indicate relatively high amounts of deviation around the mean (often as great as 100%). Some of this can be accounted for by the error inherent in the analytical procedure, although natural variability probably is high within the fish populations examined. This natural variability stems in part from the fact that the fishes were obtained from various microhabitats within the sampling region and may have been subjected to slight differences in the levels of metals dissolved in the water and present in the food from one part of the sampling area to another. Additional variation can occur in cases where heavy metals accumulate with age as was shown for mercury in *Pomatomis saltatrix* (Cross et al., 1973).

To determine possible major differences in heavy-metal levels in the food organisms compared to those found in predator fishes, we analyzed some of the commonly occurring estuarine invertebrates (Table 3). These do not always compare with fish-food organisms on a species-for-species basis; however, representatives of the important groups of crustaceans were analyzed (i.e.,

TABLE 2

LEVELS OF SELECTED TRACE METALS IN MUSCLE TISSUES OF FISHES FOR WHICH FOOD HABITS HAVE BEEN ELABORATED FROM GEORGIA FISHES.*

Fish species examined	No. of samples	Cadmium	Copper	Lead	Mercury	Zinc
Batrachoididae						
Opsanus tau	5	0.06 ± 0.03	1.8 ± 0.8	0.16 ± 0.16	2.74 ± 1.64	45 ± 26
Sciaenidae						
Bairdiella chrysura	5	0.12 ± 0.12	2.3 ± 1.7	0.06 ± 0.05	1.07 ± 0.77	21 ± 6
Cynoscion regalis	7	0.05 ± 0.02	1.9 ± 0.8	0.09 ± 0.05	0.44 ± 0.05	26 ± 7
Leiostomus xanthurus	34	0.04 ± 0.02	1.8 ± 0.9	0.08 ± 0.13	0.23 ± 0.13	22 ± 13
Micropogon undulatus	27	0.04 ± 0.03	2.3 ± 1.4	0.07 ± 0.09	0.31 ± 0.22	25 ± 19
Stellifer lanceolatus	32	0.04 ± 0.02	1.8 ± 0.8	0.13 ± 0.23	0.50 ± 0.37	26 ± 8
Bothidae						
Ancylopsetta quadrocellata	1	0.22	5.2	0.08	0.46	51
Citharichthys spilopterus	1	0.07	1.2		0.17	24
Etropus crossotus	3	0.07	0.9	0.01	0.10	21
Scophthalmus aquosus	1	0.02	2.0	0.01	1.03	31
Cynoglossidae						
Symphurus plagiusa	17	0.03 ± 0.02	1.6 ± 1.0	0.09 ± 0.16	0.63 ± 0.58	21 ± 8

*All values in ppm on a dry-weight basis and include standard deviation in cases where four or more samples were available.

TABLE 3

LEVELS OF SELECTED TRACE METALS IN INVERTEBRATE ORGANISMS OF THE TYPE COMMONLY CONSUMED BY GEORGIA ESTUARINE FISHES*

Species and tissue examined	No. of samples	Cadmium	Copper	Lead	Mercury	Zinc
Decapoda						
Palaemonetes pugio (whole animal)	3	0.06	74	0.04	0.13	58
Trachypeneus constrictus (muscle)	1	0.11	56	0.03		55
Xiphopeneus kroyeri (muscle)	4	0.36 ± 0.56	22 ± 6	0.06 ± 0.02	0.26 ± 0.02	60
Penaeus aztecus (muscle)	14	0.07 ± 0.01	18 ± 5	0.20 ± 0.23	0.17 ± 0.07	56 ± 5
Penaeus setiferus (muscle)	82	0.04 ± 0.03	16 ± 4	0.12 ± 0.20	0.23 ± 0.15	53 ± 14
Hexapanopeus augustifrons (muscle)	1	0.06	13	0.07		58
Menippe mercenaria (muscle)	2	0.13	43		1.57	290
Callinectes sapidus (muscle)	23	0.07 ± 0.08	31 ± 12	0.05 ± 0.05	0.68 ± 0.33	185 ± 95
Callinectes sapidus (egg mass)	5	0.08 ± 0.03	41 ± 14	0.94 ± 1.30	0.20 ± 0.11	160 ± 26
Callinectes sapidus (gills)	4	0.22 ± 0.39	60 ± 44	0.84 ± 1.09	0.18 ± 0.04	92 ± 21
Amphipoda						
Gammarus species	3	0.01	30			70
Copepoda						
Pseudodiaptomus coronatus and *Acartia tonsa* (mixed sample)	1	0.01	19	0.23		100
Mysidacea						
Neomysis americana	5	0.40 ± 0.52	25 ± 11	0.03 ± 0.03	0.06 ± 0.06	87 ± 30

*All values in ppm on a dry-weight basis and include standard deviation in cases where four or more samples were obtained.

decapods, amphipods, and mysids). We have assumed that values from the crab and shrimp species analyzed are valid for other decapod crustacean species and that *Gammarus* sp. is representative of amphipod crustaceans. The copepod and mysid analyses were conducted on species that were dominant food organisms in many fish stomachs.

Cadmium values for invertebrates were generally consistent with the data (Table 3). Cases in which the mean value exceeded 0.20 ppm were those which were associated with high standard deviations. Copper values were nearly an order of magnitude higher than those in fish muscle. This is expected since crustaceans have a physiological requirement for copper in blood pigment, whereas the fishes do not. Lead values compared closely with those of the fish with the exception of *Callinectes sapidus* eggs and gills where higher mean values were found. The high standard deviations of egg and gill values indicated a wide natural range in values. *Opsanus tau*, which feeds largely on crabs, demonstrated

a lead level slightly higher on the average than that of the other fish species examined (Table 2).

With the exception of the stone crab, *Menippe mercenaria* (for which only one analysis is available), the values for mercury in the invertebrates were below 1.0 ppm. Among the decapod crustaceans consumed by fish, most were shrimp rather than crabs, except for *O. tau,* which consumes mainly crabs. The high level of mercury in *O. tau* as compared with the other fish may reflect high levels of the same element in crabs that it eats. This does not explain elevated levels of mercury in *B. chrysura, S. aquosus,* and *S. plagiusa,* which feed on very few, if crabs, but prefer other invertebrates that do not have high levels of mercury. Zinc values in the invertebrates analyzed were somewhat elevated compared to fishes.

With the exceptions noted above, there were no obvious positive correlations between the trace-metal levels in the invertebrates and those in the fishes which fed upon them. There is no indication that the metals examined are being concentrated up the food web from invertebrates to fishes with the possible exceptions of lead and mercury in *O. tau.*

Under natural conditions, i.e., those which the organisms have faced throughout much or most of their evolutionary history, normal physiological control mechanisms are able to control heavy-metal uptake. The data obtained during our study, although they do show rather high degrees of variability, can be assumed to elaborate the heavy-metal picture as it exists under relatively natural conditions. The estuarine system of the southeastern United States under study has not been highly contaminated by heavy-metal pollution, although some exceptions do exist. The data presented in this paper may be useful as a baseline with which future changes within the study area can be correlated.

Laboratory studies into the effects of heavy metals on fish and invertebrates have often involved acute and chronic toxicity studies or experiments in which elevated levels of metals individually or in combination have been used to elicit marked physiological or behavioral responses (e.g., Eaton, 1973; Eisler, 1967, 1971, 1972; Eisler and Gardner, 1973; Gardner and Yevich, 1970; Pickering and Gast, 1972). Future studies into the mechanisms by which heavy metals are incorporated into fish and invertebrates both from their food and from the medium should be undertaken using levels of metals which do not exceed background to an extent sufficient to elicit harmful effects on the test organisms. Such studies will be valuable in explaining field observations.

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REFERENCES

Cross, F. A., T. W. Duke, and J. N. Willis, 1970, Biogeochemistry of Trace Elements in a Coastal Plain Estuary: Distribution of Manganese, Iron, and Zinc in Sediments, Water, and Polychaetous Worms, *Chesapeake Sci.*, **11**: 221-234.

——, L. H. Hardy, N. Y. Jones, and R. T. Barber, 1973, Relation Between Total Body Weight and Concentrations of Manganese, Iron, Copper, Zinc, and Mercury in White Muscle of Bluefish (*Pomatomus saltatrix*) and a Bathyldemersal Fish *Antimora rostrata*, *J. Fish. Res. Board Can.*, **30**: 1287-1291.

——, J. N. Willis, and J. P. Baptist, 1971, Distribution of Radioactive and Stable Zinc in an Experimental Marine Ecosystem, *J. Fish. Res. Board Can.*, **28**: 1783-1788.

Duke, T. W., 1963, Biogeochemical Cycling of Radionuclides in the Estuarine Environment, *Proc. Annu. Conf. Southwest. Assoc. Game Fish Comm.*, **17**: 315-323.

——, J. N. Willis, and T. J. Price, 1966, Cycling of Trace Elements in the Estuarine Environment. I. Movement and Distribution of Zinc-65 and Stable Zinc in Experimental Ponds, *Chesapeake Sci.*, **7**: 1-10.

Eaton, J. G., 1973, Chronic Toxicity of a Copper, Cadmium, and Zinc Mixture to the Fathead Minnow (*Pimephales promelas* Rafineque), *Water Res.*, **7**: 1723-1736.

Eisler, R., 1972, Cadmium Uptake by Marine Organisms, *J. Fish. Res. Board Can.*, **29**: 1367-1369.

——, 1971, Cadmium Poisoning in *Fundulus heteroclitus* (Pisces: Cyprinodontidae and Other Marine Organisms, *J. Fish. Res. Board Can.*, **28**: 1225-1234.

, 1967, Acute Toxicity of Zinc to the Killifish, *Fundulus heteroclitus*, *Chesapeake Sci.*, **8**: 262-264.

——, and G. R. Gardner, 1973, Acute Toxicity to an Estuarine Teleost of Mixtures of Cadmium, Copper, and Zinc Salts, *J. Fish. Biol.*, **5**: 131-142.

Gardner, G. R., and P. P. Yevich, 1970, Histological and Hematological Responses of an Estuarine Teleost to Cadmium, *J. Fish. Res. Board Can.*, **27**: 2185-2196.

Odum, E. P., and A. A. de la Cruz, 1967, Particulate Organic Detritus in a Georgia Salt-Marsh–Estuarine Ecosystem, in *Estuaries*, G. H. Lauff (Ed.), pp. 383-388, American Association for the Advancement of Science, Publication 83, Washington, D. C.

——, and A. A. de la Cruz, 1963, Detritus as a Major Component of Ecosystems, *AIBS (Amer. Inst. Biol. Sci.) Bull.*, **13**: 39-40.

Pickering, Q. H., and M. H. Gast, 1972, Acute and Chronic Toxicity of Cadmium to the Fathead Minnow (*Pimephales promelas*), *J. Fish. Res. Board Can.*, **29**: 1099-1106.

Rahn, W. R., Jr., 1973, The Role of *Spartina alterniflora* in the Transfer of Mercury in a Salt-Marsh Environment, M.S. Thesis, Georgia Institute of Technology.

Stickney, R. R., G. L. Taylor, and R. W. Heard III, 1974, Food Habits of Georgia Estuarine Fishes. I. Four Species of Flounder (Pleuronectiformes: Bothidae), *Fish. Bull.*, **72**: 515-525.

——, G. L. Taylor, and D. B. White, 1975, Food Habits of Five Species of Young Southeastern United States Estuarine Sciaenidae, *Chesapeake Sci.*, **16**: 104-114.

——, H. L. Windom, D. B. White, and F. Taylor, 1972, Mercury Concentration in Various Tissues of the Bottlenose Dolphin (*Tursiops truncatus*), *Proc. Annu. Conf. Southeast. Assoc. Game Fish Comm.*, **26**: 634-636.

Windom, H. L., 1973, Mercury Distribution in Estuarine–Nearshore Environment, *J. Waterways Harbors Div., Amer. Soc. Civil Eng.*, **99**: 257-264.

——, K. C. Beck, and R. Smith, 1971, Transport of Trace Metals to the Atlantic Ocean by Three Southeastern Rivers, *Southeast. Geol.*, **12**: 169-181.

——, and R. G. Smith, 1972, Distribution of Cadmium, Cobalt, Nickel, and Zinc in Southeastern United States Continental Shelf Waters, *Deep-Sea Res.*, **19**: 727-730.

——, R. Stickney, R. Smith, D. White, and F. Taylor, 1973, Arsenic, Cadmium, Copper, Mercury, and Zinc in Some Species of North Atlantic Finfish, *J. Fish. Res. Board Can.*, **30**: 275-279.

Wolfe, D. A., and T. R. Rice, 1972, Cycling of Elements in Estuaries, *Fish. Bull.*, **70**: 959-972.

CONCENTRATIONS OF TOTAL MERCURY AND METHYL MERCURY IN FISH AND OTHER COASTAL ORGANISMS: IMPLICATIONS TO MERCURY CYCLING

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ABSTRACT

Total and methyl mercury concentrations were determined for a variety of aquatic organisms from several estuaries of the southeastern United States. Methyl mercury was not detected in *Spartina alterniflora*, the prominent marsh plant of this region, but represented a substantial fraction (about 70%) of the mercury in muscle tissues of several aquatic animals. The relative quantity of mercury present in the methylated form in fish was unrelated to total mercury concentrations or species but was dependent on the type of tissue examined. Less methylated mercury was found in liver and spleen tissue than in muscle.

The transport of metals through aquatic ecosystems is dependent on the chemical form of the metal and the chemical and physical characteristics of the surrounding media. The chemical form of mercury may be important to its fate in marine coastal environments. Inorganic mercury can occur as Hg_2^{2+}, Hg^{2+}, or as Hg^0. The latter is volatile and easily lost to the atmosphere. Since these forms may be in equilibrium in water or sediments, the concentration and flux of unbound mercury is dependent on such conditions as Eh and pH and other chemicals present (Wood, 1974). Such physical disturbances as the movement of gases through the system, which could strip out volatile forms of the metal, may also affect the mercury flux. The fate of mercury is further complicated by the occurrence of organic species of the metal which can be biochemically formed and degraded in natural systems. The predominant stable organic mercury compound that can be formed in natural environments is methyl mercury.

The potential importance of organic mercury gained more attention when it was learned that it could be formed in natural systems by bacteria (Jensen and Jernelöv, 1969; Langley, 1973; Spangler et al., 1973). The decomposition of

methyl mercury to methane and Hg^0 in sediments has also been demonstrated experimentally (Spangler et al., 1973). Organic mercury compounds are commonly associated with organic substances. In particular methyl mercury adheres to the sulfhydryl portions of amino acid compounds. For this reason methyl mercury compounds are rapidly removed from aqueous solution by living organisms.

To assess the potential role of methyl mercury in mercury-transfer processes in southeastern coastal ecosystems, we analyzed a variety of organisms collected in coastal regions for total and methyl mercury. The results presented here represent the initial phase of a more comprehensive study of mercury-transfer mechanisms in marine ecosystems.

METHODS

Samples of fish and other biological species were collected from various locations along the South Carolina, Georgia, and Florida coasts. A map of the sampling area is provided by Stickney et al. (this volume). *Spartina alterniflora* was separated into leaves, roots, and stems. Muscle tissues were removed from a variety of Osteichthyes, Chondrichthyes, and Crustaceans. The liver and spleen tissues from some species were also analyzed. Tissues were kept frozen in plastic bags until analysis. Dry weights were determined by drying subsamples at 110°C and measuring the weight change.

Samples for total-mercury analyses were wet digested overnight in concentrated sulfuric and nitric acids on a water bath at 60°C. After digestion the samples were diluted and further oxidized with potassium permanganate and potassium disulfate. Mercury was reduced to its zero valence by addition of stannus sulfate. Samples were then aerated with a peristaltic pump into a cold-vapor atomic absorption system for analysis, and the resulting absorption was compared with that of standards. The standard deviation of analysis at the levels encountered was ±10%.

Methyl mercury was extracted from the tissues by the procedure of Uthe, Solomon, and Grift (1972). The final benzene extract was analyzed on a gas chromatograph equipped with an electron-capture detector. A 3.6-m by 3-mm-OD glass column containing 5% Hi Eff 10B (Applied Science) on Supelcoport (60/80 mesh) maintained at 180°C was used to isolate the methyl mercury compounds. Detection limits were 0.01 ppm Hg on a wet-weight basis. The accuracy and precision of the methyl mercury procedure were estimated by determining the net recoveries of added methyl mercury in quantities similar to those encountered naturally. From a series of 22 samples of several biological specimens the average recovery of methyl mercury was determined to be 100% with a standard deviation of ±7%.

RESULTS

Tissue samples from representative organisms of the southeastern Atlantic coastal ecosystem were analyzed for total and methyl mercury (Table 1). *Spartina alterniflora* contained higher concentrations of total mercury in the roots than in the stems or leaves. Methyl mercury was not detected in the plant tissues. The levels of mercury in muscle tissue of the various species of Osteichthyes generally ranged between 0.1 and 1 ppm (dry weight), the higher values of *Arius felis* (sea catfish) and *Opsanus tau* (oyster toadfish) be[illegible] exceptions. Not including the latter two species, the range of concentrations [illegible] often as great among different specimens of the same species as between different species.

In contrast to Osteichthyes, muscle tissues of Chondrichthyes contained higher concentrations of mercury. The various species of sharks contained mercury at levels between 2 and 6 ppm in muscle tissues, with an average concentration of about 4 ppm. Stingrays also exhibited high mercury levels, ranging from an average of 1.5 ppm for *Dasyatis sayi* to 3.2 ppm for *Dasyatis americana.*

In agreement with other studies that have reported total and methyl mercury concentrations (Lockhart et al., 1972; Kamps, Carr, and Miller, 1972; Rivers, Pearson, and Shultz, 1972), these data indicate that methyl mercury is the predominant form of the metal in fish muscle (Table 1). The percentage of mercury which was methylated in fish muscle was apparently independent of size or species and averaged about 70% of the total for the fish examined. Although there is considerable variation among individual samples in the amount of mercury methylated, the average was similar for muscle tissues of Osteichthyes and Chondrichthyes (Fig. 1).

Of the crustaceans examined, blue crab muscle gave yields of total and methyl mercury similar to Osteichthyes. Shrimp, which contained less mercury than the other specimens examined, also had a lower average percent of methyl mercury.

In contrast to muscle tissue, samples of spleen and liver from shar[illegible] contained proportionally low levels of methyl mercury (Fig. 1). Spleens of si[illegible] specimens of *Negaprion brevirostris* (lemon shark) averaged about 10 ppm total mercury of which only about 0.2 ppm was in methylated form. Livers of five specimens of the same species averaged 5.5 ppm with 0.05 ppm in methylated form. The relative quantity of methylated mercury in the livers of other species of sharks and other fish was higher, ranging from 3% for *Carcharhinus milberti* (sand bar shark) to 48% of total mercury for flounder (Table 1). However, in all specimens examined the relative amount of methylated mercury was lower in livers and spleens than in muscles of the same species.

TABLE 1

CONCENTRATIONS (ppm DRY WEIGHT) OF TOTAL MERCURY AND METHYL MERCURY IN TISSUES OF COASTAL ORGANISMS FROM THE SOUTHEASTERN UNITED STATES

Organism and tissue examined	No. of samples	Total mercury		Methyl mercury	
		Av.	Range	Av.	Range
Osteichthyes					
Anguillidae, freshwater eels					
Anguilla rostrata (American eel) muscle	1	1.2		0.85	
Clupeidae, herrings					
Brevoortia tyrannus (Atlantic menhaden) muscle	2	0.30	0.14–0.47	0.25	0.21–0.29
Ariidae, sea catfishes					
Arius felis (sea catfish) muscle	3	1.8	1.5–2.2	1.41	1.1–1.6
Batrachoididae, toadfishes					
Opsanus tau (oyster toadfish) muscle	1	2.9		1.4	
Cyprinodontidae, killifishes					
Fundulus heteroclitus (mummichog) muscle	1	0.47		0.14	
Serranidae, sea basses					
Centropristis striata (black sea bass) muscle	2	0.84	0.49–1.2	0.47	0.21–0.72
Rachycentridae, cobias					
Rachycentron canadus (cobia) muscle	1	0.93		0.70	
Sparidae, porgies					
Archosargus probatocephalus (sheepshead) muscle	1	0.75		0.46	

(Table continues on following page.)

TABLE 1 (Continued)

Organism and tissue examined	No. of samples	Total mercury Av.	Total mercury Range	Methyl mercury Av.	Methyl mercury Range
Sciaenidae, drums					
Micropogon undulatus (Atlantic croaker) muscle	6	0.38	0.20–0.84	0.25	0.09–0.50
Bairdiella chyrsura (silver perch) muscle	2	0.46	0.32–0.60	0.39	0.33–0.46
Cynoscion regalis (weakfish) muscle	1	0.47		0.23	
Cynoscion nebulosus (spotted sea trout) muscle	1	0.73		0.73	
Leiostomus xanthurus (spot) muscle	5	0.25	0.16–0.38	0.20	0.08–0.27
Menticirrhus americanus (southern kingfish) muscle	1	0.36		0.13	
Stellifer lanceolatus (star drum) muscle	2	0.65	0.50–0.79	0.35	0.27–0.42
Bothidae, lefteye flounder					
Paralichthys lethostigma (southern flounder) Muscle	6	0.64	0.39–0.92	0.36	0.14–0.54
Liver	1	0.10		0.05	
Ancylopsetta quadrocellata (ocellated flounder) muscle	1	0.46		0.41	
Etropus crossotus (fringed flounder) muscle	1	0.10		Nd*	
Citharichthus spilopterus (bay whiff) muscle	1	0.17		0.16	
Cynoglossidae, tonguefishes					
Symphurus plagiusa (blackcheek tonguefish) muscle	1	0.10		0.16	

Chondrichthyes					
Carcharhinidae, requiem sharks					
Negaprion brevirostris (lemon shark)					
Muscle	4	3.8	3.2–4.6	3.1	3.0–3.1
Spleen	6	10.4	1.1–1.5	0.17	Nd–0.55
Liver	5	5.5	3.9–8.3	0.05	Nd–0.07
Carcharbinus leucas (bull shark)					
Muscle	1	10.2		3.9	
Spleen	1	4.6		0.24	
Carcharbinus limbatus (blacktip shark)					
Muscle	2	0.75	0.66–0.85	0.52	0.40–0.65
Liver	1	1.30		0.06	
Carcharbinus falciforms (silky shark)					
Muscle	1	1.79		0.74	
Liver	1	0.75		0.03	
Squalidae, dogfish sharks					
Squalus acanthias (spiny dogfish) muscle	1	4.0		3.0	
Sphyrnidae, hammerhead sharks					
Sphyrna lewini (scalloped hammerhead)					
muscle	1	3.4		0.72	
Dasyatidae, stingrays					
Dasyatis sabina (Atlantic stingray)					
muscle	4	2.6	0.30–3.8	2.4	0.24–3.4
Dasyatis sayi (bluntnose stingray)					
muscle	2	1.5	1.3–1.7	0.78	0.31–1.2
Crustacea					
Portunidae, crab					
Callinectes sapidus (blue crab)					
muscle	8	0.45	0.50–1.1	0.31	0.15–0.57

(Table continues on following page.)

TABLE 1 (Continued)

Organism and tissue examined	No. of samples	Total mercury		Methyl mercury	
		Av.	Range	Av.	Range
Penaeidae, shrimp					
Penaeus setiferus (white shrimp)					
muscle	9	0.31	0.04–0.65	0.17	0.01–0.47
Penaeus aztecus (brown shrimp)					
muscle	10	0.17	0.07–0.26	0.08	0.01–0.24
Xiphopeneus kroyeri (shrimp)					
muscle	3	0.26	0.24–0.28	0.06	0.01–0.09
Palaemonidae					
Palaemonectes pugio	1	0.13		0.06	
Angiospermae					
Gramineae					
Spartina alterniflora					
Roots	8	0.78	0.40–1.4	Nd	
Stems	9	0.23	0.12–0.28	Nd	
Leaves	8	0.23	0.23–0.37	Nd	

*Nondetectable.

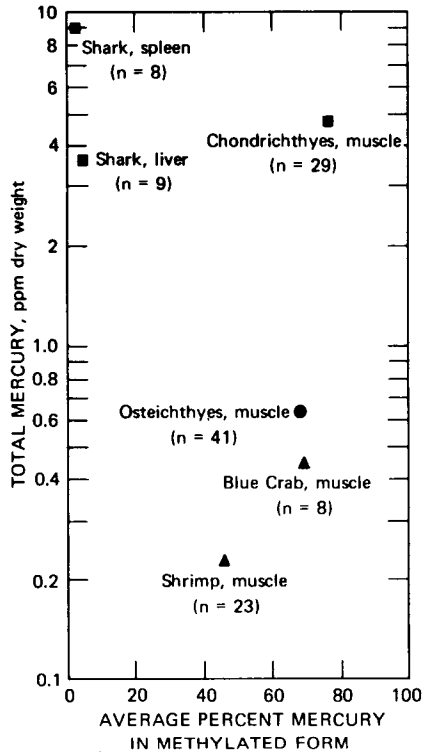

Fig. 1 Comparison of total mercury with percent methylated mercury in tissues of coastal organisms.

DISCUSSION

The higher levels of mercury found in tissues of Chondrichthyes compared to other species may result from the high position of these organisms in the food chain. Other reasons could be metabolic differences or that specimens of this class were generally older than the other organisms collected. Concentrations of mercury increase with body weight (age) in several species of fish (Cross et al., 1973).

Because of its relative stability in biological systems and its unique biochemical characteristics, methyl mercury apparently is metabolized differently by fish and other marine organisms than is inorganic mercury. Differences in the metabolic utilization of these two types of mercury help to provide a logical explanation of mercury accumulation in fish. Stickney et al. (this volume) found that mercury is concentrated in fish to a greater degree, relative to its

concentration in food sources, than Cd, Cu, Pb, and Zn. The latter were not quantitatively taken up from food supplies, but mercury was accumulated in amounts greater than could be explained by food sources alone. This difference would be expected if the fish were exposed to methyl mercury. Mercury absorbed into the fish is transferred through the animal via its blood stream until removed by the liver and spleen. Inorganic mercury is stored in these tissues until removed through the kidney by excretion. Methyl mercury is apparently not excreted to a great extent but is accumulated in the muscles (Jernelöv and Lann, 1971). In the case of pike, whether radioactive methyl mercury w introduced orally in protein-bound or free ionic form, the resulting radioactiv in fish flesh was protein bound (Miettinen et al., 1969). Burrows and Krenkel (1973) suggest that a portion of methyl mercury may be degraded to the inorganic form in the liver. Other forms of organic mercury are degraded to the inorganic form and then excreted (Jernelöv and Lann, 1971). For example, when guppy, snail, *Elodea* sp., and coontail were exposed to phenyl mercury, it was converted to the inorganic form. Exposure of these organisms to phenylmercuric acetate did not have a significant effect on their levels of methyl mercury (Fang, 1973).

Radioisotopic studies made with molluscs have shown that mercury administered in different forms is excreted at different rates. Inorganic mercury ion was excreted more rapidly than phenyl mercury, but methyl mercury was retained much longer (half time of 86 to 435 days) than either of the other two forms. The retention of methyl mercury depended on the age and size of the animals. Younger animals had the shortest half time (Miettinen et al., 1969).

Under natural conditions the mercury present in fish reflects to some degree the mercury in the surrounding environment. For example, fish moved from a contaminated to a decontaminated lake showed a decrease in mercury content of about 30% in a year (Lockhart et al., 1972). It was suggested that the decrease could have been caused in part by dilution during growth. The concentrations of total mercury relative to methyl mercury in livers and spleens may be indicative of the quantity of inorganic mercury or nonmethyl organic forms to which the fish have been exposed over a relatively short period of time, whereas mercury in muscle tissue represents accumulation of methyl mercury over a long period of time.

The importance of organic mercury in transferring the metal through low levels of the marine food chain is still unclear. An evaluation of marine zooplankton for total mercury indicated that its concentration in these organisms was of the same order of magnitude as for some fish, but the form of the metal was not determined (Williams and Weiss, 1973).

Mercury can be methylated by bacteria in sediments, but it apparently does not accumulate in natural sediments or in the water (Spangler et al., 1973). Methyl mercury accounts for only a small ($<0.01\%$) percent of the total mercury in estuarine sediments (Andren and Harriss, 1973). If marsh sediments

are the site of methylation, it would be of interest to know the mode of transport of the methyl mercury from the sediment to the fish. Methyl mercury has a relatively high volatility and could be released with gases formed in the sediments. Counteracting this, methyl mercury tends to associate with organic matter (especially proteins), which could prevent its release from sediments. Another potential mechanism for transfer of mercury into the water from marsh sediments would be biological transport through the marsh plants. The absorption and translocation of methyl mercury by terrestrial plants has been reported (Haney and Lipsey, 1973). Preliminary studies in our laboratory have shown that methyl mercury potentially can be transported upward through *Spartina* plants. If the mercury is released to the water column, it could be taken up by fish. That fish can readily remove methyl mercury from surrounding waters has been demonstrated by studies in which methyl mercury production was monitored by measuring methyl mercury taken up by exposed fish (e.g., Langley, 1973; Hannerz, 1968). This could explain the higher mercury levels in finfish than in the intermediate food-chain members.

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REFERENCES

Andren, A. W., and R. C. Harriss, 1973, Methylmercury in Estuarine Sediments, *Nature*, **245**: 256-257.

Burrows, W. D., and P. A. Krenkel, 1973, Studies on Uptake and Loss of Methyl-Mercury-203 by Bluegills (*Lepomis macrochirus* Raf.), *Environ. Sci. Technol.*, **13**: 1127-1130.

Cross, F. A., L. H. Hardy, N. Y. Jones, and R. T. Barber, 1973, Relation Between Total Body Weight and Concentrations of Manganese, Iron, Copper, Zinc, and Mercury in White Muscle of Bluefish (*Pomatomus saltatrix*) and a Bathyal-Demersal Fish (*Antimora rostrata*), *J. Fish. Res. Board Can.*, **30**: 1287-1291.

Fang, S. C., 1973, Uptake and Biotransformation of Phenylmercuric Acetate by Aquatic Organisms, *Arch. Environ. Contam. Toxicol.*, **1**: 18-26.

Haney, A., and R. L. Lipsey, 1973, Accumulation and Effects of Methyl Mercury Hydroxide in a Terrestrial Food Chain Under Laboratory Conditions, *Environ. Pollut.*, **5**: 305-316.

Hannerz, L., 1968, Experimental Investigations on the Accumulation of Mercury in Water Organisms, in *Statens undersökning och försöksanstalt för sötvattensfisket, Drottningholm, Sweden*, **48**: 120-176.

Jensen, S., and A. Jernelöv, 1969, Biological Methylation of Mercury in Aquatic Organisms, *Nature*, **223**: 753-754.

Jernelöv, A., and H. Lann, 1971, Mercury Accumulation in Food Chains, *Oikos*, **22**: 403-406.

Kamps, L. R., R. Carr, and H. Miller, 1972, Total Mercury Monomethylmercury Content of Several Species of Fish, *Bull. Environ. Contam. Toxicol.*, **8**: 273-279.

Langley, D. G., 1973, Mercury Methylation in an Aquatic Environment, *J. Water Pollut. Contr. Fed.*, **45**: 44-51.

Lockhart, W. L., J. F. Uthe, A. R. Kenney, and P. M. Mehrle, 1972, Methylmercury in Northern Pike (*Esox lucius*): Distribution, Elimination, and Some Biochemical Characteristics of Contaminated Fish, *J. Fish. Res. Board Can.*, **29**: 1519-1523.

Miettinen, J. K., M. Tillander, K. Rissanen, V. Miettinen, and Y. Ohmomo, 19[illegible] Distribution and Excretion Rate of Phenyl- and Methylmercury Nitrate in Fish Muss[illegible] Molluscs, and Crayfish, in *Proceedings of the 9th Japan Conference on Radioisotopes*, May 13–15, Tokyo, Japan Atomic Industrial Forum, Inc.

Rivers, J. B., J. E. Pearson, and C. D. Shultz, 1972, Total and Organic Mercury in Marine Fish, *Bull. Environ. Contam. Toxicol.*, **8**: 257-266.

Spangler, W. J., J. L. Spigarelli, J. M. Rose, and H. M. Miller, 1973, Methyl Mercury Bacterial Degradation in Lake Sediments, *Science*, **180**: 192-193.

Uthe, J. F., J. Solomon, and B. Grift, 1972, Rapid Semimicro Method for the Determination of Methyl Mercury in Fish Tissue, *J. Ass. Offic. Anal. Chem.*, **55**: 583-589.

Williams, P. M., and H. V. Weiss, 1973, Mercury in the Marine Environment: Concentration in Sea Water and in a Pelagic Food Chain, *J. Fish. Res. Board Can.*, **30**: 293-295.

Wood, J. M., 1974, Biological Cycles for Toxic Elements in the Environment, *Science*, **183**: 1049-1052.

NITROGEN REGENERATION BY THE CTENOPHORE Mnemiopsis Leidyi

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ABSTRACT

Measurements of biomass and nitrogen excretion rates were made for *Mnemiopsis leidyi* in Narragansett Bay, R. I. Excreted nitrogen, primarily in the form of ammonia, was constant over time for individuals, and a direct linear function of size for a sample of the population at a given temperature. The excretion rate was very temperature dependent, ranging from 0.4 to 1.5 μg atom of NH_3 per gram of dry weight per hour between 15.8 and 24.5°C. The nitrogen flux through the Narragansett Bay ctenophore population was calculated for 2 years. The 1971 maximum was about 60 μg atoms NH_3 –N $m^{-3} day^{-1}$ compared to a 1972 peak of about 10 μg atoms m^{-3} day^{-1}. Excretion rates for Narragansett Bay were applied to ctenophore biomass and temperature data from four Atlantic estuaries, and calculated fluxes of ammonia were similar. Ctenophore ammonia excretion was estimated to be comparable to that of other zooplankton during the period of ctenophore abundance. However, both these nitrogen sources are small when compared to the estimated flux from the benthos in Narragansett Bay in the late summer.

Animals have the potentially important role in ecosystems of regulating the flow of nutrients, either directly through excretion or indirectly by such mechanisms as biodeposition (Kuentzler, 1961). Numerous marine environments have been observed to be nutrient depleted during at least part of the year, and it has been determined that during these periods phytoplankton growth may be nitrogen limited (Ryther and Dunstan, 1971). Organisms excreting large amounts of nitrogen in a form readily used by phytoplankton could therefore be very important in the entire pattern of plankton dynamics.

Excretion of nitrogen by zooplankton, particularly crustaceans, can be important to phytoplankton growth (Harris, 1959; Martin, 1968; Jawed, 1973). Ammonia–nitrogen is of special interest since it is taken up preferentially by many phytoplankton (MacIssac and Dugdale, 1972) and is the primary form of nitrogen excreted by many zooplankton (Corner and Newell, 1967; Butler, Corner, and Marshall, 1969; Jawed, 1969).

The comb jelly *Mnemiopsis leidyi* is a seasonally conspicuous member of the zooplankton in the coastal waters along most of the eastern United States south of Cape Cod (Mayer, 1912; Nelson, 1925; Burrell, 1968; Miller, 1974). Although these animals have been cited as important predators on smaller zooplankton (Bishop, 1967; Miller, 1970), they have not been evaluated with respect to the importance of their role in nutrient regeneration. This paper presents the results of an investigation of nitrogen excretion rates for *M. leidyi* and combines these results with biomass data to estimate the ammonia flux from ctenophores for several Atlantic coast estuaries. This flux is compared with calculations of excretion for other zooplankton in these locations and evaluated with respect to other nutrient sources.

MATERIALS AND METHODS

Individual *M. leidyi,* ranging from 0.4 to 38.0 g live weight (0.013 to 1.283 g dry weight), were collected from Narragansett Bay in beakers by hand to minimize disturbance to the animals. Within a few hours of collection, the organisms were transferred to containers that had been prerinsed with dilute hydrochloric acid, rinsed with distilled water, and filled with filtered (filter tube, 0.5-μ retension) bay water of 31‰ salinity. Smaller organisms were placed in 300-ml biochemical oxygen demand bottles, and larger animals in 500-ml Erlenmeyer flasks. All containers were tightly stoppered, incubated in the dark at a temperature within 2°C of the ambient bay temperature, and gently shaken every 4 to 5 hr to ensure thorough mixing of nutrients and gases. After incubating at least 12 hr, organisms were removed, and their wet weight was determined. Because of their delicate nature, the organisms were drained but not blotted before weighing. Dry weights were taken after the organisms were dried at 100°C for 1 week.* The concentration of ammonia in the incubation water was determined (Solorzano, 1969), and samples were analyzed for urea (McCarthy, 1970), nitrite, and nitrate (Strickland and Parsons, 1968, as modified for the Technicon Autoanalyzer). In some cases ammonia samples were removed at frequent intervals during the incubation to confirm that the excretion rate for an individual organism was constant through time.

RESULTS

Form of Excreted Nitrogen

The analyses of urea, nitrate, and nitrite samples indicated that *M. leidyi* does not excrete these substances in appreciable amounts. Together these

*Mean of 117 determinations, wet weight = dry weight x 29.62 ± 0.65.

compounds amounted to less than 5% of the ammonia–nitrogen excreted by the animals.

Excretion with Time

Time series experiments indicated that the excretion rate by an individual animal is constant with time (Fig. 1). Organisms tested at a higher temperature

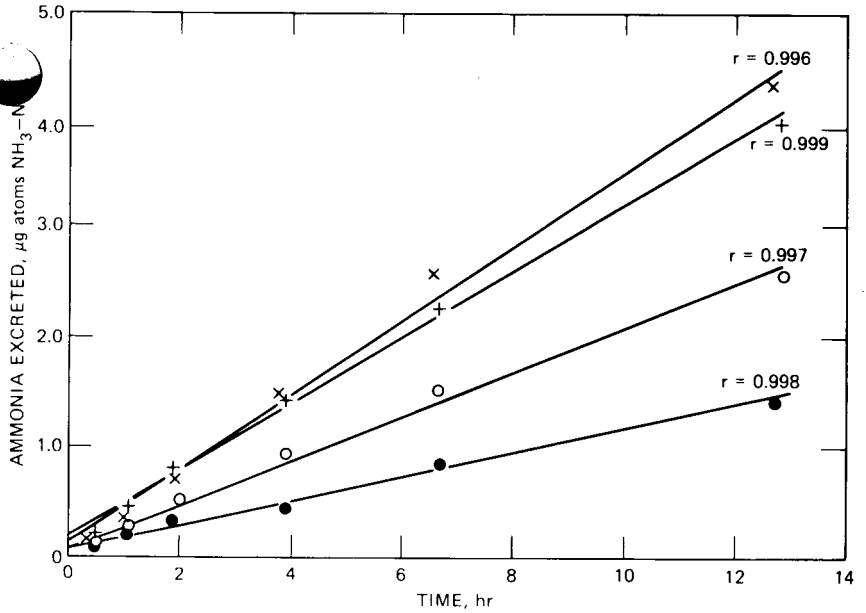

Fig. 1 Ammonia excreted over time for four individual *Mnemiopsis leidyi* at 20°C. Correlation coefficients (r) given for each regression line.

for a longer period of time yielded similar strongly linear results but with a decrease of about 10% in the 22-hr sample. This depressed excretion rate is believed to be due to the high ammonia concentration of greater than 20 μg atoms/liter in the water. Because of these findings, however, efforts were made to terminate incubations before 20 hr. In the few cases where this time was exceeded, results were consistent with the shorter incubations. Since these observations indicated a constant ammonia excretion rate, the rate for an individual could be determined with a single terminal sample, given the initial concentration. Control bottles provided the initial concentration and demonstrated that no change had occurred in the filtered water during incubation. To see if any unwanted nitrogen sources were introduced with the ctenophores, we conducted tests at 15 and 20°C in which the *Mnemiopsis* were transferred to different flasks after the first hour of a 17-hr incubation. The subsequent nitrogen increase in the prerinse flasks was generally less than 15% of that in the

experimental flasks. Since some of this increase was undoubtedly due to small fragments of the *Mnemiopsis* left in the water, the nitrogen contribution by extraneous microorganisms is probably small. This procedure maintained a closed system; so respiration as well as excretion could be determined. Respiration results will not be discussed here except to note that oxygen consumption and ammonia excretion agreed closely at all temperatures, yielding an oxygen to nitrogen ratio by atoms of 13:1 with an overall correlation coefficient for all observations of 0.98.

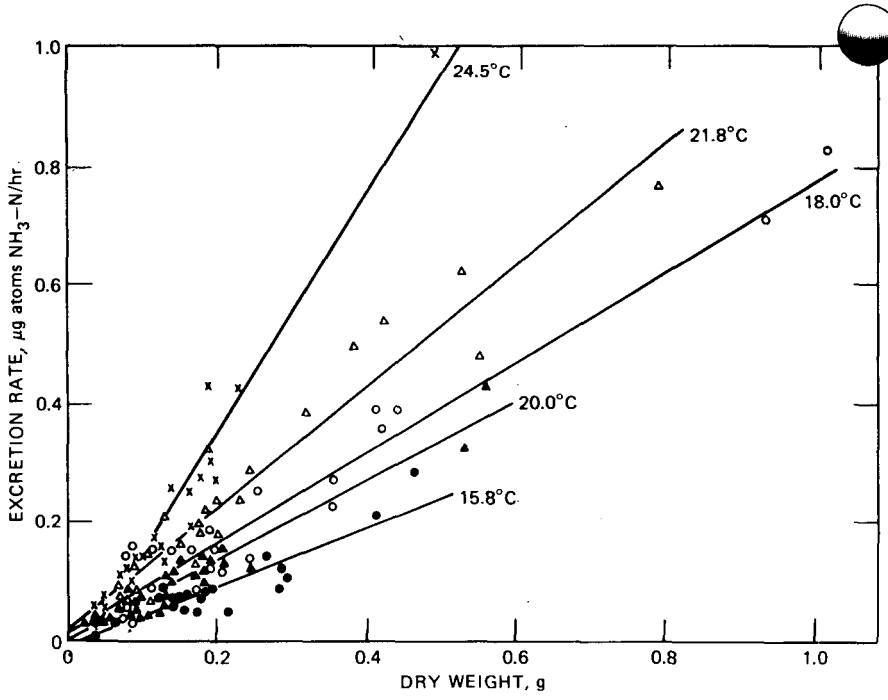

Fig. 2 Ammonia excretion rate for individual *M. leidyi* vs. dry weight for a range of temperatures.

Excretion Rate with Size

Individual excretion rates were determined using the single terminal-sample method for 134 animals at several different temperatures. At a given temperature the excretion rate per individual seems to be a direct linear function of size (Fig. 2 and Table 1). Although an attempt was made to test a variety of sizes, most organisms were relatively small because they were the most abundant and readily collected. The two very large animals used in the 18°C run (29 g and 38 g wet weight) were among the largest observed in 3 years of collecting in Narragansett Bay, and it is significant that their excretion rates do not depart appreciably from the regression line established by all the data.

TABLE 1

NUMERICAL PARAMETERS ASSOCIATED WITH THE EXCRETION RATE OF INDIVIDUAL *M. LEIDYI* AS A FUNCTION OF DRY WEIGHT AT FIVE TEMPERATURES*

Temp., °C	Regression coefficient, μg atoms NH_3 –N hr^{-1} g^{-1}	Correlation coefficient	Rate-weight exponent b	Standard error of b
15.8	0.51	0.92	1.08	0.11
18.0	0.76	0.98	1.12	0.08
20.0	0.67	0.97	0.88	0.06
21.8	1.03	0.96	1.04	0.08
24.5	2.05	0.98	1.12	0.07

*Regression and correlation coefficients are for least-squares lines given in Fig. 2; estimates and standard errors for the exponent of the equation $Y = aW^b$ are determined from log-log regression of excretion rate and size data.

The relation between metabolic rate and size of the organism is often expressed with the following equation (Brody, 1945):

$$Y = aW^b$$

where Y = metabolic rate
a = a constant for the species and temperature
W = weight of the individual
b = the rate–weight exponent

Using the data in Fig. 2, we calculated values of b for each temperature group (Table 1). These values of b are all close to 1.0, indicating that the *M. leidyi* ammonia excretion per unit weight is constant for all sizes. This result contrasts with values of b equal to about 0.7 to 0.8 found for many organisms where the relative proportion of surface area to volume seems to strongly influence metabolic rate (Brody, 1945; Kleiber, 1961). However, as Bertalanffy (1968) points out, this "surface law" is not universal and there are some parameters that do not decrease with increasing size. Although excretion rate might be expected to conform to the rule, the discrepancy here may reflect the simple nature of the ctenophore.

Excretion Rate with Temperature

The tendency for the weight-specific excretion rate to increase with temperature is clear, although the correlation coefficient is only 0.76 (Fig. 3). The data were fitted with an exponential expression as the most theoretically

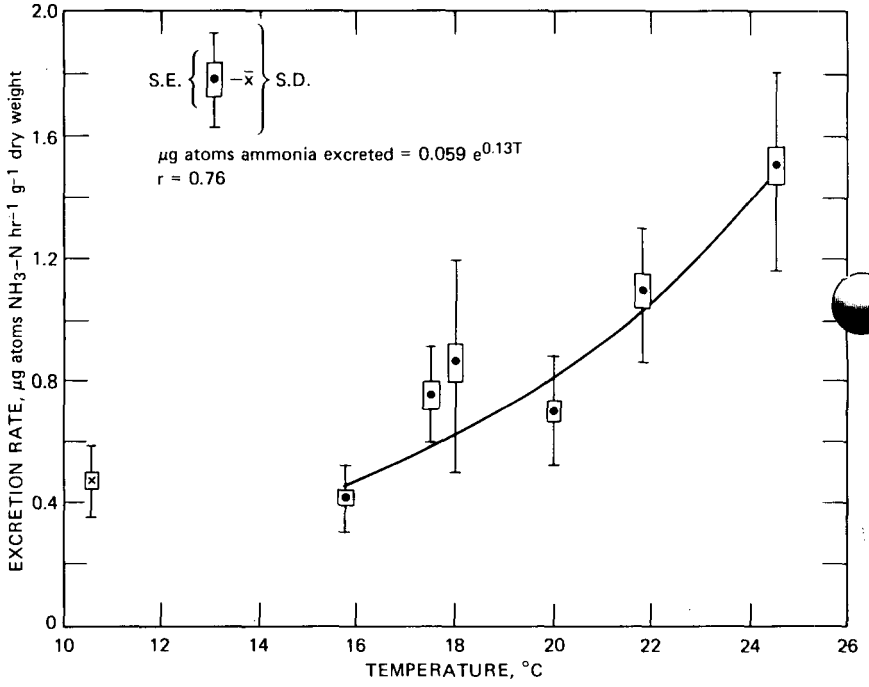

Fig. 3 ***Mnemiopsis leidyi*** **ammonia excretion rate per gram dry weight vs. temperature. The mean observed rate as well as the standard error of the mean and standard deviation of the observations are given for all temperatures tested. The mean of the observations at 10.3°C is marked by an X and is not included in the regression since these organisms received different pretreatment.**

sound (Brody, 1945), although for these six runs a straight line fits the data nearly as well (r = 0.75). Excretion rates for organisms run at 10.3°C were not included in the regression and are represented by a different symbol in Fig. 3 since they were caught by net and held 2 days before being tested. Including these 10.3°C results would yield slightly lower correlation coefficients (r = 0.71 for linear regression, r = 0.72 for logarithmic transformation).

Ammonia Flux from Narragansett Bay Ctenophores

Ctenophores are abundant in Narragansett Bay for less than 4 months of the year, but, when present, their biomass can be very impressive. By coupling average biomass estimates for 20 sampling stations with excretion estimates based on observed field temperatures, we have calculated the total daily flux of ammonia from *M. leidyi* for 2 consecutive years (Fig. 4).

The calculated excretion closely tracks the biomass estimate, departing only slightly in the fall as the water cools. The 1971 season was slightly shorter but

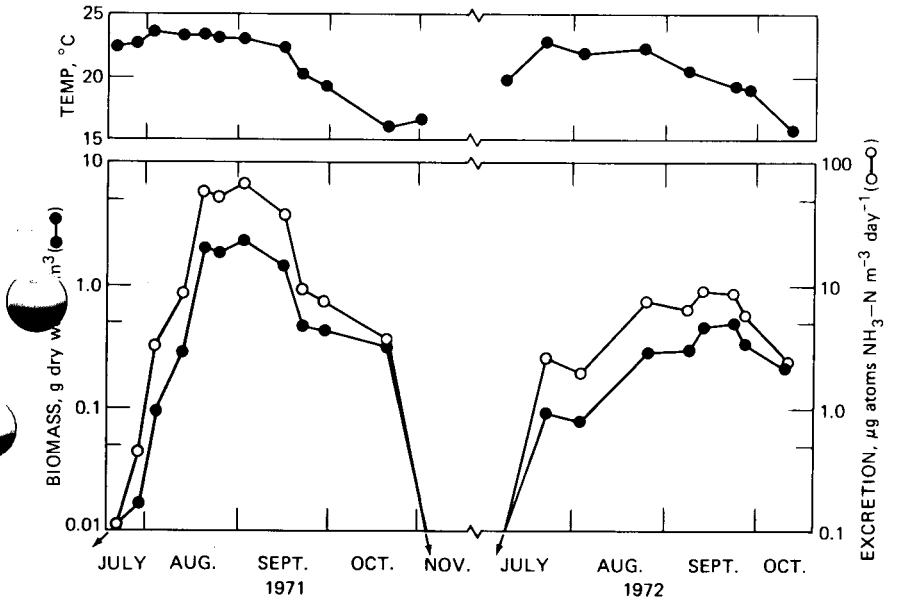

Fig. 4 Seasonal patterns of *M. leidyi* biomass and calculated ammonia excretion rate with corresponding average surface temperature for Narragansett Bay. Note log scale for biomass and excretion.

attained a peak biomass of about 2 g dry weight/m^3, more than four times the 1972 maximum. Because the 1971 biomass peak occurred slightly earlier when the water was warmer, maximum ammonia excretion was about six times greater. Integrating the calculated ammonia excretion over the entire season, the 1971 total was 2250 µg atoms NH_3—N/m^3 and the 1972 total was 500 µg atoms/m^3. During the period of maximum abundance, the 1972 population excreted ammonia daily equivalent to only about 3% of the standing stock of ammonia in the water; the 1971 population contributed about 15% per day.

DISCUSSION

Comparison with Other Marine Organisms

The ammonia excretion per milligram dry weight of *M. leidyi* is comparable to excretion rates reported for other jellies and for various species of fish, though substantially lower than rates reported for many zooplankton (Table 2). The ash content of *M. leidyi* was 80%, which compares favorably with values of about 70% estimated by Thayer et al. (1973). This high ash content of *M. leidyi* accounts for part of the large discrepancy between their rate and that of the zooplankton. When expressed on an ash-free dry-weight basis, the excretion rate

TABLE 2

COMPARISON OF AMMONIA EXCRETION RATES FOR SEVERAL MARINE ORGANISMS

Organism	Excretion rate*		References
	μg atom NH_3-N mg^{-1} day^{-1}	μg atom NH_3-N mg^{-1} day^{-1} (ash-free dry weight)†	
Ctenophore	0.01–0.04	0.05–0.2	This paper
Jellyfish and ctenophore	0.02–0.06	0.07–0.2	Jawed, 1973
Small coastal zooplankton (primarily *Acartia sp.*)	1.0–4.0	1.3–5.1	Harris, 1959; Martin, 1968; Mayzaud, 1973
Larger copepods (primarily *Calanus sp.*)	0.2–0.8	0.2–0.9	Corner et al., 1965; Corner and Newell, 1967; Butler et al., 1969; Jawed, 1973
Chaetognath	0.9	1.2	Beers, 1964
Mysids and euphausiids	0.15	0.18	Jawed, 1969
Benthic fish (sculpin, flounder, perch)	0.006–0.018	0.007–0.02	Wood, 1958
Pelagic fish (anchovy, mackerel)	0.05–0.20	0.06–0.24	McCarthy and Whitledge, 1972

*Weights are dry weights.
†Conversions to ash-free dry weight made using Curl (1962) and Thayer et al. (1973).

is more similar to that of the large zooplankton forms and active pelagic fish. Thus this is probably a more meaningful basis for comparison.

Comparison with Other Estuaries

Quantitative estimates of ctenophore biomass have been made for at least four Atlantic estuaries (Table 3). *Mnemiopsis leidyi* is the prevalent species in three of these locations, while in Biscayne Bay *M. mccraydi* is dominant. Despite marked differences in salinity and temperature regimes, the four estuaries develop very similar ctenophore biomass maximums although the seasonal timing varies. In Biscayne Bay, Fla., the peak of ctenophore abundance is in the cooler part of the year (Baker, 1973), whereas in Narragansett Bay the maximum occurs during late summer. The Pamlico River, N. C., represents an

TABLE 3

COMPARISON OF CALCULATED EXCRETION RATES AND RELATED PARAMETERS IN FOUR ESTUARIES WHERE CTENOPHORES HAVE BEEN QUANTITATIVELY SAMPLED

Location	Narragansett Bay, R. I.	York River, Va.*	Pamlico River, N. C.†	Biscayne Bay, Fla.‡
Salinity range, ‰	28–33	0–32	0–20	25–40
Annual temperature range, °C	1–24	2–27	4–30	19–31
Season of ctenophore maximum	Late summer	Winter, summer	Spring, fall	Fall–winter
Temperature during maximum, °C	20–24	2–7, 17–27	16–24	23–25
Maximum biomass, g dry weight/m^3	0.5–2.0	0.5, >0.9	0.7–2.2	0.6–1.2
Calculated excretion at biomass maximum based on Fig. 3, μg atoms NH_3–N m^{-3} day^{-1}	10–60	<5, >30	20–100	20–35
Biomass of other zooplankton during ctenophore maximum, mg dry weight/m^3	25–50§	3¶	5–11**	15–30
Calculated estimate of other zooplankton excretion, § μg atoms NH_3–N m^{-3} day^{-1}	25–150	3–9	5–33	15–90

*Burrell, 1968.
†Miller, 1974.
‡Baker, 1973.
§Martin, 1968.
¶ From Herman et al.; Burrell's values were an order of magnitude smaller.
**Peters, D. S., as cited in Miller, 1970; substantiated by Williams et al., 1968.

intermediate case with spring and fall peaks (Miller, 1970). In most cases it seems that ctenophores are abundant only when the water temperature is in the range of 16 to 27°C. In contrast to this trend, however, the York River, Va., produces a large secondary peak during the winter when the water temperature is only 2 to 7°C (Burrell, 1968). This presence of large ctenophore biomass during the winter has been substantiated by studies in the Patuxent River, another Chesapeake Bay estuary (Herman, Mihursky, and McErlean, 1968).

Estimates of excretion for these locations (Table 3) have been made using the regression equation for Narragansett Bay ctenophores presented in Fig. 3. It is likely that this calculation overestimates the excretion in the warmer waters of

the Pamlico River and Biscayne Bay since the organisms there are adapted to ambient temperatures. Nevertheless, the calculations should represent an approximation of actual rates.

A quantitative comparison of the relative importance of ctenophores and other zooplankton requires an estimate of the excretion rate for the other zooplankton during the season when ctenophores are abundant. Although the excretion rates per unit weight reported by Martin (1968) for Narragansett Bay in the late summer and fall are much higher than his results for other times of the year, the rates are similar to those obtained by Harris (1959) and Mayzaud (1973) working with comparable species at similar temperatures. Considering these results and the current work of G. Vargo on zooplankton excretion in Narragansett Bay (personal communication), a range of 1.0 to 3.0 μg atoms mg^{-1} dry weight day^{-1} seems to be a good estimate of the excretion rate of zooplankton in this estuary during the late summer and fall. For biomass levels observed during this season (Martin 1968), this range of rates suggests a zooplankton excretion from nonctenophores of 25 to 150 μg atoms NH_3–N m^{-3} day^{-1} (Table 3). Thus, in Narragansett Bay, nitrogen regeneration within the water column by ctenophores appears to be comparable to that of other zooplankton. Although considerable uncertainty is involved, similar calculations based on biomass estimates in other estuaries also seem to be in this range (Table 3).

Evaluation of the Role as Nutrient Recyclers

To evaluate whether or not the nitrogen flux from ctenophores is significant to the system as a whole, we must examine other potentially important nitrogen sources. In Narragansett Bay the nutrient flux from the benthos during the summer has been shown to be several times larger than that from zooplankton, including ctenophores (Hale, this volume). In a fairly well mixed estuary like Narragansett Bay, this tremendous input undoubtedly overshadows nitrogen contributions by other sources such as ctenophores, other zooplankton, fish, and even sewage except in localized areas.

Of course, sedimentary releases may not be as great in all systems. And, in deeper coastal waters like Long Island Sound or in highly stratified waters where nutrients from the bottom are largely unavailable to near-surface phytoplankton, ctenophores may seasonally provide a major nutrient source equal to or greater than that of other zooplankton.

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REFERENCES

Baker, L. D., 1973, The Ecology of the Ctenophore *Mnemiopsis mccraydi* Mayer, in Biscayne Bay, Florida, M.S. Thesis, Rosentiel School of Marine and Atmospheric Science, University of Miami.

[illegible]s, J. R., 1964, Ammonia and Inorganic Phosphorus Excretion by Planktonic Chaetognath *Sagitta hispida* Conant, *J. Cons. Cons. Perman. Explor. Mer*, **29**: 123-129.

Bertalanffy, L. von, 1968, *General System Theory: Foundations, Development, Applications*, George Braziller, Inc., New York.

Bishop, J. W., 1967, Feeding Rates of the Ctenophore *Mnemiopsis leidyi*, *Chesapeake Sci.*, **8**(4): 259-261.

Brody, S., 1945, *Bioenergetics and Growth*, Van Nostrand Reinhold Company, Cincinnati.

Burrell, V. G., Jr., 1968, The Ecological Significance of a Ctenophore *Mnemiopsis leidyi* (A. Agassiz) in a Fish Nursery Ground, Master's Thesis, Department of Biology, College of William and Mary.

Butler, E. I., E. D. S. Corner, and S. M. Marshall, 1969, On the Nutrition and Metabolism of Zooplankton. VI. Feeding Efficiency of *Calanus* in Terms of Nitrogen and Phosphorus, *J. Mar. Biol., Ass. U.K.*, **49**: 977-1001.

Corner, E. D. S., and B. S. Newell, 1967, On the Nutrition and Metabolism of Zooplankton. IV. The Forms of Nitrogen Excreted by *Calanus*, *J. Mar. Biol. Ass. U. K.*, **47**: 113-120.

——, C. B. Cowey, and S. M. Marshall, 1965, On the Nutrition and Metabolism of Zooplankton. III. Nitrogen Excretion by *Calanus*, *J. Mar. Biol. Ass. U. K.*, **45**: 429-442.

Curl, H., Jr., 1962, Analyses of Carbon in Marine Plankton Organisms, *J. Mar. Res.*, **20**: 181-188.

Harris, E., 1959, The Nitrogen Cycle in Long Island Sound, *Bull. Bingham Oceanogr. Collect.*, **17**: 31-65.

Herman, S. S., J. A. Mihursky, A. J. McErlean, 1968, Zooplankton and Environmental Characteristics of the Patuxent River Estuary, 1963–1965, *Chesapeake Sci.*, **9**(2): 67-82.

Jawed, M., 1973, Ammonia Excretion by Zooplankton and Its Significance to Primary Productivity During Summer, *Mar. Biol.*, **23**: 115-120.

——, 1969, Body Nitrogen and Nitrogenous Excretion in *Neomysis rayii* Murdoch and *Euphausia pacifica Hansen*, *Limnol. Oceanogr.*, **14**: 748-754.

Kleiber, M., 1961, *The Fire of Life*, John Wiley & Sons, Inc., New York.

[illegible]enzler, E. J., 1961, Phosphorus Budget of a Mussel Population, *Limnol. Oceanogr.*, **6**: 400-415.

McCarthy, J. J., 1970, A Urease Method for Urea in Seawater, *Limnol. Oceanogr.*, **15**: 309-313.

——, and T. E. Whitledge, 1972, Nitrogen Excretion by Anchovy (*Engraulis mordax* and *E. ringens*) and Jack Mackeral (*Trachurus semmetricus*), *Fish. Bull.*, **70**: 395-401.

MacIsaac, J. J., and R. C. Dugdale, 1972, Interactions of Light and Inorganic Nitrogen in Controlling Nitrogen Uptake in the Sea, *Deep-Sea Res.*, **19**: 209-232.

Martin, J. H., 1968, Phytoplankton Relationships in Narragansett Bay. III. Seasonal Changes in Zooplankton Excretion Rates in Relation to Phytoplankton Abundance, *Limnol. Oceanogr.*, **13**: 63-71.

Mayer, A. G., 1912, *Ctenophores of the Atlantic Coast of North America,* Publication No. 162, Carnegie Institute of Washington.

Mayzaud, P., 1973, Respiration and Nitrogen Excretion of Zooplankton. II. Studies of the Metabolic Characteristics of Starved Animals, *Mar. Biol.,* **21**: 19-28.

Miller, R. J., 1974, Distribution and Biomass of an Estuarine Ctenophore Population *Mnemiopsis leidyi* (A. Agassiz), *Chesapeake Sci.,* **15**: 1-8.

——, 1970, Distribution and Energetics of an Estuarine Population of the Ctenophore, *Mnemiopsis leidyi,* Ph.D. Thesis, Department of Zoology, North Carolina State University.

Nelson, T. C., 1925, On the Occurrence and Food Habits of Ctenophores in New Jersey Inland Coastal Waters, *Biol. Bull.,* **48**: 92-111.

Ryther, J. H. and W. M. Dunstan, 1971, Nitrogen, Phosphorus, and Eutrophication in Coastal Marine Environment, *Science,* **171**: 1008-1013.

Solorzano, L., 1969, Determination of Ammonia in Natural Waters by the Phenol Hypochlorite Method, *Limnol. Oceanogr.,* **14**(5): 799-801.

Strickland, J. D. H., and T. R. Parsons, 1968, *A Practical Handbook of Seawater Analysis,* J. C. Stevenson (Ed.), Fisheries Research Board of Canada, Bulletin No. 167.

Thayer, G. W., W. E. Schaaf, J. W. Angelovic, and M. W. LaCroix, 1973, Caloric Measurements of Some Estuarine Organisms, *Fish. Bull.,* **71**: 289-296.

Williams, R. B., M. B. Murdoch, and L. K. Thomas, 1968, Standing Crop and Importance of Zooplankton in a System of Shallow Estuaries, *Chesapeake Sci.,* **9**: 42-51.

Wood, J. D., 1958, Nitrogen Excretion in Some Marine Teleosts, *Can. J. Biochem. Physiol.,* **36**: 1237-1242.

THE ROLE OF BENTHIC COMMUNITIES IN THE NITROGEN AND PHOSPHORUS CYCLES OF AN ESTUARY

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ABSTRACT

A study of net sediment–water fluxes of ammonia, nitrate, nitrite, and inorganic phosphate was conducted in Narragansett Bay, R. I., from July 1973 to January 1974 to examine the role of benthic communities in the nutrient cycles of this estuary. Bottom chambers were used to obtain in situ measurements from an *Ampelisca abdita* (amphipod) community, a *Nepthys incisa–Nucula annulata* (polychaete–bivalve) community, and a *Mercenaria mercenaria* (bivalve) community. Oxygen uptake was used as a measure of metabolism. Over a temperature range from 3.2 to 22.4°C, ammonia flux at the sediment surface varied from −4.28 to 276.10 μmoles m^{-2} hr^{-1}. Nitrate was transported in both directions across the sediment–water interface, varying from −66.31 to 43.43 μmoles m^{-2} hr^{-1}. Nitrite flux was relatively unimportant. Phosphate uptake and release ranged from −9.43 to 41.63 μmoles m^{-2} hr^{-1}. Few significant differences ($p < 0.05$) were found among the three communities. Temperature exerted a strong influence on the fluxes of ammonia and phosphate. The fluxes measured can have significant effects on the nutrient concentrations of the overlying water.

Studies of marine benthic communities in the past have often centered on the structural nature of the community. Recently, benthic ecologists have begun to examine the functional aspects of the community, including questions of the role of the benthos and the nature of their coupling with the planktonic community in the larger marine ecosystem (Hargrave, 1973).

A major function attributed to the benthos in shallow-water marine ecosystems is the regeneration of inorganic nutrients. The benthos receive organic matter in the form of sinking phytoplankton, zooplankton, nekton, and detritus from the overlying water. Inorganic nutrients are regenerated as products of benthic metabolism and are returned to the overlying water, where they are again available to the phytoplankton for use in primary production.

Although this return of inorganic nutrients to the overlying water has been recognized for many years, the actual rates in marine environments are poorly known. The sediments may hold some of the regenerated nutrients in storage by sorption reactions with clay minerals (Lee, 1970) and by increased concentrations in the interstitial water (Okuda, 1960). Sediments may act as a buffer on the concentrations of some nutrients in the overlying water (Pomeroy, Smith, and Grant, 1965).

Mortimer (1941, 1942) examined the fluxes of several inorganic nutrients across the sediment–water interface in English lakes. Since then there has been a substantial amount of literature concerned with phosphorus flux in lakes (e.g., Gumerman, 1970; Li et al., 1972) and some recent literature on nutrients other than phosphorus (Byrnes, Keeney, and Graetz, 1972; Kemp and Mudrochova, 1972).

In marine environments there have been several studies of phosphorus exchange at the sediment–water interface (Miller, 1952; Jitts, 1959), but flux rates on an areal basis are rarely given. Pomeroy, Smith, and Grant (1965) measured flux rates of phosphorus from cores taken in the intertidal zone of Doboy Sound, Ga. Despite the fact that nitrogen, and not phosphorus, is generally considered the limiting nutrient in marine environments (Goldman, Tenore, and Stanley, 1973), there have been few studies on nutrients other than phosphorus. A notable exception is the work of Okuda (1960), and there are ongoing studies by the Askö laboratory in Sweden and by Hartwig (1973) in California. Measurements of sediment–water nutrient flux have usually been made by determining the concentration gradient of the nutrient in the interstitial and the overlying water and then calculating the flux based on the diffusion coefficient for that nutrient (Bray, Bricker, and Troup, 1973), or by taking a sediment core and measuring the flux between the core and the overlying water in the laboratory (Okuda, 1960). Except for the studies by the Askö laboratory and those of Hartwig, in situ measurements of sediment–water nutrient flux are lacking in the literature.

This study was made to quantify the nutrient regeneration role of the benthos by making in situ measurements of the net sediment–water flux of ammonia, nitrate, nitrite, and inorganic phosphate in Narragansett Bay, R. I. Some preliminary attempts were made to determine the factors controlling the fluxes. Oxygen uptake by the benthos was measured to provide an estimate of community metabolism.

METHODS

The Benthic Communities

Narragansett Bay is a partially mixed estuary, approximately 325 km^2 in area, with a mean depth of 8.8 m (Hicks, 1959). Three stations representing a wide variety of sediment and animal types were selected for measurement of

sediment–water nutrient flux (Fig. 1 and Table 1). Station A was on a coarse sand with a biotic community dominated by the tube-dwelling amphipod *Ampelisca abdita.* A sandy-silt bottom characterized station B, where the dominant organisms were *Nepthys incisa* (polychaete) and *Nucula annulata,* a small bivalve. Station C was on a sandy silt and was dominated by the quahog, or hard clam, *Mercenaria mercenaria.* The dissimilarity of the three communities is indicated by the low overall indexes of affinity (Sanders, 1960), which were

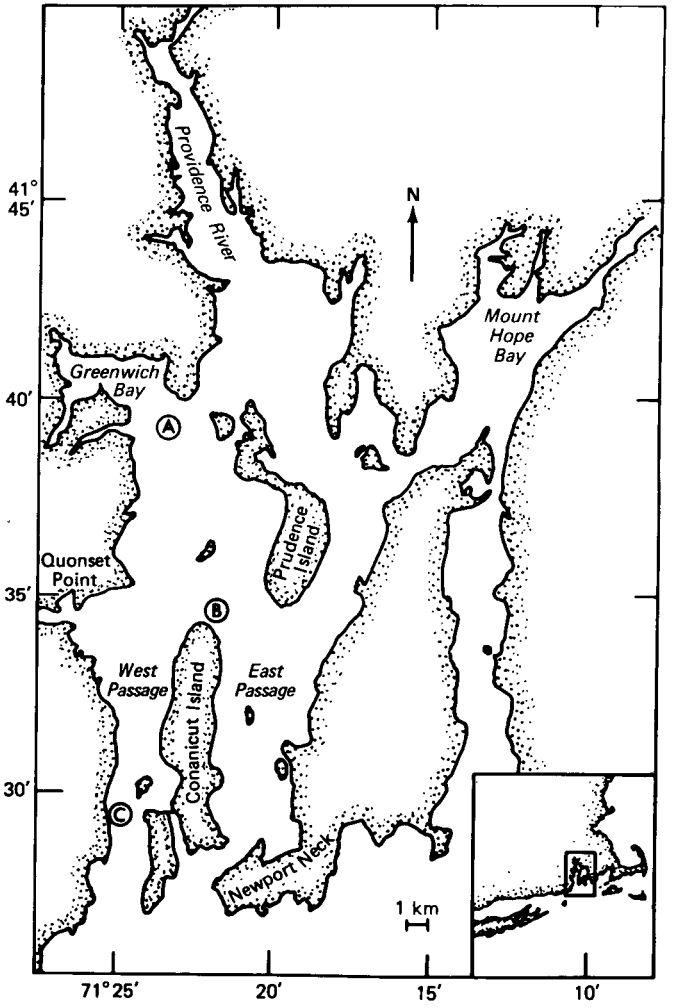

Fig. 1 Location of stations A, B, and C in Narragansett Bay, R. I. Station A, *Ampelisca abidta.* Station B, *Nepthys incisa–Nucula annulata.* Station C, *Mercenaria mercenaria.*

TABLE 1

ANIMAL AND SEDIMENT CHARACTERISTICS AT EACH STATION

Station	Depth, m	Dominant organisms	Total number individuals, No./m²	Total biomass,* g/m²	Sediment type	Percent silt–clay	Percent clay	Percent organic matter
A	5.8	*Ampelisca abdita*	16,636	6.06	Sand	6.75	3.04	1.53
B	7.3	*Nepthys incisa–Nucula annulata*	7,682	7.80	Sandy silt	73.09	18.66	4.54
C	6.1	*Mercenaria mercenaria*	3,154	26.79	Sandy silt	58.24	9.26	4

*Dry organic weight.

2.2% for numbers of individuals and 2.7% for biomass. Bottom-water salinities ranged from about 29.5‰ at station A toward the head of the bay to about 32‰ at station C near the mouth of the bay.

We used a Smith–McIntyre grab (0.1 m^2) to take five replicate quantitative samples once at each station to characterize the communities. The macrofauna (defined here as all animals not passing a 0.75-mm mesh) were counted, and their dry ash-free weight was determined. A core subsample was taken from an additional Smith–McIntyre grab for sediment grain-size analysis and organic-matter content. The pipette method, following the techniques of Buchanan (1971), was used for the sediment grain-size analyses of the fine fractions; the coarse fractions were dry sieved. Percent organic matter was estimated from loss on combustion for a combustion period of 5 hr at 550°C.

Flux Measurements

Net exchanges of dissolved substances across the sediment–water interface can be determined in situ by entrapping in a bottom chamber a known volume of water exposed to a known area of sediment and monitoring over time the concentration of the substance whose flux is to be measured. Following this principle, four bottom chambers were constructed from 12-in.-diameter polyvinyl chloride pipe cut in half longitudinally (Fig. 2). The chambers were designed to allow a submersible pump to be attached for future studies of the effect of current flow on nutrient flux. Some preliminary measurements with a current flow were obtained.

Scuba divers, who were careful not to disturb the sediments, placed the chambers over the benthic communities; three or four chambers were used simultaneously at a particular station to provide an estimate of community variability. Initial samples and final samples were taken from the valve at the top of each chamber using a 700-ml syringe. The time period between the two samples was usually 2 to 4 hr. Two series of long-term (70 hr) measurements in

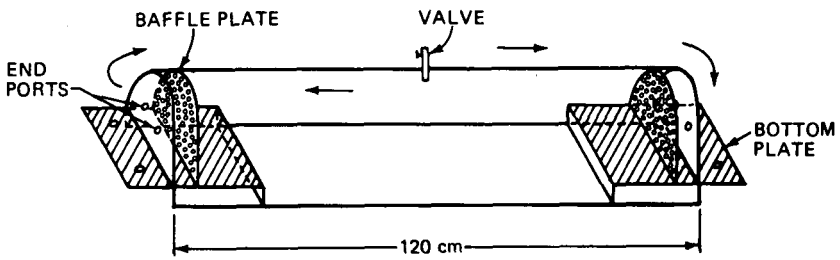

Fig. 2 Bottom chamber used for in situ measurement of oxygen and nutrient fluxes. The chambers were staked to the bottom or fitted with a heavy iron collar to sink the edges to a depth of 4 cm. Water could be drawn from one end by a submersible pump and returned through tubing to the other end. Baffles and end bottom plates provided uniform flow across the sediment, which was exposed only in the central part of the chamber. Bottom area, 2400 cm^2; volume, 27.0 liters.

July and August had indicated that increases in nutrient concentrations inside the chambers did not affect the rates of nutrient release during the first 20 hr. The divers gently circulated the water inside each chamber before taking the final sample by using the sampling syringe at the end ports of the chamber.

On deck, oxygen samples were withdrawn from the syringe by a glass siphon and "pickled" for later laboratory analysis (Strickland and Parsons, 1968). The nutrient samples were filtered with Gelman type A glass-fiber filters and preserved (ammonia: Degobbis, 1973; phosphate: Gilmartin, 1967) for later laboratory analysis of ammonia (Solorzano, 1969), nitrate and nitrite (Technicon Autoanalyzer), and inorganic phosphate (Strickland and Parsons, 1968). Oxygen and ammonia determinations were made on the same day the samples were taken; the other samples were frozen in polyethylene bottles and analyzed 1 to 6 months later.

Dark bottles were incubated simultaneously beside the chambers to provide a correction for oxygen and nutrient changes caused by plankton in the water inside the chambers. The corrections for July through September were estimated from later measurements. Environmental parameters measured just above the sediment–water interface included temperature and the concentrations of dissolved oxygen, ammonia, nitrate, nitrite, and inorganic phosphate. Oxygen and nutrient fluxes were measured six times at each station from July 1973 to January 1974 over a temperature range from 22.4 to 3.2°C.

The word "phosphate" in this paper refers to dissolved inorganic phosphate; "ammonia" refers to the sum of ammonia and the ammonium ion, which are in equilibrium in seawater. A net flux of a nutrient from the sediment is referred to as "release," whereas a net flux in the opposite direction is referred to as "uptake."

RESULTS

Over a temperature range from 3.2 to 22.4°C, oxygen uptake by the sediments and associated benthos varied from 4.73 mg m^{-2} hr^{-1} in December to 107.31 mg m^{-2} hr^{-1} in October. The mean for all measurements (not equally distributed over the temperature range) was 37.76, with a 95% confidence interval of ±6.26 mg m^{-2} hr^{-1}. There were no significant differences ($p > 0.05$) in weighted averages (corrected for temperature differences) among the three stations. Oxygen uptake showed a good correlation with temperature (Fig. 8). The maximum value (107.31 mg m^{-2} hr^{-1}) was obtained from an exceptionally dense area of the *Ampelisa* community and was not included in the regression. Since there were no significant differences ($p > 0.05$) in slopes or intercepts among stations, as shown by analysis of covariance, one regression line is fitted to all the data. Extrapolating the regression line to −1°C, which is approximately the minimum temperature of Narragansett Bay, gives a positive intercept, indicating an oxygen uptake at this low temperature.

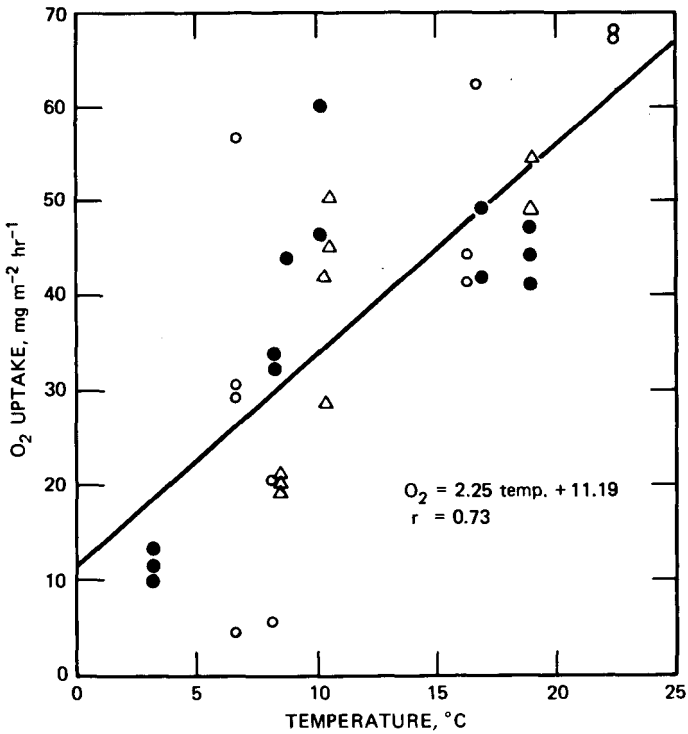

Fig. 3 Benthic oxygen uptake as a function of temperature. No significant differences ($p > 0.05$) in slopes or intercepts were found among stations. ○, *Ampelisca.* ●, *Nepthys–Nucula.* △, *Mercenaria.*

Ammonia release, which ranged from −4.28 to 276.10 μmoles m^{-2} hr^{-1}, with an overall sample mean of 84.54 ± 21.09 μmoles m^{-2} hr^{-1}, dominated the flux of nitrogen at the sediment–water interface. The weighted average of station A (97.4 μmoles m^{-2} hr^{-1}) was significantly greater ($p < 0.05$) than that of station B (59.6 μmoles m^{-2} hr^{-1}); the weighted average of station C was 70.1 μmoles m^{-2} hr^{-1}. Ammonia release from each community showed a good correlation with temperature (Fig. 4). The negative intercepts of all three regression lines predict a net uptake of ammonia at low temperatures. Since ammonia is a waste product of metabolic processes, a regression of ammonia release on oxygen uptake also gave a good correlation (Fig. 5).

Nitrate flux showed net transport in both directions across the sediment–water interface and was not correlated with temperature. Measurements of nitrate were not begun until August 23. The flux ranged from −66.31 to 43.43 μmoles m^{-2} hr^{-1}, with an overall sample mean of −1.18 ± 6.06 μmoles m^{-2} hr^{-1}. The sample mean of station B (4.03 μmoles m^{-2} hr^{-1}) was significantly greater ($p < 0.05$) than the sample mean of station C (−8.31 μmoles m^{-2} hr^{-1}); the sample mean of station A was −1.45 μmoles m^{-2} hr^{-1}.

Satisfactory nitrite measurements were not obtained until September 13. On most occasions, nitrite was not detectable inside the chambers. When present,

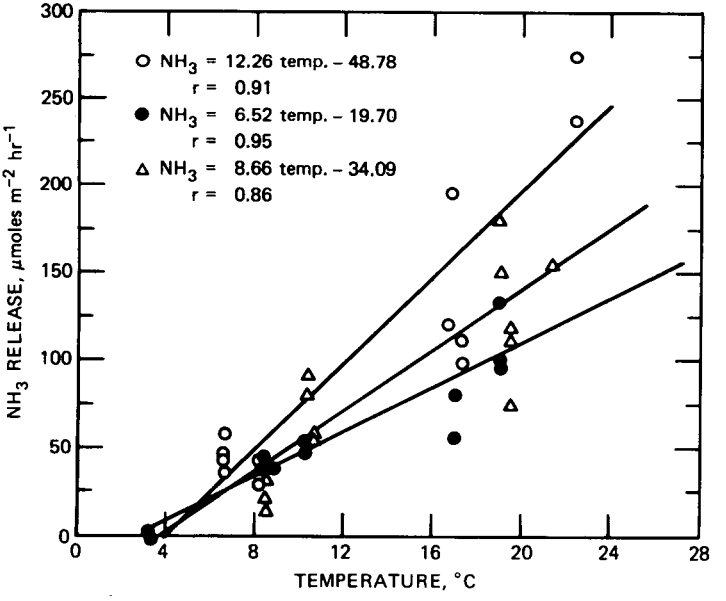

Fig. 4 Benthic ammonia release as a function of temperature. The slope of station A is significantly greater ($p < 0.05$) than that of station B. ○, *Ampelisca*. ●, *Nepthys–Nucula*. △, *Mercenaria*.

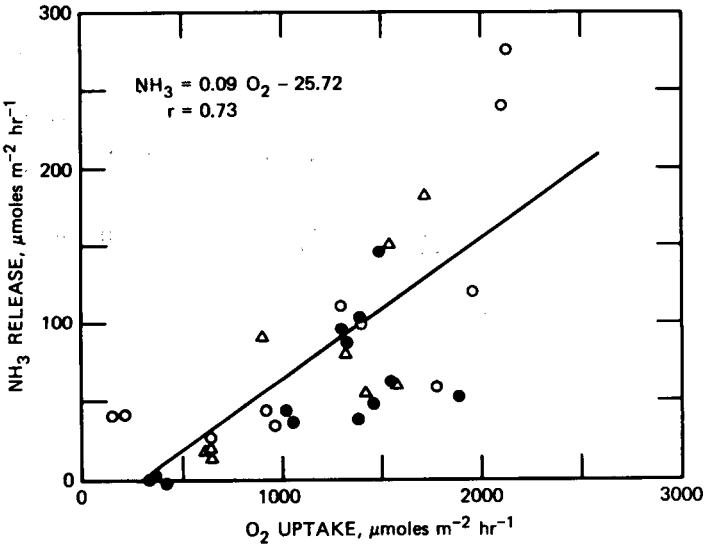

Fig. 5 Benthic ammonia release as a function of oxygen uptake. No significant differences ($p > 0.05$) in slopes or intercepts were found among stations. ○, *Ampelisca*. ●, *Nepthys–Nucula*. △, *Mercenaria*.

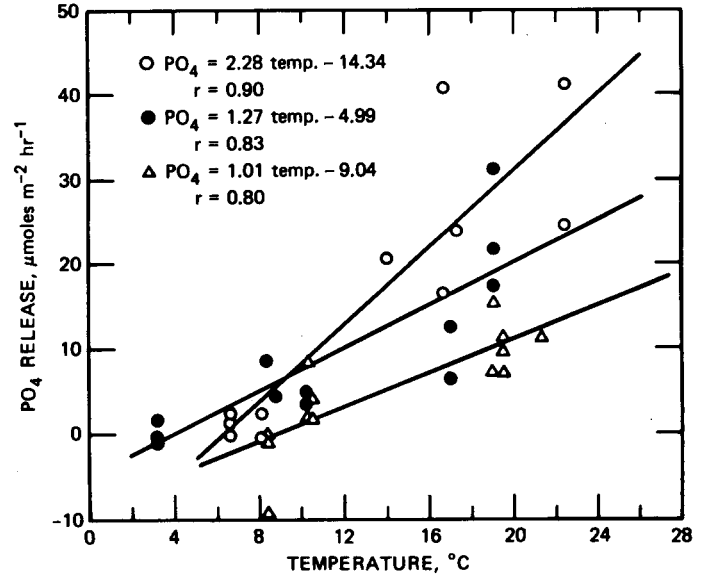

Fig. 6 Benthic phosphate release as a function of temperature. The slope of station A was significantly greater ($p < 0.05$) than the slopes of stations B and C. The intercepts, but not the slopes, of stations B and C were significantly different. ○, *Ampelisca*. ●, *Nepthys–Nucula*. △, *Mercenaria*.

nitrite fluxes were always out of the sediment and did not show a good relationship with temperature. Over a temperature range from 3.2 to 19.0°C, nitrite release varied from 0.00 to 10.35 μmoles m^{-2} hr^{-1}, with an overall sample mean of 1.66 ± 1.25 μmoles m^{-2} hr^{-1}. There were no significant differences ($p > 0.05$) among the sample means of the three stations.

Inorganic phosphate was released from the sediments at the higher temperatures but was taken up at lower temperatures (Fig. 6). This is in contrast to ammonia, which was almost always released by the sediments. The range was from −9.43 to 41.63 μmoles m^{-2} hr^{-1}, with an overall sample mean of ± 3.81 μmoles m^{-2} hr^{-1}. The weighted averages of both station A (13.1 μmoles m^{-2} hr^{-1}) and station B (10.2 μmoles m^{-2} hr^{-1}) were significantly greater ($p < 0.05$) than that of station C (3.0 μmoles m^{-2} hr^{-1}). Phosphate release was similar to ammonia release in showing a good correlation with temperature and a negative intercept at all three stations. The correlation of phosphate release and oxygen uptake (Fig. 7) was not so strong as the correlation of ammonia release and oxygen uptake but was, nevertheless, highly significant.

There was some evidence that the fit of certain regressions, notably that of phosphate on temperature, would have been improved by a logarithmic transformation of the y axis; however, until there are more data, this transformation is not justified.

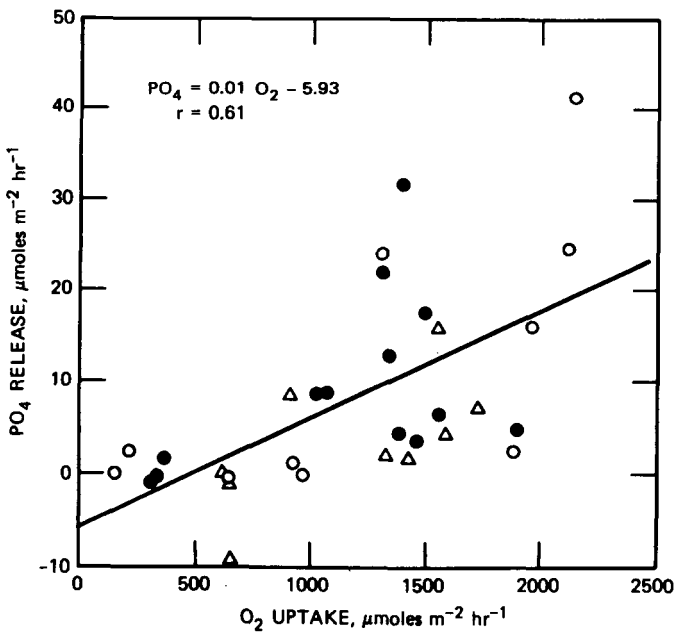

Fig. 7 Benthic phosphate release as a function of oxygen uptake. No significant differences ($p > 0.05$) in slopes or intercepts were found among stations. ○, ***Ampelisca***. ●, ***Nepthys–Nucula***. △, ***Mercenaria***.

DISCUSSION

Factors Affecting Sediment–Water Fluxes

Inorganic nutrients released from benthic communities are essentially the by-products of benthic metabolism of organic matter. Flux across the sediment–water interface occurs when there is a concentration gradient between the interstitial water and the overlying water which is large enough to overcome any tendency of the nutrient to enter into sorption reactions in the sedim[illegible] However, the actual cycles of the nutrients at the sediment–water interfac[illegible] complex. Using bottom chambers to measure net flux integrates the several processes that are occurring and measures the overall exchange with the overlying water.

There are a multitude of physical, chemical, and biological factors affecting sediment–water nutrient exchange (Hayes, 1964; Lee, 1970; McKee et al., 1970). Among the more important are animal, especially bacterial, metabolism; sorption reactions; concentration gradients and diffusion; redox potential; pH; supply of organic matter; currents; and biological reworking of the sediment.

Temperature affects several of these factors directly or indirectly and hence has a strong influence on nutrient fluxes. The rate of metabolism is probably the most important factor controlled by temperature (Hargrave, 1969), but temperature may also influence sediment compactness by controlling animal burrowing and ingestion by deposit feeders, rates of chemical reaction, diffusion coefficients, and viscosity. There are seasonal effects on sediment–water exchange, such as changes in redox potential, rate of supply of organic matter, and community structure, which may or may not be controlled by temperature but which might show a correlation with temperature. The coefficients of determination show that temperature accounted for 53% of the variability of oxygen uptake, about 82% of the variability of ammonia release, and about 71% of the variability of phosphate release.

The remainder of the variation can be explained by several parameters that could not be (or were not) controlled or measured when making in situ measurements. Some of the variation resulted from a lack of community homogeneity. The coefficients of variation for five replicate grab samples mean numbers of animals and mean biomass at each station were about 60%. contrast, the overall coefficient of variation for replicate bottom-chamber measurements of nutrient flux at the same station on the same day was about 25%. This suggests that community function shows less variability than does community structure, at least with respect to structure as defined by the classic methods of benthic studies. Other uncontrolled parameters that would be expected to vary somewhat throughout the community are sediment grain-size distribution, percent organic matter, and the concentrations of oxygen and nutrients in the interstitial water.

No strong correlations were found between nutrient fluxes and the concentrations of nutrients in the overlying water (with the possible exception of phosphate flux in December and January). Apparently there are other factors of greater importance or variability, such as animal metabolism or nutrient concentration in the interstitial water.

Oxygen Flux

Oxygen uptake by marine sediments is the result of aerobic metabolism of benthic organisms and of the reaction of oxygen diffusing into the sediment with reduced compounds diffusing out. The latter, referred to as chemical oxidation, is thought by some researchers (Teal and Kanwisher, 1961) to be a rough estimate of anaerobic metabolism since the reduced compounds are largely the by-products of anaerobic bacteria. Oxygen uptake was used as a measure of total benthic community metabolism in this study. Preliminary measurements in November, using Formalin to inhibit respiration, indicated that chemical oxidation accounted for about one-fifth the total oxygen uptake. Because molecular oxygen was used but never produced in the sediments, oxygen flux was always into the sediments. In some benthic communities oxygen production by microalgae occurs at the sediment surface, but not at the depths of the stations of this study and not under opaque chambers.

The pattern shown by the regression of oxygen uptake on temperature is a common metabolic response and is not unlike that shown by Hargrave (1969) for several benthic communities. The fraction of oxygen uptake resulting from chemical oxidation might also decrease with a decreasing temperature because of lower diffusion coefficients and because of less biological reworking of the upper layers of sediment. There is some empirical evidence from the work of McMaster (1962) for an increased sediment hardness with decreasing temperature.

Nitrogen Flux

Ammonia is the prime by-product of the metabolism of nitrogenous matter in the benthic environment. It is excreted by many benthic organisms and is produced as a result of the bacterial utilization of organic matter (Rittenberg, Emery, and Orr, 1955). This is advantageous for phytoplankton, which preferentially absorb ammonia (MacIsaac and Dugdale, 1972). The correlations of ammonia release with oxygen uptake (Fig. 5) and with temperature (Fig. 4) resulted from the relationship of metabolism and ammonia production. Some regenerated ammonia can be oxidized to nitrite and nitrate by nitrifying bacteria and then released from the sediments. In the absence of oxygen, which is not detectable in many coastal marine sediments below the uppermost centimeter or so (Kanwisher, 1962), nitrate and nitrite can serve as alternate hydrogen acceptors, being taken up by the sediments and reduced by anaerobic bacteria. The sediments in Narragansett Bay never exerted a nitrite demand on the overlying water, perhaps because there was always a sufficient supply of oxygen

and nitrate, which first serve as hydrogen acceptors. Because of the complex balance of production and uptake processes, nitrate showed little correlation with temperature. Nitrate ions, in contrast to ammonium ions (Stevenson and Tilo, 1970), show essentially no tendency to enter into sorption reactions with clay minerals (Lee, 1970); this may partially explain the variability of nitrate flux. Although ammonia may be adsorbed or oxidized, the production of ammonia in the sediments is such that, except at the coldest temperatures, these effects are surpassed, with a resulting flux several times that of nitrate or nitrite.

There are few values given in the literature for nitrogen flux on an areal basis. Rittenberg, Emery, and Orr (1955) calculated an annual regeneration of ammonia for the Santa Barbara Basin which gives an hourly rate of 1.8 μmoles m^{-2} hr^{-1}. The fluxes reported by Hartwig (1973) for a subtidal sand off California for ammonia, nitrate, and nitrite are comparable with those of Narragansett Bay.

Phosphorus Flux

Because phosphorus exists in marine environments only in the 5^{+} oxidation state (Riley and Chester, 1971), the phosphorus cycle is not as complex as the nitrogen cycle. Nevertheless there are complicating factors in the sediment–water flux of phosphate. Phosphate is released from the autolysis of bacterial cells (Lear, 1964); it is also produced by several animals, and protozoans (Pomeroy, 1970). Phosphate is assimilated by bacteria (Lear, 1964) and undergoes adsorption to clays (Carritt and Goodgal, 1954; Jitts, 1959). Because phosphate exchange is influenced by metabolic processes, phosphate release from the sediments to the overlying water is correlated with oxygen uptake (Fig. 7) and temperature (Fig. 6) in the same manner as ammonia release. The correlations are not as high as those of ammonia, probably because of the lesser quantities of phosphate produced, sorption processes, and bacterial assimilation.

Pomeroy, Smith, and Grant (1965) stated that the sediments act as a buffer on the concentration of the overlying water, maintaining a phosphate concentration in the water of Doboy Sound, Ga., of about 1 μg-atom/liter. When metabolic activity is low, the data shown in Fig. 6 may support this hypothesis for Narragansett Bay. At colder temperatures the net flux began to go into the sediments (probably because of sorption reactions) when the concentration of phosphate in the overlying water began to increase above 1 μg-atom/liter. However, phosphate concentration in the overlying water was well above 1 μg-atom/liter during the warmer months when phosphate release was high; evidently metabolic activity in the sediments during the higher temperatures was great enough to maintain a strong concentration gradient.

On the basis of laboratory measurements on cores, Pomeroy, Smith, and Grant (1965) estimated a phosphate flux of 0.04 μmoles m^{-2} hr^{-1} for undisturbed sediments in Doboy Sound; the overall mean of phosphate fluxes measured in Narragansett Bay was two orders of magnitude greater (9.6 μmoles

m^{-2} hr^{-1}). In addition to the different techniques used, possible reasons for the disparity are differences in clay mineralogy and in the source of organic matter (*Spartina* in Doboy Sound salt marshes and plankton in Narragansett Bay). From the concentration gradient and the diffusion coefficient, Bray, Bricker, and Troup (1973) calculated a phosphate release in Chesapeake Bay of 0.5 μmoles m^{-2} hr^{-1}; this value is also low compared with Narragansett Bay. As pointed out by Lee (1970), there are several factors, such as animal reworking of the sediment and turbulent mixing, which may lead to a greater flux than concentration gradients and diffusion coefficients would predict. Further, this method neglects macrofaunal excretion. Phosphate fluxes reported by Hartwig (1973) are within the same range as those of Narragansett Bay.

Community Similarities and Differences

Significant differences ($p < 0.05$) in nutrient fluxes could be demonstrated among the three stations in only a few cases. Care must be used in the interpretation of such results, but, until more data are available, it is interesting that the three stations, so widely different in sediment and animal types, were so similar in the fluxes of oxygen and nutrients. Thus benthic communities that were dissimilar in community structure exhibited a certain similarity in community function. However, the species composition of the meiofauna and the microfauna was not determined; probably these organisms account for a large proportion of the total metabolism of the community (Kanwisher, 1962; Pomeroy, 1970). Some preliminary measurements using antibiotics inside the chambers to inhibit bacterial respiration indicated the importance of bacteria in regenerative processes.

In general, the *Ampelisca* community (station A) showed a greater release of nutrients than the *Nepthys–Nucula* community (station B), and the *Mercenaria* community (station C) showed the lowest release. Usually a lower rate of nutrient regeneration would be expected from a sandy sediment than from a muddy sediment; the higher rate at station A probably resulted from the dense *Ampelisca* population overlying the sand. The *Ampelisca* tubes protruding from the sand also increased the surface area to 5 to 10 m^2 per square meter of bottom, thus increasing the attachment area for bacteria and other microorganisms. Although not statistically significant, nutrient releases were more closely related to total numbers of individuals per square meter than to total biomass. This suggests a greater metabolic rate for the smaller organisms (the amphipods) in accordance with the work of Zeuthen (1953).

The pattern of the slopes of oxygen uptake and ammonia release (Fig. 4) as functions of temperature was station A > station B > station C. Also, the slope of phosphate release as a function of temperature (Fig. 6) was greater at station A than at the other two stations. The implication of this pattern is that the epifaunal *Ampelisca* community is more sensitive to changes in temperature than the two infaunal communities.

Nutrient Ratios

According to the classic Redfield ratio (Redfield, Ketchum, and Richards, 1963), 276 atoms of oxygen are required to oxidize 106 atoms of carbon, 16 atoms of nitrogen, and 1 atom of phosphorus, which is the ratio of the latter three elements in marine plankton. For several reasons this ratio should not hold strictly true for the uptake of molecular oxygen and the release of nitrogen and phosphorus by the sediments and associated benthos. In Narragansett Bay the overall atomic ratio calculated for these fluxes was 532 oxygen; 14 nitrogen: 1 phosphorus. Thus the benthic communities regenerated nitrogen and phosph in approximately the same ratio as that of the organic matter input to the bottom. The regeneration ratio was calculated only when there was a release of phosphate from the sediment. The nitrogen value is the net sum of ammonia, nitrate, and nitrite. Neglected are some forms of nitrogen and phosphorus which might be expected to be released, e.g., dissolved organic nitrogen, dissolved organic phosphorus, and nitrogen gas. Taking these forms into consideration would lower the oxygen value, but probably not by 256 atoms. Furthermore, the theoretical ratio should probably require only 212 atoms of oxygen (Redfield, Ketchum, and Richards, 1963) since all the ammonia is not oxidized to nitrate. The high oxygen value may be a result of the chemical oxidation of such substances as hydrogen sulfide, during which oxygen is taken up and no nitrogen or phosphorus is released. Also, sorption reactions might tend to bind nitrogen or phosphorus that had been regenerated.

Relative Importance of the Benthos

There is not yet enough data on the nutrient cycles of Narragansett Bay to assess precisely the relative importance of the benthos. However, rough calculations indicate that in August, when benthic release rates are at the maximum, the benthos are the most important source of ammonia and phosphate to Narragansett Bay. Benthic releases in August provide four to six times as much ammonia and phosphate to the bay as do river runoff and sewage input (the sewage input is mainly to the upper part of the bay; Nixon and Oviatt (1974). Zooplankton regeneration in August (Martin, 1968) is approximately 2% of benthic ammonia regeneration and 14% of benthic phospha regeneration. The relative importance of the various sources in August, howev does not apply to the rest of the year. Benthic nutrient releases decrease with decreasing temperature, and there may even be a net uptake during the winter. Zooplankton biomass is low in August; at other times of the year, especially in the winter, zooplankton regeneration may exceed benthic regeneration. River runoff is low in August and may increase by a factor of 6 in the spring; sewage input is relatively constant.

As measured by the bottom chambers in this study, there is very little ammonia or phosphate released from the sediments in the winter. These results

may not be representative of the real conditions in Narragansett Bay because (1) all the flux measurements were made without a current flow inside the chamber and (2) winter storms may resuspend sediments, thereby exposing interstitial water. Current flow can increase metabolism (Nixon et al., 1971); it also removes the microlayer immediately over the sediment surface in which concentrations of nutrients could increase, inhibiting diffusion. Results from the preliminary work in this study with a recirculating current flow through the chambers indicate an increased flux of oxygen, ammonia, and phosphate at all three stations. The rates of current flow used (1 to 3 cm/sec) were an order of magnitude less than the average tidal velocity in the bay. Storms and abnormal tides may cause greater than normal current velocities, resulting in the resuspension of sediments and bringing interstitial water into contact with the overlying water. The concentrations of ammonia and phosphate in the interstitial water of estuarine sediments can be two to three orders of magnitude greater than the concentrations in the overlying water (Okuda, 1960; Bray, Bricker, and Troup, 1973). An effort was made at each station to qualitatively test the effect of resuspended sediments on the overlying water by measuring the nutrient concentrations in a chamber before and after a vigorous stirring that had the effect of resuspending the uppermost layer of sediment. In all three cases, resuspension caused the concentration of oxygen to decrease (a result of reduced compounds being released from the sediment) and the concentrations of ammonia and phosphate to increase. Another possible effect not observed inside chambers is the effect of the subtidal pump of Riedl, Huang, and Machan (1972). These investigators, as well as Webb and Theodor (1968), have demonstrated a pulsating water flow in and out of sandy sediments which is related to the passage of surface waves. Considering the preceding information, it is likely that the bottom-chamber measurements of nutrient fluxes are underestimates.

Benthic oxygen and nutrient fluxes can have considerable effect on the overlying water column. Assuming that in August the average fluxes of the three stations apply to the entire bay (an upper estimate), that there are no other gains or losses, and that there is instantaneous mixing, it would take approximately 3.2 days for the benthos to double the ammonia concentration (1.5 μg-atom/liter in August) of the bay (a volume of 28.32×10^8 m^3) and 16.9 days to double the phosphate concentration (1.5 μg-atom/liter). The daily oxygen uptake by the benthos is about 1.9% of the total oxygen content of the overlying water column. The daily ammonia release is about 31.2% of the water content; daily phosphate release is about 5.9%. These benthic releases alone can supply virtually all the nutrients required by the phytoplankton (Martin, 1968) in Narragansett Bay in August. These estimates provide some appreciation of the potential effect of the benthos on the ecosystem in which they exist.

The sediment–water fluxes measured in Narragansett Bay are probably representative of temperature estuaries. The bay has a high productivity and a rich benthos; however, the benthic oxygen uptake rates are comparable with

those reported in the literature for other areas of similar depth and temperature. Given the good correlation of ammonia and phosphate release with oxygen uptake in Narragansett Bay, it may be possible, using these regression equations as a first approximation, to calculate nutrient fluxes for other areas in which benthic oxygen uptake data are already in existence.

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REFERENCES

Bray, J. T., O. P. Bricker, and B. N. Troup, 1973, Phosphate in Interstitial Waters of Anoxic Sediments: Oxidation Effects During Sampling Procedure, *Science*, **180**: 1362-1364.

Buchanan, J. B., 1971, Measurement of the Physical and Chemical Environment. Sediments, in *Methods for the Study of Marine Benthos*, International Biological Program Handbook No. 16, pp. 30-52, N. A. Holmes and A. D. McIntyre (Eds.), Blackwell Scientific Publications, Oxford, England.

Byrnes, B. H., D. R. Keeney, and D. A. Graetz, 1972, Release of Ammonium-N from Sediments, in Proceedings of the Conference for Great Lakes Research, *Int. Ass. Great Lakes Res.*, **15**: 249-259.

Carritt, D. E., and S. Goodgal, 1954, Sorption Reactions and Some Ecological Implications, *Deep-Sea Res.*, **1**: 224-243.

Degobbis, D., 1973, On the Storage of Seawater Samples for Ammonia Determination, *Limnol. Oceanogr.*, **18**: 146-150.

Gilmartin, M., 1967, Changes in Inorganic Phosphate Concentration Occurring During Seawater Sample Storage, *Limnol. Oceanogr.*, **12**: 325-328.

Goldman, J. C., K. R. Tenore, and H. I. Stanley, 1973, Inorganic Nitrogen Removal from Wastewater: Effect on Phytoplankton Growth in Coastal Marine Waters, *Science*, **180**: 955-956.

Gunerman, R. C., 1970, Aqueous Phosphate and Lake Sediment Interaction, in Proceedi[illegible] of the Conference for Great Lakes Research, *Int. Ass. Great Lakes Res.*, **13**: 673-682.

Hargrave, B. T., 1973, Coupling Carbon Flow Through Some Pelagic and Benthic Communities, *J. Fish. Res. Board Can.*, **30**: 1317-1326.

——, 1969, Similarity of Oxygen Uptake by Benthic Communities, *Limnol. Oceanogr.*, **14**: 801-805.

Hartwig, E. O., 1973, Scripps Howard Institute of Oceanography, personal communication.

Hayes, F. R., 1964, The Mud–Water Interface, *Oceanogr. Mar. Biol. Annu. Rev.*, **2**: 121-145.

Hicks, S. D., 1959, The Physical Oceanography of Narragansett Bay, *Limnol. Oceanogr.*, **4**: 316-327.

Jitts, H. R., 1959, The Adsorption of Phosphate by Estuarine Bottom Deposits, *Aust. J. Mar. Freshwater Res.*, **10**: 7-21.

Kanwisher, J., 1962, Gas Exchange of Shallow Marine Sediments, in *Symposium on the Environmental Chemistry of Marine Sediments*, Graduate School of Oceanography, University of Rhode Island Occasional Publication No. 1.

Kemp, A. L. W., and A. Mudrochova, 1972, Distribution and Forms of Nitrogen in a Lake Ontario Sediment Core, *Limnol. Oceanogr.*, **17**: 855-867.

Lear, D. W., Jr., 1964, Bacterial Participation in Phosphate Regeneration in Marine Ecosystems, Ph. D. Thesis, Graduate School of Oceanography, University of Rhode Island, Kingston.

, G. F., 1970, *Factors Affecting the Transfer of Materials Between Water and Sediments*, University of Wisconsin, Water Resources Center Literature Review No. 1, Madison, Wisconsin.

Li, W. C., D. E. Armstrong, J. D. H. Williams, R. F. Harris, and J. K. Syers, 1972, Rate and Extent of Inorganic Phosphate Exchange in Lake Sediments, *Soil Sci. Soc. Amer. Proc.*, **36**: 279-285.

MacIsaac, J. J., and R. C. Dugdale, 1972, Interactions of Light and Inorganic Nitrogen in Controlling Nitrogen Uptake in the Sea, *Deep-Sea Res.*, **19**: 209-232.

Martin, J. H., 1968, Phytoplankton–Zooplankton Relationships in Narragansett Bay. III. Seasonal Changes in Zooplankton Excretion Rates in Relation to Phytoplankton Abundance, *Limnol. Oceanogr.*, **13**: 63-71.

McKee, G. D., L. P. Parrish, C. R. Hirth, K. M. Mackenthum, and L. E. Keup, 1970, Sediment–Water Nutrient Relationships, Parts 1 and 2, *Water Sewage Works*, **117**: 203-206, 246-249.

McMaster, R. L., 1962, Seasonal Variability of Compactness in Marine Sediments: a Laboratory Study, *Geol. Soc. Amer. Bull.*, **73**: 643-646.

Miller, S. M., 1952, Phosphorus Exchange in a Subtropical Marine Basin, *Bull. Mar. Sci. Gulf Caribb.*, **1**(4): 257-265.

Mortimer, C. H., 1941 and 1942, The Exchange of Dissolved Substances Between Mud and Water in Lakes, *J. Ecol.*, **29**: 280-329 and **30**: 147-201.

Nixon, S. W., and C. A. Oviatt, 1974, Graduate School of Oceanography, University of Rhode Island, Kingston.

——, C. A. Oviatt, C. Rogers, and K. Taylor, 1971, Mass and Metabolism of a Mussel Bed, *Oecologia (Berlin)*, **8**: 21-30.

Okuda, T., 1960, Metabolic Circulation of Phosphorus and Nitrogen in Matsushima Bay (Japan) with Special Reference to Exchange of These Elements Between Seawater and Sediments, *Trab. Inst. Oceanogr. Univ. Recife. (Brazil)*, **2**(1): 7-153.

Pomeroy, L. R., 1970, The Strategy of Mineral Cycling, *Annu. Rev. Ecol. Syst.*, **1**: 171-190.

——, E. E. Smith, and C. M. Grant, 1965, The Exchange of Phosphate Between Estuarine Water and Sediments, *Limnol. Oceanogr.*, **10**: 167-172.

dfield, A. C., B. H. Ketchum, and F. A. Richards, 1963, The Influence of Organisms on the Composition of Seawater, in *The Sea*, Vol. 2, pp. 26-77, M. N. Hill (Ed.), Wiley-Interscience, New York.

Riedl, R. J., N. Huang, and R. Machan, 1972, The Subtidal Pump: a Mechanism of Interstitial Water Exchange by Wave Action, *Mar. Biol.*, **13**: 210-221.

Riley, J. P., and R. Chester, 1971, *Introduction to Marine Chemistry*, Academic Press, Inc., New York.

Rittenberg, S. C., K. O. Emery, and W. L. Orr, 1955, Regeneration of Nutrients in Sediments of Marine Basins, *Deep-Sea Res.*, **3**: 23-45.

Sanders, H. L., 1960, Benthic Studies in Buzzards Bay. III. The Structure of the Soft-Bottom Community, *Limnol. Oceanogr.*, **5**: 138-153.

Solorzano, L., 1969, Determination of Ammonia in Natural Waters by the Phenolhypochlorite Method, *Limnol. Oceanogr.*, **14**: 799-801.

Stevenson, F. J., and S. N. Tilo, 1970, Nitrogenous Constituents of Deep-Sea Sediments, in *Advances in Organic Chemistry, 1966*, pp. 237-263, G. D. Hobson and G. C. Speers (Eds.), Pergamon Press, Inc., New York.

Strickland, J. D. H., and T. R. Parsons, 1968, *A Practical Handbook of Seawater Analysis*, Fisheries Research Board of Canada, Bulletin 167.

Teal, J. M., and J. Kanwisher, 1961, Gas Exchange in a Georgia Salt Marsh, *Limnol. Oceanogr.*, **6**: 388-399.

Webb, J. E., and J. Theodor, 1968, Irrigation of Submerged Marine Sands Through Wave Action, *Nature*, **220**: 682-683.

Zeuthen, E., 1953, Oxygen Uptake and Body Size in Organisms, *Quart. Rev. Biol.*, **28**: 1

RIVER INPUT OF INORGANIC PHOSPHORUS AND NITROGEN TO THE SOUTHEASTERN SALT-MARSH ESTUARINE ENVIRONMENT

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ABSTRACT

The Black, Pee Dee, Santee, Cooper, Savannah, Ogeechee, Altamaha, Satilla, and St. Johns rivers account for 95% of the continental runoff to the southeastern salt-marsh estuarine ecosystem between Georgetown, S. C., and Jacksonville, Fla. The supply of inorganic phosphorus and nitrogen to this system by these rivers was determined by bimonthly analysis of the dissolved PO_4, NH_3, and NO_3 content of the rivers. The annual supply of inorganic phosphorus is adequate to supply the total phosphorus required by the approximately one million acres of *Spartina* salt marsh receiving the runoff. The annual supply of inorganic nitrogen can supply only about 20% of that required, suggesting that much of the nitrogen in the salt-marsh vegetation is from other sources or is recycled within the estuarine ecosystem. Input of nitrogen by atmospheric fallout is probably insignificant, as is the river supply of organic and particulate nitrogen.

Rivers are the most important source of new nutrients to coastal ecosystems. Nitrogen and phosphorus occur in river water in both organic and inorganic form, the major inorganic forms being phosphate, nitrate, and ammonia. Because of their relatively high solubility, these substances are readily leached from the soils of drainage basins. Generally, they are biologically more available than organic forms.

Nine rivers (the Pee Dee, Black, Santee, and Cooper in South Carolina; the Savannah, Ogeechee, Altamaha, and Satilla in Georgia; and the St. Johns in Florida) account for 95% of the total discharge of fresh water to the salt-marsh estuarine environment between Georgetown, S. C., and Jacksonville, Fla. Between June 1972 and July 1973, these rivers were sampled at bimonthly intervals at several stations just above the estuarine zone. The samples were analyzed for ammonia, nitrate, and phosphate to determine the dependence of primary production of the dominant salt-marsh vegetation (*Spartina alterniflora*) on this supply of river-borne nutrients.

METHODS

Samples were collected in 8-liter Niskin bottles, filtered through 0.45-μm, Millipore filters, and immediately frozen in polypropylene bottles. The salinity of each sample was determined to ensure that dilution with seawater did not influence nutrient concentrations. Ammonia was determined colorimetrically as indophenol blue, which is formed by the reaction of hypochlorite with slightly alkaline ammonia solution in the presence of phenol and nitroprusside ions (Koroleff, 1972). Nitrate was determined by a cadmium reduction meth (Strickland and Parsons, 1968), and phosphate was determined by the techni of Murphy and Riley (1962). Blanks were determined using quartz distilled water.

RESULTS

The results of the analyses of bimonthly samples were used to determine the average concentration of ammonia, nitrate, and phosphate for each river over the period studied (Table 1). These results are based on 20 to 30 determinations

TABLE 1

INORGANIC NITROGEN AND PHOSPHORUS TRANSPORTED BY SOUTHEASTERN RIVERS

	Annual discharge, 10^{12} liters/year	Average nutrient concentrations, μg atoms/liter			Annual nutrient discharge, 10^6 g atoms/year		
		NH_3-N	NO_3-N	PO_4-P	NH_3-N	NO_3-N	PO_4-P
Pee Dee	16.1	1.3	8.1	0.6	21	130	9.7
Black	1.7	1.6	10.5	0.5	3	18	0.8
Santee	3.9	2.3	4.8	0.3	9	19	1.2
Cooper	20.5	2.6	6.0	0.4	53	123	8.2
Savannah	13.7	4.1	17.7	0.8	56	242	11.0
Ogeechee	3.7	1.3	5.0	0.6	5	19	2.2
Altamaha	15.2	1.1	6.3	0.3	17	96	4.6
Satilla	2.7	1.3	4.8	0.4	4	13	1.1
St. Johns	6.6	1.3	11.0	1.9	9	73	12.
Total	84.1				177	733	51.3

each. These data and the total discharge of each river were used to compute the annual input of inorganic phosphorus and nitrogen (Table 1). This computation indicates total nitrogen and phosphorus inputs of 910 and 51 × 10^6 gram atoms/year, respectively, assuming that the concentrations remained constant over the time of study. To a large degree this assumption appears true. The discharge of nutrients by the four major rivers (Pee Dee, Cooper, Savannah, and

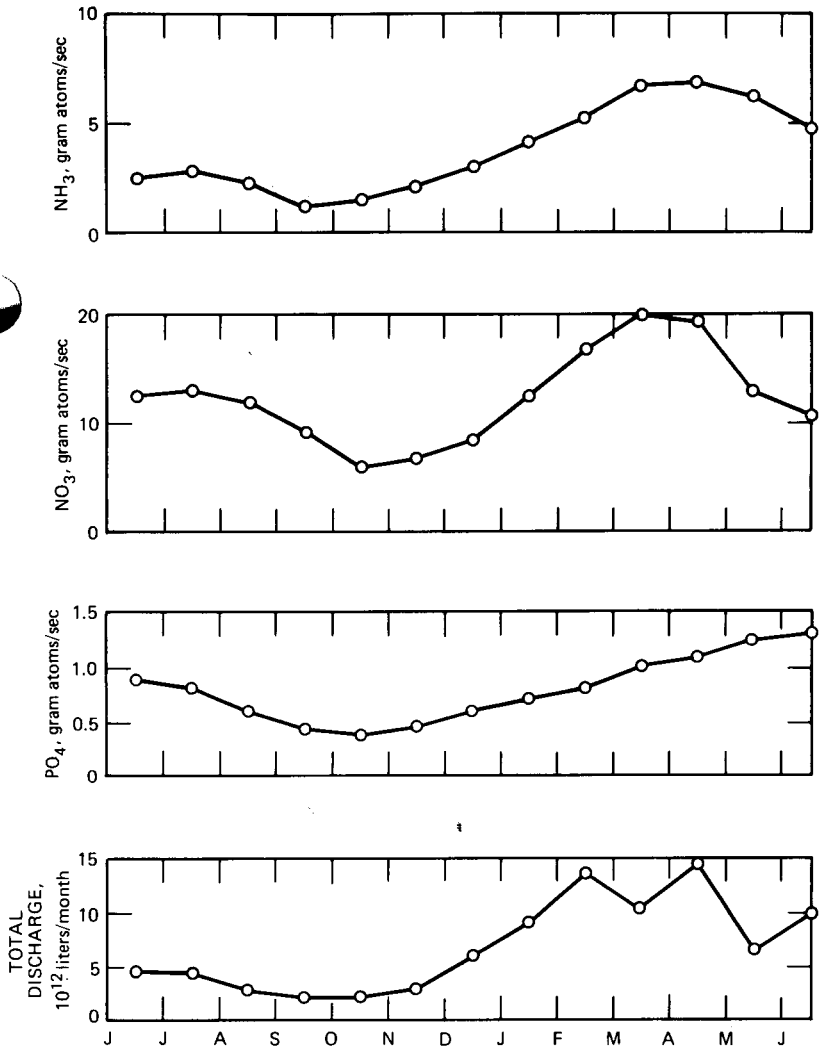

Fig. 1 Seasonal variations in the discharge rate of NH_3, NO_3, and PO_4 by the combined flow of the Pee Dee, Cooper, Savannah, and Altamaha rivers. Total monthly discharge of the nine major rivers is also shown.

Altamaha) was determined using average monthly water discharges reported by the U. S. Geological Survey and nutrient concentrations determined for the same period of time. These data were used to construct a curve for the variations in discharge of the various nutrients over the year. The summations of the curves for the four rivers are shown in Fig. 1. Integrating these curves over a year gives a total discharge of the nutrients for the four rivers of about 70% of that computed for the four rivers from Table 1. This discrepancy is evidently due to a

seasonal variation in the concentrations of the nutrients, which appears to be lower during the winter than in the summer. Most of this variation, however, is due not to changes in the concentration of nutrients but to variations in the total discharge of the river systems.

DISCUSSION

The concentrations of nitrogen and phosphorus in the dominant salt-marsh vegetation (*Spartina alterniflora*) are 2.3 and 0.02%, respectively (Udell et al., 1969; Burkholder, 1956). The annual production of salt marshes in the study area is between 500 and 1000 g dry material/m^2 (Keefe, 1972). This amounts to an annual uptake by the marshes of 800 to 1600 and 3 to 6 mg atoms/m^2 of nitrogen and phosphorus, respectively. The total area of salt marshes receiving the runoff from the nine rivers studied is about 4×10^9 m^2. From the data in Table 1, the annual river inputs of nitrogen and phosphorus to the marshes are 220 and 10 mg atoms/m^2, respectively. Clearly, river input of inorganic phosphate easily accounts for the total annual requirement of *Spartina* salt marshes. The supply of inorganic nitrogen, however, represents only about 20% of that required by salt-marsh vegetation. This suggests that other sources of nitrogen make up the deficit or that much of the nitrogen annually accumulated by *S. alterniflora* is recycled within the salt marshes.

Besides rivers there are two other possible major sources of nitrogen in southeastern estuaries: (1) atmospheric input and (2) the input of nitrogen in organic and suspended form by rivers.

Rainout is the most efficient way of removing nitrogen compounds from the atmosphere and depositing them on the earth's surface. In the coastal areas of the southeastern United States, the dominant form of nitrogen in rainwater is nitrate, which occurs at concentrations of about 0.2 to 0.3 mg/liter (Junge, 1958). The average annual rainfall in the coastal areas of Georgia and South Carolina is about 130 cm. Rain would therefore add an insignificant 4 mg atoms $N\ m^{-2}\ year^{-1}$.

The concentrations of dissolved organic matter in southeastern rivers is about 10 mg/liter, of which about 1% is nitrogen (Beck, Reuter, and Perdue, 1974). The average suspended load is about 15 mg/liter (Windom, 1974). If it is assumed that the suspended load also contains about 1% or less of available nitrogen, the total annual supply of nitrogen in both forms is estimated at 375 mg atoms N/m^2 in addition to that supplied as dissolved NO_3 and NH_3 (Table 1). Although the estimate is probably high, it is still insufficient to sustain primary salt-marsh production.

A large portion of the nitrogen annually accumulated in *S. alterniflora* therefore is probably recycled from plant detritus accumulated in salt-marsh sediments. This supports the contention of others (Ryther and Dunstan, 1971) that nitrogen limits production in coastal marine environments. The study of

nutrient fluxes through estuaries using a large-scale budget approach also clearly agrees with results of studies of isolated estuaries (Pomeroy et al., 1969; Pomeroy et al., 1972).

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REFERENCES

Beck, K. C., J. H. Reuter, and E. M. Perdue, 1974, Organic and Inorganic Geochemistry of Some Coastal Plain Rivers of the Southeastern United States, *Geochim. Cosmochim. Acta*, **38**: 341-364.

Burkholder, P. P., 1956, Studies of the Nutritive Value of *Spartina* Grass Growing in the Marsh Areas of Coastal Georgia, *Bull. Torrey Bot. Club*, **83**: 327-334.

Junge, C. E., 1958, The Distribution of Ammonia and Nitrate in Rainwater over the United States, *Trans. Amer. Geophys. Union*, **39**: 241-248.

Keefe, C. W., 1972, Marsh Production: A Summary of the Literature, *Contrib. Mar. Sci.*, **16**: 163-181.

Koroleff, F., 1972, Direct Determination of Ammonia in Natural Waters as Indophenol Blue, Institute of Marine Research, Helsinki, Finland, personal communication.

Murphy, J., and J. P. Riley, 1962, A Modified Single Solution Method for the Determination of Phosphate in Natural Waters, *Anal. Chim. Acta.*, **27**: 31-38.

Pomeroy, L. R., R. E. Johannes, E. P. Odum, and B. Roffman, 1969, The Phosphate and Zinc Cycles and Productivity of a Salt Marsh, in Symposium on Radioecology, Proceedings of the Second National Symposium, May 15–17, 1967, D. J. Nelson, and F. C. Evans (Eds.). USAEC Report CONF-670503, pp. 412-419.

——, L. R. Shenton, R. D. H. Jones, and R. J. Reimold, 1972, Nutrient Flux in Estuaries, in *Nutrients and Eutrophication*, Vol. 1, American Society of Limnology and Oceanography, pp. 274-291.

Ryther, J. H., and W. M. Dunstan, 1971, Nitrogen, Phosphorus and Eutrophication in Coastal Marine Environments, *Science*, **171**: 1008-1013.

Strickland, J. D. H., and T. R. Parsons, 1968, *A Practical Handbook of Sea Water Analysis*, Fisheries Research Board of Canada.

Well, H. F., J. Zarudsky, T. E. Doheny, and P. R. Burkholder, 1969, Productivity and Nutrient Values of Plants Growing in the Salt Marshes of the Town of Hempstead, Long Island, *Bull. Torrey Bot. Club*, **19**: 42-51.

Windom, H. L., 1974, Heavy Metal Fluxes Through Salt-Marsh Estuaries, in Proceedings of 2nd International Estuarine Symposium, in press.

NUTRIENT FLUX AND CYCLING IN FRESHWATER ECOSYSTEMS

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ABSTRACT

Flux and cycling of matter describe the biogeochemistry of an aquatic ecosystem. The flux of matter across ecosystem boundaries is facilitated by the movement of air, water, and animals, and identifying the ecosystem's boundaries is critical to a quantitative evaluation of these fluxes. A lake's metabolism reflects the biogeochemistry (output of water and materials) of its watershed. Meteorologic inputs of nutrients usually represent a major proportion of the total annual input for nutrient-poor lakes. In nutrient-rich lakes, however, geologic inputs dominate. Gaseous flux across the air–water interface may be appreciable but has not been widely studied. Nitrogen fixation and denitrification play important roles in the nitrogen balance for lake ecosystems, and on an annual basis carbon dioxide flux across the air–water interface of lake ecosystems may be very large. Careful hydrologic measurements are imperative for the construction of quantitative material-balance data for lakes. Studies are needed to relate measured nutrient loading to calculated loading values for large lake ecosystems. Models have been proposed to relate the specific loading of phosphorus and nitrogen to the standing crop (chlorophyll) or trophic state in lakes. Allochthonous inputs of organic carbon may represent a significant fraction of the total organic carbon input for lakes, but allochthonous inputs predominate in small stream ecosystems in forested regions. Material-balance studies for stream ecosystems should provide some insight into the proposed assimilative capacity of the ecosystems. Nutrients may be cycled very rapidly within the ecosystem's boundaries among living components or nonliving components or both. Turnover rates for seston vary from minutes for phosphorus to hours and days for nitrogen and to hours and weeks for carbon. A four-compartment model has been proposed to describe the cycling of phosphorus in lake ecosystems. The sediments of lakes may act as sinks for nutrients moving within a landscape; more than 50% of the annual phosphorus input to a lake may accumulate in the sediments. Aquatic and terrestrial ecosystems interact and respond to a series of inputs and outputs, which functionally link the biogeochemistry of these systems within a landscape.

Knowledge of nutrient dynamics in aquatic ecosystems is poorly integrated. Various aspects have been studied for many years (e.g., chemical equilibria,

nutrient uptake kinetics by phytoplankton, and standing stock of chemical elements) and are known in some detail, but few attempts have been made to assemble and relate the components as parts of a functioning ecosystem. Likewise, I have not attempted to evaluate and interrelate all the components by means of a comprehensive literature review. Rather I have sketched a framework for considering the role of nutrients in freshwater ecosystems, a framework in which the flow and storage of nutrients might be integrated and compared.

In my view the biogeochemistry of an aquatic ecosystem consists of two basic parts, interconnected and interdependent to be sure but amenable to different quantification procedures and conceptual approaches. These two components are nutrient flux and nutrient cycling. Flux refers here to movement, input and output across the ecosystem's boundaries. Quantification of flux is the basis for constructing budgets and observing balancing mechanisms. The biota and nonliving components within the ecosystem's boundaries respond to and are tempered by the external fluxes. Cycling refers to the exchanges among various living or nonliving components, or both, within the ecosystem. The overall structure and function of an aquatic ecosystem are determined by external fluxes and internal cycles. The ecosystem approach attempts to connect and interrelate these two components within a functional unit of nature, such as a landscape, and an ecosystem context provides the framework for relating isolated bits of knowledge.

NUTRIENT FLUX AND THE FRESHWATER ECOSYSTEM

The ecosystem's boundaries must be carefully defined before quantitative biogeochemical studies are begun. This should be an obvious requirement, but many examples can be found in the literature where improper definition of boundaries contributes to a misleading view of ecosystem processes and flux rates. Boundaries must often be determined at the convenience of the investigator rather than on the basis of known functional relationships with adjacent ecosystems. For a lake, however, the lateral boundaries are clear—the shoreline. The upstream and downstream boundaries of running-water ecosystems usually must be determined arbitrarily. The upper boundary for aquatic ecosystems can be taken to be the air–water interface, but the lower vertical boundary is often arbitrarily set at the maximum sediment depth normally utilized by most benthic organisms. Ideally, all boundaries should represent the plane at which short-term exchanges are irreversible (flux). We have found it useful and convenient to partition the nutrient input and output fluxes for an ecosystem according to the principal vehicles of transport, i.e., air, water, and animals (Bormann and Likens, 1967; Likens and Bormann, 1972). Thus inputs and outputs of water and nutrients can be identified and categorized into meteorologic, geologic, and biologic vectors (Fig. 1). This model (Fig. 1) illustrates the functional relationships of inland aquatic ecosystems to the larger watershed and airshed systems of a landscape.

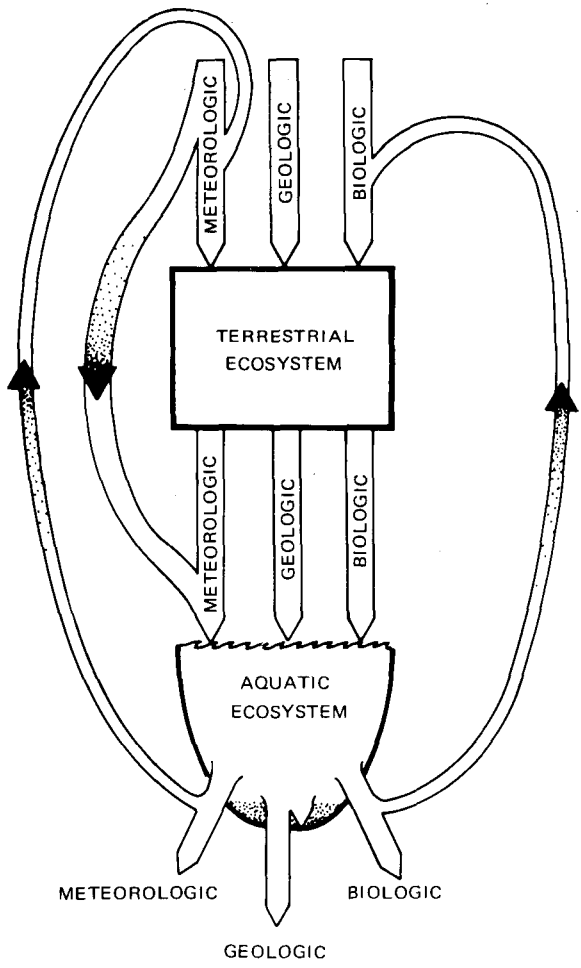

Fig. 1 Diagrammatic model of the functional linkages between terrestrial and aquatic ecosystems. Nutrients may be moved across ecosystem boundaries by meteorologic, geologic, or biologic vectors. [From G. E. Likens and F. H. Bormann, Linkages Between Terrestrial and Aquatic Ecosystems, *BioScience*, 24(8): 447 (1974).]

Nutrients without a prominent gaseous phase at normal biological temperatures (e.g., calcium, potassium, and phosphorus) are input to freshwater ecosystems primarily in precipitation (meteorologic vector) and in drainage waters (geologic vector); output losses are primarily to deep sediments and in outflows (geologic vectors). Nutrients with a prominent gaseous phase (e.g., nitrogen, carbon, and sulfur) move across the ecosystem's boundaries as gases (meteorologic vector) in addition to the input and output fluxes mentioned.

Biological vectors may transport appreciable quantities of nutrients, e.g., in fish migrations, but the details of the process are poorly known (Likens and Bormann, 1974b).

Since aquatic ecosystems are a part of landscapes and since boundaries are often arbitrarily determined, knowledge of the connections between aquatic and terrestrial ecosystems is vital to prediction or management of input–output fluxes. For example, the geologic input for an aquatic ecosystem is the geologic output from the adjacent terrestrial ecosystem and as such represents one of the most important linkages between ecosystems in the biosphere (cf. Likens and Bormann 1972, 1974b).

The input of nutrients to an ecosystem, in humid regions particularly, is caused largely by hydrologic factors (i.e., input of rain or snow and runoff). Since runoff often varies over orders of magnitude (whereas its nutrient content usually varies by less than an order of magnitude, particularly in undisturbed ecosystems), detailed study of the movement of water is of the utmost importance in calculating quantitative nutrient fluxes.

Because of constraints of space and knowledge, I shall consider primarily nutrients of somewhat greater biological interest, i.e., nitrogen, phosphorus, carbon, sulfur, and potassium. In some instances, however, almost nothing is known about the flux and cycling of these critical nutrients. For example, we do not know the amount, form, and variation of phosphorus in precipitation or the uptake, storage, and release of potassium by bacteria, phytoplankton, and zooplankton.

METEOROLOGIC FLUX

Measurements of inputs in precipitation are necessary to construct a quantitative nutrient balance (input and output) for a freshwater ecosystem. However the input of chemicals in precipitation may affect the ecosystem in two divergent ways, as nutrient sources (e.g., nitrogen, phosphorus, and potassium) or as toxic substances (e.g., PCB's, pesticides, and radioisotopes). Here I consider only the nutrient inputs.

There have been a few comprehensive studies of precipitation chemistry in the United States, but most have been limited to either regional or short-term considerations, or both (e.g., MacIntire and Young, 1923; Wilson, 1926; Collison and Mensching, 1932; Leland, 1952; Carroll, 1962; Junge, 1963; Whitehead and Feth, 1964; Gambell and Fisher, 1966; Lodge et al., 1968; Pearson and Fisher, 1971; Likens, 1972a; Likens and Bormann, 1972). Data from these studies suggest that the input of nutrients and other chemicals via precipitation may have significant effects on the ecological and geological relationships in terrestrial and aquatic ecosystems, but the effects have rarely been specified or quantified. Moreover, there have been few detailed studies of precipitation chemistry that include measurements of nitrogen, sulfur, and phosphorus over

periods of more than a year or two, and I know of no detailed synoptic studies for the United States which consider these three important nutrients concurrently. Until recently little consideration was given to the ecological importance of these inputs for freshwater ecosystems, with the notable exception of work by Gorham (1958; 1961). Because detailed information on precipitation chemistry is now accumulating for the northeastern United States (e.g., Pearson and Fisher, 1971; Likens, 1972a) and since we have monitored precipitation chemistry at Hubbard Brook in the White Mountains of New Hampshire for 11 years (e.g., Likens et al., 1971), I shall focus primarily on the chemistry of precipitation in this region.

Precipitation chemistry is highly variable—within a storm and from storm to storm—on a seasonal or annual basis. Therefore weighted averages rather than arithmetic averages must be used to characterize bulk precipitation chemistry over a period of time in which there are numerous precipitation events. Arithmetic averages may be grossly misleading. Precipitation input normally occurs as wet and dry fallout (e.g., Whitehead and Feth, 1964), and both must be collected and analyzed. Little is known about the relative ecological importance of dissolved vs. particulate materials, wet vs. dry fallout, or chemical form (speciation) of precipitation inputs to aquatic ecosystems.

Hydrogen ion contributes 69% of the cation milliequivalents, and sulfate represents 62% of the anion milliequivalents in precipitation at Hubbard Brook. Likewise, hydrogen ion and sulfate generally dominate the precipitation chemistry throughout the northeastern United States (Likens, Bormann, and Johnson, 1972). Thus the rain is acid (pH, 4.1) and represents a potentially serious environmental problem in the entire northeastern United States (Likens, Bormann, and Johnson, 1972; Likens and Bormann, 1974a). Precipitation may also contain significant amounts of various other cations and anions, including phosphorus. Usually the concentration of phosphorus is very small in rain and snow [1 to 5 μg P/liter at Hubbard Brook; 5 to 8 μg P/liter at Ithaca, New York (Likens, 1972a); 13 μg P/liter in the northeastern region of the United States (Pearson and Fisher, 1971); 21 μg P/liter in northern Minnesota (Wright, 1974); 9 μg P/liter in north central Florida (Brezonik et al., 1969)], but the annual input may be significant. There is some suggestion that phosphorus concentrations in urban areas are higher than those in rural areas (Weibel, 1969), and there may be appreciable amounts of particulate phosphorus in some samples of precipitation (Fredriksen, 1972). In general, however, the sources and relative proportions of inorganic and organic (dissolved and particulate) phosphorus in precipitation are unknown, and there are no long-term records of phosphorus in precipitation for the United States.

Some long-term measurements of precipitation show an appreciable change in sulfur, hydrogen-ion, and nitrogen chemistry during the past 30 years in the northeastern United States (Likens and Bormann, 1974a). Sulfate concentrations decreased by about 60% in the mid-1950s. Precipitation has become more

acidic. Nitrate concentrations have increased about fourfold in central New York State since 1945. Nitrate levels in precipitation in rural New Hampshire have more than doubled since 1956. These changes, which could have significant ecological effects on aquatic ecosystems, are presumably related to man's activities within the airsheds (Likens, 1972a).

The input of dissolved inorganic calcium, potassium, hydrogen ion, nitrogen, phosphorus, and sulfur in precipitation may be a significant component of the total annual nutrient input for a lake (Table 1). The relative magnitude and

TABLE 1

ANNUAL INPUTS OF WATER AND NUTRIENTS IN PRECIPITATION TO VARIOUS LAKE ECOSYSTEMS*

Material	Mirror Lake, N. H.†		Clear Lake, Ont.‡		Cayuga Lake, N. Y.§	
	kg/ha	% of total	kg/ha	% of total	kg/ha	% of total
Calcium	1.2	1.2	14	45	11	0.2
Potassium	0.47	2.1	1.0	31	1.1	0.5
Sulfur (SO_4—S)	9.6	11.1			18	1.3
Phosphorus (total P)	0.04	17	0.35	61	0.18	1.9
Nitrogen (NO_3—N + NH_4—N)	6.6	78	9.9	75	10	6.5
Hydrogen ion	0.98	96			1.1	99.9
Water (10^6 liters/ha)	10	22	12	57	10	9.0
$\frac{\text{Area of lake}}{\text{Area of watershed}}$	0.17		0.71		0.04	

*Inputs are in kilograms per hectare of lake surface.
†Likens et al., 1975.
‡Schindler and Nighswander, 1970.
§Likens, 1974.

ecological importance of direct nutrient inputs in precipitation are determined by several factors, including climate (e.g., annual precipitation), chemistry of precipitation, runoff characteristics, geology, soils and vegetation of the watershed, watershed use or level of disturbance, and the ratio between lake-surface area and watershed area. Thus a comparison of precipitation inputs, based on percent of total inputs, can be informative for an individual lake or lake type (e.g., soft water) but must be treated carefully when we are comparing different lakes. Clear Lake, Ontario, and Mirror Lake, New Hampshire, are relatively small nutrient-poor lakes with undisturbed forested drainage basins on granitic substrates (Table 1). Cayuga Lake, New York, is a large eutrophic lake surrounded by sedimentary geologic substrates and a watershed disturbed by urban and agricultural activities. The amount of water input in precipitation to all three of these lakes is approximately the same on a unit-area basis; however,

the percentage value (of total) for Clear Lake is much higher because the drainage area is proportionally much smaller. The drainage area for Cayuga Lake is about 24 times larger than its surface area, whereas the drainage area and surface area are roughly similar for Clear Lake. Nevertheless, the precipitation input of nitrogen and phosphorus to Mirror Lake and Clear Lake, and to a lesser extent to Cayuga Lake, represents a large proportion of the annual total input. Likewise, inputs of dissolved nitrogen, phosphorus, and potassium in precipitation may equal or exceed losses in drainage waters from undisturbed terrestrial ecosystems (Likens and Bormann, 1974b).

GASEOUS FLUX

The flux of gases across a freshwater ecosystem's boundaries has only recently received serious attention. Thus the quantities of H_2S, CH_4, N_2, and CO_2 which pass across the air–water interface and the subsequent response of living and nonliving components inside the aquatic ecosystem are poorly known.

Nitrogen

Data on flux and utilization of gaseous nitrogen in freshwater ecosystems are informative even though extrapolations to annual considerations and for the entire ecosystem have been based on relatively few short-term measurements. The annual fixation rate in the English Lake District was estimated at 0.04 to 0.29 g N/m^2, or less than 1% of the annual input (Horne and Fogg, 1970). The annual rate for Lake Erken, Sweden, was 0.23 to 0.73 g N/m^2, which would increase the annual nitrogen input to the lake by 40% (Granhall and Lundgren, 1971). The annual rate for Clear Lake, California, was 1.8 g N/m^2, or 43% of the annual input (Horne and Goldman, 1972). For Lake Mendota, Wisconsin, it has been estimated that nitrogen fixation, primarily by blue-green algae, annually provides about 7% of the total annual nitrogen input for the lake (Torrey, 1972, Sonzogni and Lee, 1972). Keeney, Chen, and Graetz (1971) estimated that, of the nitrogen entering the lake in seepage waters, some 63% was lost by denitrification in the sediments—or about 9% of the total annual input (Sonzogni and Lee, 1972). Sonzogni and Lee believe, however, that this value for denitrification in the sediments is much too high. Denitrification rates in the water were measured at 8 to 20 μg N $liter^{-1}$ day^{-1} (Brezonik and Lee, 1968), hence an additional amount of nitrogen would be lost through denitrification in the pelagic region [~5% of the total annual nitrogen input (Sonzogni and Lee, 1972)]. If these values were reliable and comparable, then ~7% more nitrogen would be lost by denitrification than would be added by biological fixation in Lake Mendota each year. Vollenweider (1968) believes that normally denitrification processes quantitatively exceed fixation in lakes; he estimated the rate of nitrogen loss by denitrification for various Swiss lakes at 3 to 57 mg m^{-2} day^{-1}

A very high denitrification rate (200 to 300 mg m^{-2} day^{-1}) has been observed in Lake Orta (Vollenweider, 1963).

Blue-green algae have been thought to be the major source of nitrogen fixation in freshwater ecosystems, but Keirn and Brezonik (1971) suggested that bacteria in anoxic regions may contribute significantly to the nitrogen fixation in freshwater ecosystems. They suggested that for Lake Mize, Florida, the annual rate of bacterial nitrogen fixation (limited to the anoxic hypolimnion) was 1.12 g N/m^2 in 1970 and 4.56 g N/m^2 in 1969, or about 14 and 56%, respectively, of the total annual nitrogen input to the lake. Moreover Brezonik and Harper (1969) suggested that nitrogen fixation in anoxic waters of a small meromictic lake, Lake Mary in northern Wisconsin, contributed about 0.33 to 0.42 g N m^{-2} $year^{-1}$. Keirn and Brezonik (1971) also observed nitrogen fixation by acetylene reduction in the sediments of several lakes in Florida. It is unknown how much of this nitrogen would be released or available to organisms in the overlying waters.

Carbon

The exchange rate of CO_2 across the air–water interface has been measured during the summer by the radon method in nutrient-poor lakes of the Canadian Shield (Schindler et al., 1972, Emerson, Broecker, and Schindler, 1973). This method is based on the radioactive decay of dissolved ^{226}Ra and measurement of the subsequent evasion of ^{222}Rn to the atmosphere. Results indicated that the invasion rate for Lake 227 was 17 ± 8 mmoles CO_2 m^{-2} day^{-1} or 0.204 g C m^{-2} day^{-1} (Emerson, Broecker, and Schindler, 1973). A similar value was obtained by determining a direct total carbon balance for the lake (Schindler et al., 1972). It is apparent that if this rate were to apply for only half the year (during the other half the lake might be covered with ice) a very large amount of inorganic carbon could be fluxed in this way. In fact, Schindler et al. (1972) argued convincingly that the invasion of atmospheric carbon dioxide is adequate to support eutrophication of any freshwater body given an adequate supply of nitrogen and phosphorus. Carbon dioxide is biologically fixed in the freshwater ecosystem by photosynthesis and chemosynthesis and is released by respiration.

GEOLOGIC FLUX

Undisturbed terrestrial ecosystems tend to have relatively small losses of dissolved substances and particulate matter in drainage waters. Structural or functional disturbance can upset these natural relationships, grossly accelerate output from terrestrial ecosystems, and thus increase the input to adjacent ecosystems. For example, at Hubbard Brook in New Hampshire, experimental deforestation increased annual total phosphorus loss in drainage waters tenfold, or to a level similar to the output per unit area from agricultural watersheds tributary to Cayuga Lake, New York, and increased inorganic nitrogen loss by

about fiftyfold, or to a level 6 to 25 times greater than the output from agricultural watersheds tributary to Cayuga Lake (Hobbie and Likens, 1973; Likens, 1974). Under such circumstances precipitation inputs become relatively much less important and terrestrial inputs dominate (Table 2). For example, a lake with an undisturbed forested watershed may receive 20 to 80% of its phosphorus and 50 to 80% of its inorganic nitrogen input from precipitation falling directly on the lake surface, but, when the watershed is disturbed (usually by man), only 2 to 25% of the phosphorus and 3 to 40% of the nitrogen inputs come from direct precipitation even though the absolute amounts provided by precipitation in each case are approximately the same.

INPUT–OUTPUT BALANCE

General input–output considerations apply to both standing- and running-water ecosystems. However, an obvious difference is the major throughput (e.g., Fisher and Likens, 1973) that occurs in most running-water ecosystems. Because of this, rivers and streams have been treated largely as "pipes" or conduits for the movement of water and materials instead of as the actual functioning ecosystems that they are. I know of so few careful studies of material balance or nutrient cycling in stream ecosystems that I was unable to formulate any meaningful general statements or relationships based on published data (see Keup, 1968; Ball and Hooper, 1961; Davis and Foster, 1958; Elwood and Nelson, 1972; Nelson et al., 1969, Hall, 1972). It would seem that careful material-balance studies within stream ecosystems would provide a very fruitful area of inquiry. I have relied here on material-balance studies of lakes.

Nutrient-budget data for lakes have been obtained by measurement and by calculation. Unfortunately, because of the diversity of parameters and temporal variations, quantitative measurement requires a huge expense in time, labor, and money. Hence only a few careful nutrient-balance studies or budgets have been attempted for lakes from real data. Flux depends on measurements of both hydrologic and chemical factors. Many studies have reliable chemical measurements or reliable hydrologic measurements, but not both. For large complex lake systems, the problem of quantitative measurement would seem to be insurmountable without a large and well-funded team of scientists and engineers. Faced with this dilemma workers have sought generalizations relative to the export of chemicals and nutrients from terrestrial ecosystems (Tables 3 and Figs. 2 and 3). By combining such information with data on land use, we can calculate inputs for lakes (e.g., Table 5). The land-use designations in Fig. 3 are obviously oversimplifications since most drainage areas are used simultaneously for a variety of activities. This figure attempts to generalize about the major activity affecting the export of nutrients in drainage waters. Export per unit area of watershed (milligrams per square meter per year) may not be a good indication of the total input, or loading, for a lake, or it may be indicative of

TABLE 2

SOURCES OF NITROGEN AND PHOSPHORUS FOR VARIOUS LAKES AS PERCENTAGES OF TOTAL ANNUAL INPUT

Source	Disturbed watersheds								Undisturbed watersheds					
	Lake[a] Mendota	Lake[b] Rotorua	Lake[c] Mälaren	Lake[d] Canandaigua	Cayuga[e] Lake	Lake[f] Erie	Lake[g] Erie	Lake[g] Ontario	Clear[h] Lake	Rawson[i] Lake	Mirror[j] Lake	Dogfish[k] Lake	Lake[g] Superior	Lake[g] Huron
Phosphorus														
Precipitation	6	2	4	2	2	4	4	4	61	50	17	82	46	27
Urban runoff and waste water	35	14	39	46	98	96	96	96	39	50	83	18	54	73
Rural runoff and groundwater	59	83	57	52										
Nitrogen														
Precipitation	17	6	4	3	7		18	28	75	50	78		47	62
Urban runoff and waste water	11	11	25	6	93		82	72	25	50	22		53	38
Rural runoff and groundwater	66	83	71	91										
Fixation	7	?	?	?	?		?	?	?	?	?		?	?

[a]Sonzogni and Lee, 1974; [b]Fish, 1969; [c]Vollenweider, 1968; [d]Hetling and Sykes, 1973; [e]Likens, 1974; [f]Weibel, 1969; [g]Elder, 1974; [h]Schindler and Nighswander, 1970; [i]Schindler et al., 1972; [j]Likens et al., 1975; [k]Wright, 1974.

TABLE 3

ESTIMATED EXPORT OF NITROGEN AND PHOSPHORUS IN RUNOFF FROM AN AREA WITH A POPULATION DENSITY OF 150 PERSONS PER SQUARE KILOMETER*

Source	Nitrogen, g m^{-2} $year^{-1}$	Phosphorus, g m^{-2} $year^{-1}$
Lower Limit†		
Urban wastes		
Wastes of human origin	0.66	0.08
Detergents (50%)		0.04
Runoff from highways	0.07	0.01
Industrial wastes	0.07	0.01
Subtotal	0.80	0.14
Rural runoff		
Arable	0.23	0.01
Meadows and grasslands	0.53	0.01
Forests	0.10	0.01
Subtotal	0.86	0.03
Total	1.66	0.17
Upper limit‡		
Urban wastes		
Wastes of human origin	0.66	0.08
Detergents (50%)		0.04
Runoff from highways	0.07	0.01
Industrial wastes	0.07	0.01
Subtotal	0.80	0.14
Rural runoff		
Arable	0.58	0.05
Meadows and grasslands	1.33	0.05
Forests	0.10	0.01
Subtotal	2.01	0.11
Total	2.81	0.25

*Modified from Vollenweider's data (1968).

†10% nitrogen and 1% phosphorus from farmland, forests, etc.

‡25% nitrogen and 5% phosphorus from farmland, forests, etc.

TABLE 4

ESTIMATED "AVERAGE" QUANTITIES OF NITROGEN AND PHOSPHORUS FROM VARIOUS SOURCES*

Source	Nitrogen, g m^{-2} $year^{-1}$	Phosphorus, g m^{-2} $year^{-1}$
Rainfall	0.80	0.030
Forested area	0.25	0.008
Pastured area	0.85	0.017
Cultivated cropland	0.75	0.44
Citrus farms	2.2	0.018
Muck farms	0.11	0.14
Urban area	0.80	0.350
Feedlot runoff	80	30
Domestic sewage	3900†	800†
Septic tanks		
Immediate	2400‡	140‡
Remote	970‡	14‡
Domestic ducks	480§	90§

*Adapted and modified from reviews by Brezonik and Shannon, 1971; Loehr, 1974; Dillon and Kirchner, 1975; Chapin and Uttormark, 1973 (see these papers for original references). These estimates should be considered only as approximate guides since they may not reflect the range of values that result from differences in soils, climate, management, etc.

†Grams per capita per year.

‡Grams per septic tank per year.

§Grams per duck per year.

productivity or some other ecological response since the total input depends on the size of the watershed draining to the lake and the relative input depends on the effective volume of the lake and its flushing rate. Also annual values disguise the temporal variations in quantity and quality of export from a watershed.

A few workers have attempted to obtain quantitative data on nutrient inputs outputs for an entire lake system by measuring all precipitation and runoff puts (e.g., Table 6). Rawson Lake is one of the small nutrient-poor lakes in the Experimental Lakes Area of Ontario which D. Schindler and co-workers are studying in great detail. Data on nutrient inputs and outputs for this lake exist for a 4-year period. In contrast Cayuga Lake is a large nutrient-rich lake in the Finger Lakes Region of New York. Well over 100 tributaries enter this 61-km-long lake; this poses a monstrous sampling problem. Annual nutrient inputs to Cayuga Lake exceed those to Rawson Lake by several orders of magnitude (Table 6).

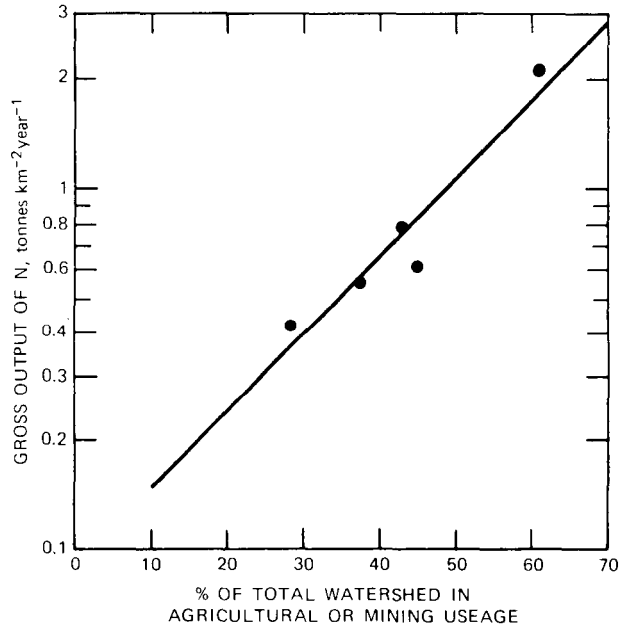

Fig. 2 Relationship between the gross export of nitrogen (NO_3^- + NH_4^+) in drainage water and the percentage of total watershed in agricultural usage for five streams draining into the southern portion of Cayuga Lake, New York. The regression line is significant; F ratio probability is <2.5%; correlation coefficient is 0.95 (Likens, 1974).

Unfortunately few data of any sort are available on nutrient budgets for most lakes. I have freely mixed the results from calculated and measured budgets in an attempt to derive a generalization, and at the same time I fully realize the numerous pitfalls that this entails. Moreover, information relative to the chemical form measured (i.e., whether values represent total or total dissolved, include organic fractions, etc.) is frequently lacking or ambiguous. On the basis of data given in Tables 2 and 5 however, it is apparent that, when precipitation inputs of nitrogen and phosphorus dominate the nutrient budgets for a lake, total nutrient loading is small and the lake is likely to be oligotrophic. When runoff from a disturbed watershed overwhelms the precipitation input, the lake is likely to be nutrient rich and eutrophic (Table 7). Although this conclusion seems logical and is embodied in the definition of cultural eutrophication (Hasler, 1947), data are too few to fully elaborate it. For example, some careful experimental studies of adjacent undisturbed and disturbed watersheds on various geologies and soil types are necessary to properly characterize the relative importance of precipitation and runoff inputs to diverse freshwater

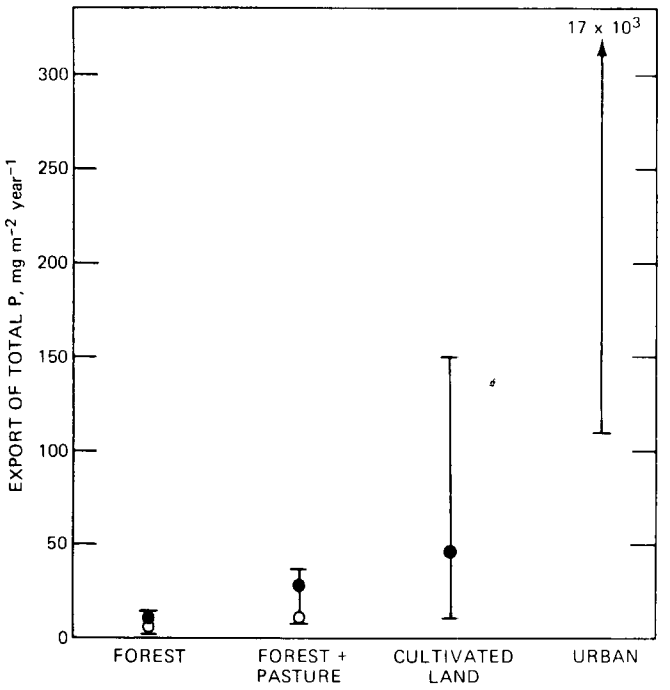

Fig. 3 Relationship between watershed use and annual export of total phosphorus in drainage water. Vertical bars are ranges. ●, means for watersheds on sedimentary geologies (forest: n = 8, $\bar{x}$ = 11.7, $s_{\bar{x}}$ = 1.32; forest + pasture: n = 4, $\bar{x}$ = 23.3, $s_{\bar{x}}$ = 5.37; cultivated land: n = 11, $\bar{x}$ = 44, $s_{\bar{x}}$ = 9.44). ○, means for granitic watersheds (forest: n = 25, $\bar{x}$ = 4.9, $s_{\bar{x}}$ = 0.58; forest + pasture: n = 6, $\bar{x}$ = 10.2, $s_{\bar{x}}$ = 1.51). Seven forested watersheds on volcanic rock in the state of Washington, having a mean export of 72 mg P m^{-2} year^{-1} (Sylvester, 1961; Emery, Moon, and Welch, 1973), are not included in the calculation of means for forested granitic watersheds. Data are derived largely from a review by Dillon and Kirchner (1975).

systems. Likewise the importance of other differences between these inputs unknown. For example, most of the phosphorus entering a lake from precipitation is presumably in inorganic form and is readily available to organisms, but much of the phosphorus input from runoff is in particulate form (both organic and inorganic, especially when the watershed has been disturbed). Moreover, runoff or precipitation inputs may be very seasonal and ostensibly out-of-phase with each other, particularly if the lake freezes over or snow accumulates, or both. That is, nutrient inputs contained in snow falling throughout the winter season may accumulate and may not appear in melt water or runoff until spring. Likewise, runoff or precipitation inputs may differ and

TABLE 5

SOURCES OF NITROGEN AND PHOSPHORUS AS PERCENT OF TOTAL INPUT FOR SELECTED LAKES IN NORTH CENTRAL FLORIDA*

Lake	Trophic status	Nutrient	Sewage and urban runoff	Septic tanks	Fertilized area	Pasture and cleared area	Forest area	Rainfall on lake surface
Santa Rosa	Ultraoligotrophic	N	0	13	0	0	47	40
		P	0	11	0	0	30	59
Santa Fe	Oligotrophic	N	7	2	5	8	41	37
		P	15	2	1	3	25	54
Orange	Mesotrophic	N	1	<1	10	15	57	17
		P	5	<1	2	9	49	35
Newnan's	Eutrophic	N	8	1	2	18	56	15
		P	22	1	<1	10	41	26
Hawthorne	Eutrophic	N	36	32	<1	5	14	13
		P	57	23	<1	2	6	12
Dora	Hypereutrophic	N	17	2	74	<1	1	6
		P	72	1	14	<1	1	12

*From the data of Brezonik and Shannon, 1971. Nutrient inputs estimated from information on land use and population characteristics of the lake's watershed (see Table 4).

TABLE 6

INPUT–OUTPUT BALANCE (TONNES/YEAR) FOR CAYUGA LAKE, NEW YORK,* 1970–1971 AND RAWSON LAKE, ONTARIO,† 1970–1973

Element	Precipitation input	Runoff input	Total input	Discharge output	Percent retained
		Cayuga Lake*			
Phosphorus	3	167	170	61	64
Nitrogen	179	2,565	2,744	513	81
Potassium	19	3,480	3,499	3,969	−12
Sulfur	313	24,671	24,984	31,983	−22
		Rawson Lake†			
Phosphorus	0.018	0.017	0.035	0.010	71
Nitrogen	0.339	0.346	0.686	0.275	60
Carbon‡	2.435	19.005	21.440	10.074	53
Potassium	0.059	0.442	0.501	0.434	13
Sulfur§	0.055	0.362	0.416	0.331	20

*Modified from the data of Likens (1974).
†Modified from the data of Schindler et al. (1975).
‡Three years only.
§One year only.

TABLE 7

SOURCES OF NITROGEN AND PHOSPHORUS AS PERCENTAGES OF THE TOTAL ANNUAL INPUT*

	Precipitation		Runoff	
	N	P	N	P
Oligotrophic lakes	56	50	44	50
Eutrophic lakes	12	7	88	93

*Based on data for 18 lakes.

may be out of phase with the periods of greatest biological activity in the lake. About 69% of the annual runoff input of molybdate reactive phosphorus, 82% of the nitrate, and 74% of the potassium for Cayuga Lake occurred during November to April, or the "nongrowing season" (Fig. 4), whereas only 47, 66, and 43%, respectively, of the direct annual precipitation input occurred during this period (Likens, 1974).

Data on nutrient inputs (particularly nitrogen and phosphorus) have been used to calculate loadings for freshwater lakes, on the basis of either surface area

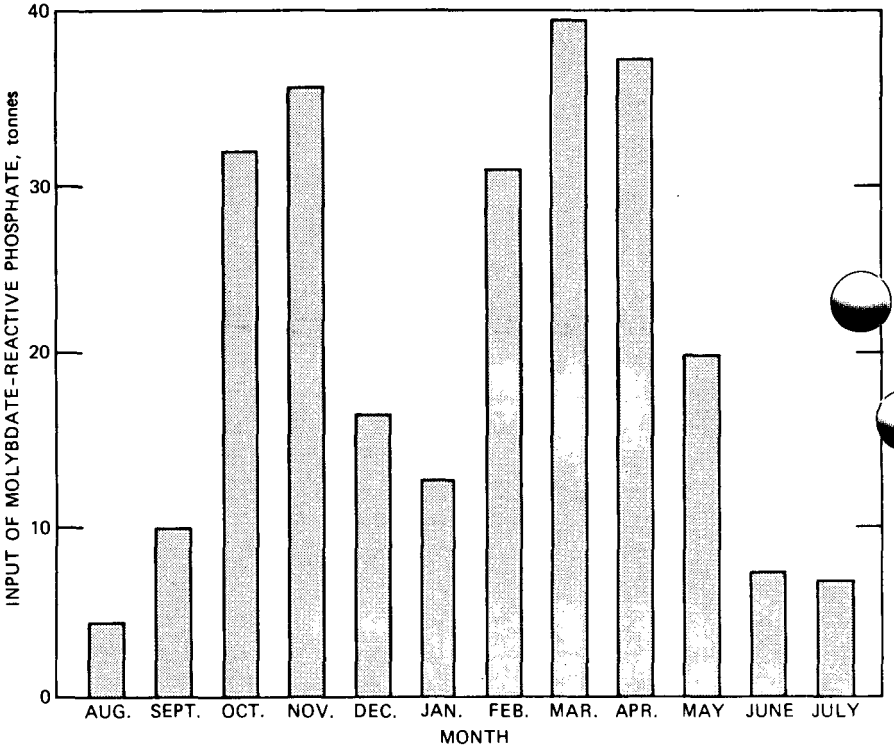

Fig. 4 Weighted monthly runoff input of molybdate-reactive phosphorus to Cayuga Lake, New York, during 1970-1971.

(surface loading) or volume (volumetric loading) of the lake (Table 8). Using surface-loading data and mean depths from lakes throughout Europe and North America, Vollenweider (1968) proposed specific loading values for nitrogen and phosphorus, which may be acceptable or, alternatively, may cause serious cultural eutrophication. Critical nutrient-loading rates in the Finger Lakes of New York (Oglesby, 1974), in some lakes in southern Ontario (Dillon, 1974a), and in a large number of lakes in north central Florida (Brezonik and Shannon, 1971) were found to be somewhat higher than the limits proposed by Vollenweider, but these lakes did not show the predicted levels of eutrophication. The predictive nature of Vollenweider's original nutrient loading–mean depth relationship has been improved by including the mean residence time of the water as part of the calculation. Dillon (1975) proposed that a plot of $L(1 - R)/\rho$, where L is phosphorus loading, R is the retention coefficient of phosphorus in the lake, and ρ is the hydraulic flushing rate vs. $\bar{z}$, the mean depth, provides a better quantitative relationship for predicting the trophic state of diverse lakes. Dillon's model relates loading to "effective" nutrient concentra-

tion in the lake. It is then possible to rationalize phosphorus loading and trophic state since a relationship between total phosphorus concentration at spring overturn and phytoplankton standing crop (summer chlorophyll) has been established for many lakes throughout the world (Fig. 5). Predictive reliability should improve as these empirical models are quantitatively refined and combined.

TABLE 8

NUTRIENT LOADING FROM PRECIPITATION AND RUNOFF* FOR CAYUGA LAKE, NEW YORK, 1970–1971

Nutrient	Volumetric loading, mg liter^{-1} year^{-1}	Surface loading, g m^{-2} year^{-1}
Bicarbonate	17.06	925
Calcium	6.80	369
Chloride	2.43	132
Magnesium	1.63	88.2
Sodium	1.52	82.5
SO_4–S	1.42	76.8
NO_3–N	0.243	13.2
SiO_2–Si	0.229	12.4
Potassium	0.195	10.6
NH_4–N	0.017	0.913
Total phosphorus	0.014	0.739
PO_4–P	0.009	0.472
Hydrogen ion	0.002	0.0867

*Seneca River is excluded since it inputs to the lake just above the outlet.

In a similar but ostensibly more elaborate attempt to derive management answers, Brezonik and Shannon (1971) developed an index of trophic state (TSI) based on seven trophic indicators (including nutrient loading) using multivariate statistical analysis techniques. The TSI values were then used to relate watershed usage and trophic conditions in a large number of lakes in northern Florida. Such empirical or statistical approaches for predicting trophic status or trends in freshwater ecosystems are necessarily general and are subject to exception, but I believe they are useful and provide a basis for management. Undoubtedly these models will be elaborated as more information and knowledge are obtained about the linkages between terrestrial and aquatic ecosystems.

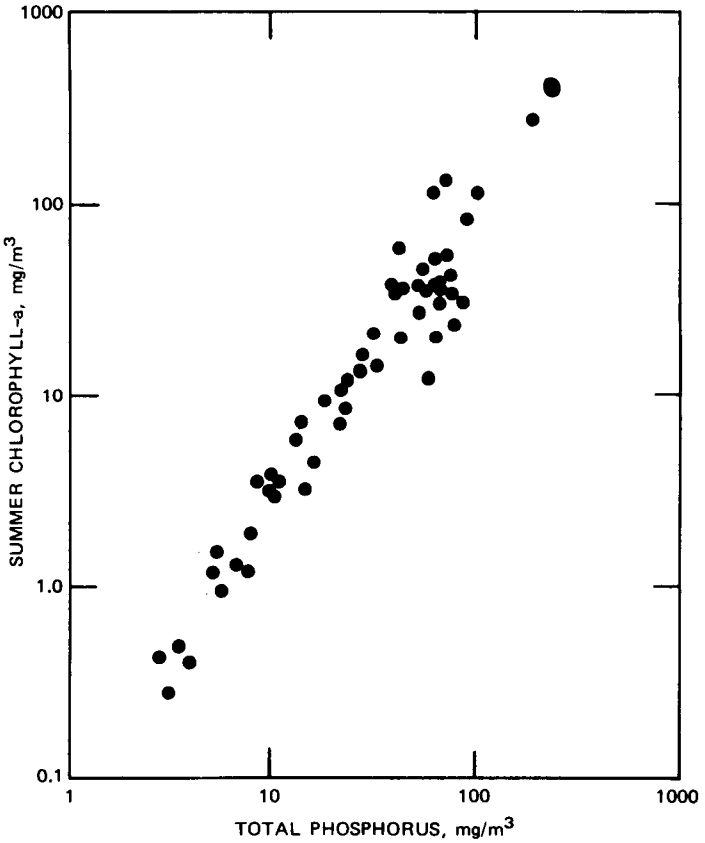

Fig. 5 Relationship between average summer chlorophyll concentration and total phosphorus concentration at spring overturn in lakes throughout the world [From P. J. Dillon and F. H. Rigler, The Phosphorus–Chlorophyll Relationship in Lakes, *Limnology and Oceanography*, 19(5): 768 (1974).]

NUTRIENT CYCLING AND THE FRESHWATER ECOSYSTEM

Within the ecosystem's boundaries, water provides the medium whereby nutrients may be dissolved, adsorbed, absorbed, complexed, ingested, fixed, exchanged, excreted, exuded, leached, precipitated, oxidized, reduced, etc.—i.e., cycled. Nutrients tend to occur or exchange between three basic compartments: available inorganic nutrients, organic matter, and primary and secondary minerals (Fig. 6). Note that organic matter (living and dead) links the two major functional components of ecosystems, energy flow and nutrient cycling. Available inorganic nutrients are those dissolved in water or on exchange

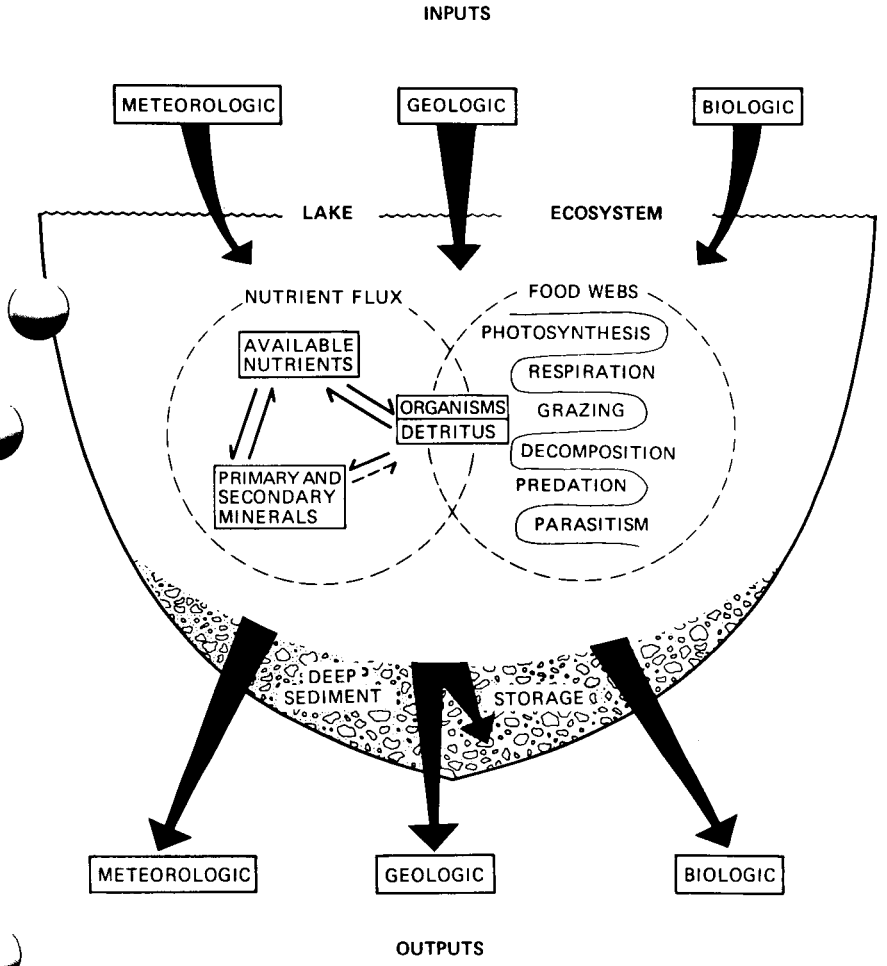

Fig. 6 A diagrammatic model for nutrient cycling in a freshwater ecosystem. (From G. E. Likens and F. H. Bormann, An Experimental Approach to Nutrient–Hydrologic Interactions in New England Landscapes, in *Coupling of Land and Water Systems*, A. Hasler (Ed.), p. 8, Ecological Studies 10, Springer-Verlag, Inc., New York, 1975.)

surfaces of pelagic particulate matter or bottom sediments. Nutrients incorporated in living and dead organic matter, in dissolved or particulate form, both in the pelagic region and in the sediments, comprise the organic-matter compartment. Nutrients incorporated within primary and secondary minerals in the sediments or suspended in the water constitute the primary and secondary mineral compartment. Another useful categorization of compartments is dissolved, as suspended particulates or as settled and substrate particulate

materials. Some such scheme of bookkeeping is necessary to integrate the exceedingly complex and diverse and often rapid cycling that occurs in natural ecosystems.

Recently the cycling of carbon, nitrogen, and phosphorus has been reviewed for freshwater systems (Brezonik, 1973; Golterman, 1973; Keeney, 1973; Kerr et al., 1973; Rigler, 1973; Syers, Harriss, and Armstrong, 1973; Wetzel and Rich, 1973). Thus my attempt here will be to highlight these reviews and to elaborate on or point out gaps in our knowledge where possible.

Carbon

Robert G. Wetzel and his colleagues developed an elaborate diagram to describe the distribution and flux of carbon in a lake ecosystem (Fig. 7). The interactions depicted by this diagram are very informative. I should point out that the diagram is a gross oversimplification of natural interactions, and yet this simplified model may be too complex to fully evaluate or to simulate on a computer. With much painstaking effort the standing stocks and exchange between many of the compartments have been evaluated to produce something of a total organic carbon budget for a small (5-ha) hard-water lake (Lawrence) in Michigan and a small (15-ha) soft-water lake (Mirror) in New Hampshire (Table 9). These data are more or less comparable although different measurement procedures and assumptions were used and neither study measured gaseous flux. The amount of net phytoplankton production (^{14}C) in both lakes is essentially the same, but it represents a much larger percentage of the total autochthonous input in Mirror Lake (Table 9). The other autochthonous inputs in Lawrence Lake are large and result in a total autochthonous fixation of carbon that is more than threefold greater than that in Mirror Lake. Macrophytes and attached algae often fix significant amounts of carbon in lakes, and these inputs must be measured and considered in analyses of the trophic status of freshwater ecosystems (Likens, 1972b).

The total allochthonous inputs are similar in size for both lakes, and most of the allochthonous organic carbon is input as dissolved material (Table 9). The relatively high percentage of particulate inputs in Mirror Lake may in part represent measurement anomalies, but it reflects largely the higher dissolved organic matter concentrations in tributaries to Lawrence Lake and the densely forested shoreline and drainage area of the essentially undisturbed Mirror Lake watershed. Input of shoreline litter (leaves, etc.) was negligible in Lawrence Lake but contributed 37% of the total allochthonous input to Mirror Lake. Surprisingly, organic carbon in direct precipitation during July to January averaged 3.1 mg/liter and, when extrapolated over the year, represented 16% of the total allochthonous inputs for Mirror Lake (Jordan and Likens, 1975).

The output components for each lake were proportionally similar in magnitude (Table 9). Most of the outflow losses occur as dissolved organic matter since the lake is a settling basin for particulate matter. Ecosystem

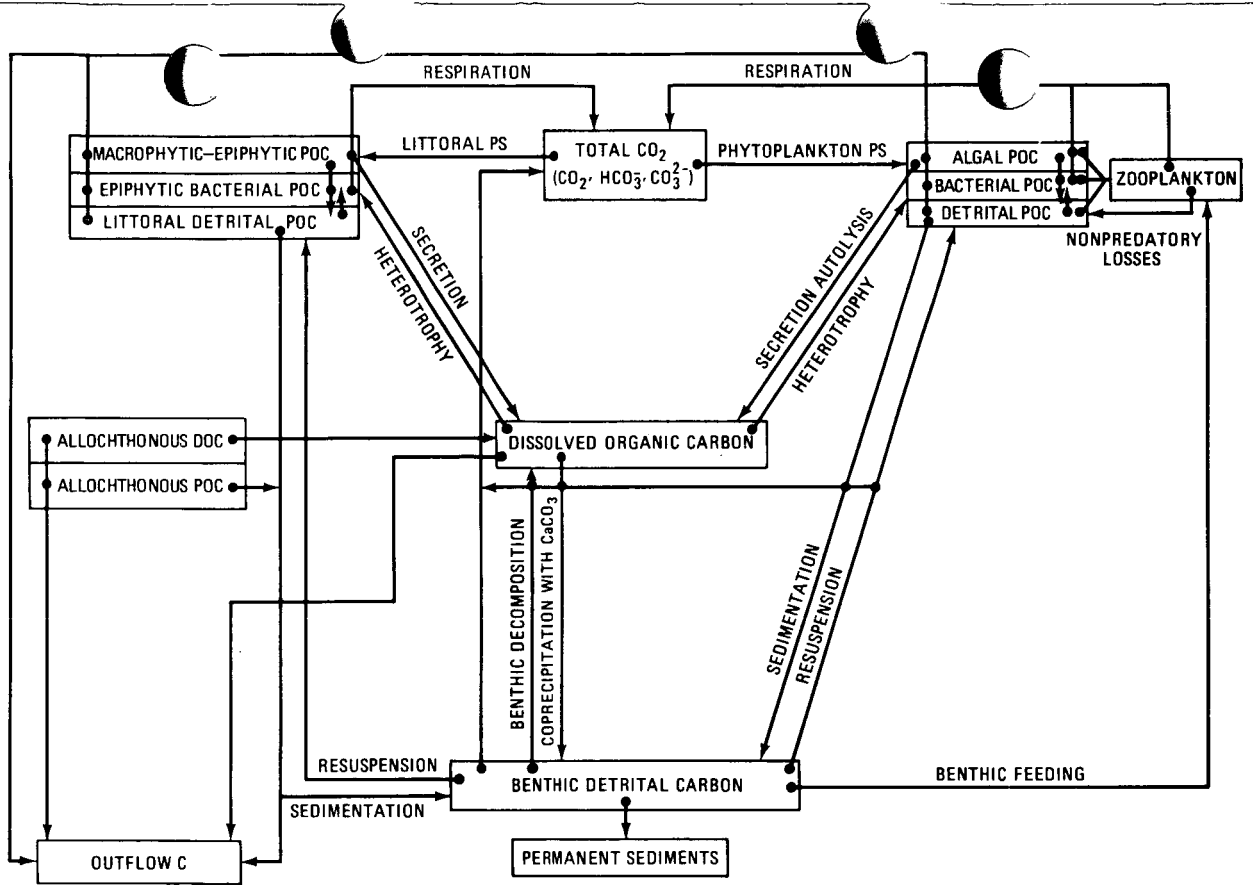

Fig. 7 A diagrammatic model for carbon in a hard-water lake. DOC is dissolved organic carbon; POC is particulate organic carbon; PS is photosynthesis. (From Wetzel and Rich, 1973.)

TABLE 9

ANNUAL ORGANIC CARBON FLUXES FOR LAWRENCE LAKE, MICHIGAN, AND MIRROR LAKE, NEW HAMPSHIRE*

	Lawrence Lake		Mirror Lake	
	g C m^{-2} $year^{-1}$	% of subtotal	g C m^{-2} $year^{-1}$	% of subtotal
Inputs				
Autochthonous (net)	193.0	88	54.0	75
Phytoplankton†	(52.6)	(24)	(47.0)	(65)
Periphyton	(41.9)	(19)	(1.3)	(2)
Macrophytes	(91.4)	(42)	(1.7)	(2)
Bacteria (chemosynthesis)	(7.1)	(3)	(4.0)	(6)
Allochthonous	25.1	12	17.9	25
Particulate	(4.1)	(2)	(6.6)	(9)
Dissolved	(21.0)	(10)	(11.3)	(16)
Subtotal	218.1	100	71.9	100
Outputs				
Respiration‡	159.7	74	54.0	75
Sedimentation	16.8	8	7.6	11
Outflow	38.6	18	10.2	14
Dissolved	(35.8)	(17)	(9.2)	(13)
Particulate	(2.8)	(1)	(1.0)	(1)
Subtotal	215.1	100	71.8	100

*Derived from the data of Wetzel et al. (1972) and Jordan and Likens (1975).
†^{14}C-method.
‡Does not include plant respiration.

respiration (loss of CO_2, including plant respiration) accounted for 83% of the total organic carbon inputs for both lakes, assuming that respiration was 40% of gross primary production. Benthic rather than planktonic respiration predominated in each case. Fisher and Likens (1973) found that about 34% of the annual organic carbon input for Bear Brook, New Hampshire, was lost as respiration. Unlike the lake ecosystem, which acts as a settling basin, the stream ecosystem exports 66% of the annual organic carbon input.

Nitrogen

Like that of carbon, the nitrogen cycle in freshwater ecosystems includes a complex assemblage of gaseous, dissolved inorganic and organic, and particulate-matter components. It is probably fair to state that the specific roles of phytoplankton and zooplankton species (particularly bacteria, fungi, and protozoa) in the cycling of nitrogen in freshwater ecosystems is not well known. With a few exceptions (e.g., Kuznetzof, 1968), our basic knowledge was extrapolated largely from an understanding of interactions in agricultural soils.

Inorganic nitrogen that has been incorporated into protoplasm by assimilation may be released to the water by leaching, excretion or exudation, autolysis, and decomposition. Organic nitrogenous compounds are decomposed to ammonia (ammonification), and the ammonia (ammonium in most aqueous solutions) is oxidized to nitrite and nitrate (nitrification). Apparently algae can assimilate either inorganic or organic forms of nitrogen. Although early studies suggested that nitrate was the major nitrogen source and there are species differences, ammonium now appears to be the major source for most freshwater plants (cf. Brezonik, 1973; Keeney, 1973). Assimilation rates may be quite rapid surface waters.

Isotopic (^{15}N) studies indicate that turnover rates for inorganic nitrogen are rapid, on the order of hours or days (Brezonik, 1973). Excretion of organic nitrogenous substances (e.g., amino acids) by phytoplankton and zooplankton, coupled with ammonification, provide an important mechanism facilitating the mineralization of nitrogen. In addition, direct autolysis of plant and animal cells may account for 30 to 50% of nitrogen mineralized (Brezonik, 1973).

Nitrification may be negligible in surface waters of lakes, possibly because the nitrifying bacteria are unable to compete with algae for ammonium (Brezonik, 1973). However, nitrification may be substantial in deeper waters and particularly in sediments (Keeney, 1973). Nitrification occurring in deeper waters that are anoxic may feed the denitrification process and thus contribute to a loss of "available" nitrogen from the functional cycle of the system. Little is known about the magnitude, seasonal variations, and relative importance of autotrophic and heterotrophic nitrification in freshwater ecosystems.

Phosphorus

Our understanding of phosphorus dynamics in freshwater ecosystems has had a major upsurge in the past 20 years, largely because of the work of F. H. Rigler and his students (Rigler, 1956; 1973; Chamberlain, 1968; Lean, 1973a; 1973b). Studies at Heart Lake, a small eutrophic lake in Ontario, illustrate some of the current ideas. Radioisotopes and Sephadex gel filtration were used to develop a four-compartment model to describe the transfer of biologically pertinent forms of phosphorus in the epilimnion of the lake during summer (Fig. 8). Relative compartment size and transfer rates were based on an assumed steady-state distribution 4.5 hr after inoculation and incubation with radioactive phosphorus. The particulate matter compartment was by far the largest, and the uptake of $^{32}PO_4$ by seston was rapid, some 50% appeared on filters within 2 min. Two other organic compartments were proposed: a so-called colloidal fraction, which had a molecular weight in excess of 5×10^6 and probably was composed of very fine nonliving particulate matter, and an XP fraction, which was anionic and very labile and had a molecular weight of about 250. Lean (1973a; 1973b) concluded that the XP compound was excreted by organisms, then rapidly combined with colloidal substances in lake water, and in the process

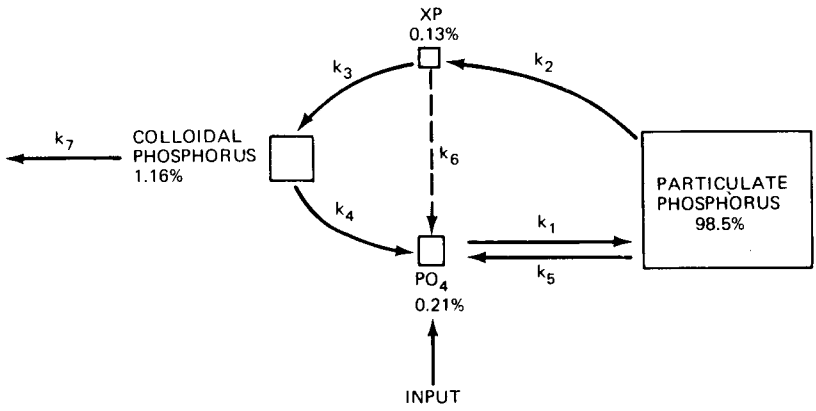

Fig. 8 A model for phosphorus distribution and transfer in the epilimnion of a lake during summer. Rate constants for this model were: K_1 (uptake of PO_4) = 0.9 min^{-1}; K_2 (release of XP) and K_3 (binding of XP to colloidal P) = 0.022 min^{-1}; K_4 (hydrolysis of colloidal P to PO_4) = 0.0017 min^{-1}; K_5 (release of PO_4 by seston); K_6 (direct hydrolysis of XP to PO_4); and K_7 (colloidal P becomes biologically unavailable). [From D. R. S. Lean, Movements of Phosphorus Between Its Biologically Important Forms in Lake Water, *Journal of Fisheries Research Board of Canada*, 30(10): 1525-1536 (1973).]

released inorganic phosphate from the colloid. The model suggested that colloidal phosphorus was not generated directly by the seston. This latter point certainly would be worthy of additional study.

Although Lean's model is enlightening, it is too early to apply it in describing the overall phosphorus dynamics of lake ecosystems. His short-term experiments must first be related quantitatively to the phosphorus fluxes for the ecosystem.

It is significant to note that the standing stock of PO_4–P predicted by Lean's model is exceedingly small (0.21%) but is rapidly cycled. The total phosphorus content in Heart Lake during the period of study was 44 μg/liter; thus, on the basis of this model, the lake water would contain only 0.0 μg PO_4–P/liter (Lean, 1973a; 1973b). We have known for some time that inorganic phosphorus is rapidly cycled in aquatic ecosystems (e.g., Pomeroy, 1960; Whittaker, 1961). Such rapid cycling, coupled with the small standing stock of inorganic phosphorus, suggests that measurements of ambient concentrations of inorganic phosphorus in lake water are of little diagnostic value for predicting trophic status or metabolic potential for a lake. Regulatory and management agencies are currently making such measurements, however, at great effort and expense.

The methodological problems of measuring phosphorus in its various forms and the associated difficulties of making ecological interpretations from these data are legion. For many freshwater ecosystems phosphorus is undoubtedly a prime nutrient in controlling eutrophication (Schindler, 1974). Phosphorus exists as dissolved and particulate matter and in organic and inorganic forms, all of which are measured and reported in varying degrees of ambiguity in the literature. Previously Rigler (1964; 1966; 1968) suggested that the actual inorganic phosphorus content of lakes may be extremely low and may be grossly overestimated by the commonly used molybdenum blue method. Molybdate-reactive phosphorus may not equal inorganic PO_4 because: (1) Filtration during sample preparation may rupture cells, releasing PO_4—P or organic phosphorus. (2) Acid used in the analytical procedure may hydrolyze organic phosphorus to PO_4—P. (3) There may be colorimetric interferences. Considering these difficulties and his results, Rigler (1973) stated that "the concentration of (PO_4—P) is assumed to be as yet unmeasurable in the trophogenic zone of most lakes" (p. 541). Lean's data (1973a; 1973b) seem to support this conclusion although there are relatively few data from divergent lake types (e.g., nutrient poor vs. nutrient rich). Overriding all this confusion is the important unanswered question, Which of the various forms of phosphorus, as measured by any of the analytical procedures, is biologically (readily) available to phytoplankton, periphyton, macrophytes, bacteria, and fungi? For example, what proportion of the total molybdate response is attributable to the organic colloidal fraction (the proportion may vary with concentration of total phosphorus), and is the colloidal fraction biologically available?

Rigler (1973) believes that at least three biological mechanisms facilitate internal cycling by returning particulate phosphorus to dissolved inorganic phosphorus: (1) direct release by ultraplankton, (2) excretion by zooplankton, and (3) enzymatic hydrolysis of organic compounds containing phosphorus. The literature does not allow an adequate comparison of these mechanisms, and again these data are quite ambiguous. Rigler (1973) estimated that the release from ultraplankton and zooplankton may be of about equal importance; a tentative rate constant of 0.019 hr^{-1} for loss of phosphorus from ultraplankton has been suggested. Excretion of phosphorus from zooplankton depends on temperature, body size, feeding rate, and probably other environmental factors. Data on excretion by zooplankton are highly variable and are difficult to compare (e.g., Rigler, 1961; 1973; Barlow and Bishop, 1965; Hargrave and Geen, 1968; Peters, 1972; Peters and Lean, 1973). I certainly cannot improve on this situation (much of the problem could have been alleviated if the details of experimental techniques and results had been more clearly presented in the literature). I would suggest that a tentative median value for zooplankton excretion might be around 200 μg P (g dry weight)$^{-1}$ hr^{-1}. Goltèrman (1973) believes that phosphorus is rapidly liberated from dying cells in the epilimnion by autolysis. His results showed that 50% of the particulate phosphorus was mineralized by enzyme hydrolysis within a few hours.

Rigler (1973) calculated an epilimnetic turnover time of 20 to 45 days for phosphorus in three lakes (Table 10). The theoretical residence time for a total lake ecosystem is of some interest here. Peterson (1974) estimated that the water in Cayuga Lake contains approximately 171 tonnes of total phosphorus. The average weighted concentration would be 18.2 μg P/liter. Since runoff and precipitation input of total phosphorus in 1970–1971 was 170 tonnes/year (Table 7), theoretically the total phosphorus in the lake water could be renewed from these sources each year. It is probably significant that the mean residence time for phosphorus in six other lake ecosystems averaged 1.1 years (0.3 to 2.0 years) although the water residence time averaged 7.1 years and ranged from 0 to 25 years (Megard, 1971; Sonzogni and Lee, 1974). The theoretical renewal time for water in Cayuga Lake during 1970–1971 was 5.1 to 5.6 years; however, the weighted average concentration in runoff was 101 μg P/liter, which is 5.5-fold greater than the average lake concentration (Likens, 1974). Such values for renewal or flushing time for Cayuga Lake (and most other lakes) are only theoretical for several reasons: (1) They are based on the total volume of the lake, as though mixing were complete and continuous (obviously renewal time for the hypolimnion would be slow relative to the epilimnion during the thermally stratified period). (2) They ignore current patterns in the lake, of which little is known. (3) They are based on an annual period, which obscures seasonal variation in hydrology and chemistry. (4) They include a major input from the Seneca River, which enters this long, narrow lake just above the outlet. (5) They are generally limited by the quality of data relative to inputs, outputs, and lake volume.

Sedimentation

Nutrients added to a lake are largely utilized by organisms, incorporated into the biomass, and ultimately sedimented as organic or inorganic materials. Thus lake sediments may serve as important sinks for nutrients moving within a landscape. Budget and loading data from several North American and European lakes (reviewed by Vollenweider, 1968; Mackenthun, 1973; Wright, 1974) indicated that some 20 to 93% of the annual total phosphorus input and 12 to 90% of the inorganic nitrogen input (gaseous exchange not considered) are retained within the lake. A majority of these lakes retained more than 50% of the nitrogen and phosphorus that was input annually. In Rawson Lake, a small nutrient-poor lake in the Canadian Shield, significant amounts of the phosphorus, nitrogen, carbon, and sulfur annual inputs were retained within the lake (Table 6). The amount of nitrogen and phosphorus retained varied from 51 to 72%, and from 67 to 79%, respectively, during the 4-year study. For Cayuga Lake, New York, some 86% of the nitrate, 74% of the molybdate-reactive phosphate, and 64% of the total phosphorus input were retained or possibly, in the case of nitrogen, were lost to the atmosphere. In contrast, the annual input of potassium exceeded the output during two of the years, and output

TABLE 10

CALCULATED RATE CONSTANTS FOR DAILY TRANSPORT OF PHOSPHORUS FROM THE EPILIMNION IN THREE LAKES*

Lake	Area, ha	Estimated rank order of littoral vegetation	Phosphorus turnover time,† day	Rate constants, day^{-1}		
				Total loss	To littoral	To hypolimnion and sediments
Toussaint	4.7	1	20	0.05	0.01	0.04
Upper Bass	5.8	2	27	0.04		
Linsley Pond	9.4	3	45	0.02	0.02	0

*From F. H. Rigler, a Dynamic View of the Phosphorus Cycle in Lakes, in *Environmental Phosphorus Handbook*, E. J. Griffith, A. M. Beeton, J. M. Spencer, and D. T. Mitchell (Eds.), p. 564, John Wiley & Sons, Inc., New York, 1973.

†One divided by rate constant for total loss.

exceeded input in the other two years in Rawson Lake. Annual input and output of potassium were nearly balanced in Cayuga Lake (Table 6).

The rate of nutrient loss or sedimentation from the pelagic region depends on a variety of environmental factors, including pH, temperature, redox potential, concentration of nutrient, chelating agents, organic matter, etc., and there are few empirical data (e.g., Hutchinson and Bowen, 1950). Rigler (1973) calculated rate constants for phosphorus loss from the epilimnion of three small lakes (Table 10). The daily loss to the hypolimnion and sediments, mostly through sinking of organic particulate matter, was 2% in Linsley Pond and 1% in Toussaint Lake. Rigler reported that Bosch obtained daily values of 1.4 to 2.5 for total phosphorus loss from the trophogenic zone of Horew Bay, Lake Lucerne, using sediment traps. However, Golterman (1973) doubted these results from Lake Lucerne for several reasons. In Toussaint Lake an additional 4% of the total phosphorus in the epilimnion was lost to the littoral region each day. Vollenweider (1968) calculated the mean rate of phosphorus exchange for the sediments of the eutrophic lake, Baldeggersee. Under anaerobic conditions the sediments released PO_4–P at a rate of 9 to 10 mg m^{-2} day^{-1}, but under aerobic conditions sediments took up PO_4–P at a mean rate of 9 mg m^{-2} day^{-1}. He pointed out that these rates may equal or exceed the loading from external sources.

Sedimentation is unquestionably of critical importance to nutrient cycling and metabolism in lakes. Careful and imaginative studies under a variety of natural conditions would undoubtedly reveal much about the mechanisms that regulate the availability of nutrients in aquatic ecosystems.

CONCLUDING REMARKS

The flux of nutrients and other materials across ecosystem boundaries is facilitated by movement of air, water, and animals. Although relatively few studies have been done to quantify these fluxes, it is obvious that ecosystems depend on and respond to such inputs and outputs of water, nutrients, and toxic materials.

Direct nutrient inputs in rain and snow are important to the biogeochemistry of aquatic ecosystems. This may be the dominant source of nutrients when a lake is nutrient poor or when its drainage basin is undisturbed, or both. More study is needed to evaluate the ecological effects of recent increases in concentration of nutrients and toxic materials (e.g., acids, heavy metals, and pesticides) in precipitation. Knowledge of gaseous exchanges across the air–water interface is very meager. Total input–output budgets for carbon, nitrogen, sulfur, etc., must await a careful evaluation of these fluxes.

The total influx of nutrients in water draining into aquatic ecosystems depends on the volume of discharge and the nutrient concentration. The ecological implications of adding nutrients to aquatic ecosystems in intermittent

large concentrations and in small volumes as opposed to adding the same total input in continuously smaller concentrations but in larger volumes and over long periods is not well known. This has important ramifications for the management of point and nonpoint sources of nutrients and pollutants.

Some careful comparisons between measured and calculated geologic inputs for a lake ecosystem are necessary to see if the added cost in time and money involved in quantitative measurements are required. Since the hydrologic measurements are so important, possibly a temporary compromise would be to concentrate measurements on these parameters.

Material-balance studies in stream ecosystems should be done. The relative flux and utilization of carbon, nitrogen, and phosphorus could be very informative relative to the overall function and the so-called assimilative capacity of the stream ecosystem.

Functional loading of nutrients will depend on yield per unit area and total area of the drainage basin, as well as on the volume and residence time of water in a lake. Disturbance within the terrestrial watershed may dramatically change the concentration or volume, or both, of runoff to a lake. Little is known about the ecological effects on aquatic ecosystems of changes in nutrient ratios in runoff inputs. This could be a fruitful area of inquiry.

Useful predictive models have been developed to relate the loading of the critical nutrients nitrogen and particularly phosphorus to chlorophyll-a concentrations, standing crop of phytoplankton, and transparency in lakes (e.g., Vollenweider, 1968; Dillon, 1974a; 1974b; 1975; Bachmann and Jones, 1974). These empirical relationships undoubtedly will serve as bases for management and further study as the models are elaborated.

Chemical speciation and form must be carefully evaluated in future studies of nutrient flux and cycling. For example, which of the phosphorus fractions is measured by the molybdate test? Is molybdate-reactive phosphorus a more useful measurement in eutrophic waters? Which of the dissolved phosphorus fractions are available to algae and macrophytes?

Much effort is needed to elucidate the complex internal-cycling parameters in aquatic ecosystems. To gain maximum understanding, however, these studies should not be done in isolation of nutrient fluxes for whole ecosystems. Rather, real progress in our understanding of aquatic ecosystems will depend, in my opinion, on our ability to relate and integrate nutrient-flux and cycling parameters. For example, knowledge of internal nutrient-turnover rates is critical to understanding nutrient availability in lakes, but these rates must be dynamic, i.e., linked to the continuous flux of ecosystem inputs and outputs.

Turnover rates for seston vary from minutes for phosphorus to hours and days for nitrogen and hours and weeks for carbon. In contrast, nutrient residence times for total aquatic ecosystems usually range from weeks to years, depending on rates of sedimentation, mixing, and throughput. Integrating these variables should lead to new levels of sophistication in diagnosing and managing aquatic ecosystems.

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REFERENCES

Bachmann, R. W., and J. R. Jones, 1974, Phosphorus Inputs and Algal Blooms in Lakes, *Iowa State J. Res.*, 49(2): 155-160.

Ball, R. C., and F. F. Hooper, 1961, Translocation of Phosphorus in a Trout Stre Ecosystem, in *Radioecology*, V. Schultz and A. W. Klement, Jr. (Eds.), pp. 217-238, Reinhold Publishing Corporation, New York.

Barlow, J. B., and J. W. Bishop, 1965, Phosphate Regeneration by Zooplankton in Cayuga Lake, *Limnol. Oceanogr., Suppl.*, **10**: R15-R24.

Bormann, F. H., and G. E. Likens, 1967, Nutrient Cycling, *Science*, **155**(3761): 424-429.

Brezonik, P. L., 1973, Nitrogen Sources and Cycling in Natural Waters, Report EPA-660/3-73-002, U. S. Environmental Protection Agency, Washington, D. C.

——, and C. L. Harper, 1969, Nitrogen Fixation in Some Anoxic Lacustrine Environments, *Science*, **164**: 1277-1279.

——, and G. F. Lee, 1968, Denitrification as a Nitrogen Sink in Lake Mendota, Wisconsin, *Environ. Sci. Technol.*, **2**: 120-125.

——, and E. E. Shannon, 1971, Trophic State of Lakes in North Central Florida, Publication No. 13, University of Florida, Water Resources Research Center, Gainesville.

——, W. H. Morgan, E. E. Shannon, and H. D. Putnam, 1969, Eutrophication Factors in North Central Florida Lakes, 23(8): 1-101, Florida Engineering and Industrial Experiment Station, Gainesville.

Carroll, D., 1962, Rainwater as a Chemical Agent of Geologic Processes: A Review, Water-Supply Paper 1535-G, U. S. Geological Survey.

Chamberlain, W. M., 1968, A Preliminary Investigation of the Nature and Importance of Soluble Organic Phosphorus in the Phosphorus Cycle of Lakes, Ph. D. Thesis, University of Toronto.

Chapin, J. D., and P. D. Uttormark, 1973, *Atmospheric Contributions of Nitrogen and Phosphorus*, Technical Report 73-2, The University of Wisconsin Water Resources Center, Madison.

Collison, R. C., and J. E. Mensching, 1932, *Lysimeter Investigations.* II. *Composition of Rainwater at Geneva, N. Y., for a 10-Year Period*, Technical Bulletin No. 193, New York Experiment Station, Geneva.

Davis, J. J., and R. F. Foster, 1958, Bioaccumulation of Radioisotopes Through Aquatic Food Chains, *Ecology*, **39**: 530-535.

Dillon, P. J., 1975, The Phosphorus Budget of Cameron Lake, Ontario: The Importance Flushing Rate to the Degree of Eutrophy of Lakes, *Limnol. Oceanogr.*, **20**(1): 28-39.

——, 1974a, The Prediction of Phosphorus and Chlorophyll Concentrations in Lakes, Ph. D. Thesis, University of Toronto.

——, 1974b, *A Manual for Calculating the Capacity of a Lake for Development*, Limnology and Toxicity Section, Water Resources Branch, Ministry of the Environment, Rexdale, Ontario.

——, and W. B. Kirchner, 1975, The Effects of Geology and Land Use on the Export of Phosphorus from Watersheds, *Water Res.*, **9**: 135-148.

——, and F. H. Rigler, 1974, The Phosphorus–Chlorophyll Relationship in Lakes, *Limnol. Oceanogr.*, **19**:(5): 767-773.

Elder, F. C., 1974, Canada Center Inland Waters, personal communication.

Elwood, J. W., and D. J. Nelson, 1972, Measurement of Periphyton Production and Grazing Rates in a Stream Using ^{32}P Material Balance Method, *Oikos* **23**: 295-303.

Emerson, S., W. Broecker, and D. W. Schindler, 1973, Gas-Exchange Rates in a Small Lake as Determined by the Radon Method, *J. Fish. Res. Board Can.*, **30**(10): 1475-1484.

Emery, R. M., C. E. Moon, and E. B. Welch, 1973, Enriching Effects of Urban Runoff on the Productivity of a Mesotrophic Lake, *Water Res.*, **7**: 1505-1516.

Fish, G. R., 1969, Lakes: The Value of Recent Research to Measure Eutrophication and to Indicate Possible Causes, *J. Hydrol. (N.Z.)*, **8**(2): 77-85.

Fisher, S. G., and G. E. Likens, 1973, Energy Flow in Bear Brook, New Hampshire: An Integrative Approach to Stream Ecosystem Metabolism, *Ecol. Monogr.*, **43**(4): 421-439.

driksen, R. L., 1972, Nutrient Budget of a Douglas-Fir Forest on an Experimental Watershed in Western Oregon, in *Research on Coniferous Forest Ecosystems,* Proceedings of a Symposium held at Bellingham, Washington, J. F. Franklin, L. J. Dempster, and R. H. Waring (Eds.), pp. 115-131, Forest Service, U. S. Department of Agriculture, Pacific Northwest Forest and Range Experiment Station, Portland, Ore.

Gambell, A. W., and D. W. Fisher, 1966, Chemical Composition of Rainfall, Eastern North Carolina and Southeastern Virginia, Water-Supply Paper 1535-K, U. S. Geological Survey.

Golterman, H. L., 1973, Vertical Movement of Phosphate in Freshwater, in *Environmental Phosphorus Handbook,* E. J. Griffith, A. M. Beeton, J. M. Spencer, and D. T. Mitchell (Eds.), pp. 509-538, John Wiley & Sons, Inc., New York.

Gorham, E., 1961, Factors Influencing Supply of Major Ions to Inland Waters, with Special Reference to the Atmosphere, *Geol. Soc. Amer., Bull.*, **72**: 795-840.

——, 1958, The Influence and Importance of Daily Weather Conditions in the Supply of Chloride, Sulphate and Other Ions to Fresh Waters from Atmospheric Precipitation, *Phil. Trans. Roy. Soc. London, Series B,* **241**: 147-172.

Granhall, U., and A. Lundgren, 1971, Nitrogen Fixation in Lake Erken, *Limnol. Oceanogr.*, **16**(5): 711-720.

Hall, C. A. S., 1972, Migration and Metabolism in a Temperate Stream Ecosystem, *Ecology,* **53**(4): 585-604.

Hargrave, B. T., and G. H. Geen, 1968, Phosphorus Excretion by Zooplankton, *Limnol. Oceanogr.*, **13**: 332-342.

Hasler, A. D., 1947, Eutrophication of Lakes by Domestic Drainage, *Ecology,* **28**: 383-395.

Hetling, L. J., and R. M. Sykes, 1973, Sources of Nutrients in Canadarago Lake, *J. Water Pollut. Contr. Fed.*, **45**: 145-156.

Hobbie, J. E., and G. E. Likens, 1973, The Output of Phosphorus, Dissolved Organic Carbon and Fine Particulate Carbon from Hubbard Brook Watersheds, *Limnol. Oceanogr.*, **18**(5): 734-742.

Horne, A. J., and G. E. Fogg, 1970, Nitrogen Fixation in Some English Lakes, *Proc. Roy. Soc. (London), Ser. B,* **175**: 351-366.

——, and C. R. Goldman, 1972, Nitrogen Fixation in Clear Lake, California. I. Seasonal Variation and the Role of Heterocysts, *Limnol. Oceanogr.*, **17**(5): 678-692.

Hutchinson, G. E., and V. T. Bowen, 1950, Limnological Studies in Connecticut. IX. A Quantitative Radiochemical Study of the Phosphorus Cycle in Linsley Pond, *Ecology,* **31**: 194-203.

Jordan, M., and G. E. Likens, 1975, An Organic Carbon Budget for an Oligotrophic Lake in New Hampshire, U.S.A., *Verh. Int. Verein. Limnol.*, **19**, in press.

Junge, C. E., 1963, *Air Chemistry and Radioactivity,* Academic Press, Inc., New York.

Keeney, D. R., 1973, The Nitrogen Cycle in Sediment–Water Systems, *J. Environ. Qual.*, **2**(1): 15-29.

——, R. L. Chen, and D. A. Graetz, 1971, Importance of Denitrification and Nitrate Reduction in Sediments to the Nitrogen Budget of Lakes, *Nature*, **233**: 66-67.

Keirn, M. A., and P. L. Brezonik, 1971, Nitrogen Fixation by Bacteria in Lake Mize, Florida, and in Some Lacustrine Sediments, *Limnol. Oceanogr.*, **16**(5): 720-731.

Kerr, P. C., D. L. Brockway, D. F. Paris, and S. E. Craven, 1973, Carbon Cycle in Sediment–Water Systems, *J. Environ. Qual.*, **2**(1): 46-52.

Keup, L. E., 1968, Phosphorus in Flowing Waters, *Water Res.*, **2**: 373-386.

Kuznetzof, S. I., 1968, Recent Studies on the Role of Microorganisms in the Cycling of Substances in Lakes, *Limnol. Oceanogr.*, **13**(2): 211-224.

Lean, D. R. S., 1973a, Movements of Phosphorus Between Its Biologically Important Forms in Lake Water, *J. Fish. Res. Board Can.*, **30**(10): 1525-1536.

——, 1973b, Phosphorus Dynamics in Lake Water, *Science*, **179**: 678-680.

Leland, E. W., 1952, Nitrogen and Sulfur in the Precipitation at Ithaca, New York, *Agr[illegible] J.*, **44**(4): 172-175.

Likens, G. E., 1974, *Water and Nutrient Budgets for Cayuga Lake, New York*, Technical Report 82, Cornell University, Water Resources and Marine Sciences Center, Ithaca, N. Y.

——, 1972a, Eutrophication and Aquatic Ecosystems, in *Nutrients and Eutrophication*, G. E. Likens (Ed.), pp. 3-13, Special Symposium, Vol. 1, American Society of Limnology and Oceanography, Lawrence, Kans.

——, 1972b, *The Chemistry of Precipitation in the Central Finger Lakes Region*, Technical Report 50, Cornell University, Water Resources and Marine Sciences Center, Ithaca, N. Y.

——, and F. H. Bormann, 1975, An Experimental Approach to Nutrient–Hydrologic Interactions in New England Landscapes, in *Coupling of Land and Water Systems*, A. D. Hasler (Ed.), Ecological Studies 10, pp. 7-29, Springer–Verlag, Inc., New York.

——, and F. H. Bormann, 1974a, Acid Rain: A Serious Regional Environmental Problem, *Science*, **184**: 1176-1179.

——, and F. H. Bormann, 1974b, Linkages Between Terrestrial and Aquatic Ecosystems, *BioScience*, **24**(8): 447-456.

——, and F. H. Bormann, 1972, Nutrient Cycling in Ecosystems, in *Ecosystem Structure and Function*, J. Wiens (Ed.), pp. 25-67, Oregon State University Press, Corvallis.

——, F. H. Bormann, and N. M. Johnson, 1972, Acid Rain, *Environment*, **14**(2): 33-40.

——, F. H. Bormann, R. S. Pierce, and D. W. Fisher, 1971, Nutrient–Hydrologic Cycle Interaction in Small Forested Watershed-Ecosystems, in *Productivity of Forest Ecosystems*, P. Duvigneaud (Ed.), pp. 553-563, Proceedings of the Brussels Symposium, 1969, UNESCO Publications, Paris.

——, N. M. Johnson, R. S. Pierce, and F. H. Bormann, 1975, Water and Nutrient Budgets for Mirror Lake, New Hampshire, in prep.

Lodge, J. R., Jr., et al., 1968, Chemistry of United States Precipitation, Final Report on the National Precipitation Sampling Network, National Center for Atmospheric Research, Boulder, Colo.

Loehr, R. C., 1974, Characteristics and Comparative Magnitude of Non-Point Sources, *Water Pollut. Contr. Fed.*, **46**: 1849-1872.

MacIntire, W. H., and J. B. Young, 1923, Sulfur, Calcium, Magnesium and Potassium Content and Reaction of Rainfall at Different Points in Tennessee, *Soil Sci.*, **15**: 205-227.

Mackenthun, K. M., 1973, Eutrophication and Biological Associations, in *Environmental Phosphorus Handbook*, E. J. Griffith, A. M. Beeton, J. M. Spencer, and D. T. Mitchell (Eds.), pp. 613-632, John Wiley & Sons, Inc., New York.

Megard, R. O., 1971, Eutrophication and the Phosphorus Balance of Lakes, Presented at the 1971 Winter Meeting, American Society of Agricultural Engineers, Chicago, Ill., pp. 1-24 (cited by Sonzogni and Lee, 1974).

Nelson, D. J., N. R. Kevern, J. L. Wilhm, and N. A. Griffith, 1969, Estimates of Periphyton Mass and Stream Bottom Area Using ^{32}P, *Water Res.*, **3**: 367-373.

Oglesby, R., 1974, Department of Natural Resources, Cornell University, personal communication.

Pearson, F. J., Jr., and D. W. Fisher, 1971, Chemical Composition of Atmospheric Precipitation in the Northeastern United States, Water-Supply Paper 1535-P, U. S. Geological Survey.

Peters, R. H., 1972, Phosphorus Regeneration by Zooplankton, Ph. D. Thesis, University of Toronto.

——, and D. Lean, 1973, The Characterization of Soluble Phosphorus Released by Limnetic Zooplankton, *Limnol. Oceanogr.*, **18**(2): 270-279.

erson, B., 1974, Section of Ecology and Systematics, Cornell University, personal communication.

Pomeroy, L. R., 1960, Residence Time of Dissolved Phosphate in Natural Waters, *Science*, **131**: 1731-1732.

Rigler, F. H., 1973, A Dynamic View of the Phosphorus Cycle in Lakes, in *Environmental Phosphorus Handbook*, E. J. Griffith, A. M. Beeton, J. M. Spencer, and D. T. Mitchell (Eds.), pp. 539-572, John Wiley & Sons, Inc., New York.

——, 1968, Further Observations Inconsistent with the Hypothesis That the Molybdenum Blue Method Measures Orthophosphate in Lakewater, *Limnol. Oceanogr.*, **13**: 7-13.

——, 1966, Radiobiological Analysis of Inorganic Phosphorus in Lakewater, *Verh. Int. Verein. Limnol.*, **16**: 465-470.

——, 1964, The Phosphorus Fractions and Turnover Time of Phosphorus in Different Types of Lakes, *Limnol. Oceanogr.*, **9**: 511-518.

——, 1961, The Uptake and Release of Inorganic Phosphorus by *Daphnia magna* Straus, *Limnol. Oceanogr.*, **6**: 165-174.

——, 1956, A Tracer Study of the Phosphorus Cycle in Lakewater, *Ecology*, **37**: 550-562.

Schindler, D. W., 1974, Eutrophication and Recovery in Experimental Lakes: Implications for Lake Management, *Science*, **184**: 897-899.

——, and J. E. Nighswander, 1970, Nutrient Supply and Primary Production in Clear Lake, Eastern Ontario, *J. Fish. Res. Board Can.*, **27**(11): 2009-2036.

——, G. J. Brunskill, S. Emerson, W. S. Broecker, and T. H. Peng, 1972, Atmospheric Carbon Dioxide: Its Role in Maintaining Phytoplankton Standing Crops, *Science*, **177**: 1192-1194.

——, R. W. Newbury, J. A. Cherry, P. C. Campbell, and K. Beaty, 1975, Annual Chemical Regimes in the Rawson Lake (Lake 239) Watershed, Experimental Lakes Area, Freshwater Institute, Fisheries Research Board of Canada, (in press).

Sonzogni, W. C., and G. F. Lee, 1974, Diversion of Wastewaters from Madison Lakes, *J. Environ. Eng. Div., Amer. Soc. Civ. Eng.*, **100**: 153-170.

——, and G. F. Lee, 1972, *Nutrient Sources for Lake Mendota—1972*, Report of the Water Chemistry Program, University of Wisconsin, Madison.

ers, J. K., R. F. Harriss, and D. E. Armstrong, 1973, Phosphate Chemistry in Lake Sediments, *J. Environ. Qual.*, **2**(1): 1-14.

Sylvester, R. O., 1961, Nutrient Content of Drainage Water from Forested, Urban and Agricultural Areas, in *Algae and Metropolitan Wastes*, pp. 80-87, SEC TR, W61, U. S. Public Health Service, R. A. Taft Sanitary Engineering Center, Cincinnati, Ohio.

Torrey, M. L. S., 1972, Biological Nitrogen Fixation in Lake Mendota, Ph. D. Thesis, University of Wisconsin, Madison.

Vollenweider, R. A., 1968, *Scientific Fundamentals of the Eutrophication of Lakes and Flowing Waters, with Particular Reference to Nitrogen and Phosphorus as Factors in Eutrophication*, UN Organization for Economic and Cultural Development, DAS/CSI/68, **27**: 1-159.

——, 1963, Studi Sulla Situazione Attuale del Regime Chimico e Biologico del Lago di Orta, *Mem. Ist. Ital. Idrobiol., Dott. Marco de Marchi,* **16**: 21-125.

Weibel, S. R., 1969, Urban Drainage as a Factor in Eutrophication, in *Eutrophication: Causes, Consequences and Correctives,* pp. 383-403, Publication 1700, National Academy of Sciences–National Research Council, Washington, D. C.

Wetzel, R. G., and P. H. Rich, 1973, Carbon in Freshwater Systems, in *Carbon and the Biosphere,* G. M. Woodwell and E. V. Pecan (Eds.), USAEC Report 720510, pp. 241-263.

——, P. H. Rich, M. C. Miller, and H. L. Allen, 1972, Metabolism of Dissolved and Particulate Detrital Carbon in a Temperate Hard-Water Lake, *Mem. Ist. Ital. Idrobiol. Dott. Marco de Marchi,* **29**(Suppl.): 185-243.

Whitehead, H. C., and J. H. Feth, 1964, Chemical Composition of Rain, Dry Fallout, and Bulk Precipitation at Menlo Park, California, 1957-1959, *J. Geophys. Res.,* **69**(18): 3319-3333.

Whittaker, R. H., 1961, Experiments with Radiophosphorus Tracer in Aquarium Microcosms, *Ecol. Monogr.,* **31**: 157-188.

Wilson, B. D., 1926, Nitrogen and Sulfur in Rainwater in New York, *J. Amer. Soc. Agron.,* **18**: 1108-1112.

Wright, R. F., 1974, *Forest Fire: Impact on the Hydrology, Chemistry and Sediments of Small Lakes in Northeastern Minnesota,* Interim Report 10, University of Minnesota Limnological Research Center, Minneapolis.

THE SANTEE SWAMP AS A NUTRIENT SINK

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ABSTRACT

A water-quality survey was conducted in the Upper Santee Swamp in South Carolina during the winter and early spring of 1973. Among the parameters measured were (1) dissolved oxygen, (2) temperature, (3) pH, (4) turbidity, (5) reactive phosphate, (6) total phosphate, (7) nitrite, (8) nitrate, (9) ammonia, (10) heterotrophic bacteria, (11) total coliforms, and (12) fecal coliforms. The Wateree and Congaree rivers, whose dissected confluent floodplains make up the Santee Swamp, transported very heavy nutrient loads in the various forms of nitrogen and phosphorus and had high turbidity and oxygen levels. The primary source of flowing waters in the swamp during this period was overflow of the Wateree River. There was a significant reduction in nutrient concentrations (particularly phosphorus) and in bacterial counts (including fecal coliforms) with little or no oxygen depletion as the waters coursed through the swamp.

One of the most prominent features and least understood ecosystems of the southeast coastal plain is the river floodplain swamp. These forested wetlands, an integral part of the stream basin, are subject to extended periods of inundation when stream discharge exceeds bank capacity. The time of inundation (the hydroperiod) and the water depth over the floor of the floodplain are quite variable but generally occur with seasonal periodicity, the maximum depths and hydroperiods occurring during the late winter and early spring months. Penfound (1952) characterized two distinct swamp types according to the hydroperiod: (1) swamp forests, characterized by long hydroperiods (inundated throughout most of the growing season), a muck substratum, tree-type vegetation, and a general lack of shrubs; and (2) river floodplain swamps,

characterized by short hydroperiods, an alluvium substratum, and mixed tree- and shrub-type vegetation. The Santee Swamp, discussed in this paper, represents a combination of the two types.

The plant communities of these forested wetlands have been described in the studies of Lindsey et al. (1961), Monk (1966), Oosting (1942), Penfound (1952), and Sharitz, Irwin, and Christy (1974). These studies detail species composition, zonation, and succession patterns for the respective systems. There are few holistic studies of the faunal communities of these systems. Goff (1952) characterized the animal community of a floodplain in Illinois, and Gr (1973) described the composition of the invertebrate populations of the litter layer of the Upper Santee Swamp. Most references to swamp fauna are species lists and/or life-history studies.

Odum (1969) classified the river floodplain swamp as an ecosystem with a fluctuating water level and placed it in the same category as salt marshes and the Everglades. Several recent studies (Carter et al., 1973; Day et al., 1974; Reiners, 1972) have demonstrated net productivity values ranging between 990 and 1170 $g\ m^{-2}\ year^{-1}$ for these swamps. These values are comparable to those measured in the salt marshes (Teal, 1962) and tend to substantiate Odum's description of the two systems as comparable and as among the world's most productive. Except for these few studies, little or no data are available in the literature for other functional ecosystem processes.

River floodplains and their associated swamp drainages have generally been speculated to be nutrient sinks. This phenomenon has now been documented for various types of marshes. Valiela, Teal, and Van Raalte (1972) demonstrated such a phenomenon for tidal salt marshes; Grant and Patrick (1970), for tidal fresh water marshes; and Lee, Bently, and Amundson (1970), for riverine freshwater marshes in Wisconsin. If we speculate for the floodplain swamps, it follows that, when the nutrient- and silt-laden floodwaters periodically inundate these areas, the loss of water velocity and the enhanced exposure to the reactive surfaces of the soils and vegetation would result in deposition and assimilation of nutrients to the soils as sediments and to vegetation as biomass accumulations. Wharton (1970) cited water-quality surveys for two separate swamp streams (the Alcovey and Flint rivers in Georgia) which received wastes from domestic sewage. He found that there was a simultaneous decrease in both biochemical oxyg demand and fecal coliforms with an increase in dissolved oxygen concentrati in the waters of the two rivers. Documentation of the functional role of the floodplain swamp as a nutrient sink during periods of inundation has been neglected, however.

The prime objective of our study was to determine whether, as in the case of the marshes, a river floodplain swamp could demonstrate a capacity to act as a nutrient sink, e.g., to decrease nutrient concentrations in the flood waters flowing through it.

STUDY AREA

The Upper Santee Swamp, Sumter County, S. C., is located approximately 40 miles south of Columbia and extends from the confluence of the Congaree and Wateree rivers along the east side of the Santee River south to the backwater areas of Lake Marion, approximately 8 miles downstream of the confluence (Fig. 1). In the past 30 years the swamp has been subjected to significant modifications resulting from the construction of an impoundment on the Santee River (Lake Marion) known as the Santee–Cooper Hydroelectric Project. The area was partially logged, beginning in 1939 and continuing until 1941 when the rising waters of the impoundment halted the logging operation. The effect of the impoundment has been to increase the hydroperiod throughout the floodplain and to increase significantly permanent inundation in certain areas, to the extent that the Santee is essentially a flow-through swamp throughout the year.

The Santee Swamp, with its extended hydroperiod, its flow-through nature, and a history of heavy nutrient loads in its source rivers, provides an excellent site in which to investigate the nutrient-sink phenomenon. Historically, according to state water-quality surveys, the Congaree and Wateree rivers bear heavy nutrient loads from sewage discharges from the city of Columbia (16,000,000 gallons per day) into the Congaree and from heavy influxes from agricultural runoff into the Wateree. According to the surveys of the South Carolina Department of Health and Environmental Control, however, Lake Marion, which is approximately 5 miles downstream of the confluence of the two rivers, generally has not shown the eutrophication symptoms typical of shallow impoundments receiving comparable nutrient loads.

Physiographically the area can be divided into four habitat types: (1) the riparian province, consisting of current river channels, assorted crossbraided sloughs, guts, creeks, and oxbow lakes; (2) the oak island province, an area of higher elevation which is only periodically inundated; (3) areas of lower elevation more or less permanently inundated with flowing waters; and (4) the backwater reaches of upper Lake Marion (Fig. 1).

METHODOLOGY

Water samples from 26 stations were collected bimonthly from January 1973 through April 1973. Sampling stations were selected so that the study area was divided into four transects roughly approximating the breaks between physiographic regions (Fig. 1). All samples were collected at a depth of 1 ft below the surface in acid-rinsed or sterile glass bottles for microbiological determination, stored on ice in transit to the laboratory, and processed within 6 hr after collection.

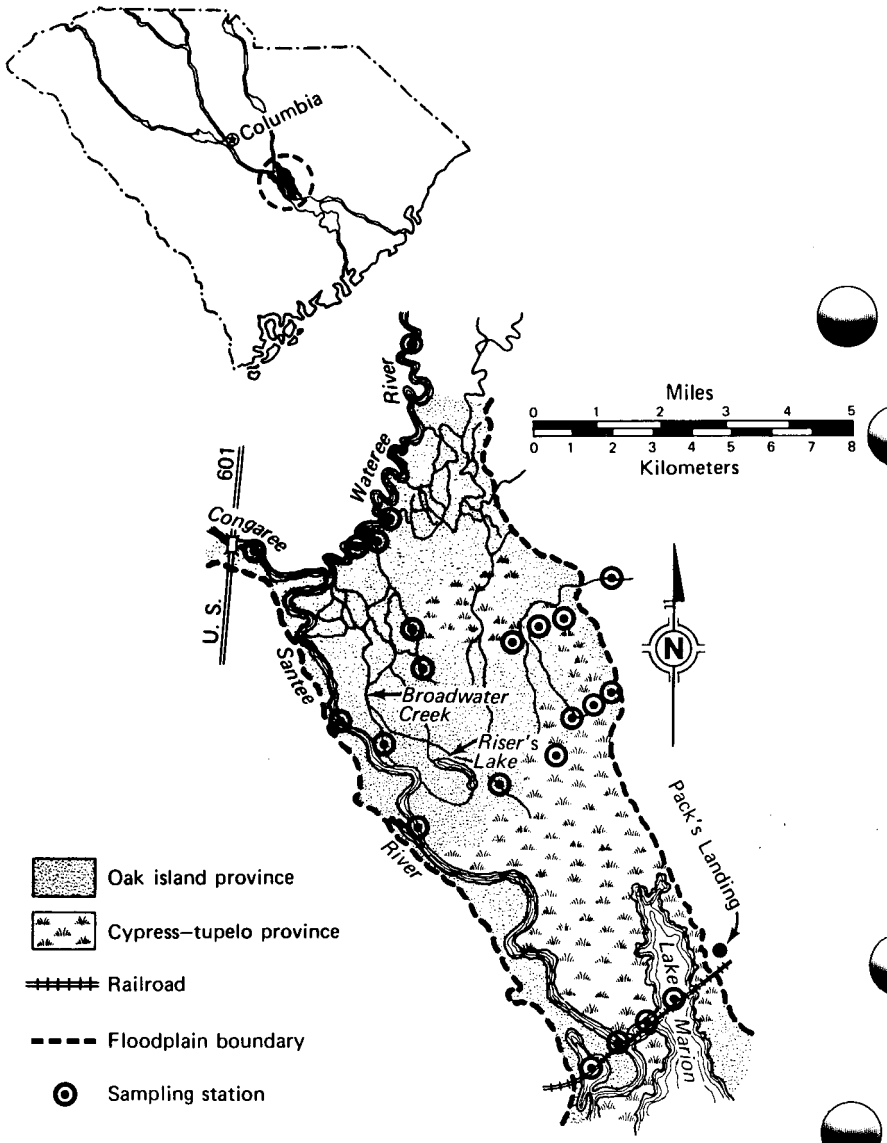

Fig. 1 Map of the Upper Santee Swamp showing sampling stations.

The following physical measurements were made:

1. Water temperatures were recorded at the time of sample collection at each of the stations.

2. Dissolved oxygen concentrations were determined by the standard Winkler method for samples taken at each station.

3. The pH of the samples was determined immediately after arrival at the laboratory.

4. Turbidity was determined by turbidiometer.

The following chemical determinations were made on samples filtered through prewashed and ignited glass-fiber filters (except for total phosphate, which was determined on unfiltered samples):

1. Reactive phosphate–phosphorus, dissolved organic phosphorus, and total phosphorus were analyzed by the technique of Murphy and Riley (1962).

2. Nitrate– and nitrite–nitrogen were analyzed according to the techniques of Strickland and Parsons (1968).

3. Ammonia–nitrogen was analyzed according to Solorzano (1969).

The following biological determinations were made:

1. Total bacterial populations were estimated by standard plate counts (USPHS) as recommended in Standard Methods (American Public Health Association et al., 1971).

2. Total coliform populations were determined by the most probable number (MPN) technique as outlined in Standard Methods.

3. Fecal coliform populations were determined by the MPN technique as outlined in Standard Methods.

RESULTS

Physical Measurements

Flow Patterns

The major flow patterns of water masses across the basin were traced by examination of isopleth plots of turbidity (Fig. 2). The normal flow pattern was indicated by the penetration of the turbid water from the rivers into the swamp basin, but reverse tongues of less-turbid lake water penetrating back into the swamp were obvious when the lake pool level was abnormally high.

Data for the first sampling date, Jan. 27, 1973, are missing. On the second sampling date, Feb. 16, the water level in the lake was abnormally high. This was caused in part by the melt runoff of a severe snow storm (100-year storm) which dropped 22 in. of snow in the immediate vicinity and lesser amounts over the entire watershed one week before the sampling date. The lake level was raised to prevent downstream flooding, and the less-turbid lake water intruded back into the swamp (Fig. 2). Turbidity ranged from 80 Jackson turbidity units (JTU) at the upper reaches in the vicinity of the river confluence to 30 JTU at the normal pool level in the vicinity of the railroad trestle. Discharge, as calculated at the U. S. Geological Survey (USGS) provisional discharge station immediately below the confluence of the two rivers, was 40,500 cfs.

Flow patterns on the third sampling date, Mar. 3, were more indicative of the pattern observed for the remainder of the study (Fig. 2). On this particular

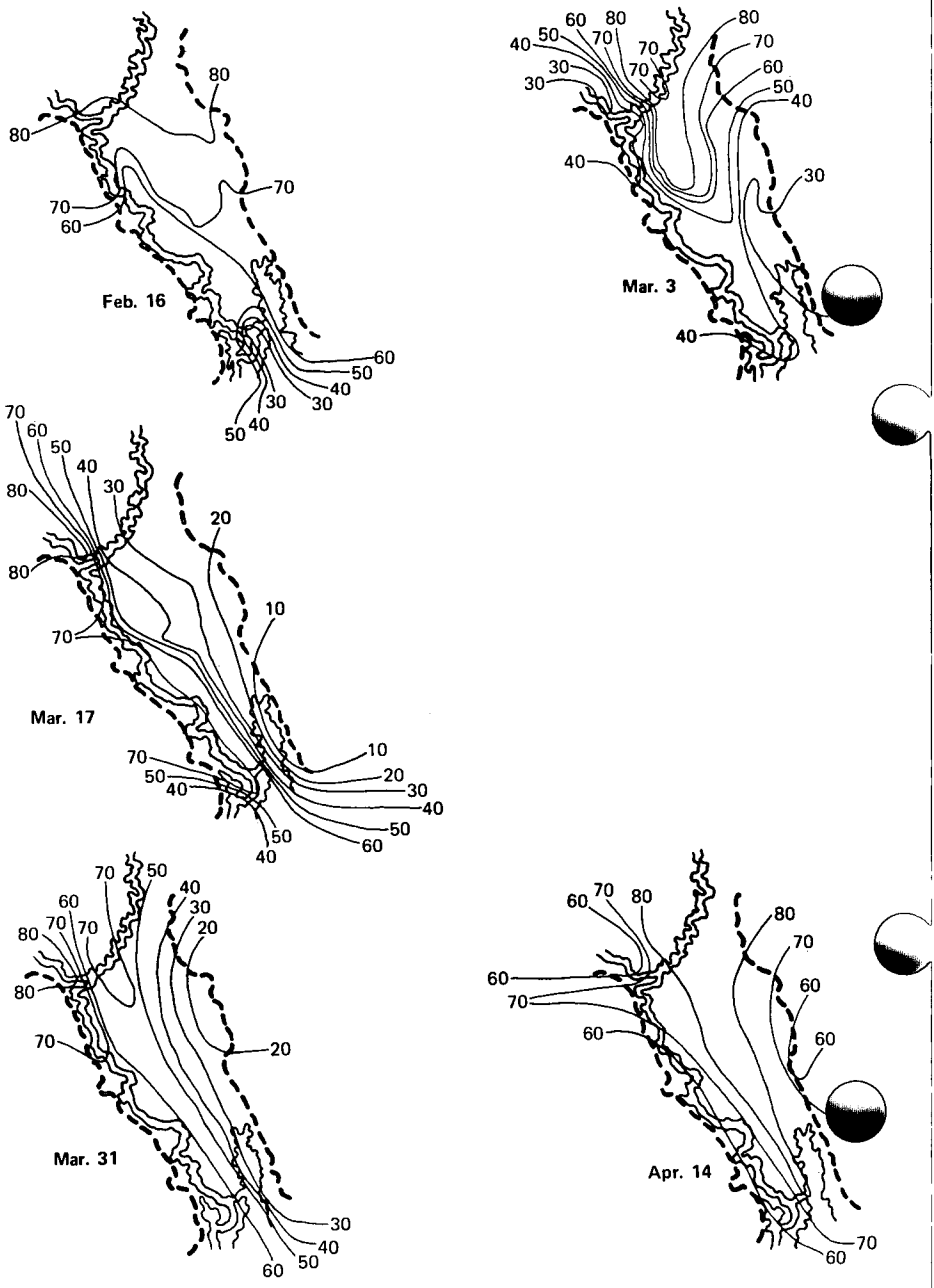

Fig. 2 Turbidity distribution pattern; values are in Jackson turbidity units.

day, the Wateree River was extremely turbid (~90 JTU), and the Congaree was somewhat less turbid (~30 JTU). From the isopleth plots it was evident that the water from the Wateree was spilling over into the upper reaches of the swamp, flowing in a general north–northeast to south–southeast direction across the basin to a point just south of the oak island province, where the flow pattern became somewhat less obvious. In the oak island province, the turbidity dropped rapidly from 80 to 40 JTU, which is comparable with the level noted in the backwater province in the vicinity of the railroad crossing. The waters of the Congaree flowed into the Santee River channel and were generally confined to the channel with no lateral intrusion into the swamp. Turbidity levels were virtually unchanged from the confluence to the backwater province. Provisional discharge of the Santee at the USGS station was 16,600 cfs.

On the fourth sampling date, Mar. 17 (Fig. 2), the Congaree was more turbid (~80 JTU) than the Wateree (~30 JTU). The pattern of flow was not as obvious as on the previous sampling date. It appeared that the Wateree was contributing the major flow into the swamp, with the water maintaining the same level of turbidity (30 JTU) from the point of entry, just above the confluence, to the backwater areas. Discharge in the Santee River was 31,700 cfs.

The turbidity and flow patterns for the next two sampling dates, Mar. 31 and Apr. 14, (Fig. 2) were similar to those described for the Mar. 3 sampling period. Santee discharge for the two dates was 34,000 and 51,900 cfs, respectively.

The pH

The pH values for the three rivers ranged from 6.6 to 7.1. The highest pH occurred when discharge was lowest. Values for the interior swamp stations generally ranged from 6.5 to 6.8. The variation in pH between stations was generally greater on the days of lowest discharge into the Santee River.

Temperature

Water temperature ranged from 6 to 9°C on Feb. 17, from 10.2 to 14°C on Mar. 3, from 16 to 19°C on Mar. 17, and from 14 to 16°C on Mar. 31. No data are available for Jan. 27 and Apr. 14.

olved Oxygen

On Jan. 27 oxygen concentrations for the three rivers ranged from 7.8 to 11.7 mg/liter and for all swamp stations from 7.4 to 11.6 mg/liter. On Feb. 17, concentrations for the rivers varied between 10.1 and 12.6 mg/liter and for the swamp from 6.9 and 9.9 mg/liter. On Mar. 3, river concentrations ranged from 9.2 to 10.2 mg/liter, and swamp concentrations ranged from 3.1 to 5.2 mg/liter. On Mar. 17, the range for river samples was from 5.2 to 8.3 mg/liter and for swamp samples from 4.6 to 6.9 mg/liter. The range of concentrations for river samples on Mar. 31 was 7.0 to 8.7 mg/liter and for swamp samples from 4.6 to

7.7 mg/liter. On the last sampling day, Apr. 14, the range for river stations was from 6.5 to 8.1 mg/liter, and swamp stations varied from 6.5 to 7.8 mg/liter.

Nutrient Analyses

Reactive Phosphate–Phosphorus

Data for all reactive phosphate concentrations are summarized in the isopleth plots for each sampling period (Fig. 3). Maximum values for phosphate–phosphorus concentrations for all sampling periods were observed in the Wateree River where concentrations ranged from 109 μg of phosphorus per liter of water on Mar. 17 to 393 μg P/liter on Jan. 27. Concentration values for the Congaree River ranged from 95 μg P/liter on Mar. 3 to 256 μg P/liter on Jan. 27. Concentrations in the Santee River closely reflected those observed in the Congaree. The isopleth plots show little or no variation in the phosphorus concentrations between the upstream stations on the Santee (in the vicinity of the confluence) and the downstream stations (in the vicinity of the transition zone between riparian and backwater provinces near the railroad trestle). This was in contrast to the patterns observed in the flow of water through the swamp. As noted in the discussion of turbidity, the primary source of flow into the upper swamp was spillover from the Wateree River. We see from the isopleth maps that this was also the primary source of phosphate–phosphorus to the swamp. The concentrations in the upper reaches closely reflected the concentrations noted for the Wateree River. There was a general reduction in the concentration of reactive phosphate as the water coursed over and through the oak island province. The greatest reduction was by an approximate factor of 2 on Jan. 27, and the least reduction, a factor of approximately 0.75, was noted on Mar. 17. Generally, after flowing through the swamp, water entering the backwater province carried significantly reduced concentrations, commonly from 75 to 100 μg P/liter.

Total Phosphorus

The distribution patterns of total phosphorus concentrations closely resembled those described for reactive phosphorus (Fig. 4). Concentrations in the Wateree River ranged from 875 μg P/liter on Mar. 3 to 300 μg P/liter on Mar. 31. Concentrations in the Congaree River ranged from 182 μg P/liter on Feb. 17 to 595 μg P/liter on Mar. 3. Values for the Santee River from the backwater provinces to the confluence of the Wateree and the Congaree generally showed consistent concentrations for each sampling period (Fig. 4). The patterns across the swamp basin were similar to those demonstrated by reactive phosphate–phosphorus concentrations. On Feb. 17, an abnormally high concentration was recorded (~500 μg P/liter) at one of the stations at the lower end of the oak island province. This was a localized "hot spot." Concentrations

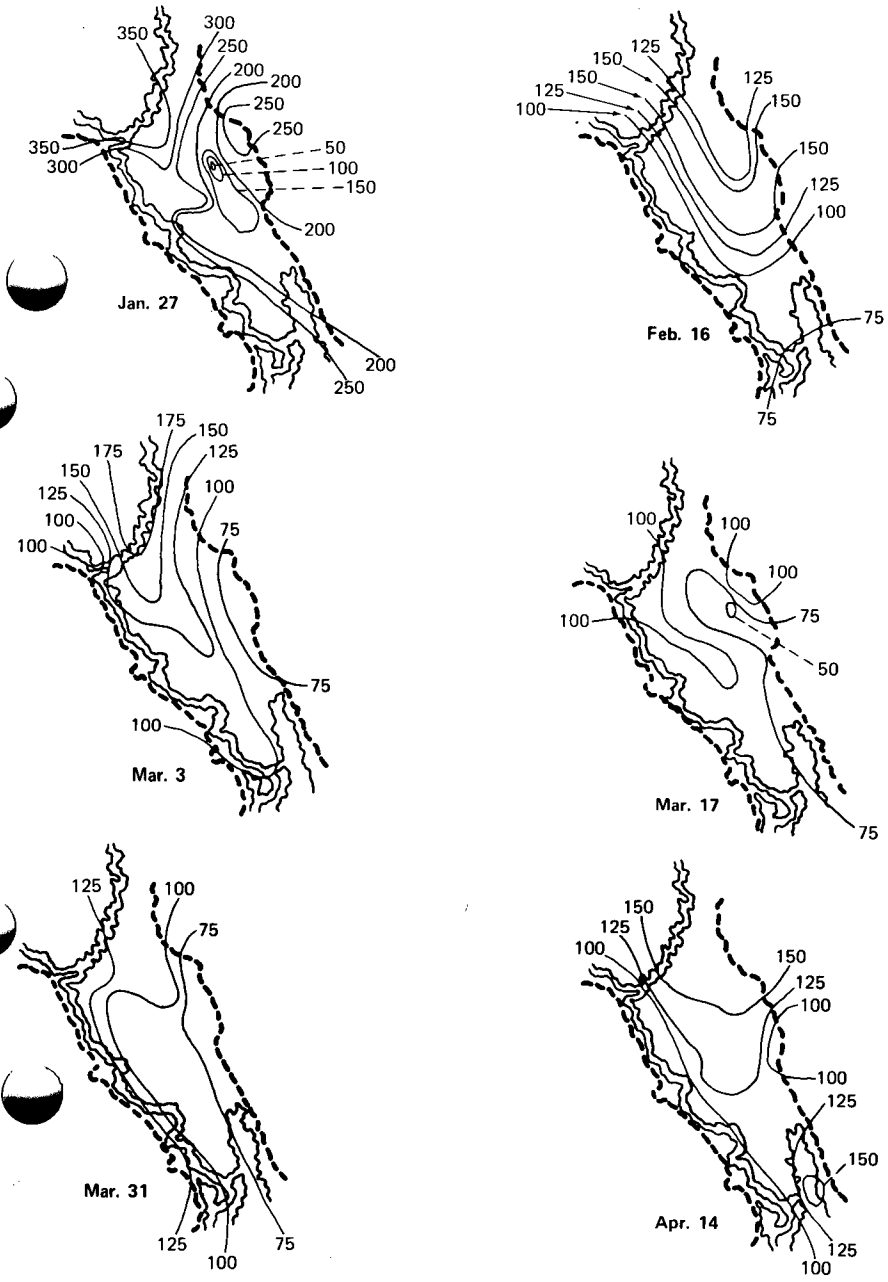

Fig. 3 Distribution patterns of reactive phosphate (PO_4—P) concentrations in micrograms of phosphorus per liter of water.

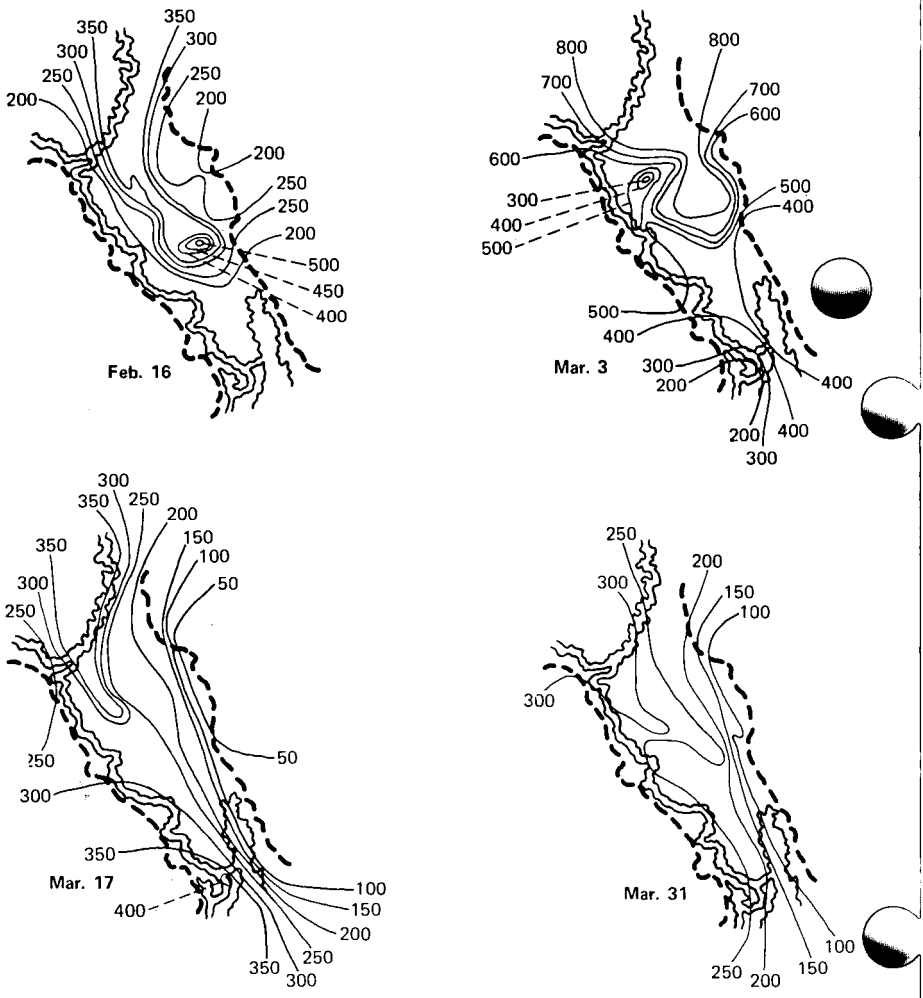

Fig. 4 Total phosphorus distribution patterns in micrograms of phosphorus per liter of water.

were 200 μg P/liter in the areas immediately surrounding this station, and was a general concentration reduction as the waters coursed through the swamp from the river source (the Wateree River primarily). The reductions were of the order of two- to threefold, the greatest reduction occurring in the week of Mar. 31 (from 300 μg P/liter at the source to 100 μg P/liter in the vicinity of the transition zone).

In summary, the general trend observed for the phosphates, both total and reactive, was a significant reduction in concentration as the water passed from the river source to the lower swamp provinces. These reductions were generally

of the order of 50%, depending on flow. Concentrations in the Congaree River were essentially unchanged in passage from the confluence to the backwater provinces of Lake Marion.

Ammonia–Nitrogen

Data for ammonia–nitrogen concentrations are summarized by isopleth plots for each sampling period in Fig. 5. Concentration values for the Wateree River (ranging from ~250 μg N/liter on Apr. 14 to ~250 μg N/liter on Jan. 27) were consistently higher than the concentrations noted for the Congaree for respective sampling periods. Concentrations in the Congaree River ranged from 15 μg N/liter on Mar. 3 to 161 μg N/liter on Jan. 27. The isopleth maps show that ammonia–nitrogen was carried into the swamp from the Wateree River. There were, however, isolated hot spots in the basin and backwater areas where concentrations exceeded those noted for the two river sources. On four of the six sampling dates (Mar. 31 and Apr. 14 being the exceptions), the concentrations entering the backwater province from the upper swamp basins were lower than the concentrations noted in the spillover area or the hot spots.

In summary, ammonia appeared to be entering the swamp from the river sources as well as being generated in local areas within the swamp. Reduction of concentrations with passage through the swamp was not observed consistently but was evident on occasion.

Nitrate–Nitrogen

Nitrate–nitrogen concentrations for each sampling period are presented in Fig. 6. In contrast to previous trends in nutrient concentrations, there was little or no difference in nitrate–nitrogen concentrations between the Congaree and Wateree river systems. Concentrations for both rivers ranged from ~125 to 300 μg N/liter. The low concentrations were observed on Jan. 27, and the high concentrations were recorded on Mar. 3 and 31. The concentrations for the Santee River were essentially unchanged from the confluence to the downstream transition zone. Generally, the nitrate–nitrogen concentrations in the swamp basin showed a lateral zonation gradient from east to west across the basin, the highest concentrations being on the west side. This pattern was typical of all but first sampling period (Jan. 27), which showed higher concentrations (250 μg N/liter) for the oak islands area than for either of the two rivers. For the remaining sampling periods, it was apparent that nitrate–nitrogen levels entering the backwater area from the swamp basin were virtually the same as water entering from the Santee River.

In summary, nitrate concentrations, consistently high in both river systems, were essentially unaltered in passage through the swamp. Some evidence of denitrification was suggested by the lateral concentration gradients of nitrate across the basin.

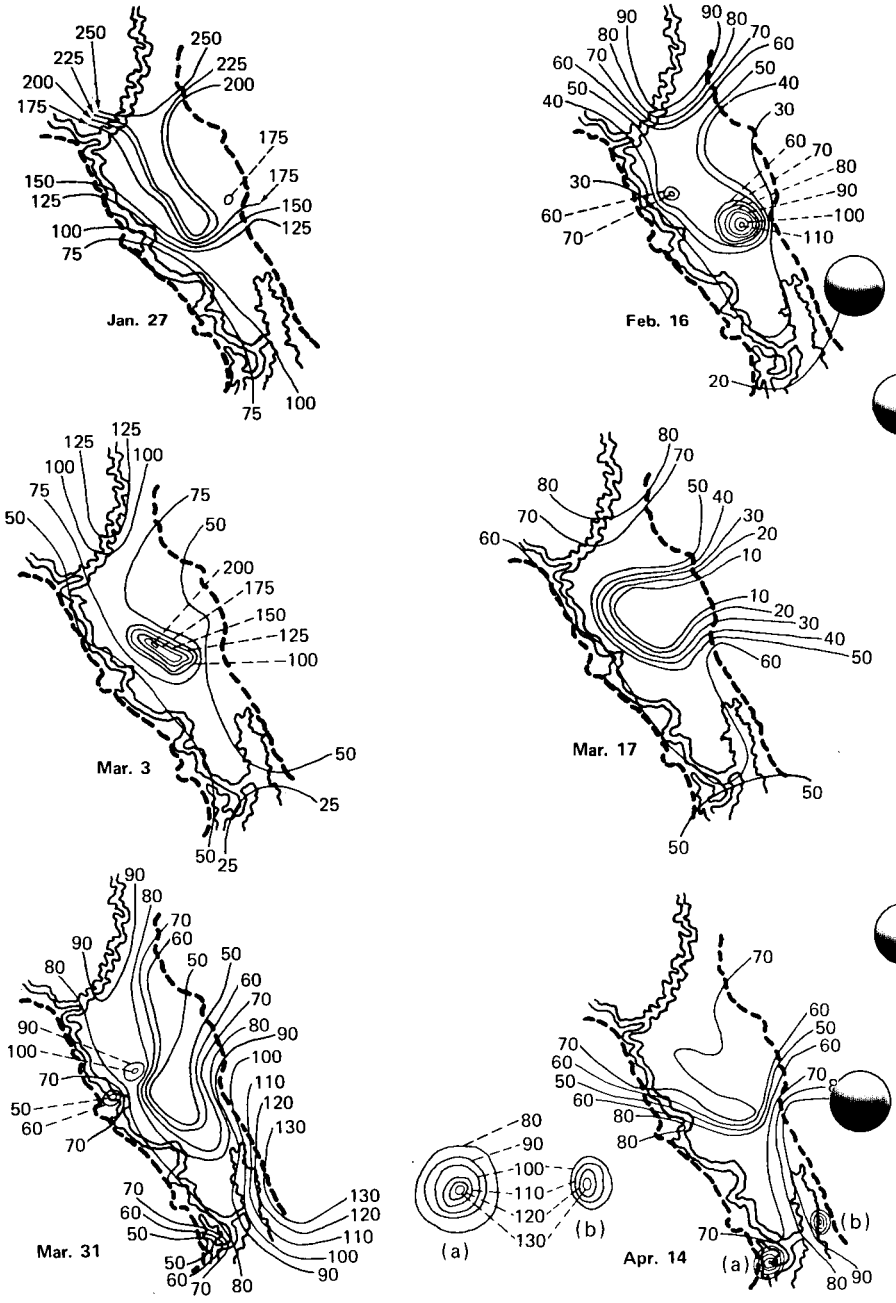

Fig. 5 Ammonia concentration distribution patterns in micrograms of nitrogen per liter of water.

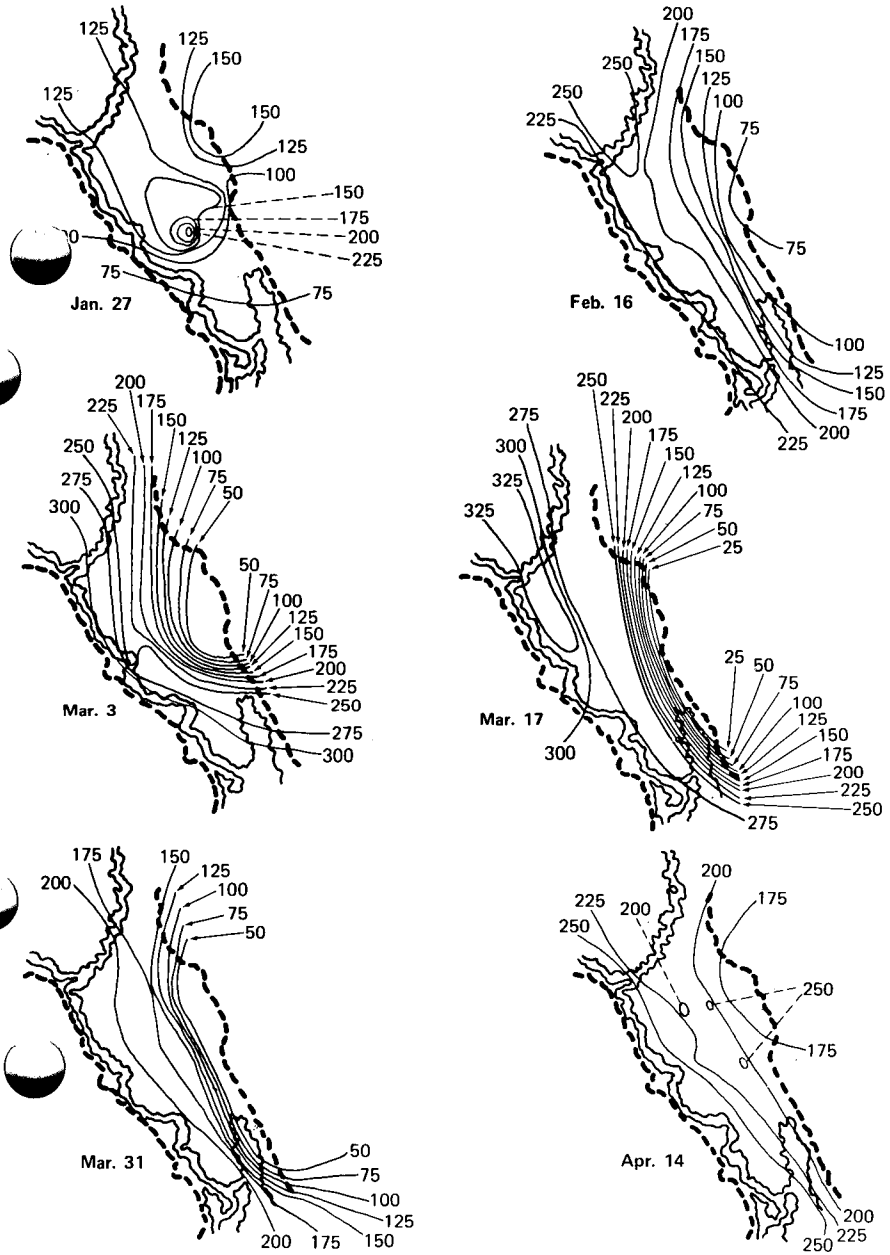

Fig. 6 Nitrate (NO_3 –N) concentration distribution patterns in micrograms of nitrogen per liter of water.

Nitrite–Nitrogen

Concentrations in the Congaree River ranged from 0.0 μg N/liter on Mar. 3 to ~15 μg N/liter on Mar. 31 and Feb. 17. In the Wateree, the concentrations varied from 5.0 μg N/liter on Jan. 27 to 28.0 μg N/liter on Feb. 17. Values in the Santee River ranged from 3.5 μg N/liter on Jan. 27 to ~16.0 μg N/liter on Feb. 17. Concentration values for the swamp stations varied from 0.0 μg N/liter to 25.0 μg N/liter over the period of the study. No discernable temporal or spatial patterns in concentration distributions were evident.

Aerobic Heterotrophs

Data for aerobic heterotrophs are summarized in Fig. 7. The information is presented as averages compiled from selected stations to represent regional trends in the basin. Population values for the three river systems, ranging from approximately 50,000 to 60,000 cells/ml, were statistically inseparable from the values reported for the upper and lower tiers of stations in the swamp, with population values ranging from 52,000 to 44,000 cells/ml. Backwater areas on both sides of the lower Santee River were significantly lower than either river or swamp populations (17,000 and 4000, respectively). One small creek (Mill Creek) on the eastern side of the swamp basin averaged 227,000 cells/ml for the study. That this station was downstream of a small hog pen perhaps explains the high values.

Total and Fecal Coliforms

Total coliform populations (Fig. 7) in the Congaree River and subsequently in the Santee were significantly higher (averaging from 1300 to 1800 cells/10 ml) than those of the Wateree (less than 100 cells/10 ml). Values for the upper and lower swamp stations reflected the values for the Wateree (185 and 473 cells/10 ml) and were statistically inseparable. These values are comparable to the backwater areas (71 and 295 cells/10 ml). The Mill Creek station average was 1287 cells/10 ml.

Fecal coliform distributions reflected the trend of the total coliform distributions. The Congaree and Santee stations are significantly higher (145 and 102 cells/10 ml) than all but the Mill Creek station (227 cells/10 ml). P[illegible] swamp station composites were very low, with values of ~10 cells/10 ml. backwater areas on both sides of the Santee also fall statistically within this range.

DISCUSSION

It is evident from the turbidity and nutrient maps that the Wateree was the major source of water and nutrients in the swamp. The source of the nutrients

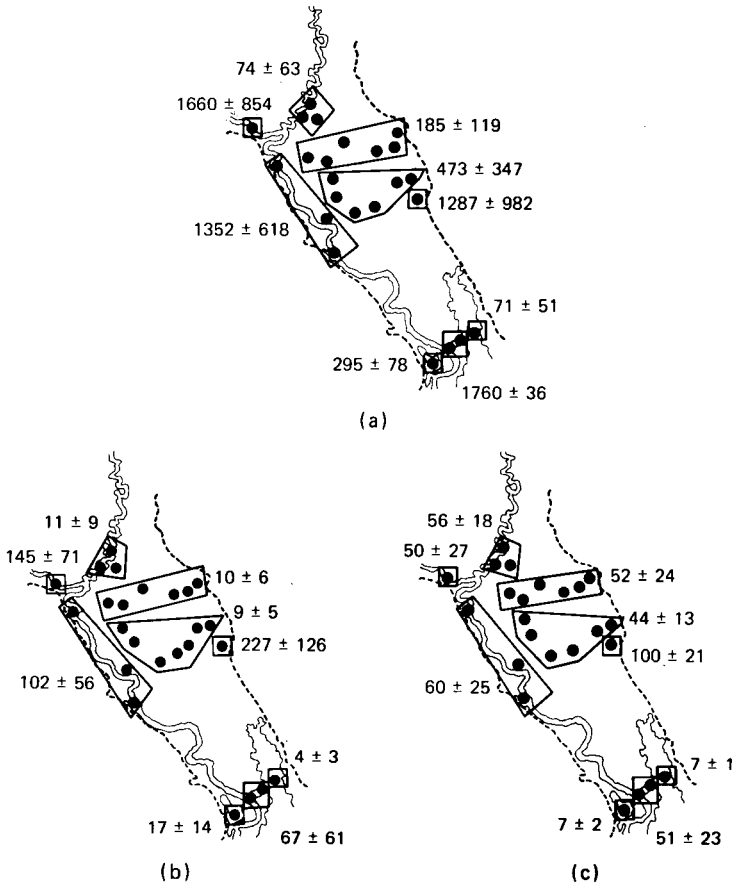

Fig. 7 Bacteriological count maps. Average data were compiled from selected stations to show regional trends. Values are given ± standard deviations. (a) Total coliforms in number of cells per 10 ml water. (b) Fecal coliforms in number of cells per 10 ml water. (c) Aerobic heterotrophs in number of cells times 10^3 per milliliter of water.

as indicated by the bacterial data, particularly coliform numbers, appeared to be cultural runoff in the Wateree Basin and a combination of domestic sewage d agricultural runoff in the Congaree.

The fact that the swamp is a nutrient sink for the phosphates particularly, is evidenced by the reduction in nutrient concentrations in the waters passing through the swamp; there is no such reduction or sink phenomenon for the waters confined to the channel of the Santee River. It is important to note here that the flow through the swamp during the study period was essentially a mass sheet flow over the floodplain floor with no significant additional stream runoff inputs; therefore concentration changes are definitely not due to dilutions.

The fate of the nutrients, particularly phosphates, lost to the sink is only speculative. Since the sink was apparent even under the highest flow regimes, during which there was no turbidity change in the waters flowing through the swamp, it appears to be primarily a biological sink. We cannot rule out the possibility that some of this loss, particularly the total phosphates, occurs as suspended silts and clays with phosphates adsorbed to them are deposited as sediment when the water velocities lessen in passage through the swamp. Woodwell (1958) has also shown that suspended pocosin soils can remove phosphate from solutions. However, Pomeroy, Smith, and Grant (1965) demonstrated that the relationship between phosphates in solution and sediments is a physicochemical equilibrium. We speculate that these sediments are at equilibrium capacity entering the swamp because of the high concentrations in the river sources and would be of little significance in reducing the reactive phosphate concentrations in passage through the swamp.

We suggest that there is extensive assimilation by the aquatic vegetation and its associated epiphytic community. Boyd (1971) cited the potential for such nutrient removal by emergent and submergent macrophytes. Extensive mats of alligator weed (*Alternathera phidoxeroides*) and *Egeria* are conspicuous (to the point of impeding navigation) in practically all the swamp waterways. In addition, Brazilian *Elodea, Ceratophyllum, Myriophyllum, Lemna,* and *Spirodela* are commonly found in lush stands in the waterways that have no shading canopy. Allen (1971) has shown also that epiphytes associated with submergent macrophytes are important in nutrient dynamics of lake waters. Certainly the tree communities are important in the utilization of nutrients deposited as sediment and could perhaps be important in maintaining the dynamic equilibrium between the sediments and waters flowing over them by drawing nutrients from the soil during growth.

Each of the biological sinks would be converting dissolved nutrients into plant biomass and exporting fractions of them, after some time lag, to the downstream impoundment by the following mechanisms: (1) through the aquatic food chain by direct grazing; (2) as dissolved organics (humics, tannins, lignins, etc.) by decomposition; and (3) as organic detritus derived by both physical and biological processes. The retention of nutrients in plant biomass would certainly vary among the different communities of plants. Pomeroy (1970) suggested that the turnover time in the forests, for example, would be the order of 10^2 to 10^4 days.

It is interesting to note that Day et al. (1974) found that a swamp in Louisiana which has had its river-water source cut off is exporting nutrients. Lee, Bently, and Amundson (1970) reported similar findings for drained marshes in Wisconsin. This suggests the sink mechanism is sensitive to manipulations by man.

We recognize the limitations of a short-term study of this nature but feel that the evidence presented here suggests a capacity of the swamp as a

provisional sink for certain nutrients, particularly phosphates. This suggests further that the swamp may play a beneficial role in abating potential eutrophication pollutants to downstream areas. Essentially the swamp may maintain and enhance the quality of the waters flowing through it. For this reason channelization and timber clearing should be evaluated in terms of effects on this role.

In conclusion, we suggest that the southeastern deciduous swamp is a highly efficient water-treatment facility with no fossil-fuel costs. It is a solar-energy-driven system, and for this reason, as well as for its aesthetic qualities, is of great economic value in the undisturbed state.

ACKNOWLEDGMENTS

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REFERENCES

Allen, H., 1971, Primary Productivity, Chemo-Organotrophy, and Nutritional Interactions of Epiphytic Algae and Bacteria on Macrophytes in the Littoral of a Lake, *Ecol. Monogr.*, 41(2): 97-127.

American Public Health Association, American Water Works Association, and Water Pollution Control Federation, 1971, Standard Methods for the Examination of Water and Waste Water, 13th ed., Publications Office, American Public Health Association, Washington, D. C.

Boyd, C. E., 1971, The Limnological Role of Aquatic Macrophytes and Their Relationship to Reservoir Management, in Reservoir Fisheries and Limnology, Special Publication No. 8, American Fisheries Society, Washington, D. C.

Carter, M., et al., 1973, South Florida Ecological Study, U. S. Environmental Protection Agency, Region IV.

Gray, J. W., Jr., Thomas Butler, Robert Allen, and James Gosselink, 1974, personal communication.

Goff, C. C., 1952, Flood-Plain Animal Communities, *Amer. Midland Natur.*, **47**: 478-486.

Grant, R. R., Jr., and Ruth Patrick, 1970, Tinicum Marsh as a Water Purifier, Conservation Foundation, Washington, D. C.

Grey, W. F., 1973, An Analysis of Forest Invertebrate Populations of the Santee–Cooper Swamp; A Floodplain Habitat. M.S. Thesis, University of South Carolina, Columbia.

Lee, G. F., J. Bently, and R. Amundson, 1970, Effect of Marshes on Water Quality, Water Chemistry Department, University of Wisconsin, Madison.

Lindsey, A. A., R. O. Petty, D. K. Sterling, and Willard Van Asdall, 1961, Vegetation and Environment Along the Wabash and Tippecanoe Rivers, *Ecol. Monogr.*, **31**: 105-156.

Monk, C. D., 1966, An Ecological Study of Hardwood Swamp in North Central Florida, *Ecology*, **47**: 649-654.

Murphy, J., and J. P. Riley, 1962, A Modified Single-Solution Method for the Determination of Phosphate in Natural Waters, *Anal. Chim. Acta*, **27**: 31-36.

Odum, E. P. R., 1969, The Strategy of Ecosystem Development, *Science*, **164**: 262-270.

Oosting, H. J., 1942, An Ecological Analysis of the Plant Communities of Piedmont, North Carolina, *Amer. Midland Natur.*, **28**: 1-126.

Penfound, W. T., 1952, Southern Swamps and Marshes, *Bot. Rev.*, **18**: 413-446.

Pomeroy, L. R., 1970, The Strategy of Mineral Cycling, *Annu. Rev. Ecol. Systemat.*, 171-190.

___, E. E. Smith, and C. M. Grant, 1965, *Limnol. Oceanogr.*, **10**(2): 167-173.

Reiners, W., 1972, Structure and Energetics of Three Minnesota Forests, *Ecol. Monogr.*, **42**(1): 71-94.

Sharitz, R. R., J. E. Irwin, and E. J. Christy, 1974, Vegetational Analyses of Swamps Differently Affected by Thermal Loading, *Oikos*, **25**: 7-13.

Solorzano, L., 1969, Determination of Ammonia in Natural Waters by the Phenol-Hypochorite Method, *Limnol. Oceanogr.*, **14**: 799-801.

Strickland, J. D. H., and T. R. Parsons, 1968, *A Practical Handbook of Seawater Analysis*, Bulletin 167, Fisheries Research Board of Canada.

Teal, J. M., 1962, Energy Flow in Salt Marsh Ecosystem of Georgia, *Ecology*, **43**: 614-624.

Valiela, I., J. M. Teal, and C. Van Raalte, 1972, Nutrient and Sewage Sludge Enrichment Experiments in a Salt Marsh Ecosystem, Intecol Symposium on Physiological Ecology of Plants and Animals in Extreme Environments, Dubrovnik, Yugoslavia, in press.

Wharton, C. H., 1970, The Southern River Swamp—A Multiple-Use Environment, Bureau of Business and Economic Research, School of Business Administration, Georgia State University, Atlanta.

Woodwell, G. M., 1958, Factors Controlling Growth of Pond Pine Seedlings in Organic Soils of the Carolinas, *Ecol. Monogr.*, **38**: 219-236.

THE ROLE OF EMERGENT MACROPHYTES IN MINERAL CYCLING IN A FRESHWATER MARSH

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ABSTRACT

Various emergent macrophytes were examined in Theresa Marsh, a 2000-ha impoundment located in southeastern Wisconsin, to evaluate their role in wetland ecosystems. Dry matter, standing crop, and monthly concentrations of nitrogen, phosphorus, and ash were measured in the above- and belowground plant components during the 1972 growing season. Soil samples taken throughout the marsh were analyzed for total nitrogen, available phosphorus and potassium, exchangeable calcium and magnesium, pH, and organic-matter content. Concentrations of the principal nutrients entering and leaving the marsh via stream flow were measured monthly throughout 1971 and 1972.

Annual dry-matter production by the macrophyte species ranged from 11 to 25 tonnes/ha and accounted for an annual nutrient accumulation of 169 kg N/ha, 37 kg P/ha, and 1000 kg ash constituents/ha. Regression analyses showed that significant ($r = 0.98$, $P > 0.01$) changes in total soil nitrogen and available phosphorus were brought about by plant uptake. There were significant ($P > 0.01$) monthly changes in available phosphorus, potassium, and exchangeable calcium in the soil, coinciding with changes in the seasonal production patterns of the vegetation. Neither nitrogen nor phosphorus seems to be a limiting variable in either the soil or water compartment. Total nitrogen and phosphorus in the marsh outflow water ranged from 1.1 to 4.31 mg/liter and 0.12 to 0.70 mg/liter, respectively. Biological activity in the marsh influences the periodicity of the outflow of a number of major elements, with the rooted emergent vegetation being chiefly responsible for the perturbations of available nutrients within the soil.

Wetlands form the interface between terrestrial and aquatic systems and, like most transitional zones, support a variety of abiotic and biotic components. Most marshes and other types of wetlands which possess overland hydrologic inputs and outputs can be considered open systems. There is a constant

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replenishment of water and nutrients from external sources, and thus these systems can be regarded as subsidized, sun-powered ecosystems. As a result of this subsidization, freshwater marshes exhibit a high biological productivity that classes them with the most productive areas in the world (Westlake, 1963; Whittaker, 1970).

Besides being sources of organic-matter production, open freshwater marshes serve in a regulatory capacity in the landscape in which they are situated. Marshes and other wetlands are important hydrologic recharge areas, and, at times of excessive rainfall and subsequent floodwater, they tend to diminish the stress on downstream waterways by modifying and easing the rate of impended flow (Niering, 1968). Marshes also may act as valves or sinks to regulate or trap the flow of nutrients from surrounding terrestrial systems (Lee, Bentley, and Amundson, 1970). This role is particularly crucial as the increasing amounts of nutrients released by urban and agricultural systems produce rapid eutrophication of waterways. Unfortunately, there has been little documentation of nutrient-cycling processes occurring in freshwater wetlands, although a variety of individual wetland species have been investigated (Boyd, 1969; 1970a; 1971; Stake, 1967; 1968; Korelyakova, 1970; Maystrenko et al., 1969). The purposes of this study were to investigate the nutrient dynamics in a freshwater marsh and, in particular, to determine the role of the emergent macrophytes in the overall mineral cycle.

SITE DESCRIPTION

Theresa Marsh is a wildlife reclamation area owned and operated by the Wisconsin Department of Natural Resources and is located in southeastern Wisconsin (43°31′N, 88°25′W). The total area is approximately 2025 ha and contains a 600-ha shallow water impoundment. The surrounding drainage basin consists of nearly 19,000 ha, of which over 90% is under cultivation or in pasture for dairy cattle. This area, which includes some of the most productive agricultural land in the state, supports crops of oats, sweet and fodder corn, peas, and alfalfa hay, which receive large amounts of fertilizers annually.

Vegetation within the marsh includes portions of lowland forest, shrub carr, and submergent aquatics. The primary portion of the marsh is composed of sedge meadow and emergent aquatic communities.

Annual mean temperature for this area is 7.6°C, and precipitation averages 71.4 cm. The average annual growing season is 130 days.

The principal source of water into the impoundment is through three stream inflows (Kohlsville Creek, Lomira Creek, and Rock River), each of which differs in channel size, volume or flow, and distance the water must flow and mix within the marsh before reaching the point of overflow (Fig. 1). Channelization of the individual streams within the marsh tends to reduce the amount of mixing

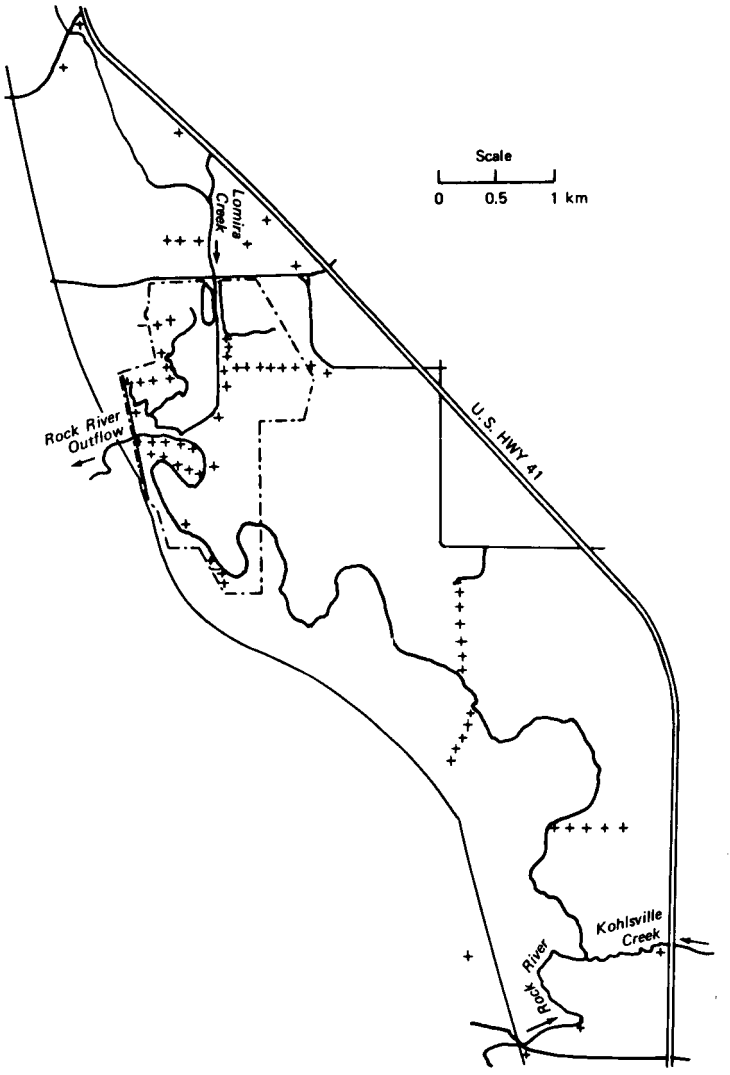

Fig. 1 Map of Theresa Marsh, Wisconsin, Department of Natural Resources Conservation Area, showing the three inflows and one outflow. +, soil sampling sites. Area enclosed inside dashed lines (— · — ·) is principal area of vegetation and soil sampling during 1972.

of inflow water. The marsh was drained in early 1971 and reflooded the same year as part of a carpicide program.

METHODS

Sampling Techniques

The standing crop of emergent macrophytes, including both above- and belowground structures, was sampled once each month during the 1972 growing season. Samples for productivity measurements were taken using 1-m^2 quadrats randomly placed within monotypic stands of vegetation. Samples for nutrient analysis were taken from these and other sites throughout the marsh (Klopatek, 1974). Above- and belowground structures of the plants were separated by cutting off the aboveground portions immediately above the belowground structures. Thus any unfair bias due to the amount of structure above or below the soil surface was eliminated. Vegetational components were either weighed directly in the field or were returned to the laboratory for fresh-weight determinations. Dry weights were obtained after drying the material in a forced-air oven at 75°C for a minimum of 72 hr.

Soil samples were taken at approximately 25 locations in the marsh, including the sites sampled for vegetation. Sampling was undertaken concurrently with the vegetation sampling (except during the winter months) and at other times during the year. Each sample consisted of three subsamples taken from the −3- to −15-cm depth. This depth range was chosen because it contained the majority of all belowground structures of emergent macrophytes.

Water samples of the three inflow channels and one outflow channel of the marsh were taken once or twice a month from June 1971 to October 1972.

Chemical Analysis

Total nitrogen content of the vegetation was measured by the macro-Kjeldahl process (Black, 1965), and total phosphorus was measured by a modified version of the procedures described by Dixon (1968). Ash content was determined by placing a measured amount of dried plant material in a muffle furnace at 500°C for 4 hr.

Determinations of soil pH, organic-matter content, total nitrogen, Bray P-2 available phosphorus, available potassium, and exchangeable calcium and magnesium were conducted by the Wisconsin State Soils Laboratory using the procedures of Schulte and Olsen (1970). Nutrient analysis of all water samples was conducted by the Wisconsin Department of Natural Resources Water Laboratory following standard methods (American Public Health Association, 1971).

VEGETATION

Determining the primary production in the marsh is the necessary starting point for investigating nutrient-cycling processes. Primary production is also the best criterion for evaluating the effects of nutrient subsidies and indicates that Theresa is among the more productive sites studied. Average production estimates, based on the measured standing crop values and including corrections for estimated litter loss in some species, are listed in Table 1.

TABLE 1

ANNUAL NET PRODUCTION RATES OF SELECTED VEGETATION, THERESA MARSH, WISCONSIN, 1972

Species	Annual net production, g m^{-2} $year^{-1}$
Typha latifolia	2456
T. latifolia and *Sparganium eurycarpum*	2877
Scirpus fluviatilis	1533
Carex lacustris	1186
Phalaris arundinacea	2028
Salix interior	1902

The growth of *Phalaris arundinacea* is a prime example of the effect of subsidization; aboveground production (1353 g m^{-2} $year^{-1}$) is well above most values previously reported for this species, even in studies employing substantial fertilizer applications and management (Ramage et al., 1958; Pringle and Van Ryswyk, 1967). In contrast, *Carex lacustris* shows the lowest net production of the species studied, 1186 g m^{-2} $year^{-1}$ (peak standing crop plus 10% for litter loss); this value is comparable to that found by others (Bernard, 1973; Bernard and McDonald, 1974). Increased production by *C. lacustris* may require different climatic conditions (increased temperature, more sunshine, etc.) rather than additional nutritional subsidization. Whatever the situation, the production of emergent plants, together with that of algae and free-floating and submergent macrophytes (McNelly and Klopatek, 1973), indicates a tremendous annual turnover of organic matter and nutrients. Total annual net primary production for Theresa Marsh is probably 28 to 35 tonnes/ha. Nutrient concentrations in the emergent macrophytes varied with species, sampling site, and plant part; most values (Table 2) fell within the ranges previously listed in the literature (Boyd, 1969; Stake, 1968; Van Dyke, 1972). For a given species, however, nutrient levels varied as much as four- or fivefold between the beginning and end

TABLE 2

NITROGEN, PHOSPHORUS, AND ASH CONCENTRATIONS IN EMERGENT MACROPHYTES, THERESA MARSH, WISCONSIN, DURING THE 1972 GROWING SEASON

Species and sampling time	Nitrogen, %			Phosphorus, %			Ash, %		
	Roots	Shoots	Spikes	Roots	Shoots	Spikes	Roots	Shoots	Spikes
Scirpus fluviatilis									
May 17		3.25			0.748			10.58	
June 11	2.88	2.58		0.814	0.639		11.09	7.79	
July 15	1.52	1.60		0.560	0.445		8.46	7.53	
Aug. 15	1.10	1.56		0.395	0.180		6.63	4.86	
Sept. 16	1.24	1.10		0.468	0.082		4.73	5.09	
Carex lacustris									
June 11	1.17	1.70		0.260	0.292		4.50	7.18	
July 15	0.98	1.10		0.224	0.313		4.44	6.09	
Aug. 15	0.90	0.60		0.234	0.158		4.05	3.55	
Sept. 22	0.80	0.82		0.181	0.210		3.65	3.34	
Phalaris arundinacea									
June 11	1.48	1.51		0.253	0.236		4.54	7.65	
July 15	1.32	0.92		0.163	0.129		3.43	5.69	
Aug. 15	1.14	0.89		0.146	0.152		4.65	5.49	
Sept. 16	0.66	0.66		0.135	0.084		2.89	4.79	
Typha latifolia									
May 17	2.32	2.45		0.249	0.629		4.60	11.24	
June 10	2.00	2.41		0.220	0.484		6.64	13.47	
July 15	1.40	0.60	2.00	0.273	0.176	0.437	10.12	9.88	9.38
Aug. 15	1.17	0.44	2.11	0.291	0.168	0.405	9.14	9.25	5.10
Sept. 16	1.58	0.56	2.04	0.314	0.181	0.403	6.83	8.59	4.78
Oct.		0.84			0.224			9	

of the growing season; this indicates the importance of recording the phenological stage at the time of sampling. Unfortunately, since few studies of belowground structures have been reported, evaluation of the actual nutrient dynamics of the vegetation is limited.

By coupling the level of nutrients in the plant (percent dry weight) with the actual amount of nutrients accrued by the vegetation (grams per square meter), we can divide the seasonal aboveground nutrient cycle into four phases. In phase 1 the plant tissue contains its highest concentration of nutrients (nitrogen, phosphorus, and ash constituents), and growth is perhaps in a lag phase, depending on external environmental parameters (i.e., light and temperature). Normally this occurs at the beginning of the growing season, but it may occur in late fall if new overwintering shoots are formed. Phase 2 is the period of peak nutrient uptake, at which time the majority of nutrient accumulation occurs. This phase takes place over a relatively short time span and, as pointed out by Boyd and Vickers (1971), does not necessarily coincide with the period of peak dry-matter production. At Theresa the peak uptake phase immediately preceded the time of peak production of *Typha latifolia* (Fig. 2) but accompanied the peak production of *Scirpus fluviatilis* (Fig. 3) and *P. arundinacea. Carex lacustris* (Fig. 4) displayed two main periods of nutrient accumulation; the first accompanied its production of new shoots that overwinter till the following growing season (Bernard, 1973). In agreement with the finding here, Stake (1967, 1968) found that the period of peak nitrogen uptake often precedes that of phosphorus.

Phase 3, the period when maximum nutrient accumulation has occurred, may or may not accompany the peak standing crop. At first this period may not seem to be a major phase in itself; at this point, however, a major "switching" occurs in the life cycle of the plant. The energies of the plant can now be applied to belowground growth, and there may be a subsequent translocation of nutrients to the belowground structures or a release of nutrients to the aquatic environment. Peak nitrogen accumulation in *S. fluviatilis* was correlated with peak standing crop, but maximum phosphorus accumulation was reached earlier. In *T. latifolia* peak nutrient accumulation occurred after peak standing crop had been reached, but this was misleading because of probable microbial enrichment, which is discussed later.

Phase 4 marks the time of decline and leveling off of nutrient concentration the plant tissue. In this phase the nutrient level drops to a plateau where loss in nutrients is caused primarily by loss in dry matter, with the rate depending on whether the plant part is under water (Boyd, 1971). This leveling-off phase is not static; it may also bring about an increase in nutrients. In *T. latifolia* the nitrogen content of the shoots and leaves increased at the end of the growing season. A similar phenomenon also occurred in *S. fluviatilis* and *Polygonum lapathifolium* (a transient wet-soil-adapted species) at the end of the 1971 growing season. The increase in nutrients, which has also been reported by

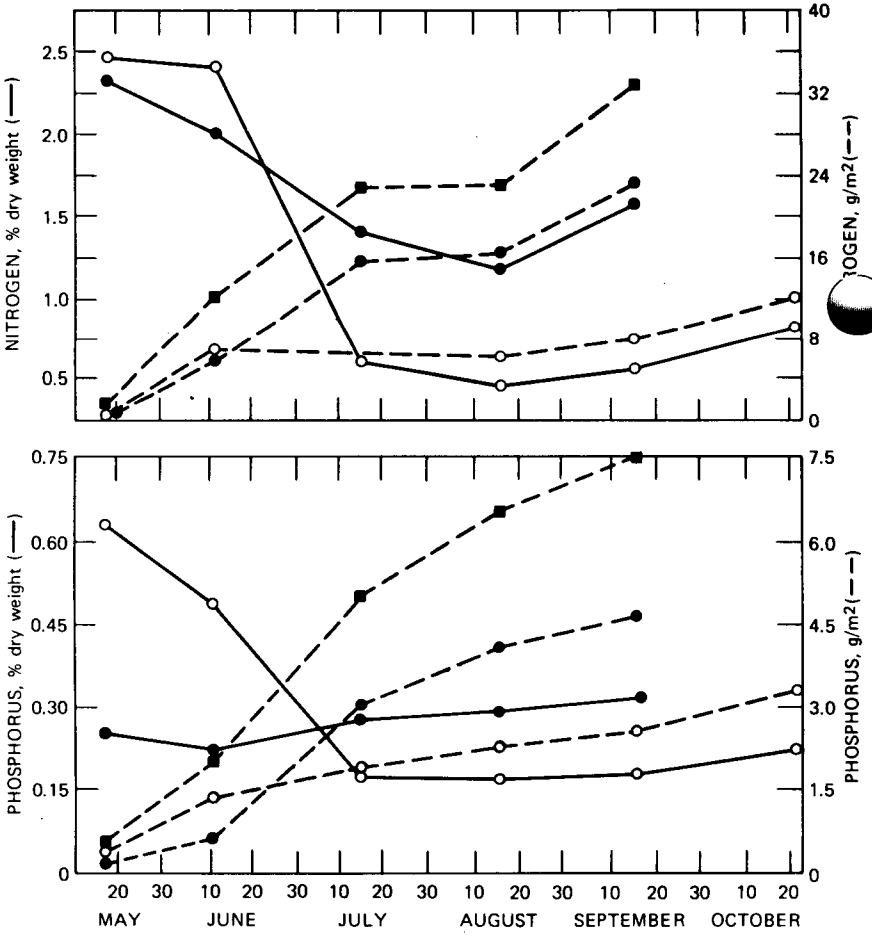

Fig. 2 Seasonal change in nitrogen and phosphorus content and the accumulation of nitrogen and phosphorus in *Typha latifolia* of Theresa Marsh in 1972. ○, shoots. ●, roots and rhizomes. ■, total.

others (Boyd, 1970b; Kaushik and Hynes, 1968), is thought to be microbial enrichment by fungi and/or bacteria colonizing on the dead plant tissue a accumulating nutrients from the surrounding water. *Carex lacustris* a displayed increases in phosphorus and ash constituents at the end of the growing season, but this was attributed to epiphytic algae.

The pattern of nutrient changes in belowground structures is less discernible than that in aboveground structures. Part of the reason is that the longevity of roots and rhizomes differs among species. The difference is exemplified in comparisons of ash concentrations of belowground structures of *T. latifolia* with those of *S. fluviatilis* and *C. lacustris*. In *T. latifolia* the highest ash content

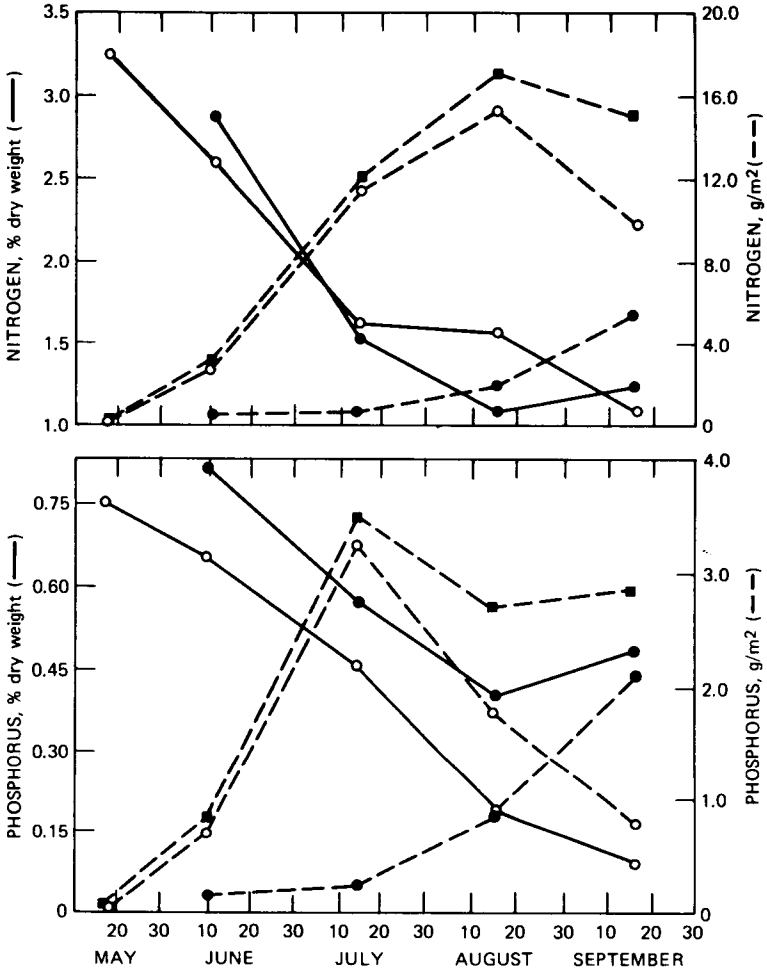

Fig. 3 Seasonal change in the nitrogen and phosphorus content and the accumulation of nitrogen and phosphorus in *Scirpus fluviatilis* of Theresa Marsh during 1972. ○, shoots. ●, roots and rhizomes. ■, total.

curred in the middle of the growing season and corresponded to lowest y-matter concentration and to the period of peak aboveground productivity. In *S. fluviatilis* and *C. lacustris* the highest ash content occurred in the beginning of the growing season and corresponded to the production of new roots and rhizomes, which have a life-span of 12 months (Bernard, 1973; Klopatek, 1974) in contrast to *T. latifolia* rhizomes, which live from 12 to 24 months (Fiala, 1971).

Nitrogen and phosphorus patterns also varied in the belowground components of the different species. *Typha latifolia* and *S. fluviatilis* (also *Sparganium*

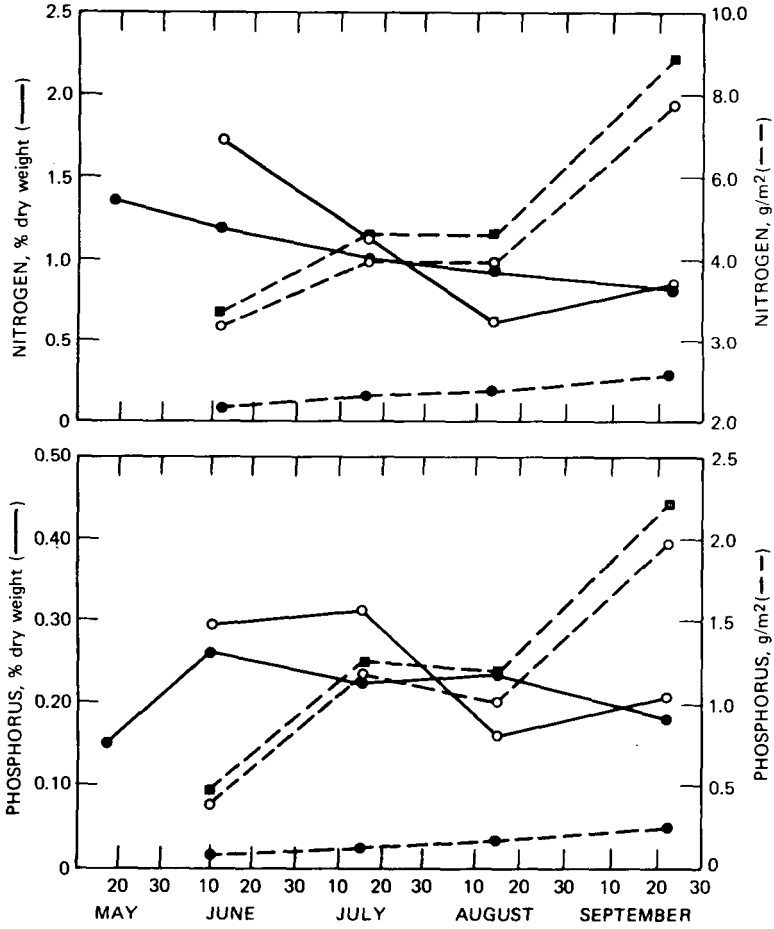

Fig. 4 Seasonal change in nitrogen and phosphorus content and the accumulation of nitrogen and phosphorus in *Carex lacustris* of Theresa Marsh in 1972. ○, shoots. ●, roots and rhizomes. ■, total.

eurycarpum, which is not reported on here) exhibited an increase in the concentration of both nitrogen and phosphorus at the end of the growing season. *Carex lacustris* did not follow this pattern, possibly because of the r shoot production in the fall, which demonstrated a significant increase in nutrient concentrations. These nutrients would presumably be available for new growth the following spring. *Phalaris arundinacea* did not show any increase in the root nutrient concentrations in the fall.

Phase 1 in the belowground biomass occurs at the beginning of the growing season when nutrient levels are at their peak and apparently are supporting the development of new above- and belowground structures. The second phase

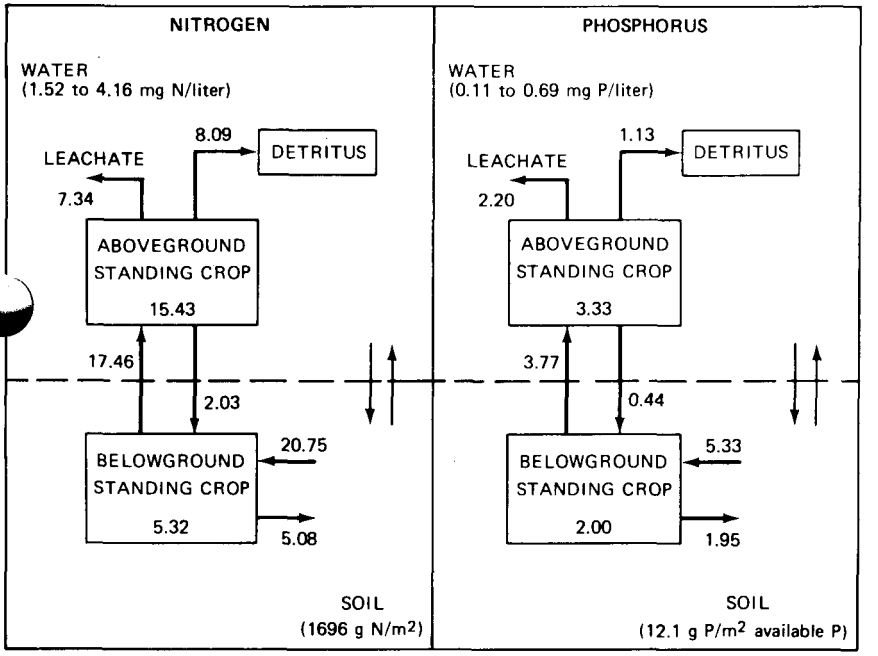

Fig. 5 Flow of nitrogen and phosphorus through a *Scirpus fluviatilis* stand. Flows are in grams per square meter per year, and compartments are grams per square meter in standing crop.

includes the outflowing of nutrients from storage into the aboveground production. At this time nutrient concentrations reach their lowest levels. Phase 3 is the switching over from above- to belowground production, with subsequent maximum accumulation of nutrients in the belowground structures. Nutrients not only enter the roots and rhizomes through normal uptake patterns but also may be translocated downward from the shoots and leaves. This period also accompanies the time of peak growth of the belowground organs of *S. fluviatilis*, *C. lacustris*, and *T. latifolia*. The fourth phase covers the end of the growing season and the period of dormancy throughout the winter months when little nutrient activity is thought to occur.

Figure 5 depicts the annual nitrogen and phosphorus budgets for *S. fluviatilis*. By combining the above- and belowground nutrient patterns with the biomass changes, we can see a more complete picture of the nutrient dynamics. Leaching losses were determined as the amount of nutrients lost by the shoots and leaves which could not be attributed to biomass loss or to an increase in belowground nutrients. A ^{32}P study of *S. fluviatilis* showed no leaching losses of phosphorus to occur before peak aboveground standing crop had been reached. Leachate losses occurring after the growing season were based on nutrient

concentrations of dead aboveground tissue collected between the 1971 and 1972 growing seasons. The amount of nutrient translocated back to the roots and rhizomes was estimated to be half the total nutrients lost by aboveground structures after the peak aboveground standing crop had been reached and not accounted for in the aboveground tissue at the time of complete senescence. Although no actual data were available, this was felt to be a reasonable estimate.

Using *S. fluviatilis* as an example (Fig. 5), we readily see that emergent macrophytes are responsible for pumping considerable amounts of nutrients out of the soil system. Combining the accumulation of nutrients by all the different species yields an average total of 169 kg N/ha, 37 kg P/ha, and 10[illegible] kg ash constituents/ha taken up within the marsh. These nutrients a[illegible] immobilized for the majority of the growing season; only one-fourth to one-third of the totals are returned directly to the soil through translocation and decomposition of and leaching from belowground structures. The remainder is released to the water to be further utilized in other biological processes, to re-enter the soil, or to flow out of the marsh system. The implications of the vegetation interactions with soil and water are discussed later.

SOIL NUTRIENTS

Marsh soils of Alfisol–Mollisol landscapes are generally more fertile than the soils that surround them (Cook and Powers, 1958). The soils of Theresa Marsh are no exception to this pattern; nutrient concentrations maintained in the marsh (Table 3) were considerably higher than those in the upland soils on its periphery and surpass the concentrations required for sustained production of neighboring agricultural crops (Walsh and Schulte, 1970).

The Histosols of the marsh differ from the surrounding upland soils primarily because of their submergence. Submergence causes an anaerobic state to exist within the root zone of the soil, and this results in a lowered redox potential. The reduced state changes the availability of many nutrients and in some cases, e.g., with phosphorus, alters the form of the element to enhance plant uptake (Ponnamperuma, 1972). The anaerobic state of the marsh soils also perpetuates the buildup of organic matter. During the 1972 growing season, no month-to-month statistical differences were noted in organic-matter content; monthly average values ranged from 40.4 to 43.4% (Table 3). Individual samp[illegible] varied from a low of 8.9% to a high of 72.5%. The mineral portion of the soil is [illegible] silt loam that reflects the nature of the surrounding upland soils.

Seasonal changes in the pH of submerged soils are minimal because of the dominant influence of the redox system (Stumm and Morgan, 1970) and other buffering systems such as $CaCO_3$ (Keeney, 1973). Soil pH showed no distinct seasonal pattern during 1972 (values averaged between 6.3 and 6.5) and was most closely correlated with organic-matter content; correlation coefficients varied from $r = -0.65$ to -0.86 ($P > 0.01$), with only one value less than -0.76.

TABLE 3

MONTHLY AVERAGES AND STANDARD DEVIATIONS OF MEASURED CHEMICAL SOIL PARAMETERS, THERESA MARSH, WISCONSIN, DURING THE 1972 GROWING SEASON

Parameter	May	June	July	August	September
pH	6.4 ± 0.5	6.5 ± 0.6	6.5 ± 0.6	6.4 ± 0.5	6.4 ± 0.6
Organic matter, %	43.2 ± 13.9	43.4 ± 14.6	41.0 ± 14.8	40.4 ± 15.2	42.6 ± 17.1
Total nitrogen, %	1.84 ± 0.62	1.88 ± 0.57	1.77 ± 0.48	1.75 ± 0.60	1.84 ± 0.67
Available phosphorus, ppm (Bray P-2)	123 ± 57	50 ± 24	68 ± 38	203.4 ± 113.4	164.3 ± 93
Available potassium, ppm	133 ± 76	169 ± 67	161 ± 58	230 ± 60	222 ± 117
Exchangeable calcium, ppm	12,060 ± 2989	5720 ± 1566	12,730 ± 3283	9542 ± 2073	9713 ± 2417
Exchangeable magnesium, ppm	2318 ± 578	1219 ± 238	2300 ± 647	2080 ± 413	2060 ± 527

Histosols falling into this pH range are essentially fully base saturated (Buol, Hole, and McCracken, 1972).

Buckman and Brady (1969) pointed out that, although the processes of mineralization, immobilization, and leaching occur continually in the soil, the

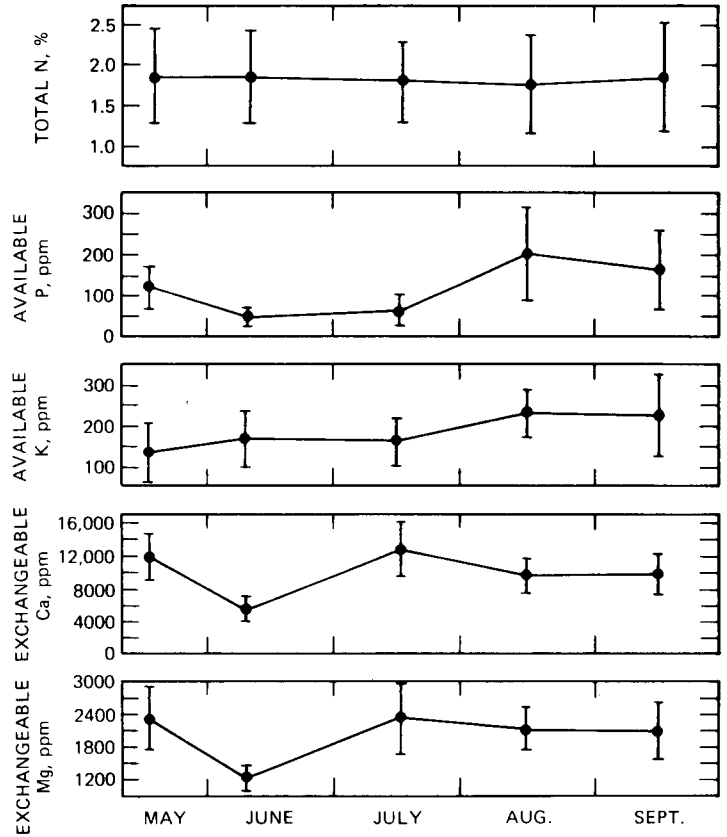

Fig. 6 Changes in monthly averages of soil nutrients in Theresa Marsh, Wisconsin, during the 1972 growing season. Bars (I) indicate one standard deviation from the mean.

total amount of nitrogen present is fairly constant throughout the year. As can be seen in Fig. 6, this was the case at Theresa Marsh; no statistical differences occurred during 1972. In agreement with the findings of Boyd (1970c), total nitrogen content was positively correlated with organic matter content ($r = 0.75$ to 0.95, $P > 0.01$).

Bray P-2 available phosphorus, on the other hand, showed two significant changes (Fig. 6). A sharp decrease occurred between the May and June sampling

dates, with the low level continuing through July and coinciding with the period of peak uptake by the emergent macrophytes. In August there was a reversion to the high levels of May. Black (1968) and Fried and Broeshart (1967) stated that, although uptake of phosphorus by the vegetation may occur, the rate of renewal of phosphorus in the soil solution is rapid enough to maintain an equilibrium in the soil. This does not seem to be the case in the emergent macrophyte root zone in Theresa Marsh.

Like phosphorus, available potassium displayed a significant increase between the July and August sampling dates (Fig. 6), but, unlike phosphorus, it showed no significant decrease in the early part of the growing season—lowest levels of available potassium occurred during the month of May, however (Table 3). The exchangeable form of potassium exists in a state of dynamic equilibrium with the nonexchangeable form (Reitemeier, 1957). Thus, if there is any drastic change in the amount of available (hence exchangeable) potassium, we might assume that it is a reflection of the uptake by rooted vegetation (given that the concentration in the overlying water remains fairly constant). Higher plants often exhibit luxury uptake of potassium; this drains the pool of the available element. With the changeover from above- to belowground production by the vegetation, the uptake of potassium ceases, and there is a subsequent increase of available potassium within the soil. Potassium translocated from the shoots and leaves to the roots and rhizomes may also be leached from the plant. Unfortunately, without potassium analysis of the plants, we cannot substantiate this hypothesis.

Both available calcium and magnesium exhibited a number of changes in the soils of Theresa Marsh during 1972 (Fig. 6), showing an increase from April (not shown) to May, a decrease in June, and an increase in July. High levels in May can be attributed to the large algal production at this time (Granert, 1973). Algal production results in the release of CO_2, the subsequent formation of $Ca(HCO_3)_2$, and the precipitation of $CaCO_3$ and $MgCO_3$ from the overlying water (Ruttner, 1963; Planter, 1970a). The low values in June (Table 3) coincide with the period of maximum uptake of ash constituents by the emergent macrophytes, and the higher values in July and the remainder of the growing season reflect the fact that the majority of accumulation of all ash constituents by the vegetation had already occurred by this time. Typically, exchangeable calcium was correlated with organic-matter content of the soil (Buckman and Brady, 1969), with correlation coefficients varying from $r = 0.70$ to 0.86 ($P > 0.05$). The only exception to this was the month of June, when the coefficient was only 0.35. This strengthens the hypothesis that emergent macrophytes were the controlling influence in the amount of exchangeable calcium in the soil during this period. Exchangeable magnesium was not significantly correlated with organic matter, and correlations with calcium were extremely low (0.19 to 0.40). The amount of exchangeable magnesium in the soil followed a pattern similar to that of calcium.

WATER NUTRIENTS

The hydrological transport of materials into and out of the marsh is the key to maintaining the marsh as an open system. Quantifying the mineral cycles within or through the marsh would require not only monitoring the stream inflows and outflow but also evaluating the rates of evapotranspiration, gas exchange, surface runoff, and subsurface flow. Despite the complex hydrology of the marsh, however, it is still possible to obtain valuable information about processes occurring within it from comparisons of the nutrient concentrations in inflow and outflow waters (Table 4).

TABLE 4

RANGE OF VARIOUS NUTRIENTS IN INFLOW AND OUTFLOW WATERS, THERESA MARSH, WISCONSIN, 1971 AND 1972

Nutrient	Marsh outflow, mg/liter	Inflows, mg/liter		
		Lomira Creek	Kohlsville Creek	Rock River
NO_2	<0.01–0.04	<0.01–0.04	<0.01–0.04	<0.01–0.06
NO_3	0.10–1.68	0.07–2.03	0.17–2.16	<0.03–1.51
NH_4	0.13–1.59	0.10–2.61	0.07–1.69	0.03–5.81
Organic nitrogen	0.65–2.22	0.54–1.74	0.33–1.51	0.77–2.23
Total nitrogen	1.52–4.16	1.13–5.19	1.72–4.06	1.38–8.32
Dissolved phosphorus	0.10–0.50	0.17–2.40	0.02–0.30	0.04–0.69
Total phosphorus	0.11–0.69	0.17–2.42	0.05–0.31	0.05–0.78
Potassium	0.9–9.1	3.6–19.6	1.4–4.5	1.4–4.8
Calcium	56–168	60–130	55–112	60–137
Magnesium	23–73	32–71	31–72	31–69

When we examine the changes in concentrations of various nitrogen species in the outflow water (Fig. 7), the sizable export of nitrogen from the marsh after the 1971 drawdown is immediately obvious. In fact, the months of June a July 1971 were the only sampling periods during the study when all nitrog species were in higher concentrations in the outflow water than in the inflow waters. The nitrogen export, which resulted from increased organic-matter decomposition caused by soil aeration and subsequent leaching of the released nitrate and soluble organic nitrogen, is a characteristic result of the drawdown of marshes (Bentley, 1969; Amundson, 1970).

In April, after the spring flushing of the marsh caused by runoff and ice melt (the ice contained 2.20 mg organic N/liter and 2.36 mg NH_4–N/liter), there was

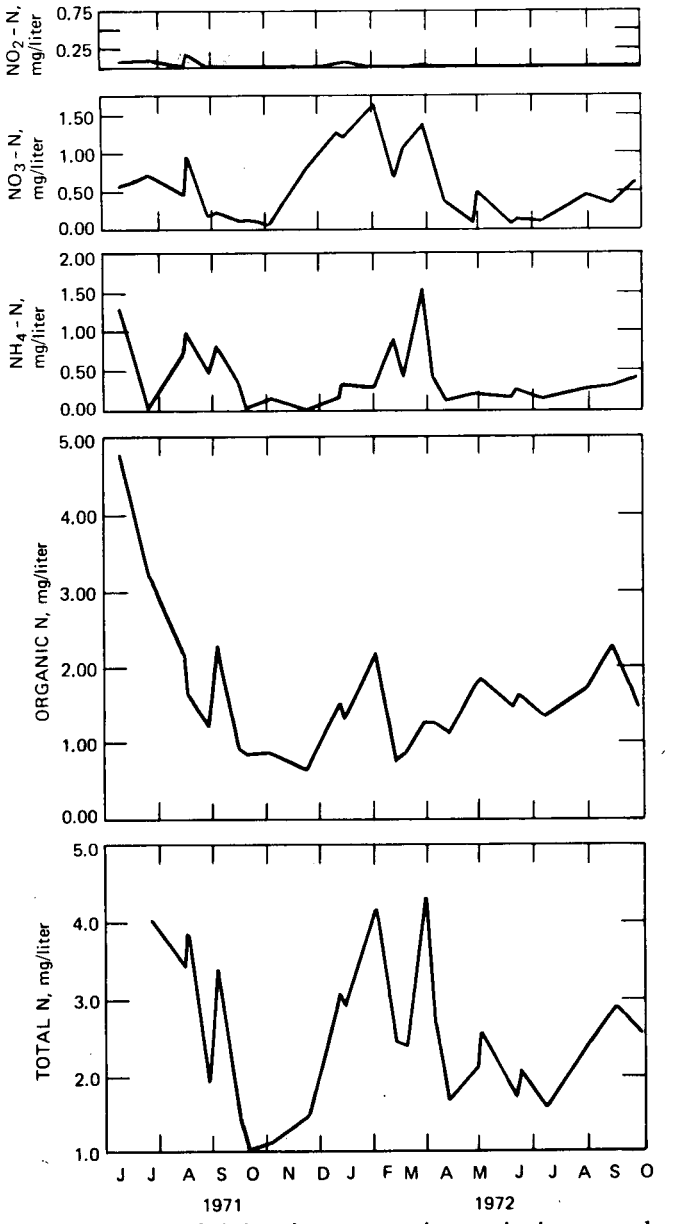

Fig. 7 Concentrations of nitrite, nitrate, ammonia, organic nitrogen, and total nitrogen in the outflow water of Theresa Marsh, 1971 and 1972.

a sharp decline in the level of nitrogen, particularly ammonia and nitrate. This coincided with an algal bloom (*Tribonema* sp.) throughout the marsh, even though an extensive covering of ice remained. In June and July the total inorganic nitrogen level in the outflow was less than 0.30 mg/liter, but levels within the marsh were as high as 0.60 mg NH_4–N/liter; this indicates that organic nitrogen is being mineralized. Lowest levels of total nitrogen occurred during the growing season in 1972. Nitrogen levels in the outflow water were significantly reduced in comparison with levels in the inflow water, during late July and early August, a time of peak growth of submerged and free-floating macrophytes (McNelly and Klopatek, 1973). This possibly indicated substan denitrification occurring in the marsh. In 1971 and at the end of the 19 growing season, there was an increase in the amount of nitrogen leaving the marsh, presumably due to the decomposition of the various marsh vegetation, with organic nitrogen being the chief mode of nitrogen export from the marsh. Comparisons between the inflow and outflow water at this time showed a minimum of 1.0 and 0.40 mg organic N/liter released from the marsh system in September and October, respectively.

Interpreting the changing phosphorus levels (Fig. 8) in the marsh outflow water is difficult because of the relatively high levels (up to 2.46 mg dissolved P/liter and 3.79 mg total P/liter) entering the north end of the marsh. Thus on the surface the annual cycle of phosphorus in the marsh outflow appears to be a reflection of the amount entering via the Lomira Creek input. When we compare phosphorus to a biologically conservative element such as chlorine, however, we note a reduction of greater than 50% in the phosphorus content of the water. The greatest reduction of phosphorus occurred during late July and mid-August when levels were lower in the outflow than in the inflows (similar to nitrogen). At no time did phosphorus appear in quantities low enough to be considered limiting (Sawyer, 1947; Vollenweider, 1968); with one exception, levels of dissolved phosphorus were continually equal to or greater than 0.10 mg/liter.

Available phosphorus in the soil and phosphorus levels in the inflow and outflow waters showed negligible correlation. Total phosphorus entering the marsh in the inflow streams accounted for only about 35% (r^2) of the variation in the marsh outflow water during the growing season. When the average accrued phosphorus (grams per square meter) in the aboveground portions of emergent macrophytes was included in the regression analysis, however, o 90% ($P > 0.01$) of the variability was accounted for. Total phosphorus in the outflow water and the aboveground structures of the emergent macrophytes was negatively correlated ($r = -0.95$, $P > 0.01$). This suggests that significant leaching of phosphorus from the plants may have taken place or that the phosphorus patterns in the emergent macrophytes are similar to the overall pattern of uptake and release by the other primary producers in the marsh. Like nitrogen, phosphorus was released in the autumn of 1971 and 1972.

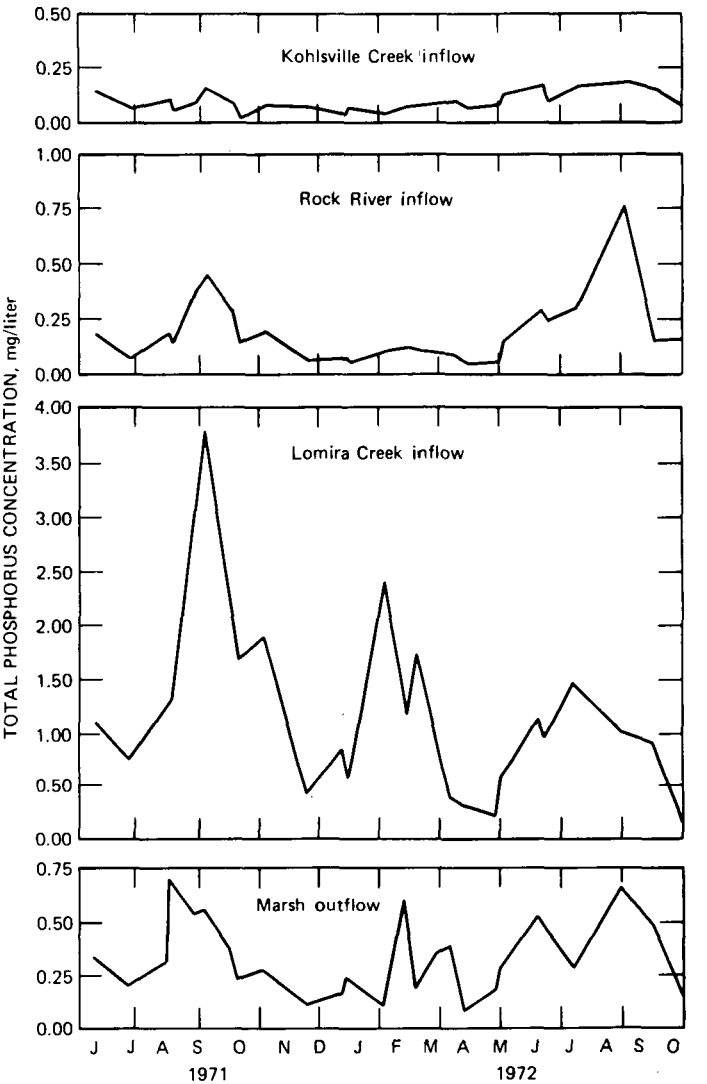

Fig. 8 Concentrations of total phosphorus in inflow and outflow waters of Theresa Marsh, 1971 and 1972.

Assessment of the flux of potassium through the marsh is complicated by the Lomira Creek input, which showed concentrations two to four times that of the other two inflows (Table 4). These high levels mask the effects of the marsh. The cycling of potassium in aquatic ecosystems is poorly understood in regard to both the interchange between the water and sediment and the pathways and concentration in the biotic compartments. Seasonal trends are difficult to

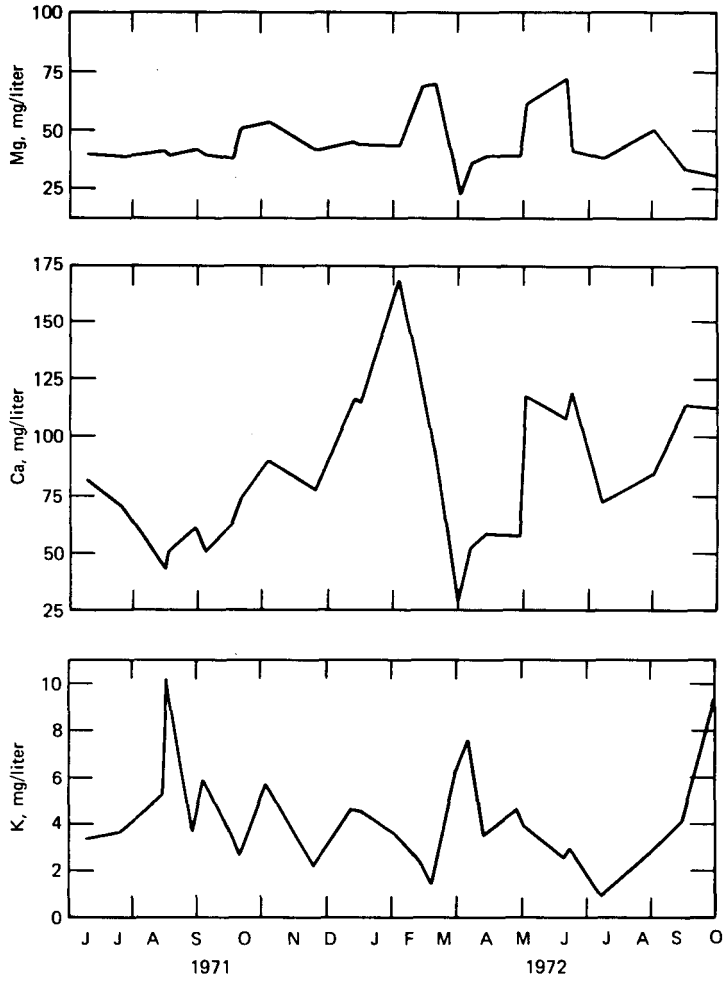

Fig. 9 Concentrations of magnesium, calcium, and potassium in outflow water of Theresa Marsh, 1971 and 1972.

ascertain (Fig. 9); however, where we compare inflow and outflow water, notice two important periods. July 1972 was the only sampling date when there was less potassium in the outflow water than in any of the inflows. This reduced outflow coincides with or follows the period of peak dry-matter production by emergent macrophytes, which necessarily utilize large quantities of potassium. An increase in the potassium content of the outflow water occurred in August 1972, as in 1971. This higher outflow level continues into September and October and corresponds with the leaching period, during which loss of

potassium from macrophytes would be expected to occur (Planter, 1970b), and with the dramatic increase noted in available potassium within the soil.

High concentrations of both calcium and magnesium in the water flowing into and out of the marsh reflect the dominant dolomitic rocks of the drainage basin. The annual cycle of both calcium and magnesium in the outflow water (Fig. 9) was similar to that found by Bentley (1969). Highest amounts of calcium and magnesium in the outflow water occurred during January and February when the marsh was under an ice cover. As ice forms, calcium, magnesium, and other ions tend to remain in solution, thus increasing their proportion in the water. In February, when the outflow water contained 119 mg Ca/liter and 70 mg Mg/liter, the ice had only 14.1 mg Ca/liter and 5.6 mg Mg/liter. After ice formation, lesser concentrations of calcium were found in the outflow than in the inflow water, whereas there were little if any differences between the levels of magnesium. This can probably be attributed to the precipitation of calcium as $Ca(HCO_3)_2$ (or $CaCO_3$) caused by the release of CO_2 into the water by the microbial decomposers (Ruttner, 1963). Magnesium, by comparison, has a greater solubility than calcium either as $Mg(HCO_3)_2$ or $MgCO_3$.

Lowest concentrations of both calcium and magnesium occurred during the period of spring flush when melt water acted as a dilutant.

In April and early May, after spring runoff had subsided, calcium and magnesium concentrations in the outflow water remained low, and both ions were in lower concentrations than in the inflow waters. Presumably these elements were being precipitated as carbonates since, at this time, the marsh experienced a substantial algal bloom. The decrease of calcium in the water paralleled the previously discussed increase of exchangeable calcium in the soil. In late May and in June, calcium again increased in the marsh outflow water. This increase coincided with a significant decrease of exchangeable calcium in the soil and with the time of maximum uptake of ash by emergent macrophytes. During June outflow concentrations of calcium were higher than inflows. In July the outflow level of calcium again decreased and was accompanied by an increase in soil exchangeable calcium. This may indicate a replenishment period during which the calcium, rapidly taken up by plants earlier, was being replaced from the water. Outflow and inflow concentrations were approximately equal during July, but in the following months the outflow levels were higher than the inflow levels. The increase in outflow of calcium, like that of potassium, indicated the leaching of ions from plant tissues, plus an overall increase of respiration within the system.

It seems reasonable to assume that these cations, especially potassium, exist in a mobile state within the marsh system and that the transfer of these cations between the water and soil compartments is in part dependent on the uptake–release pattern of the emergent macrophytes.

DISCUSSION

As noted earlier, freshwater marshes must be considered open systems with a more or less constant inflow and outflow of water, nutrients, and energy. It was also stated that freshwater marshes may be classified as sun-powered subsidized ecosystems. This study demonstrates that Theresa Marsh receives a substantial nutrient subsidy entering from the surrounding drainage basin. The added nutrients are not only of natural origin (i.e., from precipitation, erosion, weathering, and natural decomposition processes) but also include significant subsidies from man such as sewage, industrial waste, and fertilizer runoff from agricultural lands.

This study did not attempt to investigate the various sources of nutrient inputs but rather aimed to elucidate the role of emergent macrophytes in the nutrient-cycling processes taking place in the complex biogeochemical reaction site called Theresa Marsh.

To evaluate the functional role of the emergent macrophytes in the marsh ecosystem from a nutrient-dynamics point of view, we must examine both the ontogeny of the species and their patterns of nutrient uptake and release. Numerous investigators have correlated the nutrient content of submergent macrophytes with that of the surrounding water (Gerloff and Krumbholz, 1966; Gossett and Norris, 1971; Boyd and Walley, 1972). When attempts were made to compare levels of soil and water nutrients with those in emergent macrophytes, however, the correlations were poor or nonexistent (Stake, 1967; 1968; Boyd and Hess, 1970).

Emergent macrophytes are thought to derive their nutrients from the soil (Sculthorpe, 1967) rather than from the surrounding water. Thus, to correlate the changes occurring within the soil, we must account for the total amount of nutrients accumulated by the vegetation. For this purpose, three variable linear regression equations were employed to compare the changes in the amount of nutrients (grams per square meter) in the belowground (X) and the aboveground (Y) standing crops and the level of nutrients in the soil (Z) in monotypic stands of *T. latifolia*, *S. fluviatilis*, and *C. lacustris*. Results of the regression analysis are found in Table 5. Only for the *T. latifolia* nitrogen relationship was there a lack of significance; this is probably explained by the microbial enrichment of the aboveground structures.

The highly significant correlation values between both *S. fluviatilis* and *C. lacustris* (and to a lesser extent *T. latifolia*) and total soil nitrogen is somewhat surprising since, in continually waterlogged soils, ammonia is regarded as the sole plant-available nitrogen (Patrick and Mahapatra, 1968). A possible and perhaps probable explanation is that ammonia in the anaerobic marsh soil is in constant proportion to the total nitrogen present. In submerged soils, mineralization of nitrogen results in the formation of ammonia (Ponnamperuma, 1972). Ellenberg (1971) stated that the rate of mineralization of nitrogen in beech-forest soils is

TABLE 5

CORRELATION COEFFICIENTS AND REGRESSION EQUATIONS FOR RELATIONSHIPS BETWEEN SOIL NUTRIENTS AND NUTRIENTS ACCUMULATED IN ABOVE- AND BELOWGROUND STANDING CROPS OF THREE EMERGENT MACROPHYTES*

Species	Nutrient	Regression equation†	Correlation coefficient (r)
Typha latifolia	Nitrogen	$Z = 0.476 - 0.070X + 0.326Y$	0.87
	Phosphorus	$Z = -0.12 - 28.30X + 109.91Y$	0.98‡
Scirpus fluviatilis	Nitrogen	$Z = 1.005 - 0.026X + 0.006Y$	0.99¶
	Phosphorus	$Z = 22.984 - 60.848X + 0.334Y$	0.84‡
Carex lacustris	Nitrogen	$Z = 1.798 + 0.414X + 0.091Y$	0.99¶
	Phosphorus		0.99¶

*Soil nutrients are total nitrogen (%) per available phosphorus (ppm); nutrients in standing crops are in g/m^2.

†Variables are Z, soil nutrients; Y, nutrients in aboveground standing crop; and X, nutrients in belowground standing crop.

‡Significant at the 0.10 level of probability.

¶Significant at the 0.01 level of probability.

controlled by the nitrogen uptake rate of the beech tree roots. Applying this concept to the submerged marsh soils, we can postulate that the emergent macrophytes control the mineralization rate and, therefore, the amount of ammonia present. This, in turn, affects the change in total soil nitrogen. Uptake by *T. latifolia, S. fluviatilis,* and *C. lacustris* accounted for a total of 1.0, 0.6, and 0.3%, respectively, of the total soil nitrogen at each of the locations.

The significant correlations with phosphorus are not unexpected; Patrick and Mahapatra (1968) reported that Bray P-2 available phosphorus is perhaps the best measure of phosphorus availability to lowland rice grown on submerged soils. What is surprising is the magnitude of the correlation coefficients, which indicates that the emergent macrophytes are perhaps the factor controlling the flux of available phosphorus in the soil during the growing season.

The significance of these correlations is threefold: (1) Total nitrogen and available phosphorus (Bray P-2) in the soil at Theresa Marsh appear to be adequate indicators of nutrient availability. This may be difficult to explain for nitrogen, but an equilibrium may exist between total nitrogen and ammonia. (2) Emergent macrophytes are acquiring their nutrients from the soil, as has been suggested by other investigators. (3) During the growing season the macrophytes are the controlling influence on available nutrients within the soil. Correlations were not attempted between the ash content of the vegetation and the pertinent cation changes within the soil because of the number of ash

constituents not measured in the soil. Superficially, however, their pattern seems to follow nitrogen and phosphorus, though perhaps at a much more rapid rate.

Thus the macrophytes can be thought of as nutrient pumps, taking in nutrients from the soil and immobilizing them, at least temporarily, in below- and aboveground structures. By taking in phosphorus, the plants may facilitate a greater exchange of phosphorus from the water to the underlying soil; this rate may be extremely slow, however (Pomeroy et al., 1969). Through plant uptake of cations such as potassium, ammonia, calcium, and magnesium, base exchange sites in the soil are freed and can, in turn, accept new cations moving through the interstitial water. The critical times for these transfers appear to be: (1) the period of peak dry-matter production (June to July); (2) the period when the plant shifts from above- to belowground storage (August); and (3) the period of senescence of aboveground structures, with the resulting loss of nutrients through leaching and decomposition.

Changes in soil-nutrient levels, water-nutrient levels, and accumulation of plant nutrients all tend to substantiate these theories. Neither calcium nor potassium levels in the plant tissue are available as yet, and these are necessary for further substantiation.

The marsh is more than just a simple emergent macrophyte—soil—water system. In addition to available nutrient levels, we need more information to predict the total elemental changes in the soil. For example, both total nitrogen and exchangeable calcium were closely correlated with soil organic matter, but little, if any, correlation was found between available phosphorus or potassium and any of the other measured soil parameters. Furthermore, to properly evaluate the nutrient-sink concept, we must measure the total amount and the flux of an element such as phosphorus in the soil.

Nitrogen displayed a variety of patterns. Denitrification reactions appeared to occur throughout the year, especially during the summer. At the peak of the growing season, nitrogen was constrained within the marsh, but outflow was never restricted sufficiently to prevent algal growth in downstream waters. Levels of inorganic nitrogen in the inflow waters and in the marsh never appear to be below limiting levels, and organic nitrogen serves as the prime mode of nitrogen transport out of the marsh, particularly from late fall to early spring.

The level of phosphorus in the marsh water was never low enough to become limiting; rather phosphorus concentrations were often many times those st for eutrophic waters. Phosphorus levels of water flowing out of the marsh w reduced noticeably during the growing season. We may speculate that, in comparison to other elements, phosphorus is taken up in the marsh throughout the entire year, except for the end-of-growing-season release that follows leaching and decomposition of primary producers. No direct relationship was found between available phosphorus in the soil and that flowing into and out of the marsh. Phosphorus accrued in the aboveground structures of the macrophytes when levels in the outflow water dropped. This suggests that much of the

phosphorus flowing into the marsh may be taken up by the primary producers, including algae and submergent and free-floating macrophytes, to be released later through leaching and decomposition.

Potassium, calcium, and magnesium concentrations throughout the year appeared dependent on emergent-macrophyte uptake and leaching loss, total respiration in the marsh, and the various physical and chemical characteristics of the water.

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REFERENCES

American Public Health Association, 1971, *Standard Methods for the Examination of Water and Wastewater,* 13th ed., Washington, D. C.

Amundson, R. W., 1970, Nutrient Availability of a Marsh Soil, M.S. Thesis, University of Wisconsin, Madison.

Bentley, E. M., III, 1969, The Effect of Marshes on Water Quality, Ph. D. Thesis, University of Wisconsin, Madison.

Bernard, J. M., 1973, Production Ecology of Wetland Sedges: The Genus *Carex, Pol. Arch. Hydrobiol.,* **20**: 207-214.

——, and J. G. MacDonald, 1974, Primary Production and Life History of *Carex lacustris, Can. J. Bot.,* **52**: 117-123.

Black, C. A. (Ed.), 1965, *Methods of Soil Analysis.* Part 2. *Chemical and Microbiological Properties,* American Agronomy Society, Madison, Wis.

——, 1968, Soil–Plant Relationships, 2nd ed., John Wiley & Sons, Inc., New York.

Boyd, C. E., 1971, The Dynamics of Dry Matter and Chemical Substances in a *Juncus effusus* Population, *Amer. Midland Natur.,* **86**: 28-45.

——, 1970a, Production, Mineral Accumulation, and Pigment Concentrations in *Typha latifolia* and *Scirpus americanus, Ecology,* **51**: 285-290.

——, 1970b, Losses of Nutrients During Decomposition of *Typha latifolia, Arch. Hydrobiol.,* **66**: 511-517.

——, 1970c, Influence of Organic Matter on Some Characteristics of Aquatic Soils, *Hydrobiologia,* **36**: 17-21.

——, 1969, Production, Mineral Nutrient Absorption and Biochemical Assimilation by *Justicia americana* and *Alternanthera philoxeroides, Arch. Hydrobiol.,* **66**: 139-160.

——, and L. W. Hess, 1970, Factors Influencing Shoot Production and Mineral Nutrient Levels in *Typha latifolia, Ecology,* **51**: 296-300.

——, and D. H. Vickers, 1971, Relationships Between Production, Nutrient Accumulation, and Chlorophyll Synthesis in an *Eleocharis quadrangulata* Population, *Can. J. Bot.,* **49**: 883-888.

——, and W. W. Walley, 1972, Production and Chemical Composition of *Saururus cernuus* L. at Sites of Different Fertility, *Ecology,* **53**: 927-932.

Buckman, H. O., and N. C. Brady, 1969, *The Nature and Properties of Soils,* 7th ed., The Macmillan Company, New York.

Buol, S. W., F. D. Hole, and R. J. McCracken, 1972, *Soil Genesis and Classification,* Iowa State University Press, Ames.

Cook, A. H., and C. F. Powers, 1958, Early Biochemical Changes in the Soils and Water of Artificially Created Marshes in New York, *N. Y. Fish Game J.,* **5**: 9-65.

Dixon, J. P., 1968, *Modern Methods in Organic Microanalysis,* Van Nostrand-Reinhold Company, New York.

Ellenberg, H., 1971, Nitrogen Content, Mineralization and Cycling, in Symposium on Productivity of Forest Ecosystems, Brussels, 1969, P. Duvigneaud (Ed.), United Nations Educational, Scientific, and Cultural Organization and International Biological Program.

Fiala, K., 1971, Comparison of Seasonal Changes in the Growth of Underground Organs of *Typha latifolia* L. and *Typha angustifolia* L., *Hidrobiologia,* **12**: 235-240.

Fried, M., and H. Broeshart, 1967, *The Soil–Plant System in Relation to Inorganic Nutrition,* Academic Press, Inc., New York.

Gerloff, G. C., and P. H. Krumbholz, 1966, Tissue Analysis as a Measure of Nutrient Availability for the Growth of Angiosperm Aquatic Plants, *Limnol. Oceanogr.,* **11**: 529-539.

Gosset, D. R., and W. E. Norris, Jr., 1971, Relationship Between Nutrient Availability and Content of Nitrogen and Phosphorus in Tissues of the Aquatic Macrophytes *Eichornia crassipes* (Mart) Solms., *Hydrobiologia,* **38**: 15-28.

Granert, W. G., Jr., 1973, The Algal Flora of Theresa Marsh, Washington and Dodge Counties, Wisconsin, M.S. Thesis, University of Wisconsin, Milwaukee.

Kaushik, N. K., and H. B. N. Hynes, 1968, Experimental Study on the Role of Autumn-Shed Leaves in Aquatic Environments, *J. Ecol.,* **56**: 229-244.

Keeney, D. R., 1973, The Nitrogen Cycle in Sediment–Water Systems, *J. Environ. Qual.,* **2**: 15-29.

Klopatek, J. M., 1974, Production of Emergent Macrophytes and Their Role in Mineral Cycling Within a Freshwater Marsh, M.S. Thesis, University of Wisconsin, Milwaukee.

Korelyakova, I. L., 1970, Chemical Composition of the Higher Aquatic Vegetation of Kiev Reservoir, *Hydrobiol. J.,* **6**: 15-21.

Lee, G. F., E. Bentley, and R. Amundson, 1970, *Effect of Marshes on Water Quality,* University of Wisconsin Water Chemistry Program, Occasional Paper, Madison, Wisconsin.

McNelly, J., and J. M. Klopatek, 1973, *Submergent Macrophytes in Theresa Marsh,* University of Wisconsin, Milwaukee Field Station, Bulletin 6, pp. 9-14.

Maystrenko, Yu. G., A. I. Denisova, V. M. Bagnyak, and Zh. M. Aryamova, 1969, The Role of Higher Aquatic Plants in the Accumulation of Organic and Biogenic Substances in Water Bodies, *Hydrobiol. J.*, **5**: 20-31.

Niering, W. A., 1968, The Ecology of Wetlands in Urban Areas, *Gard. J.,* **18**: 177-183.

Patrick, W. H., Jr., and I. C. Mahapatra, 1968, Transformation and Availability to Rice of Nitrogen and Phosphorus in Water-Logged Soils, *Adv. Agron.,* **20**: 323-359.

Planter, M., 1970a, Physico-Chemical Properties of the Water of Reedbelts in Mikolajskie, Taltuwisko, and Sniardwy Lakes, *Pol. Arch. Hydrobiol.,* **17**: 337-356.

——, 1970b, Elution of Mineral Components Out of Dead Reed *Phragmites communis* Trin., *Pol. Arch. Hydrobiol.,* **17**: 357-362.

Pomeroy, L. R., R. E. Johannes, E. P. Odum, and B. Roffman, 1969, The Phosphorus and Zinc Cycles and Productivity of a Salt Marsh, in Proceedings of the Second National Symposium on Radioecology, D. J. Nelson and F. C. Evans (Eds.), USAEC Report CONF-670503, pp. 412-419.

Ponnamperuma, F. N., 1972, The Chemistry of Submerged Soils, *Adv. Agron.*, **22**: 29-96.

Pringle, W. L., and A. L. van Ryswyk, 1967, Response of Reed Canary Grass on Sedge-Organic Soil to Fertility Levels and Temperature in the Growth Room, *Can. J. Plant Sci.*, **47**: 305-310.

Ramage, C. H., C. Eby, R. E. Mather, and E. R. Purvis, 1958, Yield and Chemical Composition of Grasses Fertilized Heavily with Nitrogen, *Argon. J.*, **50**: 59-62.

Reitemeier, R. F., 1957, Soil Potassium and Fertility, in *Soil, The Yearbook of Agriculture*, A. Stefferod (Ed.), pp. 101-106, Superintendent of Documents, U. S. Government Printing Office, Washington, D. C.

Ruttner, F., 1963, *Fundamentals of Limnology*, 3rd ed., University of Toronto Press, Toronto, Canada.

Sawyer, C. N., 1947, Fertilization of Lakes by Agricultural and Rural Drainage, *J. New Engl. Water Works Assoc.*, **61**: 109-127.

Schulte, E. E., and C. C. Olsen, 1970, *Wisconsin Soil Testing and Plant Analysis Procedures*, Soil Fertility Series, No. 6, Soils Department, University of Wisconsin, Madison.

Sculthorpe, C. D., 1967, *The Biology of Aquatic Vascular Plants*, St. Martin's Press, Inc., New York.

Stake, E., 1968, Higher Vegetation and Phosphorus in a Small Stream in Central Sweden, *Schweiz. Z. Hydrol.*, **30**: 353-373.

——, 1967, Higher Vegetation and Nitrogen in a Rivulet in Central Sweden, *Schweiz. Z. Hydrol.*, **29**: 107-125.

Stumm, W., and J. J. Morgan, 1970, *Aquatic Chemistry*, John Wiley & Sons, Inc., New York.

Van Dyke, G. D., 1972, Aspects Relating to Emergent Vegetation Dynamics in a Deep Marsh, North-Central Iowa, Ph. D. Thesis, Iowa State University, Ames.

Vollenweider, R. A., 1968, Scientific Fundamentals of the Eutrophication of Lakes and Flowing Waters with Particular Reference to Nitrogen and Phosphorus Factors in Eutrophication, DAS/CSI/68.27, Organization for Economic Cooperation and Development, Paris.

Walsh, L. M., and E. E. Schulte, 1970, Computer-Programmed Soil Test Recommendations for Field and Vegetable Crops, Soil Fertility Series, No. 5, Soils Department, University of Wisconsin, Madison.

Westlake, D. F., 1963, Comparisons of Plant Productivity, *Biol. Rev.*, **38**: 385-425.

Whittaker, R. H., 1970, *Communities and Ecosystems*, The Macmillan Company, New York.

CHANGES IN WATER CHEMISTRY AND PRIMARY PRODUCTIVITY OF A REACTOR COOLING RESERVOIR (PAR POND)

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ABSTRACT

Water chemistry and primary productivity of a reactor cooling reservoir have been studied for 8 years. Initially the primary productivity increased sixfold, and the dissolved solids doubled. The dissolved-solids increase appears to have been caused by additions of makeup water from the Savannah River and by evaporative concentration during the cooling process. As the dissolved-solids concentrations and the conductivity of makeup water leveled off, the primary productivity stabilized. Major cation and anion concentrations generally followed total dissolved solids through the increase and plateau; however, silica concentrations declined steadily during the initial period of increased plankton productivity. Standing crops of net seston and centrifuge seston did not increase during this initial period. The collective data show the effects of thermal input to a cooling reservoir, illustrate the need for limnological studies before reactor siting, and suggest the possibility of using makeup-water additions to power reactor cooling basins as a reservoir management tool.

Par Pond has served as an impoundment for reactor cooling water at the Savannah River Plant (SRP) since the 10-km² lake was established in 1958. Since 1965 a variety of ecological and limnological studies have been conducted on the lake. A recent examination of unpublished data from some of these studies indicated hitherto unsuspected changes in lake characteristics, primary productivity, and water chemistry which are apparently related to reactor operations. In this paper the observed changes are summarized, and possible connections to reactor operations and consequences for the reservoir community are discussed. Because data available were not initially collected for this purpose, some assumptions and extrapolations were made, but these are clearly indicated in the text or by notes with the tables.

LIMNOLOGICAL MEASUREMENTS

During the period from 1965 to 1970, standard limnological measurements were made; these included measuring temperature with a thermistor thermometer, conductivity with Whitney and Beckman RB3 meters, underwater illuminance with a submarine photometer, transparency with a Secchi disk, and solar insolation with a portable pyrheliograph. Net and total seston and dissolved solids (total and volatile) were determined as described by Marshall and LeRoy (1971), except that before 1968 net seston was obtained by pouring water samples through nylon bolting cloth with 64-μm mesh openings.

Water Quality

From 1966 to the present, water-quality parameters have been measured at the Savannah River Laboratory (SRL) in conjunction with experiments conducted on Par Pond. Water samples for these measurements were collected in a polyvinyl chloride water bottle and transferred to polyethylene bottles. Major cations and silica were determined by atomic absorption spectrometry. (For a summary of procedures, see Perkin–Elmer Corp., 1973.) Chlorides were determined by the mercuric thiocyanate method (Iwasaki et al., 1956). Sulfates and bicarbonates were determined by standard procedures (American Public Health Association, 1965). From 1969 to the present, phosphates and nitrates have been measured. Orthophosphate was measured by the stannous chloride method (American Public Health Association, 1965) in Par Pond water concentrated 5- to 10-fold by boiling. Nitrate was measured by the phenoldisulfonic acid method (American Public Health Association, 1965). Field measurements were frequently made of dissolved oxygen by the Winkler method (American Public Health Association, 1965), of pH with portable pH meters, of water color with a comparator, and of turbidity with a turbidimeter.

Primary Productivity

In 1965 net primary productivity was estimated by the oxygen-change (dark bottle–light bottle) method of Gaarder and Gran (1927) on 24-hr incubations in situ near the deepest part of the lake. In subsequent years the ^{14}C method of Steemann-Nielsen (1952) was used on 3- or 4-hr incubations during midday. Although details of techniques undoubtedly varied from year to year (since the productivity determinations were not conceived as a unified series), the differences were not large enough to invalidate comparisons. For example, in 1966 and 1967 a 1-ml ampul containing 10 μCi of ^{14}C bicarbonate was broken into each bottle to be incubated, whereas in 1969 a uniform spiking solution of 100 μCi/ml was prepared and dispensed in 100-μl quantities by automatic pipet. In 1966 and 1967 counting efficiencies were corrected by use of a ^{14}C toluene internal spike. In subsequent years available radiocarbon was determined by

counting an appropriately diluted spike in a scintillation vial under nearly the same conditions of geometry as the plankton samples. The diluted spike was counted with a blank filter. Scintillation counts were made in 1966 and 1967 on a Packard 4312 (subsequently on a Beckman LS233) instrument. Further details of the ^{14}C procedure are described by Marshall and Tilly (1971).

Several mathematical manipulations were necessary to make data comparable. Oxygen-change data for 1965 were converted to carbon equivalents assuming a photosynthetic quotient of 1.0. A comparison of methods in the summer of 1969 established that net productivity (estimated by the dark bottle–light bottle oxygen-change method) in Par Pond was not significantly different from its millimolar equivalent as measured by ^{14}C uptake (Tilly and Beyers, 1972). Integrals were calculated assuming that a daily integral was equal to three times a midday 3-hr uptake value (4-hr results were prorated), as had been found in experiments performed in 1967 (Tilly, 1973). Vollenweider and Nauwerck (1961) described a similar finding for Lake Erken. In 1969 and 1970 productivity data were collected for plankton taken from a depth of 2m rather than from various depths (Marshall and Tilly, 1971). Experiments indicated that the integrals calculated by the two methods differed less than ±5%, but the curves have different shapes (Tilly, 1973).

In 1965, 1967, and 1969 to 1973, data representing all seasons were used in estimating the annual mean. In 1966 the only data available were the results of four experiments in November. These were included for comparison after it was noted that in 1969 and 1970 the November means were roughly equal to the annual averages. No productivity measurements were made on Par Pond in 1968.

PAR POND

Par Pond is a 10-km^2 reservoir impounding water from a tributary of the Savannah River, Lower Three Runs Creek. Par Pond was constructed in 1958 for use as a reactor cooling basin by the U. S. Atomic Energy Commission's Savannah River Plant. A program of limnological research was begun in 1965.

Some information about the reservoir and its relationship to the reactor system has been published (Marshall and LeRoy, 1971; Marshall and Tilly, 1971; Gibbons, 1970; and Boyd, 1970), but some features of its basic limnology were heretofore unreported. Par Pond has a mean depth of 6.2m, a maximum depth of 16m, a volume of 6.2×10^7 m^3, and a shoreline development of 4.7. During a typical year in the main (unheated) body of the lake, water color averages about 12.7 Pt–Co units; turbidity, about 1.0 Jackson turbidity unit (JTU); Secchi transparency, 2.5m; surface temperature, about 22°C; and epilimnion oxygen, about 8.6 mg/l. Annual profiles of temperature and dissolved oxygen for a cool station in Par Pond in 1960 are shown in Fig. 1. Par Pond apparently behaves like a warm monomictic lake, stratifying from April to October and

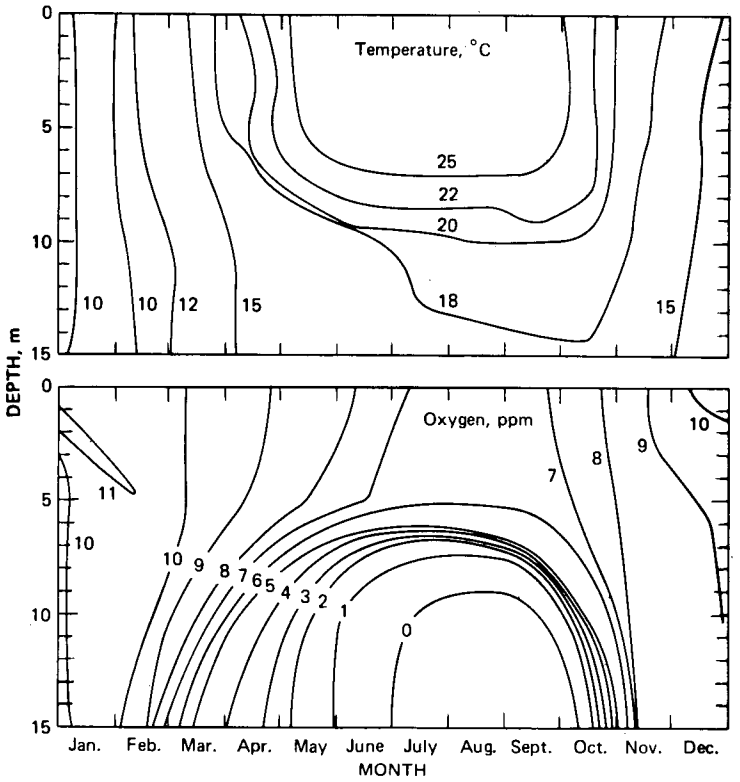

Fig. 1 Depth–time profiles of temperature and oxygen in Par Pond (January to December, 1960).

except in the arm receiving the thermal effluent, nearly homothermous the remainder of the year. As remarked by Boyd (1970) and Marshall and LeRoy (1971), the littoral community of Par Pond is unusually well developed for lakes in this vicinity, probably because water levels remain relatively stable. Large drawdowns caused by water consumption do not occur, and deficits are made up with water pumped from the Savannah River.

RESULTS AND DISCUSSIONS

Nutrient Levels

The most striking limnological change was the approximately sixfold increase and subsequent leveling in plankton primary productivity observed from 1965 to 1973 (Fig. 2). As illustrated by Fig. 3, productivity as measured by ^{14}C techniques was very highly correlated with conductivity ($r = 0.976$; $p < 0.001$; 6 df). As could be expected, good correlations were also found with total dissolved

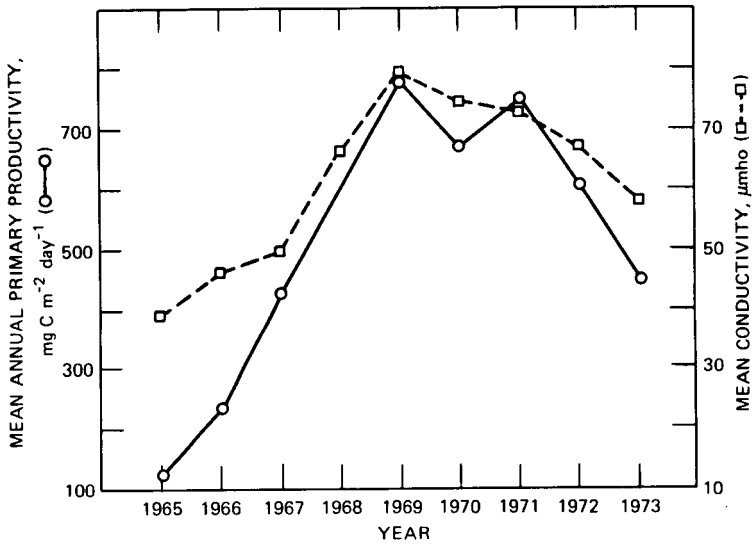

Fig. 2 Conductivity and annual plankton productivity in Par Pond (1965 to 1973).

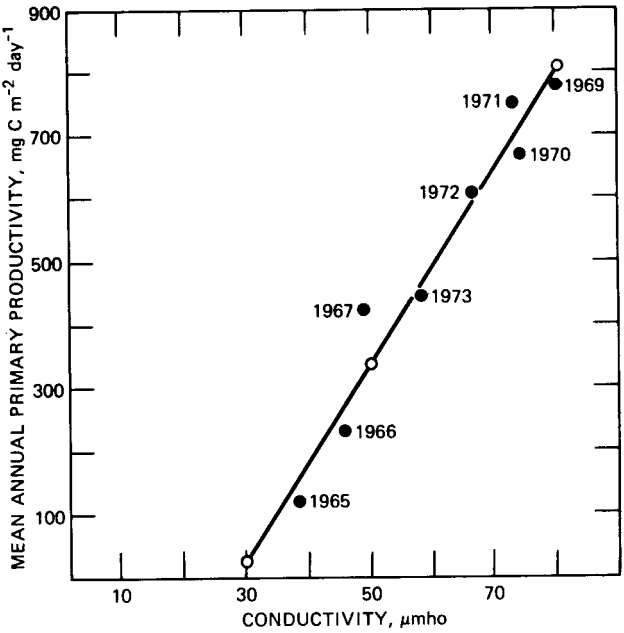

Fig. 3 Plankton productivity vs. conductivity of Par Pond (1965 to 1973). P = 15.6 µmho − 445.2; r = 0.976. ○ = least-squares points. ● = data points.

TABLE 1

PRODUCTIVITY–NUTRIENT CORRELATIONS

Nutrient	r	p*	df
Ca^{2+}	0.85	<0.01	6
Mg^{2+}	0.43	NS	6
Na^{+}	0.93	<0.1	6
K^{+}	0.81	<0.1	6
Cl^{-}	−0.12	NS	6
SO_4^{2-}	0.88	<0.01	6
HCO_3^{-}	0.89	<0.01	6
Si^{4+}	−0.73	<0.05 > 0.02	6

*NS, not significant

solids and salinity. These correlations were not as strong as for conductivity, however. Productivity correlated significantly with all major cations and anions except chloride and magnesium (Table 1). A negative correlation was found between productivity and silica concentration. Data were inadequate for computing correlations with phosphorus or nitrogen.

The productivity increase clearly appears to be a function of a general increase in nutrients. Two closely related aspects of reactor operation appear to be involved: (1) use of Savannah River water in makeup additions and (2) progressive evaporative concentration of recycled cooling water.

At the reactor, water from the Savannah River is continuously added to Par Pond water before it passes through the heat exchangers. Relative volumes added per year from 1965 to 1973 are given in Table 2. River water added annually has ranged from volumes equivalent to 0.36 to 1.25 times the average rainfall to the Par Pond drainage basin (93×10^6 m^2) and from 3 to 10 times the volume of direct rainfall into the lake. Considering the magnitude of makeup additions, it is not surprising that Par Pond water resembles Savannah River water in composition and ionic concentrations. Except for chlorides and bicarbonates, concentrations of major ions in Par Pond correlated significantly with those from the Savannah River (Table 3). Conductivities of the two systems also correlate significantly. The upward trend in Par Pond concentrations is in response to a similar steady increase in Savannah River concentrations.

Further evidence for dependence of Par Pond on the Savannah River comes from comparison with other aquatic systems in the SRP area. Surface waters in the Southeastern Coastal Plains are ordinarily relatively low in dissolved solids (Livingstone, 1963; Polisini, Boyd, and Didgeon, 1970; Tilly, 1973). Par Pond and the Savannah River alone among SRP area surface waters exhibit salinities of moderate concentrations. Pond B was a portion of the Par Pond reactor cooling system until 1964, when the reactor it served was shut down. During cooling operations Par Pond water was pumped to Pond B via the reactor, with overflow

TABLE 2

ANNUAL AVERAGES OF MONTHLY MEANS OF MEASUREMENTS MADE ON PAR POND EPILIMNION (0-7 MEANS OR COMPOSITES)*

	1965	1966	1967	1968	1969	1970	1971	1972	1973
Inorganic Ion Concentrations									
Ca, mg/l	2.07 ± 0.12	1.95 ± 0.14	2.11 ± 0.10	2.68 ± 0.30	3.18 ± 0.32	3.74 ± 0.27	3.37 ± 0.22	3.28 ± 0.16	3.28 ± 0.22
Mg, mg/l	1.20 ± 0.14	1.24 ± 0.04	1.24 ± 0.02	1.23 ± 0.03	1.67 ± 0.13	1.38 ± 0.02	1.19 ± 0.04	1.13 ± 0.03	0.96 ± 0.03
Na, mg/l	3.77 ± 0.14	5.33 ± 0.24	6.40 ± 0.09	6.51 ± 0.11	7.75 ± 0.22	7.63 ± 0.09	6.73 ± 0.23	6.29 ± 0.14	5.29 ± 0.24
K, mg/l	1.10 ± 0.03	1.17 ± 0.06	1.35 ± 0.03	1.32 ± 0.03	1.50 ± 0.04	1.56 ± 0.04	1.30 ± 0.04	1.34 ± 0.08	1.14 ± 0.11
Cl, mg/l	1.84†	3.9‡	4.7 ± 0.2	6.4 ± 1.0	7.0 ± 1.1	18.8 ± 5.4	9.5 ± 2.6	8.4 ± 1.7	5.2 ± 0.5
SO_4, mg/l	1.73†	2.0 ‡	4.1 ± 0.5	3.4 ± 0.5	5.3 ± 1.4	5.1 ± 0.7	3.4 ± 0.5	4.3 ± 1.1	3.6 ± 0.3
HCO_3, mg/l	17.5†	17.0	17.8 ± 0.6	17.4 ± 0.6	22.1	22.7	22.4 ± 0.3	20.4 ± 0.4	16.9 ± 0.5
Si, mg/l		2.87 ± 0.24	2.99 ± 0.16§	2.30 ± 0.43	1.75 ± 0.10	0.87 ± 0.09	1.72 ± 0.17	2.45 ± 0.11	1.8 ± 0.3
PO_4–P, μg/l					11 ± 2	6 ± 2	6 ± 2	12 ± 2	10 ± 3
NO_3–N, μg/l					15 ± 3	39 ± 11	33 ± 10	10 ± 2	16 ± 2
Physical Measurements									
Salinity, mg/l	29.2†	32.6	37.8	38.9	48.5	60.9	49.4	45.7	36.6
Conductivity, μmho/cm	38.5	45.7	49.2	66.0	79.2	74.4	73.0	66.5	57.6
TDS,¶ mg/l	33.5	36.7	37.1	42.7	47.4	51.7	46.5	44.5	35.6
NVDS,¶ mg/l	20.4	25.0	27.5	31.1	34.6	38.1	34.1	31.2	22.2
VS,¶ mg/l	13.1	11.7	9.6	10.4	12.8	13.6	12.4	13.3	13.4
Rainfall, in.	45.04	48.96	47.63	37.71	38.64	43.80	59.90	46.80	55.71
Relative makeup water**		3.452	3.488	1.453	1.000	1.156	1.070	1.126	1.096
Relative water replacement††		1.870	1.855	1.110	1.000	1.138	.417	1.194	1.448

TABLE 2 (continued)

	1965	1966	1967	1968	1969	1970	1971	1972	1973
Biotic Measurements									
Plankton productivity, mg C m^{-2} day^{-1}	118	229‡‡	424		777	665	746	604	443
Centrifuge seston (ash-free), mg/l	0.78	1.02	0.90	0.71	0.75	0.76	0.50	0.74	0.73
Net seston (ash-free), mg/l	0.22	0.34	0.12	0.30	0.23	0.15	0.11	0.04	0.07

*Except where noted, mean values are annual averages of epilimnion samples with monthly values equally weighted. Salinity is computed according to the method of Hutchinson (1957). Rainfall data are averages of data from measurements at two gages located within 2 miles of the lake at 100-P and Barricade 3.

†Data from St. John (1974), supplemented by information from routine monitoring.

‡April to August mean only.

§Mean of 8 months; June to January.

¶TDS is total dissolved solids, NVDS is nonvolatile dissolved solids, VS is volatile solids.

**Relative makeup water is the ratio of total makeup water added in any year to the amount added in 1969.

††Relative water replacement is the total water calculated to be delivered to Par Pond from rainfall, runoff, and makeup additions divided by the lowest sum recorded. Blanks indicate missing data.

‡‡Mean of three November experiments, combining the average rates (±10%) for 1968, 1969, and 1970.

returning to the northernmost arm of Par Pond. After 1964 the 7.7×10^5 m^2 lake was allowed to equilibrate with its own drainage basin and became independent of the Par Pond system. Sampling in Pond B was less frequent than in Par Pond, but it is clear that, although its water was relatively similar to that of Par Pond in 1964 and 1966, Pond B became progressively more dilute after reactor shutdown (Table 4). In addition, the relative ionic composition has shifted from bicarbonate domination to the chloride domination characteristic of most SRP area Coastal Plain waters (Table 5). These data further support the contention that observed increases in Par Pond nutrients are related to reactor makeup additions rather than to local influences of drainage or microclimate.

The changes in Savannah River water are probably associated with changes in the industrial and municipal pollution of the river upstream of the SRP. Degradative alterations in the condition of the river upstream of the SRP were detected about 1969 and are documented in a series of reports by the Institute of Paper Chemistry (1960–1973) and by the Academy of Natural Sciences of Philadelphia (1952 et seq.). The recent period of leveling and decline of ion concentrations and plankton productivity in Par Pond (Table 2) is coincident with the establishment of several primary and secondary waste-treatment facilities along the Savannah River above SRP.

Although makeup additions are a dominant source of nutrients to the reservoir, more than just nutrient input may be involved in the observed eutrophication. Productivity–concentration correlations are statistically weaker in relation to Savannah River water than in relation to Par Pond. Stronger evidence comes from ratios of Par Pond concentrations to Savannah River concentrations. Ratios calculated for the 1965 to 1970 interval (Fig. 4) show a general increase, with average values exceeding 1.0 during the period of highest productivity (and conductivity) and lowest makeup water additions. A few bioassay experiments were conducted in 1971 using 10-fold evaporative concentrates of Par Pond water. Additions of 100 μl of concentrate to bottles of Par Pond plankton from a depth of 2 m resulted in an average increase in ^{14}C uptake of 23% over controls. Together these observations suggest that evaporative concentration of Par Pond water occurs during recirculatory cooling and that resultant increases in nutrients stimulate primary productivity.

The correlations and observations described do not implicate any particular nutrient in the productivity changes. Experiments performed in the summer of 1971, a year when Par Pond plankton productivity was near its peak, single out only phosphate in ^{14}C uptake stimulation among some 18 nutrients tested alone or in combination (Seybert and Tilly, 1972).

The decline in silica in Par Pond during the first 6 years is interesting considering that the dominant producer organisms in Par Pond are diatoms. Schelske and Stoermer (1971) report changes in the diatom flora paralleling a decline in silica concentrations in Great Lakes water. They believe the decline in silica may be associated with eutrophication-induced increases in diatom

TABLE 3

PAR POND–SAVANNAH RIVER CORRELATIONS
(1965-1970)

	r	p	df	Precision
Ca^{2+}	0.896	<0.02	4	0.06 mg/l
Mg^{2+}	0.989	<0.002	4	0.04 mg/l
Na^{+}	0.980	<0.001	1	0.12 mg/l
K^{+}	−0.933	<0.01	1	0.02 mg/l
Cl^{-}	0.471	NS	4	0.09mg/l
SO_4^{2-}	0.964	<0.01	4	0.9 mg/l
HCO_3^{-}	−0.194	NS	4	0.9 mg/l
Conductivity	0.929	<0.01	4	1.3 μmho
Total dissolved solids	0.555	NS	4	3 mg/l

TABLE 4

CHANGES IN MAJOR IONS IN POND B
(1963-1973) (mg/l)

	1964	1966	1967	1971	1972	1973
Ca^{2+}	3.60	1.79	1.66	1.31	1.72	3.04
Mg^{2+}	2.25	0.91	0.72	0.72	0.62	0.52
Na^{+}		2.06	2.03	2.53	2.94	1.60
K^{+}		0.75	0.81	0.69	0.71	0.40
Cl^{-}	2.98	4.1	2.78	3.0	2.2	<2.42
SO_4^{2-}	2.1	2.1	3.2	0.4	1.0	2.2
HCO_3^{-}	15.5	7.2	4.6	6.1	6.8	6.6
Si^{4+}	2.49	0.52		0.42	0.88	0.52
Salinity	29.0*	18.9	15.8	14.8	16.0	16.8

*Assumes 1966 values for K^{+} and Na^{+}.

productivity and subsequent losses of silica (in diatom frustules) to the sediments. A similar phenomenon may have been occurring in Par Pond in association with the eutrophication there. By contrast, silica concentrations in the Savannah River during the interval showed no trend.

Standing Crops

Although plankton primary productivity increased in association with nutrient increase, standing crops of plankton evidently did not. Although bacteria, detritus, and naked flagellates are also present, a significant fraction of the seston in Par Pond is phytoplankton. Important changes in the phytoplankton crop should have been reflected in changes in seston fractions. Table 2

TABLE 5

IONIC COMPARISON OF SRP AREA AQUATIC SYSTEMS (1971-1972)

Ion	Concentration, meq%			
	Par Pond	Savannah River	Pond B	7 ponds*
Ca^{2+}	12.5	9.4	16.5	9.3
Mg^{2+}	7.6	9.6	11.9	10.5
Na^{+}	22.5	24.3	25.8	25.7
K^{+}	2.6	3.2	3.9	3.7
Cl^{-}	19.4	18.1	15.8	28.6
SO_4^{2-}	6.8	9.7	3.2	14.7
HCO_3^{-}	28.3	25.2	22.8	7.3
PO_4^{3-}	1.6	3.6	0.0	0.0
$NO_3(N)^{-}$	0.2	0.8	0.0	2.4

*Means of values obtained from seven local Coastal Plain ponds.

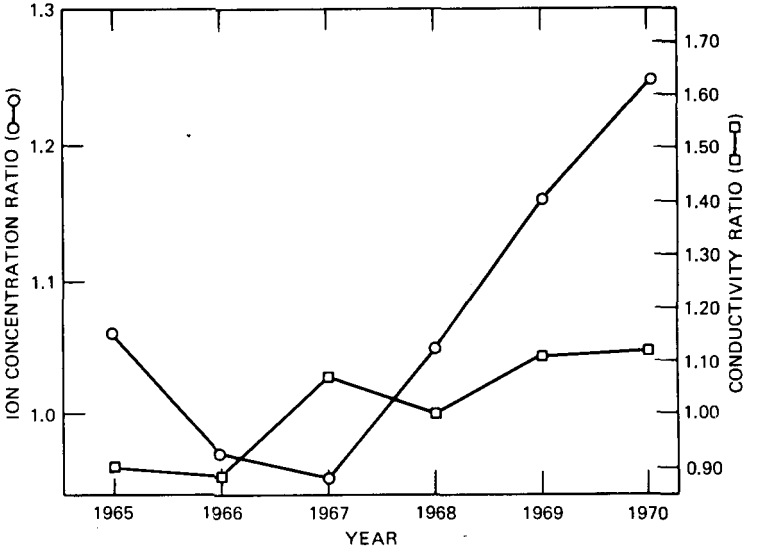

Fig. 4 Mean ratios of ion concentrations and conductivities of Par Pond to Savannah River (1965 to 1970).

shows that annual means for total seston did not follow plankton productivity but held fairly constant. The mean of annual means was 0.76 ± 0.05 mg/l ash-free dry weight. Net seston, while somewhat more variable in annual average, showed no clear trend in relation to primary productivity or in relation to total seston. The average of annual means for net seston was 0.18 ± 0.03 mg/l ash-free

dry weight. Volatile dissolved solids averaged 12.2 ± 0.05 mg/l, with no trend during the period.

Eutrophication and Succession

Margalef (1963) and Odum (1969) have proposed models in which the structural and functional changes in ecosystems during succession are equated to changes in "maturity." A lake undergoes a successional process, trending toward a steady-state terrestrial climax as it fills with biological and erosional sediments. According to these models both productivity (P) and standing crop (B) typically increase with time and then level off, and the ratio of P to B ordinarily decreases with time. In Par Pond, however, ratios based on productivity per unit of total seston per square meter steadily increased from 0.03 in 1966 to 0.18 in 1969 because P increased and B (as estimated by seston crop) remained more or less constant.

If P-to-B ratios are to be applied to the entire system, biomass information for littoral and benthic organisms should be included. Unfortunately, few data on standing crops of littoral and benthic fauna are yet available for Par Pond. Par Pond macrophytes are abundant. Their annual productivity is probably at least 370 mg C m^{-2} day^{-1} (calculations based on data from Boyd, 1974). General observations indicate a steady increase in macrophyte standing crops from 1966 to the present, but specific data are lacking. Even if macrophyte biomass were included, however, the P-to-B ratio would not be lowered significantly because macrophyte productivity increases at least linearly with standing crop.

If productivity increased while seston biomass remained constant, what became of the extra organic matter manufactured? It does not appear as an increase in the standing crop of planktonic consumers nor in dissolved organic matter. If the extra organic matter settled out to decompose on the bottom, the hypolimnetic oxygen deficit should have increased significantly since 1965. Depth–time diagrams of oxygen do not show any such trend, however. The zero isopleths in 1965 and 1970 persisted from mid-June to mid-October and descended from 8.5 m in 1965 to 9 m in 1970.

If extra organic matter settled to the bottom without being decomposed, the accumulation during the 6 years would be less than 2.5 cm of unconsolidated debris. Par Pond cores include about 20 to 25 cm of lacustrine deposits (Alberts, 1974). Allowing for some consolidation, anaerobic decomposition, and mixture with inorganic sediments, the organic accumulation would be difficult to see.

Another possibility for which indirect evidence is available is that "excess" food has been channeled to higher consumers, such as fish and turtles. According to this hypothesis, productivity increases appear in increased growth of phytoplankton, which supports an increased growth of zooplankton, which, in turn, supports an increased growth of fish.

Turnover of the lower trophic levels increases, but standing crops do not. Gibbons (1970; 1974) reported enhanced growth of Par Pond fish and turtles

and suggested that this growth is due to an increased supply of higher quality food available in Par Pond by contrast to other aquatic habitats in the area.

Continuing observations of growth rates of top carnivores during the current leveling and decline in plankton productivity will provide a partial test of the turnover hypothesis. The opportunity that exists at Par Pond to alter makeup water additions can be used to test other hypotheses concerning the relation between nutrient input, turnover, and trophic dynamics in a way that has relevance to reactor operations and to reservoir management.

REFERENCES

Academy of Natural Sciences of Philadelphia, 1952 et seq., Savannah River Biological Survey South Carolina and Georgia, Philadelphia, Pa.

Alberts, J. A., 1974, Argonne National Laboratory, personal communication.

American Public Health Association, 1965, Standard Methods for the Examination of Water and Wastewater, 12th ed., Washington, D. C.,

Boyd, C. E., 1974, Auburn University, personal communication.

——, 1970, Production, Mineral Accumulation and Pigment Concentrations in *Typha latifolia* and *Scirpus americanus, Ecology,* **51**: 285-290.

Gaarder, T., and H. H. Gran, 1927, Investigations of the Production of Plankton in Oslo Fjord. *Rapp. Procès-Verbaux Reunions, Cons. Perma. Int. Explor. Mer,* **42**: 1-48.

Gibbons, J. W., 1974, Savannah River Ecology Laboratory, personal communication.

——, 1970, Reproductive Dynamics of a Turtle *(Pseudemys scripta)* Population in a Reservoir Receiving Heated Effluent From a Nuclear Reactor, *Can. J. Zool.,* **48**: 881-885.

Hutchinson, G. E., 1957, *A Treatise on Limnology,* Vol. 1, John Wiley & Sons, Inc., New York.

Institute of Paper Chemistry, 1960-1973, A Biological Study of the Savannah River in the Vicinity of Augusta, Georgia, Appleton, Wisc.

Iwasaki, I., S. Utsumi, K. Hagino, and T. Ozawa, 1956, A New Spectrophotometric Method for the Determination of Small Amounts of Chloride Using the Mercuric Thiocyanate Method, *J. Chem. Soc. Japan,* **29**: 860-864.

Livingstone, D. A., 1963, Chemical Composition of Rivers and Lakes, in *The Data of Geochemistry,* M. Fleischer (Ed.), 6th ed., Chap. G, Professional Paper 440-G, U. S. Geological Survey.

Margalef, R., 1963, On Certain Unifying Principles in Ecology, *Amer. Natur.,* **97**: 357-374.

Marshall, J. S., and J. H. LeRoy, 1971, Iron, Manganese, Cobalt, and Zinc Cycles in a South Carolina Reservoir, in Radionuclides in Ecosystems, Proceedings of the Third National Symposium on Radioecology, May 10-12, 1971, Oak Ridge, Tenn., D. J. Nelson (Ed.), USAEC Report CONF-710501-P1, pp. 465-473.

——, and L. J. Tilly, 1971, Temperature Effects on Phytoplankton Productivity in a Reactor Cooling Pond, in Radionuclides in Ecosystems, Proceedings of the Third National Symposium on Radioecology, May 10-12, 1971, Oak Ridge, Tenn., D. J. Nelson (Ed.), USAEC Report CONF-710501-P1, pp. 645-651.

Odum, E. P., 1969, The Strategy of Ecosystem Development, *Science,* **164**: 262-270.

Perkin-Elmer Corp., 1973, *Analytical Methods for Atomic Absorption Spectrometry,* Norwalk, Conn.

Polisini, J. M., C. E. Boyd, and B. Didgeon, 1970, Nutrient Limiting Factors in an Oligotrophic South Carolina Pond, *Oikos,* **21**: 344-347.

Schelske, C. L., and E. F. Stoermer, 1971, Eutrophication, Silica Depletion, and Predicted Changes in Algal Quality in Lake Michigan, *Science* **173**: 423-424.

Seybert, D., and Tilly, L. J., 1972, Savannah River Laboratory, E. I. du Pont de Nemours & Co., Inc., unpublished data.

Steeman-Nielsen, E., 1952, The Use of Radioactive Carbon (^{14}C) for Measuring Organic Production in the Sea, *J. Cons., Cons. Perma. Int. Explor. Mer*, **18**: 117-140.

St. John, J. 1974, Savannah River Plant, E. I. du Pont de Nemours & Co., Inc., personal communication.

Tilly, L. J., 1973, Comparative Productivity of Four Carolina Lakes, *Amer. Midland Natur.*, **90**: 356-365.

—, and R. S. Beyers, 1972, Savannah River Laboratory, E. I. du Pont de Nemours & Co., Inc., and University of Georgia, unpublished data.

Vollenweider, R. A., and A. Nauwerck, 1961, Some Observations on the ^{14}C Method for Measuring Primary Production, *Verh. Int. Verein. Limnol.*, **14**: 134-139.

MINERAL PATHWAYS IN SMALL APPALACHIAN STREAMS

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ABSTRACT

Nutrient contents of benthic organisms in streams draining four small watersheds were examined. The watersheds, which were located in the southern Appalachian mountains, were each covered in a different vegetation type. Crayfish and salamanders were responsible for most of the standing-crop biomass in the detritivore and predator compartments, respectively, and also account for most of the fluxes in their compartments. They are important in the nutrient flow of small streams because they form a sink in the remineralization process. An increase in potassium concentrations and a decrease in calcium and magnesium concentrations were associated with an increase in trophic levels. Since the food material was richer in calcium and magnesium than in potassium, detritivores concentrated proportionately more potassium than calcium or magnesium. The principal mechanism of potassium release from detritus was through leaching. For calcium and magnesium, which are chemically bound in leaf tissue, the principal mechanism for release was the feeding activity of detritivores.

Since the early 1950s, the allochthonous input of detritus into running water has received much attention. Teal (1957) attributed 75% of the total energy input of Root Spring, Mass., to allochthonous detritus. Thirty percent of the food of invertebrates in Linesville Creek, Penn., was terrestrial detritus (Cummins, Coffman, and Roff, 1966). Nelson and Scott (1962) estimated that primary consumers in the Middle Oconee River, Ga., derived 66% of their energy from allochthonous detritus. Woodall and Wallace (1972) observed that certain herbivorous stoneflies were more abundant in streams receiving large amounts of deciduous detritus than in adjacent streams flowing through an old field and a pine plantation.

Bick (1959) reported that dense populations of stoneflies and crustaceans play an important role in the degradation of fallen leaves. Maciolek (1966)

found that 40 to 80% of the fine suspended organic matter in a California mountain stream was allochthonous. It has also been shown that benthic organisms are most abundant in winter when leaf input is greatest (Jones, 1950; Hynes, 1961; 1963; Woodall, 1969).

It is evident, then, that the stream subsystem is supported primarily by detritus input from the surrounding watershed. Since most nutrient losses from the watershed are via the stream, it is desirable to know the nutrient pathways within the stream subsystem and the nutrient content of stream organisms. Nutrient contents of terrestrial insects have recently appeared in the literature (Reichle, Shanks, and Crossley, 1969; Dietz, 1971), but there is almost no literature concerning nutrient content of aquatic insects.

Trophic activities of detritus-feeding arthropods and their predators are intimately involved in the distribution and transfer of nutrients during the decomposition process (Reichle, Shanks, and Crossley, 1969). Although food webs and energy budgets have been worked out for many aquatic systems (Jones, 1949; Hynes, 1970; Minshall, 1967; Odum, 1957; Teal, 1957; Welch, 1967), there is still inadequate information on the ingestion and egestion rates of aquatic organisms; therefore most of the fluxes used in this study were taken from the literature. Small streams are in many ways analogous to the adjacent soil–litter communities, and it is in the terrestrial realm that most work on rates of nutrient uptake by invertebrates has been done (Van Hook, Reichle, and Auerbach, 1970; Moulder, Reichle, and Auerbach, 1970; Kowal and Crossley, 1971; Gist, 1972).

The objectives of our research were to determine the whole-body concentrations of calcium, potassium, and magnesium in the major benthic stream fauna and to describe the pathways of these minerals in four small streams flowing through different cover types.

STUDY AREA

The Coweeta Hydrologic Laboratory, established by the U. S. Forest Service in 1934, is located in the Southern Appalachians in western North Carolina. Four watersheds were selected within an area of less than 1 mile^2. They were called the old-field, hardwood, white-pine, and coppice watersheds. Each stream was monitored by a gaging station at a v-notch weir.

The old-field watershed had been clear-cut in 1941 and 1958. After the 1958 cutting, the watershed was planted in Kentucky 31 fescue, which was killed with herbicide in 1966 and 1967. Since April 1968 the vegetation has been allowed to revert naturally to the hardwood forest. The hardwood-watershed vegetation has not been disturbed since the laboratory was established. The white-pine watershed was planted in white pines (*Pinus Strobus* L.) in 1956, after several years of annual clear-cutting. The coppice forest was a result of treatments in 1940 and 1962 in which all woody vegetation was cut and left in place. Woodall

and Wallace (1972) have described the vegetation of the watersheds in more detail.

The streams were about ½ m wide in the area where benthic fauna were sampled, but occasionally their width approached 2 m. Water depth ranged from less than 3 cm in areas where the stream bed was wide to about 15 cm in narrow areas.

METHODS

The lower portion of each stream (300 to 400 m) was divided longitudinally into four sections. A stratified random-sampling technique was used for quantitative samples (see Woodall and Wallace, 1972). Sampling began at the weir and proceeded toward the source so that no substrate would be disturbed before it was sampled. One sample was collected from each section of each stream monthly from Aug. 12, 1968, to July 18, 1969. A similar set of samples was collected at irregular intervals from Nov. 9, 1970, to Oct. 28, 1971. During the 1970-to-1971 period, qualitative samples were also collected.

A Surber square-foot sampler (Usinger, 1963) with a nylon mesh of 17 threads per centimeter was used for sampling. Since rocks and sand could be worked by hand to a depth of several inches and since most escapement of larger animals could be seen in the clear water, we felt that the Surber sampler was the best piece of equipment for these collections. The sampler was placed in the deepest part of the stream at each location, and the substrate within the sampler was disturbed by hand. The sampler was removed from the stream when it appeared that all detritus and benthic organisms had been washed into the net. Samples were transferred to a plastic bag, stored in crushed ice, and returned to the laboratory, where they were processed within 24 hr. Each sample was washed in a sieve of 10 meshes/cm (Weber, 1973), and the retained organisms and detritus were separated by hand. We feel that additional refinements in the collecting of smaller insects would not have changed their share of the measured nutrient flux enough to effect the conclusions of the study. Samples were dried at 105°C for 24 hr and desiccated over $CaCl_2$ at least 24 hr to ensure constant weight.

Densities were determined from quantitative samples, but it was also necessary to sample qualitatively to obtain enough organisms for stomach and nutrient analyses.

Samples were digested in concentrated HNO_3, analyzed on an atomic absorption spectrophotometer, and then burned in a mixture of acetylene and breathing air. One percent lanthanum chloride was added to the samples and blanks for magnesium and calcium analysis to suppress interference of phosphate and sulfate ions.

RESULTS AND DISCUSSION

The stream system was divided into a generalized five-compartment model (Fig. 1). Primary producers were put into two compartments, detritus and periphyton (attached algae). Since fungi seemed to be of only minor importance in experimentally manipulated leaves (Woodall, 1972), they were not included as part of this model.

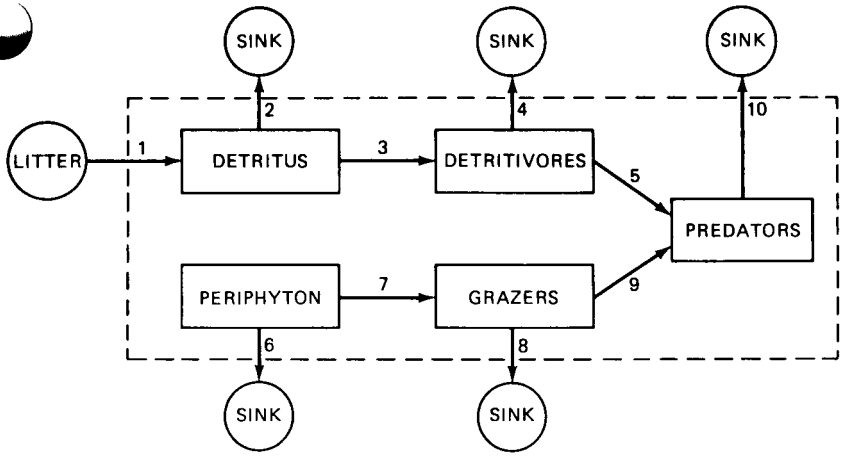

Fig. 1 General food-web diagram of a small southern Appalachian stream.

The consumers were put into three major compartments, detritivores, grazers, and predators. Organisms were assigned to these compartments on the basis of stomach analyses and of data in the literature. If an organism's diet consisted of various amounts of detritus, periphyton, and/or other animals, its standing crop was apportioned among the compartments based on the percentage of different types of food items eaten.

Sixteen groups of organisms are included in this discussion. All other organisms in the stream comprised less than 6% of the total biomass. Organisms their nutrient concentrations are listed in Table 1. Seasonal abundance and average dry weights per individual (Woodall, 1972) were combined to obtain standing-crop biomass. This was combined with nutrient concentrations to derive the standing crops of each element.

The rates of mineral leaching in leaves vary greatly from the rate of biomass loss. Potassium leaches almost immediately upon contact with water, but almost no calcium and magnesium leaching occurs (Woodall, 1971; 1972). Nutrient concentrations in litter and detritus are summarized in Table 2. The hardwood and coppice values were derived from the data of Cromack (1972) and Woodall

TABLE 1

NUTRIENT CONCENTRATIONS IN MAJOR TAXA

Taxon	Compartment*†	Calcium, mg/g	Potassium, mg/g	Magnesium, mg/g
Cambarus	D	100.3	1.9	2.3
Ephemerella	D, G	7.7	2.3	2.9
Stenonema	D	3.8	1.9	1.9
Paraleptophlebia	D	8.7	1.9	4.5
Lanthus	C	1.7	4.8	1.2
Peltoperla	D	3.5	1.8	1.6
Isogenus	P	3.9	1.7	1.2
Elmidae (Adult)	D	4.2	1.3	1.4
Elmidae (Larvae)	D	3.7	2.0	2.4
Rhyacophila	P, G, D	7.9	1.7	2.0
Diplectrona	P, G, D	3.5	2.7	1.4
Parapsyche	P, G, D	3.0	1.9	1.2
Chironomidae	P, G, D	7.9	2.1	3.3
Tipula	P, D	4.3	7.3	2.3
Eriocera	P, G, D	3.8	7.1	2.0
Desmognathus	P	39.3	2.3	2.2

*Abbreviations are D, detritivore; P, predator; and G, grazer.
†The proportion assigned to each compartment is reported in Woodall (1972).

(1972). Since no data were available on leaching of pine needles or old-field litter, deciduous values were used. Concentrations of nutrients in unleached litter were taken from the Cromack data for pine needles and from data collected by Coweeta personnel for old-field litter.

The product of the mass of detritus and the percent composition of nutrients yielded the standing crop of nutrients in the detritus of each stream. The ranges of the standing crops are presented in Table 3. Largest standing crops of calcium were found in the hardwood and coppice detritus since these two streams had the greatest detritus input, and calcium concentrations were also highest in this type of detritus (10 mg/g). The old-field stream had least detritus biomass and the lowest detrital calcium concentrations and, therefore, smallest standing crops of detrital calcium. The pine stream was intermediate between the old-field and the other two watersheds.

Potassium, the most mobile and readily leached of the cations (Carlisle, Brown, and White, 1966), was least abundant in detritus.

Both concentrations and absolute amounts of magnesium were lower in pine detritus than in the other watersheds. The largest amounts of magnesium occurred in hardwood and coppice detritus.

Table 2

CONCENTRATIONS OF NUTRIENTS IN VARIOUS TYPES OF STREAM DETRITUS AND GROUND LITTER

Nutrient and location	Old field	Hardwood	Pine	Coppice
Calcium, mg/g				
Litter	5.3	10.0	6.6	10.0
Detritus	5.3	10.0	6.6	10.0
Potassium, mg/g				
Litter	9.0	5.0	2.0	5.0
Detritus	1.0	1.0	1.0	1.0
Magnesium, mg/g				
Litter	2.0	2.0	1.0	2.0
Detritus	2.0	2.0	1.0	2.0

TABLE 3

RANGE OF SEASONAL STANDING CROPS OF CATIONS IN FOUR SMALL SOUTHERN APPALACHIAN STREAMS

Trophic level	Calcium, mg/g	Potassium, mg/g	Magnesium, mg/g
Detritus	100–2000	30–220	60–430
Detritivores	1–800	1–23	0.6–22
Detritivores*	1–12	1–10	0.6–6
Grazers	0.2–1.1	0.1–2	0.1–0.5
Predators	4–50	1–5	0.7–3.5
Predators†	0.3–1.9	0.4–2	0.2–0.7

*Detritivores excluding crayfish.
†Predators excluding salamanders.

Most calcium in the consumers was tied up in the detritivore compartment (Table 3) by crayfish, which concentrate calcium in their exoskeletons. That salamanders were also important concentrators of calcium was shown by the large standing crops of calcium in the predator compartment. These data are analogous to forest-floor decomposer populations, where a high percentage of primary consumers are Diplopoda. Reichle, Shanks, and Crossley (1969) suggested that in these systems the consumer trophic level represents a sink in the food-chain distribution of calcium. On the basis of our study, we suggest that, since crayfish and salamanders have a longer life span than other benthic organisms and since very little calcium is leached from leaves before they are consumed, these animals form a calcium sink not only within the food chain

but also in the entire remineralization process. Insects were responsible for less than 10% of the calcium in the consumer compartments.

The data presented in Table 4 show a decrease in calcium concentration with an increase in trophic level. More specifically, a decrease can be seen from total

TABLE 4

TROPHIC LEVEL CONCENTRATIONS OF CATIONS

Nutrient and trophic level	Old field	Hardwood	Pine	Coppice
Calcium, mg/g				
Detritus	5.3	10.0	6.6	10.0
Crayfish	100.3	100.3	100.3	100.3
Detritivores	63.6	51.8	68.4	51.9
Detritivores*	4.4	4.1	3.9	3.9
Grazers	5.2	4.3	4.2	4.3
Desmognathus	39.3	39.3	39.3	39.3
Predators	22.4	27.2	24.1	21.9
Predators†	2.9	3.7	3.0	3.5
Potassium, mg/g				
Detritus	1.0	1.0	1.0	1.0
Crayfish	1.9	1.9	1.9	1.9
Detritivores	3.0	2.2	2.2	2.6
Detritivores*	5.6	2.7	2.7	3.4
Grazers	4.9	4.1	3.2	3.3
Desmognathus	2.3	2.3	2.3	2.3
Predators	3.3	2.9	2.9	2.7
Predators†	4.4	2.9	3.6	3.9
Magnesium, mg/g				
Detritus	2.0	2.0	1.0	2.0
Crayfish	2.3	2.3	2.3	2.3
Detritivores	2.1	2.1	2.0	1.9
Detritivores*	2.1	1.9	1.8	1.9
Grazers	1.9	1.7	2.0	1.7
Desmognathus	2.2	2.2	2.2	2.2
Predators	2.0	1.9	1.8	1.8
Predators†	1.8	1.5	1.2	1.5

*Detritivores excluding crayfish.
†Predators excluding salamanders.

detritivores to total predators. These data mainly reflect calcium concentrations in the crayfish and salamanders. More interesting data are those on the decrease in calcium concentration in the detritus to insect detritivore to insect predator relationships. It is interesting to note that grazers frequently had higher calcium concentrations than detritivores. Diatoms were the most frequent algae observed

in grazer diets, and Vollenweider (1950) showed that high calcium concentrations were needed by some diatoms.

Like calcium, most potassium in the consumers was tied up in the detritivore compartment by the crayfish. This was because of their size rather than because of the concentration of potassium in the organism. The standing crop of potassium in consumer and detritus compartments (Table 3) was about an order of magnitude less than the standing crop of calcium. There was less potassium than calcium in the detritivore compartment because crayfish do not accumulate potassium as they do calcium. In this study detritivores showed at least a ofold increase in potassium concentration over the detritus compartment able 4).

If potassium concentrations in Table 4 are compared in the same manner as calcium concentrations, an increase is seen with an increase in trophic level. An exception is the insect detritivore to insect predator relationship in the old-field watershed. These data support the trophic level increase of potassium observed by Hasanen and Miettinen (1963) and by Pendleton et al. (1964).

Although the amount of magnesium in the detritus compartments was about twice the amount of potassium, the standing crops of magnesium and potassium in consumer trophic levels were similar. The salamanders contributed most of the magnesium to the predator compartment. Grazers represented a very small portion of magnesium in the total standing crop of consumers.

Even though differences in trophic levels were small, a trend toward a decrease in magnesium concentrations was associated with an increase in trophic levels (Table 4). Again, the relationship can best be seen by comparing total detritivores with total predators, insect detritivores with insect predators, or grazers with insect predators.

To establish fluxes into compartments in Fig. 1, we set limits on biomass ingestion rates using the literature as a guide. The rates of nutrient ingestion were then determined by multiplying the nutrient concentration in the food by the rate at which the food was eaten. The limits were necessarily wide because of the range of values in the literature. Egestion rates were also based on data in the literature. A few egestion rates of organic matter were found for aquatic insects, but no rates for cations exist. Egestion rates of cations cannot be determined from egestion rates of organic matter since various cations are retained in different amounts. Therefore we had to rely completely on the terrestrial erature for these rates. This is not as illogical as one might think. Small streams are, in principle, simply an aquatic extension of the forest floor. Organisms in streams perform the same function as and often have nutrient concentrations similar to organisms involved in terrestrial litter decomposition.

On the basis of the data in Table 5, lower and upper limits of 10 and 30% of body weight per day were placed on detritivore ingestion. A daily egestion rate of 60% of ingested organic matter was chosen for detritivores since *Pteronemobius*, a litter feeder, and *Pteronarcys*, a detritivore (Table 4), had rates of 60 and 62%, respectively. Egestion rates of 25% for calcium and 50% for

Table 5

INGESTION RATES OF CONSUMERS REPORTED AS PERCENT OF DRY BODY WEIGHT AND EGESTION RATES REPORTED AS PERCENT OF INGESTION

Organism	Ingestion rate	Egestion		References
		Rate	Commodity	
Detritivores				
Pteronarcys	30	62	Excreta	McDiffett, 1969
Peltoperla	10			Wallace, Woodall, and Sherberger, 1970
Litter saprovores	10–25			Gist, 1972
Stream detritivores	11			Kilmer and Cummins, 1971
Pteronemobius	40	60	Excreta	Van Hook, Reichle, and Auerbach, 1970
Diplopoda		26	Ca	Gist, 1972
Diplopoda		48	K	Gist, 1972
Grazers				
Banksiola	15	66	Excreta	Winterbourn, 1971
Predators				
Banksiola	5	30	Excreta	Winterbourn, 1971
Spiders	10	10	Excreta	Van Hook, Reichle, and Auerbach, 1970
Spiders	6–4	5	Excreta	Moulder, Reichle, and Auerbach, 1970
Spider		65	Ca	Gist, 1972; Van Hook, Reichle, and Auerbach, 1970
Spider		19–39	K	Gist, 1972; Van Hook, Reichle, and Auerbach, 1970
Stream invertebrates	2–8			Kilmer and Cummins, 1971
Amphibians	14–15			Darevskij and Terentev, 1967
Litter invertebrates	2–21			Gist, 1972
Lestes		63	Excreta	Fischer, 1967
Odonata		10	Excreta	Benke, 1972
Diplopoda		26	Ca	Gist, 1972
Coleoptera		38	Ca	Gist, 1972
Coleoptera		17	K	Gist, 1972

potassium were used; these rates were based on Gist's (1972) values for Diplopoda (Table 5) because nutrient concentrations in *Cambarus* were similar to those in Diplopoda. No egestion rates for magnesium were available for any trophic level.

The ingestion rate for an aquatic grazer (Table 5) was calculated from the data of Winterbourn (1971). The caddis fly larva he discussed ate algae during the first four instars and was predaceous during the last instar. During the grazing period the ingestion rate was 15% of body weight per day. The same ingestion rates used for detritivores were used for grazers since both are herbivorous and since 15% is within the limits placed on detritivore ingestion. No egestion ingestion rates could be determined because no nutrient data were available for periphyton.

Egestion from the grazer compartment was set as 66% of ingestion. This value, taken from Winterbourn's data, is very close to the egestion rates given by McDiffett (1969) for a detritivore and by Van Hook, Reichle, and Auerbach (1970) for a litter feeder (Table 5).

Ingestion rates for terrestrial invertebrate predators are given in Table 5. The food requirements of amphibians amount daily to some 15% of their own biomass (Darevskij and Terentev, 1967). The limits on predator ingestion rates were set at 5 and 15%, based on the caddis fly and amphibian rates from the literature.

The egestion rate of organic matter was set at 38% of ingestion for predators, based on the data of Winterbourn (1971), Benke (1972), and Fischer (1967). Egestion rates of 40% for calcium and 30% for potassium were based on the data of Gist (1972) and Van Hook, Reichle, and Auerbach (1970), which were determined using radioactive-tracer techniques. These values can now be assigned to the general model (Fig. 1). The fluxes quantified were ingestion and egestion. Most insect mortality was assumed to be predatory. Crayfish and salamander mortality and migration were not included in the model.

A detailed tabulation of the seasonal fluxes for each watershed can be found in Woodall (1972).

Leaching (pathway 2, Fig. 1) was responsible for about 20% of the weight loss from the detritus compartment. It accounted for 89% of the potassium flux from old-field detritus, 80% from hardwood and coppice detritus, and 50% from pine detritus. Additional fluxes of potassium were attributed to invertebrate feeding. Gist found that leaching (including microbial activity) from the litter accounted for a greater proportion of the total potassium flux than of the corresponding calcium flux. Best (1971) reported that 50 to 60% of potassium movement and about 35% of the calcium movement was due to leaching. Cromack (1972) and Carlisle, Brown, and White (1966) also showed that major potassium movement is through leaching.

Under laboratory conditions (Woodall, 1971; 1972) leaching accounted for only a small fraction of calcium and magnesium flux. Invertebrate feeding activity was responsible for most of the calcium and magnesium flux from

detritus. Calcium is found in plant cell walls where it reacts with pectic acid to form relatively insoluble salts in the middle lamella. Inside vacuoles, calcium precipitates as crystals of calcium oxylate and also forms insoluble salts in other ways (Salisbury and Ross, 1969). It is reasonable to believe that most calcium would be released to the water after the leaf was digested. Since the magnesium ion is bound in the center of the chlorophyll molecule (Salisbury and Ross, 1969), digestion probably plays a major role in the release of this element into the water.

Fluxes into the detritivore compartment (pathway 3) were considerably larger than fluxes into the predator compartment (pathways 5 and 9 combi[illegible] because of the lower ingestion rates of predators and a smaller compartment size. The cation that had the greatest flux into the detritivore compartment was calcium. The magnesium flux to detritivores was greater than the potassium flux in all watersheds except pine, where the two were the same. Peak fluxes in all watersheds corresponded to peaks in consumer biomass, and crayfish accounted for most of the consumer biomass. Fluxes into the predator compartment were usually lower than corresponding fluxes into the detritivore compartment. Fluxes to and from the grazer compartment contributed less than 10% (usually about 1 or 2%) of the total flux of any commodity.

Since Cromack's yearly input data for the hardwood and pine watersheds were available, we found it desirable to compare these data with our calculated total yearly ingestion of detritivores in these two stream areas. Calculated ingestion in the hardwood stream ranged from 101 to 302 g m^{-2} $year^{-1}$, and Cromack's litter input figure was about 270 g m^{-2} $year^{-1}$. Woodall (1969) reported that 30 to 40 g/m^2 of detritus remained in these streams in summer. Kilmer and Cummins (1971) suggested that 25% of leaf material was degraded by the stream's mechanical activity (abrasion and flushing) and by leaching (67 g in this example). This means that about 170 g of detritus should have been eaten by midsummer; this is near the middle of the range calculated.

In the pine stream the calculated ingestion was 141 to 424 g m^{-2} $year^{-1}$, and Cromack's figure for total input was about 300 g m^{-2} $year^{-1}$. If Kilmer and Cummins' 25% (75 g) is subtracted from pine needle-detritus input and Woodall's 30 to 40 g remaining in the stream is taken into account, about 190 g of detritus is left to be eaten; this is within the calculated range of ingestion.

If egestion is about 60%, a considerable amount of egested finely divi[illegible] detritus is available for consumption by groups such as filter feeders, which may depend on this source for most of their detrital food. If we assume that all detritus is eaten, the available food could be increased 2.5 times.

Examining nutrient requirements of detritivores in the hardwood stream, we see that ingestion of calcium was calculated to be between 1014 and 3020 mg m^{-2} $year^{-1}$. The total amount available in detritus for the year was 2700 mg/m^2. The calculated ingestion of potassium was 101 to 302 mg m^{-2} $year^{-1}$, and the amount available annually was 270 mg/m^2. The data for magnesium fit equally

well. Ingestion was calculated to be 203 to 604 mg m^{-2} $year^{-1}$, and the amount available in detritus was 540 mg m^{-2} $year^{-1}$.

In the pine stream 1980 mg m^{-2} $year^{-1}$ of calcium was available in detritus, and 934 to 2802 mg/m^2 was the calculated ingestion. Three hundred milligrams of potassium was available from the annual detritus input, and the calculated ingestion was 142 to 426 mg m^{-2} $year^{-1}$. Magnesium values were the same as potassium.

On the basis of this discussion, it appears that the ingestion rates calculated from the literature are probably very close to the actual ingestion rates of the compartments.

SUMMARY AND CONCLUSIONS

1. Crayfish and salamanders were responsible for most of the standing-crop biomass in the detritivore and predator compartments, respectively.

2. Crayfish and salamanders also accounted for most of the fluxes in their compartments and may be important in small stream nutrient flow because they form a sink in the remineralization process.

3. An increase in potassium concentrations was associated with an increase in trophic level.

4. A decrease in calcium and magnesium concentrations was associated with an increase in trophic level.

5. Since the food material was richer in calcium and magnesium than in potassium, detritivores concentrated proportionately more potassium than calcium or magnesium.

6. The principal mechanism of potassium release from detritus was through leaching.

7. The principal mechanism for release of calcium and magnesium, which are chemically bound in leaf tissue, was the feeding activity of detritivores.

8. Largest standing crops of cations in detritus were found in hardwood and coppice streams. This was attributed to greater standing crops of detritus and to higher concentrations of cations in this type of detritus than in pine and old-field detritus.

9. Calcium was more abundant in detritus than potassium and magnesium.

10. Because of their small size, Coweeta streams are unique among aquatic studies. Detritus probably has a greater influence in these streams than in larger streams having a greater flow.

11. Streams are important in the watersheds because they are the primary mechanism of nutrient removal from the system. Invertebrate breakdown of leaf material enhances this role.

12. Since the ingestion rates calculated from the literature were in agreement with the amount of detritus available for consumption, we concluded that rates are comparable between different types of systems.

13. This close agreement of ingestion and available food explains why there is no long-term accumulation of detritus in the streams. Since some organisms eat fine detritus egested by others, the amount of available detrital food could be effectively increased up to 2.5 times.

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REFERENCES

Benke, A. C., 1972, An Experimental Field Study on the Ecology of Coexisting Larval Odonates, Ph. D. Thesis, University of Georgia, Athens.

Best, G. R., 1971, Potassium, Sodium, Calcium and Magnesium Flux in a Mature Hardwood Forest Watershed and an Eastern White Pine Watershed at Coweeta, M.S. Thesis, University of Georgia, Athens.

Bick, H., 1959, cited in H. B. N. Hynes, 1970, *The Ecology of Running Waters*, University of Toronto Press, Toronto, Canada.

Carlisle, A., A. H. F. Brown, and E. J. White, 1966, The Organic Matter and Nutrient Elements in Precipitation Beneath a Sessile Oak Canopy, *J. Ecol.*, **54**: 87-98.

Cromack, K., 1972, Oregon State University, personal communication.

Cummins, K., W. Coffman, and P. Roff, 1966, Trophic Relationships in a Small Woodland Stream Ecosystem, *Verh. Int. Verein. Limnol.*, **16**: 627-638.

Darevskij, T. S., and Pavel V. Terentev, 1967, Estimation of Energy Flow Through Amphibian and Reptile Populations, in *Secondary Productivity of Terrestrial Ecosystems*, pp. 181-197, K. Petrusewicz (Ed.), Panstwowe Wydawnictwo, Warsaw, Poland.

Deitz, A., 1971, Changes with Age in Some Mineral Constituents of Worker Honey Bees. I. Phosphorous, Calcium, Magnesium, Sodium, and Iron, *J. Ga. Entomol. Soc.*, **6**: 51-3.

Fischer, Z., 1967, cited in H. E. Welch, 1968, Relationships Between Assimilation Efficiencies and Growth Efficiencies for Aquatic Consumers, *Ecology*, **49**: 755-759.

Gist, C., 1972, Analysis of Mineral Pathways in a Cryptozoan Foodweb, Ph. D. Thesis, University of Georgia, Athens.

Hasanen, E., and J. K. Miettinen, 1963, Cesium-137 Content of Fresh-Water Fish, *Nature*, **200**: 1018-1019.

Hynes, H. B. N., 1970, *The Ecology of Running Waters,* University of Toronto Press, Toronto, Canada.

——, 1963, Imported Organic Matter and Secondary Productivity in Streams, in Proceedings of Sixteenth International Congress of Zoology, pp. 324-329, J. A. Moore (Ed.), Washington, D. C.

——, 1961, The Invertebrate Fauna of a Welch Mountain Stream, *Arch. Hydrobiol.,* **57**: 344-388.

Jones, J. R. E., 1950, A Further Ecological Study of the River Rheidol: The Food of the Common Insects of the Main-Stream, *J. Anim. Ecol.,* **19**: 159-174.

——, 1949, A Further Ecological Study of Calcareous Streams in the "Black Mountain" District of South Wales, *J. Anim. Ecol.,* **18**: 142-159.

mer, W. E., and K. W. Cummins, 1971, Toward a Dynamic Model of a Temperature Zone Woodland Stream, Section A-4, in Annual Report, NSF GI-20, H. E. Koenig and W. E. Cooper (Eds.), National Science Foundation, Office of Interdisciplinary Research, Washington, D. C.

Kowal, N. E., and D. A. Crossley, Jr., 1971, The Ingestion Rates of Microarthropods in Pine Mor Estimated with Radioactive Calcium, *Ecology,* **52**: 444-452.

Maciolek, J. A., 1966, cited in H. B. N. Hynes, 1970, *The Ecology of Running Waters,* University of Toronto Press, Toronto, Canada.

McDiffett, W. F., 1969, The Transformation of Energy by a Stream Detritivore, *Pteronarcys scotti* (Plecoptera), Ph. D. Thesis, University of Georgia, Athens.

Minshall, G. W., 1967, Role of Allochthonous Detritus in the Trophic Structure of a Woodland Springbrook Community, *Ecology,* **48**: 139-149.

Moulder, B. C., D. E. Reichle, and S. I. Auerbach, 1970, Significance of Spider Predation in the Dynamics of Forest Floor Arthropod Communities, USAEC Report ORNL-4452, Oak Ridge National Laboratory.

Nelson, D. J., and D. C. Scott, 1962, Role of Detritus in the Productivity of a Rock-Outcrop Community in a Piedmont Stream, *Limnol. Oceanogr.,* **7**: 396-413.

Odum, H. T., 1957, Trophic Structure and Productivity of Silver Springs, Florida, *Ecol. Monogr.,* **27**: 55-112.

Pendleton, R. C., R. D. Lloyd, C. W. Mays, and B. W. Church, 1964, Trophic Level Effect on the Accumulation of Cesium-137 in Cougars Feeding on Mule Deer, *Nature,* **204**: 708-709.

Reichle, D. E., M. H. Shanks, and D. A. Crossley, 1969, Calcium, Potassium and Sodium Content of Forest Floor Arthropods, *Ann. Entomol. Soc. Amer.,* **62**: 57-62.

Salisbury, F. B., and Cleon Ross, 1969, *Plant Physiology,* Wadsworth Publishing Company, Inc., Belmont, Calif.

Teal, J. M., 1957, Community Metabolism in a Temperate Cold Spring, *Ecol. Monogr.,* **27**: 283-302.

Usinger, R. L. (Ed.), 1963, *Aquatic Insects of California,* University of California Press, Berkeley, Calif.

n Hook, R. I., D. E. Reichle, and S. I. Auerbach, 1970, Energy and Nutrient Dynamics of Predator and Prey Arthropod Populations in a Grassland Ecosystem, USAEC Report ORNL-4509, Oak Ridge National Laboratory.

Vollenweider, R. A., 1950, cited in L. Provasoli, J. J. A. McLaughlin, and I. J. Pinter, 1954, Relative and Limiting Concentrations of Major Mineral Constituents for the Growth of Algal Flagellates, *Trans. N. Y. Acad. Sci.,* **16**: 412-417.

Wallace, J. B., W. R. Woodall, and F. F. Sherberger, 1970, Breakdown of Leaves by Feeding of *Peltoperla maria* (Plecoptera: Peltoperlidae), *Ann. Entomol. Soc. Amer.,* **63**: 562-567.

Weber, C. I., 1973, Biological Field and Laboratory Methods for Measuring the Quality of Surface Waters and Effluents, U. S. Environmental Protection Agency, Cincinnati, Ohio.

Welch, H. E., 1967, Energy Flow Through the Major Macroscopic Components of an Aquatic Ecosystem, Ph. D. Thesis, University of Georgia, Athens.

Winterbourn, M. J., 1971, An Ecological Study of *Banksiola crotchi* Banks (Trichoptera: Phryganidae) in Marion Lake, British Columbia, *Can. J. Zool.*, **49**: 637-645.

Woodall, W. R., 1972, Nutrient Pathways in Small Mountain Streams, unpublished Ph. D. Thesis, University of Georgia, Athens.

——, 1971, Changes in Nutrient Concentrations in Water Caused by Feeding of *Pteronarcys scotti* Nymphs (Plecoptera: Pteronarcidae), paper presented at the Georgia Entomological Society Meeting, Savannah, Mar. 17–19, 1971, unpublished.

——, 1969, A Comparison of Aquatic Insects in Four Different Watersheds, M.S. Thesis, University of Georgia, Athens.

——, and J. B. Wallace, 1972, Benthic Fauna in Four Small Southern Appalachian Strea *Amer. Midland Natur.*, **88**: 393-407.

ORGANICALLY COMPLEXED COPPER, ZINC, AND CHELATING AGENTS IN THE RIVERS OF WESTERN PUERTO RICO

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ABSTRACT

The method for determining soluble chelators gives their concentration in copper-equivalent chelating capacity units in fresh or slightly brackish (<3% salinity) water. The mean concentration of chelators in the Río Guanajibo for December 1973 and January 1974 was 0.4 mg of copper per liter of water (N = 21, SD = 0.2) and for February 1974, 0.9 mg/liter (N = 8, SD = 0.4). The combined mean for the Río Añasco and Culebrinas was 0.5 mg/liter (N = 7, SD = 0.4) in January and February 1974. The mean concentration of ionic copper was 0.5 μg/liter (N = 7, SD = 0.6) and of ionic zinc, 0.2 μg/liter (N = 8, SD = 0.1) in the Río Guanajibo from November 1972 to February 1973. The concentration of organically bound copper was 0.3 μg/liter (N = 7, SD = 0.2) and that of organically bound zinc was 0.6 μg/liter (N = 8, SD = 0.6); this indicates that there was more than a sufficient quantity of chelator available in the river to complex all the soluble copper. The presence of a high ratio of Ca^{2+} to Cu^{2+} probably prevents the formation of larger concentrations of organically complexed copper. The mean concentration of chelating agents in the Guanajibo River seems to be directly related to the increased organic input from municipalities and a sugar mill. The concentration of chelators in tropical rivers appears to be higher than that found in Canadian lakes. The mean concentration for particulate organic carbon (POC) was 3653 μg atoms/liter (SD = 3653, N = 29). The dissolved reactive phosphate (DRP) ranged from a mean of 1.1 μg atoms/liter. No significant correlation could be found between POC, DRP, and the concentration of chelators.

As part of the continuing study of trace-metal transport from the terrestrial to marine environments at the Puerto Rico Nuclear Center (Lowman et al., 1965; 1966; 1967; Lowman and Ting, 1973), an attempt has been made to use the method described by Kunkel and Manahan (1973) in tropical rivers and seawater to determine the concentration of soluble strong chelators. The importance of chelators in trace-metal transport has been investigated (Goldberg, 1957; Johnston, 1964; Barber and Ryther, 1969; Fukai, 1969; Schnitzer, 1971; Barber and Zeitlin, 1972; Lewis, Whitfield, and Raminarine, 1972; Manahan,

1972; Kunkel and Manahan, 1973), and hypotheses have been made as to their importance in marine waters (Duursma, 1970; Stumm and Morgan, 1970). Consequently the increased input of organic material from untreated domestic, industrial, and agricultural wastes to the rivers on the west coast of Puerto Rico may be changing the behavior of trace elements in the aquatic environments by increasing the concentration of chelators (Bender, Matson, and Jordan, 1970).

The presence of organic chelators in tropical rivers has not been demonstrated because there was no adequate method. A method has been found (Kunkel and Manahan, 1973), however, which, although it does not specifically identify the soluble organic chelators, can give a quantitative estimate of [redacted] concentration. The presence of soluble organic chelators in tropical seawater has been shown (Hood, 1967; Slowey and Jeffries, 1967; Fukai, 1969; Lowman and Ting, 1973). The concentration of the complexing agents varied from 0 to 0.04 mg of Cu^{2+} per liter of water in Canadian lakes (Gächter, Lum-Shue-Chan, and Chau, 1973).

The concentration of soluble strong heavy-metal chelators was monitored in the three major rivers on the west coast of Puerto Rico, Culebrinas River, Anasco River, and Guanajibo River, with major emphasis on the Guanajibo River (see Fig. 1). The concentration of soluble strong chelators in the water and its relationship to rainfall, known sources of pollution, concentration of particulate organic carbon, and dissolved reactive phosphate were studied during the period from December 1973 to January 1974. The presence of sugar-mill wastes can be detected by high concentrations of particulate matter (Biaggi, 1968). The increase in dissolved reactive phosphate can act as a tracer for municipal sewage. When we say "strong chelators," we refer to chelators with a $\log K \geqslant 13$, where K refers to the formation constant of a ligand–metal complex.

METHODS

The sampling sites in the three watersheds are shown in Fig. 1. Two sets of samples were collected with a polyethylene sampler and immediately placed in two clean 500-ml linear polyethylene bottles and stored in the dark on ice. A drop of 1 : 1 (v/v) toluene and carbon tetrachloride was added to the first bottle to prevent changes in the dissolved inorganic phosphate. When the second sample arrived at the laboratory, it was divided into two aliquots, one of which was used for the detection of strong heavy-metal chelators and the other for particulate organic carbon. The concentrations of the particulate, ionic, and organic forms of trace metals were determined in 10-liter water samples collected at the same locations but at different times. All samples were filtered through 0.4-mμ pore-size filters within 3 hr of collection.

The filtered, preserved sample was analyzed for dissolved reactive phosphate by the single-solution method (Strickland and Parsons, 1968) with a spectrophotometer at 885 nm. The standard error of the regression coefficient was 0.0035 for the standard curve.

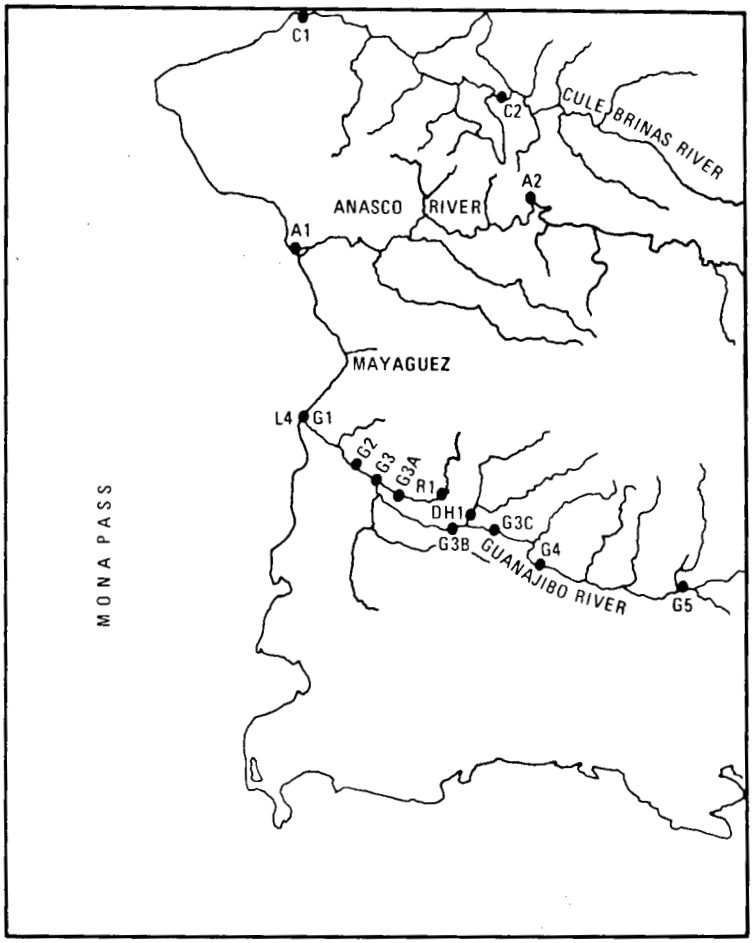

Fig. 1 West coast of Puerto Rico, showing sampling sites in three watershed areas.

Soluble Strong Heavy-Metal Chelators

One aliquot of the second 500-ml sample was filtered through a filter previously rinsed with low-carbon water. The low-carbon water was obtained by double-glass distilling tap water over $K_2S_2O_8$ and H_3PO_4. This was necessary to maintain low blank values. Our regular distillation procedure apparently did not eliminate soluble organic compounds. Filtering apparatus was washed in hot acid dichromate and rinsed with low-carbon water. Samples were analyzed in duplicate with two blanks prepared in low-carbon water.

The method for determining copper-equivalent chelating capacity depends on the following relationships:

$$Cu^{2} + 2OH \rightarrow Cu(OH)_2 \quad (1)$$

$$K_s = (Cu^{2+})(OH^-)^2 = 3 \times 10^{-20} \quad (2)$$

Therefore at pH 10 the quantity of copper in solution is extremely small—below the practical detection limit of conventional atomic absorption spectrophotometry, as shown in the following equation:

$$(Cu^{2+}) = \frac{K_s}{(OH^-)^2} = \frac{3 \times 10^{-20}}{(1 \times 10^{-4})^2} = 3 \times 10^{-12}$$

A 50.0-ml subsample of the filtered water was used to determine the equivalent copper chelating capacity. After adding 5 ml of $5 \times 10^{-3} M$ $CuSO_4$ we slowly adjusted the pH to 10 ± 0.2 with $5 \times 10^{-2} M$ Na_2CO_3. A blue copper precipitate developed. If it did not, additional copper was added. The sample was then boiled until the precipitate changed to light blue gray or brown. The volume of cooled sample was brought back to 50.0 ml with low-carbon water (adjusted to pH 10 with $5 \times 10^{-2} M$ Na_2CO_3). The sample was filtered through a 0.4-mμ pore-size filter, which was preclogged with precipitated $Cu(OH_2)$ to prevent the loss of fine Cu^+ particles. The filtrate was acidified with nitric acid. Copper remaining in solution (i.e., the chelated copper) was analyzed in the filtrate with an atomic absorption spectrophotometer under standard conditions (Perkin-Elmer Corp., 1973). The concentration of soluble strong heavy-metal chelating agents in the original sample was then expressed in milligrams per liter, copper equivalent chelating capacity, i.e., the number of milligrams of copper which can be chelated by the chelating agents present in 1 liter of solution.

The biggest problem with this method was in obtaining low blank values. Three factors caused high blanks:

1. Organic material leached by hot distilled water from plastic carboys.
2. Fine $Cu(OH)_2$ precipitate leaked through the 0.4-mμ pore-size filters.
3. Precipitated $Cu(OH)_2$ redissolved by acidified distilled water or acid cleaning solutions.

The blanks were maintained at less than 0.03 mg of Cu^{2+}-equivalent chelating capacity per liter when:

1. Low-carbon double-glass distilled water was used.
2. The 0.4-mμ filter was preclogged with $Cu(OH)_2$ precipitate to decrease its pore size before the $Cu(OH)_2$ precipitate of the sample was filtered.
3. All glassware, filters, and equipment coming in contact with the sample were given a final rinse with alkaline (pH 10) low-carbon water to prevent the precipitated $Cu(OH)_2$ from redissolving.

To determine the precision of the method, we collected a 2-liter sample from a settling pond at the Anasco sugar mill. We then determined the concentration of strong heavy-metal chelators for eight replicates. The results gave a mean of

0.6 mg/liter copper-equivalent chelating capacity with a standard deviation of 0.09 mg/liter. To further check the precision, we determined the concentration of chelator in 10 replicate 50.0-ml samples containing $5 \times 10^{-5} M$ Na_2EDTA in distilled water to simulate natural chelators. The samples contained 0.2 mg/liter copper-equivalent chelating capacity with a standard deviation of 0.009 mg/liter. The theoretical stoichiometric quantity should have been $5 \times 10^{-5} M$ Cu^{2+} (0.32 mg/liter). Another determination for chelators was made using duplicate 50.0-ml aliquots containing 1, 2, 3, 4, and $5 \times 10^{-6} M$ Na_2EDTA in distilled water. This experiment was repeated using 1, 2, and $5 \times 10^{-6} M$ Na_2EDTA in distilled water. regression coefficients for the linear least-squares fit were tested for the two ndard curves and were not significantly different at the $p < 0.05$ level (t test). The results for the two experiments were then pooled, and a linear regression least-squares fit was calculated for the combined data. The analysis of variance showed the linear regression coefficient to be significantly different from zero. The deviations from regression were zero at the $p < 0.005$ level. The resulting linear regression equation was:

$$Y = 0.4 + 0.8X \tag{4}$$

where Y is the estimated concentration of chelators expressed as the soluble copper-equivalent chelating capacity $\times 10^{-6} M$, and X is the known concentration of added $Na_2EDTA \times 10^{-6} M$.

The observed and theoretical concentration of soluble chelator, expressed in copper-equivalent chelating capacity $\times 10^{-6} M$, can be computed from the pooled regression equation (Eq. 4). The method could not be used for samples $>3‰$ in salinity because of numerous interferences in that complex media.

Particulate Organic Carbon

Glass filters were used in determining particulate organic carbon (POC). The filters were cleaned by combustion at 450 to 500°C for 8 hr in a muffle furnace, then weighed to constant weight, and stored, wrapped in clean aluminum foil, in a desiccator. A 250-ml sample was vacuum filtered (¼ to ⅓ atm) through a glass filter. The filter was sucked dry, removed, held over the fumes of concentrated HCl for a few seconds to release the inorganic carbon, and then returned to the ter apparatus. One milliliter of $0.32M$ Na_2SO_4 was added to the filter to ove excess salts, and it was sucked dry again. This was repeated. The filter was rewrapped in its original aluminum foil, dried at 60 to 70°C for 24 hr, stored in a desiccator, reweighed until a constant weight was reached, and then carefully added to the sample receptacle of a carbon, hydrogen, and nitrogen analyzer. The particulate organic carbon and nitrogen were calculated using known amounts of acetanilide (10.36% N, 17.78% C) as a standard. Six replicate samples taken from station G2 on Feb. 18, 1974 were used for precision tests. The results were 782 ± 122 SD μg of carbon per liter (a coefficient of variation of 15.6%).

Particulate, Ionic, and Organic Forms of Copper and Zinc

Ten-liter surface samples were collected in acid-washed plastic containers and filtered through 142-mm diameter, 0.45-mμ pore-size filters washed with acid and rinsed with distilled water in an all-plastic holder. The filtering was completed within 8 hr of sample collection. The filters, both samples and blanks, were then dry ashed at 400°C, dissolved with concentrated HCl, and diluted to 20 ml with distilled water. This was referred to as the particulate fraction. The filtrate was allowed to flow through a Chelex-100 (50- to 100-mesh) column and then through an Amberlite XAD-2 column at 5 ml/min.

The ionic fractions of the metals were retained on the Chelex-100 col (Riley and Taylor, 1968) and the organic complexes were retained on the Amberlite XAD-2 column (Lowman, personal communication; Grieser and Pietrzyk, 1973, as quoted in Chu and Pietrzyk, 1974). The retention of inorganic ^{58}Co was 91% on the Chelex-100 column, but only 0.6% of the organic ^{57}Co was retained on the Chelex-100 column (Lowman and Ting, 1973).

Preparation of Columns

The Chelex-100 resin was pretreated by washing with 6*N* HCl and then with distilled water until all traces of HCl were removed. A 20-ml slurry of the washed and treated resin was placed in a 1.5-cm-ID by 10-cm plastic column and kept covered with liquid.

Ten grams of Amberlite XAD-2 resin was placed in a 1.5-cm-ID by 10-cm column, treated with 100 ml of 1*N* HCl, and rinsed with 100 ml of distilled water. The two columns were then connected in series, with the Chelex-100 column on top.

The Chelex-100 column was eluted with 40 ml of hot concentrated HCl, and the acid extracts were dried down to approximately 5 ml and then diluted to 20 ml with distilled water. A Chelex-100 blank was treated in the same way.

The Amberlite XAD-2 resin was removed and dried and then ashed at 400°C. The ashes were dissolved with concentrated HCl and taken to 10 ml with distilled water. The Amberlite blank was treated in the same way.

All the fractions were analyzed on an atomic absorption spectrophotometer under standard conditions (Perkin-Elmer Corp., 1973) with known concentrations of metals dissolved in acid and distilled water to prepare calibration cur The data are in a preliminary form, and no precision has been determined for the method at this time.

RESULTS

The Guanajibo River was the most extensively studied of the three rivers. There were nine sampling stations from the mouth (G1) to the head of the river at Sabana Grande (G5) and one station at the river–ocean mixing zone (L4) (see

Fig. 1). Results for the concentrations of soluble strong heavy-metal chelators are shown in Table 1. The concentration of soluble chelators was significantly higher ($P < 0.05$, t test) on Feb. 13, 1974 (0.9 mg/liter copper-equivalent chelating capacity, N = 8, SD = 0.4), than on either Dec. 5, 1973, or Jan. 17, 1974 (combined mean 0.4 mg/liter capacity, N = 21, SD = 0.2). The combined mean for the Anasco and Culebrinas rivers was 0.5 mg/liter (N = 7, SD = 0.4).

TABLE 1

CONCENTRATION* OF STRONG HEAVY-METAL CHELATORS IN THE GUANAJIBO RIVER†

Station	Sampling date						
	12/5/73	1/17/74	2/13	7/11	7/16	7/24	7/29
G1	0.6	0.5	1.0	UD	UD	UD	UD
G2	0.4	0.5	0.4	0.2	UD	UD	UD
G3	0.8	0.7	NS	UD	UD	0.3	UD
G3A	0.4	0.5	0.4	UD	UD	UD	UD
G3B	0.1	0.2	1.3	UD	UD	UD	UD
G3C	UD	0.2	1.5	UD	UD	0.1	UD
G4	0.4	0.2	0.7	UD	UD	UD	UD
G5	0.7	0.6	NS	NS	NS	NS	UD
R1	UD	0.2	1.3	NS	UD	UD	UD
DH1	0.2	0.3	0.6	NS	UD	UD	UD

*Expressed as milligrams of Cu^{2+}-equivalent chelating capacity per liter.
†The abbreviations are UD, undetected with the present method, and NS, not sampled.

The mean concentration of particulate organic carbon (POC) was not significantly different from one sampling period to the next. The mean concentration of POC was 3653 μg atoms/liter (N = 29, SD = 3653). The two highest values occurred on Feb. 13, 1974, at stations G2 (1430 μg atoms/liter) and G3 (20,000 μg atoms/liter). The concentration of dissolved reactive phosphate (DRP), sampled from November 1972 to January 1974, ranged from a mean of 1.1 μg atoms/liter at station G5 (N = 15, SD = 2.3) to 6.6 μg atoms/liter at the river mouth (N = 11, SD = 0.3). In general, the DRP increased toward the river mouth, being highest at stations G3C and G3B and lowest at G5. The peak concentration of DRP and POC seemed to be centered around sampling stations G3, G3B, and G3C. The concentration of strong heavy-metal chelators also appeared to be greatest near stations G3A, G3B, and G3C. There was no significant correlation between the concentration of soluble chelators and POC or DRP. The undetectable or low levels of soluble chelators during July 1974 coincided with the halt of sugar harvesting and refining (June to December) and with the rainy season (Table 2) and the resulting increase in the clay–silt load of the river. Although the data on

TABLE 2

MONTHLY RAINFALL IN (CM) FOR THE GUANAJIBO RIVER WATERSHED, 1973–1974

Month	Year 1973	1974
January	1.47	5.68
February	4.73	7.60
March	4.43	6.84
April	2.70	9.58
May	4.58	3.14
June	10.58	7.52
July	7.33	23.01
August	18.90	4.55*
September	16.37	
October	16.93	
November	10.61	
December	3.80	
Total	102	68.2

*For Aug. 1–11 only.

particulate, ionic, and organically complexed forms of Cu^{2+} and Zn^{2+} were preliminary (Table 3) the results indicated that a large portion of the dissolved Cu^{2+} and Zn^{2+} (44 and 75%, respectively) was organically bound. There was no significant difference (t test) in the organically complexed Zn^{2+} or Cu^{2+} from stations G1 to G5. The particulate fraction of Cu^{2+} increased from the upper river (R1 + G5) to the mouth (G1). There was no significant difference in the particulate Zn^{2+} for the river stations and no significant change between the river stations (G1 + G5 + R1) and the river–ocean mixing zone (L4) for the mean ionic Zn^{2+} or Cu^{2+}. The mean particulate Zn^{2+} and Cu^{2+} for the river stations decreased, however, while the mean organic Zn^{2+} and Cu^{2+} increased in the river–ocean mixing zone.

DISCUSSION

The quantities of soluble chelators for the period from December 1973 to January 1974 were consistently high at stations G3 and G5 and low at G3C. The concentration of soluble chelators seemed to increase after station G3A, which is just below the Eureka Central, a sugar mill. The high values at Sabana Grande (G5), where the water was always very shallow and clear, were probably due to a low concentration of particles, either clay–silt or iron and aluminum oxides in the water. The low clay–silt concentrations and resulting clarity could cause an increase in algal productivity with an increase in production of soluble organic

TABLE 3

CONCENTRATION (μG/LITER) OF MEAN IONIC, ORGANIC, AND PARTICULATE FORMS OF Cu^{2+} AND Zn^{2+} IN RIO GUANAJIBO

	Ionic	Organic	Particulate	Total metal
			Zn^{2+}	
Stations G1 to G5				
Mean	0.2	0.6	3.8	4.6
S.D.	0.1	0.6	1.0	1.7
N	8	8	8	8
Soluble forms of the mean, %	25	75		
River–ocean station, January 1973	0.1	1.0	0.8	1.9
Percent of total	9	91		
			Cu^{2+}	
Stations G1 to G5				
Mean	0.5	0.4	2.1	3.0
S.D.	0.5	0.3	2.1	2.9
N	7	7	7	7
Soluble forms of the mean, %	56	44		
Mixing zone station, January 1973	0.2	0.8	0.5	1.5
Soluble forms, %	20	80		

chelating substances (Fogg and Westlake, 1955). The greatest change came in February, when the peak values were located just below the town of San German at station G3C. San German discharges municipal sewage into the Guanajibo River. The values of soluble chelators in the Guanajibo River were highest during February. These higher values were probably due to the increased organic load from the sugar mill, the decreased rainfall, which caused a decrease in concentration of clay–silt particles, and the increase in organic matter due to low runoff. The 2 : 1 expanding lattice of kaolinite clay has the ability to adsorb organic material (Smith, Samuels, and Cernuda, 1951). Also, a similar role for the iron and aluminum oxides was suggested by Smith et al. (1951). The soils in the Guanajibo watershed contain 15 to 20% free iron oxides, aluminum oxides, and kaolinite (Smith et al., 1951).

Although there were more than enough chelating agents in the river water to complex all the soluble Cu^{2+} and Zn^{2+} present, only a fraction of the soluble

Cu^{2+} (~44%) was organically complexed (Table 3). Up to 75% of the soluble Zn^{2+} was organically complexed, however (Table 3). A possible explanation for the fact that soluble Cu^{2+} and Zn^{2+} were not totally complexed is that there is a high Ca^{2+}-to-Cu^{2+} ratio (3000), which may prevent the formation of larger concentrations of organically complexed Cu^{2+} and Zn^{2+} because of the competition of the Ca^{2+} ion for the soluble chelators (Stumm and Morgan, 1970). However, more of the copper may have complexed with the particulate organic material, as suggested by Stumm and Morgan (1970). The particulate organic carbon in the Guanajibo River ranges from 49 to 20,000 μg/liter.

Chau and Lum-Shue-Chan (1974) reported 33% of soluble Zn^{2+} and 70% of soluble Cu^{2+} to be strongly bound in lake waters near Sudbury, Ontario. The strongly bound metal was determined as the difference between total metal and labile metal. The labile metal was the metal measured on the untreated sample by differential pulse anodic stripping voltammetry. The total metal was the amount measured by the same method after persulfate oxidation of the filtered sample (0.45-mμ pore-size filter). The labile metal includes the ionic metal, acetate exchangeable metal, and some of the strongly bound metal when the ligand-to-metal ratio was greater than one (Chau and Lum-Shue-Chan, 1974).

The concentration of soluble chelators in our study appears to be directly related to the input of organic material from municipalities and from a sugar mill and inversely related to the increase in particulate matter in the river during the rainy season (May to November). The presence of organically complexed Cu^{2+} and Zn^{2+} was shown and the percentages agreed with the results of other investigators (Chau and Lum-Shue-Chan, 1974). The concentration of soluble organic strong chelators was much greater than the known concentration of soluble organically complexed Zn^{2+} or Cu^{2+} in the Guanajibo River. The particulate fractions of Cu^{2+} and Zn^{2+} for the Guanajibo River were 70 and 83%, respectively, of the mean total metal concentration. The quantitative importance of soluble chelators in total trace-metal transport, as shown by Zn^{2+} and Cu^{2+}, was not as important as the particulate material. The relationship of organic particulate material to complex metals has not been investigated, however.

The method used, although not as sensitive as differential pulsed anodic stripping, was of sufficient precision if precautions were taken to ensure low blanks. The inability to reproduce the stoichiometric slope of 1 when copper-equivalent chelating capacity was plotted against the concentration of EDTA was probably the result of insufficient time for copper to reach equilibrium with the available ligands. A minimum time of 2 hr was found necessary in Canadian lake waters (Gächter, Lum-Shue-Chan, and Chau, 1973).

The ability of organic particulate material to complex trace metals will be investigated using the technique of density gradient centrifugation (Lamners, 1962).

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REFERENCES

er, D. R., and H. Zeitlin, 1972, Metal Ion Concentration in Sea Surface Microlayer and Size Separated Atmospheric Aerosol Samples in Hawaii, *J. Geophys. Res.*, **77**: 5076-5086.

——, and J. H. Ryther, 1969, Organic Chelators Affecting Primary Production in the Cromwell Current Upwelling, *J. Exp. Mar. Biol. Ecol.*, **3**: 191-199.

Bender, M. E., W. R. Matson, and R. A. Jordan, 1970, On the Significance of Metal Complexing Agents in Secondary Sewage Effluents, *Environ. Sci. Technol.*, **4**: 520-521.

Biaggi, N., 1968, The Sugar Industry in Puerto Rico and Its Relation to the Industrial Waste Problems, *J. Water Pollut. Contr. Fed.*, **40**(8): 1423-1433.

Chau, Y. K., and Ken Lum-Shue-Chan, 1974, Determination of Labile and Strongly Bound Metals in Lake Water, *Water Res.*, **8**: 383-388.

Chu, Chi-Hong, and D. J. Pietrzyk, 1974, High Pressure Chromatography on XAD-2, A Porous Polystyren-Diviny [l] Benzene Support—Separation of Organic Bases, *Anal. Chem.*, **46**(3): 330-336.

Duursma, E. K., 1970, Organic Chelation of ^{60}Co and ^{65}Zn by Leucine in Relation to Sorption by Sediments, in Organic Matter in Natural Waters, D. W. Hood (Ed.), pp. 387-397, Institute of Marine Science, University of Alaska, Publication No. 1.

Fogg, G. E., and D. F. Westlake, 1955, The Importance of Extra-Cellular Products of Algae in Fresh Water, *Int. Ass. Theor. Appl. Limnol., Commun.*, **12**: 219-232.

Fukai, R., 1969, On the Chelation of Some Radionuclides in a Sea Water Medium, *Rapp. Comm. Int. Mer. Medit.*, **19**(5): 935-936.

Gächter, R., Ken Lum-Shue-Chan,, and Y. K. Chau, 1973, Complexing Capacity of the Nutrient Medium and Its Relation to Inhibition of Algal Photosynthesis of Copper, *Schweiz. Z. Hydrol.*, **35**: 252-261.

Goldberg, E. D., 1957, Marine Geochemistry, Chemical Scavengers of the Sea, *J. Geol.*, **62**: 249-265.

Grieser, M. D., and D. J. Pietrzyk, 1973, Liquid Chromatography on a Porous Polystyrene–Divinylbenzene Support, *Anal. Chem.*, **45**: 1348-1353.

Hood, D. W., 1967, Chemistry of the Oceans: Some Trace Metal-Organic Associations and Chemical Parameter Differences in Top One Meter of Surface, *Environ. Sci. Technol.*, **1**(4): 303-305.

Johnston, R., 1964, Sea Water, the Natural Medium of Phytoplankton. II. Trace Metals and Chelation, and General Discussion, *J. Mar. Biol. Ass. U.K.*, **44**: 87-109.

Kunkel, R., and S. E. Manahan, 1973, Atomic Absorption Analysis of Strong Heavy Metal Chelating Agents in Water and Waste Water, *Anal. Chem.*, **45**(8): 1465-1468.

Lamners, W. T., 1962, Density Gradient Separation of Plankton and Clay from River Water, *Limnol. Oceanogr.*, **7**: 224-229.

Lewis, A. G., P. H. Whitfield, and A. Raminarine, 1972, Some Particulate and Soluble Agents Affecting the Relationship Between Metal Toxicity and Organisms Survival in the Calanoid Copepod *Euchaeta japonica*, *Mar. Biol.*, **17**: 215-221.

Lowman, F. G., and R. Y. Ting, 1973, The State of Cobalt in Sea Water and Its Uptake by Marine Organisms and Sediments, in *Radioactive Contamination of the Marine Environment,* Symposium Proceedings, Seattle, Wash., 1972, pp. 369-384, International Atomic Energy Agency, Vienna (STI/PUB/313).

——, R. A. Stevenson, R. McClin and S. Lugo Ufret, 1967, The Effects of River Outflows Upon the Distribution Patterns of Fallout Radioisotopes in Marine Organisms, in *Radioecological Concentration Processes,* Proceedings of the International Symposium, Stockholm, April 25–29, 1966, B. Aberg and F. P. Hungate (Eds.), Pergamon Press, Inc., New York.

——, D. K. Phelps, R. McClin, V. R. de Vega, I. O. de Padovani, and R. J. Garcia, 1966, Interaction of the Environmental and Biological Factors on the Distribution of T[illegible] Elements in the Marine Environment, in *Disposal of Radioactive Wastes into Oceans and Surface Waters,* Symposium Proceedings, Vienna, 1966, pp. 250-[illegible], International Atomic Energy Agency, Vienna (STI/PUB/126).

——, et al., 1965, Investigations of Trace Element Distribution in Marine Waters and Sediments, in *5th Inter-American Symposium on the Peaceful Application of Nuclear Energy,* Valparaiso, Chile, Mar. 9–13, 1964, pp. 241-259, Pan American Union, Washington, D. C.

Manahan, S. E., 1972, *Environmental Chemistry,* Willard-Grant Press, Inc., Boston, Mass.

Perkin-Elmer Corp., 1973, Analytical Methods for Atomic Absorption Spectrophotometry, Norwalk, Conn.

Riley, J. P., and D. Taylor, 1968, Chelating Resins for the Concentration of Trace Elements from Sea Water and Their Analytical Use in Conjunction with Atomic Absorption Spectrophotometry, *Anal. Chim. Acta,* 40: 479-485.

Schnitzer, M., 1971, in *Organic Compounds in Aquatic Environments,* Samuel D. Faust and J. V. Hunter (Eds.), Marcel Dekker, Inc., New York.

Slowey, J. F., and L. M. Jeffreys, 1967, Evidence for Organic Complexed Copper in Sea Water, *Nature,* 214: 377-379.

Smith, R. M., G. Samuels, and C. F. Cernuda, 1951, Organic Matter and Nitrogen Build-Ups in Some Puerto Rican Soil Profiles, *Soil Sci.,* 72(6): 409-427.

Strickland, J. D. H., and T. R. Parsons, 1968, *A Practical Handbook of Seawater Analysis,* Bulletin No. 167, 2nd ed., Fisheries Research Board of Canada, Ottawa, Ont.

Stumm, W., and J. J. Morgan, 1970, *Aquatic Chemistry,* Wiley-Interscience, Inc., New York.

UPTAKE AND ELIMINATION OF RADIOTUNGSTEN IN BLACK BULLHEADS

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ABSTRACT

Black bullheads, *Ictalurus melas* (Rafinesque), accumulated radiotungsten from food and water. Whole-body activity reached a plateau after the fish had been in tagged water 4 days (mean temperature 14°C). Whole-body elimination of radiotungsten varied with the method of uptake. Fish that had accumulated radiotungsten from water had a single exponential component of elimination with a biological half-life of 2.75 days. Fish that had received radioisotope in a single feeding lost activity at two rates; one component had a biological half-life of 14 hr and the second 6 days. The bone, skin, flesh, blood, and gills contained the greatest percentages of whole-body activity after 1 day of uptake from tagged water; after 8 days, the flesh, gills, bone, and gut together contained 78.6% of the total activity. The bone had the longest biological half-life (8.0 days) of the tissues examined and contained 69.8% of the whole-body activity after 16 days of elimination.

The distribution and kinetics of tungsten in biological systems are not well known. Tungsten is a transition metal chemically similar to uranium, chromium, and molybdenum. Because the radioisotopes of tungsten (^{181}W, ^{185}W, and ^{187}W) comprise a large fraction of the radioactivity after certain types of nuclear detonations (Lane, 1963; Essington, Nishita, and Steen, 1965), the role of tungsten in biological systems and its movement through food chains are of importance. Very few studies on tungsten metabolism in animals have been done, however. The purpose of this research was to study the uptake and turnover of radiotungsten in the black bullhead, *Ictalurus melas* (Rafinesque).

Studies have shown that ingested or injected radiotungsten is eliminated by rats principally via urine and that initially the blood-rich organs exhibit high concentrations of tungsten. The studies also showed that radiotungsten eventually localizes in the bone, with a relatively long retention time (Hamilton, 1951; Wase, 1956; Ballou, 1960; Fleshman, Krotz, and Silva, 1966; Kaye, 1968).

There is virtually no information available on tungsten cycling or metabolism in poikilothermic vertebrates. Since some invertebrates had been shown to accumulate radiotungsten (Kaye and Crossley, 1968; Reed and Martinedes, 1971), it was of interest to examine the uptake and elimination of tungsten in a poikilothermic vertebrate such as a fish.

METHODS

Black bullheads, *I. melas*, were collected from a pond at the Oak Ridge National Laboratory. Experimental fish ranged from 48 to 156 g in weight and from 16 to 22.5 cm in length. In the laboratory the bullheads were held in large (500-liter) stainless-steel tanks containing flowing spring water (12 to 16°C). Fish were held for at least 3 days in spring water before being used in experimentation.

Tungsten-187 in the form K_2WO_4 in 0.7*N* KOH solution with a specific activity of 91.823 mCi/mg was obtained from Oak Ridge National Laboratory, and ^{181}W in the form W(V1) in 0.5*N* HCl and 0.1*N* HF with a specific activity of 17.0 mCi/mg was obtained from Nuclear Science and Engineering Corporation.

Several types of experiments were performed. In the first, the whole-body uptake of ^{187}W from water was studied. Experimental containers were plastic utility tubs, 45 cm in diameter at the top and 22 cm deep, fitted with polyethylene covers and aerated. Four fish were placed in 10 liters of radiotungsten-tagged water at a concentration of 2×10^4 dis min^{-1} ml^{-1}. The fish remained in the tagged water for 6 days, during which time they were removed daily, rinsed for 1 min in spring water, and counted with a scintillation counter. The water concentration of ^{187}W was not maintained during the 6-day uptake period.

A second experiment dealt with the whole-body elimination of ^{187}W by fish exposed to a water concentration of 2×10^4 dis min^{-1} ml^{-1} for 24 hr in containers similar to those described. After 24 hr a whole-body count was made on each fish with the scintillation counter. The fish were then placed in large (190-liter) stainless-steel kettles containing flowing spring water that ranged from 12 to 16°C. Whole-body counts were made daily over a 7-day excretion period. The experiment was terminated after 7 days because of the short physical half-life (24 hr) of ^{187}W.

In a third experiment the whole-body elimination of ^{187}W after accumulation from food was studied. Five bullheads were placed in individual utility tubs containing 10 liters of aerated spring water. Night crawlers (*Lumbricus* sp.) were injected with 0.3 ml of ^{187}W solution with an activity of 3.596×10^5 dis min^{-1} ml^{-1} to give an activity of 1.08×10^5 dis/min per worm. Each fish was immediately fed one tagged worm and was allowed to remain undisturbed for 2 to 3 hr to facilitate digestion. After this time the fish were counted in the same way as in the water-uptake experiment and placed in a large

stainless-steel kettle like that described. The counting procedure was also the same as in the previous experiment.

Separate experiments were performed to determine radiotungsten uptake and turnover by individual tissues. In the tissue-uptake experiment, 12 bullheads were placed in 50 liters of ^{181}W-tagged water at a concentration of 1.3×10^4 dis min^{-1} ml^{-1}. Three fish were sampled after 24 hr in the tagged water, three after 48 hr, four after 4 days, and two after 8 days. A blood sample was collected from each fish by severing the caudal peduncle. Samples were taken of skin, flesh, liver, gall bladder and bile, spleen, stomach, gut, gonads, kidney, heart, bone, and gills. The skin sample consisted of a strip of skin taken from each side of the fish and freed of flesh; the flesh sample was taken from the dorsal musculature; the bone sample consisted of a portion of the spinal column scraped clean of flesh; and the internal organs were counted whole. The gills were removed and counted intact. The remainder of the fish was cut up and counted as residue. Counting was done on a single-channel gamma spectrometer with a well-type NaI(Tl) crystal.

In the study of radiotungsten elimination by tissues, 18 bullheads were put into 50 liters of ^{181}W-tagged water at a concentration of 1.3×10^4 dis min^{-1} ml^{-1}, allowed to accumulate radiotungsten for 4 days, and then removed and rinsed in spring water. Three fish were then sacrificed, and their tissues were sampled and counted as in the uptake experiment. The remaining 15 fish were placed in a stainless-steel kettle containing 190 liters of flowing spring water (12 to 16°C). Three fish for each period were sacrificed after 1, 2, 4, 8, and 16 days of radiotungsten elimination.

The tissue uptake and elimination data were normalized to a 50-g fish and converted to a percentage of the whole-body activity. The fractions of the whole-body weight comprised by each tissue were taken from Krumholz (1956). His data, which were from the dissection of yellow bullheads (*I. natalis*), compared well with the data for selected black bullhead tissue in this study. Biological half-lives were calculated for the tissues in the elimination study and were plotted according to least-squares regression analyses.

Whole-body uptake and elimination curves were plotted, and the biological half-lives for elimination of radiotungsten after uptake from food and water were calculated. The whole-body elimination curves were subjected to the "peel off" method to determine the contribution of each component to the total curve (Wang and Willis, 1965). Extrapolating the long component back to t = 0 and subtracting the contribution of this portion from the total apparent activity gave the initial component of elimination.

RESULTS AND DISCUSSION

Bullheads accumulated radiotungsten from water steadily during the first 4 days of the uptake experiment. The whole-body activity after 4 days was 2×10^6 dis/min and remained at that level till the end of the experimental

period (6 days) (Fig. 1). Since freshwater fish do not normally drink water, the accumulation of radiotungsten may have been due to uptake by tissues, such as gills and skin.

Since the whole-body uptake experiment lasted only 6 days, it is not known if additional uptake would occur over a longer period of time. The plateau reached after 4 days of whole-body uptake may not represent a true equilibrium situation since the amount of radioactivity in the experimental water was not held constant during the study. Because stable tungsten analyses were not available, the specific activity (ratio of radiotungsten to total tungsten), which is a measure of mineral equilibrium in the fish, could not be calculated (Reed & Nelson, 1967).

Whole-body elimination of radiotungsten varied with the manner of intake. Fish that had accumulated radiotungsten from water for 4 days lost activity

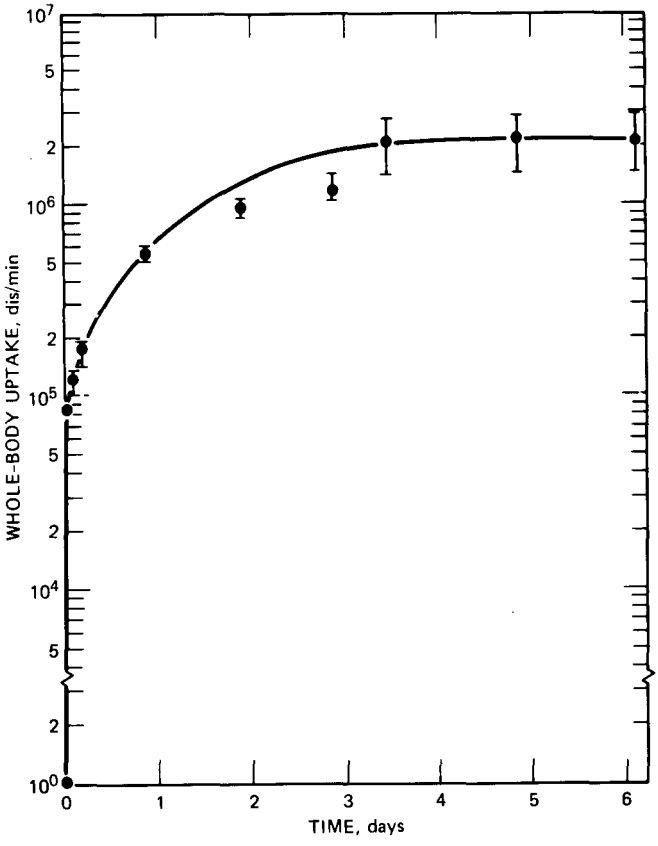

Fig. 1 Whole-body uptake (±1 standard error) of ^{187}W from water by black bullheads. Each point represents the mean of four fish.

steadily during the 7-day excretion period. Twenty-four percent of the initial activity was lost during the first 4 hr of excretion, probably via gut elimination [Fig. 2(a)]. The remaining 76% was excreted in an exponential fashion, with a biological half-life of 2.75 days. There were no available data for comparison with this portion of the experiment, but fish that received radiotungsten in a single feeding had an elimination curve [Fig. 2(b)] similar to those shown in several experiments with rats (Wase, 1956; Ballou, 1960; Kaye, 1968). A rapid component of elimination (T_{b_1}) with a biological half-life of 14 hr accounted for early losses in activity [Fig. 2(b)]. This may have been caused by elimination through the gastrointestinal tract.

A second component had a biological half-life (T_{b_2}) of 6 days. Since the elimination curve had not reached a plateau after 7 days, it is possible that one or more additional components of excretion would be evident if the experiment were continued over a longer period of time. Elimination of radiotungsten by various tissues reflects this hypothesis also since the long components of the tissue-excretion curves had biological half-lives from 2.1 to 8.0 days, whereas long-term studies with rats showed that one component with a half-life of 1100 days was present in bone (Kaye, 1968).

The greatest percentage of whole-body activity during the period of radiotungsten uptake from water was present in the bone, flesh, skin, gills, gut, and blood. Bone decreased in percent of total activity but still accounted for 23% after 8 days of exposure (Table 1). Skin and blood also lost activity relative to the total body, and at the end of the 8-day exposure period, these components contained 13.85 and 7.46%, respectively, of the whole-body activity (Table1). Flesh increased in activity during the uptake period and after 8 days contained 20.3% of the whole-body activity. The gut also showed increases and contained 10.72% of the whole-body activity. The gonads, spleen, gall bladder, and bile increased in activity during exposure, but these tissues combined were responsible for only 1.51% of the total activity after 8 days (Table 1). Only slight changes occurred in the proportion of radiotungsten in the heart, stomach, kidney, and liver, which ranged from 0.2 to 4.6% of the whole-body activity after 8 days of tissue uptake.

Losses of activity by tissues were followed for 16 days. During this time all tissues examined decreased rapidly in activity, with biological half-lives from 2.1 to 8.0 days.

As in studies with rats, the bone of bullheads had the longest biological half-life (8.0 days) of all the tissues examined. The gills, with their cartilaginous supportive structure, also had a relatively long half-life (5.1 days). The bone initially contained 32.2% of the whole-body activity, and, after 16 days of whole-body elimination, it contained 69.8% (Table 2). This trend is in agreement with studies on rats, in which more than 99% of the total body burden was in the bone after 100 days (Kaye, 1968). In bullheads the gills contained 9.4% of the total activity initially, and after 16 days they still contained 8.3% (Table 2).

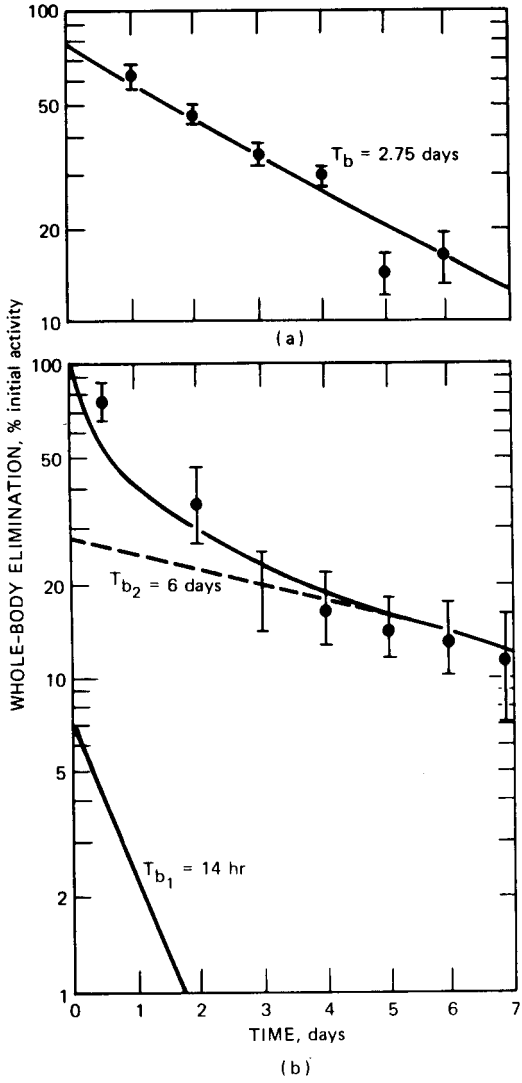

Fig. 2 (a) Whole-body elimination (±1 standard error) of ^{187}W by black bullheads after 4 days of radioisotope uptake from water. The biological half-life is 2.75 days. Each point represents the mean of six fish. (b) Whole-body elimination (±1 standard error) of ^{187}W by black bullheads after uptake in a single feeding. The biological half-lives of two components of elimination are indicated by T_{b_1} and T_{b_2}. Each point represents the mean of five fish.

TABLE 1

UPTAKE OF ^{181}W FROM WATER BY BLACK BULLHEAD TISSUES EXPRESSED AS A PERCENTAGE OF WHOLE-BODY ACTIVITY*

Tissue	N†	1 day	N†	2 days	N†	4 days	N†	8 days
Blood	3	9.05 ± 0.96	3	9.55 ± 1.86	4	7.01 ± 0.64	2	7.46 ± 0.97
Skin	3	16.70 ± 0.63	3	17.48 ± 1.33	4	10.41 ± 0.96	2	13.85 ± 1.46
Flesh	3	14.32 ± 0.70	3	17.63 ± 0.74	4	16.26 ± 2.00	2	20.30 ± 3.98
Liver	3	2.86 ± 0.33	3	2.94 ± 0.08	4	2.73 ± 0.25	2	3.24 ± 0.50
Stomach	3	5.21 ± 0.56	3	3.10 ± 0.28	4	4.05 ± 0.62	2	4.57 ± 1.65
Gut	3	3.71 ± 0.40	3	6.66 ± 2.71	4	9.12 ± 2.81	2	10.72 ± 6.49
Kidney	3	3.57 ± 0.16	3	3.60 ± 0.66	4	2.35 ± 0.35	2	4.39 ± 0.76
Heart	3	0.22 ± 0.04	3	0.25 ± 0.03	4	0.22 ± 0.03	2	0.21 ± 0.03
Bone	3	32.22 ± 1.83	3	29.46 ± 1.40	4	35.96 ± 3.29	2	23.68 ± 15.83
Gills	3	11.03 ± 2.48	2	11.08 ± 3.08	4	10.68 ± 1.17	2	10.02 ± 0.66
Spleen	3	0.07 ± 0.02	3	0.10 ± 0.02	4	0.25 ± 0.07	2	0.12 ± 0.01
Gonads	3	0.98 ± 0.39	3	0.46 ± 0.32	4	0.95 ± 0.47	2	1.11 ± 0.84
Bile and bladder	1	0.03	3	0.09 ± 0.02	1	0.06	2	0.28 ± 0.17

*Mean $\frac{\text{tissue (dis/min)}}{\text{whole-body (dis/min)}}$ ± 1 SE (%).

†Number of samples.

Increases in activity in the kidney and liver correspond to results from experiments with rats (Hamilton, 1951; Wase, 1956; Ballou, 1960; Kaye, 1968) and were probably due to urinary excretion in the case of the kidney and to radiotungsten losses from the flesh, skin, and blood to both liver and kidney (Table 2). In contrast to data from experiments with rats, the spleen decreased in activity and contained only 0.03% of the total activity after 16 days. This may be due to differences in hemopoiesis between fishes and mammals.

The gut and stomach, devoid of contents, had biological half-lives of 3.8 and 3.3 days, respectively. These tissues contained 10.5% of the initial whole-body activity, but after 16 days the stomach had dropped from 4.4 to 0.85%, and the gut decreased from 6.2 to 3.6%. These results differ from those reported in studies with rats, in which gastrointestinal tract elimination accounted for 40% or more of the radiotungsten losses (Ballou, 1960; Fleshman, Krotz, and Silva, 1966; Kaye, 1968). This difference may be due to the method of radiotungsten administration or treatment of gut and stomach contents. The rats were injected either intraperitoneally or intramuscularly or were fed the radioisotope, whereas the bullheads accumulated radiotungsten from water.

This study has shown that black bullheads are capable of accumulating and retaining radiotungsten from both water and food. The distribution of the radioisotope among the various tissues was quite similar to distributions reported

TABLE 2

ELIMINATION OF ^{181}W FROM BLACK BULLHEAD TISSUES AFTER 4 DAYS OF UPTAKE FROM WATER EXPRESSED AS A PERCENTAGE OF WHOLE-BODY ACTIVITY*

Tissue	Initial	1 day	2 days	4 days	8 days	16 days
Blood	9.03 ± 0.84	6.07 ± 0.57	5.85 ± 0.39	3.98 ± 0.04	1.71 ± 0.10	0.46 ± 0.08
Skin	12.43 ± 1.18	12.10 ± 3.25	11.76 ± 2.15	6.95 ± 3.10	4.71 ± 0.72	2.65 ± 0.47
Flesh	13.56 ± 0.89	12.93 ± 2.16	11.78 ± 1.31	9.74 ± 1.04	5.04 ± 0.46	3.32 ± 0.20
Liver	1.89 ± 0.12	2.45 ± 0.37	2.15 ± 0.10	2.90 ± 0.69	2.67 ± 0.39	3.12 ± 0.34
Stomach	4.38 ± 2.07	3.09 ± 0.21	2.64 ± 0.36	2.21 ± 0.66	1.28 ± 0.17	0.85 ± 0.11
Gut	6.16 ± 2.84	5.63 ± 1.03	4.29 ± 0.60	3.79 ± 1.44	2.68 ± 1.03	3.58 ± 0.80
Kidney	9.69 ± 6.27	3.56 ± 0.45	4.54 ± 0.45	3.53 ± 0.63	7.34 ± 1.86	6.27 ± 0.32
Heart	0.16 ± 0.02	0.17 ± 0.06	0.12 ± 0.01	0.14 ± 0.04	0.07 ± 0.02	0.01 ± 0.01
Bone	32.17 ± 5.35	44.75 ± 4.51	46.73 ± 2.34	54.85 ± 2.38	64.72 ± 1.51	69.79 ± 1.55
Gills	9.41 ± 1.07	8.78 ± 0.81	9.05 ± 1.01	9.43 ± 0.91	8.88 ± 1.13	8.33 ± 0.30
Spleen	0.12 ± 0.04	0.11 ± 0.01	0.39 ± 0.29	0.09 ± 0.03	0.09 ± 0.02	0.03 ± 0.02
Gonads	0.85 ± 0.34	0.15 ± 0.03	1.06 ± 0.57	1.17 ± 0.24	0.75 ± 0.34	1.54 ± 0.76
Bile and bladder (N = 2)	0.14 ± 0.01	0.09 ± 0.04	0.20 ± 0.08	0.46 ± 0.22	0.02 (N = 1)	0 (N = 2)

*Mean $\frac{\text{tissue (dis/min)}}{\text{whole-body (dis/min)}}$ ± 1 SE (%), N = 3.

in studies with rats. Radiotungsten was eliminated at different rates depending on the method of uptake. The bone was the critical tissue in terms of body burden regardless of the method of accumulation. Additional experiments would be of interest to determine the long-term pattern of radiotungsten distribution in bullheads and other fish species.

ACKNOWLEDGMENTS

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REFERENCES

Ballou, J. E., 1960, Metabolism of ^{185}W in the Rat, USAEC Report HW-64112, General Electric Company, Hanford Atomic Products Operation, Richland, Wash.

Essington, E. H., H. Nishita, and A. J. Steen, 1965, Release and Movement of Radionuclides in Soils Contaminated with Fallout Material from an Underground Thermonuclear Detonation, *Health Phys.*, 11(8): 689-698.

Fleshman, D., S. Krotz, and A. Silva, 1966, The Metabolism of Elements of High Atomic Number, in Program Book for the Advisory Committee for Biology and Medicine of the United States Atomic Energy Commission. Part II, USAEC Report UCRL-14739(Pt. 2), pp. 69-86, California University, Livermore, Lawrence Livermore Laboratory.

Hamilton, J. G., 1951, The Metabolic Properties of Various Materials, in Medical and Health Physics Quarterly Report, July, August, and September, 1951, USAEC Report AECD-3354, University of California, Radiation Laboratory.

Kaye, S. V., 1968, Distribution and Retention of Orally Administered Radiotungsten in the Rat, *Health Phys.*, 15: 399.

___, and D. A. Crossley, Jr., 1968, Radiotungsten Retention by Two Insect Species, *Health Phys.*, 14: 162-165.

Krumholz, L. A., 1956, *Observations of the Fish Population of a Lake Contaminated by Radioactive Wastes*, American Museum of Natural History, New York.

Lane, W. B., 1963, Some Radiochemical and Physical Measurements of Debris from an Underground Nuclear Detonation, USAEC Report PNE-29F, Naval Radiological Defense Laboratory, San Francisco.

Reed, J. R., and B. A. Martinedes, 1971, Uptake and Retention of Tungsten-181 by Crayfish (*Cambarus longulus longerostris* Ort.), in Radionuclides in Ecosystems, Proceedings of the Third National Symposium on Radioecology, May 10–12, 1971, Oak Ridge, Tenn., D. J. Nelson (Ed), USAEC Report CONF-710501(Pt. 1), pp. 390-393, U. S. Atomic Energy Commission, Oak Ridge National Laboratory, and The Ecological Society of America.

___, and D. J. Nelson, 1967, Radiostrontium Uptake in Blood and Flesh of Bluegills, *Lepomis macrochirus* Rafinesque, in Proceedings of the Second National Symposium on Radioecology, Ann Arbor, Mich., May 15–17, 1967, D. J. Nelson and F. C. Evans

(Eds.), USAEC Report CONF-670503, pp. 226-233, U. S. Atomic Energy Commission, The Ecological Society of America, and The University of Michigan.

Wang, C. H., and D. L. Willis, 1965, *Radiotracer Methodology in Biological Science*, p. 32, Prentice-Hall, Inc., Englewood Cliffs, N. J.

Wase, A. W., 1956, Absorption and Distribution of Radiotungstate in Bone and Soft Tissues, *Arch. Biochem. Biophys.*, **61**: 272-277.

MOBILIZATION OF MERCURY FROM FRESHWATER SEDIMENTS BY HUMIC ACID

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ABSTRACT

Mercury added to freshwater systems rapidly ends up in the sediments, from which several pathways of mobilization are possible. Data are presented on the release of elemental mercury (Hg^0) formed during the interaction between added inorganic mercury (Hg^{2+}) and natural humic acid. The release of Hg^0 varies with the ratio between humic acid and mercury. Release is quite substantial when there is a moderate excess of humic acid but slows considerably when there is less humic acid than mercury. A great excess of humic material totally inhibits the reaction. In whole sediments, therefore, the amount of humic acid present should have a great effect on the amount of mercury released.

The mercury cycle has received much attention lately because of perturbations caused by man's activities. These are generally localized imbalances but can have very serious consequences, as seen in Minamata, Japan. On a global scale, Hammond (1971) estimated that since 1900 losses of mercury to the environment from both fossil-fuel burning and agricultural and industrial uses have amounted to 10^5 tons. Even if all this mercury reached the oceans, it is considerably less than the 10^8 tons already present there. Miller et al. (1972) report that museum specimens of tuna caught as long ago as 1878 show the same levels of mercury as recent specimens; this indicates that there has been no change in the concentration of mercury in the oceans. In more restricted freshwater or estuarine areas, however, the addition of only a few pounds of mercury each day can have far-reaching effects, which are only beginning to be understood.

Figure 1 shows some of the reactions that take place when inorganic mercury (Hg^{2+}) is added to water. It is rapidly and strongly taken up by the sediments (Jenne, 1970), where it may remain or may undergo any of several transformations. If sulfide is present, insoluble mercuric sulfide will be formed.

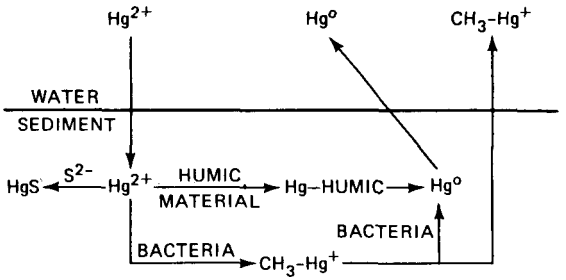

Fig. 1 Mercury transformations in a water–sediment system. Not all possible reactions or intermediate compounds are shown here, and some of the processes may be reversible. All three forms of mercury shown in the water are readily taken up by the biota.

Uptake by bacteria can lead to the formation of methylmercury, which may be released to the water (Wood, 1974) or broken down by demethylating bacteria to release elemental mercury (Hg^0) (Spangler et al., 1973). Another possible reaction involves uptake by humic materials in the sediment and subsequent reduction to Hg^0. Strohal and Huljev (1971) found that mercuric ion forms a strong complex with humic acids. Szilagyi (1971) showed that soil humic material is capable of reducing ferric iron to ferrous iron in aqueous solution, and Szalay and Szilagyi (1967) described a similar reduction of vanadium. If mercuric ion (Hg^{2+}) could also be reduced by humic acid, elemental mercury (Hg^0) would be produced. In fact, Bongers and Khattak (1972) found that Hg^{2+} added to sediments was released as Hg^0, and we have shown that this reduction is mediated by humic acid in purified form (Alberts et al., 1974). This paper presents further data on the interaction between mercury and humic acids and the mobilization of Hg^0.

MATERIALS AND METHODS

The volatilization of elemental mercury was carried out in the apparatus shown in Fig. 2. Mercury of known specific activity was added to the reaction flask (as $HgCl_2$ with $^{203}Hg(NO_3)_2$ as a tracer), and humic acid was introduced in purified form (10% ash). The reaction solution was buffered with borate–boric acid prepared by adding boric acid to a saturated sodium borate solution until the desired pH (between 6 and 9) was obtained. All reactions were carried out at ambient temperature (23 to 25°C). The sediment from which the humic material was extracted came from a farm pond near the University of Georgia. The mud was shaken with a fivefold (w/v) excess of 0.1*N* KOH for 12 hr and then centrifuged at 14,000 rpm to separate all solids. The supernatant was acidified to pH 1 with concentrated HCl to precipitate the humic acid, which was then separated by centrifugation. The humic acid was shaken for 48 hr with

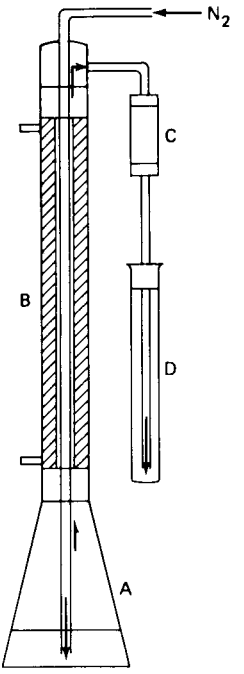

Fig. 2 Experimental apparatus for volatilization of elemental mercury. A, reaction flask. B, water-filled condenser. C, anhydrone trap. D, mercury trap containing 20 ml of 5% (w/v) potassium permanganate and 5 ml of 18*N* sulfuric acid. A stream of gas (N_2 or air) is passed down the tube into the reaction flask and then out through the anhydrone trap and the mercury trap, where volatile mercury species are removed.

several changes of 1% HF–HCl, redissolved in 0.1*N* KOH, dialyzed against distilled water until the pH was near neutral, and freeze-dried.

The mercury trap quantitatively removed all volatile mercury species. The identity of the species involved was determined by passing the untrapped effluent gas through the beam of an atomic absorption spectrophotometer set to determine elemental mercury. A positive response was noted. A further test involved placing a trap containing cysteine in the gas flow; this would complex both ionic and organic forms of mercury (Clarkson and Greenwood, 1970). Since no retention of mercury was observed, we concluded that the volatile form was indeed elemental mercury. The trapped mercury was quantified by radioactive measurement in a scintillation counter with a 2- by 2-in. NaI crystal. The mercury trap was treated with 5 ml of 25% (w/v) hydroxylamine hydrochloride to clear the permanganate and any precipitate, and an aliquot of this solution was counted. After correcting for background and decay, we divided the sample counts by the specific activity of the mercury in the reaction

flask to determine the amount of mercury present in the trap. Material balances for mercury done at the conclusion of a run accounted for 80 to 90% of the mercury initially added. Losses to the glassware and the anhydrone trap are possible and may also occur during the addition of hydroxylamine hydrochloride.

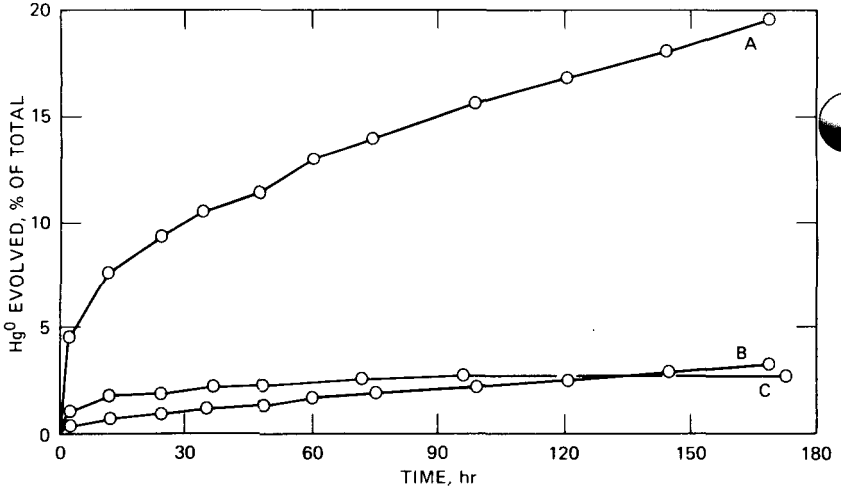

Fig. 3 Volatilization of Hg^0 in the presence of purified humic acid. Each reaction flask contained Hg^{2+} and humic acid in varying ratios and was buffered at pH 7.2. Humic acid-to-mercury ratios were A, 50 : 1; B, 1 : 2; C, 1000 : 1. Total mercury in A and B was 200 μg and in C, 10 μg.

RESULTS

Figure 3 illustrates the reduction of inorganic mercury to the elemental form in the presence of humic acids. When the ratio (by weight) of humic acid to mercury is 50 : 1, a significant fraction of the total mercury added initially is volatilized over the course of about a week. When the ratio is greatly decreased, to 1 : 2, so is the rate of reaction, particularly over the first 48 hr. However, release of Hg^0 does continue at a steady rate over the next 120 hr. A large excess of humic acid to mercury, 1000 : 1, almost totally halts the reaction after a small initial release. Further data presented in Table 1 indicate that the release of mercury is relatively insensitive to the ratio of humic acid to mercury over a large range and only at the extremes does it seriously inhibit the reaction.

Other factors affecting the rate of release of Hg^0 include pH and the presence of sulfide (S^{2-}). Alberts et al. (1974) showed that release is inversely pH dependent between pH 6.5 and 9.0, and further unpublished results extend this range to pH 4.1. The addition of sulfide to the reaction flask (as Na_2S) has

TABLE 1

THE EFFECT OF THE HUMIC ACID : Hg^{2+} RATIO BY WEIGHT ON THE RELEASE OF Hg^0

Humic acid : Hg^{2+}	Hg^0 evolved after 100 hr,* % of total
1000 : 1	2.5 (5)
400 : 1	11.5 (1)
50 : 1	14.5 (3)
5 : 1	12.8 (2)
1 : 2	2.6 (5)

*Figure in parentheses is the number of determinations at each ratio.

the effect of totally halting the reaction, presumably because of the formation of mercuric sulfide (HgS). The use of either air or nitrogen to sparge the solution has no effect on the reaction, and the addition of some other common cations (Fe^{3+}, Al^{3+}, Ca^{2+}, Mg^{2+}, Na^+, K^+) is also without effect.

DISCUSSION

The interaction between mercury and humic acid, with the subsequent mobilization of elemental mercury, is a complex problem of unknown importance in the mercury cycle. Using simplified systems containing inorganic mercury and purified humic acid, we obtained seemingly contradictory results. At levels of humic acid 50 times greater than the mercury present, a substantial amount of the mercury is released as Hg^0. A 100-fold decrease in the amount of humic acid causes a decrease in both the rate and the cumulative amount of elemental mercury released. However, a large increase in the amount of humic acid relative to mercury also depresses the reaction, inhibiting it almost totally. One possible explanation of these results is that two processes are actually taking place. The reduction of Hg^{2+} to Hg^0 is mediated by humic acid, but the actual mechanism is not known. We think that the electrons required may come from free radicals associated with humic acid (Alberts et al., 1974). The humic acid molecule may participate directly in the reaction or may be more of a catalyst in aiding the reduction process. Another process taking place could be a strong complexation of the mercury by the humic acid molecule. If excess humic acid could effectively bind all the mercury and immobilize it in either the ionic or elemental form, we would expect the inhibition of release. This was observed.

If we extend these observations to the possible release of elemental mercury from sediments, the organic content of the sediments becomes an important

factor. Where humic acid concentration is high, small amounts of mercury are likely to be entirely complexed and release of Hg^0 will not occur. Sediments of lower organic content may actively release Hg^0, however. When the humic acid concentration of a given sediment remains constant, a steady increase in the mercury concentration will eventually lead to an excess of mercury over that able to be complexed and Hg^0 will be released. If the additions of mercury are halted, the excess will be reduced, and the residual mercury firmly bound to the humic acid will remain in the sediment. The presence of sulfide will complicate this scheme and probably lead to the permanent removal of more mercury to the sediment (Fagerstrom and Jernelov, 1972). At any one ti therefore, most of the mercury present in a given sediment will be immobilized there, with only a small fraction available for release as either elemental or methylmercury.

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REFERENCES

Alberts, J. J., J. E. Schindler, R. W. Miller, and D. E. Nutter, Jr., 1974, Elemental Mercury Evolution Mediated by Humic Acid, *Science*, **184**: 895-897.

Bongers, L. H., and M. N. Khattak, 1972, Sand and Gravel Overlay for Control of Mercury in Sediments, Water Pollution Control Research Series, 16080 HVA 01/72, Environmental Protection Agency.

Clarkson, T. W., and M. R. Greenwood, 1970, Selective Determination of Inorganic Mercury in the Presence of Organomercurial Compounds in Biological Material, *Anal. Biochem.*, **37**: 236-243.

Fagerstrom, T., and A. Jernelov, 1972, Some Aspects of the Quantitative Ecology of Mercury, *Water Res.*, **6**: 1193-1202.

Hammond, A. L., 1971, Mercury in the Environment: Natural and Human Factors, *Science*, **171**: 788-789.

Jenne, E. A., 1970, Atmospheric and Fluvial Transport of Mercury, in *Mercury in th Environment*, U. S. Geological Survey, Professional Paper No. 713, pp. 40-45.

Miller, G. E., P. M. Grant, R. Kishore, F. J. Steinkruger, F. S. Rowland, and V. P. Guin 1972, Mercury Concentrations in Museum Specimens of Tuna and Swordfish, *Science*, **175**: 1121-1122.

Spangler, W. J., J. L. Spigarelli, J. M. Rose, R. S. Flippin, and H. H. Miller, 1973, Degradation of Methylmercury by Bacteria Isolated from Environmental Samples, *Appl. Microbiol.*, **25**: 488-493.

Strohal, P., and D. Huljev, 1971, Investigation of Mercury-Pollutant Interaction with Humic Acids by Means of Radiotracers, in *Nuclear Techniques in Environmental Pollution*, Symposium Proceedings, Salzburg, 1970, pp. 439-446, International Atomic Energy Agency, Vienna (STI/PUB/268).

Szalay, A., and M. Szilagyi, 1967, The Association of Vanadium with Humic Acids, *Geochim. Cosmochim. Acta,* **31**: 1-6.

Szilagyi, M., 1971, Reduction of Fe^{3+} Ion by Humic Acid Preparations, *Soil Sci.,* **111**: 233-235.

Wood, J. M., 1974, Biological Cycles for Toxic Elements in the Environment, *Science,* **183**: 1049-1052.

REDISTRIBUTION OF CESIUM-137 IN SOUTHEASTERN WATERSHEDS

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ABSTRACT

Sediment samples from 14 southeastern agricultural reservoirs and surface samples from representative soils from the contributing watershed areas were analyzed for ^{137}Cs. The concentrations of ^{137}Cs measured reflect the nature of the watershed, its cover, its use, and man's activities. Since the redistribution of ^{137}Cs was assumed to result from soil erosion, recent erosion rates can be calculated from the measured ^{137}Cs accumulations in sediments and from the decreases in the ^{137}Cs calculated to have been deposited on upland soils. Measured concentrations of ^{137}Cs ranged from 14 to 158 nCi/m^2 in surface soils. As much as 525 nCi/m^2 of ^{137}Cs was measured in the deposited sediment profile. Watershed budgets for ^{137}Cs were calculated for three representative watersheds using available sediment survey information and the measured ^{137}Cs concentrations.

Watersheds are often considered the smallest ecosystem unit for practical management by man (Odum, 1971). The biochemical cycles of nutrients and other chemical elements within or through this watershed ecosystem must be understood before these ecosystems can be properly managed. With the increasing use of atomic energy to produce power, the movement of radioactive materials in watershed ecosystems must be understood so that decisions on locating nuclear reactors and on the release of radioactive materials from these reactors can be made to ensure safety and sustain the ecosystems.

Fallout of ^{137}Cs and ^{90}Sr from the nuclear bomb tests of the 1950s and early 1960s is distributed over the world in regional patterns. A study of distribution of ^{137}Cs in watershed components can provide much information on the cycling of this nuclide within a given watershed ecosystem. Once in contact with the soil, ^{137}Cs becomes strongly adsorbed on the finer soil fractions, and further downward movement by physiochemical processes is limited (Tamura, 1964). Therefore most of the redistribution of ^{137}Cs within

watershed ecosystems should be related to the erosion cycle in the watershed (Ritchie, Spraberry, and McHenry, 1974).

In this paper we show the distribution and movement of fallout ^{137}Cs in selected southeastern watershed ecosystems.

MATERIALS AND METHODS

Watersheds

Fourteen watersheds in the southeastern United States were selected for this study. Reservoirs control all the surface runoff from these watersheds. The watersheds and the controlling reservoirs are briefly characterized in Table 1. Land use on the watersheds is a mixture of cropland, pasture, and forest. Parts of each watershed have been cultivated; however, at the time of sampling (1970–1972), Powerline and Salem Fork No. 11A had no cultivated areas. All the watersheds studied have a considerable acreage of land devoted to pasture, improved or unimproved. The forests consist primarily of oaks, (*Quercus* sp.), hickories (*Carya* sp.), and pines (*Pinus* sp.). Both planted and naturally reseeded pine stands exist. The dominance of forest type and land use varied among watersheds.

Sampling

Soil samples were collected in 2.5- or 5.0-cm increments to a depth of 10 cm at sites representative of the different land-use conditions on the watershed. The surface litter was included in the surface soil sample.

Sediment samples from within the reservoir were taken in 5- or 10-cm increments with an 8.1-cm-diameter corer. The volumetric cores were taken from the accumulated sediment profiles at several locations within the reservoir. The samples were dried in the laboratory at 70°C for 48 hr and then passed through a 12.5-mm sieve. The dried and screened samples (2 to 3 kg) were sealed in plastic Marinelli beakers and allowed to stand at least 2 weeks before radiological analyses.

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Gamma-ray spectrometric analyses were made using a 1024-channel pulse-height analyzer and a 10- by 12.5-cm NaI(Tl) crystal as the detector. The energy scan was from 0 to 2.82 MeV (Ritchie and McHenry, 1973). A computer program for the least-squares resolution of gamma-ray spectra was used to reduce the spectra (Schonfeld, 1966). Typical statistics for precision of measurements have been published (Ritchie and McHenry, 1973). The detection limit of the system is less than 0.03 pCi/g. This value translates into 1.5 nCi/m^2 for a soil or sediment with a density of 1.00.

TABLE 1

LOCATION AND CHARACTERISTICS OF SELECTED SOUTHEASTERN RESERVOIRS AND WATERSHEDS

Watershed	Location (county and state)	Year of reservoir construction	Watershed area, ha	Reservoir capacity, m^3	Dominant soils
North Fork Broad River No. 14	Stephens, Ga.	1954	311	347×10^3	Hapludults
Lake Mary	Tift, Ga.	1929	233	(12-ha area)	Paleudults and hapludults
Walker Pond	Tift, Ga.	1960	24	12×10^3	Paleudults and hapludults
Plum Creek No. 4	Shelby, Ky.	1954	370	493×10^3	Hapludalfs
Rock Creek No. 2 (Lake Bernard Frank)	Montgomery, Md.	1966	3238	0.97×10^6	Hapludults
Askalmore (Y-17a-2)	Tallahatchie, Miss.	1959	1551	2.38×10^6	Hapludalfs
East Cypress (LT-14a-6)	Lafayette, Miss.	1962	947	1.05×10^6	Paleudults
Murphy	Marshall, Miss.	1953	55	28×10^3	Paleudults and fragiudults
Powerline	Lafayette, Miss.	1953	126	38×10^3	Paleudults
Puss Cuss (LT-14a-1)	Lafayette, Miss.	1962	4040	5.59×10^6	Paleudults
Smith	Marshall, Miss.	1953	88	28×10^3	Paleudults and fragiudults
Third Creek No. 7A	Alexander, N. C.	1954	1254	1.09×10^6	Hapludults
Third Creek No. 21	Iredell, N. C.	1954	417	517×10^3	Hapludults
Salem Fo[illegible]11A	Harrison, W. Va.	1954	75	63×10^3	[illegible]ochrepts

Sedimentation

A number of the watersheds reported here were used in a federal interagency study of the trap efficiencies of small agricultural reservoirs. These reservoirs were surveyed at intervals to determine the volume of accumulated sediment. The data are available in a series of reports compiled at the USDA Sedimentation Laboratory (Dendy and Champion, 1973).

EXPERIMENTAL RESULTS

The fallout of ^{137}Cs on the study watersheds was estimated from the concentrations of ^{137}Cs measured under forest or other undisturbed, uneroded cover. The values measured, together with those calculated from published U. S. Atomic Energy Commission (AEC) reports for three selected stations within the area, are given in Table 2. The data from the AEC monitoring stations were taken from Health and Safety Laboratory Fallout Quarterly Summary Reports (1970–1973) as ^{90}Sr concentrations and were converted to ^{137}Cs concentrations according to the method of Gustafson (1969). The magnitude of the measured ^{137}Cs concentrations on undisturbed watershed sites is of the same order as that reported for the AEC monitoring sites in the region. Where a range of values is indicated in Table 2, two or more sites are involved in the summarized data. For example, in the Plum Creek watershed in Kentucky, the values from two pastures and one forested site are shown in Table 2 as a mean value with the standard error and the range of values.

Cultivation affects both the distribution of the fallout ^{137}Cs within the soil profile and the total amount found. The ^{137}Cs is distributed throughout the plow depth, and, unlike the undisturbed sites, the concentration of ^{137}Cs in the surface soil is no longer predominant. Other studies conducted at the USDA Sedimentation Laboratory (Ritchie et al., 1970, 1973) have also indicated this effect. Data from Third Creek No. 7A in Alexander County, N. C. (Table 3), illustrate this effect. The soil samples collected were taken only to a depth of 10 cm. However, the average depth of plowing in the area was deeper, perhaps as much as 15 or 20 cm. The measured ^{137}Cs concentrations in the cultivated soils this particular North Carolina watershed should be increased accordingly, as own in Table 3. The data shown in Table 3 do indicate that considerable amounts of ^{137}Cs fallout have been lost from the cultivated areas. Similar losses were observed on cultivated portions of other watersheds. The losses may be ascribed to soil erosion and perhaps to some removal of ^{137}Cs in harvested crops.

There are numerous reports in the literature concerning the adsorption and retention of ^{137}Cs at or near the surface of the soil (McHenry, Ritchie, and Gill, 1973; Benson, 1960). The data presented in Table 3 for undisturbed sites (pine)

TABLE 2

CUMULATIVE ^{137}Cs FALLOUT MEASURED AT UNDISTURBED SITES AND THE DISTRIBUTION OF ^{137}Cs CALCULATED FOR SELECTED SOUTHEASTERN WATERSHEDS

Watershed	Concentration of ^{137}Cs fallout, nCi/m^2			Total ^{137}Cs, mCi		
	Mean ± SE	Range	Calculated deposition	Input to watershed*	Found in watershed soils	Found in reservoir sediments
North Fork Broad No. 14	136 ± 11	105–167	136	423	452	7
Lake Mary	84	84	84	196	193	6†
Walker Pond	111 ± 36	66–182	111	27	22	1†
Plum Creek No. 4	113 ± 7	100–124	113	418	437	14
Rock Creek No. 2	116 ± 9	107–126	116	3756	3545	18
Askalmore	118 ± 10	104–146	118	1830	1718	44†
East Cypress	132 ± 5	109–153	132	1250	1067	4†
Murphy	153 ± 5	137–168	153	84	64	9
Powerline	158 ± 3	152–162	158	199	184	11
Puss Cuss	125 ± 6	96–158	125	5050	4396	114†
Smith	156 ± 11	142–177	156	137	101	9
Third Creek No. 7A	116 ± 27	89–143	116	1455	1173	11
Third Creek No. 21	98	98	98	409	359	7†
Salem Fork No. 11A	119 ± 12	100–140	119	89	89	2
AEC monitoring stations:						
Birmingham, Ala., 1957–1972			121			
Columbia, S. C., 1959–1972			73			
New York City, 1954–1972			163			

*Calculated from the undisturbed sampling sites.

†Based on estimated sediment accumulation.

TABLE 3

DISTRIBUTION OF ^{137}Cs IN SOILS UNDER DIFFERENT COVER (THIRD CREEK NO. 7A, ALEXANDER COUNTY, NORTH CAROLINA)

Cover	Depth, cm	Concentration of ^{137}Cs, nCi/m^2	
		Per sample	Total
Wheat	0–5	19.56	
	5–10	18.53	76.18*
Corn	0–5	19.27	
	5–10	20.29	79.12*
Corn	0–5	10.08	
	5–10	9.21	38.58*
Tobacco	0–5	27.09	
	5–10	29.60	113.38*
Pine	0–5	78.62	89.06
	5–10	10.44	
Pine	0–5	109.48	143.05
	5–10	33.57	

*Assumed plow depth of 20 cm.

give additional verification. Similar data were obtained for all watersheds considered in this study.

Assuming that all the fallout ^{137}Cs was adsorbed, or fixed, on particles at the soil surface and that little downward movement occurred subsequently, measurements of ^{137}Cs in soil profiles should produce totals equivalent to the total fallout. If the soils were cultivated, the accumulated ^{137}Cs would be distributed, of course, throughout the depth of tillage, as indicated above, and not in the immediate surface soil as is the case in undisturbed forested and grassed areas.

We (Ritchie et al., 1970, 1973; Ritchie, McHenry, and Gill, 1974) have calculated the relative amounts of fallout ^{137}Cs accumulated in the sediments found in the reservoir controlling the runoff from the watershed. Similar calculations were made for each of the study watersheds. The data are summarized in Table 2. The ^{137}Cs fallout was taken as the mean measured for t. The ^{137}Cs watershed input column is the product of the assumed fallout times the watershed area. The ^{137}Cs contents in the "watershed soils" column were determined using the average ^{137}Cs concentration measured in the soil samples. This value is expressed on a watershed basis. Values for cultivated soils have been increased to reflect the plow-depth concentration. The ^{137}Cs contents in the "reservoir sediments" column were determined on the basis of the measured ^{137}Cs found in the sediments and of the amount of accumulated sediment calculated from sediment survey records. In six of the watersheds no values for measured sediment were available, and estimates of the accumulated

sediment were made on the basis of available information. Sediment-accumulation records were available for the early life of some of the reservoirs, and in those reservoirs the calculated rates of sedimentation were extrapolated to the date of sample collection.

The data shown in Table 2 indicate that most of the fallout ^{137}Cs falling on southeastern watersheds is still on that watershed, undoubtedly adsorbed by the (finer) soil particles. Some ^{137}Cs has been removed from the watershed. A portion of this ^{137}Cs is found in the reservoir sediments. On an area basis there has been an increase of ^{137}Cs in these reservoir sediments over that in the watershed soils. The concentration of ^{137}Cs in these selected reservoirs, concentration factor, on an area basis is:

North Fork Broad No. 14	2.0
Plum Creek No. 4	2.7
Rock Creek No. 2	5.3
Powerline	2.8
Third Creek No. 7A	1.6
Salem Fork No. 11A	3.1

The total ^{137}Cs activity found in the reservoir sediments is only a small percentage of that existing on the watershed. For watersheds with complete data, ^{137}Cs loss from the watershed was calculated. This loss may be due to crop removal or to soil erosion and movement of the radioactivity from the watershed through the reservoir as outflow.

A complete budget of the incoming, existing, and removed ^{137}Cs was obtained for three of the study watersheds located in north Mississippi, i.e., for Murphy, Powerline, and Smith watersheds. This was possible because a record of the land use was obtained when the soil and sediment samples were collected. We have partially reported the data collected for the study watersheds (Ritchie, McHenry, and Gill, 1974). Representative data collected from the Murphy watershed, Fig. 1, show the ^{137}Cs input to the entire watershed, its distribution in the watershed soils by cover types, and the assumed loss calculated on the uneroded areas. The input to the reservoirs, fallout and runoff, is calculated and compared with the quantity measured in the reservoir. The difference between the calculated ^{137}Cs input to and the measured content in the reservoir is assumed lost from the watershed. Trap efficiencies calculated for Murphy, Powerline, and Smith reservoirs for incoming ^{137}Cs were 38, 53, and 25%, respectively. The percentages of ^{137}Cs calculated lost from the watersheds were 12, 3, and 15%, respectively, of that assumed deposited.

Two mechanisms are assumed to account for the loss of ^{137}Cs from the study watersheds—erosion and crop removal. No data are available on the ^{137}Cs content of the crops grown on most of the study watersheds. On Powerline, where no cultivation existed, half the ^{137}Cs removed from the

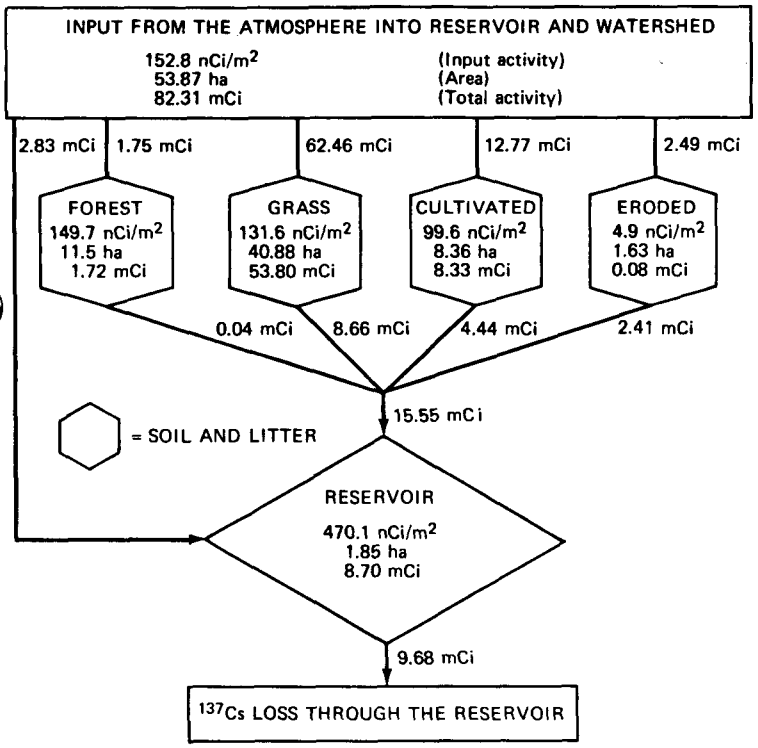

Fig. 1 Distribution of fallout ^{137}Cs in Murphy watershed, Marshall County, Mississippi.

watershed soils apparently passed through the reservoir, probably adsorbed on the fine clay or organic colloids. The percent lost from Smith watershed was considerably greater. Smith watershed was also the most extensively cultivated. Apparently in these particular watersheds a measurable amount of ^{137}Cs was removed with the harvested crop.

SUMMARY AND CONCLUSIONS

The concentration and distribution of fallout ^{137}Cs were determined for 14 southeastern watersheds. On the basis of the assumption that the measured ^{137}Cs concentration in uneroded and undisturbed areas represented the integrated total input, ^{137}Cs losses were calculated. In all 14 watersheds most of the ^{137}Cs fallout was still in the watershed. Some ^{137}Cs moves from the watershed, as shown by an areal buildup of ^{137}Cs in the sediments of the reservoirs controlling the outflow of the watersheds. For those watersheds with

complete records of cover, ^{137}Cs content, and sediment accumulation, only a fraction of the deposited ^{137}Cs has been removed from the watershed. The loss of ^{137}Cs was greater from cultivated watersheds than from uncultivated watersheds.

On the basis of the results from these 14 southeastern watersheds, the loss of radioactive fallout, as determined for ^{137}Cs, is very small (<5%) from uncultivated watersheds. Some ^{137}Cs is lost through soil erosion, but much of this is trapped on sediments by the controlling reservoir. Where crops are removed from the watersheds, a measurable amount of the ^{137}Cs deposited on the cultivated areas may be removed. If an agricultural watershed was gr[illegible] contaminated, little loss of the radioactivity would be expected from[illegible] watershed if no agricultural crops were removed. If procedures were adopted to flocculate the fine particles entering reservoirs with runoff waters, the losses of radioactivity from the watersheds through the reservoirs could be reduced to a very low value.

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REFERENCES

Benson, D. W., 1960, Review of Soil Chemistry Research at Hanford, USAEC Report HW-67201, Hanford Atomic Products Operation.

Dendy, F. E., and W. A. Champion (Comps.), 1973, *Summary of Reservoir Sediment Deposition Surveys Made in the United States Through 1970*, U. S. Department of Agriculture, Miscellaneous, Bulletin No. 1266.

Gustafson, P. F., 1969, ^{137}Cs in the U. S. Diet 1961–1968 and the Influence of Climatic and Agricultural Factors, in *Environmental Contamination by Radioactive Materials*, Symposium Proceedings, Vienna, 1969, pp. 135-143, International Atomic Energy Agency, Vienna, 1969 (STI/PUB/226).

Health and Safety Laboratory Fallout Program Quarterly Summary Reports 1970–[illegible] USAEC Reports HASL-237(App.), 245(App.), 259(App.), and 276(App.). (Oc[illegible] issues, 1970–1973), Health and Safety Laboratory.

McHenry, J. R., J. C. Ritchie, and A. C. Gill, 1973, Accumulation of Fallout Cesium-137 in Soils and Sediments in Selected Watersheds, *Water Resour. Res.*, 9: 676-686.

Odum, E. P., 1971, *Fundamentals of Ecology*, W. B. Sanders Co., Philadelphia.

Ritchie, J. C., and J. R. McHenry, 1973, Determination of Fallout ^{137}Cs and Natural Gamma-Ray Emitting Radionuclides in Sediments, *Int. J. Appl. Radiat. Isotop.*, 24: 575-578.

——, J. R. McHenry, and A. C. Gill, 1974, Fallout ^{137}Cs in the Soils and Sediments of Three Small Watersheds, *Ecology*, 55: 887-890.

——, J. R. McHenry, A. C. Gill, and P. H. Hawks, 1973, Distribution of Cesium-137 in a Small Watershed in Northern Mississippi, in Radionuclides in Ecosystems, Proceedings of the Third National Symposium on Radioecology, May 10–12, 1971, D. J. Nelson (Ed.), USAEC Report CONF-710501-P1, pp. 129-132, Oak Ridge National Laboratory.

——, J. R. McHenry, A. C. Gill, and P. H. Hawks, 1970, The Use of Fallout Cesium-137 as a Tracer of Sediment Movement and Deposition, in Proceedings of the Mississippi Water Resources Conference, 1970, pp. 150-162, Mississippi Water Resources Research Institute, State College, Miss.

——, J. A. Spraberry, and J. R. McHenry, 1974, Estimating Soil Erosion from the Redistribution of Fallout ^{137}Cs, *Soil Sci. Soc. Amer., Proc.*, 38: 137-139.

Bonfeld, E., 1966, Alpha M: An Improved Computer Program for Determining Radioisotopes by Least-Squares Resolution of the Gamma-Ray Spectra, USAEC Report ORNL-3975, Oak Ridge National Laboratory.

Tamura, T., 1964, Selective Sorption Reactions of Cesium with Mineral Soils, *Nucl. Safety*, 5(3): 263-268.

RADIOCESIUM CYCLING IN VEGETATION AND SOIL

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ABSTRACT

Data on cesium dynamics in vegetation and soils are reviewed. Special emphasis is placed on typical environments in the southeastern United States. Clay minerals of soil, especially micaceous types, effectively fix cesium and remove it from biotic components of ecosystems. Fallout ^{137}Cs enters food chains principally by direct deposition on vegetation; uptake by the root pathway is usually less than direct contamination of plant foliage. Cesium-137 levels in vegetation of the southeastern U. S. Coastal Plain are estimated on the basis of direct deposition from the atmosphere and root uptake from soil. Estimated concentrations, based on current concepts of ^{137}Cs dynamics in vegetation and fixation in soil, are in good agreement with observed values of ^{137}Cs in vegetation collected in 1969 and 1970. Mechanisms of direct deposition and of increased uptake by roots due to the absence of micaceous clays adequately explain the higher levels of ^{137}Cs in vegetation of the Coastal Plain and thus are responsible for the elevated ^{137}Cs reported for milk of the Tampa, Fla., milkshed.

Considerable interest has been shown in the dynamics, fate, and effect of ^{137}Cs in the biosphere because it is a predominant long-lived product in the fission of nuclear explosives and reactors. Approximately 6% of the total fission of ^{235}U is ^{137}Cs. Cesium-137 has been widely distributed as global fallout; low le occur in all parts of the biosphere. Because it is readily assimilated into bo tissues, ^{137}Cs becomes a major contributor to radiation dose to living organisms.

Adequate technology currently exists in the nuclear fuel cycle to control releases so that ^{137}Cs from nuclear waste will not exceed the current levels caused by fallout from nuclear explosions in the atmosphere. Unless atmospheric testing resumes, we would not expect to again experience elevated environmen-

tal concentrations of ^{137}Cs from fallout. Indeed, the peak level of ^{137}Cs in the world atmosphere and biotic components of ecosystems probably has already occurred according to monitoring data obtained for the past 25 years (Radiological Health Data and Reports 1963–1973; HASL 1974). The reasons are threefold: (1) in the absence of new ^{137}Cs injection to the atmosphere, the deposited quantities are diminishing owing to physical radioactive decay; (2) experimental data and fallout monitoring results show that the greatest ^{137}Cs assimilation into biological organisms is coincident with the initial ^{137}Cs introduction into the ecosystem, i.e., direct contamination of vegetation followed by ingestion of foodstuffs by livestock or humans; (3) cesium is effectively removed from biological circulation through the mechanism of fixation by soil clays.

In this paper we review the factors that influence the cycling of cesium in terrestrial ecosystems. The review focuses on the mechanisms influencing the dynamics and fate of ^{137}Cs in pathways leading to man. A limited amount of new data confirms existing concepts of cesium cycling in biota and retention in soils. Existing knowledge of ^{137}Cs dynamics is applied to the interpretation of elevated ^{137}Cs in milk in the Tampa, Fla., milkshed.

GEOCHEMISTRY OF STABLE CESIUM

In a mineral cycling symposium (actually a misnomer because it is elements rather than minerals that cycle), it would be instructive to review the natural geochemistry of stable cesium before addressing the cycling of ^{137}Cs in biotic and abiotic components of ecosystems. The basic geochemistry of cesium provides substantial insight into the possible fate of fission-product ^{137}Cs in geological substrates. The primary minerals that contain cesium are pollucite, rhodizite, and avogadrite (Fairbridge, 1972). Cesium is isomorphically substituted for potassium and rubidium in the lattice of other minerals, e.g., cesium for potassium in the formation of biotite and leucite. Biotite can also serve as a secondary source for cesium. As the crystalline structure is decomposed in processes of mineral weathering, cesium is solubilized and immediately resorbed to clays.

There is ample geologic evidence supporting the concept of interlayer lattice fixation of cesium because only in those sedimentary deposits which contain clays or shales is the cesium abundance greater than 1 ppm. In contrast, the concentration level is in the parts per billion range in sandstone and limestone. Cesium ions are adsorbed to selective sites on clays of geologic sediments or they penetrate into interlayer voids of micaceous minerals and, for all practical purposes, are permanently fixed. Thus, beginning with a primary mineral, the sequence of events in the geochemistry of stable cesium is: mineralization from primary minerals → substitution in micaceous minerals → release in subsequent weathering processes → selective fixation (or adsorption) by clay minerals.

REACTION OF ^{137}Cs WITH CLAY MINERALS

Research in recent decades has confirmed the mechanism for fixation of ^{137}Cs by clay minerals (Shulz, Overstreet, and Barshad, 1960; Tamura and Jacobs, 1960). This mechanism is by far the most important factor in the biogeochemical cycling of cesium in terrestrial ecosystems because the degree of fixation by clays governs subsequent availability to biological organisms. In addition to adsorption by the general cation-exchange complex of soils, cesium is effectively adsorbed to selective sites, and fixation occurs with weathered potassium-depleted micaceous clays. Lomenick and Tamura (1965) report that fixation varied with different clay minerals. With micaceous-type minerals and with clays exhibiting a limited expanding lattice crystalline structure, desorption of ^{137}Cs (the inverse of fixation) was 30% of that for nonexpanding kaolinitic lattice type and fully expanding montmorillonite type minerals. The latter minerals (kaolinite and montmorillonite) are known for their nonselective cation-exchange reactions, whereas the former (mica and illite) exhibit high selectivity.

The mechanism for fixation of ^{137}Cs is related to the weathering of potassium from micaceous clays. When added to soil, cations whose radii are similar to that of potassium, such as cesium, rubidium and NH_4^+, are tightly adsorbed to these weathered micaceous minerals. If sufficient quantities of these cations are added, the expanded lattice collapses because of the favorable ionic radii of these elements and because of the neutralization of the negative charges between the clay surfaces, and cations are fixed or trapped (Arnold, 1960; Barshad, 1954). This mechanism likely accounts for fixation of potassium, cesium, rubidium, and NH_4^+ cations when added to soil in macroquantities (>10 ppm).

Different mechanisms likely prevail in the fixation of microquantities (ppb range). For example, illite and micas, as well as collapsed vermiculite (potassium saturated) and bentonite (heat treated), strongly adsorb trace levels of ^{137}Cs (Tamura and Jacobs, 1960). Fixation is considered to be largely near the edges of the interlayer spacings. Density-gradient zonal-centrifugation techniques have been used to identify clay-mineral adsorption sites of ^{137}Cs in soil (Francis and Tamura, 1972; Auerbach, Olson, and Waller, 1964) collected from the ^{137}Cs tagged *Liriodendron* forest. The dominant mineral responsible for ^{137}Cs adsorption in this soil was pedogenic chlorite (a mineral derived from weathering of mica).

Results on ^{137}Cs desorption from soils with different predominant clay minerals confirm that fixation is greatest with micaceous clays. Tracer quantities of ^{137}Cs (carrier-free solution) fixed to three podzolic soils from Tennessee were desorbed with 1*N* sodium acetate (Table 1). In the initial 0.25 hr, 32% of the ^{137}Cs was desorbed from the kaolinitic Fullerton soil, and desorption continued for 264 hr (87%). The illitic Sequoia soil showed maximum desorption (about 50%) in about 1 to 4 hr; then the soil appeared to resorb the

TABLE 1

PERCENTAGE DESORPTION OF RADIOCESIUM FROM THREE EAST TENNESSEE SOILS (A HORIZON)

Soil	Solution contact time, hr*					
	0.25	1	4	24	96	264
Fullerton (kaolinitic)	32.2	46.2	59.3	75.3	80.6	86.7
Sequoia (illitic)	47.8	50.8	49.0	37.1		17.7
Captina (mixed)	27.0	33.4	36.5	33.7	32.3	29.4

*Desorbing solution was 1*N* sodium acetate; 100 ml of solution per gram of soil; maximum desorption is underlined.

cesium, resulting in 18% desorption after 264 hr. Thus, in 1*N* sodium acetate, desorption of ^{137}Cs was a factor of almost 5 greater with kaolinitic soil compared with that for illitic soil. The Captina soil contains both kaolinite and illite in about equal quantities; its desorptive characteristic resembles that of the illitic Sequoia.

The desorption data (Table 1) provide further insight into the role of selectivity of adsorption sites in the fixation of ^{137}Cs by various clays. The adsorption of cesium occurred from a distilled-water system, and the trace level of cesium likely was adsorbed on surfaces with which it came in immediate contact without regard to selective or nonselective sites. When sodium ions were introduced during desorption, the cesium ions could be displaced from nonselective sites; the quantity displaced increased with time of contact. This type of response is typified by the kaolinite-bearing Fullerton soil. On the other hand, with the illite-bearing Sequoia and Captina soils, the desorbed cesium from nonselective sites was readsorbed on illitic selective sites (Tamura and Jacobs, 1960). Sodium ions can desorb cesium from the nonselective sites but cannot compete with cesium for the selective sites; hence the decreasing desorption observed in the illite-bearing soils represents readsorption at the selective sites.

Minerals and clays possessing selective sites (vermiculite: Sawhney, 1965; illite and hydrous mica: Tamura, 1964) have high selectivity for cesium. Francis and Brinkley (1975) provided additional information on the role of minerals and clays in the fixation of ^{137}Cs in sediments from Steel Creek below the AEC Savannah River Plant in South Carolina. The concentration of ^{137}Cs in the micaceous component was three times that of the kaolinite (3.6 to 1.1 nCi/g, respectively). Although concentration of ^{137}Cs was greatest on the micaceous clays in this sample, over 90% of the ^{137}Cs was associated with the kaolinite mineral simply because this mineral is the predominant clay in soils and sediments of the Savannah River region.

Fixation of radiocesium by soil is the major factor that determines the long-term availability to biological organisms in terrestrial ecosystems. Cesium

removal from biological circulation in ecosystems is mediated by soil clay and in particular by such cesium-fixing clay minerals as illite. Other micaceous-derived clays (vermiculite, pedogenic chlorite) also selectively adsorb cesium. Thus, in soils where these minerals predominate or are even found, the uptake of radiocesium by plants is severely restricted because the soil serves as an effective sink for fallout ^{137}Cs.

CESIUM-137 TRANSPORT IN TERRESTRIAL ECOSYSTEMS

Transport of cesium in terrestrial ecosystems involves both physical processes (by atmospheric dispersion, aerosol dynamics and deposition, by movement in hydrologic streams, and by erosion of sediments) and biological processes (assimilation of foliar deposits, root uptake, and food-chain transport). Following its incorporation into the vegetation component, the ^{137}Cs is dispersed among naturally occurring food webs. For selected food-chain pathways, the nuclide can be ingested by man. Direct deposition on vegetation and immediate incorporation into food chains dominates initial phases of biological transport. In the absence of new ^{137}Cs from atmospheric deposition, the soil–plant pathway constitutes the principal mode of ^{137}Cs transport to man.

Transport of cesium to man can be many faceted (see Fig. 1 in Kaye and Ball, 1969), but the principal pathways for ^{137}Cs are those described by Bruce and Russell (Fig. 1 in Bruce and Russell, 1969). For food-chain mechanisms Bruce and Russell conclude, "a relatively small number of critical pathways are responsible for . . . airborne radioactivity that reaches man's diet." They also conclude that the most direct route is direct foliar contamination → milk → man for exposures involving ^{137}Cs. In any case, the hazard to man from ^{137}Cs will involve these transfers; direct deposition on foliage, soil to plant, plant to animal or man. Emphasis on only these transfers admittedly is an over simplification, but it is beyond the scope of this paper to describe the innumerable pathways for both agricultural and ecological systems.

Direct Foliar Contamination

More than a decade ago Russell (1963, 1965) recognized that direct foliar contamination rather than uptake from soil was the principal mode of entry of fallout fission-product nuclides into vegetation. Others (Krieger, Kahn, and Cummings, 1967) have shown that uptake of ^{137}Cs from soil accounts for only 3% of the total burden in bluegrass, the remainder being contributed by direct deposition (Table 2).

Monitoring data illustrate the close relationship between ^{137}Cs concentration in air and ^{137}Cs in milk. A significant positive correlation ($r = 0.97$) for ^{137}Cs concentration in air and milk was observed for quarterly averages from seven milksheds across the United States from 1962 to 1967 (Wilson, Ward, and

TABLE 2

COMPUTED RELATIVE CONTRIBUTIONS OF ^{137}Cs TO BLUEGRASS FROM FALLOUT CONTAMINATION OF FOLIAGE AND FROM ROOT UPTAKE OF CONTAMINATED SOIL*

Basis	Deposition on foliage, pCi/m²	Root uptake, pCi/m²	Ratio root uptake / total
Stable cesium†	210	6	0.03
Uptake of ^{137}Cs from soil	207	8	0.04
Covered plots	154	62	0.29

*Data from Krieger, Kahn, and Cummings (1967), p. 69.

†Root uptake calculated on basis of stable cesium concentrations in vegetation and soil.

Johnson, 1969). A multiple regression model, based on fallout over the preceding 2- to 6-month period, predicted with considerable accuracy the declining concentration and seasonal variation of ^{137}Cs in milk. The high correlation of ^{137}Cs concentration in air and concentration in milk strongly implies that direct deposition on vegetation was responsible for much of the ^{137}Cs entry into the grass–cow–milk food chain. To date, the concentration of ^{137}Cs in air and milk has continued to decline (Fig. 1). The significance of these data is that levels in air and milk have decreased simultaneously by an order of magnitude since the moratorium on nuclear testing in the atmosphere. In contrast, a reverse trend would be expected a priori if concentration in milk were directly related to accumulation of ^{137}Cs in soil, i.e., levels in milk would increase with cumulative ^{137}Cs in soil.

Various investigators have demonstrated that nutrient elements (Biddulph, 1960) and fission products (Middleton, 1959; Levi, 1969) are readily assimilated by foliage. The results show that ^{137}Cs is relatively mobile within this vegetation component. From 10 to 20% of the assimilated radiocesium may be translocated to grain (Middleton, 1959) or fruiting structure (Levi, 1969). The mechanism of entry into leaf-cell protoplasm appears to involve adsorption of ...tions to negatively charged biocolloids or nondiffusible anions in the cell wall, ...llowed by active metabolic uptake into the cell (Biddulph, 1960). Initial adsorption would be mediated by surface fissures in the cutin which would allow entry of soluble fission products to anionic sorption sites or to plasmodesmic extensions to cuticle margins. However, the exact mechanism and the kinetics of ionic transport from external surfaces to internal protoplast are not known. In practice, however, it may not be essential to know the relative distribution between internal and external plant parts because both external and internal plant structures are consumed by foraging animals. The concentration of

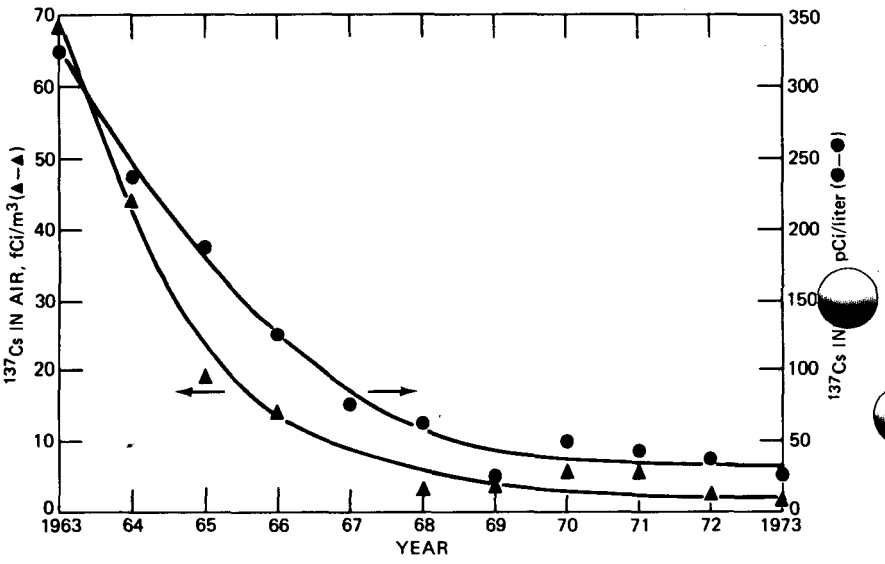

Fig. 1 Parallel relationship between concentration of ^{137}Cs in air (fCi m^{-3}) and in milk (pCi/liter). Close agreement over an order of magnitude decrease in both parameters suggests a strong relationship between direct deposition and entry of ^{137}Cs into food chains. Data taken from USAEC Health and Safety Laboratory Fallout Program (1974) and from Pasteurized Milk Network (1973).

contaminants in foodstuffs (representing both external and internal contamination) is the most important information needed for estimates of trophic transport, and the internal vs. external localization of ^{137}Cs in the leaf may be of secondary importance.

Retention and Weathering of ^{137}Cs from Contaminated Foliage

The processes of retention and weathering determine time-dependent concentrations of the contaminant in vegetation. The fraction of the incident contaminant which is retained by the vegetation depends on the physiochemical form of fallout as well as on the foliar characteristics of vegetation. For gra contaminated by aqueous spray or by fallout particles, representative retenti values are given in Table 3. The wide range of initial retention of fallout (aqueous or particulate form) is partially explained by different foliage density, but other factors, e.g., mode of deposition, morphological differences in foliage, and duration between application and measurement, may all influence estimates of initial retention. For example, the effect of leaf morphology is illustrated by the fact that 75% of total retention by sorghum was located in the leaf axil (junction of leaf blade with stem axis) (Witherspoon and Taylor, 1971). Furthermore, substantial losses may occur between the time of deposition and

initial measurements because only 11% of initial deposition of fallout simulant particles remained on fescue after 1 hr (Dahlman, 1971).

The time-dependent decreases of ^{137}Cs following direct foliar contamination are also somewhat variable. Russell (1965) reports an average weathering half-time of 14 days for vegetation contaminated by natural fallout. We have determined from experiments with ^{137}Cs-tagged fallout simulant applied to fescue grass that decrease in ^{137}Cs content of the grass mimicked a negative exponential, $Y = 0.27 + 1.59e^{-0.52t}$, where Y is retention and t is time in days. For the nonlinear regression fit, the weathering half-time is approximately 30 days. If a negative exponential loss rate is assumed, Middleton's (1959) data for aqueous-spray contamination suggest a 32-day weathering half-time. From different observations it appears, then, that approximately half the ^{137}Cs deposited on foliage is lost from grass vegetation in an interval of 14 to 30 days.

TABLE 3

RETENTION OF FALLOUT BY GRASS

Mode of application	Species	Initial retention, %	Reference
Aqueous spray, ^{137}Cs	Ryegrass	6 to 13	Kirchman et al. (1967)
Aqueous spray, ^{137}Cs	Wheat	14 to 31	Middleton (1959)
Fallout particles	Fescue	45	Dahlman (1971)
Fallout particles	Sorghum	38	Witherspoon and Taylor (1971)
Fallout particles	Fescue	69	Peters and Witherspoon (1972)
	Bluegrass	71	
	Bermuda	82	
	Zoysia	76	

Plant Uptake of Radiocesium from Soil

Soil serves as an effective sink for fallout ^{137}Cs, thus minimizing uptake by roots (see previous section on reaction of ^{137}Cs with clay minerals). Movement of radioactive cesium from soil to plants is dependent on the physical, mineral, chemical, and biological conditions of the soil. Other factors that govern uptake by plants are temperature, moisture, fertility, and pH conditions of soil. The soil–plant link limits the long-term movement of ^{137}Cs through the food chain to man. For example, after cropping for 520 days, less than 0.2% of the ^{137}Cs

added to soil is transported to the foliar portion of legumes (Nishita, Steen, and Larson, 1958).

Concentration ratios, e.g., [^{137}Cs] plant/[^{137}Cs] soil, on a gram per gram basis, have been used to express the relative concentration of radionuclides in soil and plants. Radiocesium is considered to be slightly excluded by plants, namely, concentration ratios range from 0.01 to 1 (Menzel, 1965). Thus plants usually discriminate against rather than accumulate cesium from contaminated soil. The range of ratios reported for different plants growing in soil is given in Table 4. Radiocesium in plants grown on productive agricultural soils represented by concentration ratios <1 (Nishita, Steen, and Larson, 195 Nishita, Haug, and Hamilton, 1968; Evans and Dekker, 1968; Auerbach et al., 1959, 1972). However, from highly weathered acid soils, the concentration ratio of radiocesium is often >1 (Table 4, Evans and Dekker, 1969; Fredriksson, 1970b; Marei et al., 1972). For example, radiocesium uptake from acid podzol soils in the USSR and Canada is equal to the uptake of radiostrontium. The radiocesium concentration ratio between plants and the sandy acid soils of the southeastern United States and the lateritic Brazilian soils may exceed 10 in the absence of 2 : 1 layer silicates (Cummings et al., 1969; Fredriksson, 1970b; Sharitz et al., 1975).

Uptake of radiocesium from relatively unweathered productive agricultural soils is usually low (<0.5%). In natural environments uptake of ^{137}Cs from highly weathered soils may be equal to that of radiostrontium. Although relative concentration ratios range over at least 3 orders of magnitude, the higher values usually can be explained on the basis of low clay content, low pH, and a scarcity of clays possessing the 2 : 1 layer silicates. Soil fertility, abundance of organic matter, and management practices may also influence plant uptake of ^{137}Cs to a lesser extent, but an evaluation of these factors is beyond the scope of this discussion.

Radiocesium in Plants from Foliar Deposition vs. Root Uptake

It is important to recognize the relative contribution of ^{137}Cs in plants from direct foliar deposition vs. root uptake. Few data are available which permit a comparison of root vs. foliar uptake, but, from measurements of ^{137}Cs fallou and stable cesium ratios, Krieger, Kahn, and Cummings (1967) estimated plant/soil ratio of 8×10^{-5} (discrimination factor) based on root uptake only (Table 5). Thus it would appear that in the absence of direct deposition the discrimination factor for ^{137}Cs in plants related to root uptake would be several orders of magnitude less than values given in Table 4. Russell and Bruce (1969) estimated independently that not more than 30% of the radiocesium burden in plants would originate from soil, and the real value might be closer to 10%. For example, only 3% of the ^{137}Cs burden in bluegrass is contributed by the root pathway in the Ohio region (Krieger, Kahn, and Cummings, 1967), and in

TABLE 4

RELATIVE CONCENTRATION OF CESIUM IN PLANTS AND SOIL

Plant	Soil characteristics	Ratio*	Reference
Beans	pH 6.8; sand, 33%; silt, 46%; clay, 20%;	0.013 to 0.027	Nishita, Haug, and Hamilton (1968)
Red clover	178 Swedish soils	0.10 to 1.32	Fredriksson (1970a)
Oats	4 Canadian soils; pH 5.2 to 7.8; under different potassium and NH_4 fertility regimes	0.05 to 5.68	Evans and Dekker (1969)
Cereal, forage, and vegetable crops	pH 7.5; organic matter, 6.9%; cation-exchange complex, 24.2 meq/100 g	0.004 to 0.471	Evans and Dekker (1968)
Persicaria	Flooded and nonflooded conditions	0.003 to 1.35	Pendleton and Uhler (1960)
Grasses	Podzolic sand and podzol carbonate clays	0.3 to 8.2†	Marei et al. (1972)
Clover	Cropping 60 to 520 days; pH 6.8; sand, 33%; silt, 46%; clay, 20%	0.06 to 0.352	Nishita, Steen, and Larson (1958)
Winter rape	Brazilian laterite soil, pH 4.6; organic matter, 4.8%	0.89 to 13.2	Fredriksson (1970b)
Red maple leaves	Flood-plain sediment; predominantly kaolinite clay; sandy texture‡	0.2 to 5.4	Ragsdale and Shure (1973)
Sagittaria latifolia leaves	Flood-plain sediment; kaolinite-type clay, sandy texture‡		Sharitz et al. (1975)
	Low-level ^{137}Cs	20§	
	High-level ^{137}Cs	1.5	
Oats	Soils from southeastern United States	0.02 to 72¶	Cummings et al. (1969)
Millet	White Oak Lake bed soil (field plots)	0.03	Auerbach et al. (1959)
Millet	White Oak Lake bed soil (continuous cropping in pots)	0.03	Auerbach et al. (1972)
Aspergillus	White Oak Lake bed soil	0.01	Auerbach et al. (1974)

*Ratio of quantity in plant to quantity in soil on a per unit weight basis.

†Ratios based on units of pCi/liter in grass per pCi/kg in soil; thus, to compare with other ratios in Table 4, Marei's ratios should be adjusted upward to account for the possibility of a grass density of <1.0 kg/liter.

‡Data on soil texture and clay minerology taken from Brisbin et al. (1974), assuming that their data (Table 3, p. 24) from transects A and B would represent soil and sediment conditions for the delta (Sharitz et al., 1975) and the swamp forest (Ragsdale and Shure, 1973).

§The large ratio (20) may possibly reflect natural surface contamination of *S. latifolia* leaves by contaminated water or sediment because the species is typically emersed or submersed in aquatic environments.

¶Assuming at least 200 g of soil in 1-pt containers.

TABLE 5

RELATIVE CONCENTRATION IN BLUEGRASS AND SOIL MINUS CONTRIBUTION BY DIRECT FOLIAR CONTAMINATION*

Basis	^{137}Cs (pCi) or stable Cs (mg/m^2) concentration		Ratio bluegrass / soil
	Soil	Bluegrass	
^{137}Cs-contaminated soil	79,000	8	0.00009
Stable cesium	750	0.055	0.00007

*Data from Krieger, Kahn, and Cummings (1967).

Colorado negligible ^{137}Cs (<1%) is taken up by alfalfa and corn from soil (Johnson, Wilson, and Lindsay, 1966).

Internal Dynamics of Radiocesium in Plants

Radiocesium is highly mobile once it gains entry to internal tissues of the plant (Resnik, Lunt, and Wallace, 1969; Middleton, 1959). Few data are available on the internal dynamics of radiocesium in plants with the exception of data from Middleton (1959), Levi (1969), Witherspoon (1964), Waller and Olson (1967), Brown (1964), and Dahlman, Auerbach, and Dunaway (1969). Data from Dahlman, Auerbach, and Dunaway (1969) illustrate the internal redistribution of an external tag of ^{134}Cs to fescue grass (*Festuca arundinaceae*) (Fig. 2). Extensive mobility is exhibited: 25% of the radiocesium absorbed by foliage is redistributed to roots over the initial 2-week period; approximately 25% moved to the inflorescence; at the time of flowering ^{134}Cs moved out of the roots into the inflorescence.

The first experimental data on the cycling of cesium in forest ecosystems were obtained from Witherspoon's (1964) experiments at Oak Ridge in 1960. When ^{134}Cs was introduced into the bole of white oak trees, 39% moved immediately to the canopy and 61% remained in the bole or was transferred directly via roots to soil. At the end of the second growing season, 18% of the original inoculum was in litter and 19% in soil. Cesium-134 in the foliar component was rapidly recycled as leaf fall and rainout. Over 50% of the leaf burden was returned to woody tissues before leaf fall. This experiment was the first of its kind to demonstrate the extensive mobility of cesium in the biological components of ecosystems.

In a separate study on ^{137}Cs cycling in tulip poplar, Waller and Olson (1967) found similar percentages remaining in the bole (woody compartment) after the second growing season (Table 6). The fraction that cycled through the

canopy to the forest floor was also similar for both systems. More attention was given to underground processes in the tulip poplar experiments, and it was determined that 30% of the initial tag moved through the roots and was fixed in the soil before the end of the first growing season. By analyzing the ^{137}Cs concentrations in the clay fraction at various soil depths, Francis and Tamura (1971) confirmed that radiocesium originated from roots. The concentration in clay at the 6-cm depth was twice that at the 2- and 4-cm depths. The only

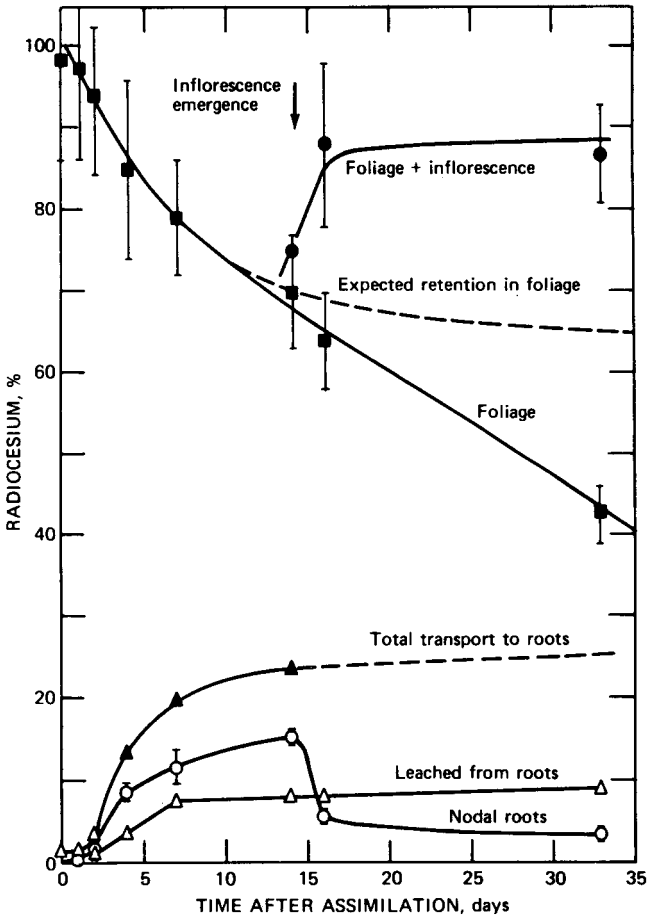

Fig. 2 Distribution of radiocesium in different organs of fescue following foliar assimilation. Cesium-134 was applied to foliage surface by emerging leaves in solution for 5 min. The extrapolated estimate of expected retention by foliage is based on an absence of transfer to developing inflorescence. The large error terms for foliage and inflorescence are attributed to variable initial retention on surface microsites and intercellular spaces.

TABLE 6

DISTRIBUTION OF CESIUM IN PLANT AND SOIL COMPONENTS OF WHITE OAK AND TULIP POPLAR SPECIES AT THE END OF THE SECOND GROWING SEASON

Compartment	Percentage distribution* White oak		Tulip poplar	
Bole	48	48	53	53
Canopy	(39)		(27)	
Roots	14		9	
			(30)	
Soil	18	51	36	47
Litter	19		2	
			(7)	
Export			2	2
Total		99		102

*Values in parentheses denote percentage of total cesium cycled through the compartment.

mechanism that explains the higher concentrations 6 cm beneath the surface is prompt transfer through the root pathway.

Distribution in root, soil, and litter components was different for the two systems (white oak vs. *Liriodendron*), but the summation percentages show somewhat similar concentrations in aboveground and belowground compartments (Table 6). The results illustrate the extensive initial mobility of cesium when it is introduced into trees. In both ecosystems, from 27 to 40% is cycled upward to the canopy, approximately 30% reaches the forest floor, approximately 30% moves directly to the root system, and most of that quantity moving to the roots appeared in soil in the tulip poplar community.

MODELS OF ENVIRONMENTAL TRANSPORT OF ^{137}Cs

Models of radiocesium dynamics in terrestrial ecosystems have been formulated using the extensive data bases on ^{137}Cs cycling in forests and ^{137}Cs transport in the grass–cow–milk–man food chain. Another very meaningful application of models of ^{137}Cs dynamics is the prediction of the radiologic hazard to man using data on deposition, retention, and plant uptake from soil and concepts of food-chain transport and systems-analysis techniques. For example, Booth, Kaye, and Rohwer (1971) estimated radiocesium transport and the resultant dose to man for the soil–grass–cow–milk–man pathway of exposure. In their predictions concepts and data similar to those described in this paper were coupled with systems-analysis modeling techniques; ^{137}Cs

concentrations in ecosystem components and dose to man were estimated for constant fallout input to the landscape, for equilibrium conditions, and for an average geographical location. The model estimates were compared with monitoring data for milk; agreement was relatively good because, for example, the predicted radiocesium content of milk was 62% of a 6-month observed average in 1970 (Booth, Kaye, and Rohwer, 1971). Such agreement would probably be acceptable for generic applications, and the accuracy of the model probably could be improved by considering site-specific parameters and by quantifying the nonlinear ecologic and climatic variations. In any event, it appears, on the basis of this successful application, that the concepts, techniques, data, and models do indeed describe the important relationships in terrestrial ecosystems. The quantitative data are adequate for modeling and describing the dynamics of ^{137}Cs in pathways leading to man.

RADIOCESIUM DYNAMICS IN ECOSYSTEMS OF THE SOUTHEASTERN UNITED STATES

The elevated cesium concentration in milk of the Tampa, Fla., milkshed has received close attention in the past decade (Pasteurized Milk Network, 1963–1973; Porter et al., 1967). Important questions related to this phenomenon are (1) Is sufficient information available to explain the reason for elevated ^{137}Cs in milk at Tampa? and (2) is a special mechanism responsible for increased uptake by vegetation (with a consequent increase in milk) such as that postulated by Gamble (1971)? Gamble contends that increased uptake is due to root–mycorhizal relationships. An assessment of these questions, using extant information on the biospheric behavior of ^{137}Cs, is required before additional research is commissioned. We submit that existing concepts and data are adequate to explain the elevated ^{137}Cs of the Florida milkshed. An assessment of the problem is made with information developed in previous sections of this paper.

The existing evidence indicates that direct deposition of fallout ^{137}Cs contributes substantially to the entry of ^{137}Cs into food chains. Wilson, Ward, and Johnson (1969) concluded that the concentration of ^{137}Cs in milk of the Tampa milkshed depended on both direct input from the atmosphere and on uptake from soil. It is interesting that their predicted values in milk decreased in relation to a lower air concentration of ^{137}Cs, and that the predicted and observed ^{137}Cs values for milk showed good agreement in the mid-1960s. That the close relationship of ^{137}Cs concentration in air and milk continued through 1973 (Fig. 1) is strong circumstantial evidence that direct deposition on vegetation still plays an important role in ^{137}Cs dynamics in the grass–cow–milk pathway.

Elevated levels of ^{137}Cs in Tampa milk are attributed to feeding dairy cattle Pangola (*Digitaria decumbens*) hay that contained 2 to as much as 10 times more

^{137}Cs than other dairy-feed components (Porter et al., 1967). The mechanism of how Pangola hay accumulated more ^{137}Cs than other feeds was not determined, but both direct deposition on foliage and uptake by roots are the likely pathways, although substantial uptake by graminaceous plants may also occur at the base of tillers and stoloniferous structures on the soil surface (Russell, 1963).

For plants simultaneously exposed to both atmospheric and soil sources of ^{137}Cs, uptake via the root pathway would be expected to account for 1 to 3% (a maximum of 30%) of the plant burden. Cesium-137 uptake through plant roots is inversely related to the fixing capacity and clay content of soil and directly related to the sand content of 43 soils from the southeast, including at least five soils from Florida (Cummings et al., 1969, 1971). From their experiments, greatest plant uptake is observed for humic gley-type soils (characterized by highly weathered kaolinitic clays and sandy texture). An average of 2.8% of added ^{137}Cs was assimilated into oat seedlings in pot culture. These observations are consistent with extensive literature data (Table 4), namely, higher ^{137}Cs uptake (ratios >1) is reported for sandy, acid, highly weathered soil, particularly in the absence of 2 : 1 expanding lattice clays.

The evidence indicates that direct deposition of ^{137}Cs on foliage and appreciable root uptake (2.8% of ^{137}Cs in soil) may both be responsible for increased levels of ^{137}Cs in Florida milk. It is difficult to delineate the exact responsible mechanisms because no deliberate measurements have been made of direct deposition of fallout on Florida vegetation, its retention on foliar surfaces, and the subsequent incorporation into livestock feed. In continental environments direct deposition appears to account for at least 95% of the ^{137}Cs content of forage (Johnson, Wilson, and Lindsay, 1966; Kreiger, Kahn, and Cummings, 1967). Ward, Johnson, and Wilson (1966) estimate a net deposition velocity (V)* of 0.001 m/sec, and their results indicate that at least an equivalent quantity of ^{137}Cs is deposited by rainfall. According to Gifford and Pack (1962), a value of 0.001 m/sec for V probably is realistic for ^{137}Cs.

Upper and lower limits of ^{137}Cs deposition are estimated in Table 7. When we recognize that direct deposition is affected by ecosystem features (vegetation surfaces and density, soil exposure) and meteorologic conditions (rainfall, atmo-

*Net deposition represents the fraction on vegetation after weathering losses have occurred. It represents the quantity available for subsequent ingestion by a consuming animal. It is a convenient expression because its determination does not require knowledge of fractional retention, kinetics of weathering, and intraplant redistribution. Further, net deposition velocity (V) is conveniently used with air concentration to estimate ground concentration (D), i.e., D = VAt, where A = air concentration (curies per cubic meter) and t is time in seconds. The units of V are meters per second and of D are curies per square meter.

TABLE 7

ESTIMATED RELATIVE CONTRIBUTION OF ^{137}Cs TO VEGETATION VIA ATMOSPHERIC DEPOSITION AND ROOT UPTAKE

Duration, days	Source	^{137}Cs concentration, pCi/m^3 air or pCi/kg soil	^{137}Cs concentration in vegetation		
			Direct deposition, pCi/kg		Root uptake,‡ pCi/kg
			Dry*	Total†	
30-day growing season	Air§	5.6×10^{-3}	56	112	
300 Growing season	Air	5.6×10^{-3}	560	1120	
	Soil¶	205			860

*Dry deposition (D) is calculated according to $D = A \times V \times t/M$, where A = air concentration (see footnote §), V = deposition velocity = 0.001 m/sec, t = time in seconds (2.6×10^6 sec per 30 days and 2.6×10^7 sec per 300 days), and M = mass of vegetation in kg/m^2 (0.2 kg/m^2 for unfertilized pasture).

†Total deposition (dry + wet) is approximately twice dry deposition according to Ward et al. (1966).

‡Root uptake (R) is calculated from $R = S \times f \times Z$, where S = soil concentration (see footnote ¶), f = fraction of total assimilated [2.8% according to Cummings et al. (1969, 1971)], Z = mass of soil in effective rooting zone, a 10-cm depth was selected for this analysis. A diffuse root system extends deeper than 10 cm, but Gamble (1971) shows most of the ^{137}Cs in the top 10 cm of soil.

§Air concentration in pCi/m^3; average of midyear values for 1969, 1970 data (Fig. 2) and HASL (1974), pp. B-78, B-79.

¶Soil concentration taken from Gamble (1971).

spheric mixing), we realize that the estimates are by no means exact; they should be regarded as approximations for purposes of discussion. These calculations suggest that we would expect only a nominal direct deposit of radiocesium on foliage over a 1-month growing period, but for longer periods, e.g., 10 months, dry deposition could account for possibly more ^{137}Cs in vegetation (1120 pCi/kg) than would be expected from root uptake (860 pCi/kg), using the average percentage uptake (f) of 2.8% (Cummings et al., 1969). This percentage uptake value is an order of magnitude greater than the upper-limit percentage uptake commonly reported for agricultural soils (0.3%; United Nations Scientific Committee on the Effects of Atomic Radiation, 1962). Thus, for either a lower f value or for a higher V, the direct-deposition mechanism would account for

substantially more ^{137}Cs in forage than that attributed to root uptake especially when chronic fallout deposition is estimated over a full growing season or longer.

In Table 7 total ^{137}Cs in forage is estimated for both direct deposition and uptake from soil, and the estimates are compared with measured values reported for southern Georgia and Florida. Total estimated ^{137}Cs in Florida plants, approximately 2000 pCi/kg for both direct deposition and root uptake, compares favorably with many reported values for vegetation growing on humic gley-type soils in southeastern Georgia (Cummings et al., 1971). The average ^{137}Cs concentrations reported for leaves were 1000, 1800, 1600, and 2800 pCi/kg for gallberry, wax myrtle, smilax, and swampberry, respectively. The grand average (1800 pCi/kg) for these species is in good agreement with estimated deposition and uptake for a growing season (2000 pCi/kg). The average ^{137}Cs concentration for mixed grasses was 6100 pCi/kg, three times the estimated 2000 pCi/kg. The discrepancy between estimated and observed concentrations may be due to a higher effective deposition on grass foliage or possibly to increased uptake at the base of graminaceous plants, as described by Russell (1963). Substantially higher values (factors of 5 to 10) were observed for leaves of red bay, palmetto, holly, and deer's tongue and for mosses. The discrepancies between observed and estimated values for these species are not easily explained, although local soil factors (acid pH, low clay content, absence of 2 : 1 expanding lattice clays) or long periods (several growing seasons) of direct deposition on evergreen foliage may account for some of the difference. Total estimated ^{137}Cs in vegetation (2000 pCi/kg) also agrees favorably with a range of values that Gamble (1971) reports for Florida vegetation in 1969 and 1970: for pine needles, 270 pCi/kg; scrub oak leaves, 2700 pCi/kg; palmetto fronds, 2400 pCi/kg; hardwood forest leaf litter, 900 and 1300 pCi/kg, for a grand average of 1500 pCi/kg.

It appears from this assessment that the elevated concentrations of ^{137}Cs in vegetation of coastal-plain ecosystems and for the Tampa, Fla., milkshed can be explained on the basis of current knowledge of radiocesium dynamics in terrestrial environments. The combination of direct deposition of ^{137}Cs on vegetation and the high fractional transfer (approximately 3%) in the soil-root pathway can account for the levels of ^{137}Cs observed in many species that grow on sandy, acid, kaolinitic soils—sometimes classified as humic gley's—of Florida. Low cesium-fixing capacity due to mineralogical characteristics and low clay content are probably important soil factors responsible for increased plant uptake. A new, yet unidentified factor, e.g., mycorhizal, symbiotic enhancement of uptake (Gamble, 1971), is not required to explain the elevated levels of ^{137}Cs in vegetation and milk, although the possible existence of such a mechanism is not disputed. Direct deposition of fallout on vegetation appears to be an important mode of contamination; otherwise the concentration of ^{137}Cs in milk—a function of concentration in forage—would not decrease in tandem with the order of magnitude decrease in ^{137}Cs in the atmosphere which has been reported in the past decade.

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REFERENCES

ld, P. W., 1960, Nature and Mode of Weathering of Soil—Potassium Reserves, *J. Sci. Food Agr.*, **6**: 285-292.

Auerbach, S. I., et al., 1972, Environmental Sciences Division Annual Progress Report for Period Ending September 30, 1972, Radionuclide Cycling in Terrestrial Environments, p. 2, USAEC Report ORNL-4848, Oak Ridge National Laboratory.

——, et al., 1974, Environmental Sciences Division Annual Progress Report for Period Ending September 30, 1973, Terrestrial Radionuclide Cycling and Effects, p. 48, USAEC Report ORNL-4935, Oak Ridge National Laboratory.

——, et al., 1959, Health Physics Division Annual Progress Report for Period Ending July 31, 1959, Ecological Research, pp. 18-54, USAEC Report ORNL-2806, Oak Ridge National Laboratory.

——, J. S. Olson, and H. D. Waller, 1964, Landscape Investigations Using Cesium-137, *Nature*, **201**: 761-764.

Barshad, I., 1954, Cation Exchange in Micaceous Minerals, *Soil Sci.*, **78**: 55-76.

Biddulph, O., 1960, Radioisotopes in Plants: Foliar Entry and Distribution, in *Radioisotopes in the Biosphere*, pp. 73-85, R. S. Caldecott and L. A. Snyder (Eds.), University of Minnesota Center for Continuation Study.

Booth, R. S., S. V. Kaye, and P. S. Rohwer, 1971, A System Analysis Methodology for Predicting Dose to Man from a Radioactively Contaminated Terrestrial Environment, in Radionuclides in Ecosystems, D. J. Nelson (Ed.), pp. 877-893, USAEC Report CONF-710501-P2.

Brisbin, I., et al., 1974, Patterns of Radiocesium in the Sediments of a Stream Channel Contaminated by Production Reactor Effluents, *Health Phys.*, **27**: 19-27.

Brown, G. N., 1964, Cesium in *Liriodendron* and Other Woody Species: Organic Bonding Sites, *Science*, **143**: 368-369.

Bruce, R. S., and R. Scott Russell, 1969, Agricultural Aspects of Acute and Chronic Contamination Situations, in *Environmental Contamination by Radioactive Materials*, Seminar Proceedings, Vienna, 1969, pp. 79-89, International Atomic Energy Agency, Vienna (STI/PUB/226).

mings, S. L., L. Bankert, A. R. Garrett, Jr., and J. E. Regnier, 1969, ^{137}Cs Uptake by at Plants as Related to the Soil Fixing Capacity, *Health Phys.*, **17**: 145-148.

——, J. H. Jenkins, T. T. Fendley, L. Bankert, P. H. Bedrosian, and C. R. Porter, 1971, Cesium-137 in White-Tailed Deer as Related to Vegetation and Soils of the Southeastern United States, in Radionuclides in Ecosystems, D. J. Nelson (Ed.), pp. 123-128, USAEC Report CONF-710501-P1.

Dahlman, R. C., 1971, Prediction of Radionuclide Contamination of Grass from Fallout Particle Retention and Behavior, in *Survival of Food Crops and Livestock in the Event of Nuclear War*, Upton, L. I., Sept. 15, 1970, AEC Symposium Series, No. 24 (CONF-700909).

——, S. I. Auerbach, and P. B. Dunaway, 1969, Behavior of ^{137}Cs-Tagged Particles in a Fescue Meadow, in Environmental Contamination by Radioactive Materials, Seminar

Proceedings, Vienna, 1969, pp. 153-165, International Atomic Energy Agency, Vienna (STI/PUB/226).

Evans, E. J., and A. J. Dekker, 1969, Effect of Nitrogen on ^{137}Cs in Soils and Its Uptake by Oat Plants, *Can. J. Soil. Sci.*, **49**: 343-355.

——, and A. J. Dekker, 1968, Comparative Cesium-137 Content of Agricultural Crops Grown in Contaminated Soil, *Can. J. Plant Sci.*, **48**: 183-188.

Fairbridge, Rhodes W. (Ed.), 1972, Cesium: Element and Geochemistry, in *The Encyclopedia of Geochemistry and Environmental Sciences* (Encyclopedia of the Earth Science Series, Vol. 4A), pp. 147-148, Van Nostrand Reinhold Company, New York.

Francis, C. W., and F. S. Brinkley, 1975, Preferential Adsorption of ^{137}Cs to Micaceous Mineral in an Environmentally Contaminated Sediment, to be published.

——, and T. Tamura, 1972, An Evaluation of Zonal Centrifugation as a Research To[ol] Soil Science. II. Characterization of Soil Clays, *Soil Sci. Soc. Amer., Proc.*, **36**: 372-3[77]

——, and T. Tamura, 1971, Cesium-137 Soil Inventory of a Tagged Liriodendron Forest, 1962 and 1969, in Radionuclides in Ecosystems, D. J. Nelson (Ed.), pp. 140-149, USAEC Report CONF-710501-P1.

Fredriksson, L., 1970a, Plant Uptake of Fission Products. III. Uptake of Cesium-137 by *Trifolium protense* as Influenced by the Potassium and Calcium Level in the Soil, *Lantbrukshoegsk. Ann.*, **36**: 41-60.

——, 1970b, Plant Uptake of Fission Products, IV. Uptake of Strontium-90 and Cesium-137 from Tropical and Subtropical Soils, *Lantbrukshoegsk. Ann.*, **36**: 61-89.

Gamble, J. F., 1971, A Proposed Mechanism for the Recycling of Radiocesium in Florida Soil Plant Systems, in Radionuclides in Ecosystems, D. J. Nelson (Ed.), pp. 133-139, USAEC Report CONF-710501-P1.

Gifford, F. A., Jr., and D. H. Pack, 1962, Surface Deposition of Airborne Material, *Nucl. Safety*, **3**(4): 76-80.

Johnson, J. E., D. W. Wilson, and W. L. Lindsay, 1966, Transfer of Fallout Cesium-137 from Soil to Dairy Cattle Feeds, *Soil Sci. Soc. Amer., Proc.*, **30**: 416-417.

Kaye, S. V., and S. J. Ball, 1969, Systems Analysis of a Coupled Compartment Model for Radionuclide Transfer in a Tropical Environment, in Symposium on Radioecology, D. J. Nelson and F. C. Evans (Eds.), pp. 731-739, USAEC Report CONF-670503.

Kirchmann, R., E. Fagniart, and S. Van Pujmbroeck, 1967, Studies on Foliar Contamination by Radiocesium and Radiostrontium, in *Radioecological Concentration Processes*, B. Aberg and F. P. Hungate (Eds.), pp. 475-483, Pergamon Press, Inc., New York.

Krieger, H. L., B. Kahn, and S. Cummings, 1967, Deposition and Uptake of ^{90}Sr and ^{137}Cs in an Established Pasture, in *Radioecological Concentration Processes*, B. Aberg and F. P. Hungate (Eds.), pp. 59-72, Pergamon Press, Inc., New York.

Levi, E., 1969, The Penetration and Adsorption of Cesium in Bean Leaves, *Act. Bot. Neer.*, **18**: 455-461.

Lomenick, T. F., and T. Tamura, 1965, Naturally Occurring Fixation of Cesium-137 on Sediments of Lacustrine Origin, *Soil Sci. Soc. Amer., Proc.*, **29**: 383-387.

Marei, A. N., R. M. Barkhudarov, N. J. Novikova, E. V. Petukhova, L. D. Dubova, and V[.] Briganina, 1972, Effect of Natural Factors on Cesium-137 Accumulation in the Bo[dy] of Residents in Geographical Regions, *Health Phys.*, **22**: 9-15.

Menzel, R. G., 1965, Soil–Plant Relationships of Radioactive Elements, *Health Phys.*, **11**: 1325-1332.

Middleton, L. J., 1959, Radioactive Strontium and Cesium in the Edible Parts of Crop Plants After Foliar Contamination, *Int. J. Radiat. Biol.*, **4**: 387-402.

Nishita, H., R. M. Haug, and M. Hamilton, 1968, Influence of Minerals on Strontium-90 and Cesium-137 Uptake by Bean Plants, *Soil Sci.*, **105**: 237-243.

——, A. J. Steen, and K. H. Larson, 1958, Release of Strontium-90 and Cesium-137 from Vina Loam upon Prolonged Cropping, *Soil Sci.*, **86**: 195-201.

Pasteurized Milk Network, 1973, *Radiol. Health Data*, **14**: 671 (and previous years' reports, 1963–1972).

Pendleton, R. C., and R. L. Uhler, 1960, Accumulation of Cesium-137 by Plants Grown in Simulated Pond, Wet Meadow, and Irrigated Field Environments, *Nature*, **185**: 707-708.

Peters, L. N., and J. P. Witherspoon, 1972, Retention of 44 to 88 m Simulated Fallout Particles by Grasses, *Health Phys.*, **22**: 261-266.

Porter, C. R., C. R. Phillips, M. W. Carter, and B. Kahn, 1967, The Cause of Relatively High ^{137}Cs Concentrations in Tampa, Florida, Milk, in *Radioecological Concentration Processes*, B. Aberg and F. P. Hungate (Eds.), pp. 95-101, Pergamon Press, Inc., New York.

dale, H. L., and D. J. Shure, 1973, Food/Plain Transfer and Accumulation of ^{137}Cs om a Reactor Effluent Stream, in *Environmental Behaviour of Radionuclides Released in the Nuclear Industry*, Symposium Proceedings, Aix-en-Provence, 1973, pp. 243-253, International Atomic Energy Agency, Vienna (STI/PUB/345).

Report of the United Nations Scientific Committee on the Effects of Atomic Radiation, 1962, 17th Session Supplement No. 16A 5216: 289-310.

Resnik, M. C., O. R. Lunt, and A. Wallace, 1969, Cesium, Potassium, Strontium, and Calcium Transport in Two Different Plant Species, *Soil Sci.*, **108**: 64-73.

Russell, R. S., 1965, An Introductory Review: Interception and Retention of Airborne Material on Plants, *Health Phys.*, **11**: 1305-1315.

——, 1963, The Extent and Consequences of the Uptake by Plants of Radioactive Nuclides, *Ann. Rev. Plant Physiol.*, **14**: 271-294.

——, and R. S. Bruce, 1969, Environmental Contamination With Fallout from Nuclear Weapons: A Review, in *Environmental Contamination by Radioactive Materials*, Seminar Proceedings, Vienna, 1969, pp. 3-13, International Atomic Energy Agency, Vienna (STI/PUB/226).

Sawhney, B. L., 1965, Sorption of Cesium from Dilute Solutions, *Soil Sci. Soc. Amer. Proc.*, **29**: 25-28.

Sharitz, Rebecca R., S. L. Scott, J. E. Pinder III, and S. K. Woods, 1975, Uptake of Radiocesium from Contaminated Floodplain Sediments by Herbaceous Plants, *Health Phys.*, **28**: 23-28.

Shulz, R. K., R. Overstreet, and I. Barshad, 1960, On the Soil Chemistry of Cesium-137, *Soil Sci.*, **89**: 16-27.

Tamura, T., 1964, Selective Sorption Reactions of Cesium with Soil Minerals, *Nucl. Safety*, **5**(3): 262-268.

——, and D. G. Jacobs, 1960, Structural Implications in Cesium Sorption, *Health Phys.*, **2**: 391-398.

USAEC Health and Safety Laboratory Fallout Program, 1974, Quarterly Summary Report, *Appendix B*: 73-82, USAEC Report HASL-281.

Ward, G. M., J. E. Johnson, and D. W. Wilson, 1966, Deposition of Fallout Cesium-137 on Forage and Transfer to Milk, *Public Health Rep. (U.S.)*, **81**: 639-645.

er, H. D., and J. S. Olson, 1967, Prompt Transfer of Cesium-137 to the Soils of a Tagged *Liriodendron* Forest, *Ecology*, **48**: 15-25.

Wilson, D. W., G. M. Ward, and J. E. Johnson, 1969, A Quantitative Model of the Transport of ^{137}Cs from Fallout to Milk, in *Environmental Contamination by Radioactive Materials*, Seminar Proceedings, Vienna, 1969, pp. 125-134, International Atomic Energy Agency, Vienna (STI/PUB/226).

Witherspoon, J. P., 1964, Cycling of Cesium-134 in White Oak Trees, *Ecol. Monogr.*, **34**: 403-420.

——, and F. G. Taylor, Jr., 1971, Retention of 1–44 μ Simulated Fallout Particles by Soybean and Sorghum Plants, *Health Phys.*, **21**: 673-677.

ACCUMULATION AND MOBILITY OF CESIUM IN ROOTS OF TULIP POPLAR SEEDLINGS

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ABSTRACT

Tulip poplar, *Liriodendron tulipifera* L., seedlings were stem-well tagged with cesium, periodically harvested, and separated into root and shoot compartments to determine seasonal cesium distributions in different root-diameter classes and to delineate element pathways to forest soils. The cesium concentration (μCi/g) in roots <0.1 cm in diameter averaged 1.5 and 3.0 times greater than in roots in the 0.5- to 0.1-cm- and 1.0- to 0.5-cm-diameter classes, respectively. Roots contained 24% of the seedling pool of cesium in 1 week and about 40% in 7 weeks after inoculation. Sixty-five percent of the seedling content was in the root system 8 months after tagging. On an annual basis, roots of the <0.5-cm-diameter classes contained an average of 36% of the seedling pool (root and shoot) and 72% of the root pool of cesium. This is important because small roots constituted a considerable portion of the annual turnover in these root systems. Soil content of cesium (3.37 μCi) at the termination of the study and analysis of treatment effects (aboveground inputs to soil allowed or not allowed) indicated that root processes contributed twice as much cesium to the soil during the study period as the combined aboveground processes contributed.

It is generally acknowledged that the inorganic elements in ecosystems are mobile and are continuously cycled within and among ecosystems. Much knowledge has been accumulated for cycling rates of materials for aboveground compartments, but belowground compartments have received little attention because of difficulties encountered in removing roots and observing root syst in situ. We must have knowledge of the behavior of isotopes in natural syst for proper nuclear waste disposal and feasible application of nuclear energy (Odum, 1959). An understanding of the cycling of various chemical elements is

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essential for efficient management of forest production (Auerbach, Olson, and Waller, 1964; Waller and Olson, 1967; Witherspoon, 1964; and Thomas, 1969).

Results from relatively recent studies (Witherspoon, 1964; Waller and Olson, 1967; Sandberg, Olson, and Clebsch, 1969) indicate that the turnover of material from tree roots may be important as compared with aboveground transfer. The objectives of this study were to interpret accumulation and to estimate the transfer of cesium from roots of seedlings (field grown in potted forest soils) to the soil in which they were grown by use of techniques not [illegible]able to field studies. Roots were separated into diameter and condition [illegible] or live) classes in an effort to determine the role of each class in the accumulation of cesium and turnover to soil. Witherspoon (1964) indicated that in small white oak trees (*Quercus alba* L.) roots less than 0.5 mm in diameter [illegible]ontained approximately 13 times as much cesium per unit weight as roots up to [illegible]0 mm in diameter. All aboveground cesium inputs were eliminated for 50% of the seedlings so that the budgets for soils with and without aboveground inputs could be studied.

MATERIALS AND METHODS

Three hundred field-grown potted tulip poplar (*Liriodendron tulipifera* L.) seedlings were each stem-well tagged with about 11 μCi of ^{134}Cs. The seedlings were approximately 2 years old at the time of potting. Nine trees were randomly selected from each of two treatments (aboveground transfers to soil were excluded or were allowed to occur normally) at 6-week intervals for 1 year. Treatment 1 (exclusion of aboveground transfers to soil) consisted in placing the plants under a greenhouse roof that allowed several meters clearance between the polyethylene sheeting and the plants. The structure was open-ended to allow air flow. In treatment 2, which allowed aboveground transfers to occur [illegible]ormally, fallen leaves and other litter (bud scales, etc.) were allowed to fall or [illegible]ere placed on the soil surface to decay normally through the study period. Plants under the canopy were artificially watered. Precipitation was monitored, and water equal to precipitation was applied to plants either on the day rainfall occurred or on the following day. Seedlings (nine from each treatment) were [illegible]sted, and root systems were divided into the following root-size (diameter) [illegible]ondition classes: (1) roots over 1.0 cm, (2) roots 1.0 to 0.5 cm, (3) roots 0.5 to 0.1 cm, (4) roots <0.1 cm, and (5) dead roots. Dead roots were separated by color. Aboveground plant parts were separated into leaf and old and new stem components. New stem represented any growth accrued after seedlings broke dormancy. Soil samples were collected for cesium analysis by thoroughly mixing each pot of soil for each seedling three to four times and removing 2- to 3-g samples after each mixing. This provided a composite sample of 10 to 12 g of soil from each seedling. Soil leachate was sampled and analyzed for cesium throughout the study period. Plant materials were dried, weighed, and analyzed

for ^{134}Cs. Details of root removal, processing, and analyses are reported elsewhere (Cox, 1972). A cesium balance was maintained for plant and soil components.

Oven-dried plant and soil materials were counted in a gamma spectrometer system containing a well-type NaI-crystal detector. Samples were placed in 25- by 150-mm glass tubes and counted in the 0.55 to 0.84 MeV portion of the gamma spectrum where ^{134}Cs exhibits characteristic photopeaks. Efficiency and decay corrections were made against standards for similar plant-tissue components and soils.

RESULTS AND DISCUSSION

Cesium Concentrations

In comparison with other seedling parts, the ^{134}Cs concentration in small roots reached high levels 7 days after the seedlings were tagged. By July 15, the <0.1-cm-diameter roots contained over 2.1 μCi of radiocesium per gram (dry weight), whereas the concentration in roots in the 0.5- to 0.1-cm class was about 1.2 μCi/g (dry weight). Leaf concentration was about 1.0 μCi/g (dry weight). Average annual biomass and cesium content and concentration values for the seedling parts are given in Table 1. Concentration of cesium in the <0.1-cm root-size class was about 1.5 and 3.0 times greater than in roots in the 0.5- to 0.1-cm- and 1.0- to 0.5-cm-diameter classes, respectively. Leaves exhibited an average concentration (0.85 μCi/g) considerably lower than that in the <0.5-cm-diameter classes.

Cesium-134 concentrations at all periods were inversely related to the diameter of the roots. Seasonal concentrations varied simultaneously among all diameter classes, with the greater variation occurring in the smaller roots. Growth dilution, leaching, exudation, sloughing, translocation from soil and shoot parts, and other processes account for the seasonal changes in concentration.

Seasonal Distribution of Cesium Pools in Plant Parts

Cesium rapidly shifted from above- to belowground plant parts (Table 2). One week after tagging (July 15) about 15% of the plant content of cesium was in leaves, and 57% remained in the old stem tissue. By August 25 (sample 2) the leaves reached their maximum content of 16% and by the October harvest decreased to 12%. This was attributed primarily to transfer back into woody components. Waller and Olson (1967) found that during October, before leaf fall, there was a remobilization of cesium in yellow poplar. In this study, each seedling transferred an estimated maximum average of approximately 0.95 μCi of ^{134}Cs to the soil by rainout and leaf fall after October 6. Estimates of leaf drop and foliage leaching before this date showed that these processes

TABLE 1

RELATIVE COMPARISON OF AVERAGE ANNUAL ^{134}Cs CONCENTRATION, CONTENT BY PLANT PART, AND BIOMASS OF YELLOW POPLAR SEEDLINGS GROWN IN POTTED FOREST SOILS*

Source	Biomass,† g (dry weight)	% total weight	^{134}Cs,† μCi/g	Content, μCi	% Cs
Shoot parts					
Old stem	6.80 (0.20)	54	0.50 (0.03)	3.4	38
New stem	0.32 (0.03)	3	0.81 (0.17)	0.3	2
Leaves‡	1.40 (0.13)	13	0.85 (0.07)	1.2	12
Root-diameter classes, cm					
>1.0	0.45 (0.07)	3	0.17 (0.03)	0.1	3
1.0–0.5	1.58 (0.06)	12	0.66 (0.03)	1.0	12
0.5–0.1	1.14 (0.05)	9	1.24 (0.06)	1.4	15
<0.1	1.13 (0.05)	9	1.91 (0.09)	2.2	23
Dead roots	0.15 (0.01)	1	0.31 (0.03)	0.1	<1

*Percentage distributions provide a relative look at cesium in relation to biomass in plant parts.

†Values in parentheses are standard errors of the mean. N = 144.

‡Averages for the five sampling periods when leaves were present. Percent columns do not total 100% since N = 90 for leaves.

contributed about 0.10 μCi to the soil. Therefore a return of about 1.05 μCi of ^{134}Cs was estimated as maximum input for the leaf component. As much as 5% of the total radiocesium leached from tagged *Liriodendron* trees has been attributed to stem flow (Waller and Olson, 1967). Stem-flow contributions were judged as insignificant in this seedling study, however, because the stems exhibited very little surface area and were very smooth.

Summation of data in Table 2 shows that over 24% of the plant budget of radiocesium transferred to the root system in a period of 7 days, and the root system contained about 40% by August 25. The root portion of plant cesium exceeded 50% by October 6 and did not drop below this level throughout the rest of the study period. From late August to mid-November, the root pool of cesium increased over 20%. This fall transfer to the root pool coincided with senescence. The root pool contained over 65% of the plant pool of radiocesium

TABLE 2

SEASONAL DISTRIBUTION OF CESIUM POOLS IN ABOVE- AND BELOWGROUND PARTS OF *LIRIODENDRON* SEEDLINGS*

Date	Old stem	New stem	Leaves	Root classes				
				>1.0	1.0–0.5	0.5–0.1	<0.1	Dead
July 15	57.1	2.5	15.2	0.8	7.5	8.1	8.2	0.6
	(4.6)	(0.9)	(1.8)	(0.4)	(1.6)	(1.3)	(1.2)	(0.28)
Aug. 25	42.5	2.2	15.7	3.3	8.7	10.8	15.8	0.7
	(4.0)	(0.4)	(2.7)	(1.1)	(1.5)	(1.3)	(2.1)	(
Oct.6	30.1	2.5	12.3	1.5	12.8	14.0	26.0	.0
	(1.6)	(1.0)	(1.4)	(0.8)	(1.2)	(1.0)	(1.4)	(0.07)
Nov. 17	36 0	1.2	0.0	2.1	13.6	17.0	28.9	0.2
	(2.5)	(0.1)	(0.0)	(1.1)	(1.2)	(1.5)	(1.7)	(0.03)
Jan. 3	36.5	1.6	0.0	3.5	12.2	17.8	27.1	0.4
	(2.7)	(0.2)	(0.0)	(1.2)	(0.9)	(1.4)	(2.2)	(0.07)
Feb. 14	39.5	1.6	0.0	2.3	14.5	16.5	24.7	0.4
	(2.6)	(0.2)	(0.0)	(1.1)	(1.1)	(1.1)	(2.0)	(0.06)
Mar. 27	28.3	1.4	2.4	5.0	12.6	19.2	30.1	0.5
	(1.9)	(0.2)	(0.5)	(1.4)	(0.7)	(1.2)	(2.1)	(0.1)
May 8	34.4	1.7	9.1	4.5	11.5	14.7	24.1	0.5
	(2.5)	(0.2)	(0.6)	(1.2)	(1.2)	(1.1)	(2.2)	(0.08)
Grand mean	37.9	1.8	6.9	2.9	11.7	14.8	23.1	0.4
	(1.2)	(0.2)	(0.7)	(0.4)	(0.5)	(0.5)	(0.9)	(0.05)

*Values in parentheses are standard errors of the mean. Because of rounding, percentages may not sum to 100%. N = 18.

by March 27. Content in the root system decreased about 12% and shoot content increased 12%, however, between the March and May harvest periods; this indicates a shift of cesium aboveground during leaf development. Although it is not indicated here, the soil content showed little change (1%) in this period. During this time the old-stem content increased from 28 to 33% of the total plant radiocesium, leaves gained 5%, and new stems gained the remainder. By May 1972 the old-stem, new-stem, and leaf compartments contained 38, 2, and 9% of the plant radiocesium, respectively. The remainder (about 51%) of the seedling content of cesium was in the root system.

Root-Diameter-Class Distribution of Cesium

One week after tagging (July 15), the three smallest root-diameter classes (Table 2) contained about equal portions of radiocesium. With time, however, more of the isotope concentrated in the smallest diameter roots (<0.1 cm). After August 25 the <0.1-cm roots contained over 40% of the radiocesium in the root pool, and the 0.5- to 0.1-cm class averaged about 27% of the root pool. Therefore the <0.5-cm root-diameter classes contained over 65% of the root

pool of cesium. This is of major importance since roots <0.5 cm in diameter constitute a considerable portion (>90%) of the annual turnover by mortality in these root systems (Cox, 1972).

Major net losses in the seedling root biomass and cesium pool due to death and decay occurred in late summer (August), winter (between November and March harvests), and spring (May). The total dead root material accounted for during these periods alone averaged about 0.76 g of dry weight or ~1.2 μCi of cesium per seedling. The average annual cesium concentration (1.6 μCi/g) of the two smallest root-size classes (0.5 to 0.1 cm and <0.1 cm) was applied to the ual dry weight of the dead root material collected during the study to imate the cesium turnover by death and decay since all losses occurred in <0.5-cm root-diameter classes.

Above- vs. Belowground Inputs of Cesium to Soil

Analysis of treatment effects (aboveground transfers to soil were excluded or were allowed to occur normally) substantiated the importance of root processes in transfer of mobile elements to soils. Average annual ^{134}Cs concentration (± standard error) for soils under canopies where aboveground inputs were allowed (treatment 2) was 3.04 ± 0.18 nCi/g; for soils whose contributions were primarily from roots (aboveground inputs excluded, treatment 1), it was 2.19 ± 0.27 nCi/g. Analysis of variance of soil cesium concentrations for the treatments indicated a difference among treatments at the 5% probability level. This indicated, as did previous budget estimates, that approximately 33% (1.1 μCi) of the soil cesium content was transferred from shoot components by way of rain leaching and leaf drop and that the remaining 67% (~2.27 μCi) was transferred to the soil by root processes. Leachate samples did not accumulate detectable amounts of cesium activity.

The ^{134}Cs content of the soil at the end of the study (May harvest) was 3.37 ± 0.41 μCi or over 32% of the total budget (10.58 ± 0.29 μCi) for the plant and soil components. The root system contained over 38% of the cesium at the termination of the study, leaving about 30% aboveground. Sandberg, Olson, and Clebsch (1969) estimated a 32% radiocesium loss from the root system of yellow poplar seedlings to a sand mixture in one growing season. That only 25% of this was attributed to root death was probably related to the unusually good aeration vided by the sand growth medium; the remaining 75% was attributed to udation–leaching. The estimate in the present study (over 50%) is probably low since the removal of dead root material is considerably more difficult in soil than it was in sand, and only major losses were considered. Exchange phenomena, leaching, root exudation, and consumption by soil-dwelling herbivores contributed the remaining losses.

Several studies indicate that leaching and exudation of fine roots may account for sizeable cesium losses in *Liriodendron*. Waller and Olson (1967) regarded exudation and leaching processes as important root-transfer pathways

in a cesium-tagged *Liriodendron* forest on the basis of concentrations of ^{137}Cs at various depths in the soil profile. Sandberg, Olson, and Clebsch (1969) estimated that 75% of the ^{137}Cs losses in roots of *Liriodendron* seedlings grown in sand were due to leaching and exudation. The sand growth medium probably permitted high estimates because of the lack of contact phenomena. In any case, we must be careful in extrapolating data from these artificial conditions (nutrient solutions, sand, etc.) to the soil (Rovira, 1971).

Results are in agreement with field and seedling studies, which noted that small roots rapidly accumulate high concentrations of inorganic elements (Witherspoon, 1964; Waller and Olson, 1967; Sandberg, Olson, and Clebsch, 1969) and that root processes must be responsible for returning as much material to soil as aboveground processes. The high content of cesium in small roots (<0.1-cm diameter) as compared with larger roots of the yellow poplar seedlings agrees with the relative differences noted in white oak roots by Witherspoon (1964). Determining the seasonal distribution of root biomass by diameter class appears to be very important in assessing the role of roots in the accumulation and transfer of cesium, and possibly analogous elements, since most annual turnover by mortality occurs in fine roots (<0.5 cm in diameter).

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REFERENCES

Auerbach, S. I., J. S. Olson, and H. D. Waller, 1964, Landscape Studies Using ^{137}Cs, *Nature*, **201**: 761-764.

Cox, T. L., 1972, Production, Mortality, and Nutrient Cycling in Root Systems of *Liriodendron* Seedlings, Ph. D. Thesis, University of Tennessee, Knoxville.

Odum, E. P., 1959, *Fundamentals of Ecology*, 2nd Ed., W. B. Saunders Company, Philadelphia.

Rovira, A. D., 1971, Plant Root Exudates, in *Biochemical Interactions Among Plants*, pp. 19-24, National Academy of Sciences, Washington, D. C.

Sandberg, G. R., J. S. Olson, and E. E. C. Clebsch, 1969, Internal Distribution and Loss from Roots by Leaching of ^{137}Cs Inoculated into *Liriodendron tulipifera* L. Seedlings Grown in Sand Culture, USAEC Report ORNL-TM-2660, Oak Ridge National Laboratory.

Thomas, W. A., 1969, Accumulation and Cycling of Calcium by Dogwood Trees, *Ecol. Monogr.*, **39**: 101-120.

Waller, H. D., and J. S. Olson, 1967, Prompt Transfers of Cesium-137 to the Soils of a Tagged *Liriodendron* Forest, *Ecology*, **48**: 15-25.

Witherspoon, J. P., 1964, Cycling of Cesium-134 in White Oak Trees, *Ecol. Monogr.*, **34**: 403-430.

RADIOCESIUM LEVELS IN VEGETATION COLONIZING A CONTAMINATED FLOODPLAIN

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ABSTRACT

Radiocesium concentrations in herbaceous and woody plants inhabiting a floodplain contaminated by nuclear production reactor effluents were measured. Leaves and stems of herbaceous plants (*Andropogon* sp. and *Scirpus cyperinus*) contained higher concentrations of radiocesium than those of woody plants (*Alnus serrulata, Myrica cerifera,* and *Salix nigra*). *Andropogon* and *Alnus* fruits had higher concentrations than the leaves or stems. Radiocesium concentrations in fruits and leaves were significantly correlated with stem radiocesium levels in some or all of the species sampled. Mean radiocesium levels in the plant parts exceeded mean soil concentrations; this indicates concentration of radiocesium by the vegetation.

Possible release of radionuclides from nuclear reactors has produced concern over the dynamics of radioisotopes in ecosystems. Radionuclides from failed experimental fuel elements in storage at a nuclear production reactor were released into Steel Creek at the U. S. Atomic Energy Commission's Savannah River Plant from 1961 to 1970 (Marter, 1970). Of the radionuclides detected in contaminated disassembly-basin water, ^{137}Cs was judged to be of greatest biological significance because of its long half-life (~30 years). Over the 9 years of releases, average radiocesium concentrations in Steel Creek water ranged from 6 pCi/liter in 1961 to 615 pCi/liter in 1968 (Marter, 1970).

Steel Creek sediments downstream from the reactor were contaminated by ^{137}Cs, which was contained mostly within the top 20 cm of soil (Brisbin et al., 1974). Plants inhabiting the Steel Creek delta exhibit appreciable radiocesium concentrations, and in some cases plant radiocesium levels exceed soil concentrations (Sharitz et al., 1975). Studies upstream from the delta have also

shown appreciable ^{137}Cs concentrations in vegetation and insect taxa (Marter, 1970; Anderson, Gentry, and Smith, 1973).

Because of the low radiocesium fixing capacities of Steel Creek soils (Brisbin et al., 1974) and indications of ^{137}Cs concentration by vegetation (Sharitz et al., 1975), radiocesium levels in dominant plant species on the lower portion of Steel Creek were measured. In general, our objectives were to estimate ^{137}Cs concentations in the component parts of various plant species and to determine if there were relationships between parts or between species in Steel Creek. Statistical correlations have been used in other studies to predict radiocesium concentrations in the component parts of one species on the basis concentrations in another species (Ng et al., 1973).

METHODS AND MATERIALS

Herbaceous species inhabiting contaminated Steel Creek sediments include broomsedge (*Andropogon* sp.) in well-drained soils and emergent vegetation, woolgrass (*Scirpus cyperinus*), in moist areas bordering the stream banks. Dominant woody species inhabiting the stream banks and adjacent floodplain are black willow (*Salix nigra*), wax myrtle (*Myrica cerifera*), and tag alder (*Alnus serrulata*) (Anderson, Gentry, and Smith, 1973). These species occupy a diverse range of habitats, including islands in the creek, stream banks, and areas on the floodplain.

These herbaceous and woody species were sampled along transects (A and B) extending from Steel Creek to the limits of the floodplain. Transects A and B were located 15.5 and 16.2 km, respectively, downstream from the reactor (Brisbin et al., 1974) and were 150 and 170 m long, respectively. Leaf, stem (twig), fruit (inflorescence), and root samples were collected at 5-m intervals along the transects during October 1971. Only surface roots were collected from woody vegetation. Soil was washed from the roots, but some external insoluble radiocesium may have been retained.

Samples were dried several days at 80°C in a forced-draft oven before being ground. Ground samples were dried 24 hr to a constant weight in a vacuum oven at approximately 50°C and weighed. Samples were counted for radiocesium using two pulse-height analyzers with well-type NaI crystals. There was no significant difference in results from two different machines when they were calibrated against known plant standards. Radiocesium concentrations were expressed as picocuries per gram of dry weight (pCi/g). Some radioactive emissions from ^{134}Cs were present in the energy spectrum for ^{137}Cs on the counting equipment, but, since the ratio of ^{134}Cs to ^{137}Cs in Steel Creek is generally less than 1 : 20 (Marter, 1970), concentrations presented refer mainly to contamination by ^{137}Cs. Statistical significance was indicated by $P < 0.05$.

RESULTS

Radiocesium concentrations in the component parts of woody and herbaceous plants from the transects appeared to be log normally distributed. Concentrations of ^{137}Cs in the parts of other herbaceous species from Steel Creek also approximate a log-normal distribution (Sharitz et al., 1975). Therefore, the data were transformed into logarithms prior to statistical analysis (Steele and Torrie, 1960). Mean radiocesium concentrations in plants from transect A did not differ significantly from those from transect ($F_{1,793} = 2.36$); consequently data from both transects were pooled.

Radiocesium concentrations in leaves ($F_{4,404} = 52.7$, $P < 0.001$) and in stems ($F_{4,400} = 71.03$, $P < 0.001$) differed significantly among the five species sampled. Leaves and stems of herbaceous plants had higher concentrations than leaves and stems of woody plants (Table 1). *Alnus*, *Andropogon*, and *Scirpus* fruits differed significantly in their radiocesium levels ($F_{2,181} = 16.69$, $P < 0.001$). *Scirpus* roots had significantly higher concentrations than *Andropogon* roots ($F_{1,172} = 26.1$, $P < 0.001$). *Andropogon* fruits had the highest mean radiocesium levels, and *Scirpus* roots were the next highest.

Radiocesium concentrations differed significantly among plant parts within species for *Alnus*, *Andropogon*, and *Scirpus* (Table 1). Mean radiocesium levels in fruit were generally 1 to 6 times as great as those in stems and 0.75 to 3 times as great as those in leaves. Mean radiocesium concentrations in leaves were 1 to 2 times as great as those in stems. In *Myrica*, *Salix*, and *Andropogon*, the difference between mean radiocesium levels in leaves and in stems was not significant.

Radiocesium levels in the plant species and their component parts were highly variable. Coefficients of variation ranged from 56 to 96% for plant parts from *Myrica*, *Scirpus*, and *Andropogon*. *Salix* leaves and stems had coefficients of variation of 153 and 118%, respectively. *Alnus* parts were least variable, with coefficients of variation ranging from 38 to 48%.

Despite this variability, ^{137}Cs concentrations in plant parts were predictable on a local level. Mean radiocesium concentrations in the leaves, stems, fruits, and roots of the vegetation at each sampling station were correlated along transect A. A single regression equation was an adequate predictor of leaf radiocesium concentrations from stem concentrations for all five plant species (Fig. 1). The regression of stem (Y) against leaf (X) radiocesium concentration was: $\ln Y = 0.712 + 0.826 (\ln X)$. In herbaceous plants mean radiocesium concentrations in fruit were significantly regressed against mean concentrations in stems (Fig. 2). The regression of stem radiocesium (Y) against fruit radiocesium (X) was, for *Scirpus*, $\ln Y = 0.049 + 0.976 (\ln X)$, and, for *Andropogon*, $\ln Y = 0.813 + 0.768 (\ln X)$. For both *Scirpus* and *Andropogon*, a single regression equation was calculated to describe the relationship between stem (Y) and root (X) radiocesium concentrations: $\ln Y = 1.861 + 0.666 (\ln X)$ ($n = 44$,

TABLE 1

MEAN RADIOCESIUM CONCENTRATIONS IN PLANT PARTS FROM FIVE SPECIES GROWING ON A CONTAMINATED FLOODPLAIN.*

Species	Plant parts†				Degrees of freedom	F‡
	Leaves	Stems	Fruits	Roots		
Alnus serrulata						
Mean	215.6[a]	103.9[a]	625.6[a]		2115	97.80§
95% Confidence interval	183.6-253.3	92.8-116.3	499.7-783.2			
Sample size	45	57	16			
Myrica cerifera						
Mean	134.3[a]	98.9[a]			1115	3.48¶
95% Confidence interval	104.9-171.8	79.8-122.6				
Sample size	59	58				
Salix nigra						
Mean	160.8[a]	155.6[b]			1150	0.06¶
95% Confidence interval	131.1-197.2	130.9-185.0				
Sample size	73	79				
Andropogon sp.						
Mean	494.4[b]	432.2[c]	756.3[a]	411.9[a]	3340	11.10§
95% Confidence interval	436.1-560.6	380.8-490.5	633.5-902.9	345.5-491.1		
Sample size	102	103	62	77		
Scirpus cyperinus						
Mean	509.9[b]	331.3[c]	389.9[b]	746.8[b]	3437	20.24§
95% Confidence interval	439.9-591.2	285.6-384.3	335.1-453.6	641.8-868.9		
Sample size	130	108	106	97		

*Radiocesium concentration is expressed as picocuries per gram dry weight.

†Within component parts, values having the same superscript are not significantly different (Scheffe's Test, Morrison, 1967).

‡F statistics test for a significant difference in mean radiocesium levels among plant parts.

§Significant at the 0.001 level.

¶Not significant at the 0.05 level.

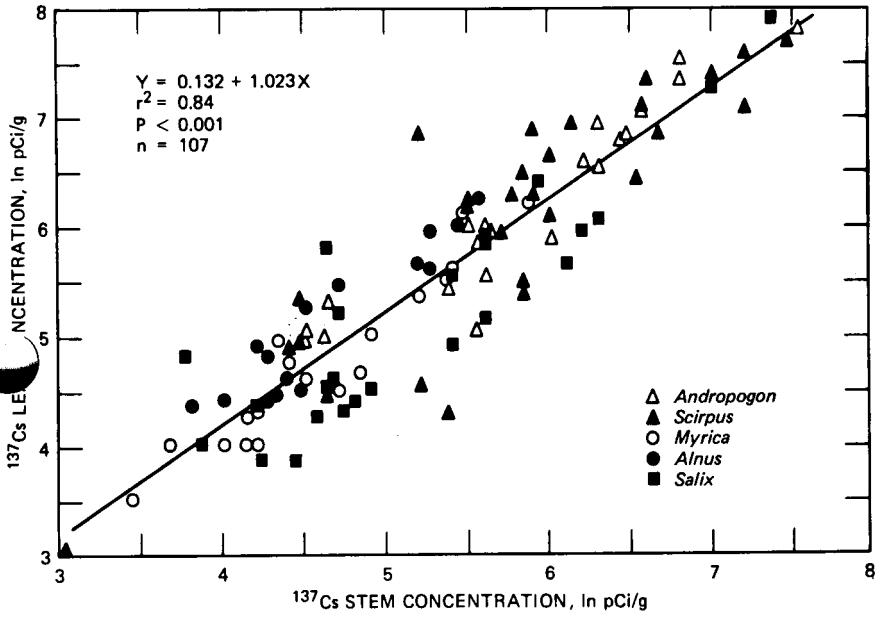

Fig. 1 Relationship between leaf radiocesium concentrations and stem radiocesium concentrations in five species of plants inhabiting a contaminated floodplain.

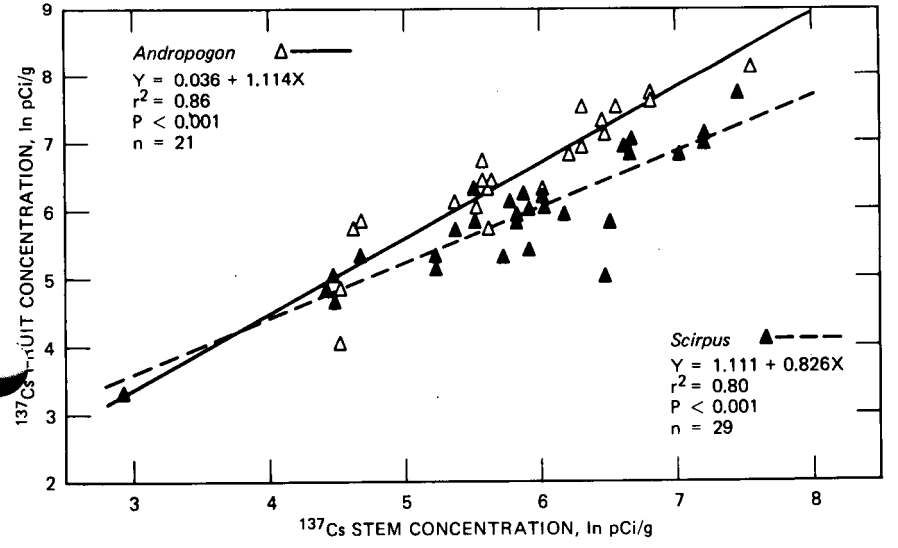

Fig. 2 Relationship between fruit radiocesium concentrations and stem radiocesium concentrations in herbaceous vegetation colonizing a contaminated floodplain.

$r^2 = 0.47$, and $P < 0.001$). Correlations in radiocesium concentrations among species were highly variable, with r values less than 0.70. Many of the correlations were significant at a low level, and concentrations in the component parts of one species could not be used to accurately predict concentrations in another species.

DISCUSSION

Radiocesium concentrations in vegetation from Steel Creek probably represent contamination from internally deposited radionuclide and not appreciable external contamination from worldwide fallout. This is a reasonable assumption considering the relatively high activities of the plants, the high soil radiocesium levels (Brisbin et al., 1974), and earlier studies demonstrating the uptake of radiocesium from contaminated substrates by vegetation under varied environmental conditions (Pendleton and Uhler, 1960; Cline, 1969; Cummings et al., 1971). Differences in mean radiocesium levels among species, as well as poor correlations in concentrations among species, suggest that radiocesium uptake by vegetation is species specific. The observed differences could be attributable to differences in uptake mechanisms or to differences in leachability among plant species (Witkamp and Frank, 1964).

Sources of variation in mean radiocesium concentrations among species include characteristics of each species niche, e.g., soil moisture (Pendleton and Uhler, 1960), soil organic matter (Barber, 1964), and soil texture (Brisbin et al., 1974). A basic distinction exists between concentrations in the aerial parts of herbaceous and woody plants. Herbaceous plants show greater contamination than woody plants, probably because their root systems are shallow and concentrated within the upper regions of the soil where a majority of the radiocesium in Steel Creek sediments is located (Brisbin et al., 1974). Roots of woody plants grow deeper into the soil where less radiocesium is concentrated.

Differences between mean leaf and stem concentrations appear minor relative to the accumulation of radiocesium in *Scirpus* and *Alnus* fruits. The accumulation of radiocesium in fruits has been observed in herbaceous plants inhabiting other contaminated environments (Auerbach and Crossley, 1958). High fruit radiocesium levels may have an impact on the gene pool of plants inhabiting contaminated areas. Morphological differences, which may have a genetic basis, exist between plants of the same species inhabiting radiocontaminated and control areas (Plummer, Crossley, and Gardiner, 1965). Regardless of whether high concentrations in fruit damage fitness by introducing mutant lethals or benefit contaminated individuals by inducing radiation heterosis (Wallace, 1968), radionuclide deposition in fruits may create a selection pressure for more or less efficient uptake mechanisms.

Relationships among leaf, stem, and fruit concentrations observed for Steel Creek vegetation will be useful in predicting radiocesium levels in aboveground

plant parts on the basis of a single component. In limited sampling programs stem and fruit concentrations can be predicted from leaf radiocesium levels. Correlations between concentrations in the component parts of other herbaceous plants, (*Polygonum* and *Sagittaria*) exist in the Steel Creek delta (Sharitz et al., 1975), but the general applicability of the equations in predicting concentrations within or outside the limits of Steel Creek is unknown. The existence of a single regression equation to describe leaf–stem radiocesium relationships in all five species implies that there is some generality to the ln Y–ln X transformed predictive model. Differences between species equations describing fruit–stem radiocesium relationships might be expected because of the wide variability in seed composition among plants. The lack of predictive relationships among plant species found in this study confirms earlier reports that predictability in radiocesium concentrations among plant species inhabiting Steel Creek is poor (Anderson, Gentry, and Smith, 1973). Species-specific radiocesium uptake by vegetation may cause relatively poor correlations in concentrations between species as compared to correlations between the component parts of the same species.

Brisbin et al. (1974) predicted that vegetation growing on Steel Creek sediments at transects A and B would exhibit a large degree of variability in radiocesium concentrations because soil radiocesium levels are extremely variable at these sites (e.g., soils only 1 m apart may vary by as much as 190% of their mean). Our results indicate that there is a large degree of variability in plant concentrations on Steel Creek but that this may not be attributable to variation in substrate radiocesium concentrations because plant concentrations are not correlated with total soil concentrations. The availability of soil radiocesium to vegetation, which is probably not reflected by total soil activity, may also be extremely variable within the floodplain sediments, giving rise to variability in plant concentrations.

Mean concentrations in the component parts of vegetation along transects A and B exceed soil radiocesium levels at the transects, which average 59.0 and 96.0 pCi/g dry weight, respectively (Brisbin et al., 1974). Sharitz et al. (1975) found that herbaceous plants growing on soils with activities less than 100 pCi/g concentrated radiocesium above soil levels. Our results agree with this observation. Steel Creek vegetation apparently concentrates radiocesium at the sampling sites. Cummings et al. (1971) report that the soils of the southeastern coastal plain generally have low radiocesium-fixing capacities and that radiocesium uptake by oats is negatively correlated with soil-fixing capacity. Desorption studies have demonstrated that radiocesium is not tightly held by Steel Creek sediments (Brisbin et al., 1974). Therefore, concentration of radiocesium by vegetation above mean soil levels is not surprising. Our study, in conjunction with others (Ragsdale and Shure, 1973; Sharitz et al., 1975), indicates that, given a large release of radiocesium, uptake by vegetation colonizing contaminated sediments may represent more of an environmental problem along streams of the southeastern coastal plain than in other ecosystems

where radiocesium may be actively fixed by soils (Lomenick and Gardiner, 1965).

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REFERENCES

Anderson, G. E., J. B. Gentry, and M. H. Smith, 1973, Relationships Between Levels of Radiocesium in Dominant Plants and Arthropods in a Contaminated Streambed Community, *Oikos*, **24**: 165-170.

Auerbach, S. I., and D. A. Crossley, Jr., 1958, Strontium-90 and Cesium-137 Uptake by Vegetation Under Natural Conditions, in *Proceedings of the Second United Nations International Conference on the Peaceful Uses of Atomic Energy*, Geneva, 1958, Vol. 18, pp. 494-499, United Nations, New York.

Barber, D. A., 1964, Influence of Soil Organic Matter on the Entry of Cesium-137 into Plants, *Nature*, **204**: 1326-1327.

Brisbin, I Lehr, Jr., et al., 1974, Patterns of Radiocesium in the Sediments of a Stream Channel Contaminated by Production Reactor Effluents, *Health Phys.*, **26**: 1-9.

Cline, J. F., 1969, The Effects of Substrate Conditions on the Uptake Rate of ^{137}Cs by Plants, in *Symposium on Radioecology*, Proceedings of the Second National Symposium, Ann Arbor, Mich., May 15–17, 1967, D. J. Nelson and F. C. Evans (Eds.), USAEC Report CONF-670503, pp. 547-552, U. S. Atomic Energy Commission, The Ecological Society of America, and The University of Michigan.

Cummings, S. L., J. H. Jenkins, T. T. Fendley, L. Bankert, P. H. Bedrosian, and C. R. Porter, 1971, Cesium-137 in White-Tailed Deer as Related to Vegetation and Soils of the Southeastern United States, in Radionuclides in Ecosystems, Proceedings of the Third National Symposium on Radioecology, Vol. 1, pp. 123-128, D. J. Nelson (Ed.), USAEC Report CONF-710501-P1.

Lomenick, T. F., and D. A. Gardiner, 1965, The Occurrence and Retention of Radionuclides in the Sediments of White Oak Lake, *Health Phys.*, **11**: 567-577.

Marter, W. L., 1970, Radioactivity in the Environs of Steel Creek, USAEC R[illegible] DPST-70-435, Savannah River Laboratory.

Morrison, D. F., 1967, *Multivariate Statistical Methods*, McGraw-Hill Book Company, New York.

Ng, Y. C., B. J. Berger, D. J. Pederson, Y. E. Ricker, and S. E. Thompson, Jr., 1973, Evaluation of the Dosage from Terrestrial Foods, in Enewetak Radiological Survey, USAEC Report NVO-140, Vol. 1, pp. 542-611, Nevada Operations Office.

Pendleton, R. C., and R. L. Uhler, 1960, Accumulation of Caesium-137 by Plants Grown in Simulated Pond, Wet Meadow, and Irrigated Field Environments, *Nature*, **185**: 707-708.

Plummer, G. L., D. A. Crossley, and D. A. Gardiner, 1965, Growth Response of Two Sedges Inhabiting a Radioactive Waste Disposal Area, *Ecology*, **46**: 346-348.

Ragsdale, H. L., and D. J. Shure, 1973, Flood Plain Transfer and Accumulation of ^{137}Cs from a Reactor Effluent Stream, in *Environmental Behavior of Radionuclides Released in the Nuclear Industry*, Proceedings Series, Aix-en-Provence, France, International Atomic Energy Agency, Vienna (STI/PUB/345).

Sharitz, R. R., S. L. Scott, J. E. Pinder III, and S. K. Woods, 1975, Uptake of Radiocesium from Contaminated Floodplain Sediments by Herbaceous Plants, *Health Phys.*, **28**: 23-28.

Steel, R. G. D., and J. H. Torrie, 1960, *Principles and Procedures of Statistics*, McGraw-Hill Book Company, New York.

Wallace, B., 1968, *Topics in Population Genetics*, W. W. Norton & Company, Inc., New York.

Tamp, M., and M. F. Frank, 1964, First Year of Movement, Distribution, and Availability of ^{137}Cs in the Forest Floor Under Tagged Tulip Poplars, *Radiat. Bot.*, **4**: 485-495.

SEASONAL VARIATION IN RADIOCESIUM CONCENTRATIONS IN THREE TREE SPECIES

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ABSTRACT

Radiocesium concentrations in leaves and stems of black willow (*Salix nigra*), wax myrtle (*Myrica cerifera*), and tag alder (*Alnus serrulata*) trees inhabiting a floodplain contaminated by production-reactor effluents were measured over 1 year. In willow and myrtle trees, leaf radiocesium levels were highest in the spring and declined during the growing season; stem levels remained relatively unchanged or exhibited a slight increase. Seasonal changes in alder tree parts depended on the site examined. The relationship among component parts was essentially consistent across species and collecting sites in the summer. The radiocesium concentrations in order of rank were: roots $\geq$ leaves $>$ stems. Species differences in component-part radiocesium levels were dependent on the part sampled and the collecting site examined. Mean soil to plant-part concentration factors in summer ranged from 0.9 to 7.6, and species means across leaves, stems, and roots averaged 2.1, 3.8, and 6.2 for alder, willow, and myrtle trees, respectively.

Radionuclide cycling in woody plants has previously been examined by innoculating vegetation with radioactive isotopes (Witherspoon, 1964; Witkamp and Frank, 1964; Waller and Olson, 1967). Although the behavior of radionuclides injected into vegetation might be different from that of radionuclides entering vegetation through roots from radioactive soil, no such differences have been demonstrated. This study focuses on radiocesium dynamics in three tree species inhabiting a contaminated southeastern floodplain. Radiocesium dynamics in trees has not been appreciably explored in southeastern ecosystems, and studies on radionuclide cycling in contaminated environments will enable us to better assess the potential impact of radioactive releases from the nuclear industry.

The study area was Steel Creek, a 20-km coastal-plain stream located on the U. S. Atomic Energy Commission's (AEC) Savannah River Plant near Aiken,

S. C. During a 9-year period, from 1961 to 1970, approximately 260 Ci of radiocesium, primarily ^{137}Cs, entered Steel Creek from facilities at two nuclear production reactors (Marter, 1970). Releases emanated from storage basins housing defective fuel assemblies. During the time that releases were occurring, large amounts of reactor cooling water also entered Steel Creek and elevated the water level. When water levels were reduced, following shutdown of one reactor and a redirection of flow from the other reactor to a cooling reservoir, the Steel Creek floodplain was exposed. Black willow (*Salix nigra*), wax myrtle (*Myrica cerifera*), and tag alder (*Alnus serrulata*) are the most common tree species now ing on the contaminated floodplain soils (Anderson, Gentry, and Smith, 3).

Previous studies have demonstrated radiocesium uptake by vegetation in the vicinity of Steel Creek (Sharitz et al., 1975; Garten et al., this volume). Our purpose was to answer the following questions: (1) Do the aboveground component parts of trees exhibit seasonal trends in radiocesium concentrations, and are these trends consistent across different locations? (2) Are radiocesium levels in component parts different among species, and are these differences consistent across different locations? (3) Is radiocesium concentrated by the woody vegetation above soil radiocesium levels?

MATERIALS AND METHODS

Individual black willow, wax myrtle, and tag alder trees were selected randomly along transects on the lower portion of Steel Creek. The transects, A, B, and C, were each over 150 m in length and located approximately 15.5, 16.2, and 16.9 km, respectively, downstream from the reactor area (see Brisbin et al., 1974, for illustration). Ten trees of each species were chosen along each transect with the exception of transect C where only willow trees were present. Leaf and stem (twig) samples were taken, when available, from each tree in fall (October 1971), winter (January 1972), spring (April 1972), and summer (July 1972). Soil samples and surface roots were dug to a depth of approximately 15 cm from the base of each tree during summer.

Plant samples were dried in paper bags at 80°C in a forced-draft oven before being ground with a Wiley mill. Subsamples in test tubes were then dried night in a vacuum oven at 50°C to a constant weight. Soil samples were ed in an oven at 80°C, pulverized and homogenized, and sifted through a 2-mm-mesh sieve to remove organic matter. Subsamples of soil and plants were counted for radiocesium using two pulse-height analyzers (gamma spectrometers) equipped with sodium iodide well-type detectors. Samples were counted for 30 min or to a preset count of 100 counts in the peak channel depending on the machine used. A nonparametric sign test of paired observations showed there was no significant difference in results from the two machines when both were calibrated against known standards ($P > 0.10$, $n = 15$). Both machines had

similar counting efficiencies, and sample activities were calculated on the basis of same-day counts of standards and backgrounds. Calculations were made by an IBM 360 computer, and concentrations are expressed as picocuries per gram dry weight.

Peak stripping techniques for omitting energies from isotopes other than ^{134}Cs and ^{137}Cs present in the samples were not used. Relative to radiocesium concentrations in Steel Creek, the contribution of other radioactive elements to the total gamma spectrum is negligible. Among the cesium isotopes the ^{134}Cs to ^{137}Cs ratio in Steel Creek is less than 1:20 (Marter, 1970); therefore concentrations presented refer mainly to ^{137}Cs.

Statistical analysis was obtained using the Statistical Analysis Sys (Service, 1972).

RESULTS

Over the study period, data on some component parts were not available. Any trees with missing observations were deleted; so all trees included in the analysis have complete records for all seasons when component parts are expected. With these constraints on the available data, complete records were obtained for seven alder trees, eight myrtle trees, and six willow trees at transect A, five trees of each species at transect B, and nine willow trees at transect C. Analysis of variance was used in the statistical analysis. A log-normal transformation was applied to the data before analysis because radiocesium data on plants from the Savannah River Plant most frequently fit a log-normal distribution (Pinder and Smith, this volume). Statistical significance was indicated by $P \leq 0.05$.

Seasonal variation in leaf and stem radiocesium concentrations was apparent to varying degrees in all tree species, and in some instances trends were dependent on environment or the transect sampled. Willow leaves and stems differed significantly in radiocesium concentrations across seasons ($F_{2,43} = 14.0$ and $F_{3,60} = 4.75$, respectively). Willow leaf radiocesium levels declined from spring to fall, but stems exhibited a slight increase in concentrations over the same period (Fig. 1). Radiocesium concentrations in both willow leaves and stems differed significantly among the three transects ($F_{2,43} = 23.7$ and $F_{2,60} = 13.6$, respectively). However, the seasonal changes in concentrati were consistent across these transects (i.e., season × transect interactions w not significant for either leaf or stem data).

Myrtle trees exhibited a pattern that was similar, in some respects, to seasonal changes in willow radiocesium concentrations. Myrtle leaf radiocesium levels differed significantly among seasons ($F_{3,37} = 41.3$) and between transects ($F_{1,37} = 6.1$). Leaf concentrations declined steadily from spring to winter, and the nonsignificant interaction between the season and transect treatment terms demonstrated this seasonal change was consistent across the two sampling

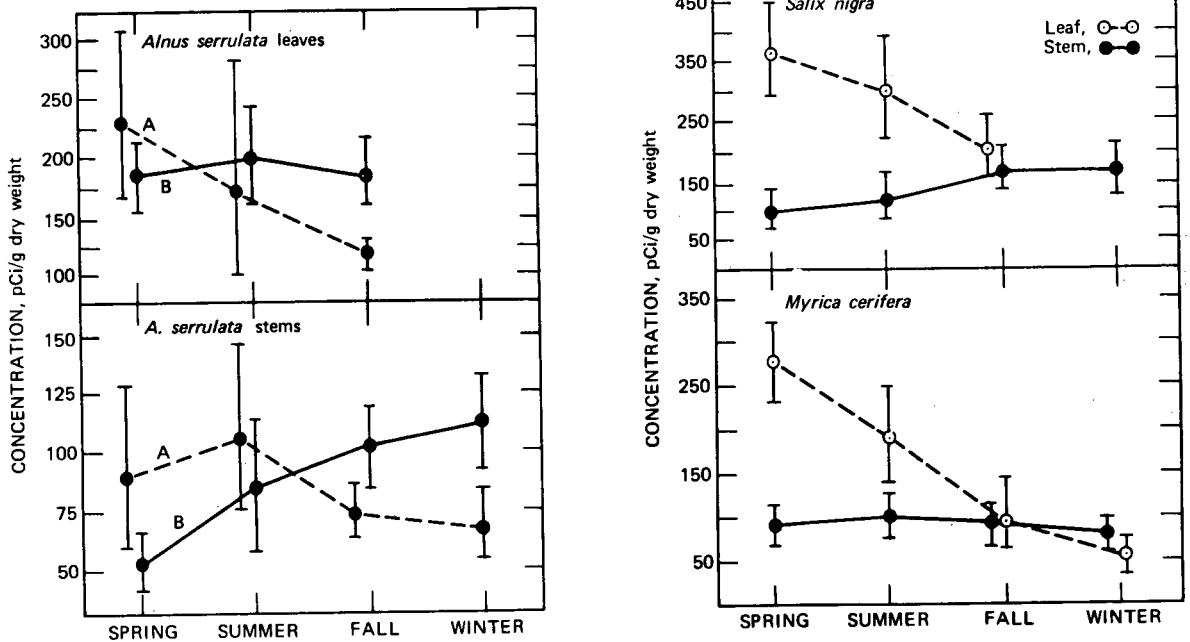

Fig. 1 Seasonal variation in mean radiocesium concentrations in the leaves and stems of black willow (*Salix nigra*), wax myrtle (*Myrica cerifera*), and tag alder (*Alnus serrulata*) trees growing on a contaminated floodplain. Sample size was 20 willow trees, 13 myrtle trees, and 7 alder trees at transect A and 5 alder trees at transect B. Vertical lines on either side of the mean show ±2 SE.

locations. Myrtle stems did not differ significantly among seasons in their radiocesium levels (Fig. 1).

Seasonal differences in alder leaf and stem radiocesium concentrations were observed (Fig. 1), but seasonal trends and differences were dependent on the transect sampled (i.e., season X transect interactions were significant for both leaves and stems, $F_{2,24} = 3.6$ and $F_{3,34} = 8.4$, respectively). Alder leaf levels decreased throughout the growing season at transect A, but concentrations remained relatively unchanged at transect B (Fig. 1). Alder stem concentrations steadily increased from spring to winter at transect B, but at transect A mean stem levels in fall and winter were somewhat lower than in spring or sum Significant seasonal differences in alder leaf and stem concentrations ($F_{2,24} = 3.6$ and $F_{3,34} = 3.1$, respectively) were therefore a function of the immediate environment in which alders were growing.

The component parts of alder, willow, and myrtle differed significantly in their summer radiocesium concentrations ($F_{2,24} = 29.5$, $F_{2,43} = 41.9$, and $F_{2,25} = 17.8$, respectively). Interaction terms (part X transect) in each univariate analysis were not significant, indicating that component-part differences were consistent across transects A and B. Multiple comparison of group means by a Scheffé test (Morrison, 1967) demonstrated the following significant differences: (1) in both willow and alder trees, root concentrations were usually greater than leaf concentrations, which were greater than stem concentrations, and (2) in myrtle trees, root and leaf concentrations were similar, and both were greater than stem concentrations (Table 1). Relationships among plant-part radiocesium levels are clearly dependent on the season when parts are collected (Fig. 1).

Differences in radiocesium concentrations among species were also assessed. Species differences were affected by habitat as indicated by a significant overall species X transect interaction term in a multivariate analysis of variance of leaf, stem, and root concentrations (Hotelling–Lawley Trace, $F = 4.6$, $df = 6,34$). Univariate analysis of variance demonstrated that the species X transect interaction was significant in an analysis of both leaf and stem concentrations. When the mean values for these component parts in Table 1 are examined, the source of the interaction becomes apparent. Considering only leaves, at transect A the radiocesium levels in the species rank as follows: willow > myrtle > alder; at transect B the reverse order is observed: alder > myrtle > willow. Mean s concentrations rank as follows at transect A: willow > alder > myrtle; transect B the reverse is observed: myrtle > alder > willow. Clearly, interspecific differences in concentrations are dependent on both the part examined and the site sampled.

Plant radiocesium concentrations were independent of soil concentrations, as indicated by no significant correlations among plant-part and soil radiocesium levels for any of the tree species. Concentration factors of plant-part radiocesium levels to soil radiocesium concentrations were calculated for each tree, using all

TABLE 1

MEAN RADIOCESIUM CONCENTRATIONS (pCi/g DRY WEIGHT) IN THE COMPONENT PARTS OF TREE SPECIES AT TRANSECTS ACROSS A CONTAMINATED FLOODPLAIN IN SUMMER

	Component part								
	Leaf			Stem			Root		
Transect	Willow	Alder	Myrtle	Willow	Alder	Myrtle	Willow	Alder	Myrtle
A	426.4	166.2	207.9	142.9	104.8	96.0	401.2	248.6	480.2
B	147.7	196.2	178.0	59.6	81.6	103.2	269.2	379.3	225.0
C	393.5			166.9			721.3		
Means* across Transects									
A and B	239.2^{a}	183.1^{a}	188.7^{a}	88.7^{b}	90.6^{b}	101.7^{b}	322.8^{c}	318.1^{c}	289.7^{a}

*Within a species, any two means sharing the same superscript are not significantly different ($P > 0.05$). Sample size was six willow, seven alder, and eight myrtle trees at transect A, five of each species at B, and nine willows at transect C.

available data from the summer sample. Individual concentration factors were extremely variable, ranging from 0.1 to 36.0 across the parts and species examined (Table 2). Mean concentration factors were greater than 1.0 for all species and parts with the exception of alder stems. Mean stem ratios differed significantly among species ($F_{2,50} = 4.2$), the concentration ratio for alder stems being significantly lower than that for myrtle stems. Alder was the only species in which there was a significant difference among parts ($F_{3,57} = 10.9$), stem ratios being significantly lower than leaf or root concentration factors.

TABLE 2

MEAN CONCENTRATION RATIOS ($\bar{X}$) OF RADIOCESIUM IN EACH PLANT PART TO SOIL RADIOCESIUM (pCi/g DRY WEIGHT) AND THE RANGE (R) OF RATIOS FOR EACH COMPONENT PART OF EACH SPECIES*

Component part	Statistic	Concentration ratios†		
		Willow	Alder	Myrtle
Leaves	$\bar{X}$	$3.8^{a,1}$	$2.3^{b,1}$	$7.1^{a,1}$
	R	0.1–30.3	0.5–11.1	0.4–33.9
Stems	$\bar{X}$	$1.3^{a,1,2}$	$0.9^{a,1}$	$3.8^{a,2}$
	R	0.1–6.1	0.2–2.8	0.2–19.8
Roots	$\bar{X}$	$6.2^{a,1}$	$3.2^{b,1}$	$7.6^{a,1}$
	R	0.6–36.0	0.7–10.2	0.9–25.9
Species mean		3.8	2.1	6.2

*Summer concentrations were used for leaves, roots, and stems. The sample size was 24 willow, 16 alder, and 13 myrtle trees.

†Within each row, means sharing the same numerical superscript are not significantly different ($P > 0.05$). Within each column, means sharing the same alphameric superscript are not significantly different ($P > 0.05$).

Despite the relatively low radiocesium concentrations in the component parts of myrtle trees (Table 1), concentration factors were highest for this species owing to the low-level soils on which it was growing ($\bar{X}_{soil} = 121.2$, $n = 13$). Radiocesium concentrations in the component parts of willow trees were relatively high (Table 1), but, because this species was growing in areas of high soil contamination ($\bar{X}_{soil} = 318.5$, $n = 24$), the mean concentration factor was lower than that for myrtle trees (Table 2). The mean soil radiocesium level at the base of alder trees was 187.2 ($n = 16$).

DISCUSSION

Seasonal changes in radiocesium concentrations observed for trees inhabiting the Steel Creek floodplain can be explained by current knowledge of

radiocesium dynamics in woody vegetation. The patterns observed in our study are in general agreement with patterns of seasonal change obtained from innoculating vegetation with radioisotopes. The spring maximum in leaf radiocesium concentrations in willow, myrtle, and alder trees (at transect A) probably results from a mobilization of radiocesium and other mineral elements within the plant as a result of actively growing foliar tissue. Witherspoon (1964) found ^{134}Cs to be highly mobile in oak trees in the spring. Once a spring maximum is attained, foliar radiocesium concentrations decline (Auerbach, Olson, and Waller 1964). Radiocesium losses from willow leaves throughout our study ranged from 46 to 61% of the maximum spring concentration, depending on the transect examined. For myrtle trees, 73 to 77% of the maximum spring foliar concentration was lost by winter. Our figures for radiocesium loss from myrtle and willow leaves are in agreement with values reported for oak and poplar trees at other sites. Witherspoon (1964) reported 51% of the total foliar ^{134}Cs content in oak trees may be lost from the leaf tissue prior to leaf abscission in the fall. In tulip poplar trees, a 53% reduction in foliar ^{137}Cs has been observed over a summer growing season (Waller and Olson, 1967).

Declining leaf radiocesium concentrations throughout the growing season have been attributed to both foliar leaching by rainfall (Auerbach et al., 1964; Waller and Olson, 1967) and to the translocation of radiocesium back into woody tissue prior to leaf fall (Witherspoon, 1964). In tulip poplar trees as much as two-thirds of the maximum ^{137}Cs in a summer tree canopy may be moved to the soil via root death, root exudation, and leaching by soil water (Waller and Olson, 1967). Radiocesium transport from foliage to roots and soil cannot be demonstrated from our data. However, increasing radiocesium concentrations in willow and in some alder stems (Fig. 1) over the growing season suggest resorption of radiocesium from leaves by the stem tissue as leaf senescence approaches. Leaching of radiocesium from willow and alder leaves is probably more important than translocation in decreasing concentrations throughout the spring and summer seasons. The cause of declining leaf concentrations in myrtle trees is unclear. Translocation of radiocesium into woody tissue is not indicated by the unchanging stem concentrations. Appreciable leaching of myrtle leaves by rainfall also seems unlikely because of the thick waxy cuticle layer characteristic of this species.

Seasonal changes in radiocesium concentrations have two consequences for the floodplain ecosystem. First, the high foliar radiocesium levels in spring and summer suggest that, per unit weight, significantly more radiocesium will be ingested by herbivores at that time. Spring and summer are times when consumers may be undergoing net growth, and consequently greater amounts of radionuclide might be incorporated into the consumer biomass during the growing season than in the fall when foliage concentrations are low. Second, the translocation of radiocesium back into woody tissue in fall will promote

retention of the element within the ecosystem and reduce the magnitude of the release of cesium in leaf fall to the decomposer food chain.

In this study we found that environment or collecting site affected both seasonal changes in radiocesium concentration in one species and the nature of species differences in the summer. The interaction of season and transect treatment terms in the analysis of alder tree radiocesium levels indicates that the microhabitat in which alders are growing has some influence on radiocesium dynamics within this species. It is not known what differences exist between transects A and B which would lead to the observed interaction. The interaction of species and transect treatment terms in the analysis of component parts of these trees suggests that the degree of uptake by a species depends on the environment it occupies. Even within a site, microenvironmental differences may be important in determining species differences. For example, myrtle and alder trees appear to be growing in drier areas on the floodplain than are willows, which grow in poorly drained soils and are the major tree species inhabiting the water-saturated delta sediments of Steel Creek. Radiocesium uptake by herbaceous vegetation has been shown to be related to the amount of soil water (Pendleton and Uhler, 1960), and soil-moisture differences may contribute to differences in radiocesium levels among species and transects on Steel Creek. Such edaphic factors as soil composition, pH, and soil nutrient content, which set limits on the distribution of a species on the floodplain, are probably also important in determining the radiocesium concentrations found in each species.

Nonsignificant correlations between soil radiocesium levels and plant component-part concentrations were observed in this study. A similar result has been reported for herbaceous plants inhabiting the Steel Creek delta (Sharitz et al., 1975). Differences between collecting sites or differences among species do not arise from differences in mean soil radiocesium concentrations alone. However, concentration factors for these species indicate an accumulation of radiocesium in the component parts of woody vegetation. In addition to considerable individual variation, soil-to-plant concentration factors can be expected to exhibit seasonal variation. Each concentration ratio reported in this study is merely a static index of radiocesium concentrations in vegetation relative to soil concentrations. Concentration-ratio data from Steel Creek are in contrast to vegetation growing on White Oak Lake bed sediments in Tennessee, where Crossley (1967) reported concentration factors of 0.027 for radiocesium. Accumulation of radiocesium in vegetation has been observed at another stream system flowing parallel to Steel Creek at the Savannah River Plant (Ragsdale and Shure, 1973). At Lower Three Runs Creek, vegetation-to-substrate radiocesium ratios range from 0.3 to 8.3 for roots and 0.1 to 5.5 for leaves (Ragsdale and Shure, 1973). Concentration factors of soil-to-plant radiocesium levels from 2.5 to 32.6 were recently reported for other areas of the world (Marei et al., 1972).

Studies are needed to determine if radionuclide concentration by vegetation in Steel Creek may be characteristic of southeastern coastal-plain streams.

Desorption studies show that radiocesium is not tightly bound by Steel Creek sediments (Brisbin et al., 1974), and radiocesium fixing capacities of soils are apparently poor throughout the entire southeast (Cummings et al., 1971). Radiocesium uptake by plants in the vicinity of Steel Creek may be related to mineral-deficient soils characteristic of southeastern ecosystems.

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REFERENCES

Anderson, G. E., J. B. Gentry, and M. H. Smith, 1973, Relationships Between Levels of Radiocesium in Dominant Plants and Arthropods in a Contaminated Streambed Community, *Oikos,* **24**: 165-170.

Auerbach, S. I., J. S. Olson, and H. D. Waller, 1964, Landscape Investigations Using Cesium-137, *Nature,* **201**: 761-764.

Brisbin, I. Lehr, Jr., et al., 1974, Patterns of Radiocesium in the Sediments of a Stream Channel Contaminated by Production Reactor Effluents, *Health Phys.,* **27**: 19-27.

Crossley, D. A., Jr., 1967, Comparative Movement of ^{106}Ru, ^{60}Co, and ^{137}Cs in Arthopod Food Chains, in Proceedings of the Second National Symposium on Radioecology, D. J. Nelson and F. C. Evans (Eds.), USAEC Report CONF-670503, pp. 687-695.

Cummings, S. L., J. H. Jenkins, T. T. Fendley, L. Bankert, P. H. Bedrosian, and C. R. Porter, 1971, Cesium-137 in White-Tailed Deer as Related to Vegetation and Soils of the Southeastern United States, in Radionuclides in Ecosystems, Proceedings of the Third National Symposium on Radioecology, D. J. Nelson (Ed.), USAEC Report CONF-710501-P2, Vol. 2, pp. 123-128.

Marei, A. N., R. M. Barkhudarov, N. J. Novikova, E. V. Petukhova, L. D. Dubova, and V. M. Briganina, 1972, Effect of Natural Factors on Cesium-137 Accumulation in the Bodies of Residents in Some Geographical Regions, *Health Phys.,* **22**: 9-15.

...rter, W. L., 1970, Radioactivity in the Environs of Steel Creek, USAEC Report DPST-70-435, Savannah River Laboratory.

...rrison, D. F., 1967, *Multivariate Statistical Methods,* pp. 32-35, McGraw-Hill Book Company, New York.

Pendleton, R. C., and R. L. Uhler, 1960, Accumulation of Cesium-137 by Plants Grown in Simulated Pond, Wet Meadow, and Irrigated Field Environments, *Nature,* **185**: 707-708.

Ragsdale, H. L., and D. J. Shure, 1973, Floodplain Transfer and Accumulation of ^{137}Cs from a Reactor Effluent Stream, in *Environmental Behavior of Radionuclides Released in the Nuclear Industry,* Symposium Proceedings, AIX-en-Provence, France, 1973, pp. 243-253, International Atomic Energy Agency, Vienna, 1973 (STI/PUB/345).

Service, J., 1972, *A User's Guide to the Statistical Analysis System,* North Carolina State University, Raleigh, N. C.

Sharitz, R. R., S. L. Scott, J. E. Pinder III, and S. K. Woods, 1975, Uptake of Radiocesium from Contaminated Floodplain Sediments by Herbaceous Plants, *Health Phys.*, **28**: 23-28.

Waller, H. D., and J. S. Olson, 1967, Prompt Transfers of Cesium-137 to the Soils of a Tagged *Liriodendron* Forest, *Ecology*, **48**: 15-25.

Witherspoon, J. P., 1964, Cycling of Cesium-134 in White Oak Trees, *Ecol. Monogr.*, **34**: 403-420.

Witkamp, M., and M. L. Frank, 1964, First Year of Movement, Distribution, and Availability of ^{137}Cs in the Forest Floor Under Tagged Tulip Poplars, *Radiat. Bot.*, **4**: 485-495.

DISTRIBUTION OF RADIOCESIUM IN VEGETATION ALONG A CONTAMINATED STREAM

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ABSTRACT

Radiocesium concentrations in leaves from four plant species were measured at eight sites along a 20-km stream contaminated by radioactive effluent from nuclear production reactors at the Savannah River Plant in South Carolina. Leaf samples from *Sagittaria latifolia, Salix nigra, Polygonum punctatum,* and *Scirpus cyperinus* averaged 488.2, 303.2, 191.7, and 86.4 pCi/g dry weight, respectively. The distribution of radiocesium in the vegetation appeared to be species specific and independent of distance from the entry point of reactor effluent into the stream. Leaf radiocesium concentrations were generally higher in plants where the rate of streamflow decreased because of man-made impoundments, fallen trees, or increased stream width. At all sites the radiocesium levels in the plant species were log normally distributed. A significant linear relationship existed for all species between the variance and the mean picocuries per gram, but each species appeared to have a different slope and intercept. Radiocesium concentrations in one plant species could not be used to predict concentrations in another.

The possibility of radioactive releases from nuclear industries has caused concern over the fate of radioactive materials in the environment. Since many nuclear facilities border rivers, it is necessary to know how the physical as well as the biological components of an aquatic environment influence the deposition and cycling of radionuclides (Rice, 1963; Parker et al., 1965; Ragsdale and Sayre, 1973). The manner of radionuclide deposition is important (Sayre, Guy, and Chamberlain, 1963), as are the factors affecting their biological uptake (Menzel, 1954; Pendleton and Uhler, 1960; Shanks and DeSelm, 1963; Davis, 1963).

Steel Creek, a 20-km stream located at the Savannah River Plant in South Carolina, has received large quantities of radiocesium (Marter, 1970). Radiocesium not only is concentrated in the stream sediments but also is readily

available to the biota (Anderson, Gentry, and Smith, 1973; Brisbin et al., 1974; Sharitz et al., 1975). In addition, the wide floodplains along Steel Creek are areas of extensive local deposition. These characteristics provide an environment where depositional patterns of radioactive effluent in a stream can be related to uptake of radiocesium by the biota.

Our primary purpose was to determine the pattern of radiocesium contamination in vegetation along Steel Creek and to relate the extent of contamination to the physical aspects of the stream. We also determined the frequency distribution of radiocesium in four plant species from eight different locations along Steel Creek to see whether radiocesium uptake by vegetation is species specific and/or dependent on local conditions.

STUDY AREA

From 1961 to 1970, approximately 261 Ci of radiocesium were released into Steel Creek from nuclear production reactors (Fig. 1). Yearly releases ranged from 5.2 to 53.3 Ci (Marter, 1970). A history and description of Steel Creek is given elsewhere (Anderson, Gentry, and Smith, 1973; Brisbin et al., 1974; Marter, 1970).

Eight sampling sites were chosen along the creek. A wide range of habitats, varying from high unflooded creek banks to low floodplains, support vegetation. Small islands interrupt the channel at many locations, becoming increasingly abundant at the downstream sites. Both coarse- and fine-particle sediments are found at all sites; however, sands are deposited more abundantly along the stream banks and on the channel islands. Fine-particle clays are characteristic of the floodplain marshes, and highly organic sediments are found in the stream delta and in backwater areas.

Five sites were located at road or railroad crossings (sites 2, 4, 5, 6, and 7) where streamflow was restricted to one channel. There was no restriction of streamflow at sites 3 or 8. At site 1, near the entry point of the effluent (Fig. 1), a man-made impoundment had caused soil to be deposited on the floodplain, and a marsh approximately 20 m wide had developed. At all sites above site 5, the floodplain was narrow (14 to 75 m), and the stream formed one main channel. Downstream from site 5 the floodplain widened to 75 to 400 m, and the broad floodplain supported a frequently flooded marsh. Site 8 was located on the delta approximately 2 km from the Savannah River where vegetation is flooded continuously during winter and spring. Here the main channel divides into many small channels separated by marsh and numerous islands.

MATERIALS AND METHODS

Leaf samples from four plant species were collected at each site during November 1973. Black willow (*Salix nigra*), arrowhead (*Sagittaria latifolia*),

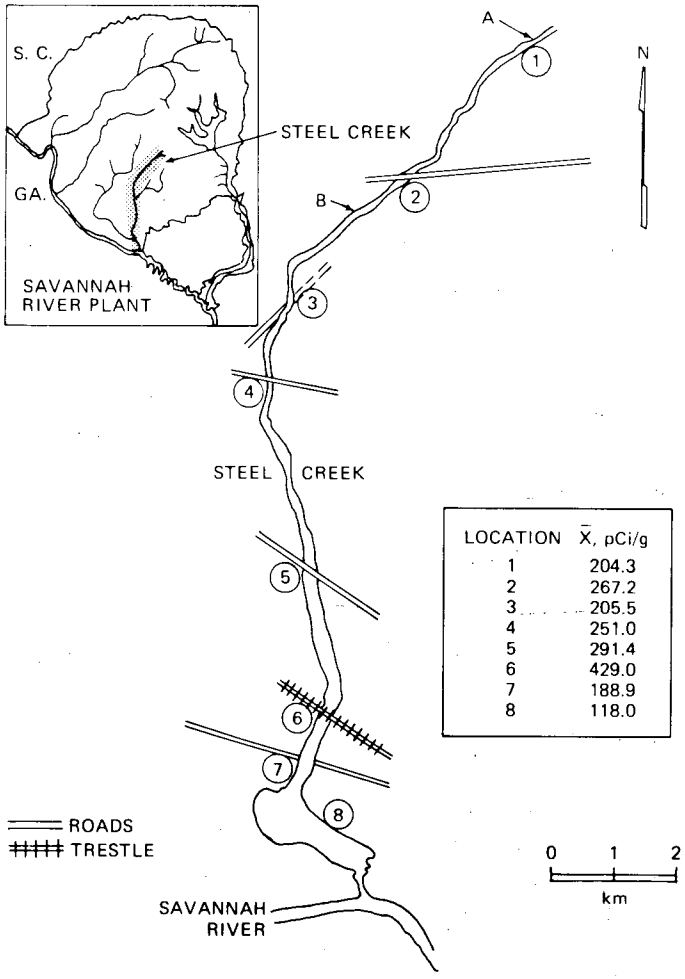

Fig. 1 Map of Steel Creek indicating sampling locations (1 to 8) and points of radiocesium release into the stream (A and B) (a greater amount of radiocesium was released at point A). Mean radiocesium concentrations of all plants sampled at each location are given.

smartweed (*Polygonum punctatum*), and woolgrass (*Scirpus cyperinus*) were collected at each location (except for *Polygonum* at site two). At each site 34 to 53 plants of each species were collected; each individual plant was at least 1 m from another plant of the same species. Each sample was dried to a constant weight at 80°C in a forced-draft oven, ground, and counted for radiocesium with a pulse-height analyzer either for 100 counts in the peak channel or for 30 min. The two counters used gave statistically equivalent results when calibrated against known plant standards. The radioactivity of ^{137}Cs and ^{134}Cs could not

be separated by the counting procedures, but it is unlikely that ^{134}Cs contributes significantly to the total radioactivity (Marter, 1970). Radiocesium concentration was expressed as picocuries per gram of dry weight. Statistical significance was indicated by $P \leq 0.05$.

RESULTS

The frequency distributions of the 31 data sets did not differ significantly from the log-normal distribution and the ln X transformed data did not differ significantly from the normal distribution when tested by the Kolomogorov-Smirnov test of goodness of fit (Sokal and Rohlf, 1969). All data were log normally transformed prior to statistical analysis (Sokal and Rohlf, 1969).

There were significant differences among sites for *Polygonum* ($F_{6,331} = 37.63$), *Sagittaria* ($F_{7,361} = 6.06$), *Salix* ($F_{7,271} = 6.90$), and *Scirpus* ($F_{7,397} = 16.26$), as well as differences among species across sites ($F_{7,1389} = 9.42$). Significant differences between locations for each species are given in Table 1. *Sagittaria* leaves had the highest radiocesium concentration at all sites except 1, where *Salix* was higher (Table 1). However, mean radiocesium concentration in *Sagittaria* leaves did not differ significantly from *Polygonum* at sites 3, 4, and 6 or from *Salix*, except at sites 5 and 6. Mean leaf radiocesium concentrations in *Polygonum* and *Salix* did not differ significantly at sites 3, 4, and 7. Radiocesium levels in *Scirpus* leaves were significantly lower than all other species at all sites except 5, where there was no significant difference between *Scirpus* and *Polygonum* leaves. Radiocesium levels in *Polygonum* and *Scirpus* leaves were highest at site 6, in *Salix* leaves at site 1, and in *Sagittaria* leaves at site 5. The mean radiocesium levels for *Salix* at site 1 and *Sagittaria* at site 5 did not differ significantly from their respective means at site 6. The locational mean for all species was highest at site 6, and all species had the lowest mean radiocesium concentrations at site 8 (Fig. 1). The Roy–Sheffé test (Steel and Torrie, 1960) was used to determine differences between species and location radiocesium concentrations.

Relationships between the mean and the variance can supply information on the frequency distribution of the data sets. Log-normal distributions have a linear relationship between the mean and variance (Sokal and Rohlf, 1969). There were significant linear relationships between the mean and variance for species examined in this study. For *Scirpus* and *Sagittaria* the coefficient of determination (r^2) was less than 0.6 but was statistically significant. In all species one or more points exhibited a variance much higher than expected for the mean and did not appear to fit the calculated relationship. These points corresponded to the sites at which the coefficient of variation was highest within species (Table 1). At these sites a greater number of points than expected fell above the mean. A bimodal distribution could account for such an observation. After dividing the data points into groups of high and low values, we calculated

TABLE 1

MEAN RADIOCESIUM CONCENTRATIONS (pCi/g DRY WEIGHT) FOR SPECIES AT EACH LOCATION ALONG STEEL CREEK*

Location†	*Polygonum punctatum*	*Sagittaria latifolia*	*Salix nigra*	*Scirpus cyperinus*
1	155.5^{a}	496.8^{bc}	595.2^{c}	37.1^{a}
	(30.2)	(98.5)	(93.8)	(70.2)
2		441.3^{ab}	280.7^{ab}	152.4^{c}
		(74.0)	(140.8)	(134.7)
3	256.0^{b}	340.0^{ab}	248.4	81.4^{b}
	(59.3)	(57.8)	(91.0)	(73.3)
4	328.8^{b}	471.1^{abc}	390.1^{ab}	64.6^{cb}
	(47.6)	(81.1)	(78.1)	(68.4)
5	132.7^{a}	961.5^{c}	304.9^{ab}	177.6^{c}
	(65.2)	(71.2)	(88.0)	(62.7)
6	635.5^{c}	766.9^{c}	363.4^{abc}	190.2^{c}
	(82.9)	(122.7)	(74.4)	(61.9)
7	143.2^{a}	483.5^{abc}	216.4^{ab}	83.0^{b}
	(54.6)	(149.8)	(63.6)	(73.9)
8	115.8^{a}	257.9^{a}	178.8^{a}	35.2^{a}
	(37.6)	(182.3)	(61.6)	(74.7)
Species mean	191.7	488.2	303.2	86.4

*Values in parentheses are coefficients of variation of the untransformed data. Any two means in the same species column with the same superscript are not significantly different at 0.05 level. Sample sizes ranged from 42 to 53 for *Polygonum*, 34 to 50 for *Sagittaria*, 34 to 35 for *Salix*, and 50 to 51 for *Scirpus*.

†Locations are numbered consecutively in downstream order (see Fig. 1). *Polygonum punctatum* was not present at location 2.

two means. Replacing the original values with the two new ones resulted in significant linear relationships for all species, with $P < 0.01$ and $r^2 > 0.9$ in each case (Fig. 2).

There were no significant correlations among species means. The uptake of radiocesium at each site appeared to be species specific and highly variable. *Sagittaria* was the most variable of the four species studied, with a range in leaf radiocesium levels from 54.8 to 8513.7 pCi/g. The range for *Salix* was 19.7 to 4024.2 pCi/g; for *Polygonum*, 51.5 to 4209.4 pCi/g; and for *Scirpus*, 7.1 to 1992.8 pCi/g. The coefficient of variation (Table 1) for each species increased in areas where the species grew across a wide range of soil types and moisture conditions. *Salix* and *Scirpus* occupied a wide habitat range at site 2; for *Polygonum* and *Sagittaria*, the greatest range of habitats occurred at sites 5 to 8, where the stream widened and marsh and island habitats were formed.

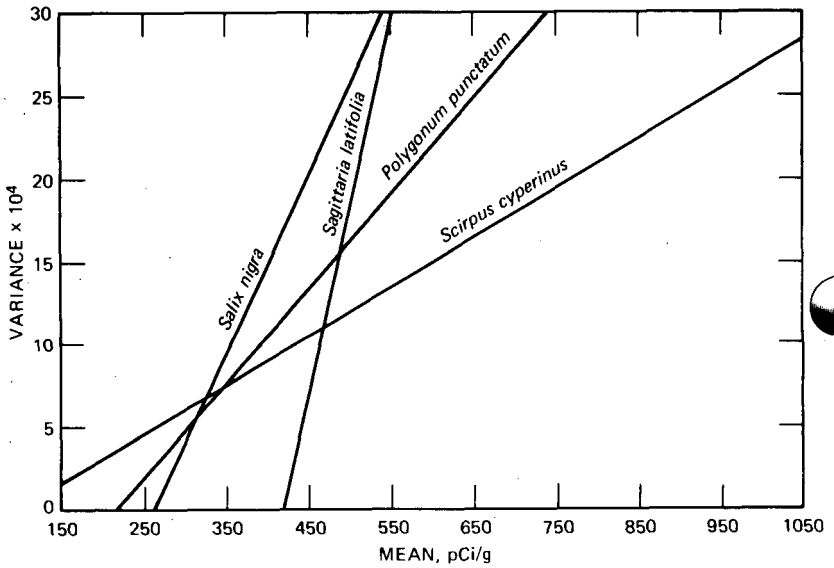

Fig. 2 Relationship of variance (Y) to mean (X) radiocesium concentrations for four species. Equations for each species are given as Y = aX + b, where a = 0.0034 ± 0.0004, b = 91.64 ± 32.60, and r^2 = 0.98 for *Scirpus*; a = 0.0005 ± 0.0001, b = 410.96 ± 155.46, and r^2 = 0.91 for *Sagittaria*; a = 0.0017 ± 0.0003, b = 219.78 ± 88.27, and r^2 = 0.93 for *Polygonum*; and a = 0.0009 ± 0.0001, b = 262 ± 64.43, and r^2 = 0.95 for *Salix*. All slopes are significantly different from zero at $P \leq 0.05$.

DISCUSSION

With the exception of *Scirpus*, concentrations of radiocesium reported in this study are similar to those previously given by others for the same species and locations (Anderson, Gentry, and Smith, 1973; Sharitz et al., 1975; Garten et al., this volume). We found concentrations of radiocesium in *Scirpus* leaves that were lower than those previously reported (Garten et al., this volume). Seasonal variation may account for some of the difference. Since *Scirpus* leaves sampled in this study were collected in late fall, much of the radiocesium may have been leached out (Auerbach, Olson, and Waller, 1964) or transported back to the roots and soil. For these reasons the values presented in Table 1 are probably conservative estimates of the radiocesium concentrations in leaves of the vegetation along Steel Creek. Since the sampling was completed within 2 weeks, seasonal changes in radiocesium concentrations probably have little effect on the locational differences within each species. Not all, or even many, of the variables required to account for differences among species were measured. Our

main interest was the pattern of radiocesium levels in vegetation along the stream.

The lack of significant correlations between species means suggests that there is no single species that can be used to predict radiocesium levels in other plant species. Sharitz et al. (1975) found that radiocesium levels in the leaves of a plant correlated with those in leaves of nearest neighbors of the same species. Anderson, Gentry, and Smith (1973) also found correlations between radiocesium levels in different plant species. Although there may be correlations between species in a local area, such relationships are not apparent from data collected over different locations in our study. Rather each species appears to act independently of other species.

Although the radiocesium concentrations appeared to be log normally distributed in all species, the slopes and intercepts were not the same for the species examined when the variances were graphed against the means (Fig. 2). This suggests that factors influencing radiocesium contamination are different for each species. Some species also were found to have bimodal frequency distributions of radiocesium concentrations; this suggests that different factors may also influence radiocesium levels within a species. Some of these factors are undoubtedly related to the physical aspects of the stream and include soil nutrients and moisture. For example, observed differences between coarse and fine soils (Brisbin et al., 1974) may influence the uptake of radiocesium by plants such that discrete groups of high- and low-level concentration can be recognized. In addition, Anderson, Gentry, and Smith (1973) found that radiocesium levels in Steel Creek vegetation were higher on islands than on the floodplain. In our study, bimodal frequency distributions may have resulted from combining two distributions with different means.

Two points can be made concerning the distribution of radiocesium in vegetation along Steel Creek. First, a gradient of decreasing radiocesium levels in vegetation from site 1 (the point of reactor discharge to the creek) to site 8 (the delta) cannot be demonstrated for any of the species examined. We have no available data on the levels of radiocesium in sediments at the eight sampling locations, but we infer that the observed pattern of radiocesium in vegetation along the creek is due to differences among locations in the degree of deposition of radiocontaminated sediments. Therefore, in areas where streamflow is restricted and water velocity decreases (e.g., site 6, where a railroad trestle channels the creek into a narrow passage), sediments and radiocesium will accumulate. A general pattern of radiocesium levels in vegetation along the creek supports this interpretation. At sites 2, 4, 5, and 6, where major obstructions in the form of bridges cross the stream, the locational means are greater than at sites 1, 3, 7, and 8, where streamflow is not impeded (Fig. 1). This trend is consistent for each species, with some exceptions (e.g., *Salix* leaves at site 1), which may be due to factors previously discussed. Radiocesium concentrations at site 8 are the lowest among all species. This may be because of the high proportion of fine sediments on the delta which bind radiocesium more tightly

than do the coarser soils (Brisbin et al., 1974) characteristically found upstream. Also the collection of plants on the edge of the delta may have biased the radiocesium levels at this site downward.

The fate of radionuclides in aquatic ecosystems appears to be highly dependent on the physical characteristics of the system studied (Sayre, Guy, and Chamberlain, 1963). The high foliar radiocesium concentrations at all locations sampled along Steel Creek indicate that radiocesium is readily available to biota at many points along the stream, not just where the streamflow is reduced (Parker et al., 1965). From studies of an adjacent stream at the Savannah River Plant, Ragsdale and Shure (1973) concluded that the physical characteristics of floodplains are related to the deposition of radioactive material. If releases occur during high water, the probability of deposition on the floodplain increases. Natural narrowing of the stream or the presence of man-made obstructions, such as bridges and impoundments, affects the deposition of contaminated soils and therefore influences radionuclide levels in plants. Radionuclides deposited in high concentrations along a stream can then be deposited downstream at a later time by recurrent flooding and erosion.

When we evaluate the possible influences of radioactive releases on aquatic systems, the physical factors as well as the biological factors need to be considered (Ragsdale and Shure, 1973) to determine whether a system will accumulate radionuclides. Aquatic systems should be surveyed to determine where contamination might accumulate. The accessibility of possible contamination to the biota and to the public should be considered. Such studies should be conducted as an initial step in determining the environmental impact of possible radionuclide releases into aquatic ecosystems.

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REFERENCES

Anderson, G. E., J. B. Gentry, and M. H. Smith, 1973, Relationships Between Levels of Radiocesium in Dominant Plants and Arthropods in a Contaminated Streambed, *Oikos*, **24**: 165-170.

Auerbach, S. I., J. S. Olson, and A. D. Waller, 1964, Landscape Investigations Using Cesium-137, *Nature (London)*, **201**: 761-764.

Brisbin, I. L., Jr., et al., 1974, Patterns of Radiocesium in the Sediments of a Stream Channel Contaminated by Production Reactor Effluents, *Health Phys.*, **27**: 19-27.

Davis, J. J., 1963, Cesium and Its Relationship to Potassium in Ecology, in *Radioecology*, Proceedings of the First National Symposium on Radioecology, V. Schultz and A. W. Klement, Jr. (Eds.), pp. 539-556, Reinhold Publishing Corporation, New York.

Marter, W. L., 1970, Radioactivity in the Environs of Steel Creek, USAEC Report DPST-70-435, E. I. Du Pont de Nemours and Co., Aiken, S. C., Savannah River Laboratory.

Menzel, R. G., 1954, Competitive Uptake by Plants of Potassium, Rubidium, Cesium, Calcium, Strontium, and Barium from Soils, *Soil Sci.*, **77**: 419-425.

Parker, H. M., R. F. Foster, I. L. Ophel, F. L. Parker, and W. C. Reinig, 1965, North American Experience in the Release of Low-Level Waste to Rivers and Lakes, in *Proceedings of the Third International Conference on the Peaceful Uses of Atomic Energy, Geneva, 1964*, Vol. 14, pp. 62-71, United Nations, New York.

Pendleton, R. C., and R. L. Uhler, 1960, Accumulation of Caesium-137 by Plants Grown in Simulated Pond, Wet Meadow, and Irrigated Field Environments, *Nature (London)*, **185**: 707-708.

Ragsdale, H. H., and D. J. Shure, 1973, Floodplain Transfer and Accumulation of ^{137}Cs from a Reactor Effluent Stream, in *Environmental Behavior of Radionuclides Released in the Nuclear Industry*, Proceedings Series, Aix-en-Provence, France, 1973, International Atomic Energy Agency, Vienna (STI/PUB/345).

Rice, T. R., 1963, Accumulation of Radionuclides by Aquatic Organisms, in *Studies of the Fate of Certain Radionuclides in Estuarine and Other Aquatic Environments*, Proceedings of a Symposium held in Savannah, Ga., J. J. Sabo and P. H. Bodrosian (Eds.), U. S. Public Health Service Publication No. 999-R-3.

Sayre, W. W., H. P. Guy, and A. R. Chamberlain, 1963, Uptake and Transport of Radionuclides by Stream Sediments, Professional Paper 433-A, U. S. Geological Survey.

Shanks, R. E., and H. R. DeSelm, 1963, Factors Related to Concentration of Radiocesium in Plants Growing on a Radioactive Waste Disposal Area, in *Radioecology*, Proceedings of the First National Symposium on Radioecology, V. Schultz and A. W. Klement (Eds.), pp. 97-101, Reinhold Publishing Corporation, New York,

Sharitz, R. R., S. L. Scott, J. E. Pinder, III, and S. K. Woods, 1975, Uptake of Radiocesium from Contaminated Floodplain Sediments by Herbaceous Plants, *Health Phys.*, **28**: 23-28.

Sokal, R. R., and F. J. Rohlf, 1969, *Biometry*, W. H. Freeman and Company, San Francisco.

Steel, R. G. D., and J. H. Torrie, 1960, *Principles and Procedures of Statistics*, McGraw-Hill Book Company, Inc., New York.

EFFECTS OF AGE, SEX, AND PELAGE PHENOTYPE ON THE ELEMENTAL COMPOSITION OF THE OLD-FIELD MOUSE

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ABSTRACT

Whole-body elemental composition was examined in laboratory-raised old-field mice (*Peromyscus polionotus*) ranging in age from 0 to 42 days. Effects of age, sex, and pelage phenotype on dry-weight, live-weight, and lean-dry- and lean-live-biomass concentrations of 13 elements were determined with analysis of variance. Age was the major factor affecting the concentrations of elements. Only one element, either sodium or sulfur, in each of the four expressions of concentration was not significantly affected by age. Sex had a significant effect on only two elements, potassium and zinc, when expressed as dry-weight concentrations and did not have a significant effect on any elements when expressed as live-weight or lean-dry- or lean-live-biomass concentrations. Pelage phenotype had a significant effect on concentrations of strontium when expressed as live-weight or lean-dry- or lean-live-biomass concentrations but not when expressed as a dry-weight concentration. Pelage phenotype had no effect on other elemental concentrations.

Ecological studies of elemental cycling have produced considerable information on the whole-body elemental composition of animals. To use this information in a general way, investigators have attempted to develop predictive equations for various groups of organisms. Beyers et al. (1971) postulated constancy in composition for most elements, so that an average value could be used for adult small mammals. Small but statistically significant differences were found, however, when inter- and intraspecific comparisons were made. Intraspecific differences reported were due to age, size, and sex (Briese, 1973; Sella, 1973), reproductive condition (Briese, 1973); and genetic factors (Evans and King, 1955; Wiener, Field, and Wood, 1969). In addition, intraspecific differences in elemental concentrations of mammals have been reported over season (Hyvarinen, 1972; Briese, 1973; Evans, 1973; Nabholz, 1973; Sella, 1973) and locality (Nabholz, 1973; Sella, 1973).

We studied three factors that appear to play a role in intraspecific differences. Effects due to age, sex, and two naturally occurring pelage phenotypes (dark and light brown, described in Dawson, Smith, and Carmon, 1969) were analyzed in nonreproducing laboratory-raised *Peromyscus polionotus*. Since animals were maintained in the laboratory, changes due to spatial and temporal shifts in the diet were eliminated.

METHODS AND MATERIALS

Old-field mice, *Peromyscus polionotus*, were maintained in a laboratory colony at the Savannah River Ecology Laboratory. Pairs of mice, at least 7 to 8 generations removed from the original stock captured in Field 3-412, were housed in plastic cages (18.4 by 29.2 cm) which contained vermiculite as litter. Water and laboratory chow were provided ad libitum. The animal room was maintained at 25 ± 2°C, with lights on at 0700 and lights off at 1900 EST.

Pairs were checked daily for the presence of new litters. Only litters of three or more mice were used, and larger litters were reduced to three. Mice were weighed, individually marked with India ink under the skin (described in Carmon, Golley, and Kennedy, 1964), and replaced in the cage. Pups were weighed at weekly intervals up to 42 days. At 21 days, mice were weaned, toe clipped, and placed in separate cages with water and laboratory chow provided ad libitum. Only litters in which all three individuals survived were used in the analyses of body and elemental composition.

Mice were sacrificed at weekly intervals from 0 to 42 days by suffocation so that no fluids were lost. Animals were killed in the late afternoon when there was a minimum of material in the gastrointestinal tract. Live weight was recorded, and mice were placed in tared vials, frozen and then freeze dried to a constant weight. When specimens were so small (e.g., 0- to 7-day-old mice) that analyses could not be performed on one mouse, samples were lumped (only mice of the same age, sex, and pelage phenotype were used).

Dry specimens were ground until homogeneous in a CRC micro-mill with cool water circulating around the grinding vessel to aid in the retention of fat. Before analyses samples were stored in a desiccator. Fat was extracted from an 0.1.5-g subsample in a Goldfisch fat extractor. Samples were refluxed for a period of 3.5 hr with petroleum ether as the solvent.

Concentrations of 13 elements (Ca, P, K, Na, Mg, Fe, Zn, Al, Mn, Sr, B, Mo, and Ba) were determined with a Jarrell–Ash direct-reading 1.5-m emission spectrograph. Results for barium were not used because of the low concentration level (<1 ppm in most specimens). Techniques were similar to those for plant samples (Jones and Warner, 1969), with the following exceptions: (1) subsamples (0.5 to 1.0 g) of specimen were dried at 60°C before ashing and were ashed at 450°C for 8 hr and (2) concentrations of standards were modified for the range of concentrations of different elements found in animal tissue.

Sulfur was determined with a Leco sulfur analyzer (apparatus described in Jones and Isaac, 1972). Preparation of subsamples was similar to that for plants (Jones and Isaac, 1972) except that the subsample (0.5 to 0.8 g) of mouse tissue was dried at 60°C before weighing and was ashed at 500°C for 1 hr.

Concentrations of elements are expressed with respect to dry whole body (water removed), whole body, lean dry body (water and fat removed), and lean live body (only fat removed).

RESULTS

Dry-Weight Concentrations

Effects of age, sex, and pelage phenotype and of the interactions of these variables on dry-weight concentrations of elements were examined with analysis of variance. Age had a significant effect on all elements except sulfur (Table 1). Changes with age in mean dry-weight concentrations varied for different elements (Table 2). Calcium, aluminum, and manganese increased in concentration to 21 days and then stabilized. Phosphorus, boron, and molybdenum concentrations decreased from 0 to 7 days, then increased to 21 days, and subsequently leveled out. Potassium, sodium, and sulfur decreased in concentration from 0 to 21 days and then remained constant. Iron, magnesium, and zinc decreased in concentration from 0 to 14 days, increased to 21 days, and then varied little to 42 days. Strontium concentration increased from 0 to 7 days, decreased to 14 days, increased to 35 days, and decreased markedly at 42 days.

Sex had a significant effect on only two elements, potassium ($F = 4.67$, $df = {}^{1}/_{138}$, $P < 0.05$) and zinc ($F = 3.67$, $df = {}^{1}/_{138}$, $P < 0.05$). Both had a slightly higher mean for males: potassium, males = 10264 ppm, females = 10238 ppm; zinc, males = 131 ppm, females = 124 ppm.

Pelage phenotype did not have a significant effect on any of the dry-weight elemental concentrations.

Thirteen of the 52 possible interactions were significant on dry-weight concentrations. None of the age–sex interactions were significant. The age–pelage phenotype interactions were significant for potassium, magnesium, and strontium. Phosphorus, magnesium, iron, and aluminum were affected by the sex–pelage phenotype interactions. The interactions between age, sex, and pelage phenotype were significant for Na, Fe, Al, Sr, B, and Mo.

Live-Weight Concentrations

Age had a significant effect on live-weight concentrations of all elements except sodium (Table 1). Concentrations of Ca, P, S, Mg, Fe, Zn, Al, and B demonstrated similar trends by increasing to 21 days and then leveling out to 42 days (Table 2). Manganese and molybdenum increased to 21 days, remained constant to 35 days, and then increased to 42 days. Potassium decreased from 0

TABLE 1

SUMMARY OF F-VALUES FOR THE EFFECT OF AGE (0 TO 42 DAYS) ON ELEMENTAL CONCENTRATIONS* OF 13 ELEMENTS IN *Peromyscus polionotus*†

Element‡	DWB	LWB	LDB	LLB
Ca	**32.04**	**26.15**	**38.32**	**52.15**
P	**4.24**	**44.74**	**11.04**	**53.65**
K	**46.79**	*2.54*	**13.91**	**4.95**
S	1.93	**20.14**	1.99	**20.56**
Na	**46.61**	0.98	**17.60**	1.31
Mg	**21.70**	**38.69**	**21.17**	**42.22**
Fe	**14.41**	**32.75**	**16.90**	**36.61**
Zn	**4.77**	**22.42**	**9.93**	**28.39**
Al	**25.60**	**44.60**	**30.81**	**47.80**
Mn	**26.80**	**36.42**	**34.21**	**39.53**
Sr	**19.88**	**29.28**	**22.24**	**31.12**
B	**7.34**	**28.53**	**13.38**	**32.03**
Mo	**15.66**	**68.95**	**26.85**	**70.01**

*Values were determined from analyses of variances of age, sex, and pelage phenotype and the interactions of these simple variables.

†Abbreviations are DWB, dry-weight biomass; LWB, live-weight biomass; LDB, lean-dry biomass; and LLB, lean-live biomass. Values in italics are for $P < 0.05$, and values in boldface are for $P < 0.001$.

‡The degrees of freedom for each element are $^{1}/_{138}$, except for sulfur, which is $^{1}/_{107}$.

to 7 days, increased to 14 days, and then stabilized. Strontium increased to 35 days and then decreased to 42 days.

Sex did not have a significant effect on any of the live-weight elemental concentrations.

Pelage phenotype had a significant effect on only one element, strontium ($F = 4.88$, $df = {}^{1}/_{138}$, $P < 0.05$). Strontium had a slightly higher mean for the dark pelage phenotype ($\bar{X} = 2.1$ ppm) than for the light-brown pelage phenotype ($\bar{X} = 1.7$ ppm).

Six of the 52 possible interactions were significant on live-weight concentrations. The age–sex interactions were significant for only manganese. The age–pelage phenotype interactions were significant for magnesium and molybdenum. The sex–pelage phenotype interactions were not significant for any elements. The age–sex–pelage phenotype interactions were significant for strontium, boron, and molybdenum.

Lean-Dry-Biomass Concentrations

Age had a significant effect on the lean-dry-biomass concentrations of all elements except sulfur (Table 1). Changes with age in mean lean-dry-biomass concentrations varied with different elements (Table 3) and, in general, followed the same trends as those for live-weight concentrations with age.

TABLE 2

SUMMARY OF MEANS BASED ON DRY-WEIGHT AND LIVE-WEIGHT CONCENTRATIONS OF 13 ELEMENTS IN *Peromyscus polionotus* DETERMINED AT WEEKLY INTERVALS FROM 0 TO 42 DAYS*†

	Dry-weight concentration, ppm							Live-weight concentration, ppm						
Element	0	7	14	21	28	35	42	0	7	14	21	28	35	42
Ca	5694	10500	14966	25079	21383	26155	20188	998	2347	4289	6946	6542	6461	6358
	(1616)	(2521)	(1599)	(1985)	(2146)	(3928)	(1977)	(282)	(581)	(494)	(893)	(627)	(992)	(750)
P	17550	17067	17503	19096	18275	19955	17422	3075	3809	4981	5848	5612	6003	6069
	(745)	(1073)	(1009)	(921)	(834)	(2030)	(811)	(151)	(286)	(296)	(257)	(266)	(455)	(246)
K	15706	11947	10107	9357	9492	10118	8306	2748	2658	2874	2863	2904	3050	2872
	(789)	(1296)	(502)	(436)	(499)	(745)	(500)	(80)	(287)	(135)	(128)	(138)	(162)	(121)
S	4407	4346	4265	4237	4012	4100	3767	776	973	1230	1303	1245	1246	1309
	(326)	(323)	(244)	(367)	(329)	(309)	(235)	(75)	(92)	(68)	(95)	(93)	(78)	(151)
Na	5838	4179	3262	2865	2870	3110	2736	1007	933	930	879	883	938	948
	(276)	(392)	(305)	(242)	(165)	(289)	(241)	(51)	(93)	(86)	(69)	(57)	(74)	(75)
Mg	448	413	355	609	721	836	622	79	91	101	186	221	251	214
	(47)	(75)	(25)	(89)	(82)	(101)	(66)	(9)	(15)	(7)	(26)	(25)	(26)	(19)
Fe	338	257	221	350	388	396	312	59	57	63	107	119	120	108
	(27)	(52)	(11)	(32)	(46)	(36)	(24)	(4)	(10)	(3)	(9)	(15)	(9)	(7)
Zn	133	117	108	142	117	141	135	23	26	31	43	36	42	47
	(8)	(7)	(4)	(16)	(9)	(17)	(10)	(1)	(2)	(2)	(5)	(3)	(5)	(3)
Al	55	68	67	122	119	128	101	10	15	19	37	37	39	35
	(5)	(13)	(4)	(13)	(15)	(13)	(9)	(1)	(3)	(1)	(4)	(5)	(3)	(3)
Mn	3.5	4.1	5.0	13.3	17.1	17.0	17.6	0.6	0.9	1.4	4.0	5.2	5.2	6.1
	(0.6)	(0.7)	(0.8)	(2.7)	(3.0)	(2.0)	(2.8)	(0.1)	(0.2)	(0.2)	(0.8)	(0.9)	(0.7)	(0.8)
Sr	4.4	5.0	4.2	6.2	8.5	11.2	6.1	0.8	1.1	1.2	1.9	2.6	3.3	2.1
	(0.5)	(0.9)	(0.7)	(1.0)	(1.4)	(1.9)	(0.7)	(0.1)	(0.1)	(0.2)	(0.3)	(0.4)	(0.5)	(0.2)
B	3.4	3.1	3.3	4.3	4.0	4.3	4.2	0.6	0.7	0.9	1.3	1.2	1.3	1.4
	(0.3)	(0.3)	(0.4)	(0.4)	(0.2)	(0.4)	(0.3)	(0.1)	(0.1)	(0.1)	(0.1)	(0.1)	(0.1)	(0.1)
Mo	2.0	1.9	2.0	2.2	2.4	2.4	2.3	0.3	0.4	0.6	0.7	0.7	0.7	0.8
	(0.1)	(0.2)	(0.1)	(0.1)	(0.1)	(0.1)	(0.1)	(0.03)	(0.05)	(0.03)	(0.04)	(0.04)	(0.04)	(0.04)

*Sample sizes for all elements except sulfur are: 0 = 16, 7 = 15, 14 = 29, 21 = 28, 28 = 24, 35 = 22, and 42 = 32. Sample sizes for sulfur are: 0 = 14, 7 = 13, 14 = 21, 21 = 19, 28 = 17, 35 = 19, and 42 = 30.

†Values in parentheses are two standard errors.

TABLE 3

SUMMARY OF MEANS BASED ON LEAN-DRY- AND LEAN-LIVE-BIOMASS CONCENTRATIONS OF 13 ELEMENTS IN *Peromyscus polionotus* DETERMINED AT WEEKLY INTERVALS FROM 0 TO 42 DAYS*†

Element	Lean-dry-biomass concentration, ppm							Lean-live-biomass concentration, ppm						
	0	7	14	21	28	35	42	0	7	14	21	28	35	42
Ca	6183	12799	20450	33220	27957	33558	29950	1014	2447	4655	8283	7062	8402	7896
	(1788)	(3175)	(2431)	(2383)	(2497)	(4275)	(2731)	(292)	(611)	(555)	(595)	(664)	(980)	(703)
P	19011	20545	23653	25453	24069	25706	26061	3116	3955	5389	6333	6070	6455	6885
	(943)	(1454)	(1459)	(1283)	(1127)	(2027)	(1247)	(158)	(301)	(334)	(283)	(307)	(459)	(298)
K	17027	14369	13678	12453	12485	13096	12375	2793	2768	3114	3104	3144	3288	3261
	(941)	(1474)	(691)	(544)	(631)	(788)	(631)	(166)	(294)	(153)	(137)	(156)	(172)	(135)
S	4875	5245	5843	5605	5338	5333	5611	810	1011	1335	1399	1351	1344	1484
	(394)	(419)	(333)	(455)	(386)	(345)	(290)	(84)	(97)	(76)	(102)	(102)	(86)	(82)
Na	6314	5008	4417	3821	3796	4012	4083	1034	966	1006	950	956	1009	1073
	(293)	(452)	(410)	(319)	(275)	(318)	(370)	(42)	(95)	(93)	(74)	(68)	(79)	(86)
Mg	492	496	480	803	944	1079	917	81	95	109	201	238	271	241
	(55)	(87)	(36)	(110)	(102)	(114)	(83)	(9)	(16)	(8)	(28)	(26)	(27)	(20)
Fe	367	309	298	469	511	511	463	60	59	68	116	129	129	122
	(30)	(61)	(14)	(48)	(57)	(39)	(29)	(5)	(11)	(3)	(10)	(16)	(10)	(7)
Zn	145	142	146	189	153	181	200	24	27	33	47	39	46	53
	(9)	(7)	(7)	(21)	(11)	(20)	(13)	(1)	(2)	(2)	(5)	(3)	(5)	(3)
Al	60	82	91	162	156	165	150	10	16	21	40	39	42	40
	(6)	(16)	(6)	(19)	(19)	(14)	(11)	(1)	(3)	(1)	(4)	(5)	(3)	(3)
Mn	3.8	4.9	6.7	17.6	22.6	22.2	26.0	0.6	0.9	1.5	4.4	5.7	5.6	6.9
	(0.6)	(0.8)	(1.0)	(3.6)	(4.0)	(2.8)	(3.5)	(0.1)	(0.2)	(0.2)	(0.9)	(1.0)	(0.7)	(0.9)
Sr	4.8	6.1	5.4	8.1	11.1	14.3	9.0	0.8	1.1	1.2	2.0	2.8	3.6	2.4
	(0.5)	(1.1)	(0.9)	(1.2)	(1.7)	(2.1)	(1.0)	(0.1)	(0.2)	(0.2)	(0.3)	(0.4)	(0.5)	(0.3)
B	3.7	3.8	4.5	5.7	5.3	5.7	6.1	0.6	0.7	1.0	1.4	1.3	1.4	1.6
	(0.3)	(0.4)	(0.6)	(0.5)	(0.3)	(0.6)	(0.5)	(0.1)	(0.1)	(0.1)	(0.1)	(0.1)	(0.2)	(0.1)
Mo	2.1	2.2	2.7	3.0	3.1	3.2	3.5	0.3	0.4	0.6	0.7	0.8	0.8	0.9
	(0.2)	(0.2)	(0.1)	(0.2)	(0.2)	(0.2)	(0.2)	(0.03)	(0.06)	(0.04)	(0.05)	(0.04)	(0.05)	(0.05)

*Sample sizes for all elements except sulfur are: 0 = 16, 7 = 15, 14 = 29, 21 = 28, 28 = 24, 35 = 22, and 42 = 32. Sample sizes for sulfur are: 0 = 14, 7 = 13, 14 = 23, 21 = 19, 28 = 17, 35 = 19, and 42 = 30.

†Values in parentheses are two standard errors.

Sex had no significant effects on any of the lean-dry-biomass concentrations of elements.

Pelage phenotype had a significant effect on one element, strontium ($F = 5.15$, $df = {}^{1}/_{138}$, $P < 0.05$). Strontium had a slightly higher mean in the dark pelage phenotype ($\bar{X} = 9.5$ ppm) than in the light-brown pelage phenotype ($\bar{X} = 7.6$ ppm).

Eight of the 52 possible interactions were significant in lean-dry-biomass concentrations. The age–sex interactions were significant for only manganese. The age–pelage phenotype interactions were significant for magnesium, zinc, and molybdenum. The sex–pelage phenotype interactions were not signifi[cant] for any of the elements. The age–sex–pelage phenotype interactions [were] significant for four elements, sodium, strontium, boron, and molybdenum.

Lean-Live-Biomass Concentrations

Age had a significant effect on the lean-live-biomass concentrations of all elements except sodium (Table 1). Changes with age in mean lean-live-biomass concentrations varied with different elements (Table 3) and were generally similar to changes in the live-weight concentrations with age.

Sex did not have a significant effect on the lean-live-biomass concentrations of any of the elements.

Pelage phenotype had a significant effect on only one element, strontium ($F = 5.92$, $df = {}^{1}/_{138}$, $P < 0.05$). Strontium had a slightly higher mean in the dark pelage phenotype ($\bar{X} = 2.3$ ppm) than in the light-brown pelage phenotype ($\bar{X} = 1.8$ ppm).

Five of the 52 possible interactions were significant on lean-live-biomass concentrations. The age–sex and sex–pelage phenotype interactions were not significant for any elements. The age–pelage phenotype interactions were significant for only zinc and molybdenum. The age–sex–pelage phenotype interactions were significant for strontium, boron, and molybdenum.

DISCUSSION

Age was the major factor affecting the elemental composition of the old-field mouse. Only two elements, sulfur expressed as dry- and lean-[dry] biomass concentrations and sodium expressed as live- and lean-live-biomass concentrations, did not change significantly with age (Table 1). Changes with age were of two general types, increase in concentrations to asymptotic levels and decrease in concentrations to asymptotic levels, although some elements were much more irregular in the trends than others. Stabilization at asymptotic levels, or "chemical maturity," was expected from the results of work with other mammals (Moulton, 1923; Bailey, Kitts, and Wood, 1960; Sheng and Huggins, 1971). In addition, it was also apparent that, as Sheng and Huggins (1971)

reported for the beagle, chemical maturity was attained at different ages for specific elements. Briese (1973) also found significant effects due to age (calculated from body measurements in field-caught animals) in cotton rats for Al, Ca, Cu, K, Mg, Mn, Na, P, and Sr but not for B, Ba, Fe, Mo, N, and Zn; however, she did not look at chemical maturity in these animals.

Sex was a significant factor for only two elements, potassium and zinc, and then only when expressed as dry-weight concentrations. Wiener et al. (1974) examined the effect of sex on dry-weight concentrations of 15 elements in four samples of field-caught *Peromyscus* and one sample of *Perognathus*; significant effects were found for only 3 of the 75 possible tests. In field-caught cotton rats, Briese (1973) found significant differences for barium and strontium but not for 13 other elements. Sella (1973) found differences for iron and manganese but not for zinc. Briese (1973) also reported significant interactions between sex and/or season and size for Ba, Ca, P, Sr, and Zn and suggested that some differences are related to the reproductive condition of the females. In our laboratory study, since all females were nulliparous, effects due to reproductive condition were minimal.

Pelage phenotype had no simple effect on the concentrations of elements, except for strontium expressed as live-weight or lean-dry- or lean-live-biomass concentrations. No other comparable data are available for the effects of a single gene locus on whole-body elemental concentration, but a single gene effect on the concentration of potassium in the red blood cells of sheep has been reported (Evans and King, 1955). Breed also had a significant effect on the concentration of copper in the blood of sheep (Wiener et al., 1969). Major genetic differences had an effect on gross body composition among inbred lines of house mice (Dawson, 1970) and subspecies of deer mice (Hayward, 1965). Differences in elemental composition would also be expected for major genetic differences associated with inbred lines or subspecies of mice. It is unlikely, however, that allelic differences at a single locus would alter whole-body elemental composition.

Significant effects of certain factors on elemental composition may be confounded by the gross body components. Kaufman and Kaufman (1974) found that pelage phenotype had a significant effect on percent protein and percent ash, sex had a significant effect on percent water, and age had a significant effect on all four major body components. Eight significant interactions of the 16 possible indicate that the main effects are not changing independently and thus complicate the interpretation. Because of this, the type and number of significant effects on elemental concentration depend on the form of expression of concentrations.

Many factors, such as species, age, size, sex, reproductive condition, and spatial, temporal, and genetic variables, can alter the concentrations of elements in animals (Gentry et al., 1974). Studies that have examined one or more of these factors in small mammals have typically examined dry-weight concentra-

tions in field-caught animals (Beyers et al., 1971; Briese, 1973; Nabholz, 1973; Sella, 1973; Gentry et al., 1974; Wiener et al., 1974). We used four expressions of concentration to examine the effects of age, sex, and pelage phenotype under laboratory conditions with other variables controlled, and, although our concentration data are probably not directly extrapolatable to field situations, two findings have general application: (1) age (size) has a major effect on elemental composition and (2) the effects and the magnitude of these effects as influenced by different variables change with the form of the expression of concentration data. Since age has a major effect on elemental concentration, we suggest that variability due to age (size) be removed before the effects of other variables are examined. In addition, we suggest that in future studies consideration be given to the form of expression of the concentration values since differences between the forms of expression can exist.

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REFERENCES

Bailey, C. B., W. D. Kitts, and A. J. Wood, 1960, Changes in the Gross Chemical Composition of the Mouse During Growth in Relation to the Assessment of Physiological Age, *Can. J. Anim. Sci.*, **40**: 143-155.

Beyers, R. J., M. H. Smith, J. B. Gentry, and L. L. Ramsey, 1971, Standing Crops of Elements and Atomic Ratios in a Small Mammal Community, *Acta Theriologica*, **16**: 203-211.

Briese, L. A., 1973, Variations in Elemental Composition and Cycling in the Cotton Rat, *Sigmodon hispidus*, M. S. Thesis, University of Georgia, Athens.

Carmon, J. L., F. B. Golley, and G. Kennedy, 1964, A Rapid Technique for Identifying Young Mice, *J. Mammology*, **45**: 306-307.

Dawson, N. J., 1970, Body Composition of Inbred Mice (*Mus musculus*), *Comp. Biochem. Physiol.*, **37**: 589-593.

Dawson, W. D., M. H. Smith, and J. L. Carmon, 1969, A Third Independent Occurrence of the Brown Mutant in *Peromyscus*, *J. Hered.*, **60**: 286-288.

Evans, D. M., 1973, Seasonal Variations in the Body Composition and Nutrition of the V (*Microtus agrestis*), *J. Anim. Ecol.*, **42**: 1-18.

Evans, J. V., and J. W. King, 1955, Genetic Control of Sodium and Potassium Concentration in the Red Blood Cells of Sheep, *Nature (London)*, **176**: 171.

Gentry, J. B., L. A. Briese, D. W. Kaufman, M. H. Smith, and J. G. Wiener, 1974, Elemental Cycling in Small Mammal Populations, in *Small Mammals: Their Productivity and Population Dynamics*, F. B. Golley, K. Petrusewicz, and L. Ryszkowski, (Eds.), Cambridge University Press, London, in press.

Hayward, J. S., 1965, The Gross Body Composition of Six Geographic Races of *Peromyscus*, *Can. J. Zool.*, **43**: 297-308.

Hyvarinen, H., 1972, Seasonal Changes in the Copper Content of the Common Shrew, *Sorex araneus*, over a Two-Year Period, *J. Zool.*, **166**: 411-416.

Jones, J. B., Jr., and R. A. Isaac, 1972, Determination of Sulfur in Plant Material Using a Leco Sulfur Analyzer, *J. Agr. Food Chem.*, **20**: 1292-1294.

——, and M. H. Warner, 1969, Analysis of Plant-Ash Solution by Spark-Emission Spectroscopy, *Develop. Appl. Spectrosc.*, **7A**: 152-160.

Kaufman, G. A., and D. W. Kaufman, 1974, Savannah River Ecology Laboratory, unpublished.

Moulton, C. R., 1923, Age and Chemical Development in Mammals, *J. Biol. Chem.*, **57**: 79-97.

Nabholz, J. V., 1973, Small Mammals and Mineral Cycling on Three Coweeta Watersheds, M. S. Thesis, University of Georgia, Athens.

[illegible]a, L. D., 1973, Trace Elements in the Cotton Rat, *Sigmodon hispidus*, on the Piedmont of Georgia, M. S. Thesis, University of Georgia, Athens.

Sheng, H. G., and R. A. Huggins, 1971, Growth of the Beagle: Changes in Chemical Composition, *Growth*, **35**: 369-376.

Wiener, G., A. C. Field, and J. Wood, 1969, The Concentration of Minerals in the Blood of Genetically Diverse Groups of Sheep. I. Copper Concentration at Different Seasons in Blackface, Cheviot, Welsh Mountain and Crossbred Sheep at Pasture, *J. Agr. Sci.*, **72**: 93-101.

——, D. W. Kaufman, G. A. Kaufman, J. B. Gentry, M. H. Smith, and P. R. Ramsey, 1974, Savannah River Ecology Laboratory, unpublished.

PREDICTION OF ELEMENTAL CONTENT IN THE OLD-FIELD MOUSE

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ABSTRACT

Elemental composition of laboratory-raised old-field mice was examined from birth to 6 weeks of age. Correlations between live weight and live-weight concentrations of 14 elements and between dry weight and dry-weight concentrations of these elements were examined, as were correlations for data transformed to natural logarithms. Equations for predicting the amounts of these elements present from both live-weight and dry-weight values were calculated. The best estimate of elemental content for live 0- to 6-week-old animals came from the prediction of the natural logarithm of the amount of each element computed from the natural logarithm of the live weight. For live trappable-size mice (3 to 6 weeks of age), the average live-weight concentration was the best estimator of elemental content. Elemental content from dry weight for both 0- to 6- and 3- to 6-week-old mice should be estimated from regression equations relating the logarithm of the amount of each element to the logarithm of dry weight.

To estimate standing crops of elements in different components of an ecosystem, we must know the elemental content of the members of that component. Extensive data on the elemental content of mammals are available (Bowen, 1966), but unfortunately these data are for specific tissues and organs rather than for the whole body. For ecological studies we need the whole-body elemental content to estimate elemental standing crops from biomass data.

Gentry et al. (1974) suggested that the elemental composition of adult small mammals was constant enough to warrant the use of average whole-body elemental concentrations. In species such as the cotton rat (Briese, 1973) and the old-field mouse (Kaufman and Kaufman, this volume), however, age has a major effect on elemental composition. In addition, Sella (1973) estimated elemental concentration in cotton rats from the natural logarithm of the length of the hind foot, whereas Reid et al. (1968) and Briese (1973) reported high

predictability of the natural logarithm of the amount of an element in sheep and cotton rats, respectively, from the natural logarithm of live weight.

We examined changes in elemental content of laboratory-raised old-field mice (*Peromyscus polionotus*) from birth to 6 weeks of age with the objective of determining the usefulness of live and dry weights as predictors of elemental concentrations or amounts. We present predictive equations for estimating elemental content from live and dry weights of the mice.

METHODS AND MATERIALS

Old-field mice, *Peromyscus polionotus*, were maintained in a laboratory colony at the Savannah River Ecology Laboratory. Pairs of mice (at least 7 to 8 generations removed from the original stock) were housed in plastic cages (18.4 by 29.2 cm) which contained vermiculite as litter. Water and laboratory chow were provided ad libitum. The animal room was maintained at 25 ± 2°C, with lights on at 0700 and lights off at 1900 EST.

Mice were sacrificed in the late afternoon at weekly intervals from 0 to 42 days (details of procedures are given in Kaufman and Kaufman, this volume). Live weight was recorded, and mice were placed in tared vials and frozen. Then specimens were freeze-dried to a constant weight. When specimens were so small (e.g., 0- to 7-day-old mice) that all analyses could not be performed from one mouse, samples were lumped and an average weight was used. Dry specimens were ground in a CRC micro mill until homogeneous and then stored in desiccators until analysis.

Concentrations of 13 elements (Ca, P, K, Na, Mg, Fe, Zn, Al, Mn, Sr, B, Mo, and Ba) were determined with a Jarrell-Ash direct-reading 1.5-m emission spectrograph (techniques are described in Kaufman and Kaufman, this volume). Results for barium were not used because of the low concentration level (not measurable, <1 ppm in most specimens). Sulfur was determined with a Leco sulfur analyzer (apparatus is described in Jones and Isaac, 1972). Nitrogen was determined by the standard micro-Kjeldahl technique (Association Official Agricultural Chemists, 1960) on a 0.04 to 0.06-g subsample.

Elemental concentrations in dry-weight biomass (DWB) were the concentration values from the samples analyzed. Amounts of the elements in a mouse were then calculated as the product of the DWB of a mouse and the elemental concentration in the DWB for that mouse. Live-weight concentrations were calculated by dividing the amount of the element in an animal by its live-weight biomass (LWB).

RESULTS

In 0- to 6-week-old mice, the live-weight concentrations of all elements except potassium and sodium were highly correlated to live weight although

predictability (r^2) was extremely low for most elements (Table 1). Significant correlations between dry-weight concentrations and dry weight were found for all elements except phosphorus, iron, and zinc (Table 1). Again predictability was low for most elements. Correlation of the natural logarithm of live-weight concentration against the natural logarithm of live weight was higher than concentration against live weight for all 12 significant correlations, although predictability was still low for many elements (Table 1). Predictability was increased by transforming the dry-weight data to natural logarithms for all but two (those for nitrogen and sulfur) of the significant correlations (Table 1).

Coefficients of determination (r^2) for estimating elemental amounts in 0-6-week-old mice for live-weight and dry-weight data with both log-transformed and nontransformed data are given in Table 1. Predictability of elemental amounts from both live and dry weights was greater with log-transformed data. Predictive equations relating the natural logarithm of elemental amount to the natural logarithm of weight (live and dry) are given in Table 2. Average values (Table 3) can be used for the live-weight concentrations of potassium and sodium and the dry-weight concentrations of phosphorus, iron, and zinc but should not be used for other elements because of the correlations between concentration and weight (Table 1).

Predicting the live-weight elemental concentration of trappable-sized mice (3 weeks or older) by use of either live weight or the natural logarithm of live weight is impossible for most elements and is not feasible for the others (Table 1). Dry-weight elemental concentration is correlated to dry weight for 9 of 14 elements; and correlations of log-transformed data are also significant for 9 of 14 elements (Table 1). However, less than 35% of the variability in elemental concentration would be accounted for by any of the 18 regression equations.

Regression equations for estimating the amount of different elements in a 3- to 6-week-old mouse from either its live or dry weight are given in Table 2. However, average concentrations (Table 3) would be the best estimator for 9 of the 14 elements with live weight and 4 of 14 elements with dry weight (see r^2 values in Table 1).

DISCUSSION

To study elemental flow through a population or elemental cycling in an ecosystem, we must calculate the elemental content of different components. Calculations of the elemental standing crops of different components depend on estimates of the elemental composition of individual organisms. These estimates could be the average elemental concentrations or concentration values that are specific for various parameters, such as age, size, or sex. Age- or size-related estimates are important because (1) organisms appear to undergo elemental changes until chemical maturity is reached (Moulton, 1923; Bailey, Kitts, and Wood, 1960; Sheng and Huggins, 1971) and (2) populations undergo consider-

Table 1

COEFFICIENTS OF DETERMINATION (r^2) FOR REGRESSION EQUATIONS RELATING LIVE-WEIGHT ELEMENTAL CONCENTRATION TO LIVE WEIGHT AND DRY-WEIGHT ELEMENTAL CONCENTRATION TO DRY WEIGHT (TOP LINE) AND ELEMENTAL AMOUNT TO BOTH LIVE AND DRY WEIGHTS (BOTTOM LINE) IN *Peromyscus polionotus**

	0 to 6 weeks old				3 to 6 weeks old			
	Live weight†		Dry weight†		Live weight†		Dry weight†	
Element	Linear	Log	Linear	Log	Linear	Log	Linear	Log
N	**0.22**	**0.33**	**0.49**	**0.48**	0.00	0.01	**0.31**	**0.30**
	0.92	**0.97**	**0.90**	**0.97**	**0.76**	**0.81**	**0.75**	**0.80**
Ca	**0.40**	**0.64**	**0.16**	**0.46**	*0.04*	*0.04*	**0.20**	**0.21**
	0.74	**0.87**	**0.68**	**0.87**	**0.34**	**0.36**	**0.25**	**0.30**
P	**0.45**	**0.63**	0.00	0.00	0.00	0.00	**0.18**	**0.18**
	0.92	**0.96**	**0.89**	**0.96**	**0.76**	**0.78**	**0.71**	**0.76**
K	0.03	0.03	**0.48**	**0.59**	0.00	0.00	**0.24**	**0.23**
	0.92	**0.95**	**0.85**	**0.95**	**0.77**	**0.81**	**0.63**	**0.71**
S	**0.24**	**0.41**	**0.19**	**0.12**	0.01	0.01	**0.23**	**0.23**
	0.89	**0.95**	**0.86**	**0.95**	**0.69**	**0.71**	**0.64**	**0.68**
Na	0.01	0.02	**0.42**	**0.53**	0.00	0.01	**0.09**	**0.08**
	0.79	**0.88**	**0.76**	**0.87**	**0.58**	**0.62**	**0.51**	**0.57**
Mg	**0.43**	**0.52**	**0.11**	**0.13**	0.02	*0.05*	0.03	0.01
	0.75	**0.88**	**0.66**	**0.85**	**0.44**	**0.50**	**0.29**	**0.37**
Fe	**0.35**	**0.43**	0.02	0.02	0.00	0.00	**0.11**	**0.09**
	0.81	**0.90**	**0.76**	**0.88**	**0.51**	**0.58**	**0.43**	**0.51**
Zn	**0.36**	**0.47**	0.00	0.00	0.02	0.03	0.02	0.01
	0.82	**0.93**	**0.80**	**0.93**	**0.58**	**0.61**	**0.55**	**0.59**
Al	**0.42**	**0.66**	**0.14**	**0.33**	0.00	0.00	**0.11**	**0.09**
	0.79	**0.92**	**0.74**	**0.91**	**0.45**	**0.52**	**0.37**	**0.46**
Mn	**0.49**	**0.70**	**0.33**	**0.51**	**0.09**	**0.20**	0.01	*0.06*
	0.70	**0.88**	**0.67**	**0.87**	**0.45**	**0.57**	**0.39**	**0.50**
Sr	**0.26**	**0.38**	**0.05**	**0.09**	0.00	0.01	*0.05*	0.02
	0.57	**0.81**	**0.50**	**0.78**	**0.21**	**0.33**	**0.12**	**0.23**
B	**0.46**	**0.55**	**0.09**	**0.11**	*0.05*	*0.05*	0.01	0.01
	0.84	**0.92**	**0.84**	**0.93**	**0.63**	**0.67**	**0.62**	**0.67**
Mo	**0.62**	**0.70**	**0.13**	**0.17**	**0.13**	**0.13**	0.01	0.00
	0.92	**0.96**	**0.93**	**0.96**	**0.79**	**0.81**	**0.83**	**0.83**

*Linear (concentration = a + b weight) and log (ln concentration = ln a + b weight) relationships were examined. Sample sizes are 166 (sulfur has only 133) for 0 to 6 weeks old and 106 (sulfur has only 85) for 3 to 6 weeks old.

†The r^2 values in italics indicate associated r values significant at $P < 0.05$ and the values in boldface, at $P < 0.01$.

Table 2

SUMMARY OF PREDICTIVE EQUATIONS FOR ESTIMATING ELEMENTAL AMOUNT FROM BOTH LIVE AND DRY WEIGHTS IN *Peromyscus polionotus**†

Element	Live weight		Dry weight	
	b ± 2SE	ln a ± 2SE	b ± 2SE	ln a ± 2SE
		0 to 6 weeks old		
N	1.143 ± 0.032	−3.947 ± 0.062	0.856 ± 0.023	−2.347 ± 0.023
Ca	2.041 ± 0.121	−0.372 ± 0.235	1.528 ± 0.090	2.486 ± 0.088
P	1.343 ± 0.041	1.004 ± 0.079	1.005 ± 0.030	2.884 ± 0.029
K	1.042 ± 0.036	0.970 ± 0.069	0.776 ± 0.029	2.431 ± 0.028
S	1.234 ± 0.049	−0.279 ± 0.096	0.923 ± 0.036	1.450 ± 0.036
Na	0.953 ± 0.055	−0.009 ± 0.106	0.709 ± 0.043	1.328 ± 0.042
Mg	1.616 ± 0.093	−3.012 ± 0.179	1.189 ± 0.077	−0.738 ± 0.075
Fe	1.416 ± 0.075	3.710 ± 0.145	1.051 ± 0.060	5.699 ± 0.058
Zn	1.344 ± 0.059	2.939 ± 0.110	1.004 ± 0.044	4.822 ± 0.042
Al	1.719 ± 0.080	1.930 ± 0.155	1.281 ± 0.063	4.340 ± 0.061
Mn	2.263 ± 0.129	−1.339 ± 0.250	1.678 ± 0.103	1.839 ± 0.101
Sr	1.626 ± 0.125	−0.662 ± 0.242	1.196 ± 0.100	1.628 ± 0.097
B	1.479 ± 0.067	−0.817 ± 0.130	1.109 ± 0.049	1.252 ± 0.048
Mo	1.459 ± 0.047	−1.323 ± 0.091	1.095 ± 0.033	0.717 ± 0.032
		3 to 6 weeks old		
N	0.962 ± 0.092	−3.550 ± 0.202	0.752 ± 0.074	−2.231 ± 0.080
Ca	0.780 ± 0.203	2.427 ± 0.445	0.555 ± 0.167	3.552 ± 0.181
P	1.019 ± 0.106	1.724 ± 0.232	0.790 ± 0.088	3.127 ± 0.095
K	1.001 ± 0.096	1.062 ± 0.211	0.742 ± 0.092	2.475 ± 0.099
S	0.945 ± 0.133	0.356 ± 0.296	0.724 ± 0.110	1.666 ± 0.123
Na	1.060 ± 0.162	−0.243 ± 0.355	0.798 ± 0.136	1.242 ± 0.145
Mg	1.291 ± 0.252	−2.217 ± 0.551	0.875 ± 0.222	−0.309 ± 0.240
Fe	1.036 ± 0.174	4.623 ± 0.381	0.764 ± 0.148	6.090 ± 0.160
Zn	1.177 ± 0.184	3.334 ± 0.404	0.912 ± 0.148	4.955 ± 0.160
Al	1.004 ± 0.199	3.561 ± 0.414	0.745 ± 0.157	4.979 ± 0.170
Mn	1.782 ± 0.305	−0.152 ± 0.670	1.318 ± 0.258	2.369 ± 0.2
Sr	1.188 ± 0.333	0.384 ± 0.729	0.789 ± 0.279	2.157 ± 0.3
B	1.196 ± 0.165	−0.165 ± 0.361	0.943 ± 0.129	1.466 ± 0.139
Mo	1.232 ± 0.119	−0.810 ± 0.260	0.984 ± 0.087	0.856 ± 0.094

*Regression equations were of the form ln amount = ln a + b ln live weight or ln amount = ln a + b ln dry weight. Coefficients of determination are given in Table 1. Sample sizes are 166 (sulfur has only 133) for 0 to 6 weeks old and 106 (sulfur has only 85) for 3 to 6 weeks old.

†All equations have associated r values that are highly significant ($P < 0.01$).

TABLE 3

MEAN ± 2 STANDARD ERRORS FOR LIVE- AND DRY-WEIGHT CONCENTRATIONS* FOR *Peromyscus polionotus* FROM THE LABORATORY AND FOR FIELD-CAUGHT MICE*

	Laboratory				Field†	
	Live weight		Dry weight			
Element	0 to 6 weeks old, ppm	3 to 6 weeks old, ppm	0 to 6 weeks old, ppm	3 to 6 weeks old, ppm	Mean ± 2SE, ppm	Range, ppm
N	25,356 ± 554	26,617 ± 603	8.90 ± 0.15 pph	8.39 ± 0.18 pph	10.75 ± 0.27 pph	9.61–12.65 pph
Ca	5679 ± 427	7236 ± 347	1.88 ± 0.12 pph	2.30 ± 0.12 pph	3.15 ± 0.20 pph	1.64–4.33 pph
P	5272 ± 188	5893 ±153	1.81 ± 0.04 pph	1.86 ± 0.05 pph	2.31 ± 0.12 pph	1.79–2.94 pph
K	2873 ± 59	2918 ± 69	1.02 ± 0.03 pph	0.92 ± 0.03 pph	1.15 ± 0.07 pph	0.88–1.75 pph
S	1198 ± 41	1280 ± 41	0.41 ± 0.01 pph	0.40 ± 0.01 pph		
Na	927 ± 29	912 ± 35	0.33 ± 0.01 pph	0.29 ± 0.01 pph	0.37 ± 0.02 pph	0.28–0.45 pph
Mg	171 ± 12	215 ± 13	580.2 ± 35.1	685.2 ± 43.9	1090 ± 100	600–1810
Fe	93.8 ± 5.2	112.8 ± 5.1	322.1 ± 15.3	356.8 ± 17.1	303 ± 34	176–546
Zn	37.1 ± 1.8	42.4 ± 2.1	127.5 ± 4.8	133.5 ± 6.9	107 ± 11	65–190
Al	29.0 ± 2.0	36.6 ± 1.8	97.1 ± 5.4	115.7 ± 6.0	198 ± 33	103–461
Mn	3.69 ± 0.42	5.17 ± 0.42	11.93 ± 1.04	16.22 ± 1.40	15.0 ± 4.9	2–46
Sr	1.91 ± 0.17	2.41 ± 0.20	6.50 ± 0.53	7.70 ± 0.69	28.7 ± 5.5	8–61
B	1.13 ± 0.06	1.33 ± 0.06	3.84 ± 0.15	4.17 ± 0.18	5.2 ± 0.5	3–7
Mo	0.65 ± 0.03	0.75 ± 0.02	2.20 ± 0.05	2.34 ± 0.06	3.0 ± 0.2	2.5–3.8

*Samples sizes are 166 (sulfur has only 133) for 0 to 6 weeks old and 106 (sulfur has only 85) for 3 to 6 weeks old. Mean ± 2 SE and range of dry-weight concentrations are also listed for 26 species of field-caught rodents (some elements were examined in only 25 species).

†Field summary from Gentry et al. (1974).

able change in age and size structure. Since age is difficult to assess and weight (which is partly dependent on age) is much easier to determine in field populations, we should base estimates of elemental content on weight and not age to facilitate field use of the values.

We examined the relationship between live-weight concentrations and live weight as well as dry-weight concentrations and dry weight since both have been studied. Live-weight estimators are more useful than dry-weight estimators for converting field biomass into elemental standing crops. For both log-transformed and nontransformed data, these relationships had a majority of significant correlations (12 of 14 for live weight and 11 of 14 for dry weight). Sodium and potassium were not correlated with live weight, and phosphorus, iron, and zinc were not correlated with dry weight (Table 1). Predictability of most of the regression equations is quite low, however (Table 1). For the significant correlations it is not advisable to use average values for all animals (0 to 6 weeks) with no regard for size. Therefore, for population studies the best approach in estimating elemental content is to use regression equations of log-transformed data (Table 2) as Briese (1973) did for cotton rats and Reid et al. (1968) did for sheep.

When only animals of trappable size (assumed to be 3 weeks or older in our study) are considered, predicting concentration from live weight is impossible (Table 1). Therefore, under field conditions when only trappable animals are being considered, average live-weight concentration is probably the best estimator to use since the predictability of the amount of many elements from live weight is also low (Table 1). If dry-weight values are to be used, it is not advisable to use average concentration data since a majority of the dry-weight concentrations were correlated to dry weight (Table 1). The best estimates of elemental content in trappable-size mice from dry weight would be from the regression equations relating the natural logarithm of the amount of each element to the natural logarithm of dry weight (Tables 1 and 2).

In relating our laboratory data to field situations, we compared our average values for 0- to 6- and 3- to 6-week-old mice to the range and average values for field-caught rodents using dry-weight concentrations (Table 3). Concentrations of N, Mg, Al, Sr, Mo, and Ba in 0- to 6-week-old mice were below the range for field-caught animals (Table 3). The concentrations of macroelements in the 3- to 6-week-old laboratory old-field mice were lower than those in the field-caught animals. This difference is probably related to the much greater fat content of laboratory animals (Kaufman and Kaufman, 1974). Other differences may be caused by differences in the elemental content of the diet of field and laboratory animals.

Although the concentration data from our study may not be directly extrapolatable to the field, the major conclusion, that concentrations change with size and age (Table 1; Kaufman and Kaufman, this volume), is relevant to work with field populations. Therefore, studies of elemental flow through

populations should be concerned with calculating standing crops from size-specific estimators, even though average dry-weight concentration values of small mammals are probably sufficient for the small-mammal component in an ecosystem study (Gentry et al., 1974).

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REFERENCES

Association Official Agricultural Chemists, 1960, Methods of Analysis, Washington, D. C.

Bailey, C. B., W. D. Kitts, and A. J. Wood, 1960, Changes in the Gross Chemical Composition of the Mouse During Growth in Relation to the Assessment of Physiological Age, *Can. J. Anim. Sci.*, **40**: 143-155.

Bowen, H. J. M., 1966, *Trace Elements in Biochemistry*, Academic Press, Inc., New York.

Briese, L. A., 1973, Variation in Elemental Composition and Cycling in the Cotton Rat, *Sigmodon hispidus*, M.S. Thesis, University of Georgia, Athens.

Gentry, J. B., L. A. Briese, D. W. Kaufman, M. H. Smith, and J. G. Wiener, 1974, Elemental Cycling in Small Mammal Populations, in *Small Mammals: Their Productivity and Population Dynamics*, F. B. Golley, K. Petrusewicz, and L. Ryszkowski (Eds.), Cambridge University Press, London, in press.

Jones, J. B., Jr., and R. A. Isaac, 1972, Determination of Sulfur in Plant Material Using a Leco Sulfur Analyzer, *J. Agr. Food Chem.*, **20**: 1292-1294.

Kaufman, G. A., and D. W. Kaufman, 1974, Savannah River Ecology Laboratory, unpublished.

Moulton, C. R., 1923, Age and Chemical Development in Mammals, *J. Biol. Chem.*, **57**: 79-97.

Reid, J. T., et al., 1968, Some Peculiarities in the Body Composition of Animals, in *Body Composition in Animals and Man*, pp. 19-44, National Academy of Sciences, Washington, D. C.

Sella, L. D., 1973, Trace Elements in the Cotton Rat, *Sigmodon hispidus*, on the Piedmont of Georgia, M.S. Thesis, University of Georgia, Athens.

Sheng, H. G., and R. A. Huggins, 1971, Growth of the Beagle: Changes in Chemical Composition, *Growth*, **35**: 369-376.

CHEMICAL COMPOSITION OF WHITE-TAILED DEER: WHOLE-BODY CONCENTRATIONS OF MACRO- AND MICRONUTRIENTS

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ABSTRACT

Wet- and dry-weight concentrations of six macronutrients (Ca, K, Mg, N, Na, and P) and five micronutrients (Cu, Fe, Mn, Mo, and Zn) were determined for whole-body samples from 27 white-tailed deer (*Odocoileus virginianus*). Information on the nutrient composition of deer was combined with biomass data to estimate standing crops of nutrients in deer herds at the Savannah River Plant and to predict exportation of nutrients from the Savannah River Plant system during annual deer hunts. Nutrient standing crops in deer were small relative to those of primary producer components of temperate forest ecosystems. Similarly, annual loss of nutrients by harvest of deer was negligible in comparison with annual nutrient budgets of southeastern forests.

Investigation and modeling of nutrient cycles in natural ecosystems have added considerable insight to our understanding of ecosystem structure and function. In addition, studies of the interrelationships of populations of primary consumers and nutritional cycles of forages are answering many of the questions that have long perplexed population biologists (see Klein, 1965, 1970; Schultz, 1964, 1969). Prerequisite to the quantitative modeling of nutrient flux within an ecosystem or through a population is knowledge of standing crops of nutrients within various system components. Since estimates of standing crops of nutrients in the biological components of an ecosystem are generally derived as the product of the biomass density of the component multiplied by the concentration of each nutrient within the component (Beyers et al., 19[illegible] Sturges, Holmes, and Likens, 1974), knowledge of the nutrient composition of ecosystem components is essential.

White-tailed deer (*Odocoileus virginianus*) occur in most North American temperate forests and are abundant at the Savannah River Plant (Urbston, 1967). The impact of deer on nutrient cycles in temperate forests apparently has

not been investigated. This report presents preliminary data on the nutrient composition of white-tailed deer and combines these data with available biomass figures to estimate standing crops of nutrients in deer herds on the Savannah River Plant site and amounts of nutrients lost from the Savannah River Plant system by removal of deer during annual hunts.

METHODS AND MATERIALS

Wet- and dry-weight whole-body concentrations of six macronutrients (Ca, K, Mg, N, Na, and P) and five micronutrients (Cu, Fe, Mn, Mo, and Zn) were determined for 27 white-tailed deer shot at the Savannah River Plant. Carcasses (stomach and intestinal contents included) were frozen whole, sawed into smaller units, and ground in a meat grinder. Samples were then freeze dried and further homogenized in a Wiley mill, and three to six subsamples of the homogenate, each weighing approximately 250 g, were analyzed for each deer. Chemical analysis was performed by arc spectrography (Jones and Warner, 1969) for all elements except nitrogen, which was measured by the Kjeldahl method (Jackson, 1956). Chemical analyses were conducted at the Georgia Soil Testing and Plant Analysis Laboratory in Athens, Georgia.

RESULTS

Results of chemical analyses are given in Table 1 as mean wet- and dry-weight whole-body concentrations. Linear regression of nutrient concentration on body weight indicated no significant change in concentrations with respect to body weight. Coefficients of variation for macronutrient concentrations averaged less than those for micronutrient concentrations. Only three of the 11 elements (Mg, Mn, and Mo) had coefficients of variation greater than 25% (Table 1). Since coefficients of variation for wet- and dry-weight concentrations were similar for each element, the concentrations given in Table 1 should provide reasonable estimates of the nutrient composition of white-tailed deer.

Urbston (1967) estimated a minimum density of 41 white-tailed deer per square mile (approximately 0.16 deer per hectare) at the Savannah River Plant. This estimate is probably conservative since the deer population was in a state of expansion at the time of Urbston's study. The mean wet weight of 4691 deer killed during annual hunts at the Savannah River Plant from 1965 to 1973 (unpublished data) was 44.54 kg. This figure should accurately estimate average wet weight of deer at the Savannah River Plant, since individuals of both sexes and all age classes are taken and little discrimination between deer is shown by hunters. Multiplying the density estimate of 0.16 deer per hectare, by the wet-weight value of 44.54 kg per deer, we obtained a wet-weight biomass density

TABLE 1

AVERAGE WHOLE-BODY NUTRIENT COMPOSITION AND STANDING CROPS FOR WHITE-TAILED DEER AND EXPORTATION OF NUTRIENTS BY HARVEST OF DEER AT THE SAVANNAH RIVER PLANT

	Wet-weight concentration* (mean ± 2 SE)	CV†	Dry-weight concentration* (mean ± 2 SE)	CV†	Standing crop‡	Nutrient loss§
Macronutrient	mg/g	%	mg/g	%	g/ha	g/ha/year
Nitrogen	31.2 ± 0.8	6.6	104.0 ± 2.3	5.7	222.5	16.2
Calcium	9.28 ± 0.76	21.3	30.9 ± 2.6	21.5	66.2	4.8
Phosphorus	6.78 ± 0.47	18.1	22.6 ± 1.6	18.3	48.3	3.5
Potassium	2.86 ± 0.15	13.8	9.53 ± 0.50	13.6	20.4	1.5
Sodium	1.16 ± 0.05	11.5	3.88 ± 0.19	12.9	8.3	0.60
Magnesium	0.27 ± 0.03	29.4	0.91 ± 0.10	28.9	1.9	0.14
Micronutrient	μg/g	%	μg/g	%	mg/ha	mg/ha/year
Iron	49.5 ± 3.8	19.9	164.5 ± 10.8	17.1	353	26
Zinc	20.6 ± 1.5	19.5	68.4 ± 4.7	17.8	147	11
Manganese	8.56 ± 1.23	37.3	28.5 ± 4.0	36.2	61	4.5
Copper	7.83 ± 0.53	17.5	26.1 ± 1.8	17.9	56	4.1
Molybdenum	0.91 ± 0.11	30.8	3.0 ± 0.3	29.9	6	0.5

*Concentration data are means for 27 deer.

†Coefficient of variation.

‡Based on an estimated density of 0.16 deer/ha with a mean live weight of 44.54 kg/deer.

§Based on an estimated annual removal of 900 deer from the 780-km^2 Savannah River Plant.

(D) of 7.13 kg/ha for deer at the Savannah River Plant. Standing crop for each nutrient (S_i) was estimated by the equation

$$S_i = DC_i$$

where C_i is wet-weight whole-body concentration of a particular nutrient (from Table 1). Dry-weight nutrient concentrations from Table 1 would be used if D were in units of dry weight. Predicted standing crops of nutrients in deer are also given in the table.

In 1965 deer hunts were begun on a trial basis at the Savannah River Plant. Since 1967 approximately 900 deer have been harvested annually ($\bar{X} = 903$; range, 699 to 1162). The Savannah River Plant has a land area of about 300 miles^2 or 780 km^2. Hence, this rate of removal is equivalent to 1.15 deer per square kilometer per year or 0.52 kg wet-weight biomass per hectare per year if 44.54 kg is the mean wet weight of deer killed in hunts. Nutrient exportation was calculated on a per-hectare scale using wet-weight concentrations and a biomass value of 0.52 kg ha^{-1} year^{-1} (Table 1).

DISCUSSION

Information concerning nutrient composition of consumer components of temperate forests is becoming increasingly available (Reichle, Shanks, and Crossley, 1969; Beyers et al., 1971; Nabholz, 1973; Sturges, Holmes, and Likens, 1974; Gentry et al., 1974). Except for manganese, our values for whole-body elemental concentrations in deer are within the range of concentrations given by Wiener et al. (1974) for 16 species of xeric rodents from various locations in the southwestern United States. This seems surprising when differences in size, diet, and physiology between southeastern deer and southwestern rodents are considered. Deer and rodents have certain physiological requirements in common which apparently necessitate the maintenance of body pools of nutrients within defined bounds. Such factors as age (Sheng and Huggins, 1971), sex (Briese, 1973), species (Nabholz, 1973; Wiener et al., 1974), location (Sella, 1973; Wiener et al., 1974), and season (Briese, 1973; Nabholz, 1973; Sella, 1973) can affect the chemical composition of mammals in various ways. However, Wiener et al. (1974) concluded that for rodents generic means (i.e., average whole-body elemental concentrations for congeneric species) are suitable estimators of body concentrations for most elements. If this is true of deer, our data for nutrient composition should be applicable to populations of deer in other geographic areas.

Since few quantitative data on nutrient flux and standing crops in southeastern forests are currently available, it is difficult to assess the importance of deer in nutrient-cycling processes solely on the information given here. Our estimates of standing crops of nutrients in deer are much higher than

those given for small-mammal (Beyers et al., 1971; Nabholz, 1973) and avian (Sturges, Holmes, and Likens, 1974) communities inhabiting temperate forest ecosystems. A comparison of nutrient pools in deer relative to those in primary producers is not feasible since data on nutrient standing crops are not available for primary producer components of southeastern forests. However, our values for nutrient standing crops in deer are small relative to estimates of nutrient pools in the vegetational component of certain other temperate forests (Ovington, 1962; Duvigneaud and Denaeyer-De Smet, 1970).

Our calculations of nutrient loss by removal of deer are approximately 30% of Crisp's (1966) estimates of nutrient exportation from a grazed pasture by removal of sheep and wool and approximately twice the values given by Sturges et al. (1974) for maximum nutrient loss resulting from annual migration of birds from northern hardwood forests. Crisp (1966) and Sturges et al. (1974) concluded that nutrient exportation due to sale of sheep and wool and to migration of birds, respectively, was negligible in relation to other system outputs of nutrients and was, therefore, unimportant. Similarly, our estimates of nutrient loss by removal of deer are minuscule in comparison to nutrient budgets for southeastern Piedmont forests (see Wells, Whigham, and Lieth, 1972). However, further information concerning ingestion, egestion, and turnover of nutrients by deer will be required before their importance in nutrient-cycling processes in temperate forest ecosystems can be more fully evaluated.

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REFERENCES

Beyers, R. J., M. H. Smith, J. B. Gentry, and L. L. Ramsey, 1971, Standing Crops of Elements and Atomic Ratios in a Small Mammal Community, *Acta Theriologica*, **16**: 203-211.

Briese, L. A., 1973, Variations in Elemental Composition and Cycling in the Cotton Rat, *Sigmodon hispidus*, M.S. Thesis, University of Georgia, Athens.

Crisp, D. T., 1966, Input and Output of Minerals for an Area of Pennine Moorland: The Importance of Precipitation, Drainage, Peat Erosion and Animals, *J. Appl. Ecol.*, **3**: 327-348.

Duvigneaud, P., and S. Denaeyer-De Smet, 1970, Biological Cycling of Minerals in Temperate Deciduous Forests, in Ecological Studies, Vol. 1, *Analysis of Temperate Forest Ecosystems,* pp. 199-225, D. E. Reichle (Ed.), Springer-Verlag New York, Inc., New York.

Gentry, J. B., L. A. Briese, D. W. Kaufman, M. H. Smith, and J. G. Wiener, 1974, Elemental Flow and Standing Crops for Small Mammal Populations, in *Small Mammals: Their Productivity and Population Dynamics,* F. B. Golley, K. Petrusewicz, and L. Ryszkowski (Eds.), Cambridge University Press, London, in press.

Jackson, M. L., 1956, Soil Chemical Analysis: Advanced Course, Department of Soil Science, University of Wisconsin, Madison, Wis.

Jones, J. B., Jr., and M. H. Warner, 1969, Analysis of Plant–Ash Solutions by Spark-Emission Spectroscope, *Develop. Appl. Spectrosc.,* **7A**: 152-160.

n, D. R., 1970, Food Selection by North American Deer and Their Response to Over Utilization of Preferred Plant Species, in *Animal Populations in Relation to Their Food Resources,* pp. 25-44, A. Watson (Ed.), Blackwell Scientific Publications Ltd., Oxford, England.

—, 1965, Ecology of Deer Range in Alaska, *Ecol. Monogr.,* **35**: 259-284.

Nabholz, J. V., 1973, Small Mammals and Mineral Cycling on Three Coweeta Watersheds, M.S. Thesis, University of Georgia, Athens.

Ovington, J. D., 1962, Quantitative Ecology and the Woodland Ecosystem Concept, *Advances Ecol. Res.,* **1**: 103-192.

Reichle, D. E., M. H. Shanks, and D. A. Crossley, Jr., 1969, Calcium, Potassium, and Sodium Content of Forest Floor Arthropods, *Ann. Entomol. Soc. Amer.,* **62**: 57-62.

Schultz, A. M., 1969, A Study of an Ecosystem: The Arctic Tundra, in *The Ecosystem Concept in Natural Resource Management,* pp. 77-93, G. M. Van Dyne (Ed.), Academic Press, Inc., New York.

—, 1964, The Nutrient-Recovery Hypothesis for Arctic Microtine Cycles. II. Ecosystem Variables in Relation to Arctic Microtine Cycles, in *Grazing in Terrestrial and Marine Environments,* pp. 57-68, D. J. Crisp (Ed.), Blackwell Scientific Publications Ltd., Oxford, England.

Sella, L. D., 1973, Trace Elements in the Cotton Rat, *Sigmodon hispidus,* on the Piedmont of Georgia, M.S. Thesis, University of Georgia, Athens.

Sheng, H. P., and R. A. Huggins, 1971, Growth of the Beagle: Changes in Chemical Composition, *Growth,* **35**: 369-376.

Sturges, F. W., R. T. Holmes, and G. E. Likens, 1974, The Role of Birds in Nutrient Cycling in a Northern Hardwoods Ecosystem, *Ecology,* **55**: 149-155.

Urbston, D. F., 1967, Herd Dynamics of a Pioneer-Like Deer Population, *Proc., Annu. Conf. Southeast. Assoc. Game Fish Comm.,* **21**: 42-50.

Wells, C. G., D. Whigham, and H. Lieth, 1972, Investigation of Mineral Nutrient Cycling in an Upland Piedmont Forest, *J. Elisha Mitchell Sci. Soc.,* **88**: 66-78.

Wiener, J. G., D. W. Kaufman, G. A. Kaufman, J. B. Gentry, M. H. Smith, and P. R. Ramsey, 1974, Chemical Composition of Rodents: Use of Whole-Body Concentrations for Estimation of Standing Crops of Elements, submitted to *Ecology.*

RADIOCESIUM CONCENTRATIONS IN WHOLE-BODY HOMOGENATES AND SEVERAL BODY COMPARTMENTS OF NATURALLY CONTAMINATED WHITE-TAILED DEER

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ABSTRACT

Radiocesium concentrations were determined for various tissues, organs, and other body compartments of 17 white-tailed deer collected from contaminated habitats on the AEC Savannah River Plant. Highest levels of radiocesium concentration were found in skeletal muscle, feces, kidney, and adrenal tissue, which averaged between 50 to 70 pCi radiocesium/g (dry weight). Liver and bone showed the lowest average values. With the exception of feces and rumen contents, nearly all tissues and organ compartments showed significant positive linear correlations between their respective radiocesium levels. Analyses of whole-body homogenates indicated that the deer examined averaged 9.91 pCi radiocesium/g (whole-body wet weight). These values were best predicted from the radiocesium contents of skeletal muscle, using the relationship: pCi radiocesium/g dry whole-body weight = 3.33 + 0.60 (pCi/g dry skeletal muscle). Calculation of a weighted "predictive index" indicated that concentrations in skeletal muscle best predicted the overall pattern and levels of radiocesium distribution within all compartments of the deer body. Radiocesium concentrations in the brain, heart, and liver, respectively, followed muscle in order of predictive ability.

Deer frequently constitute a major portion of the herbivore biomass in an ecosystem. Thus they may have a special importance when it comes to describing and quantifying the cycling and contamination patterns of radionuclides or other pollutants in these systems. Deer are also popular game animals frequently consumed by man as food. Thus they can serve as vectors by which various radionuclides or other contaminants directly enter human food chains. It is important to understand not only the processes by which wild deer become contaminated but also the distribution of such substances in various organs, tissues, and other body compartments of the deer's body. Of special concern in this regard is the establishment of predictive relationships which allow estimation of the degrees of contamination of those particular portions, such as

skeletal muscle, which are selectively eaten by man. Moiseyev et al. (1967) demonstrate the important differences in tissue radiation-exposure rates which can be produced by differential concentrations of radionuclides in the various organs or tissues.

Because of the large body size, direct estimation of the total radionuclide body burdens of deer is quite difficult and time consuming. Such information must be obtained, however, if the contamination levels of deer populations are to be quantitatively related to those of other herbivore populations, such as mice, inhabiting the same ecosystems. Prime consideration should be given to establishment of predictive relationships that allow the estimation of total body burdens of deer without the necessity of either whole-body counting or time-consuming carcass homogenization and subsampling procedures. An indirect method of rapidly estimating the radiocesium content of deer muscle, under field conditions, is described by Rabon and Johnson (1973).

The distribution of radiocesium within the bodies of several species of cervids has been described (Ekman and Greitz, 1967; Moiseyev et al., 1967; Plummer, Pullen, and Provost, 1967; Hakonson and Whicker, 1971b). All these studies are in general agreement; skeletal muscle tends to accumulate the highest concentrations as well as the greatest percentage of total radiocesium body burden in these deer. However, in three of these studies the number of animals examined was too small (N = 1 to 9) to permit the calculation of reliable predictive relationships between the various body compartments. Plummer, Pullen, and Provost (1967) calculated predictive relationships involving various body compartments related to wet-weight radiocesium concentrations in the tongue alone. Moreover, the studies by Ekman and Greitz (1967) and Hakonson and Whicker (1971b) used animals that were sacrificed shortly after being given single orally administered doses of ^{134}Cs solutions in the laboratory. Such deer might show different patterns of isotope uptake and organ concentration as compared to free-living deer that have been contaminated through natural food-web pathways.

In the present study an opportunity was afforded to examine the patterns of radiocesium distribution in the various body compartments of white-tailed deer collected from the resident herd on the AEC Savannah River Plant (SRP). The 300 square miles of the SRP encompass a variety of terrestrial habitats located both the Savannah River Pleistocene Coastal Terraces and the Aiken Plateau graphic subregions of portions of Aiken, Barnwell, and Allendale counties in South Carolina. Detailed descriptions of the SRP habitats are given by Jenkins and Provost (1964) and Norris (1963). Brief histories and major ecological relationships of the SRP deer herd are summarized by Jenkins and Provost (1964), Urbston (1967), and Rabon (1968). Concentrations of 11 chemical elements in whole-body homogenate, from the same deer used in the present study, are described by Wiener et al., this volume. As indicated by Rabon (1968), Marter (1970), and Brisbin et al. (1974), a number of the terrestrial and swampland habitats inhabited by the SRP deer herd have been contaminated

over the past 15 to 20 years with several radionuclides, chiefly radiocesium, which have been released periodically into production-reactor effluent streams. Previous studies (Rabon, 1968; Marter, 1970) of the radiocesium contents of muscle samples of SRP deer suggest that many animals had sufficient concentrations of both natural fallout and reactor-released radiocesium to serve as ideal subjects for description of the patterns of radiocesium distribution within several body compartments as well as total-body homogenate. The ecological and health-related significance of the radiocesium contamination levels found in this deer herd are discussed at length by Jenkins and Fendley (1968) and Marter (1970).

In this study the term "body compartment" is used to designate a specific portion of the deer's total carcass. Such compartments include rumen contents and feces as well as the various organs and such tissues as muscle and bone.

MATERIALS AND METHODS

Seventeen deer were collected either as road kills or by shooting. In shooting, efforts were made to collect deer both from areas of known high radiocesium contamination and from less contaminated habitats. Deer were collected during several seasons to sample periods of varying susceptibility to dietary radiocesium contamination (Rabon, 1968). These procedures were expected to allow the study of specimens with varying levels of total-body burden.

Fresh biopsy samples, weighing approximately 4 g, were taken from each deer for radiocesium analysis. The body compartments sampled included: thigh skeletal muscle, heart, rumen contents, feces, liver, lung, spleen, kidney, adrenal gland, brain, and bone (shank portion of femur). All biopsy samples, plus the remaining total carcass, were then frozen until further processing. For a uniform total-body homogenate, the remaining whole carcass, while frozen solid, was chopped and band sawed into smaller (10 to 20 cm) cubes, which were then passed several times through a Hobart model 4732 meat grinder with a grinder plate equipped with 15-mm openings. Six 250-g aliquots were then randomly taken from the whole-body homogenate of each deer and refrozen for subsequent analysis along with the organ biopsy samples. All samples, including aliquots of whole-body homogenate, were freeze-dried to a constant weight and ground to a fine powder on a model No. 3 Wiley mill equipped with a 2-mm grinder screen. A single aliquot weighing between 1 and 2 g was then taken of each sample and placed in a 1.5- by 11-cm glass counting tube for radiocesium determination. Determinations were made on a Nuclear Chicago pulse-height analyzer equipped with a 3-in. NaI crystal and a 2-in. well. All powdered samples were packed to a constant counting geometry in the bottom of the counting tube. Thirty-minute counts of the samples were compared to 30-min same-day counts of background and 30-min counts of phantoms containing a known

amount of radiocesium homogenized into dried powdered biological material. Counter sensitivity for the radiocesium determination procedures described was 5.48 pCi/g (dry weight), and samples whose radiocesium concentrations were less than twice this value were not considered to be significantly distinguishable from background. All values were finally expressed as picocuries radiocesium per gram dry tissue weight. Values reported here for radiocesium levels in whole-body homogenate represent the averages of all aliquots processed and counted for each individual deer.

Although radiocesium contents, as expressed in this study, included some contribution from the ^{134}Cs energy peak, it is unlikely that this isotope contributed significantly to the counts observed. Marter (1970) has shown the ratio of ^{137}Cs to ^{134}Cs to be approximately 20 : 1 in biota from the areas where most of the deer were collected. Other gamma-emitting isotopes were present in only relatively small amounts in these habitats (Marter, 1970) and had energy spectrums that were widely separated from the $^{134-137}Cs$ energy peaks. They were, therefore, considered unlikely to contribute significant errors to the radiocesium analyses (Anderson, Gentry, and Smith, 1973).

RESULTS

Radiocesium contents of the various tissues, organs, and other body compartments are shown in Fig. 1. The highest levels were found in kidney and adrenal tissue, which averaged 68.60 and 65.71 pCi/g (dry weight), respectively. Bone and liver contained the lowest levels, averaging 12.41 and 14.56 pCi/g (dry weight), respectively. All compartments examined had average radiocesium levels that were significantly distinguishable from background, i.e., greater than 10.96 pCi/g (dry weight). The highest value observed was 340.76 pCi/g (dry weight) for a sample of adrenal tissue.

Correlation coefficients for linear relationships between radiocesium contents of the various body compartments of the deer are presented in Table 1. Correlations involving bone were not included in Table 1 because of low sample sizes resulting from sample losses during laboratory preparation. With the exception of those relationships involving feces and rumen contents, only the relationship between adrenal and kidney tissue failed to show a statistically significant ($P < 0.05$) correlation. Feces showed statistically significant correlations with only 3 of the other 10 possible correlations, while rumen contents showed significant correlations with 7 of the other 10. There was a highly significant correlation between the radiocesium levels found in rumen contents and feces, although the predictability of this relationship was not great ($r^2 = 0.48$).

The radiocesium levels of the various body compartments are plotted in Fig. 2 as linear functions of increasing radiocesium levels in the whole-body homogenate. Only three organs, brain, liver, and lung, increased in radiocesium

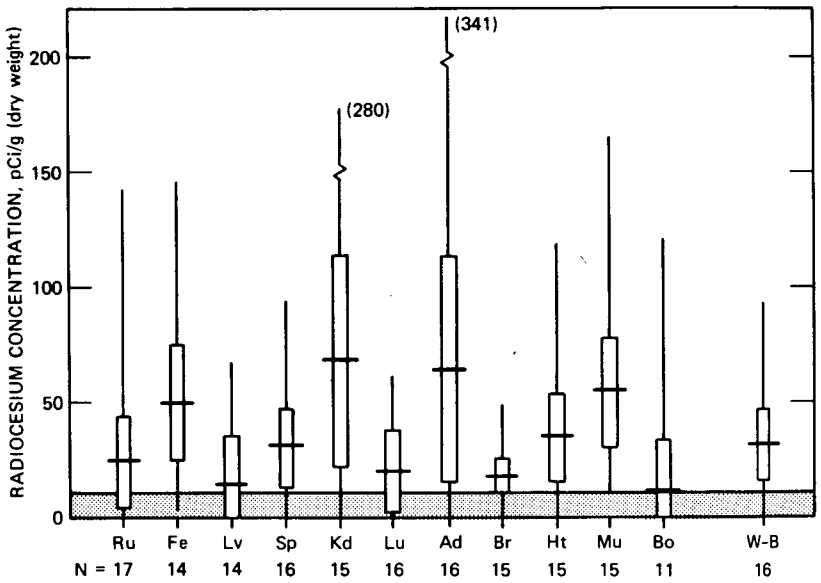

Fig. 1 Radiocesium concentrations in several tissues, organs, and other body compartments of white-tailed deer from the AEC Savannah River Plant. Horizontal lines represent means, rectangles represent ±2SE, and vertical lines represent ranges. Values falling within the shaded area are not significantly distinguishable from background, as determined by twice the calculated counting sensitivity of 5.48 pCi/g (dry weight). Ru, rumen contents; Fe, feces; Lv, liver; Sp, spleen; Kd, kidney; Lu, lung; Ad, adrenal; Br, brain; Ht, heart; Mu, skeletal muscle; Bo, bone; and W-B, whole-body homogenate.

TABLE 1

CORRELATION COEFFICIENTS FOR LINEAR RELATIONSHIPS BETWEEN RADIOCESIUM CONCENTRATIONS, EXPRESSED AS PICOCURIES PER GRAM DRY WEIGHT, OF VARIOUS TISSUES, ORGANS, AND OTHER BODY COMPARTMENTS OF WHITE-TAILED DEER FROM THE AEC SAVANNAH RIVER PLANT[1,2]

	Rumen contents	Feces	Liver	Spleen	Kidney	Lungs	Adrenal	Brain	Heart	Skeletal muscle	Whole-body homogenate
Rumen contents	1.00	0.69**	0.92**	0.77**	0.74**	0.82**	0.48	0.51	0.60*	0.48	0.53*
Feces	13	1.00	0.33	0.54	0.88**	0.67*	0.23	0.44	0.34	0.31	0.67*
Liver	11	10	1.00	0.93**	0.96**	0.91**	0.86**	0.86**	0.93**	0.92**	0.85**
Spleen	15	12	14	1.00	0.90**	0.91**	0.78**	0.85**	0.95**	0.86**	0.85**
Kidney	12	11	12	14	1.00	0.93**	0.51	0.75**	0.80**	0.75**	0.79**
Lungs	15	13	13	15	14	1.00	0.56*	0.89**	0.79**	0.71**	0.70**
Adrenal	15	12	12	15	14	15	1.00	0.81**	0.87**	0.83**	0.75**
Brain	14	11	12	14	14	14	14	1.00	0.89**	0.96**	0.86**
Heart	14	11	13	15	13	14	14	13	1.00	0.94**	0.90**
Skeletal muscle	14	13	11	13	12	13	13	13	12	1.00	0.91**
Whole-body homogenate	15	12	12	14	14	14	14	14	13	13	1.00

[1] Numbers below the diagonal indicate the number of observations contributing to the respective correlation analyses.

[2] Single and double asterisks indicate significant correlations at the 0.05 and 0.01 probability levels, respectively.

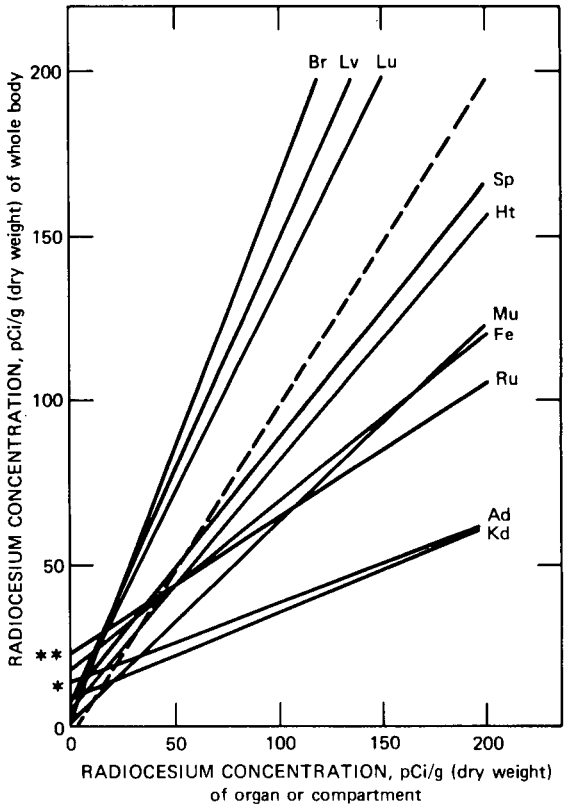

Fig. 2 Changes in the concentrations of radiocesium in several tissues, organs, and other body compartments of white-tailed deer from the AEC Savannah River Plant, as related to increasing whole-body concentrations. Each continuous line represents a statistically significant linear fit. The dotted line represents a plot for the condition when radiocesium concentration in a particular body compartment would be equal to that in the average whole-body homogenate. Regression coefficients and coefficients of determination for these relationships are given in Table 2. Single and double asterisks designate Y-intercepts that are significantly different from zero at the 0.05 and 0.01 probability levels, respectively. Br, brain; Lv, liver; Lu, lung; Sp, spleen; Ht, heart; Mu, skeletal muscle; Fe, feces; Ru, rumen contents; Ad, adrenals; and Kd, kidney.

content at rates that were less than that of the whole body. The remaining compartments, especially adrenal and kidney tissue, increased in radiocesium content at relatively greater rates than the whole body.

Only adrenal tissue and rumen contents showed Y-intercept values that differed significantly from zero (Fig. 2). Values for the Y-intercepts, slopes, and coefficients of determination (r^2) for these relationships are presented in Table 2, as are similar values for linear relationships between these same body

TABLE 2

REGRESSION ANALYSES OF THE VARIATION IN RADIOCESIUM CONCENTRATIONS OF WHOLE-BODY HOMOGENATES AND SKELETAL-MUSCLE SAMPLES FROM WHITE-TAILED DEER (AEC SAVANNAH RIVER PLANT) AS FUNCTIONS OF RADIOCESIUM CONCENTRATIONS OF VARIOUS OTHER BODY COMPARTMENTS

Body compartment	Skeletal muscle				Whole-body homogenates			
	F (df)	Y-intercept	Slope	r^2	F (df)	Y-intercept	Slope	r^2
Rumen contents	3.63(1,12)[1]	42.66**[2]	0.53	0.23	5.18(1,13)*	23.15**	0.41*	0.29
Feces	1.17(1,11)	43.73	1.08	0.10	8.23(1,10)*	18.36	0.51*	0.45
Liver	48.59(1,9)**	21.00*	2.20*	0.84	26.02(1,10)**	10.35	1.42**	0.72
Spleen	31.83(1,11)**	15.51	1.17**	0.74	31.49(1,12)**	9.82	0.78**	0.72
Kidney	12.62(1,10)**	22.43	0.42**	0.56	20.80(1,12)**	11.42	0.29**	0.63
Lungs	11.44(1,11)**	17.79	3.38**	0.51	11.43(1,12)**	9.80	1.29**	0.49
Adrenal	25.30(1,11)**	29.22*	0.37**	0.70	15.30(1,12)**	15.85*	0.22**	0.56
Brain	159.37(1,11)**	−0.85	2.95**	0.94	34.58(1,12)**	5.55	1.66**	0.74
Heart	79.63(1,10)**	10.25	1.18**	0.89	46.91(1,11)**	7.77	0.75**	0.81
Whole-body homogenate	55.12(1,11)**	4.86	1.38**	0.83				
Skeletal muscle					55.12(1,11)**	3.33	0.60**	0.83

[1] All calculations are based on radiocesium concentrations expressed as pCi per gram dry weight of tissue.

[2] Single and double asterisks represent either significant treatment effects (F values), significant deviations from a Y-intercept of zero, or significant deviations from a slope of zero, at the 0.05 and 0.01 levels of probability, respectively.

compartments and skeletal muscle. Liver, adrenal tissue, and rumen contents showed Y-intercepts that were significantly greater than zero with respect to regressions against skeletal muscle. Excluding the relationships of skeletal muscle to feces and rumen contents, all the body compartments examined showed significant linear regressions against muscle and whole-body homogenates. All slopes were positive and differed significantly from zero. The levels of predictability varied greatly for these relationships, however, ranging from $r^2 = 0.94$ (brain—skeletal muscle) to $r^2 = 0.29$ (rumen contents—whole-body homogenate).

DISCUSSION

The relative radiocesium concentrations of the various organs, tissues, and other body compartments of the deer examined in this study may be compared with similar values published by other investigators for deer as well as for other mammalian species. Book, Connolly, and Longhurst (1972) were not able to show a correlation between fallout radiocesium concentrations of deer skeletal muscles and rumen contents, principally because of a seasonal fluctuation in the rumen radiocesium levels which was not reflected in the levels in the muscles. Since our deer were collected in several different seasons, such a seasonal variation might also have resulted in the failure of the rumen contents to show significant correlations with the radiocesium concentrations of skeletal muscles and several other body compartments (Table 1).

Owing to the highly uneven spatial distribution of radiocesium in the various Savannah River Plant habitats (Brisbin et al., 1974), deer probably receive periodic pulses of radiocesium in their diet, even within a given season, as they range throughout areas where vegetation varies widely in nuclide concentration. This would help to explain the failure of samples of rumen contents and feces to show significant correlations with many of the other body compartments since radiocesium concentrations of the gut contents would simply reflect the degree of contamination of the animal's more recent meals. Long-term averages of radiocesium intake would be reflected in the radionuclide concentrations of muscle, brain, and other organs.

Ekman and Greitz (1967) provide an extensive analysis of the orga- compartment contamination dynamics and the implications of such pulse as well as long-term continuous radiocesium dietary intake patterns in deer. These investigators indicate that the percent of total body burden per kilogram of muscle can decrease from 26.9 to 7.5% in 60 days after the cessation of continuous radiocesium intake. The fact that our deer showed a significant fit to a constant linear relationship between the radiocesium concentrations of skeletal muscle and the whole-body homogenate (Tables 1 and 2) suggests that on the SRP they generally do not encounter radiocesium-free diets for extended periods during any season. Apparently even those habitats which have not directly

received radiocesium-contaminated effluent releases still have fallout levels in their vegetation sufficiently high to allow the maintenance of the observed ratio between the radiocesium levels of the muscles and the total body burdens of the deer in such areas.

Several other studies of the intercompartmental distribution of radiocesium are confirmed by our findings that the radiocesium concentrations of skeletal muscle and kidneys are among the highest and those of the liver and bone are among the lowest of all compartments examined (Furchner, Trafton, and Richmond, 1964; Ekman and Greitz, 1967; Moiseyev et al., 1967; Plummer, [illegible]en, and Provost, 1967; Hakonson and Whicker, 1971b). Few such studies [illegible]ve examined adrenal tissue. However, when calculated on a wet-weight basis, skeletal muscle actually showed a higher radiocesium concentration than adrenal tissue (Table 3). Mule deer studied by Hakonson and Whicker (1971b) failed to show relatively high radiocesium concentrations in adrenal tissue following administration of single oral dosages of ^{134}Cs in drinking water. Data from Hakonson and Whicker (1971b), however, are only reported on a wet-weight basis. It is also possible that certain differences might arise owing to single laboratory-administered radionuclide dosages as opposed to body burdens acquired by feeding over extended periods on contaminated food resources in natural food chains.

Whole-body homogenate of the deer averaged 32.11 pCi radiocesium/g (dry weight) (Fig. 1). The dry-weight/wet-weight ratios of approximately 80 samples of this homogenate averaged 30.87%; the live deer thus contained whole-body radiocesium burdens that averaged 9.91 pCi/g (wet weight). This value is quite a bit lower than the corresponding figure for skeletal muscle, which averaged 16.52 pCi/g (wet weight) (Table 3). This would suggest that the use of radiocesium data from deer-muscle samples, compared with whole-body counts of such smaller herbivores as insects, mice, or rabbits (Jenkins and Fendley, 1968), tends to overestimate the contamination levels of the deer relative to the other species being considered.

As shown in Table 2, skeletal muscle would make the best predictor of whole-body burdens of radiocesium in these deer, using the regression equation defined by the coefficients presented there ($r^2 = 0.83$). Care should be taken, however, before such a regression equation is used to predict whole-body [illegible]dens of deer from skeletal-muscle samples, unless thigh musculature is used. [illegible]fferent skeletal muscles of reindeer may show different patterns of radiocesium accumulation following orally administered nuclide doses (Ekman and Greitz, 1967). However, as Ekman and Greitz point out, such differences between different skeletal muscles decrease with time. Since our data are derived from deer exposed to long-term continuous radiocesium uptake, this factor probably did not contribute an important source of error. The procedure described by Rabon and Johnson (1973) for the indirect field estimation of radiocesium concentrations in deer muscle could also, within the limits of error

described by those investigators, form a basis for the application of the predictive relationships described in the present study.

Radiocesium contents of the skeletal muscles were nearly three times as high as those reported by Rabon (1968) for muscle samples from SRP deer during the winter season when, according to that investigator, body burdens are expected to be the greatest. Our values for SRP deer skeletal muscle were still considerably lower than those radiocesium values reported by other workers for white-tailed deer from fallout-contaminated habitats of the southeastern lower coastal plain (Jenkins and Fendley, 1968; Jenkins and Fendley, 1971). Data presented by Jenkins and Fendley (1968) for radiocesium concentrations in rumen contents of southeastern deer are not directly comparable to those obtained in this study since the former are not presented on a dry-weight basis and no reliable dry/wet conversion factors are available for such rumen contents whose percentage water composition may vary widely. Our average dry-weight value of 24.29 pCi radiocesium/g rumen contents is again nearly threefold greater than comparable values given by Rabon (1968) for the rumen contents of SRP deer. The deer in our study apparently spent more time in proximity to the more highly contaminated SRP habitats than those studied by Rabon (1968) from the same general area.

The radiocesium concentrations found in this study suggest a trophic-level concentration factor of 2.27 for the ratio of muscle to rumen-content radiocesium levels calculated on a dry-weight basis. However, since the relationship between muscle and rumen-content radiocesium levels was not significant (Tables 1 and 2), this ratio could vary considerably between samples. The value of 2.27, however, is close to a concentration factor of 3.3 reported by Jenkins and Fendley (1968) for deer contaminated with fallout radiocesium and calculated on a wet-weight basis. Considering whole-body homogenate rather than muscle radiocesium levels, the concentration factor shown by our deer with respect to their food supply was only 1.32. Moreover, the relationship between these two compartments was statistically significant (Tables 1 and 2).

An important use that can be made of such data as have been collected in this study is to ask which of the various tissues, organs, or other body compartments would best predict the pattern and levels of radiocesium distribution in all other compartments of the deer's body. Such a question is often of great practical importance when financial or logistic restrictions make impossible to sample and analyze all body compartments from each individual animal. For such evaluations feces and rumen contents would obviously not make suitable predictors of other compartments because their radiocesium concentrations are not well correlated with concentrations in some of the other body parts (Table 1). Therefore these two compartments, along with whole-body homogenate, which is so difficult to prepare that it is an unsuitable predictor, were eliminated from consideration in this regard.

The values of the other organs or tissues can be quantified by a predictive index (P.I.) whose numerical value is directly proportional to the usefulness of

the compartment in question as a predictor of the radiocesium contents of the other compartments. This P.I. is greatest for those body compartments which show the highest coefficients of correlation (r) with all others. That is, $P.I._k$ is directly proportional to $\Sigma_{j=1}^{t} z_{j \cdot k}$, where $P.I._k$ is the predictability index of the k*th* compartment, z is the standard normal deviate transformation (Steel and Torrie, 1960) of the coefficient of correlation between the j*th* and k*th* compartments, and t is the total number of body compartments.

However, when the merits of a given compartment are being evaluated as a predictor of total-body radiocesium distribution and concentration, it is most important for the compartment in question to show good predictability for those others which, by virtue of their (1) large size or (2) high radiocesium content per gram, contain relatively larger proportions of the body's total radiocesium burden than others. For example, it would be essential for any predictor of radiocesium distribution in deer bodies to show a high correlation with levels found in skeletal muscle since this is where over 75% of the total body burden of this radionuclide is found (Hakonson and Whicker, 1971b). Therefore each value for $z_{j \cdot k}$ should be weighted for the factors of (1) relative size and (2) radiocesium concentration per gram of the j*th* compartment. Thus we can now define

$$P.I._k = \sum_{j=1}^{t} \left(P_j \frac{C_j}{C_{WB}} z_{j \cdot k} \right)$$

where t, $P.I._k$, and $z_{j \cdot k}$ are as previously defined, P_j is the percentage of total-body mass comprised by the j*th* compartment on a wet-weight basis, C_j is the radiocesium content (pCi/g wet weight) of the j*th* compartment, and C_{WB} is the radiocesium content (pCi/g wet weight) of the whole body. The expression $P_j(C_j/C_{WB})$ thus represents that proportion of the animal's total body burden which is found in the j*th* compartment.

In our case, values for $z_{j \cdot k}$ were calculated by transforming the correlation coefficients presented in Table 1, and values for P_j were taken from Hakonson and Whicker (1971a,b). Values for C_j were taken from the mean values of the present study for picocuries of radiocesium per gram dry weight and were converted to a wet-weight basis with dry/wet conversion factors for the tissues and organs of other mammals (Altman and Dittmer, 1964). The dry/wet ratio of renal tissue was assumed to be the same as that given for the spleen. The value of 9.91 pCi radiocesium/g (wet weight) was used for the whole-body burdens of the deer in this study.

Relative values and rankings with respect to P.I. values, P_j, average C_j/C_{WB}, and average $z_{j \cdot k}$ for each of nine body compartments of the deer are shown in Table 3. These rankings of P.I. numbers indicate that skeletal muscle is the best overall predictor of the pattern and levels of radiocesium distribution in the deer's body. This is undoubtedly due to the fact that skeletal muscle comprises by far the largest proportion of the total body mass of any of the compartments

TABLE 3

RANKING* OF NINE BODY COMPARTMENTS OF WHITE-TAILED DEER FROM THE AEC SAVANNAH RIVER PLANT

Body compartment	P.I.†	P_j‡	$\bar{x}z_{j \cdot k}$§	$\frac{\bar{x}C_j}{\bar{x}C_{WB}}$¶**
Muscle	214.08 (1)	47.0 (1)	1.38 (4)	1.67 (2)
Brain	159.86 (2)	0.30 (6)	1.37 (6)	0.40 (9)
Heart	145.53 (3)	0.85 (5)	1.45 (3)	1.08 (4)
Liver	136.98 (4)	1.90 (3)	1.57 (1)	0.45
Spleen	113.44 (5)	0.26 (7–8)	1.48 (2)	0.69
Adrenal	97.22 (6)	0.01 (9)	1.10 (8)	1.43 (3)
Kidney	92.89 (7)	0.26 (7–8)	1.38 (5)	1.73 (1)
Lungs	84.68 (8)	1.80 (4)	1.37 (7)	0.41 (8)
Bone	44.28 (9)	10.30 (2)	0.73 (9)	1.04 (5)

*Ranking was done with respect to the relative values for predictability index (P.I.), percentage of total-body mass comprised (P_j), average $z_{j \cdot k}$ value, and ratio of average compartment radiocesium content per gram wet weight (C_j) to the average whole-body radiocesium content per gram wet weight (C_{WB}). Numbers in parentheses indicate relative orders of ranking from highest (1) to lowest (9) values.

†See text for derivation.

‡From Hakonson and Whicker (1971a) and Hakonson and Whicker (1971b).

§Calculated from Table 1 of this study.

¶Calculated from values taken from this study and dry/wet conversion ratios from Altman and Dittmer (1964).

**Calculated as 9.91 pCi/g wet weight (see text).

listed, and, in addition, skeletal muscle showed the second highest wet-weight radiocesium concentration per gram. Given these two facts, it would probably have been intuitively obvious that skeletal muscle was the most important predictor, even without going through the described analyses and calculations. What would probably not have been intuitively obvious, however, would have been the relative importances of the other compartments in the P.I. rankings for second, third, and fourth positions. The second highest P.I. ranking, for example, was shown by the brain, which ranked sixth, sixth, and ninth, ove in the proportion of body mass, average $z_{j \cdot k}$ value, and concentration per gra categories, respectively (Table 3). The high ranking of brain in this case seems to be attributable to the fact that it showed a higher coefficient of correlation ($r = 0.96$) with skeletal muscle than any other body compartment.

Although tongue was not examined in the present study, Plummer, Pullen, and Provost (1967) indicate that this organ can be a useful predictor of radiocesium levels in other body compartments. In a real sense, however, tongue may be considered as simply a sample of skeletal muscle and therefore accorded

an appropriate first-place P.I. ranking, bearing in mind possible differences that different skeletal muscles may show in their patterns of radiocesium accumulation (Ekman and Greitz, 1967). The ease with which a tongue can be sampled from a deer carcass, however, would tend to make it a particularly appropriate sample of skeletal muscle to use.

The importance of adequately ranking the predictability value of the second, third, and fourth positions of P.I. index values lies in possible future needs to designate a single deer organ or tissue sample from which to estimate the body content and distribution of more than just one radionuclide or other environmental contaminant. Processing these same deer samples for plutonium, for example, might have shown bone, liver, brain, or spleen to have the highest P.I. values for this latter nuclide, with muscle, in this case, possibly ranking quite low. If this should prove to be the case, then designating which tissue or organ should be sampled to estimate both plutonium and radiocesium would require an optimization of the average P.I. values for each of these radionuclides for each compartment of the body. Then brain or spleen might prove to be the best single sample for analytical and predictive procedures for both these nuclides, representing a compromise between their respective patterns of distribution within the deer's body.

Interspecies inferences of patterns of radiocesium distribution between different body organs and tissues should be approached with caution because of the important differences in pattern that have been demonstrated between such species as sheep, goats, and deer (Longhurst, Goldman, and Della Rosa, 1967; Ekman and Greitz, 1967). Ekman and Greitz (1967) report that differences between reindeer and goats can be shown more clearly with respect to liver radionuclide concentrations than with respect to concentrations in other tissues, such as skeletal muscle. To be completely understood, we must interpret these interspecies differences on the basis of a firm prior knowledge of intraspecies variability in organ-distribution patterns. Variability of this type might be attributable to such factors as age, sex, and body size. The evaluation of these factors, however, will require the examination of still larger population samples.

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REFERENCES

Altman, P. L., and D. S. Dittmer (Comps. and Eds.), 1964, *Biology Data Book,* Federation of American Societies for Experimental Biology, Washington, D. C.

Anderson, G. E., J. B. Gentry, and M. H. Smith, 1973, Relationships Between Levels of Radiocesium in Dominant Plants and Arthropods in a Contaminated Streambed Community, *Oikos,* **24**: 165-170.

Book, S. A., G. E. Connolly, and W. M. Longhurst, 1972, Fallout ^{137}Cs Accumulation in Two Adjacent Populations of Northern California Deer, *Health Phys.,* **22**: 379-385.

Brisbin, I. L., Jr., et al., 1974, Patterns of Radiocesium in the Sediments of a Stream Channel Contaminated by Production Reactor Effluents, *Health Phys.,* **27**: 19-27.

Ekman, L., and U. Greitz, 1967, Distribution of Radiocesium in Reindeer, in *Radioecological Concentration Processes,* B. Aberg and F. P. Hungate (Eds.), pp. 655-673, Pergamon Press, Inc., New York.

Furchner, J. E., G. A. Trafton, and C. P. Richmond, 1964, Distribution of Cesium-137 After Chronic Exposure in Dogs and Mice, *Proc. Soc. Exp. Biol. Med.,* **116**: 375-378.

Hakonson, T. E., and F. W. Whicker, 1971a, The Contribution of Various Tissues and Organs to Total Body Mass in the Mule Deer, *J. Mammalogy,* **52**: 628-630.

——, and F. W. Whicker, 1971b, Tissue Distribution of Radiocesium in the Mule Deer, *Health Phys.,* **21**: 864-866.

Jenkins, J. H., and T. T. Fendley, 1971, Radionuclide Biomagnification in Coastal-Plain Deer, in Radionuclides in Ecosystems, D. J. Nelson (Ed.), pp. 116-122, USAEC Report CONF-710501-P1.

——, and T. T. Fendley, 1968, The Extent of Contamination, Detection, and Health Significance of High Accumulations of Radioactivity in Southeastern Game Populations, *Proc. Annu. Conf. Southeast. Ass. Game Fish Comm.,* **22**: 89-95.

——, and E. E. Provost, 1964, The Population Status of the Larger Vertebrates on the Atomic Energy Commission Savannah River Plant Site, Final Report, USAEC Report TID-19562.

Longhurst, W. M., M. Goldman, and R. J. Della Rosa, 1967, Comparison of the Environmental and Biological Factors Affecting the Accumulation of ^{90}Sr and ^{137}Cs in Deer and Sheep, in *Radioecological Concentration Processes,* B. Aberg and F. P. Hungate (Eds.), pp. 635-648, Pergamon Press, Inc., New York.

Marter, W. L., 1970, Radioactivity in the Environs of Steel Creek, USAEC Report DPST-70-435, Savannah River Laboratory.

Moiseyev, A. A., et al., 1967, Distribution of Gamma-Radiation Tissue Doses of ^{137}Cs Incorporated into the Body of a Reindeer (*Rangifer tarandus*), in *Radioecological Concentration Processes,* B. Aberg and F. P. Hungate (Eds.), pp. 649-654, Pergamon Press, Inc., New York.

Norris, R. A., 1963, *Birds of the AEC Savannah River Plant Area,* Contribution XIV from the Charleston Museum, Charleston, S. C.

Plummer, G. L., T. M. Pullen, Jr., and E. E. Provost, 1967, Cesium-137 and a Population Georgia White-Tailed Deer, in Symposium on Radioecology, D. J. Nelson and F. C. Evans (Eds.), pp. 609-615, USAEC Report CONF-67053.

Rabon, E. W., 1968, Some Seasonal and Physiological Effects on ^{137}Cs and ^{89,90}Sr Content of the White-Tailed Deer (*Odocoileus virginianus*), *Health Phys.,* **15**: 37-42.

——, and J. E. Johnson, 1973, Rapid Field Monitoring of Cesium-137 in White-Tailed Deer, *Health Phys.,* **25**: 515-516.

Steel, R. G. D., and J. H. Torrie, 1960, *Principles and Procedures of Statistics,* McGraw-Hill Book Company, New York.

Urbston, D. F., 1967, Herd Dynamics of a Pioneer-Like Deer Population, *Proc. Annu. Conf. Southeast. Ass. Game Fish Comm.,* **21**: 42-50.

RELATIONSHIP BETWEEN POTASSIUM INTAKE AND RADIOCESIUM RETENTION IN THE REINDEER

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ABSTRACT

The effect of dietary potassium on radiocesium retention was studied in reindeer fed winter diets of lichens. Potassium added to the diet markedly decreased radiocesium retention; this suggests that seasonal changes in cesium retention observed earlier in reindeer might be caused largely by nutritional factors. Data indicate that a 20-fold increase in dietary potassium results in a 2-fold decrease in radiocesium retention.

In an earlier study we described the movement of fallout radiocesium through the arctic food chain: lichens → reindeer and caribou → man, wolf, and fox (Holleman, Luick, and Whicker, 1971). Radiocesium concentrations in lichens are relatively constant, decaying with an effective half-time of 3 to 8 years (Martin and Koranda, 1971). But radiocesium kinetics in the herbivore and carnivore trophic levels of the food chain may be quite variable and may depend on the annual season. For example, during the summer months cesium turnover rates in reindeer are two to three times higher than values during winter (Holleman et al., 1971). Both potassium intake and environmental temperature have been suggested as factors that influence cesium turnover in animals (Mahlum and Sikov, 1968) and man (Furchner, Richmond, and Drake, 1965). The rates at which elements are eliminated by animals also depend on intrinsic biological factors, such as body size, age, sex, physical activity, and physical condition (Reichle, Dunaway, and Nelson, 1970). Although cesium and potassium have similar chemical and physiological properties, a ninefold increase in potassium intake resulted in only a twofold decrease in cesium retention in rats (Wasserman and Comar, 1961). If a similar relationship between potassium intake and cesium retention existed for ruminants, the relatively minor changes in potassium concentration occurring in normal livestock diets would not significantly alter cesium retention. The diet and the potassium intake of

free-grazing reindeer and caribou are highly dependent on season, however. During the winter months, September to May, the diet consists largely of lichens, which have a low potassium content. The summer diet of deciduous shrubs, sedges, and grasses has a relatively high potassium content. Therefore, potassium intake by reindeer and caribou may be highly dependent on season, assuming that during winter potassium is obtained only from plant sources and not from such sources as mineral licks. This study was undertaken to determine the effects of potassium intake on cesium retention in reindeer when the animals were maintained on a winter diet of lichens.

METHODS AND MATERIALS

The lichens used for this study were collected by hand from a mountain tundra range about 15 miles south of the Cantwell Reindeer Research Station, Cantwell, Alaska. Foreign debris was removed, and the lichens were divided into four batches. Each batch was sufficient to maintain one reindeer on an ad libitum feeding regime for approximately 35 days. Potassium (KCl) at three different concentrations was sprayed onto three batches. One batch served as the untreated control diet. Samples of each lichen batch were ashed and dissolved in nitric acid, and the solutions were then analyzed for potassium concentration by atomic absorption methods.

In 1967 the University of Alaska obtained several reindeer (*Rangifer tarandus sibericus*) from the Bureau of Indian Affairs model herd at Nome, Alaska. At present the Institute of Arctic Biology, University of Alaska, maintains a reindeer herd consisting of some of the original animals and their progeny. The four reindeer selected from the herd for this study were kept in individual pens (~10 by 10 m) and fed one of the four lichen diets ad libitum. Lichen consumption rates for each reindeer were calculated as the difference between amount fed and amount not eaten during each feeding period. Feeding periods ranged from 3 to 7 days in length. After a 10-day equilibration period on the four experimental diets, each reindeer was injected intravenously with 100 μCi of ^{134}Cs (^{134}CsCl) and whole-body counted for the gamma-ray-emitting isotope at periodic intervals for approximately 25 days thereafter. Details concerning the equipment and counting procedures have been published (Holleman, Luick, and Whicker, 1971).

The cesium retention data were analyzed by plotting the natural logarithm of the count rate vs. the time after injection of ^{134}Cs. The count rate was directly proportional to the ^{134}Cs body burden of the reindeer. The resulting curve was resolved into two exponential components by least-squares regression analysis and the conventional "peeling" process associated with multicomponent exponential elimination (Chew, 1971). The equation describing cesium retention was the sum of a fast exponential component and a slow exponential component:

$$\text{Retention} = Ae^{-at} + Be^{-bt} \quad (1)$$

where A and B = fractions of cesium eliminated by the fast and the slow components, respectively
e = Napierian base, 2.718
a and b = slopes of the two exponential components
t = time elapsed since the injection of cesium

Biological half-times for each of the exponential components were calculated as .693 divided by the respective slopes.

This study was conducted in March and April 1974. The average ambient temperature during the experimental period was −5.9°C.

RESULTS AND DISCUSSION

Data pertaining to the four reindeer used in this study and their lichen and potassium intakes are given in Table 1. Average lichen intakes for the four reindeer on a dry-weight basis ranged from 1.6 to 2.0% of body weight per day. These values were slightly less than might be expected for free-grazing reindeer (Holleman, Luick, and Whicker, 1971) or caribou (Hanson, Whicker, and Lipscomb, 1972) but agree well with previous ad libitum feeding trials of penned or restricted reindeer (Holleman and Luick, 1972) which involved animals from the Institute of Arctic Biology reindeer herd. The potassium intake for each animal was computed as the product of the average daily lichen-biomass intake and the potassium concentration of the lichens fed to that particular reindeer. Average daily intakes ranged from 0.84 to 16.0 g of potassium, a 20-fold range. This conceivably approximates the annual range of potassium intake for free-grazing reindeer and caribou (Holleman et al., 1971).

Retentions of ^{134}Cs after a single intravenous injection by the four experimental reindeer are shown in Fig. 1. Cesium retention is plotted as a percentage of the cesium body burden at the time of injection. Analysis of the curves yielded the values listed in Table 1 for the fast and slow components as described by Eq. 1.

There was no significant difference ($P < 0.05$) in the slopes of the fast components of cesium retention for reindeer 1, 2, and 3, but initial cesium retention for reindeer 4 (highest potassium intake) was significantly decreased. Previous studies (Holleman et al., 1971) indicating substantial variation in the slopes of the fast components for reindeer on identical diets confirmed that a larger sample of experimental animals is necessary to determine statistically the effect of potassium intake on the fast-elimination component. Although the effect of potassium intake on the initial retention of injected ^{134}Cs was unclear, an effect of increasing intake on the slow component was evident. The slope for the slow component ranged from 0.031 day^{-1} at the lowest potassium intake to 0.061 day^{-1} at the highest. The slopes of the slow components for the four

TABLE 1

FOOD AND POTASSIUM INTAKE AND RETENTION OF ^{134}Cs BY EXPERIMENTAL REINDEER

Variable	Experimental reindeer			
	1*	2	3	4
Sex	F	M	F	F
Age, years	7	3	4	8
Body weight, kg	94	95	88	96
Average lichen intake,† g/day	1554	1814	1737	1616
Potassium in lichen, mg/g	0.54	1.2	3.4	9.9
Average potassium intake, g/day	0.84	2.2	5.9	16.0
Slopes, day^{-1}				
Fast component‡	0.41 (0.025)	0.41 (0.047)	0.37 (0.022)	0.62 (0.028)
Slow component‡	0.031 (0.0011)	0.036 (0.00057)	0.043 (0.0013)	0.061 (0.0030)
Biological half-time of ^{134}Cs, day				
Fast component	1.7	1.7	1.9	1.1
Slow component	22.1	19.1	16.2	11.4
Intercepts, %				
Fast component	42.9	30.1	37.2	29.2
Slow component	57.1	69.9	62.8	70.8

*Animal on control diet.
†Lichens expressed on dry-weight basis.
‡Standard deviation given in parentheses.

intake rates were significantly different from each other ($P < 0.05$). Covariance analysis was used to determine significant differences in the slopes (Snedecor, 1962).

To investigate the relative effect of potassium intake on the retention of cesium by reindeer, we converted the data from absolute to relative values; i.e., the potassium intake rates were converted to units of relative increase in intake by standardizing the data with respect to the lowest intake rate. Likewise the slopes for the slow components were standardized with respect to the cesium retention associated with the lowest potassium intake. These data were plotted on logarithmic coordinates and fitted by least-squares analysis. The resulting least-squares line, the data, and the results of similar studies by Wasserman and Comar (1961) on rats are plotted in Fig. 2. The equations for the relationship

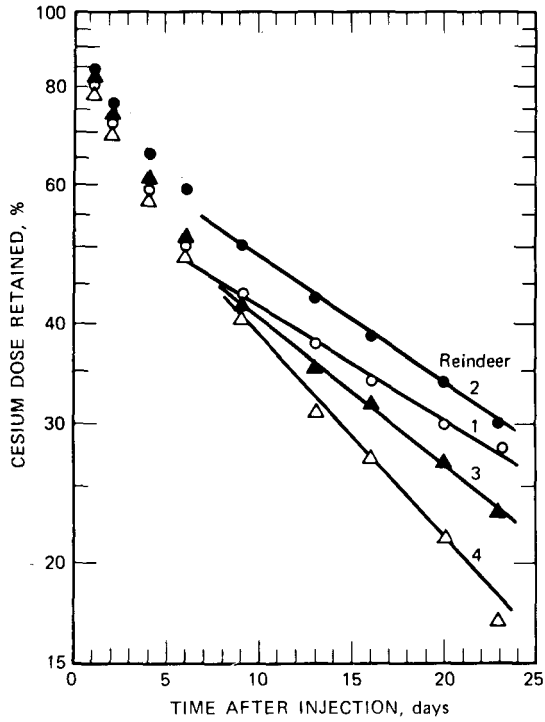

Fig. 1 Retention of cesium as a function of time after a single intravenous injection of ^{134}Cs in four experimental reindeer.

between relative increase in potassium intake (Y) and relative decrease in cesium retention (X) give $Y = X^{4.2}$ for our data ($r = 0.97$) and $Y = X^{3.2}$ for the rat data. There were no significant differences in the two equations at the 95% confidence level. The data for rats were included for comparison since similar data for other species of mammals were not available.

Previous data indicated a two- to threefold decrease in cesium retention for free-grazing reindeer from winter to summer (Holleman et al., 1971). A decrease in cesium retention due solely to an increase in potassium intake would necessitate a 20- to 100-fold increase in intake from winter to summer (Fig. 2). This could be achieved by consuming food of relatively higher potassium content, by increasing food intake, and/or by utilizing high-potassium mineral licks. Thus the potassium concentration in the untreated lichens in this study was ~0.5 mg/g of dry lichen. In contrast, the concentration of potassium in the summer diets of free-grazing reindeer and caribou, which consist chiefly of green vegetation, may be 10 times as great (Holleman et al., 1971). Also, studies of body-water turnover (Cameron and Luick, 1972) and food intake using esophageal fistulated reindeer (White et al., 1974) suggest an increase in food

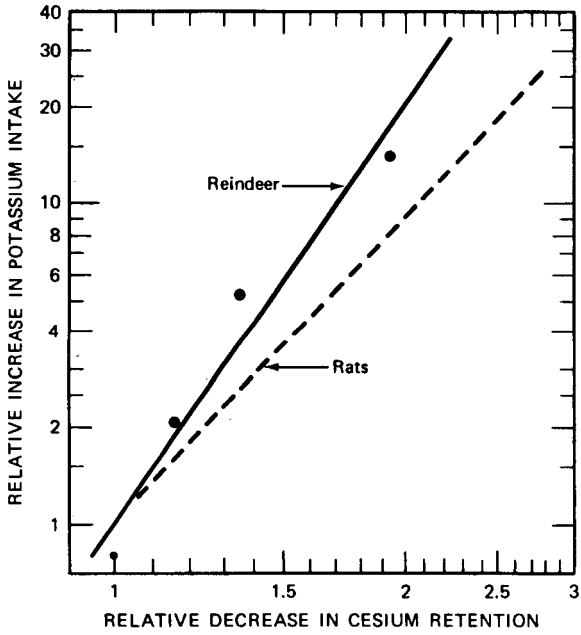

Fig. 2 Effect of potassium intake on the retention of ^{134}Cs in reindeer and rats. Experimental points are reindeer data; the curve is plotted on logarithmic coordinates and fitted by least-squares analysis.

intake in summer as compared with winter for free-grazing reindeer. This could be attributed to increased activity, growth, and reproductive activities. Lastly, mineral licks would be more available and possibly would be used to a greater extent during summer when the reindeer and caribou graze on ranges that are free of snow and ice.

ACKNOWLEDGMENT

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REFERENCES

Cameron, R. D., and J. R. Luick, 1972, Seasonal Changes in Total Body Water, Extracellular Fluid, and Blood Volume in Grazing Reindeer, *Can. J. Zool.*, **50**: 107-116.

Chew, R. M., 1971, The Excretion of ^{65}Zn and ^{54}Mn as Indices of Energy Metabolism of *Peromyscus polionotus*, *J. Mammalogy*, **52**: 337-350.

Furchner, J. E., C. Richmond, and G. H. Drake, 1965, Effects of Environmental Temperature on the Retention of Chronically Administered ^{137}Cs, *Health Phys.*, **11**: 623.

Hanson, W. C., F. W. Whicker, and J. F. Lipscomb, 1972, Lichen Forage Ingestion Rates of Free-Roaming Caribou Estimated with Fallout Cesium-137, in *Proceedings of the First International Reindeer and Caribou Symposium*, J. Luick, P. Lent, R. White, and D. Klein (Eds.), University of Alaska, Fairbanks, in press.

Holleman, D. F., and J. R. Luick, 1972, Radiocesium Cycling in Reindeer/Caribou, in *Proceedings of the First International Reindeer and Caribou Symposium*, J. Luick, P. Lent, R. White, and D. Klein (Eds.), University of Alaska, Fairbanks, in press.

——, J. R. Luick, and F. W. Whicker, 1971, Transfer of Radiocesium from Lichen to Reindeer, *Health Phys.*, **21**: 657-666.

lum, D. D., and M. R. Sikov, 1968, Effect of Environmental Temperature and Potassium Consumption on Cesium-137 Metabolism in the Rat, *Health Phys.*, **15**: 541-543.

Martin, J. R., and J. J. Koranda, 1971, Recent Measurements of Cesium-137 Residence Time in Alaskan Vegetation, in *Radionuclides in Ecosystems*, Proceedings of the Third National Symposium on Radioecology, D. J. Nelson (Ed.), USAEC Report CONF-710501-P1, Vol. 1, pp. 108-115, U. S. Atomic Energy Commission, Oak Ridge National Laboratory, and The Ecological Society of America.

Reichle, D. E., P. B. Dunaway, and D. J. Nelson, 1970, Turnover and Concentration of Radionuclides in Food Chains, *Nucl. Safety*, **11**: 43-55.

Snedecor, G. W., 1962, *Statistical Methods*, Iowa State University Press, Ames, Iowa.

Wasserman, R. H., and C. L. Comar, 1961, The Influence of Dietary Potassium on the Retention of Chronically Ingested ^{137}Cs in the Rat, *Radiat. Res.*, **15**: 70-77.

White, R. G., et al., 1974, Ecology of Caribou at Prudhoe Bay, Alaska, Tundra Biome Prudhoe Bay Report, U. S. International Biological Project, No. 5311.

SEASONAL AND ANNUAL VARIATIONS IN THE QUANTITIES OF NITROGEN, POTASSIUM, PHOSPHORUS, MAGNESIUM, CALCIUM, AND MANGANESE REACHING THE FOREST FLOOR AS MAST IN PENNSYLVANIA AND VERMONT FORESTS

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ABSTRACT

Mast production was measured at monthly intervals for 5 years in two forests near Linesville, Pa., for 2 years in two parts of the virgin Tionesta Natural Area near Kane, Pa., and for 3 years in four plots at two altitudes in the Green Mountain National Forest in the vicinity of Manchester, Vt. Approximate concentrations of N, K, P, Mg, Ca, and Mn in selected parts of the species collected were determined from the literature and from spectrophotometric and combustion analyses. The most abundant of these elements reaching the forest floor as edible mast was nitrogen on all sites; the least abundant on all sites was manganese. The relative abundance of the other four elements varied from site to site. Geographic variations in the quantities of particular elements exceeded two orders of magnitude. Annual variations in the quantities of particular elements exceeded one order of magnitude in Vermont but were about half an order of magnitude in Pennsylvania. Seasonal variations were closely related to the species composition and size of the total mast crop on each site. The spatial distribution of mast reaching the forest floor was uneven and variable from year to year, especially on the Pennsylvania sites, where 60 to 80 samples were required to achieve a standard error of the mean equal to approximately 15% of the mean. Some observations concerning the fate of this mast on the study sites are presented.

Mast production is an aspect of forest ecology which is of interest to biologists from a wide variety of backgrounds and disciplines. Several decades of research have produced hundreds of papers reporting observations and experimental results from many parts of the world. A number of investigators have measured fruit or seed production of individual species and related it to crown size, age, diameter at breast height (dbh), stand density, etc. (Downs and McQuilkin, 1944; Cypert and Webster, 1948; Fowells and Schubert, 1956; Reid and

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Goodrum, 1957; Goodrum, Reid, and Boyd, 1971). Others have related the seed production of individual trees to soil conditions and a variety of climatological events (Matthews, 1955, 1963; Sarvas, 1955, 1968; Gysel, 1957; Minckler and Janes, 1965; Hawkins, 1966; Sharp and Sprague, 1967; van Vredenburch and LaBastide, 1969). Some investigators have expended considerable effort to find ways of manipulating individual trees or their immediate environments to increase fruit or seed production (Puritch and Vyse, 1972). Many have estimated and reported the relative size and variation of mast crops over extended periods of time through the use of indexes and scales using descriptive terms (good, fair, [illegible]) or numbers (Baldwin, 1942; Uhlig and Wilson, 1952; Sharp, 1958; Zasada and Viereck, 1970). Few investigators, however, have reported measurements per unit area of total mast crops or of the parts (endosperm, fleshy mesocarps, etc.) that are commonly ingested by birds or mammals (Gorecki and Gebczynska, 1962; Ovington and Murray, 1964; Myczkowski, 1967; Gysel, 1971), and apparently only Gosz, Likens, and Bormann (1972) have reported the macronutrient content of mast crops per unit area. Therefore we designed and performed (in conjunction with the long-term population study of Tryon and Snyder, 1973) a 5-year study to ascertain the dynamics, energetics, and nutritional aspects of fruit and seed production in virgin and second-growth forests in the northeastern United States.

The work reported here focuses on the seasonal and annual variations in the total quantities of selected nutrients reaching the forest floor as mast. Discussions of the energetics and variability in species composition of mast crops and of the relationship between mast crops and eastern chipmunk populations (*Tamias striatus*) will be included in papers now in preparation.

STUDY AREAS AND METHODS

Measurements were made on eight different sites, four in northwestern Pennsylvania and four in Vermont. Two of the Pennsylvania sites, referred to by Tryon and Snyder (1973) as the "Lab" site and the "Farm" site, were in a transition zone between the beech–maple forest region, mixed Mesophytic forest region, and hemlock–white pine–northern hardwoods region (Braun, 1950). The Lab site was a 4.65-ha portion of the University of Pittsburgh's [illegible]atuning Laboratory of Ecology, elevation 300 m. Second growth *Prunus* [illegible]*otina, P. virginiana, Quercus velutina,* and *Q. alba* dominated the canopy and shrub layer, although several species of *Cornus* were conspicuous in the shrub layer. *Circaea quadrisulcata, Rubus* sp., *Podophyllum peltatum, Parthenocissus quinquefolia, Impatiens capensis,* and *Maianthemum canadense* were abundant herbs, but *Prunus* seedlings and saplings were the most numerous and widespread small plants. Budbreak occurred about May 1 for the dominant trees.

The Farm site, a 3.28-ha rectangular plot near the center of a 20-ha woodlot, 4 km southeast of the Lab site, was dominated by *Fagus grandifolia, Acer*

saccharum, and *Prunus serotina* and was older and more diverse than the Lab site. Small trees outnumbered other herbaceous plants, but *Circaea quadrisulcata, Viola* sp., *Galium* sp., *Mitchella repens,* and *Trillium* sp. were frequently encountered. The elevation and dates of budbreak were similar to those of the Lab site.

The other Pennsylvania sites (Tionesta 1 and 2) were in the Allegheny section of the northern Appalachian Highlands division of the hemlock–white pine–northern hardwoods region (Braun, 1950), in the Tionesta natural area of the Allegheny National Forest, about 150 km east of the Lab site. Both were relatively level 1.44-ha squares atop 90-m high ridges at elevations near 600 m. Their canopies were dominated by *Fagus grandifolia, Acer saccharum,* and *Tsuga canadensis* in that order. *Prunus serotina* trees approximately 1 m dbh also contributed significantly to the canopy of Tionesta 2. The shrubs and herbs of both areas were sparse except in the vicinity of dead or fallen trees. Budbreak occurred about May 15.

The Vermont sites consisted of four 1.44-ha squares at two different elevations in the Green Mountain National Forest, east and south of Danby, Vt. (Tryon and Snyder, 1973). All sites were in the New England section of the northern Appalachian Highlands division of the hemlock–white pine–northern hardwoods region (Braun, 1950). At an elevation of 244 m (800 ft), the lower plots (Vermont 800-1 and Vermont 800-2) were in Braun's hemlock–hardwoods area. Sloping slightly to the west and shaded from morning sun by an easterly ridge, these plots had canopies dominated by *Fagus grandifolia, Acer rubrum,* and *A. saccharum.* Also conspicuous were *Tsuga canadensis, Betula lenta,* and *B. papyrifera.* Large segments of the forest floors were devoid of herbaceous vegetation, but tree seedlings and a variety of ferns, club mosses, and flowering plants were present. Budbreak occurred in mid-May.

The higher plots (Vermont 2800-1 and 2800-2), elevation 853 m (2800 ft), were in Braun's spruce–hardwoods area facing the west and southeast, respectively. Both canopies were dominated by *Betula lutea* and *Abies balsamea,* although *Picea rubens, B. papyrifera,* and *Acer pensylvanicum* were common. Herbaceous and shrubby vegetation was denser than on the Vermont 800 sites, *Viburnum alnifolium* being the most conspicuous small plant. Ferns and club mosses were nearly absent, but mosses, including *Sphagnum,* occurred in large patches. Budbreak occurred in late May.

For additional information on the study sites see Hough and Forbes (1943) and Graybill (1970).

In the early years of this investigation, the fruit production of the Pennsylvania sites was estimated by establishing two categories of fruits and measuring each separately during six 33-day intervals between late April and mid-November. Fruits usually produced on or within 1.3 m of the forest floor were distinguished from fruits usually produced in the higher understory and canopy and were sampled by a harvest method employing randomly placed sets

of 12 adjacent 0.5- by 4.0-m quadrats. However, the fruits produced by this category amounted to such a small percentage of the total (0 to 5% in calories) that sampling was discontinued and the category was ignored.

Fruits produced by taller plants were sampled with randomly placed 1-m-square, liquid-filled samplers adapted from Thompson and McGinnes (1963) and Ward and Leonard (1968). For details of construction and placement in the field see Graybill (1970). A total of 297 samplers were placed in the field: 81 on the Lab, 64 each on the Farm and Tionesta 1 and 2, and 6 each on the four Vermont sites. Initially, a dekaliter of water and 120 ml of Formalin (for killing birds and mammals) were poured into each sampler, creating a formalin pool that increased in volume after a few rain showers. In Pennsylvania, sampling was begun in August 1968, and samplers were serviced regularly at 2-week intervals until November of that year and between late April and mid-November of subsequent years. Each servicing included the addition of 120 ml of Formalin to each sampler. In the spring and summer, litter and fruits were removed with a 1-mm mesh net at the end of each 33-day interval. In the fall, when litterfall and fruitfall were heavy, they were removed twice during each interval. In Vermont the sampling method was generally similar to that in Pennsylvania except that sampling did not begin until August in 1970 and June in 1971 and 1972, and litter and fruits were removed at 1-week intervals during the fall period.

Litter and fruits removed from the samplers were carried to the laboratory in labeled grocery or plastic bags. There they were hand sorted either immediately (1968 to 1971 Pennsylvania samples) or after a period of storage at $-20^{\circ}C$ (1972 Pennsylvania samples and all Vermont samples). All fruit and seed parts were separated from leaves, branches, and other litter and then dried at $80^{\circ}C$ for 48 hr; identified as to species; sorted, counted, pooled by location and time interval; and stored at room temperature in plastic bags.

Dry-weight standards were established as follows for each fruit part collected during each 33-day interval. Samples of berries and fruits with fleshy mesocarps (which were often crushed while being transported from the samplers to the laboratory) were picked by hand at arbitrarily chosen locations on the Pennsylvania study areas in 1968 and 1969. In the laboratory the samples were counted and rinsed with distilled water. If they contained large stones, the fleshy parts were carefully stripped from the stones with stainless-steel knives, dried on glass petri dishes at $80^{\circ}C$, weighed, and stored in plastic bags at room temperature. Dry-weight standards for fruits without fleshy parts were determined from subsamples of the fruits removed from the samplers. We felt that large errors in mean dry weight and fraction of edible materials were likely to exist in samples collected from the forest floor. Reports by Shaw (1968) and our own field observations indicated that, in areas like the Lab and Farm sites where mammal populations were dense, selective removal of tree seeds from the forest floor was often rapid and extensive. On the other hand, our experiments with

beechnuts, acorns, cherry seeds, and maple samaras showed that dry weight and caloric value were not significantly altered by up to 5 weeks of soaking in dilute Formalin, comparable to that in the samplers, providing the pericarps were intact. The proportion of fruits which contained edible material (seed parts commonly ingested by granivores) was determined by cutting tests. The edible parts were separated from the inedible parts (bracts, woody pericarps, etc., which are not commonly ingested by granivores) with steel pliers and stainless-steel forceps, dried, and weighed.

Elemental concentrations for all fruit parts except *Prunus* mesocarps were determined during the winter of 1973 to 1974 from 1.0- to 10.0-g subsamples of the materials used for determining dry-weight standards. *Prunus* mesocarps were obtained from fruits handpicked in September 1973 in Amherst, Mass. The 1.0- to 10.0-g subsamples of fruit parts were homogenized by hand with a stainless-steel knife and further divided into 0.1- to 1.0-g subsamples for K, Mg, P, Ca, and Mn analyses and 10- to 50-mg subsamples for N determinations. Nutrient concentrations reported in Table 1 are means of measurements obtained from two of the subsamples of fruit parts. Substituted values in Table 1 were derived from our measurements of related species (*Acer pensylvanicum* and *A. spicatum* from *A. rubrum* and *A. saccharum*, and *Quercus bicolor* from *Q. alba*), except for *Pyrus* sp., which was derived from data cited by Winton and Winton (1935). For most fruit parts, nutrient concentrations were determined for one study site and time interval and then extrapolated to other sites and time intervals as needed. The size of errors resulting from this procedure is not known at this time, but an upper limit is suggested by the work of Youngberg (1952), who reported differences of 5 to 10% and 30 to 110%, respectively, in the concentration of selected elements in seeds of red pine and Norway spruce from areas of different soil fertility.

Nitrogen content of the samples was determined with an automated nitrogen analyzer based on the micro-Dumas method (Coleman Instruments Division, affiliate of Perkin-Elmer Corp., 1963). "Cuprox fines" served as the oxidizing agent.

Concentrations of K, Mg, Ca, and Mn were determined with an atomic absorption spectrophotometer equipped with a laminar-flow burner using a hydrogen–air fuel mixture. Subsamples (0.1 to 1.0 g) were prepared for analyses by a wet digestion procedure using nitric and perchloric acids (Piper, 194 Dilutions were made when concentrations exceeded the range of the spectro photometer.

Concentrations of phosphorus were determined from aliquots of the samples digested for the spectrophotometric analysis. Reagent preparation and analytical procedures followed Humphries (1956). The blue complexes formed with sample and standard phosphate solutions were compared in a spectrophotometer at 690 μ.

TABLE 1

APPROXIMATE CONCENTRATIONS OF MACRONUTRIENTS IN THE EDIBLE PARTS OF FRUITS AND SEEDS PRODUCED ON THE STUDY AREAS

Plant species and part*	Collection site and date	Dry weight,† %					
		N	K	P	Mg	Ca	Mn
Acer pensylvanicum seeds	Vermont 2800-2, October 1971	3.98	(0.500)	(0.750)	(0.140)	(0.017)	(0.050)
A. rubrum seeds	Farm, June 1971	6.01	0.325	0.828	0.158	0.016	0.048
A. saccharum seeds	Tionesta 2, November 1971	4.91	0.773	0.696	0.123	0.018	0.083
A. spicatum seeds	Vermont 2800-2, October 1971	6.31	(0.500)	(0.750)	(0.140)	(0.017)	(0.050)
Betula sp. seeds with wings	Vermont 2800-1, October 1972	1.96	0.145	0.313	0.076	0.015	0.024
Carya cordiformis seeds	Farm, October 1971	1.69	0.275	0.235	0.087	0.014	0.032
C. ovalis seeds	Lab and Farm, November 1971	2.28	0.237	0.326	0.094	0.006	0.033
C. ovata seeds	Farm, October 1971	1.84	0.180	0.250	0.091	0.019	0.045

TABLE 1 (Continued)

Plant species and part*	Collection site and date	Dry weight,† %					
		N	K	P	Mg	Ca	Mn
Fagus grandifolia seeds	Farm, November 1971	3.74	0.365	0.362	0.100	0.450	0.052
Prunus serotina							
Fleshy mesocarps	Amherst, Mass., September 1973	0.76	0.963	0.329	0.258	0.042	0.015
Seeds	Lab, Farm, and Tionesta 1, September and October 1971	5.33	0.288	0.355	0.118	0.031	0.008
Pyrus sp. whole fruits	Lab, July 1971	2.32	0.600	(0.010)	0.055	(0.030)	0.001
Quercus alba seeds	Lab, October 1971	1.12	0.800	0.180	0.059	0.050	0.017
Q. bicolor seeds		(1.00)	(0.800)	(0.180)	(0.060)	(0.050)	(0.017)
Q. rubra seeds	Lab and Farm, October 1971	1.08	0.900	0.132	0.061	0.075	0.018
Q. velutina seeds	Farm, October 1971	0.94	0.410	0.127	0.070	0.085	0.049
Vaccinium corymbosum whole fruits	Lab, August 1969	0.47	0.430	0.056	0.071	0.475	0.007
Vitis sp. flesh	Farm, October 1969	1.14	1.886	0.122	0.085	0.028	0.019

*The nitrogen content of the following fruit parts was also determined: *Abies balsamea* seeds with wings, Vermont 2800-2, September 1971, 0.76%; *Fraxinus americana* seeds, Tionesta 2, November 1971, 3.66%; *Liriodendron Tulipifera* seeds, Farm, November 1971, 4.73%; *Magnolia acuminata* seeds, Farm, November 1971, 4.24%; *Picea glauca* seeds with wings, Vermont 2800-1, October 1972, 1.87%; and *Pinus Strobus* dewinged seeds, Vermont 800-1, October 1972, 4.15%.

†Means of measurements obtained from two separate subsamples of material. Numbers in parentheses are not measurements but are derived from related species, as explained in text.

The nutrient content of edible mast reaching each sampler during each interval was calculated by multiplying together the following four measurements for each species and then summing the species: (1) the number of fruits, (2) the proportion of these fruits which contained edible material, (3) the mean dry weight (g) of edible material in fruits which contained some edible material, and (4) the calculated concentrations (percent dry weight) of nutrients in the edible material. Corrections were added to the 1968 Lab and Farm measurements to compensate for fruits that had fallen before sampling was begun in August. These corrections were determined by observing, in subsequent years, the proportion of fruits of each species which fell before and after the date sampling was initiated in 1968, and then increasing the 1968 measurements accordingly. Spring and summer fruit production was so light in Vermont that such corrections there were not deemed necessary in 1970.

RESULTS AND DISCUSSION

Concentrations of nitrogen in the fruit parts analyzed in this study (Table 1) compared favorably with most of those reported earlier (Davis, 1904; Korstian, 1927; Winton and Winton, 1935; Benson and Calderwood, 1936; Wainio and Forbes, 1941; Baumgras, 1944; King and McClure, 1944; Smith, 1950; Spinner and Bishop, 1950; Gysel, 1957; Reid and Goodrum, 1957; Watt and Merrill, 1963). Other elements in these fruit parts have received much less attention, but most of the concentrations reported for either the edible parts themselves or the edible parts plus pericarps are close to those we have observed (Winton and Winton, 1935; Wainio and Forbes, 1941; King and McClure, 1944; Spinner and Bishop, 1950; Gysel, 1957). The high potassium concentrations in *Prunus serotina* flesh and frost grape flesh substantiate reports on related species cited by Winton and Winton (1935). The concentration of calcium in our samples of *Vaccinium corymbosum* was 10 times higher than that reported by Wainio and Forbes (1941). However, calcium concentrations reported by King and McClure (1944) for whole frost grapes were nine times higher than those reported by Wainio and Forbes (1941) for the same species and plant part. Our analyses of frost grape flesh produced values for calcium even lower than those of Wainio and Forbes (1941), suggesting that calcium may be more concentrated in the seeds. For white oak seeds we observed concentrations of magnesium 40% lower than corresponding concentrations reported by Wainio and Forbes (1941); for shagbark hickory seeds our phosphorus concentrations were 30% lower than those of Wainio and Forbes (1941).

The relative abundance of the six elements in the edible mast at the Lab, Farm, and Tionesta 2 sites was $N > K > P > Mg > Ca > Mn$ (Table 2). On Tionesta 1 and the Vermont 2800-1 and 2800-2 sites, the pattern was similar except that calcium was more abundant than magnesium on the former and

phosphorus was more abundant than potassium on the latter. On the Vermont 800 plots, the order was N > Ca > P > K > Mg > Mn.

Geographic variations in the quantities of some of the nutrients reaching the forest floor as edible mast exceeded two orders of magnitude (Table 2). Calcium was more abundant on Tionesta 1 than on any other plot (0.58 kg in 1971 and 0.34 kg in 1972) because of the high density of beech trees, which produce calcium-rich seeds. All other elements reached their highest abundance on the Lab site, which contained a high density of productive oak and cherry trees. The low productivity of the Vermont 2800 sites resulted from the virtual absence of species that commonly produce a large amount of mast. The comparable data appear to be those from the Hubbard Brook Experimental Forest in New Hampshire, for the period October 1968 to October 1969 (Gosz, Likens, and Bormann, 1972). There, fruits (including bracts, pericarps, etc.) which reached the ground contained 2.8 kg N, 1.4 kg K, 0.3 kg P, 0.2 kg Mg, 0.8 kg Ca, and 0.1 kg Mn/ha. Most of these values exceed the averages of our Vermont sites but would probably be similar if the inedible parts were subtracted.

Annual variations in the production of macronutrients exceeded one order of magnitude in Vermont (see Table 2, Vermont 800-2 for potassium, Vermont 2800-1 for magnesium, and others), but the variations were about half that size in Pennsylvania. Part of this difference may be due to the smaller number of samplers in Vermont, but the complementary effect in yield described by Goodrum, Reid, and Boyd (1971) is conspicuous, particularly at the Farm and Lab sites, where the vegetation is more diverse. On both plots there are several species capable of producing large mast crops. Since they do not produce synchronously, it is unusual to observe a year in which all are highly productive or a year in which all experience crop failures. The Tionesta sites, particularly Tionesta 1, resemble Vermont 800, and we suspect that, if sampling were continued for several years, annual variations on Tionesta 1 would approach those already observed in Vermont and would exceed those observed on the Lab and Farm.

Seasonal variations in the nutrient content of mast reaching the forest floor were closely related to the species composition and size of the overall mast crop on each site. Table 3 summarizes these variations for nitrogen. Data for the other elements have not been included here but follow the same general pattern as nitrogen. The timing of fruitfall matched the times outlined by Trimble and Tryon (1967) for seed production by the major hardwood species in the northeast. Most fruits reached the ground in September and October, but red maple fell in June, some cherry in August, and some beech in early November. Annual differences in time of seedfall varied by a few weeks for most species. In years when such species as sugar maple or beech experienced large mast crops, light seedfall often continued into December and sometimes even later. Fruits of

TABLE 2

NUTRIENT CONTENT (kg ha^{-1} $year^{-1}$) OF EDIBLE MAST REACHING THE FOREST FLOORS OF THE EIGHT STUDY SITES IN PENNSYLVANIA AND VERMONT*

Site and years	Nitrogen	Potassium	Phosphorus	Magnesium	Calcium	Manganese
Lab, 1968–1972	2.411–8.332 (0.429–2.061) 4.680	1.246–4.357 (0.182–1.029) 2.900	0.471–1.620 (0.076–0.416) 0.879	0.278–1.107 (0.044–0.287) 0.578	0.070–0.253 (0.011–0.051) 0.156	0.029–0.091 (0.005–0.018) 0.062
Farm, 1968–1972	1.380–4.314 (0.243–0.738) 2.643	0.413–1.354 (0.062–0.316) 0.813	0.157–0.612 (0.025–0.131) 0.362	0.059–0.265 (0.009–0.084) 0.151	0.027–0.190 (0.007–0.031) 0.106	0.012–0.056 (0.003–0.007) 0.030
Tionesta 1, 1971–1972	4.504–4.915 (0.542–0.606) 4.710	0.538–1.107 (0.061–0.343) 0.823	0.492–0.626 (0.053–0.135) 0.559	0.198–0.296 (0.017–0.094) 0.247	0.344–0.580 (0.040–0.066) 0.462	0.057–0.068 (0.007–0.008) 0.063
Tionesta 2, 1971–1972	1.168–3.014 (0.209–0.493) 2.091	0.195–0.653 (0.036–0.203) 0.424	0.137–0.470 (0.022–0.092) 0.304	0.059–0.194 (0.010–0.056) 0.126	0.061–0.119 (0.011–0.025) 0.090	0.015–0.028 (0.003–0.004) 0.022

TABLE 2 (Continued)

Site and years	Nitrogen	Potassium	Phosphorus	Magnesium	Calcium	Manganese
Vermont 800-1, 1970–1972	0.857–1.933 (0.317–0.898) 1.457	0.075–0.188 (0.029–0.087)) 0.140	0.092–0.189 (0.031–0.087) 0.146	0.024–0.052 (0.009–0.024) 0.040	0.082–0.226 (0.037–0.108) 0.165	0.012–0.026 (0.004–0.012) 0.020
Vermont 800-2, 1970–1972	0.192–2.582 (0.085–1.470) 1.736	0.014–0.267 (0.006–0.143) 0.175	0.024–0.267 (0.009–0.141) 0.178	0.006–0.070 (0.002–0.040) 0.048	0.009–0.279 (0.007–0.170) 0.186	0.003–0.036 (0.001–0.020) 0.024
Vermont 2800-1, 1970–1972	0.065–0.946 (0.004–0.099) 0.401	0.006–0.072 (0.000–0.008) 0.049	0.011–0.154 (0.008–0.016) 0.066	0.002–0.038 (0.000–0.004) 0.016	0.000–0.007 (0.000–0.001) 0.003	0.001–0.012 (0.000–0.001) 0.005
Vermont 2800-2, 1970–1972	0.109–0.655 (0.031–0.150) 0.327	0.009–0.050 (0.002–0.011) 0.027	0.018–0.105 (0.005–0.024) 0.052	0.004–0.025 (0.001–0.006) 0.012	0.001–0.005 (0.000–0.001) 0.002	0.001–0.022 (0.000–0.005) 0.010

*Numbers without parentheses show range of values observed on each site. Numbers in parentheses are the respective standard errors of the mean. Underlined numbers are annual means.

TABLE 3

SEASONAL VARIATIONS IN THE QUANTITY (kg ha^{-1} time $interval^{-1}$) OF NITROGEN REACHING THE FOREST FLOORS OF THE EIGHT STUDY SITES IN PENNSYLVANIA AND VERMONT DURING THIS STUDY*

Site and years	Time of year					
	Apr. 26–May 28	May 29–June 30	July 1–Aug. 2	Aug. 3–Sept. 5	Sept. 6–Oct. 8	Oct. 9–Nov. 21
Lab, 1969–1972	0.000–0.012 0.004	0.000–0.063 0.020	0.000–0.643 0.316	0.669–2.752 1.510	1.061–3.701 2.080	0.380–1.992 0.898
Farm, 1969–1972	0.002–0.500 0.192	0.000–0.190 0.119	0.013–0.108 0.070	0.052–0.530 0.291	0.376–1.949 0.898	0.342–1.804 1.020
Tionesta 1, 1971–1972	0.000–<0.001 <0.001	0.001–0.038 0.020	0.002–0.101 0.052	0.050–0.689 0.370	0.066–0.305 0.186	0.267–4.560 2.414
Tionesta 2, 1971–1972	0.000–<0.001 <0.001	0.043–1.816 0.930	0.001–0.090 0.050	0.101–0.587 0.344	0.114–0.308 0.211	0.212–0.909 0.561
Vermont 800-1, 1970–1972	....	0.000–0.019 0.006	0.000–0.014 0.009	0.000–<0.001 <0.001	0.350–0.724 0.578	0.133–1.561 0.867
Vermont 800-2, 1970–1972	....	0.000–0.003 0.001	0.000–0.012 0.009	0.000–<0.001 <0.001	0.131–0.629 0.322	0.061–2.211 1.406
Vermont 2800-1, 1970–1972	....	0.000–<0.001 <0.001	0.000–0.005 0.002	0.000–<0.001 <0.001	0.027–0.534 0.207	0.039–0.408 0.193
Vermont 2800-2, 1970–1972	....	0.000–<0.001 <0.001	0.000–0.007 0.005	0.000–<0.001 <0.001	0.028–0.427 0.173	0.080–0.226 0.151

*Minimum, maximum, and mean values (underlined) for edible mast are included for each time interval and site. Dotted lines indicate that no samples were collected.

beech, sugar maple, birch, and other fall seed producers which reached the ground before September contained virtually no edible material.

The spatial distribution of nutrients in the form of mast on the forest floor was uneven and variable from year to year, especially on the Pennsylvania plots, where 60 to 80 samplers were required to achieve a standard error of the mean equal to 15% of the mean. On several occasions we attempted to reduce this number of samplers by distinguishing between those which were productive and those which were unproductive and stratifying our sampling. These attempts, however, were unsuccessful because the pattern of distribution of mast and nutrients among the samplers was not consistent from year to year. In Verm within-plot variation was much smaller, but with only six samplers the stand error of the mean was as high as 50 to 60% of the mean in some cases. Confidence intervals in Table 2 reflect variations in the spatial distribution of fruit parts but not the much smaller variations in elemental concentration of fruit parts.

The relationship between edible mast and litter was not analyzed on any of our study areas. However, if the litter production on these sites was within the ranges described by Rodin and Bazilivitch (1967) for birch forests (200 to 300 kg ha^{-1} $year^{-1}$ of mineral elements), oak forests (240 to 270 kg ha^{-1} $year^{-1}$), and beech forests (up to 350 kg ha^{-1} $year^{-1}$), then the mineral elements in edible mast ranged from less than 0.3% (on Vermont 2800) to more than 3.0% (on the Lab site) of the total mineral elements in the fallen litter. If silicon and other elements had been included in our analysis, these percentages would be slightly higher.

The fate of the nutrients reaching the forest floor as edible mast is not yet precisely known, but on all our sites eastern chipmunks appear to be the granivores that consume the largest amount of mast, and edible mast after reaching the forest floor tends to disappear within a few days. Laboratory measurements of the annual ingestion rates of chipmunks (Graybill, 1970) indicate that, if the chipmunks on these sites sustained themselves on mast alone, they consumed approximately one-half the nutrients that reached the forest floor as edible mast during that time (1969 to 1970). An analysis of the stomach contents of chipmunks from the Tionesta Natural Area during 1972 and 1973 revealed that most of their diet was indeed mast. It appears from this that the eastern chipmunk is a major channel in the movement of nutrients fr the fruits and seeds of forest trees in the area of this study.

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REFERENCES

Baldwin, H. I., 1942, *Forest Tree Seed of the North Temperate Regions with Special Reference to North America,* Chronica Botanica Company, Waltham, Mass.

Baumgras, P., Experimental Feeding of Captive Fox Squirrels, *J. Wildlife Manage.,* **8**: 296-300.

Benson, S. R., and H. N. Calderwood, 1936, The Chemical Examination of the Seed of *Abies balsamea* (L.) Miller, *J. Amer. Chem. Soc.,* **58**: 523-525.

Braun, E. L., 1950, *Deciduous Forests of Eastern North America,* The Blakiston Co., Philadelphia.

Coleman Instruments Division, 1963, Operating Directions for the Coleman Model 29 Nitrogen Analyzer, Coleman Instruments Division (Perkin-Elmer Corporation), Maywood, Ill.

Cypert, E., and B. S. Webster, 1948, Yield and Use by Wildlife of Acorns of Wat r and Willow Oaks, *J. Wildlife Manage.,* **12**: 227-231.

Davis, N. F., 1904, *Chestnut Culture in Pennsylvania,* Commonwealth of Pennsylvania Department of Agriculture Bulletin No. 123.

Downs, A. A., and W. E. McQuilkin, 1944, Seed Production of Southern Appalachian Oaks, *J. Forest.,* **42**: 913-920.

Fowells, H. A., and G. H. Schubert, 1956, *Seed Crops of Forest Trees in the Pine Region of California,* U. S. Department of Agriculture, Technical Bulletin 1150.

Goodrum, P. D., V. H. Reid, and C. E. Boyd, 1971, Acorn Yields, Characteristics, and Management Criteria of Oaks for Wildlife, *J. Wildlife Manage.,* **35**: 520-532.

Gorecki, A., and Z. Gebczynska, 1962, Food Conditions for Small Rodents in a Deciduous Forest, *Acta Theriologica,* **VI**: 275-295.

Gosz, J. R., G. E. Likens, and F. H. Bormann, 1972, Nutrient Content of Litterfall on the Hubbard Brook Experimental Forest, New Hampshire, *Ecology,* **53**: 769-784.

ybill, D. L., 1970, Food Resources and Ingestion Rates of *Tamias striatus* Populations, Ph. D. Thesis, University of Pittsburgh.

Gysel, L. W., 1971, A 10-Year Analysis of Beechnut Production and Use in Michigan, *J. Wildlife Manage.,* **35**: 516-519.

___, 1957, Acorn Production on Good, Medium, and Poor Oak Sites in Southern Michigan, *J. Forest.,* **55**: 570-574.

Hawkins, P. J., 1966, Seed Production and Litterfall Studies of *Callitris columellaris, Aust. Forest. Res.,* **2**: 3-16.

Hough, A. F., and R. D. Forbes, 1943, The Ecology and Silvics of Forests in the High Plateaus of Pennsylvania, *Ecol. Monogr.,* **13**: 299-320.

Humphries, E. C., 1956, Mineral Components and Ash Analysis, in *Modern Methods of Plant Analysis,* Vol. 1, M. Paech and M. V. Tracey (Eds.), Springer-Verlag, New York.

King, T. R., and H. E. McClure, 1944, Chemical Composition of Some American Wild Feedstuffs, *J. Agr. Res.,* **69**: 33-46.

Korstian, C. F., 1927, *Factors Controlling Germination and Early Survival in Oaks,* Yale University School of Forestry, Bulletin 19.

Matthews, J. D., 1963, Factors Affecting the Production of Seed by Forest Trees, *Forestry Abstracts,* **24**: 1-13.

___, 1955, The Influence of Weather on the Frequency of Beech Mast Years in England, *Forestry,* **28**: 107-116.

Minckler, L. S., and D. Janes, 1965, *Pin Oak Acorn Production on Normal and Flooded Areas,* University of Missouri Agricultural Experiment Station, Research Bulletin 8[illegible]

Myczkowski, S., 1967, Sklad florystyczny, struktura i produktywność roślinności wiastej platu *Fagetum carpaticum* (Floristic Composition, Structure, and Productivity of Woody Plants in a Beech Stand *Fagetum carpaticum), Studia Naturae, Seria A,* **1**: 61-94. (Text in Polish, summaries in English).

Ovington, J. D., and G. Murray, 1964, Determination of Acorn Fall, *Quart. J. Forest.,* **58**: 152-159.

Piper, C. S., 1944, *Soil and Plant Analysis,* Wiley-Interscience, New York.

Puritch, G. S., and A. H. Vyse, 1972, *Cone Production in Conifers: A Review of the Literature and Evaluation of Research Needs,* Pacific Forest Research Centre, Canadian Forestry Service, Victoria, British Columbia, Information Report BC-X-65.

Reid, V. H., and P. D. Goodrum, 1957, Factors Influencing the Yield and Wildlife Use of Acorns, in Sixth Annual Forestry Symposium, Louisiana State University and Agricultural and Mechanical College, Baton Rouge, pp. 46-79.

Rodin, L. E., and N. I. Bazilivitch, 1967, *Production and Mineral Cycling in Terrestrial Vegetation,* translated by G. E. Fogg, Oliver and Boyd Ltd., London.

Sarvas, R., 1968, Investigations into the Flowering and Seed Crop of *Picea abies, Commun. Inst. Forest. Fenniae,* **67**: 1-84.

___, 1955, Investigations into the Flowering and Seed Quality of Forest Trees, *Commun. Inst. Forest. Fenniae,* **45**: 1-37.

Sharp, W. M., 1958, *Evaluating Mast Yields in the Oaks,* Pennsylvania State University Agricultural Experiment Station, Bulletin 635.

___, and V. G. Sprague, 1967, Flowering and Fruiting in the White Oaks; Pistillate Flowering, Acorn Development, Weather and Yields, *Ecology,* **48**: 243-251.

Shaw, M. W., 1968, Factors Affecting the Natural Regeneration of Sessile Oak (*Quercus petraea*) in North Wales. I. A Preliminary Study of Acorn Production, Viability, and Losses, *J. Ecol.,* **56**: 565-583.

Smith, J. R., 1950, *Tree Crops: A Permanent Agriculture,* Harcourt Brace Jovanovich, Inc., New York.

Spinner, G. P., and J. S. Bishop, 1950, Chemical Analysis of Some Wildlife Foods in Connecticut, *J. Wildlife Manage.,* **14**: 175-180.

Thompson, R. L., and B. S. McGinnes, 1963, A Comparison of Eight Types of Mast T[illegible] *J. Forest.,* **61**: 679-680.

Trimble, G. R., Jr., and E. H. Tryon, 1967, *Seeding Characteristics of Eleven Appalachian Hardwood Species,* Northeastern Forest Experiment Station, Upper Darby, Pa.

Tryon, C. A., and D. P. Snyder, 1973, Biology of the Eastern Chipmunk, *Tamias striatus:* Life Tables, Age Distributions, and Trends in Population Numbers, *J. Mammal.,* **54**: 145-168.

Uhlig, H. G., and H. L. Wilson, 1952, A Method of Evaluating an Annual Mast Index, *J. Wildlife Manage.,* **16**: 338-343.

van Vredenburch, C. L. H. and J. G. A. LaBastide, 1969, The Influence of Meteorological Factors on the Cone Crop of Douglas Fir in the Netherlands, *Silvae Genet.*, **18**: 182-186.

Wainio, W. W., and E. B. Forbes, 1941, The Chemical Composition of Forest Fruits and Nuts from Pennsylvania, *J. Agr. Res.*, **62**: 627-635.

Ward, F. D., and R. G. Leonard, 1968, Rodents Drown in Mast Traps, *J. Mammal.*, **49**: 530.

Watt, B. K., and A. L. Merrill, 1963, *Composition of Foods: Raw, Processed, Prepared,* Handbook No. 8, U. S. Department of Agriculture.

Winton, A. L., and K. B. Winton, 1935, *The Structure and Composition of Foods,* Vol. II., John Wiley & Sons, Inc., New York.

Youngberg, C. T., 1952, Effect of Soil Fertility on the Physical and Chemical Properties of [illegible]e Seed, *J. Forest.*, **50**: 850-852.

[illegible], J. C., and L. A. Viereck, 1970, *White Spruce Cone and Seed Production in Interior Alaska, 1957–1968,* U. S. Pacific Northwest Forest Range Experiment Station Research Note PNW-129.

FALLOUT CESIUM-137 AND MINERAL-ELEMENT DISTRIBUTION IN FOOD CHAINS OF GRANITIC-OUTCROP ECOSYSTEMS

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ABSTRACT

Fallout ^{137}Cs movement is described for arthropod food chains on Panola and Arabia mountains, granite monadnocks in the Georgia Piedmont region. Food chains on mountain slopes had significant ^{137}Cs in herbivore and predator trophic levels. Food bases were identified from observation and from cesium to potassium ratios in vegetation and arthropods. Lichens are major accumulators of fallout ^{137}Cs but do not appear to be important food sources for arthropods. Cesium-137 concentrations decrease in the food chains; these decreases resemble those reported for other terrestrial arthropod chains. Aspects of ^{137}Cs movement and nutrient-element dynamics in granitic-outcrop ecosystems are discussed.

Granitic outcrops in the Piedmont region of the southeastern United States contain a variety of small, yet persistent, "island" ecosystems of varying complexity (Burbanck and Platt, 1964). In this paper we describe the movement of fallout ^{137}Cs through arthropod food chains associated with these small ecosystems. The work was suggested by reports of significant ^{137}Cs concentrations in outcrop vegetation (Plummer, 1969). We compared food-chain transport of radiocesium in outcrop areas with previously published information on arthropod food chains. Earlier research showed that ^{137}Cs concentrations decreased in higher arthropod trophic levels in a radioactive waste-disposal (Crossley, 1969) and in an experimentally tagged forest stand (Reichle and Crossley, 1967, 1969). In contrast, aquatic food chains (Pendleton, 1965) and vertebrate food chains (Hanson and Palmer, 1965; Jenkins et al., 1969) were reported to contain increasing ^{137}Cs concentrations at higher trophic levels.

Granitic-outcrop ecosystems themselves may serve as models for larger, more extensive ecosystems that accumulate radionuclides. Current ecological theory

holds that mature ecosystems tend to be conservative of nutrient elements, whereas successional or developmental stages, or ecosystems with low diversity or stability, tend to lose nutrient capital (e.g., Odum, 1969; Bormann and Likens, 1967). Such a theory does not explain the retention of radioactive fallout in many ecological systems. Some radioactive elements, such as ^{90}Sr and ^{137}Cs, are metabolized by mechanisms that are similar to those for nutrient elements. Yet the ability of such different ecosystems as alpine snow ecosystems (Osburn, 1963), arctic tundra, southeastern U. S. Coastal Plain vs. Piedmont (Jenkins et al., 1969), and granitic-outcrop ecosystems to accumulate fallout radionuclides appears unrelated to system maturity, complexity, or stability. More intensive studies of such small systems as granitic outcrops may lead to further understanding of nutrient conservation mechanisms in ecosystems in addition to providing information on the environmental behavior of radioactive materials.

MATERIALS AND METHODS

We sampled soils, plants, and arthropods on Arabia and Panola mountains, two granitic monadnocks near Atlanta, Ga., during summer 1969. The bulk of the more destructive sampling was done on Arabia mountain; Panola mountain has become a state park. Vegetation and soils were sampled in lichen–annual, annual–perennial, and mountaintop communities (Burbanck and Platt, 1964). Soil samples each consisted of 20 lumped 2-in. soil cores. Vegetation samples from lichen–annual and annual–perennial communities each consisted of a single 0.25-m^2 quadrat. All green plants and lichens were clipped with shears, collected in paper bags, dried at 50°C, and ground in a Wiley mill. Samples of *Parmelia* consisted of 0.25-m^2 quadrats of lichen, scraped from bare rock with a wire brush and screened to remove soil particles (Plummer, 1969). We took samples at weekly intervals.

Each sample of the rock grasshopper *Trimerotropis* consisted of at least 20 individuals, taken at 2-week intervals. The remaining categories of arthropods (winged and wingless herbivores and predators) were sorted from 500-sweep collections obtained at 2-week intervals. A similar collection of grasshoppers and 500-sweep samples was made at the base of each mountain. Additional 500-sweep collections were made in adjacent, nonoutcrop areas. Because of the small weights of arthropods obtained in the 500-sweep samples, the collections for the entire summer were lumped. Arthropods were dried at 50°C, weighed, and ground in a Wiley mill.

Soils, vegetation, and arthropods were analyzed for ^{137}Cs with a Packard multichannel analyzer system in a 256-channel mode. Materials were analyzed or reanalyzed in summer 1973, and results were corrected for radioactive decay to summer 1969. Counting times were 100 min (soils and vegetation) or 300 min (arthropods). Analysis for mineral-element content of samples followed a

wet-ashing procedure, with measurements performed on an atomic absorption spectrophotometer (Bausch & Lomb AC2-20).

RESULTS

Mineral-element concentrations for granitic outcrop plants are shown in Table 1. Potassium concentrations tended to be lower in lichen species, intermediate in mosses, and highest in vascular plants. Calcium concentrations were lower in lichens, but similar in mosses and vascular plants. In each, some overlap occurred between bare-rock lichens (*Parmelia*) and m (*Grimmia*). For sodium, a similar increase may occur from lichens through mosses to vascular plants, but any differences are slight. It would be difficult to separate a taxonomic (or physiological) effect from a habitat effect in these data. Plants growing in depression communities tend to have higher mineral-element contents than plants growing on bare rock. However, these comparisons involve plants that are physiologically very different.

Cesium-137 concentrations in these plants show an opposite trend; i.e., a decrease in concentration from lichens through mosses to vascular plants (Table 2). *Parmelia* lichens contained the highest concentrations found, about 200 pCi/g. *Cladonia* lichens and mosses had ^{137}Cs concentrations similar to each other (about 25 to 30 pCi/g) and were several times higher than most vascular plant species (about 8 pCi/g). These concentrations are consistent with previously published values for outcrop plants (Plummer and Helseth, 1965; Plummer, 1969). These two opposing trends in elemental content produce a drastically different ratio of ^{137}Cs to potassium in these sets of plants (Table 1). Ratios (pCi ^{137}Cs per milligram of potassium) were about 80 in *Parmelia* lichens, about 20 in *Cladonia* lichens, about 10 in mosses, and about 1 in vascular plants. Food chains based on lichens thus should have an intake of relatively more ^{137}Cs than would food chains based on vascular plants or even mosses, assuming similar assimilation efficiencies.

Concentrations of mineral elements in samples of arthropods are given in Table 2. Data are presented by location and by trophic level, with winged and wingless forms, *Trimerotropis* and *Collops*, shown separately. Mountaintop collections were made at the apex of Panola mountain, which supports a variety of vegetation. Mountain-slope collections were taken midway down the slop Panola and Arabia mountains. Mountain-base collections were made in vegeta-tion immediately at the terminations of exposed granite, and adjacent-area collections were made in vegetation nearby. *Trimerotropis* is a grasshopper; *Collops* is a beetle believed to be predaceous but perhaps omnivorous. Locations of sampling sites had no obvious effects on mineral-element concentrations in arthropods, nor were trophic-level effects demonstrable for potassium or calcium. However, a decided trophic-level effect appeared for sodium. For herbivores, sodium concentrations average about 1300 ppm; for predators, about

TABLE 1

MINERAL-ELEMENT AND FALLOUT CESIUM-137 CONCENTRATIONS* IN GRANITIC-OUTCROP PLANTS DURING SUMMER 1969

Plant species	No. of samples†	Ca	Na	K	No. of samples‡	^{137}Cs, pCi/g	Cs-to-K ratio, pCi/mg K
Lichens							
Parmelia sp.	7	795 ± 205	249 ± 76	2,450 ± 344	7	209 ± 71	85
Cladonia podocarpa	4	640 ± 182	244 ± 20	1,290 ± 152	4	27.0 ± 5.28	21
Cladonia caroliniana	4	580 ± 48	189 ± 58	1,260 ± 105	4	24.1 ± 1.34	19
Cladonia leporina	5	530 ± 83	289 ± 18	1,410 ± 140	5	31.0 ± 2.14	22
Mosses							
Grimmia sp.	3	2,270 ± 1,560	249 ± 76	1,960 ± 726	3	25.1 ± 6.9	12.8
Polytrichum commune	6	3,845 ± 944	258 ± 21	2,700 ± 313	8	23.7 ± 4.58	8.8
Vascular Plants							
Panicum sp.	4	2,020 ± 598	370 ± 99	6,190 ± 2,540	4	7.5 ± 1.79	1.2
Andropogon sp.	3	2,520 ± 420	287 ± 34	4,790 ± 2,540	5	7.7 ± 1.38	1.6
Senecio tomentosa	7	5,260 ± 371	317 ± 23	6,690 ± 371	8	7.8 ± 1.76	1.2
Viguiera porteri	10	11,120 ± 1,378	500 ± 114	11,930 ± 1,691	9	12.1 ± 3.02	1.0
Lindernia monticola	5	7,209 ± 341	817 ± 293	6,468 ± 1,040	6	6.2 ± 1.18	1.0
Hympericum sp.	3	2,553 ± 324	647 ± 280	3,178 ± 1,400	5	8.0 ± 1.27	2.5
Pinus sp.	3	2,918 ± 189	461 ± 45	3,560 ± 446	4	20.7 ± 11.58	5.81
Juncus sp.	0				2	8.0 ± 1.13	

*Values are parts per million ± standard error.

†For elemental analysis.

‡For ^{137}Cs analysis.

TABLE 2

MINERAL-ELEMENT CONTENT AND FALLOUT CESIUM-137 IN ARTHROPOD SAMPLES FROM GRANITIC OUTCROPS DURING SUMMER 1969

Arthropods	Ca, ppm	Na, ppm	K, ppm	Dry weight, g*	^{137}Cs, pCi/g	Cs-to-K ratio, pCi/mg K
Mountaintop						
Herbivores	775	1,170	11,150	1.9724	3.4 ± 0.53	0.30
Predators	1,010	3,030	9,970	0.5918	†	†
Mountain slope						
Herbivores						
Winged	605	1,840	10,040	1.4933	9.6 ± 1.03	0.96
Wingless	1,230	1,260	12,770	1.2140	10.7 ± 4.74	0.84
Predators	930	3,000	10,700	0.2140	†	†
Trimerotropis	350	1,650	10,280	5.6912	11.7 ± 0.30	1.13
Collops	1,880	2,350	7,970	0.4111	5.4 ± 2.54	0.68
Mountain base						
Grasshoppers	1,440	1,100	12,600	1.2411	4.1 ± 1.49	0.33
Adjacent area						
Herbivores						
Winged	840	1,030	8,540	1.4453	1.9 ± 0.71	1.22
Wingless	1,720	1,280	14,210	1.3888	4.1 ± 1.06	0.29
Predators						
Winged	600	810	7,430	0.4393	†	†
Wingless	1,418	3,810	11,480	0.9556	†	†
Grasshoppers	1,430	1,080	11,850	1.0050	†	†

*Values for ^{137}Cs analysis only.

†Levels of ^{137}Cs detected were not significantly different from background count rates at the 0.05 level (standard errors based on counting errors).

2600 ppm. Vascular plants (Table 1) averaged about 500 ppm. Such increases for sodium concentrations in invertebrate food chains have been reported previously for a forest-floor community (Reichle and Crossley, 1969) and a grassland community (Van Hook, 1971). Winged forms generally (one exception) had lower concentrations than wingless forms for all elements and both trophic levels. If real, such a difference might result from higher feeding rates of immatures or higher turnover rates by more active adults, or other physiological differences.

Fallout ^{137}Cs contents of arthropod samples from granitic outcrop are given in Table 2. Despite the use of lumped samples for the entire summer, weights available for analysis were small. Nevertheless, trophic level and site effects could be demonstrated for ^{137}Cs content in the arthropods. Largest concentrations were found in herbivores (about 10 pCi/g dry weight) collected in mountain-slope areas. Herbivores on the mountaintop and at the mountain base averaged about 3 to 4 pCi/g. Somewhat lower concentrations were found for herbivores in adjacent areas. The similarity of ^{137}Cs concentrations in winged or wingless herbivores suggests that dilution through insect immigration onto the mountain slopes was not significant. Most samples of predators did not

have ^{137}Cs contents statistically different from background, probably as a result of the small sample size available. Cesium-137 levels in predators were obviously lower, however, than in herbivores. *Collops,* presumably predaceous, had about 5 pCi ^{137}Cs/g in slope areas, a reduction of 50% from herbivore concentrations in slope areas. Ratios of ^{137}Cs to potassium in these samples varied with site, averaging about 0.9 in collections from slopes and about 0.3 in samples from mountaintop, mountain base, and adjacent areas.

DISCUSSION

Arthropod food chains on slopes of Panola and Arabia mountains contain fallout ^{137}Cs concentrations some three to five times higher than those in adjacent areas or on the mountaintop. Referencing the food chains to a plant base is difficult because of the great variability in ^{137}Cs concentrations in the outcrop plants, but inferences from the cesium-to-potassium ratios and information about ^{137}Cs dynamics on outcrops are suggestive.

Plummer and Helseth (1965) were able to demonstrate a downward movement of fallout ^{137}Cs in Georgia flat-rock outcrops, with a gradual removal of ^{137}Cs along drainage patterns by vegetational communities and their soils. Presumably such effects produce the higher concentrations noted here for food chains on mountain slopes in contrast to the mountaintop. The exaggerated cesium-to-potassium ratio for *Parmelia* effectively rules out this species as an important food source for the generalized arthropod food chain. For arthropods the ratio is no greater than 1 (Table 2); only the vascular plants have a similar ratio of cesium to potassium (Table 1). Some reduction in the cesium to potassium ratio in the plant-to-arthropod transfer may occur, however. Reichle and Crossley (1969) reported a 10-fold reduction in a cesium-to-potassium ratio for forest-floor food chains. They attributed the reduction in arthropods to low availability of ^{137}Cs, as well as lower assimilation of cesium relative to potassium. If such a 10-fold decrease in cesium-to-potassium ratios occurs in outcrop food chains, then the mosses *Grimmia* and *Polytrichum* may serve as food plants. The grasshopper *Trimerotropis* utilizes significant amounts of *Grimmia* (Duke and Crossley, 1975).

If we use the mosses as a food base, then transfers along food chains on granitic outcrops resemble those reported for other arthropod food chains. Comparisons can be made by normalizing concentrations in herbivores and predators to a percentage of ^{137}Cs concentrations in the vegetation. For granitic outcrops, percentage concentrations of ^{137}Cs in plants, herbivores, and predators (slopes) are approximately 100 : 40 : 20. For a forbs system (White Oak Lake bed, Oak Ridge, Tenn., Crossley, 1969), values were 100 : 30 : 26. In a forest canopy (Reichle and Crossley, 1969) values were 100 : 48 : 13, and in the associated forest-floor (Reichle and Crossley, 1969) values were 100 (litter) : 30 : 17. Thus our results confirm previous observations on terrestrial arthropod food chains. In contrast to some aquatic, arctic, or terrestrial

mammalian food chains, concentrations of ^{137}Cs decrease during trophic transfers. Furthermore, arthropod food chains on granitic outcrops do not seem to possess nutrient conservation mechanisms different from those of food chains existing in other, less impoverished areas.

Further measurements and experiments will be needed to resolve some of the aspects of nutrient and mineral-element dynamics within the outcrop systems and to determine what system properties allow for the accumulations of radioactive fallout. Certainly the presence of lichens is an important factor. Plummer (1969) estimated that *Parmelia* alone contained (in 1965) about 42% of the fallout ^{137}Cs that had fallen on outcrops since 1945. His mean value, 434 pCi/g dry weight are about twice our values (for 1969), attesting to the abilities of this plant to retain ^{137}Cs. Similarly, Plummer's values for ^{137}Cs in *Cladonia* are about twice ours. Apparently other plant values are lower by several times those given by Plummer and Helseth (1965), but not by an order of magnitude. Possibly, leaching from *Parmelia* is adequate to replenish losses from rooted-plant communities. Fragments of lichen thallus washed or blown into depression communities may be a source of nutrients on ^{137}Cs for vascular plants. The exaggerated cesium-to-potassium ratios of lichens are not easily explained. Plummer and Helseth (1965) suggest that *Parmelia* releases acids that remove potassium from the rock, perhaps adding potassium to communities downstream. *Parmelia* may cling to potassium as tenaciously as it does to ^{137}Cs. Alternatively, exaggerated cesium-to-potassium ratios may simply reflect a long time lag for the equilibration of fallout radionuclides in these communities. The presence of long time constants in nutrient cycles of outcrop ecosystems can be inferred from successional studies (Burbanck and Platt, 1964). In new experiments that are currently under way there is an attempt to evaluate nutrient and mineral-element gains and losses by communities of rooted plants.

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REFERENCES

Bormann, R. H., and G. E. Likens, 1967, Nutrient Cycling, *Science*, **155**: 424-429.

Burbanck, Madeline P., and Robert B. Platt, 1964, Granitic Outcrop Communities of the Piedmont Plateau in Georgia, *Ecology*, **45**: 292-306.

Crossley, D. A., Jr., 1969, Comparative Movement of ^{106}Ru, ^{60}Co, and ^{137}Cs in Arthropod Food Chains, in Symposium on Radioecology, Proceedings of the Second National Symposium, Ann Arbor, Mich., May 15, 1967, D. J. Nelson and F. C. Evans (Eds.), pp. 687-695, USAEC Report CONF-670503.

Duke, Kenneth M., and D. A. Crossley, Jr., 1975, Population Energetics and Ecology of the Rock Grasshopper, *Trimerotropis saxatilis.* submitted to *Ecology.*

Hanson, W. C., and H. E. Palmer, 1965, Seasonal Cycle of ^{137}Cs in Some Alaskan Natives and Animals, *Health Phys.,* **11**: 1401-1406.

Jenkins, James H., J. Robert Monroe, and Frank B. Golley, 1969, Comparison of Fallout ^{137}Cs Accumulation and Excretion in Certain Southwestern Mammals, in Symposium on Radioecology, Proceedings of the Second National Symposium, Ann Arbor, Mich., May 15, 1967, D. J. Nelson and F. C. Evans (Eds.), pp. 623-626, USAEC Report CONF-670503.

Odum, Eugene P., 1969, The Strategy of Ecosystem Development, *Science,* **18**: 262-270.

Osburn, W. S., Jr., 1963, The Dynamics of Fallout Distribution in a Colorado Alpine Tundra Snow Accumulation Ecosystem, pp. 51-72, in *Radioecology,* V. Schultz and A. W. Klement, Jr. (Eds.), Reinhold Publishing Corporation, New York.

Pendleton, R. C., 1965, Accumulation of Cesium-137 Through the Aquatic Food Web, in *Biological Problems in Water Pollution,* C. M. Tarzwell (Ed.), pp. 355-363, Health, Education, and Welfare, Public Health Service, 000-WP-25.

Plummer, Gayther L., 1969, Fallout Radioisotopes in Georgia Lichens, in Symposium on Radioecology, Proceedings of the Second National Symposium, Ann Arbor, Mich., May 15, 1967, D. J. Nelson and F. C. Evans (Eds.), pp. 571-577, USAEC Report CONF-670503.

——, and F. Helseth, 1965, Movement and Distribution of Radionuclides on Granitic Outcrops Within the Georgia Piedmont, *Health Phys.,* **11**: 1423-1428.

Reichle, David E., and D. A. Crossley, Jr., 1969, Trophic Level Concentrations of Cesium-137, Sodium, and Potassium in Forest Arthropods, in Symposium on Radioecology, Proceedings of the Second National Symposium, Ann Arbor, Mich., May 15, 1967, D. J. Nelson and F. C. Evans (Eds.), pp. 678-686, USAEC Report 670503.

——, and D. A. Crossley, Jr., 1967, Investigation on Heterotrophic Productivity in Forest Insect Communities, in *Secondary Productivity of Terrestrial Ecosystems,* K. Petrusewicz (Ed.), pp. 563-587, Panstwowe Wydawnictwo Naukoew, Warschau.

Van Hook, Robert I., Jr., 1971, Energy and Nutrient Dynamics of Spider and Orthopteran Populations in a Grassland Ecosystem, *Ecol. Monogr.,* **41**: 1-26.

RESOURCE PARTITIONING IN LEAF-LITTER FAUNAS FROM HARDWOOD AND HARDWOOD-CONVERTED-TO-PINE FORESTS

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ABSTRACT

The structure and function of litter faunas were measured from the forest floors of two forest watersheds: mature hardwood (reference) and adjacent white pine, once hardwood (experimental) forests. The biomass of some 18 combined taxa of litter animals was about one-third lower, numerical abundances were about one-half lower, and standing crops of calcium and potassium were also lower in the pine plantation than in the hardwood system. These data were synthesized as models of the cryptozoans' food webs. In the hardwood watershed, 11% of the calcium and 3% of the potassium from annual leaf-litter input were processed by the litter animals. By contrast, 2% of the calcium and 28% of the potassium from annual litter input entered the food webs of the litter fauna in the white pine watershed.

As much as 90% of the net primary production in forests does not pass through herbivore food chains before it is deposited on the forest floor as detritus and becomes available to saprozoic food chains (Whittaker, 1970; Crossley, 1970). Organisms in this latter pathway process the majority of the materials released by primary producers. Complexes of fungi, bacteria, and animals interact and utilize nutrients in these dead materials and aid in releasing nutrients (Kurche[illegible] 1960; Edwards and Heath, 1963; Crossley and Witkamp, 1964; and Witka[illegible] 1971). These nutrients may become available for uptake again by plants, transferred from the ecosystem via runoff, or retained in deep soils. The rates of release of these materials and the pathways they follow in the microfloral–

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faunal complex may largely determine whether the entire watershed system conserves its nutrients or loses them.

Coweeta Hydrologic Station in North Carolina offers a variety of natural and manipulated watersheds. Watershed 18 is a mature deciduous hardwood forest and serves as a reference forest; burning and cutting have been restricted since 1924, and before that time logging was minimal. Adjacent watershed 17 serves as an experimental system because as a mature hardwood forest it was logged in 1942; in 1956 it was planted with white pine seedlings. Subsequent cuttings of hardwood shoots have ensured that watershed 17 is essentially a young white pine plantation. Particulars of these catchments (Johnson and Swank, 1973) indicate that both watersheds are similar in slope, exposure, size, elevation, etc., but they differ, of course, in botanical composition.

Researchers at Coweeta have undertaken the determination of the movement of mineral elements—calcium and potassium—through the soil-litter fauna, using standing crops of elements, turnover rates from radioisotope measurements, and systems-analysis techniques. Gist (1972) synthesized data from the mature hardwood watershed with digital computer methods applied to a 10-compartment model. Cornaby (1975) concentrated on similar dynamics of the forest floor of the white pine watershed, using analog computer methods on a 6-compartment model. These studies were made to (1) determine numerical densities, biomasses, and standing crops of mineral elements in the soil-litter fauna; (2) measure the flow of calcium and potassium through their food webs; (3) detect the importance of the various animal groups in maintaining this flow; and (4) establish the importance of food-chain movement relative to the annual litter input of mineral elements to the forest floor. This paper compares the principal findings of these two studies.

MATERIALS AND METHODS

Field investigations were conducted at Coweeta Hydrological Station in North Carolina in fall and winter 1970 and in summer 1971 for the hardwood watershed and in fall and winter 1971 and in spring, summer, and fall 1972 for the pine system. Precipitation and temperature profiles were similar for the year period. The watersheds used are described by Johnson and Swank (1973). Forest-floor invertebrates were separated from litter on the two forest floors by pitfall trapping, Berlese extraction, and hand-retrieval techniques. Organisms were enumerated, weighed (dry-weight biomass), and prepared for whole-body analyses of chemical composition for calcium and potassium. Particulars of the sampling programs and chemical analyses are given by Cornaby (1973) and Gist and Crossley (1975). In addition, Gist (1972) and Gist and Crossley (1974) performed tracer studies, some of the results of which Cornaby (1975) used in estimating flows between populations. Exact values from radioisotope studies, as well as extensive literature reviews on feeding habits of some 20 taxa of

forest-floor invertebrates, are given by Gist (1972), Gist and Crossley (1975), and Cornaby (1975). Cromack's (1972) work on litter budgets in the two forests provided data for inputs to the forest-floor community.

RESULTS AND DISCUSSION

The conceptual models used for analysis of the role of the litter fauna in the hardwood and pine watersheds are shown in Fig. 1. Litter input of calcium and potassium goes directly to compartment X_1 (litter) where transfers may occur to any of several processors or to soil directly. Movement from animals occurs as egestion, death, and losses to predator compartments (populations). Numerous recycling pathways, including those from soil humus and/or soil microflora, to litter animals are factored into the models because connectivities represent the net balance of inputs and outputs for a given compartment. Gist (1972) annualized his summer models for both calcium and potassium dynamics. Cornaby's model (1975) was constructed to estimate only annual patterns.

Differences between the two models are such that all the data from one watershed cannot be used for simulations on the model for the other watershed. For instance, the hardwood watershed model contains a finer compartmentalization of the fauna but does not provide for animal remains. And the study of the white pine watershed included some taxa not measured on the hardwood watershed. Nevertheless, comparisons of results are possible at two levels. Standing crops and faunal compositions can be compared since they are independent of the structures of the models. Also, gross comparisons of some of the internal dynamics and total outputs of the models are fruitful.

There were large differences in numerical densities, faunal composition, and standing-crop biomasses between faunas of the two watersheds. Annual average densities of litter invertebrates averaged 65,060 individuals per square meter on the hardwood watershed and exceeded by a factor of about 2 the density of 35,830 individuals per square meter on the white pine watershed (Table 1). Cryptostigmata and Collembola combined accounted for approximately 90% of both these annual densities, but the relative contributions of these two groups differed on the two watersheds. Diplopoda were conspicuously more abundant on the hardwood watershed. Average biomass on the white pine watershed was 1.30 g/m^2, compared with 3.81 g/m^2 on the hardwood watershed (Table 1). Biomass of nearly every faunal group was smaller on the pine watershed, exceptions being Collembola and such macroinvertebrates as Gastropoda and Aranea. The Collembola, in particular, may be the dominant group of fauna in the white pine watershed, where they maintained high biomasses (500 mg/m^2).

Figure 2 shows the relative inputs of calcium and potassium to the two forest floors and indicates the degree of resource partitioning by the respective soil-litter faunas. The percentage of the annual litterfall inputs which actually entered the food chains was comparatively small. On the hardwood watershed

TABLE 1

MEAN ANNUAL DENSITIES AND BIOMASSES OF LITTER FAUNA FROM DECIDUOUS HARDWOOD AND HARDWOOD-CONVERTED-TO-WHITE PINE FORESTS (Limits for 95% confidence intervals are provided in parentheses after the mean)

Taxa	Deciduous hardwood	Hardwood converted to white pine
	Densities, individuals/m² *	
Cryptostigmata	55,630 (47,050; 64,410)	19,440 (18,570; 20,310)
Mesostigmata	1,500 (130; 2,870)	2,050 (1,760; 2,340)
Aranea (small)	400 (270; 530)	290 (250; 340)
Collembola	7,520 (6,230; 8,810)	13,220 (12,620; 13,820)
Other microarthropods	†	830 (710; 950)‡
Diplopoda	5	1
Other macroinvertebrates	2§	7¶
Totals	65,060 (56,270; 73,850)**	35,830 (33,050; 38,610)**
	Estimated biomass, mg (dry weight tissue)/m² ††	
Cryptostigmata	1,660	190
Mesostigmata	90	40
Aranea (small)	220	140
Collembola	280	500
Other microarthropods	†	40‡
Diplopoda	1,290	40
Other macroinvertebrates	270§	350¶
Totals	3,810	1,300

*Sample sizes for microarthropods were 36 and 210 0.01 per square meter for Berlesed samples of litter for hardwood and white pine forests, respectively; sample sizes for macroinvertebrates were 25 and 116 per square meter for hand-sorted samples of litter for hardwood and white pine forests, respectively. Densities are based on direct counts.

†Samples not tabulated for these two taxa (see footnote ‡).

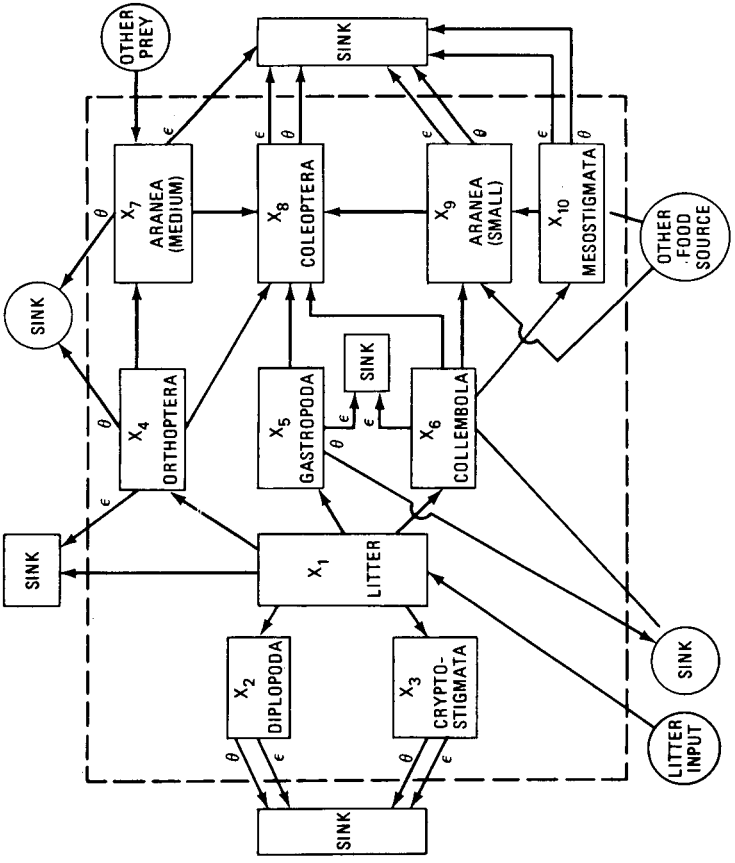
‡*Prostigmata* and Pseudoscorpionida.

§Gastropoda, Aranea (large), Carabidae, and Orthoptera.

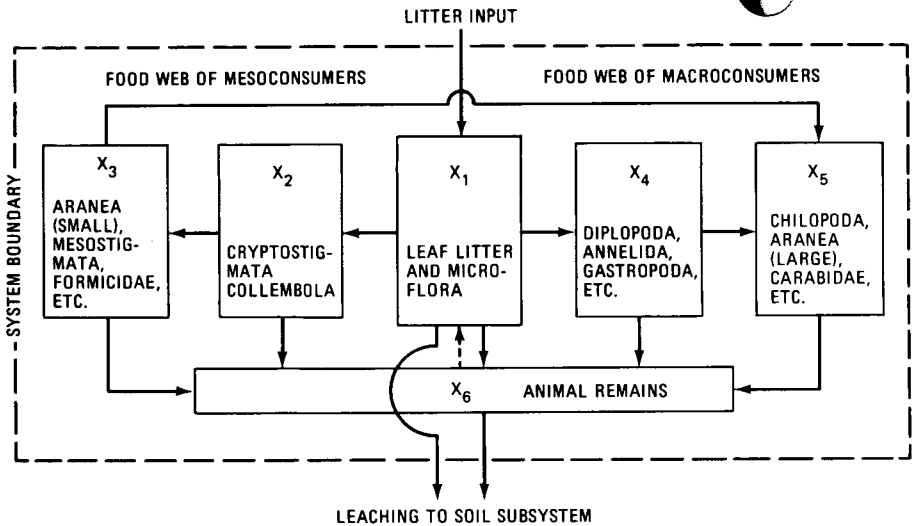
¶Gastropoda, Chilopoda, Aranea (large), Opiliones, Phalangida, Isopoda, Tettigoniidae, Carabidae, Staphylinidae, Formicidae, and Oligochaeta.

**Computation of limits for 95% confidence intervals were based on first four taxa; inclusion of last three groups would not have appreciably changed the confidence values.

††Biomass values are based on average weights per individual (based on direct weighings of many individuals) multiplied by direct counts.


OTHER PREY
SINK
X_7 ARANEA (MEDIUM)
X_8 COLEOPTERA
X_9 ARANEA (SMALL)
X_{10} MESOSTIGMATA
OTHER FOOD SOURCE
SINK
X_4 ORTHOPTERA
X_5 GASTROPODA
SINK
X_6 COLLEMBOLA
SINK
X_1 LITTER
X_2 DIPLOPODA
X_3 CRYPTO-STIGMATA
SINK
LITTER INPUT
SINK
θ
ε

(a)



(b)

Fig. 1 Conceptual models of cryptozoan food webs on two forest floors. Populations are shown as compartments and feeding interactions as connectivities where the head of an arrow indicates the direction of calcium and potassium movement and the tail identifies the donor. (a) A 10-compartment model for a mature deciduous hardwood forest (Gist, 1972) where θ = nonpredatory mortality and ϵ = egestion. (b) A 6-compartment model for a nearby hardwood-converted-to-pine forest (Cornaby, 1975).

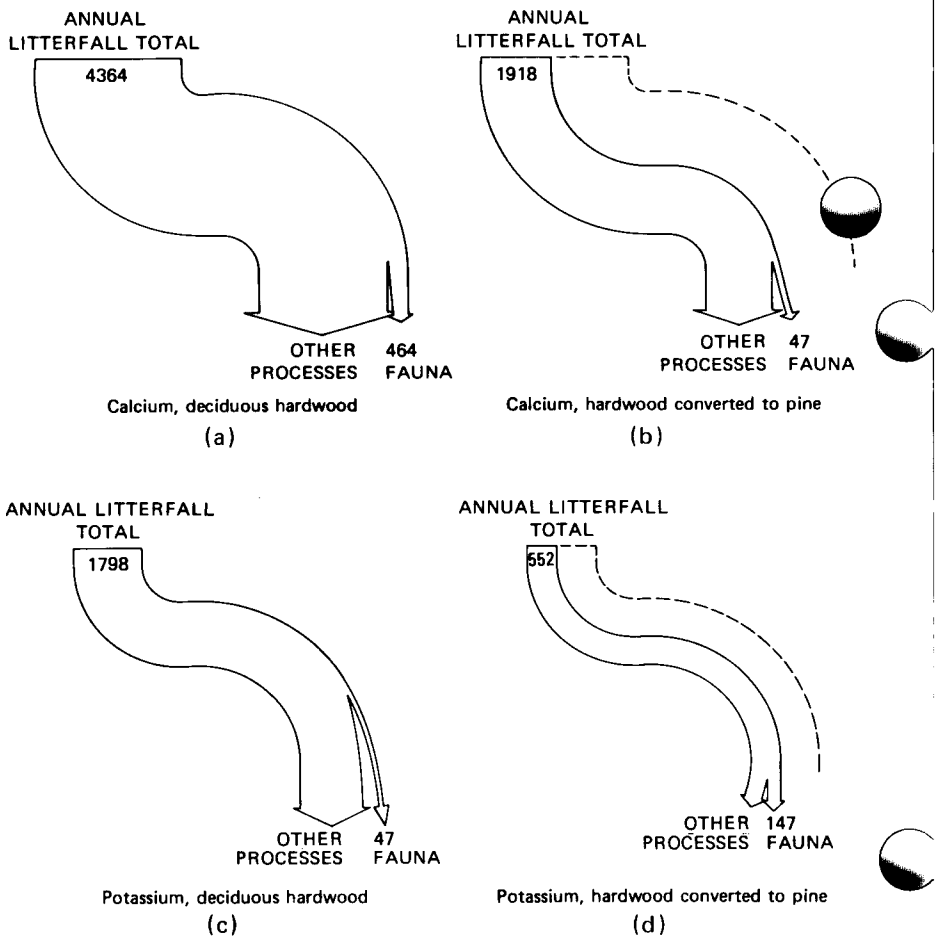


Fig. 2 Flows of calcium and potassium in a mature, deciduous hardwood forest and nearby hardwood converted to white pine forest. Differences in litter input, standing crops of litter faunas, and turnover rates of these populations, as measured with radioisotopes and systems models (see Fig. 1), resulted in the observed resource partitioning. All values are expressed as milligrams of element per square meter per year. Dotted lines show probable inputs of calcium and potassium at the time of the present study if there had been no past modifications of the two forest ecosystems.

the models showed that about 11% of annual input of calcium was ingested by animals; the remaining 89% remained in the decomposing detritus–microflora complex or moved on to the mineral soil. For potassium about 3% of the annual litter input entered the detritus food web of the hardwood forest. In the white pine watershed, the soil-litter fauna processed about 2% of the calcium input and 28% of the potassium input from annual litterfall. Although small, these percentages indicate considerable modification of nutrient movement in the litterfall pathway following hardwood replacement with white pine.

Before 1942 both watersheds were mixed hardwood forests at similar stages of development. We assume that the structure and function of the forest-floor litter fauna was similar. Furthermore, it is expected that annual litterfall would have been similar in the two forests. The logging and planting of white pine on the experimental watershed have altered nutrient cycling (Johnson and Swank, 1973) as well as the soil-litter fauna, evidently leading to differences in nutrient utilization by the complexes of organisms in the food webs.

Litter fauna used only one-tenth as much calcium in the experimental watershed as in the control (Fig. 2). For potassium the amount of this element entering the fauna was about three times larger on the experimental watershed than on the control. These changes may be the result of shifts in faunal composition, possibly as a result of calcium limitation to some faunal or process groups.

Further differences between the role of fauna in the processing of nutrients on the two watersheds appeared when the rates of utilization were compared with standing crops of elements in the litter faunas. Only values for summer are shown; however, they reveal trends typical of other seasons and of the year. The standing crop of an element was determined by multiplying observed concentrations by biomasses. The standing crop of calcium in detritivores was 560 mg/m^2 in the hardwood watershed, compared with 54 mg/m^2 in the white pine watershed. This nine-tenths reduction corresponds closely with the nine-tenths reduction in the rate of calcium intake by the fauna which was estimated to be 464 mg m^{-2} $year^{-1}$ for hardwood vs. 47 mg m^{-2} $year^{-1}$ for the white pine. The calcium contained in the standing crop of litter was similar in the two watersheds: 10.7 g/m^2 for hardwood vs. 10.4 g/m^2 for hardwood converted to pine forests. Thus the utilization rate of calcium by the fauna was related to the standing crop of fauna and perhaps to annual input of litter [Fig. 2(a,b)] but evidently not to the standing crop of litter, at least not in any obvious manner.

For potassium the relationships between standing crops and inputs were not clear. Detritivores on the hardwood watershed had a standing crop of potassium which was about three times greater than that on the white pine watershed, where about 10 mg/m^2 and about 30 mg/m^2 were observed. Yet the smaller standing crop of litter animals on the white pine watershed processed three times more potassium than did the larger standing crop in the hardwood watershed [Fig. 2(c,d)]. The litter component of the forest floors contained similar amounts of potassium with 1.8 g/m^2 vs. 2.3 g/m^2 for hardwood and pine,

respectively. Whether this difference in potassium turnover is a property of the composition of the soil-litter fauna in the white pine watershed or is due to some difference in potassium retention within the litter–detritus system (or both) remains to be resolved. Since Collembola were the dominant litter animals in terms of biomass (Table 1), studies of potassium metabolism by Collembola may reveal further insight into the behavior of this element in this forest-floor system.

These studies evaluated the role of the litter-soil fauna in cycling of calcium and potassium in litter–detritus systems. Comparisons of the results lead further questions about the context in which soil-litter fauna should considered. Each of us has expressed the opinion that soil fauna process only a small fraction of the input of mineral element into the forest floor (Crossley, 1970; Gist, 1972; Cornaby, 1975). Yet, the present results show that this is not necessarily so. Fauna processed about 28% of the annual litter input of potassium in the white pine watershed and 11% of the annual calcium input in the hardwood watershed. These are not entirely trivial numbers, when it is considered that about half the calcium input of white pine litter remains immobilized after a year. Further, both models apparently underestimate calcium input into fauna. Each model required that the annual input of calcium was about equal to the summer standing crop of detritivores. Calcium turnover for soil fauna is not well measured, but an amount three to four times that suggested by models could be reasonable (Kowal and Crossley, 1971).

It is not clear whether the food chains should be referenced to annual input of litter (as was done here) or to total annual input including throughfall. In the latter case the percentages of mineral elements passing through food chains would be reduced by factors ranging from 1.2 (calcium in the hardwood watershed) to 6 (potassium in the white pine watershed). It is also unclear what fraction of the entire litter–detritus elemental pool may be available to the soil fauna. It would be desirable to reference the feeding of soil fauna to the microflora as a food base, but our knowledge of elemental concentrations and turnovers in soil microflora is limited such that it seems impossible to do so at present (Cromack, Todd, and Monk, 1975).

Comparisons of the results of the two studies provide estimates and some explanations for the amounts of calcium and potassium being processed by the food webs of the leaf-litter faunas. The significance of these partitionings wil best understood as the results of ongoing studies on producers, consumers, a abiotic factors at Coweeta and elsewhere are synthesized from an ecosystem perspective.

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REFERENCES

Cornaby, B. W., 1975, Systems Models of Nutrient Transfer in a Cryptozoan Food Web, in Proceedings of Third Soil Microcommunities Conference, D. L. Dindel (Ed.), USERDA Report CONF-731015 (in press).

——, 1973, Population Parameters and Systems Models of Litter Fauna in a White Pine Ecosystem, Eastern Deciduous Forest Biome, Memo Report No. 73-19, U. S. International Biological Program.

Cromack, K., Jr., 1972, Litter Production and Litter Decomposition in a Mixed Hardwood Watershed and in a White Pine Watershed at Coweeta Hydrologic Station, North Carolina, Ph.D. Dissertation, University of Georgia, Athens, Ga.

——, R. L. Todd, and C. D. Monk, 1975, Patterns of Basidiomycete Nutrient Accumulation in Conifer and Deciduous Forest Litter, *Soil Biol. Biochem.* (in press).

Crossley, D. A., Jr., 1970, Roles of Microflora and Fauna in Soil Systems, in *Pesticides in the Soil: Ecology, Degradation and Movement,* International Symposium on Pesticides in the Soil, pp. 30-35, Michigan State University, East Lansing.

——, and M. Witkamp, 1964, Forest Soil Mites and Mineral Cycling, Congrés International d'Acarologie, Fort Collins, Colorado, *Acarologia,* fascicule h. s., 1964: 137-145.

Edwards, C. A., and J. W. Heath, 1963, The Role of Soil Animals in Breakdown of Leaf Materials, in *Soil Organisms,* pp. 76-78, J. Doeksen and J. van der Drift (Eds.), North-Holland Publishing Company, Amsterdam.

Gist, C., 1972, Analysis of Mineral Pathways in a Cryptozoan Food Web, Ph.D. Dissertation, University of Georgia, Athens, Ga.

——, and D. A. Crossley, Jr., 1975, The Litter Arthropod Community in a Southern Appalachian Hardwood Forest: Numbers, Biomass and Mineral Element Content, *Amer. Midland Natur.,* 93: 107-122.

Johnson, P. L., and W. T. Swank, 1973, Studies of Cation Budgets in the Southern Appalachians on Four Experimental Watersheds with Contrasting Vegetation, *Ecology,* 54: 70-80.

Kowal, N. E., and D. A. Crossley, Jr., 1971, The Ingestion Rates of Microarthropods in Pine Mor, Estimated with Radioactive Calcium, *Ecology,* 52: 444-452.

Sheva, G. F., 1960, The Role of Invertebrates in the Decomposition of the Oak Leaf Litter, *Pocvovedenie,* 4: 16-23.

Whittaker, R. H., 1970, *Communities and Ecosystems,* Collier-Macmillan Ltd., London.

Witkamp, M., 1971, Soils as Components of Ecosystems, *Annu. Rev. Ecol. Syst.,* 2: 85-110.

——, and D. A. Crossley, Jr., 1966, The Role of Arthropods and Microflora in Breakdown of White Oak Litter, *Pedobiologia,* 6: 293-303.

FOREST-FLOOR NUTRIENT DYNAMICS IN SOUTHERN APPALACHIAN HARDWOOD AND WHITE PINE PLANTATION ECOSYSTEMS

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ABSTRACT

Nutrient content and detrital biomass in the forest floor of a mature deciduous hardwood watershed and a 15-year-old white pine plantation at Coweeta Hydrologic Laboratory, N. C., were followed through one complete annual cycle, May 1970 to May 1971. Total carbon storage is significantly greater in the white pine than in the deciduous hardwood forest floor. Forest-floor biomass is probably approaching a steady state in the pine plantation, as indicated by computed turnover times. Calcium content, which is on the order of 100 kg/ha in both forest floors, is higher in the hardwood forest floor than in the pine; this reflects a considerably higher concentration of calcium in hardwood litter. Magnesium content is an order of magnitude lower than calcium. Potassium and sodium levels are very similar in both forest floors. Nitrogen and phosphorus storage is considerably higher in the white pine than in the hardwood forest floor. Summer loss rates were computed for forest-floor components.

In temperate forest ecosystems the forest floor, or aboveground detritus, is one of the major reservoirs of the elements required for ecosystem metabolism and structural maintenance. As expressed by Remezov and Pogrebnyak (1969): "In the course of the biological cycle, forest vegetation extracts the required nutrient elements from the soil and returns them to the soil, in proportions which are most favorable for its development. As a result of the succession of forest generations, the uppermost soil horizons become enriched in nutrient elements in the proportions required by the vegetation." That is, over a period of years the nutrients are concentrated where they are needed. This enrichment process depends directly on the release of nutrients from the litter.

As part of an integrated research program on the ecological structure, productivity, and biogeochemical cycling pathways of small watershed eco-

systems at Coweeta Hydrologic Laboratory, N. C., I sought to quantify the standing crops, or pools, of nutrient elements and detrital biomass in the forest floor of two watersheds and to estimate the rate at which nutrient elements are lost from the forest floor.

Although the history and description of these watersheds and of the U. S. Forest Service and International Biological Program research conducted in them have been discussed adequately elsewhere (Johnson and Swank, 1973), I will emphasize here that the watersheds are located in the highest rainfall area of eastern North America. Annual precipitation in the study watersheds averages slightly less than 200 cm/year. Temperature and moisture appear to be the two primary driving functions for litter decomposition (Witkamp, 1971). Lack of adequate moisture would not generally be a limiting factor for litter microbial decomposition in the Coweeta watersheds, and thus temperature becomes the primary driving function. Moisture is important because of its role in the physical leaching of minerals, particularly during winter or periods of high microbial mortality when immobilization (or microbial uptake) is not as effective in retarding loss.

METHODS AND MATERIALS

Two sample transects were established in each of the two watersheds. Each transect led from a stream channel to a point 60 m up on both facing slopes. The layout of the transects was affected by the watershed topography. In the hardwood watershed, transects were at midwatershed level on each of two stream channels. In the white pine watershed, transects were across the lower and upper thirds of the single channel. The transects were selected in areas with the following vegetation growth forms (see Table 1 for hardwood species distribution based on fresh litterfall composition): (1) broad-leaved deciduous with deciduous understory, (2) broad-leaved deciduous with broad-leaved evergreen understory (*Kalmia* and *Rhododendron*), and (3) needle-leaved evergreen (white pine, *Pinus Strobus* L.).

Two plots (2 by 15 m each) were established on each slope of a transect as near as practical to the stream and 60 m upslope; there was a total of 16 plots, 8 watershed. Every two months triplicate 0.25-m^2 quadrats were sampled in each plot. All the litter, including branches up to 2.5 cm in diameter, was collected from each quadrat. The litter was collected separately by forest-floor horizon, L and F in the hardwood watershed; L, F, and H in the pine watershed (Phillipson, 1971).

Litter samples were ovendried at 70°C, weighed, ground to less than 2-mm particle size, and submitted to the University of Georgia Soil Testing and Plant Analysis Laboratory, where they were again oven-dried at 70°C before being analyzed.

TABLE 1

WEIGHT AND COMPOSITION OF L LAYER (WS18), NOVEMBER 1970*

Common name	Species or component	Weight, g/m^2	% of total
Chestnut oak	*Quercus Prinus*	44.8	21.0
Red oak	*Q. rubra*	25.3	11.8
Scarlet oak	*Q. coccinea*	29.1	13.6
Black oak	*Q. velutina*	20.1	9.4
White oak	*Q. alba*	1.6	0.76
Blackjack oak	*Q. marilandica*	0.07	0.0
Red maple	*Acer rubrum*	18.1	8.5
Dogwood	*Cornus florida*	6.0	2.8
Sourwood	*Oxydendrum arboreum*	2.7	1.3
Hickory	*Carya* sp.	14.4	6.7
Tulip tree	*Liriodendron tulipifera*	4.2	2.0
Rhododendron	*Rhododendron maximum*	5.5	2.6
Mountain laurel	*Kalmia latifolia*	2.4	1.1
Fraser magnolia	*Magnolia Fraseri*	2.0	0.92
Cucumber tree	*M. acuminata*	0.25	0.12
Sassafras	*Sassafras albidum*	0.28	0.13
American chestnut	*Castanea dentata*	0.13	0.062
American beech	*Fagus grandifolia*	0.10	0.047
Black tupelo	*Nyssa sylvatica*	0.02	0.0070
Witch hazel	*Hamamelis virginiana*	0.07	0.031
Huckleberry	*Vaccinium* sp.	0.02	0.0078
Grape	*Vitis* sp.	1.9	0.87
Fern		0.35	0.16
Smilax	*Smilax* sp.	0.05	0.02
Birch	*Betula* sp.	0.18	0.078
Miscellaneous	Fruits, twigs, leaf fragments	34.3	16.0
	TOTALS	213.9	100.0

*Data are for a total of 24 0.25-m^2 quadrat samples, or a 6-m^2 area.

Litter nitrogen was determined by a micro-Kjeldahl procedure, and elements other than nitrogen were determined with a direct-reading spark emission spectrograph, after dry-ashing and uptake in nitric acid (Jones and Isaac, 1971).

The high between-plot variability of the litter chemical properties and the minimal plot sample size precluded any analysis of possible trends within a watershed, such as trends with elevation along a slope or with vegetation type. For this reason the data for each parameter and sampling period were combined by watershed and considered as one sample. This lumping of data resulted in statistically significant differences between means in many cases, both between watersheds and over time.

For a more detailed discussion of methods and a detailed data tabulation, see the International Biological Program report by Yount (1972).

RESULTS AND DISCUSSION

The total carbon storage (as represented by dry total litter weight) is significantly higher in the white pine than in the deciduous hardwood forest floor (Fig. 1). Total litter weight in the pine forest floor was fairly stable throughout the year. Swank and Schreuder (1973) reported that leaf-area index in the pine watershed stabilized at a maximum value beginning in 1969. These facts suggest that the pine forest floor should soon be approaching a steady state.

An estimate of the species composition of the leaf litter in the hardwood watershed is given in Table 1. Oak species predominate, and the chestnut oak comprises 21% of the total. The litter input to the pine forest floor is, of course, almost entirely white pine, with the exception of a small amount of herbaceous and shrub litter and leaves from a few scattered *Liriodendron* sprouts.

Three pine litter layers (L, F, and H) were easily distinguishable and separable in the field. In the hardwood forest floor, the L layer was identified as that material not bound by fungal filaments and hence free to be blown about. The F-layer material ranged from identifiable, but bound, leaves and fragments to, in many cases, particles too small to be identified, but there was no way to separate this readily in the field. Thus an H layer in the hardwood forest floor was not distinguished and in any case was at least partly incorporated into the A1 horizon; i.e., the transition from forest floor to soil was sharp in the pine

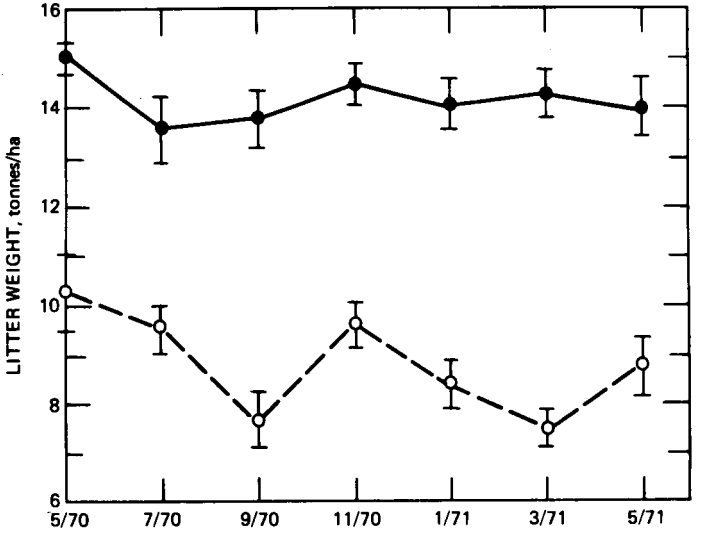

Fig. 1 Total oven-dry weight of forest-floor litter. —•—, pine. – –○– –, hardwood. Vertical lines indicate ±SE (n = 24).

watershed but rather broad in the hardwood. Because of the obvious visual and operational (sampling) division of the pine forest floor into three horizons, I preferred to use the L, F, and H designations, as in Phillipson (1971). In terms of the commonly used O1 and O2 designations, L is equivalent to O1 and F (or F + H) is equivalent to O2.

Over much of the year the amounts of calcium and magnesium present were either approximately the same or significantly greater in the hardwood forest floor than in the pine (Fig. 2). Since the reverse is true for litter dry weight (Fig. 1), this reflects a considerably higher concentration of calcium and magnesium in the hardwood litter. Calcium concentration increases from L t layers in both forest floors, but decreases slightly in the pine H layer (Table The pine H-layer calcium decrease may be due in part to mineral matter incorporated into this horizon from the soil. In contrast to the hardwood forest floor, which contained numerous fine rootlets, no roots were observed in the pine forest floor (i.e., the soil–litter transition was sharp, as noted). Hence the decrease in calcium and other elements in the pine H layer cannot be attributed

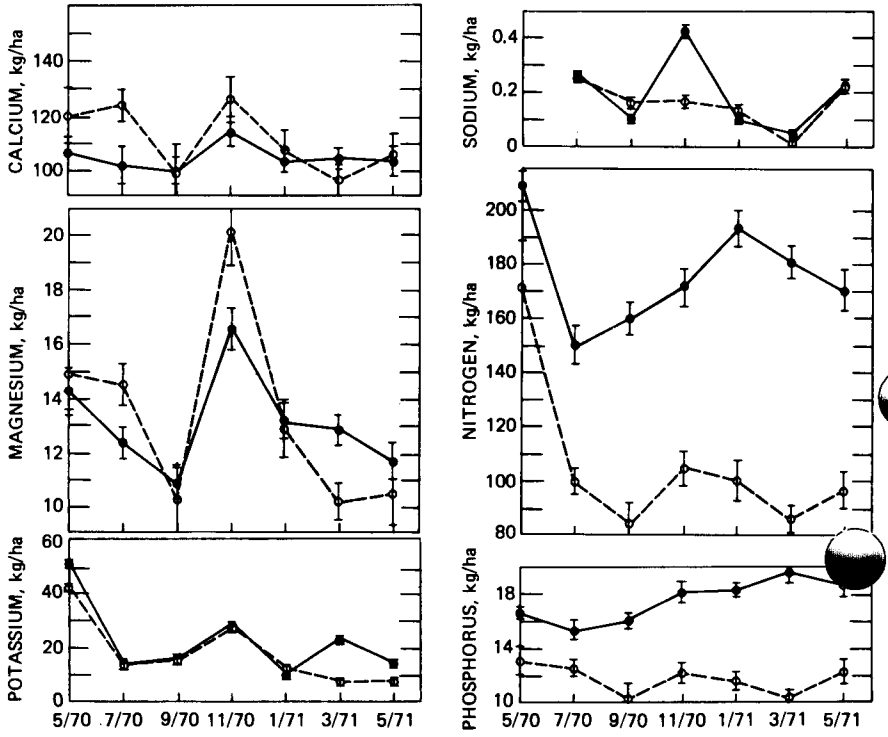

Fig. 2 Total forest-floor content of selected nutrients. —●—, pine. – –○– –, hardwood. Vertical lines indicate ±SE (n = 24).

TABLE 2

CHANGE IN CONCENTRATION* OF LITTER COMPONENTS THROUGH THE LITTER PROFILE, NOVEMBER 1970

Layer	Ash-free organic matter, %	Ca, %	Mg, %	K, %	Na, ppm	N, %	P, %
				White Pine			
L	97.0 ± 0.3	0.73 ± 0.02	0.143 ± 0.003	0.213 ± 0.003	7 ± 2	0.86 ± 0.02	0.104 ± 0.001
F	94.8 ± 0.4	0.82 ± 0.03	0.121 ± 0.004	0.210 ± 0.006	54 ± 5	1.27 ± 0.02	0.131 ± 0.002
H	71.1 ± 1.4	0.76 ± 0.03	0.095 ± 0.005	0.194 ± 0.006	25 ± 2	1.28 ± 0.02	0.129 ± 0.002
				Hardwood			
L	95.8 ± 0.1	1.05 ± 0.03	0.240 ± 0.009	0.319 ± 0.010	10 ± 2	0.76 ± 0.02	0.100 ± 0.001
F	89.5 ± 1.0	1.36 ± 0.04	0.196 ± 0.006	0.275 ± 0.007	20 ± 3	1.18 ± 0.02	0.132 ± 0.004

*Mean ±SE (n = 24).

to root uptake. Forest-floor magnesium content reaches a minimum in September, at the same time that magnesium is at a maximum in the soil (Yount, this volume). Magnesium concentration decreases continuously with litter profile depth.

Potassium levels in the forest floor of both watersheds were quite similar throughout most of the year, and sodium levels were similar in both forest floors also. There is a declining trend for certain elements between May 1970 and May 1971 (i.e., for calcium, magnesium, potassium, and nitrogen in the hardwood litter and for magnesium and nitrogen in the pine litter). The decline is greater than can be attributed to the slight decrease in total litter over the year. A li[illegible] explanation for this is that there was more leaching due to higher rainfall in e[illegible] 1971 than in 1970.

Quarterly rainfall data furnished by Swank (1971) at Coweeta support the hypothesis that more intense leaching in 1971 compared with 1970 was a major contributing factor to the lower levels of these nutrients in May 1971. The following data are from a rain gage for which continuous records are available since the beginning of hydrologic studies at Coweeta and are considered to be representative of trends within the Coweeta Basin.

Period	Total precipitation, cm		
	35-year average	1970	1971
Nov.–Jan.	48.08	41.58	41.76
Feb.–April	54.33	36.88	51.61
May–July	40.39	36.02	54.13

During the entire 6-month period before the beginning of this study, rainfall was lower than the 35-year average, and, in the immediately preceding three months (February to April 1970), it was ~25% lower. During the February-to-April quarter of 1971, however, toward the end of this study, rainfall was almost back to the 35-year average (i.e., considerably higher than in the previous spring), and it was also considerably higher than the 35-year average from May to July 1971. These data roughly correlate with the lower levels of forest-floor elements in May 1971 as compared with May 1970. In addition, the lower-than-average rainfall just before this study began may be at least par[illegible] responsible for the higher initial levels of calcium, magnesium, potassium, [illegible] nitrogen in the forest floor. That is, the earlier levels may be above normal, and the levels in May 1971 may be closer to normal or below normal. As it turned out, this study spanned a period preceded by a relatively dry winter and concluded with a relatively wet spring, compared with the 35-year average.

In contrast to calcium and magnesium, significantly more nitrogen and phosphorus were stored in the white-pine than in the hardwood forest floor. Todd (1971) reported high nitrogen fixation rates in the litter; this may help to explain these figures.

A comparison of the change in concentration of litter components through the litter profile gives some idea of the dynamics of litter decomposition and of elemental mobilities. Since the data in Table 2 are for November 1970, shortly after litterfall, the L layer represents new litter. Concentration data are more instructive for this purpose than are area-weight data because the latter are controlled by the total litter weight, which increases by a factor of from 2 to 4 times from the top to the bottom litter layer and completely obscures the concentration changes.

Particularly noteworthy here are the decreasing concentrations of ash-free ...ic matter, magnesium, and potassium through the litter profile and the ...easing concentrations of calcium, sodium, nitrogen, and phosphorus. Among the latter group of elements, calcium and sodium show a peak concentration in the middle (F) layer in the pine forest floor. Calcium maintained this peak concentration in the F layer throughout the year, but sodium shifted to a peak concentration in the H layer beginning in January 1971. This may have been due to the increased precipitation during this period.

The decreasing concentration of ash-free organic matter through the litter profile is attributable to metabolic losses of carbon dioxide and water, which decrease the carbon, hydrogen, and oxygen content of the decomposing material (Witkamp, 1971). Potassium decrease is probably due to the high solubility of potassium compounds and the lower stability of monovalent vs. divalent cations in cation-exchange complexes. In general, however, in complex systems such as forest litter and soil, with many different exchange materials present and many biochemical processes taking place, it is difficult if not impossible to generalize on the exchange behavior of cations on the basis of simple chemical arguments because the relative exchangeability (hence leachability) varies considerably with the nature of the exchanger and the concentration of the solution (Wiklander, 1964).

It is reasonable to expect that the biologically critical elements nitrogen and phosphorus would tend to be retained and to increase in concentration during decomposition. Furthermore, nonsymbiotic nitrogen fixation probably adds to the original nitrogen content of the litter.

The relative mobilities of various litter elements have been quantified by measuring the amounts of the elements present at the beginning and end of a ...n period and dividing the difference by the original amount (Attiwill, 1968; ...emezov, 1961). The resulting fractional decrease can be related to an exponential decay model (Olson, 1963); Minderman (1968) has argued that a linear decay model is equally valid. For expressing relative mobilities, however, either assumption is valid. The difference arises in the application of the original fractional decrease figures, such as in the computation of turnover times. I have chosen to apply the exponential decay model for the limiting case of free decay (no input) to estimate summer loss rate constants and turnover times for several litter components.

The period of maximum litterfall occurs at approximately the same time in both white pine and hardwood watersheds—from mid-October to early November. Litterfall in the hardwood forest is essentially complete by the middle of November. In the pine plantation, however, the time distribution of litterfall is broader, and needles tend to hang up in the dense network of branches, which further retards their fall. During the period between May and September, however, litterfall is at a minimum in both watersheds, and the conditions of the free-decay model are most closely met. This approximation is much better for some litter components than for others and is probably least valid for nitrogen, where fixation is to be expected.

The results are presented in Table 3 in the form of a mobility series in w[illegible] the k' values represent fractional losses during the period from May to September. These values can be converted, via the exponential free-decay model, to instantaneous fractional loss rate constants k, with time units of $year^{-1}$, and, if desired, to turnover times by taking the reciprocal of k. These k values, of course, apply to the summer period only.

Potassium and nitrogen mobilities (i.e., loss rate constants) in both forest floors are considerably higher than those of the litter as a whole, expressed either as dry weight or ash-free weight loss. Nitrogen mobility is much lower in the pine than in the hardwood forest floor. Of course, the mobility of nitrogen actually represents the net excess of nitrification, denitrification, and leaching over nitrogen fixation and immobilization in the litter. Thus these processes must be more closely in balance in the pine litter. Magnesium loss appears to be more closely tied to structural breakdown of the forest-floor components (i.e., to dry weight loss) in hardwood than in pine litter. In both litter types calcium and phosphorus losses are evidently closely tied to the loss rate of the forest floor as a whole.

In summary, the forest-floor nutrient pools reported on here represent the result of a number of competing processes; principally litterfall, precipitation, leaching, microbial decomposition, and microbial immobilization, or uptake. For nitrogen, the additional processes of fixation, nitrification, and denitrification must be added. These processes result in a situation in which calcium and magnesium tend to be selectively concentrated in the hardwood forest floor, nitrogen and phosphorus tend to be concentrated in the pine forest floor, and potassium and sodium are concentrated approximately equally in both forest floors.

ACKNOWLEDGMENT

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TABLE 3

RELATIVE MOBILITIES* AND DECAY CONSTANTS† OF FOREST-FLOOR COMPONENTS CALCULATED FROM STANDING-CROP DECREASE, MAY TO SEPTEMBER 1970

White pine	**K**	>	**Mg**	>	**N**	>	**Ash-free wt.**	>	**Dry wt.**	>	**Ca**	>	**P**
k′, yr^{-1}	0.688		0.237		0.235		0.0903		0.0870		0.0694		0.0422
k, yr^{-1}	3.495		0.810		0.804		0.284		0.273		0.216		0.129
Hardwood	**K**	>	**N**	>	**Mg**	>	**Ash-free wt.**	>	**Dry wt.**	>	**P**	>	**Ca**
k′, yr^{-1}	0.641		0.513		0.315		0.255		0.246		0.223		0.181
k, yr^{-1}	3.071		2.158		1.137		0.881		0.849		0.755		0.598

*$k' = \frac{X_0 - X}{X_0}$

†$k = (-1/t) \ln (1 - k')$, where $t = \frac{1}{3}$ year.

REFERENCES

Attiwill, P. M., 1968, The Loss of Elements from Decomposing Litter, *Ecology*, **49**: 142-145.

Johnson, P. L., and W. T. Swank, 1973, Studies of Cation Budgets in the Southern Appalachians on Four Experimental Watersheds with Contrasting Vegetation, *Ecology*, **54**: 70-80.

Jones, J. B., and R. Isaac, 1971, Laboratory Procedures for the Analysis of Soils, Feed, Water and Plant Tissue, Soil Testing and Plant Analysis Laboratory, University of Georgia, Athens.

Minderman, G., 1968, Addition, Decomposition and Accumulation of Organic Matter in Forests, *J. Ecol.*, **56**: 355-362.

Olson, J. S., 1963, Energy Storage and the Balance of Producers and Decomposers in Ecological Systems, *Ecology*, **44**: 322-331.

Phillipson, J., 1971, *Methods of Study in Quantitative Soil Ecology: Population, Production, and Energy Flow*, Handbook No. 18, Chap. 3, Plant Litter, U. S. International Biological Program.

Remezov, N. P., 1961, Decomposition of Forest Litter and the Cycle of Elements in an Oak Forest, *Sov. Soil Sci. (Engl. Transl.)*, **1961**: 703-711.

___, and P. S. Pogrebnyak, 1969, *Forest Soil Science*, Translated by A. Gourevitch, Y. Haver (Ed.), Israel Program for Scientific Translations, Ltd., Jerusalem. Published pursuant to agreement with the U. S. Department of Agriculture and the National Science Foundation, Washington, D. C.

Swank, W. T., 1971, Coweeta Hydrologic Laboratory, U. S. Department of Agriculture, Forest Service, personal communication.

___, and H. T. Schreuder, 1973, Temporal Changes in Biomass, Surface Area, and Net Production for a *Pinus strobus* L. Forest, Biomass Studies, pp. 171-182, International Union of Forest Research Organizations, Working Party on the Mensuration of the Forest Biomass, College of Life Sciences and Agriculture, University of Maine, Orono.

Todd, R. L., 1971, Microbial Transformations of Nitrogen in Natural and Manipulated Watersheds at Coweeta, Eastern Deciduous Forest Biome Memo Report 71-133, U. S. International Biological Program.

Witkamp, M., 1971, Soils as Components of Ecosystems, *Annu. Rev. Ecol. Systemat.*, **2**: 85-110.

Wiklander, Lambert, 1964, Cation and Anion Exchange Phenomena, in *Chemistry of the Soil*, 2nd ed., Firman E. Bear (Ed.), pp. 163-205, Reinhold Publishing Corporation, New York.

Yount, J. D., 1972, Soil and Forest Floor Chemical Dynamics in Two Contrasting Watershed Ecosystems. Eastern Deciduous Forest Biome Memo Report No. 72-53, U. S. International Biological Program.

LITTER PRODUCTION, DECOMPOSITION, AND NUTRIENT CYCLING IN A MIXED HARDWOOD WATERSHED AND A WHITE PINE WATERSHED

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ABSTRACT

Litter production and decomposition data were obtained for a mixed-hardwood watershed and for a white pine watershed. Litterfall data were obtained for leaves, stems, flowers, acorns, and miscellaneous debris in the hardwood watershed and for needles, stems, and cones in the white pine watershed. Litterfall data obtained included biomass of litter; nitrogen, phosphorus, potassium, calcium, and magnesium contents in litter; and structural organic constituents (lignin, cellulose, and total fiber) of leaf litter. Total annual litter production in the hardwood watershed (1970–1971) was 4369 kg ha^{-1} $year^{-1}$ of which 2773 kg ha^{-1} $year^{-1}$ (64%) was leaf litter. Total annual white pine litter production (1970–1971) was 3253 kg ha^{-1} $year^{-1}$, 98% of which was needle litter in the young stand (planted 1956). Litter decomposition data were obtained for weight loss rate and for loss rates of nutrients. The first-year litter breakdown rate of confined mixed-hardwood leaf litter was $k = -0.70$ $year^{-1}$; the breakdown rate of confined white pine needle litter was $k = -0.46$ $year^{-1}$. Litter decomposition rates of chestnut oak, white oak, white pine, red maple, and dogwood were significantly correlated with senescent leaf carbon-to-nitrogen ratio and sclerophyll index, the sclerophyll index giving a better statistical estimate of decomposition rate.

Nutrient cycling and energy flow are two ecological processes that delineate the structure and dynamics of ecological systems. In terrestrial ecosystems an important set of energy flows and nutrient transfers result from litterfall and in the subsequent decomposition of litter. Litterfall and litter decomposition can be thought of as separate events in terrestrial ecosystems, but such ecological

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processes as energy flow and nutrient cycling permit them to be linked together functionally in an ecosystems context.

Seventy percent of the energy fixed in net primary production in a grazed meadow ecosystem goes directly to decomposer organisms (Macfadyen, 1963). As much as 90% of terrestrial net primary production ultimately is utilized by decomposers (Whittaker, 1970; Odum, 1971). It has been suggested that decomposer organisms may be just as important in aquatic ecosystems as they are in terrestrial ones (Pomeroy, 1970). Litterfall and litter decomposition also account for a substantial portion of internal nutrient cycling in terrestrial ecosystems. In a study of a mesic oak-dominated forest floor, litt[illegible] accounted for approximately 60% (average for the elements phospho[illegible], potassium, calcium, and magnesium) of internal nutrient input to the forest floor (Carlisle, Brown, and White, 1966a; 1966b).

Biodegradation of litter is a complex process in which microorganisms and soil animals interact synergistically (Crossley, 1970; Witkamp, 1971). Both the microorganisms and soil animals are strongly influenced by such abiotic factors as soil–litter temperature and moisture. Microorganisms predominate in litter decomposition, primarily because they have enzymes capable of biodegrading structural carbohydrates including such complex end products of carbohydrate metabolism as lignin (Witkamp, 1971). As much as 90% of litter materials can be biodegraded by microorganisms (Macfadyen, 1963). Microorganisms are also important in the release and transfer of nutrients bound in the litter (Witkamp, 1971; Stark, 1972; Todd, Cromack, and Stormer, 1973). Soil animals, by interacting synergistically with the microorganisms, function as one set of biological control factors which regulate rates of litter decomposition (Edwards, Reichle, and Crossley, 1970; Ausmus and Witkamp, 1974). In turn these animals are dependent for their nutrition primarily upon the microorganisms they ingest since soil animals lack enzymes necessary to biodegrade all but the simplest forms of structural carbohydrates (Nielson, 1962).

Considerable data exist for litter production and litter nutrients in forest ecosystems, with major review papers summarizing forest-litter data from many different sources (Ovington, 1962, 1965; Olson, 1963; Bray and Gorham, 1964; Rodin and Bazilevich, 1967). For the purpose of facilitating comparison of data from many different ecosystems, total annual litter budgets are preferred; subannual budgets for major litter components usually are available in m[illegible] recent studies (Carlisle, Brown, and White, 1966b; Sykes and Bunce, 1970; G[illegible] Likens, and Bormann, 1972).

In this paper we compare nutrient cycling from litter production and litter decomposition in a mixed-hardwood ecosystem with the same nutrient-cycling processes in an adjacent white pine (*Pinus strobus* L.) watershed in the southern Appalachians. We also compare indexes of foliage-litter substrate quality obtained from the two different vegetation types and discuss nutrient cycling implications of foliage-litter nitrogen and phosphorus levels in the context of carbon allocation to such substrates as lignin and cellulose.

RESEARCH AREAS

The two forest watersheds used in this study are located within the U. S. Forest Service Coweeta Hydrologic Laboratory, Franklin, N. C. The two field sites were chosen such that litter production and litter decomposition in a mixed-hardwood ecosystem could be compared and contrasted with corresponding litter dynamics in a white pine ecosystem. The mature mixed-hardwood stand, designated by the U. S. Forest Service as watershed 18, is 12.5 ha in area. The white pine stand, planted in 1956, is 13.5 ha in area and was designated as watershed 17. Broad environmental differences between the two watersheds are minimized in that they have similar slopes, aspects, altitudinal ranges, soils, and precipitation and are contiguous for approximately one-half their vertical distances (Kovner, 1955; Johnson and Swank, 1973).

MATERIALS AND METHODS

Square traps 0.5 m on a side were used for hardwood leaf litter, flower litter, and debris. To make all traps equal regardless of ground slope, we placed each trap on wooden legs and leveled each with a spirit level during installation. The traps were checked periodically thereafter. Thirty of the litter traps were placed at random in the hardwood watershed in the fall of 1969. Acorn litter was collected from 20 60-cm by 60-cm cloth-bottomed deadfall traps.

White pine needles were collected in 200-cm by 15-cm aluminum troughs used in a throughfall study of watershed 17 (Best, 1971). Nineteen of these troughs were used; 10 were located in one random transect and 9 were located in another random transect through the watershed.

During the fall periods, leaf and needle litter were collected at approximately 2-week intervals. Since some of the white pine needles became lodged in branches, additional litter collections were made at intervals throughout the year. No hardwood collections were made in winter because little leaf litter remained on the trees after December. Beginning in late spring and continuing through the summer at monthly intervals, flower litter and debris were collected in the hardwood watershed.

Stem and branch litter were collected from 18 10-m by 10-m ground plots in the hardwood stand. During the summer of 1970, the total accumulated standing crop of woody litter was estimated. Within each plot, two 2-m by 2-m subplots, located on opposite diagonal corners of the large plots, were used to collect stem litter less than 2.5 cm in diameter. In the whole plot, woody litter 2.5 cm or greater in diameter was collected. American chestnut logs and branches were excluded from the standing crop totals since they represented litter input from a catastrophic event in the watershed. The following year collection was made of all woody litter that had fallen into the plots.

In the summer of 1970, 10 3.33-m by 3.33-m woody-litter plots were set up in the white pine stand; collections were made in the summer of 1971. Most of the dead branches remain on the trees. Consequently woody-litter input to the forest floor is as yet relatively unimportant for the white pine stand. Woody-litterfall data from the ground plots of both watersheds were corrected to a horizontal area basis for average slopes of 53% in both watersheds. This permitted comparison of woody litter from the ground plots with litter-trap data on a common basis.

Data for first-year leaf-litter breakdown of single species were obtained during two consecutive 1-year periods, beginning in the fall of 1969. Single species for which leaf-litter decomposition data were obtained included chestnut oak (*Quercus prinus* L.), white oak (*Quercus alba* L.), red maple (*Acer rubrum* L.), and flowering dogwood (*Cornus florida* L.) in the hardwood watershed and eastern white pine in the pine stand. The four species used for deciduous-litter breakdown were chosen to give a range of decomposition rates and to represent the more important species groups producing leaf litter within the system. In the hardwood stand additional leaf-decomposition data were obtained for mixed-species leaves in litter bags.

Data for litter breakdown of single species were obtained using decimeter square fiber glass litter bags (Crossley and Hoglund, 1962), each containing approximately 2.5 g of leaves. In the deciduous stand the integrated decomposition rate was obtained for mixed-hardwood leaves confined in the large, 0.125 m^2, litter bags each containing approximately 40 g of deciduous leaves. In addition to the larger size, a different bag design was used for the mixed-litter bags to permit easier entry of soil animals. The upper half of each large bag was made of 2.54-cm-mesh nylon netting, while the lower half was fine 2-mm-mesh nylon to inhibit loss of small leaf fragments from the bag. The decimeter-sized fiber glass litter bags used for single-species leaves from chestnut oak, white oak, red maple, and dogwood and needles of white pine were all 1-mm mesh.

Litter bags were removed from the field at approximately monthly intervals. The bags were weighed to determine percentage weight loss from original samples before the samples were ground in a Wiley mill for nutrient analysis.

Litter weight loss was quantified for single-species and for mixed-deciduous litter bags using the exponential decay model of Olson (1963). Nutrient loss rates from mixed deciduous litter were also quantified using the same approach.

Leaves, other small litter, and woody litter were air-dried for storage when practical or dried at 50°C when wet litter or green leaves were collected. Leaves that were to be used for decomposition studies were air-dried only to prevent possible chemical changes that might affect decomposition. For nutrient analyses, including nitrogen, litter was dried at 70°C. All final dry-weight biomass calculations were made on litter subsamples dried at 70°C. Samples were oven-dried at 50°C for analysis of organic constituents of litter. Nutrient analyses included determinations of sodium and the following major elements: nitrogen, phosphorus, calcium, potassium, and magnesium.

A micro-Kjeldahl technique was used for nitrogen determinations. Micro-Kjeldahl procedures were those of the Soil Testing and Plant Analysis Laboratory of the Agronomy Department, University of Georgia, as given in their 1971 laboratory manual (*Laboratory Procedures for the Analysis of Soils, Feed, Water, and Plant Tissue*). All other elements were determined by direct-reading spark-emission spectroscopy (Jones and Warner, 1969). Analyses for the percentage of acid-detergent fiber (cellulose and lignin) and non-cell-wall plant material followed the methods of Van Soest (1963, 1966, and 1967). The sclerophyll index was calculated following the method of Loveless (1961). Since sclerophyll index as originally proposed uses the ratio of crude fiber to crude protein × 100, crude fiber was estimated (Ellis, Matrone and Maynard, 1946) as total acid-detergent fiber × 0.64. Crude protein was calculated (Loveless, 1961) as percent nitrogen × 6.25. The percentage of carbon in leaf litter used for decomposition studies was estimated from the percentage lignin content in leaves using a regression given by Van Soest (1963).

To analyze for changes in nitrogen and total fiber, we harvested green leaves in August from several of the more important tree species in the hardwood stand and from the white pine stand. To analyze nutrient differences between senescent leaves and needles, we collected additional leaf samples in mid-October. For comparative purposes we have included a few values for western coniferous and deciduous species.

RESULTS AND DISCUSSION

Results are given as annual budgets of nitrogen, phosphorus, calcium, potassium, and magnesium in litterfall and biomass of different hardwood and white pine litterfall components in Tables 1 and 2. The leaf-litterfall category in the hardwood watershed does not include litter from shrubs, such as *Kalmia latifolia* L., *Rhododendron maximum* L., or herbaceous litter. Such litter was estimated (Day, 1971) to total 370 kg ha^{-1} $year^{-1}$. Herbaceous leaf litterfall was not estimated in the white pine stand; ground cover was sparse, however, owing to the closed canopy.

Total litter production in the hardwood watershed was 4369 kg ha^{-1} $year^{-1}$, which is within the lower 95% confidence interval of the annual litter production, totaling 4800 ± 548 kg ha^{-1} $year^{-1}$ for 11 other North American warm temperate deciduous forests (Bray and Gorham, 1964). Hardwood-litter production was only 14% greater than the mean annual litter production of 3730 ± 260 kg ha^{-1} $year^{-1}$ in 67 cool temperate deciduous forests (Bray and Gorham, 1964). In an oak-dominated British forest with a similar rainfall regime as Coweeta, on soils of low nutrient status, a total annual litter budget of 3858 kg ha^{-1} $year^{-1}$ was observed (Carlisle, Brown, and White, 1966a). On calcareous soils in Meathop Wood, Great Britain, an average total litter production of 5130 kg ha^{-1} $year^{-1}$ was reported (Sykes and Bunce, 1970).

TABLE 1

HARDWOOD WATERSHED 18: ANNUAL LITTERFALL BUDGET FOR BIOMASS AND MACRONUTRIENTS FOR 1970–1971

Category	Leaves	Stems ≤2.5 cm diameter	Stems >2.5 cm diameter	Acorns			Flowers	Debris*	Total
				Cups	Shells	Kernels			
Biomass,† kg ha^{-1} year^{-1}	2773 ± 305	706 ± 88	306 ± 145	122	120	171	6.2 ± 2.5	165 ± 37	4369
% of biomass	63.5	16.2	7.0	2.8	2.7	3.9	0.1	3.8	100.0
Macronutrients,‡ kg ha^{-1} year^{-1}									
Nitrogen	23.57	3.89	1.35	0.49	0.54	1.71	0.13	2.20	33.87
Phosphorus	3.48	0.62	0.25	0.11	0.10	0.26	0.01	0.22	5.03
Potassium	13.00	0.57	0.20	0.90	0.40	2.19	0.05	0.76	18.07
Calcium	34.11	5.57	1.73	0.43	0.41	0.15	0.03	2.16	44.49
Magnesium	6.10	0.10	0.01	0.02	0.00	0.07	0.02	0.23	6.55

*Debris category includes such fine litter fragments as bud scales, lichen fragments, and insect frass.

†Figures given are mean ±95% confidence interval of the mean.

‡Calculated as the product of average biomass, in kilograms per hectare per year, and percentage nutrient concentration on a dry-weight basis.

TABLE 2

WHITE PINE WATERSHED 17: ANNUAL LITTERFALL BUDGET FOR BIOMASS AND MACRONUTRIENTS FOR 1970–1971

Category	Needles	Stems*	Pine cones	Total
Biomass, kg ha^{-1} $year^{-1}$	3184 ± 293	38.5 ± 14.0	30.6 ± 8.1	3253
% of biomass	97.9	1.2	0.9	100.0
Macronutrients, kg ha^{-1} $year^{-1}$				
Nitrogen	26.27	0.16	0.11	26.54
Phosphorus	3.66	0.03	0.03	3.72
Potassium	5.32	0.10	0.12	5.54
Calcium	19.08	0.11	0.003	19.19
Magnesium	2.71	0.002	0.000	2.71

*Most dead stems remained attached to the trees.

Total annual litter production in the white pine watershed was 3253 kg ha^{-1} $year^{-1}$, considerably less than the mean annual litter production of 5425 ± 950 kg ha^{-1} $year^{-1}$ in 8 other North American warm temperate coniferous forests (Bray and Gorham, 1964). However, the white pine needle-litter production of 3184 ± 293 kg ha^{-1} $year^{-1}$ does not differ significantly from annual needle-litter production, averaging 3640 ± 510 kg ha^{-1} $year^{-1}$ in 10 North American warm temperate coniferous forests (Bray and Gorham, 1964). North American warm temperate forests average 37% nonneedle litter, while cool temperate forests average 23% (Bray and Gorham, 1964). On this basis, the white pine watershed at Coweeta could average 4500 to 5000 kg ha^{-1} $year^{-1}$ total annual litter production when mature. Needle-litter production did not differ significantly from white pine needle production, averaging 3386 ± 375 kg ha^{-1} $year^{-1}$ for three stands located in the northeastern United States (Chandler, 1944).

Comparing the nutrient budgets of these three northeastern white pine stands with data in Table 2 shows that the former were cycling 26% more nitrogen, 10% more potassium, 54% more magnesium, nearly the same quantities of calcium, and 46% less phosphorus. Comparison of total annual litterfall nutrient budgets in Tables 1 and 2 shows the hardwood stand was cycling more potassium, calcium, and magnesium in litterfall than the white pine stand. The appreciably greater amounts of potassium, calcium, and magnesium being cycled by the hardwood ecosystem than by the white pine watershed are consistent with other reports (Chandler, 1944; Ovington, 1962; 1965); temperate hardwood ecosystems generally cycle more cations than coniferous ecosystems with similar productivities. In the present case, total litterfall and nutrient return in litter are substantially less in the white pine watershed.

Litter from the reproductive materials and fine debris in the hardwood watershed had equal or higher percentage concentrations of all macronutrients, except calcium, as did deciduous leaf litter. Branch litter contained smaller nutrient concentrations than deciduous leaf litter. Flower litter, which was mostly from oaks, and miscellaneous debris contained relatively more macronutrients, except potassium, than did acorns. Partitioning the acorns into component parts permitted the nutrient quality of the kernels to be assessed. Acorn production in 1970 to 1971 was heavy and totaled 9.4% of total litterfall biomass. Three years of acorn production in an oak-dominated forest in Great Britain averaged 2.5% of total litter (Sykes and Bunce, 1970). Although no acorns were collected at Coweeta during the subsequent year, production seemed noticeably less.

Total litter nutrient input budgets in throughfall and litterfall are given in Table 3. Data are for potassium, calcium, magnesium, and sodium in both the hardwood and the white pine stands. Both watersheds are cycling nearly similar amounts of nutrients in throughfall, but they differ substantially in quantities

TABLE 3

COMPARISON OF LITTERFALL AND THROUGHFALL NUTRIENT BUDGETS BETWEEN HARDWOOD AND WHITE PINE STANDS FOR 1970–1971

Nutrient budgets, kg ha^{-1} $year^{-1}$	K	Ca	Mg	Na*
Hardwood				
Annual litterfall, total	18.07	44.49	6.55	0.009
Annual throughfall, total†	30.50	8.10	3.10	8.600
Total annual budget	48.57	52.59	9.65	8.609
Annual litterfall, % of total	37.2	84.6	67.9	0.1
White pine				
Annual litterfall, total	5.54	19.19	2.71	0.002
Annual throughfall, total†	30.50	6.30	2.00	7.20
Total annual budget	36.54	25.49	4.71	7.202
Annual litterfall, % of total	15.2	75.3	57.5	0.03

*Sodium concentration is 2 ppm in hardwood litter and 0.5 ppm in white pine litter.

†From Best (1971).

and in total proportions of nutrients contributed by litterfall. In terms of absolute amounts and percentage contribution by litterfall to the total nutrient budgets, the deciduous system has more elements in litterfall relative to throughfall than is the case for the white pine stand.

When the total nutrient budgets in the hardwood watershed are compared with those of a mesic oak-dominated forest in Britain (Carlisle, Brown, and White, 1966b) for the elements potassium, calcium, and magnesium, it is seen that the percentages contributed by litterfall in the Coweeta hardwood stand are all greater by an average of 22%. Total amounts of potassium and calcium cycled [illegible]weeta in both throughfall and litterfall also are greater by 20%, while 27% [illegible] total magnesium was cycled in their system. Sodium budgets are very different in the two deciduous forests, with nearly seven times more total sodium being cycled in the British oak woodland. Although detailed budgets are [illegible]ot given in Table 1, actual sodium content of litter in the British system (Carlisle, Brown, and White, 1966b) was three orders of magnitude greater than that of the hardwood litter at Coweeta.

In Table 4 the data for organic constituents in leaves show several trends. Most senescent leaves have higher total fiber and lignin but lower nitrogen and phosphorus than do leaves in the mid-growing season. For purposes of comparison with deciduous species, we had to take composite samples of all age classes of needles or leaves to obtain a representative sample for foliar nutrient and organic analyses.

It has been hypothesized that foliar sclerophyll indexes above 100 to 150 indicate a vegetation that is adapted to growing on phosphorus-deficient sites (Loveless, 1961; 1962). Species growing on such sites generally have lower protein content than vegetation with adequate phosphorus available (Loveless, 1961; 1962). Although there is some question as to when in the season to sample green leaves for sclerophyll determinations, very early season values probably would be misleading owing to higher nitrogen and phosphorus content [illegible]nd lower fiber content. When mid-August values for green hardwood leaves at [illegible]oweeta are compared, all sclerophyll indexes are high, indicating a sclerophyllous vegetation. All conifer species compared, including those from the western United States, have high sclerophyll indexes. Red alder and snowbrush are included as examples of nitrogen-fixing species. Nitrogen-fixing species might h[illegible]ow sclerophyll indexes simply because they have a readily available source [illegible]rogen, even in soils of low phosphorus availability. American chestnut survives at Coweeta only as stump sprouts.

Evidence has been presented that a phosphorus content below 0.3% is associated with a lower protein content and a high sclerophyll index (Loveless, 1961; 1962). Most phosphorus values for green leaves in the species listed in Table 4 were less than 0.2%, except yellow poplar and Douglas fir, and all were below 0.3%.

Sclerophyll vegetation occurs in both wet and dry habitats (Loveless, 1962). Phosphate deficiency is characteristic of acid soils in areas of high rainfall

TABLE 4

REPRESENTATIVE SPECIES DATA FOR FOLIAGE ORGANIC-MATTER QUALITY

Species	Location	% N	% P	% total acid detergent fiber	% lignin	Sclero-phyll index
Chestnut oak (G)*	Coweeta,	2.0	0.18	32.8	12.6	168
Chestnut oak (S)	N. C.	1.2	0.12	48.3	25.5	430
Scarlet oak (G)	Coweeta,	1.8	0.16	31.0	15.5	
Scarlet oak (S)	N. C.	0.9	0.12	34.8	16.7	597
White oak (G)	Coweeta,	2.0	0.17	26.0	9.1	132
White oak (S)	N. C.	1.0	0.12	38.2	17.2	390
Mixed hickory (G)	Coweeta,	2.1	0.18	33.7	9.2	165
Mixed hickory (S)	N. C.	1.2	0.16	42.9	16.9	351
Red maple (G)	Coweeta,	1.5	0.16	29.3	9.4	200
Red maple (S)	N. C.	1.2	0.14	30.0	12.7	260
Yellow poplar (G)	Coweeta,	2.0	0.20	29.3	7.2	146
Yellow poplar (S)	N. C.	1.0	0.12	41.1	14.6	443
Dogwood (G)	Coweeta,	2.0	0.18	22.4	3.5	115
Dogwood (S)	N. C.	1.4	0.14	21.1	3.9	160
American chestnut (G)	Coweeta,	1.9	0.18	30.3	7.6	163
American chestnut (S)	N. C.	1.0	0.10	32.8	8.8	354
White pine (G)	Coweeta,	1.4	0.17	38.8	16.4	296
White pine (S)	N. C.	0.9	0.11	54.3	31.0	617
Douglas fir (G)	Corvallis,	1.0	0.27	28.3	16.5	309
Douglas fir (S)	Ore.	0.5	0.26	38.6	24.1	815
Ponderosa pine (G)	Flagstaff, Ariz.	0.8	0.14	32.4	16.1	414
Engelmann spruce (G)	Logan, Utah	0.6	0.07	27.4	13.3	510
Red alder (G)	Blue River,	2.5	0.23	11.9	6.0	49
Red alder (S)	Ore.	2.1	0.16	19.4	9.5	94
Snowbrush (G)	Blue River,	2.0	0.13	15.7	6.1	80
Snowbrush (S)	Ore.	0.81	0.06	21.0	10.0	

*All samples represent mean values of composite samples taken from at least five different individual trees, except Ponderosa pine and Engelmann spruce. G = mid-growing season, S = senescent.

(Salisbury, 1959); Coweeta watersheds are situated in a region of high rainfall, and considerable weathering of the older Appalachian land surface has occurred (Kovner, 1955). Return of phosphorus in litterfall averages 0.11% concentration on a dry-weight basis, based on total litterfall biomass and total amount of

phosphorus given in Table 1. The white pine stand is cycling an equally low level of phosphorus in litterfall (Table 2). The critical level is 0.2% for phosphorus immobilization in decomposing litter (Alexander, 1961). Phosphorus values in decomposing litter at Coweeta are all less than 0.2%, showing that this element would tend to be immobilized by microbial organisms. First-year phosphorus loss of 34% from mixed-hardwood leaf litter was considerably lower than the first-year weight loss of 50% (Cromack, 1973). Further evidence of phosphorus deficiency in Coweeta soils comes from experimental data with these soils in which American sycamore (*Platanus occidentalis* L.) seedlings lacking mycorrhi- show phosphate-deficiency symptoms when grown in greenhouse containers t, Marx, and Monk, 1974); presence of mycorrhizal symbionts would permit survival and reproduction of tree vegetation in the infertile soils characteristic of Coweeta. Phosphorus-cycling levels remain low enough to indicate that the vegetation would have the high sclerophyll indexes observed.

High sclerophyll indexes are associated with lower foliage ash contents (Loveless, 1962). One general implication of this work is that ecosystems which are characterized by highly sclerophyllous vegetation (possibly due to phosphorus deficiency) are cycling smaller quantities of total nutrients, as reflected by ash content, than is the case for vegetation with low sclerophyll indexes (Monk, 1966). When comparative sclerophyll data become available from many of the temperate ecosystems for which litter nutrient data exist, then a better judgment can be made concerning the relationship between nutrient cycling in the system and the sclerophyll indexes of their characteristic vegetations. Assessment of the role of mycorrhizal symbionts in permitting survival and reproduction of tree vegetation in soils of low fertility is also needed.

Decomposition and nutrient-loss-rate data were obtained for both hardwood and white pine litter. On the basis of sets of litter bags put out in two consecutive years, first-year decomposition data for single species in both watersheds showed the following exponential weight loss rates: $k = -0.46$ year^{-1} for white pine, $k = -0.61$ year^{-1} for chestnut oak, $k = -0.72$ year^{-1} for white oak, $k = -0.77$ year^{-1} for red maple, and $k = -1.26$ year^{-1} for dogwood. A mixture of hardwood leaves contained in large litter bags had an annual exponential loss rate of $k = -0.70$ year^{-1}, or in terms of percentage weight loss, 50% weight loss occurred during the first year. By contrast, white pine averaged v 37% weight loss during the first year. The slowest decomposing hardwood ies was chestnut oak, which averaged 46% weight loss during the first year. Dogwood, the fastest decomposing hardwood species, averaged 68% weight loss during first-year decomposition.

Release of nutrients during first-year decomposition showed that nitrogen, phosphorus, and calcium tended to be immobilized, while magnesium and potassium were lost at greater rates than weight. The mixed-hardwood litter lost only 12% nitrogen during the first year, and there was no significant loss of nitrogen from white pine litter. Mixed-hardwood litter had a carbon-to-nitrogen ratio of 62 : 1, while white pine had a carbon-to-nitrogen ratio of 58 : 1;

carbon-to-nitrogen ratios appreciably greater than 30 : 1 result in increasing immobilization of nitrogen in the microbial populations' decomposing litter (Alexander, 1961).

Mixed hardwood litter lost 34% of phosphorus during the first year of decomposition, in contrast to a 50% weight loss; an indication that partial immobilization of phosphorus occurred. In white pine there was no significant loss of total phosphorus in first-year decomposition, but the weight loss was 37%. As indicated previously, the probable reason for the appreciably lower loss rate of phosphorus compared to weight loss from decomposing litter was the low level of phosphorus (0.12%) in foliage litterfall of both watersheds. The cri level at which phosphorus is immobilized in organic material is 0.2%.

Calcium loss rate was also less than the weight loss of the deciduous litter, e.g., a 29% first-year loss of calcium compared to a 50% weight loss. There was no significant loss of calcium from white pine litter during the same period. Evidence exists that litter- and soil-inhabiting fungi can concentrate substantial amounts of calcium (Stark, 1972; Todd, Cromack, and Stormer, 1973), quantities perhaps sufficient to result in partial immobilization of this nutrient in litter. Macronutrient quantities of calcium as well as other cations, such as potassium and sodium, can be used by fungi to neutralize oxalic acid, which is a low-energy waste product of carbohydrate metabolism in fungi (Foster, 1949). Oxaloacetic acid, a key intermediate in respiratory metabolism, is hydrolyzed to oxalic acid and acetate by oxaloacetate hydrolase in fungi (Burnett, 1968). The common metabolic production of this acid would result in substantial demand of cations, such as calcium, in the production of oxalate salts (Foster, 1949).

Potassium and magnesium loss rates were greater than weight loss rates for both mixed-hardwood litter and white pine litter. Potassium loss during the first year for hardwood litter was 83%, while potassium loss was 82% from white pine litter. Magnesium loss was 77% from mixed hardwood litter and 68% from white pine. It has been shown that ^{137}Cs (an analogue of potassium) loss rates were greater than weight loss rates for three deciduous species (Witkamp and Frank, 1969). In another study the loss rate of ^{134}Cs was also considerably greater than the weight loss rate of white oak (Witkamp and Crossley, 1966). Potassium is known to be significantly concentrated by both the vegetative and sporocarp portions of fungi-inhabiting litter (Stark, 1972; Todd, Cromack, and Stormer 1973). In contrast to calcium, which tends to form insoluble calcium ox crystals in such vegetative structures of fungi as hyphae and rhizomorphs, potassium is readily translocated in fungi where it is accumulated in sporocarps (Stark, 1972). Although potassium oxalate can be formed, it is much more soluble than calcium oxalate and would tend to be lost by leaching when excreted by hyphae. Potassium is more easily leached from litter than any other essential cation (Cromack, 1973). Magnesium was not significantly accumulated by fungi in litter substrates at Coweeta (Todd, Cromack, and Stormer, 1973), indicating a lesser use rate for the element than for potassium. Magnesium also is

not as easily leached from litter as potassium (Cromack, 1973), in part because it is less easily displaced from cation exchange sites in litter substrates than is potassium.

Weight-loss regressions were calculated from exponential loss rates of white pine, chestnut oak, white oak, red maple, and dogwood (as previously mentioned) and the chemical properties of the senescent leaves of those trees. Two simple linear regressions were calculated using the exponential weight loss rates of the species as the dependent variables and the carbon-to-nitrogen ratios [illegible] sclerophyll indexes of senescent leaves of these species (Table 4) as [illegible]pendent variables. The linear regression of exponential weight loss rate (y) and carbon-to-nitrogen ratio (x) is

$$y = -1.92 + 0.026x \quad (n = 5, r = 0.86, p = 0.06) \tag{1}$$

The data for the carbon-to-nitrogen ratio in senescent leaves of the five species used in Eq. 1 were: white pine, 58.0 : 1; chestnut oak, 42.2 : 1; white oak, 48.3 : 1; red maple, 39.2 : 1; and dogwood, 31.8 : 1. The linear regression of the exponential weight loss rate (y) and sclerophyll index (x) is

$$y = -1.34 + 0.001x \quad (n = 5, r = 0.90, p < 0.05) \tag{2}$$

Comparison of the two regressions shows that the sclerophyll index of senescent foliage is a statistically better variable with which to assess leaf decomposition rate than is the senescent leaf carbon-to-nitrogen ratio.

The sclerophyll index incorporates information about organic-matter quality for decomposition in terms of such structural compounds as cellulose and lignin, as well as crude protein nitrogen. The carbon-to-nitrogen ratio itself does not indicate the nature of the carbon substrate. Alexander (1961) presents evidence from the work of others (Fuller and Norman, 1943; Peevy and Norman, 1948; Pinck, Allison, and Sherman, 1950) that litter decomposition rates may be better predicted by knowing lignin content than by knowing the carbon-to-nitrogen ratio. The present data on sclerophyll index, which incorporates lignin and cellulose as total acid detergent fiber, plus a linear regression relating species [illegible]nin content to decomposition rate (Cromack, 1973), support his basic [illegible]othesis (Alexander, 1961).

A possible consequence of sclerophylly not considered by Loveless (1961; 1962) was that leaf-litter decomposition rates would be less in those species with high sclerophyll indexes. As discussed previously, he established relationships between high leaf sclerophyll indexes and low leaf levels of phosphorus, nitrogen, and ash. In forest ecosystems characterized by cycling low levels of nitrogen and phosphorus, the sclerophyll index can be considered an index to slower organic matter decomposition rates and release rates of such nutrients as nitrogen and phosphorus.

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REFERENCES

Alexander, M., 1961, *Introduction to Soil Microbiology*, John Wiley & Sons, Inc., New York.

Ausmus, B. S., and M. Witkamp, 1974, Litter and Soil Microbial Dynamics in a Deciduous Forest Stand, USAEC Report EDFB-IBP-78-10, Oak Ridge National Laboratory.

Best, G. R., 1971, Potassium, Sodium, Calcium, and Magnesium Flux in a Mature Hardwood Forest Watershed and an Eastern White Pine Forest Watershed at Coweeta, M.S. Thesis, University of Georgia, Athens, Ga.

—, D. Marx, and C. D. Monk, 1974, personal communication.

Bray, J. R., and E. Gorham, 1964, Litter Production in Forests of the World, in *Advances in Ecological Research*, J. B. Cragg (Ed.), Vol. 2, pp. 101-157, Academic Press, Inc., New York.

Burnett, J. H., 1968, *Fundamentals of Mycology*, St. Martin's Press, New York.

Carlisle, A., A. H. F. Brown, and E. J. White, 1966a, Litterfall, Leaf Production and the Effects of Defoliation by *Tortrix viridana* in a Sessile Oak (*Quercus petraea*) Woodland, *J. Ecol.*, **54**: 65-85.

—, 1966b, The Organic Matter and Nutrient Elements in the Precipitation Beneath a Sessile Oak (*Quercus petraea*) Canopy, *J. Ecol.*, **54**: 87-98.

Chandler, R. F., Jr., 1944, Amount and Mineral Nutrition Content of Freshly Fallen Needle Litter of Some Northeastern Conifers, *Soil Sci. Amer., Proc.*, **8**: 409-411.

Cromack, K., Jr., 1973, Litter Production and Decomposition in a Mixed Hardwood Watershed and a White Pine Watershed at Coweeta Hydrologic Station, North Carolina, Ph. D. Dissertation, University of Georgia, Athens, Ga.

Crossley, D. A., Jr., 1970, Roles of Microflora and Fauna in Soil Systems, in *Pesticides in the Soil: Ecology, Degradation and Movement*, International Symposium on Pesticides in the Soil, pp. 30-35, Feb. 25—27, 1970, Michigan State University.

—, and M. P. Hoglund, 1962, A Litter-Bag Method for the Study of Microarthropods Inhabiting Leaf Litter, *Ecology*, **43**: 571-573.

Day, F. P., Jr., 1971, Vegetation Structure of a Hardwood Watershed at Coweeta, M.S. Thesis, University of Georgia, Athens, Ga.

Edwards, C. A., D. E. Reichle, and D. A. Crossley, Jr., 1970, The Role of Soil Invertebrates in Turnover of Organic Matter and Nutrients, in *Analysis of Temperate Forest Ecosystems*, D. E. Reichle (Ed.), pp. 147-172, Springer-Verlag New York, Inc.

Ellis, G. H., G. Matrone, and L. A. Maynard, 1946, A 72% H_2SO_4 Method for the Determination of Lignin and Its Use in Animal Nutrition Studies, *J. Anim. Sci.*, **5**: 285-297.

Foster, J. W., 1949, *Chemical Activities of Fungi*, Academic Press, Inc., New York.

Fuller, W. H., and A. G. Norman, 1943, Cellulose Decomposition by Aerobic Mesophilic Bacteria from Soil. III. The Effect of Lignin, *J. Bacteriol.*, **46**: 291-297.

[illegible]z, J. R., G. E. Likens, and F. H. Bormann, 1972, Nutrient Content of Litterfall on the Hubbard Brook Experimental Forest, New Hampshire, *Ecology*, **53**: 769-784.

Johnson, P. L., and W. T. Swank, 1973, Studies of Cation Budgets in the Southern Appalachians on Four Experimental Watersheds with Contrasting Vegetation, *Ecology*, **54**: 70-80.

Jones, J. B., Jr., and M. H. Warner, 1969, Analysis of Plant-Ash Solutions by Spark-Emission Spectroscopy, *Develop. Appl. Spectrosc.*, **7A**: 152-160.

Kovner, J. L., 1955, Changes in Streamflow and Vegetation Characteristics of a Southern Appalachian Mountain Watershed Brought About by Forest Cutting and Subsequent Regrowth, Ph. D. Dissertation, State University of New York, Syracuse, N. Y.

Loveless, A. R., 1962, Further Evidence to Support a Nutritional Interpretation of Sclerophylly, *Ann. Bot., (London)*, **26**: 551-561.

——, 1961, A Nutritional Interpretation of Sclerophylly Based on Differences in the Chemical Composition of Sclerophyllous and Mesophytic Leaves, *Ann. Bot. (London)*, **25**: 168-184.

Macfadyen, A., 1963, *Animal Ecology*, Sir Isaac Pitman and Sons, London.

Monk, C. D., 1966, An Ecological Significance of Evergreenness, *Ecology*, **47**: 504-505.

Nielson, C. O., 1962, Carbohydrases in Soil and Litter Invertebrates, *Oikos*, **13**: 200-215.

Odum, E. P., 1971, *Fundamentals of Ecology*, W. B. Saunders Company, Philadelphia.

Olson, J. S., 1963, Energy Storage and the Balance of Producers and Decomposers in Ecological Systems, *Ecology*, **44**: 322-331.

Ovington, J. D., 1965, Organic Production, Turnover, and Mineral Cycling in Woodlands, *Biol. Rev.*, **40**: 295-336.

——, 1962, Quantitative Ecology and the Woodland Ecosystem Concept, in *Advances in Ecological Research*, J. B. Cragg (Ed.), Vol. 1, pp. 103-192, Academic Press, Inc., New York.

Peevy, W. J., and A. G. Norman, 1948, Influence of Composition of Plant Materials on Properties of the Decomposed Residues, *Soil Sci.*, **65**: 209-226.

Pinck, L. A., F. E. Allison, and M. S. Sherman, 1950, Maintenance of Soil Organic Matter, II. Losses of Carbon and Nitrogen from Young and Mature Plant Materials During Decomposition in Soil, *Soil Sci.*, **69**: 391-401.

[illegible]neroy, L. R., 1970, The Strategy of Mineral Cycling, in *Annual Review of Ecology and Systematics*, R. F. Johnston, P. W. Frank, and C. D. Michener (Eds.), pp. 171-190, Vol. I. Annual Reviews, Inc., Palo Alto, Calif.

Rodin, L. E., and N. I. Bazilevich, 1967, Production and Mineral Cycling in Terrestrial Vegetation, Oliver & Boyd, Edinburgh.

Salisbury, E. J., 1959, Causal Plant Ecology, in *Vistas in Botany*, W. B. Turrill (Ed.), pp. 124-144, Vol. 1. Pergamon Press, Inc., New York.

Stark, N., 1972, Nutrient Cycling Pathways and Litter Fungi, *Bioscience*, **22**: 355-360.

Sykes, J. M., and R. G. H. Bunce, 1970, Fluctuations in Litterfall in a Mixed Deciduous Woodland Over a Three-Year Period 1966–1968, *Oikos*, **21**: 326-329.

Todd, R. L., K. Cromack, Jr., and J. C. Stormer, Jr., 1973, Chemical Exploration of the Microhabitat by Electron Probe Microanalysis of Decomposer Organisms, *Nature*, **243**: 544-546.

Van Soest, P. J., 1966, Nonnutritive Residues: A System of Analysis for the Replacement of Crude Fiber, *J. Ass. Offic. Anal. Chem.*, **49**: 546-551.

——, 1963, Use of Detergents in the Analysis of Fibrous Feeds, II. A Rapid Method for the Determination of Fiber and Lignin, *J. Ass. Offic. Agric. Chem.*, **46**: 829-835.

——, and R. H. Wine, 1967, Use of Detergents in the Analysis of Fibrous Feeds. IV. Determination of Plant Cell Wall Constituents, *J. Ass. Offic. Anal. Chem.*, **50**: 50-55.

Whittaker, R. H., 1970, *Communities and Ecosystems*, Macmillan Publishing Co., Inc., New York.

Witkamp, M., 1971, Soils as Components of Ecosystems, in *Annual Review of Ecology and Systematics*, R. F. Johnston, P. W. Frank, and C. D. Michener (Eds.), pp. 85-110, Vol. 1. Annual Reviews, Inc., Palo Alto, Calif.

——, and D. A. Crossley, Jr., 1966, The Role of Arthropods and Microflora in Breakdown of White Oak Litter, *Pedobiologia*, **6**: 293-303.

——, and M. L. Frank, 1969, Loss of Weight, ^{60}Co and ^{137}Cs from Tree Litter in Three Subsystems of a Watershed, *Environ. Sci. Technol.*, **3**: 1195-1198.

CERIUM AND COBALT MOVEMENT WITH LITTER LEACHATE IN A FOREST SOIL

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ABSTRACT

Leachate containing ^{144}Ce and ^{60}Co from leaf litter of mockernut hickory (*Carya tomentosa* Nutt.) and black gum (*Nyssa sylvatica* Marsh.) trees was applied to a forest soil in three different treatments to estimate the rates at which these elements move downward after release in the litter layer: (a) single application, (b) single application at twice the concentration in (a), and (c) four periodic applications over 1 year. Regression b values describing the distribution of ^{144}Ce and ^{60}Co 4 years after the first applications did not differ significantly ($P > 0.01$) among treatments for either element, but movement by ^{144}Ce significantly exceeded that by ^{60}Co for all treatments. A combination of chemical and physical phenomena retained cerium and cobalt in the biologically active zones of soil, with the organic layer and upper 3 cm of mineral soil accounting for 68% of the ^{144}Ce and 91% of the ^{60}Co.

To interpret results from several investigations concerning the circulation of cerium and cobalt in deciduous forests, we ascertained the rates at which these elements move downward in soil after release from decomposing leaves. We chose for our study the mockernut hickory (*Carya tomentosa* Nutt.) and the black gum (*Nyssa sylvatica* Marsh.); the former accumulates rare-earth elements, including cerium, in foliage, and the latter accumulates cobalt (Thomas, 1973). The study area is part of Chestnut Ridge near Walker Branch Watershed on the U. S. Atomic Energy Commission's Oak Ridge Reservation in Tennessee. The ridgetop supported agriculture until 1943, and a clearly defined plow layer exists to a depth of 10 cm. The soil is a Fullerton silt loam, a Typic Paleudult, underlain by residual chert resting on dolomitic limestone. Chert fragments are

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common in the lower soil profile but not in the plow layer. The A1 horizon of Fullerton silt loam on the watershed is characterized by average bulk density of 1.1 g/cm^3, sand-to-silt-to-clay ratio of 34 : 63 : 3%, pH of 4.5, cation-exchange capacity of 5.6 meq/100 g, 29% base saturation, and 6.5% organic matter (Peters et al., 1970).

Vegetation consists of an oak–pine overstory dominated by black oak (*Quercus velutina* Lam.), white oak (*Q. alba* L.), shortleaf pine (*Pinus echinata* Mill.), and Virginia pine (*P. virginiana* Mill.). Christmas fern (*Polystichum acrostichoides* Michx.) contributes most to the sparse ground cover. Annual precipitation averages 135 cm, and rainfall during the study period did not deviate substantially from this amount.

A sample consisting of 300 g each of air-dried mockernut hickory and black gum leaves was crushed and added to 20 liters of precipitation containing 20 μCi/liter of ^{144}Ce and 5 μCi/liter of ^{60}Co. After 3 weeks, when the solution became concentrated with organic leachates, it was filtered to remove all visible particulate matter and stored in a translucent polyethylene carboy at room temperature.

In early January 1969, fresh leaf litter was removed temporarily from three contiguous 1-m^2 plots; the prepared solution and untagged previously collected precipitation were sprinkled evenly over the plots as follows:

High plot: 4 liters of solution and 6 liters of precipitation.

Low plot: 2 liters of solution and 8 liters of precipitation.

Periodic plot: 2 liters of solution and 8 liters of precipitation. After 3, 6, and 9 months, an additional 2 liters of solution and 8 liters of precipitation were applied to this plot. On these latter three dates, 10 liters of precipitation were added to the other two plots to equalize the water balances.

Ten liters over each plot corresponds to a 1-cm rainfall. The initial application coincided with leaching of leaf litter in the winter following abscission, and the periodic applications simulated pulses of cerium and cobalt added to soil in organic leachates from decomposing litter.

RESULTS AND DISCUSSION

In January 1973, 4 years after initiation of the study, a soil core of 2-cm diameter was taken from the center of each of nine subplots arranged in a uniform 3 by 3 pattern within each 1-m^2 plot. Because preliminary sampling indicated no detectable amounts of either radioisotope at depths greater than 9 cm, each of the cores was divided into four segments: organic material above mineral soil, 0 to 3, 3 to 6, and 6 to 9 cm. After being oven-dried at 105°C, the samples were analyzed for both radioisotopes with a 400-channel gamma analyzer. Control samples obtained near the plots provided background values. All counting data that significantly exceeded background ($P < 0.01$) were corrected for radiological decay to a common date and expressed as disintegra-

tions per minute per gram of sample weight. A segment between 9 and 12 cm was collected with one-half the cores in case any radioisotope did penetrate that deep, but none of these displayed significant counting rates. A series of samples collected outside but near the plot boundaries contained no detectable radioactivity, suggesting negligible lateral movement within the soil.

Expressing the concentrations in each segment as a percentage of that at the 0- to 3-cm depth normalized the data for each core and for each radioisotope. The normalized data then were fitted by least-squares estimates to the regression equation

$$\ln (Y) = a - b(d)$$

where Y is the relative concentration of radioisotope(%), d is the depth (cm), and a and b are constants estimated from the data. The same normalization and regression procedures were used to obtain a second set of b values by disregarding data for the organic layer and considering only the quantities of radioisotopes in mineral soil.

The estimated b values express relative penetration, with values near zero indicating an even distribution of radioisotope within the soil profile. The nearer the b value is to 1.0, the more concentrated the radioisotope is near the surface. Low b values, then, reflect greater penetration than do high ones.

Each of the four sets of b values (two elements with and without inclusion of the organic layer) were subjected to an analysis of variance to test for application-rate effects and position (row and column) effects. None of the four analyses revealed significant trends at the 0.01 level, but the average estimated b value for ^{144}Ce significantly exceeded ($P < 0.01$) that for ^{60}Co in all treatments, regardless of whether concentrations in the organic layer were included (Table 1). The overall average b values ($\bar{X} \pm SE$) for ^{60}Co are 0.357 ± 0.014 for soil, including the organic layer, and 0.272 ± 0.019 for mineral soil only. Corresponding values for ^{144}Ce are 0.103 ± 0.007 and 0.047 ± 0.007. Relative distribution of radioisotope within the cores did not differ significantly ($P > 0.01$) among treatments for either element, the average distribution for all treatments among the four soil segments being 45, 23, 17, 15% for ^{144}Ce and 78, 13, 6, 3% for ^{60}Co. Strong retention of both elements in the organic layer, even after 4 years, is expected because of the high affinity between metals and organic matter (Mortensen, 1963).

Although rapid downward movement of cobalt is not to be anticipated (Tiller, Hodgson, and Peech, 1963; Lomenick and Gardiner, 1965), even in soil of rather low clay content (Jones, Riceman, and McKenzie, 1957), the ^{60}Co penetrated even less than expected. On the other hand, ^{144}Ce migrated deeper than anticipated. Kulikov and Korobitsyn (1968) found 86 to 88% of the ^{144}Ce applied to the soil surface to be retained within 2 cm after two growing seasons, and Nishita and Essington (1967) reported practically no downward movement of ^{144}Ce after leaching a variety of contaminated soils with water. Other results

TABLE 1

REGRESSION b VALUES FOR MIGRATION IN SOIL OF ^{144}Ce AND ^{60}Co APPLIED AT DIFFERENT RATES, WITH AND WITHOUT CONSIDERATION OF THE ORGANIC SOIL LAYER*

Application rate	^{144}Ce	^{60}Co
High, single application		
Organic and mineral soil	0.112 ± 0.015	0.363 ± 0.021
Mineral soil only	0.056 ± 0.014	0.239 ± 0.040
Low, single application		
Organic and mineral soil	0.096 ± 0.012	0.371 ± 0.033
Mineral soil only	0.037 ± 0.008	0.293 ± 0.034
Low, periodic applications		
Organic and mineral soil	0.100 ± 0.011	0.337 ± 0.020
Mineral soil only	0.047 ± 0.005	0.284 ± 0.026

*$\bar{X}$ ± SE; n = 9.

show an extremely slow diffusion rate for cerium (Prokhorov and Tien-in, 1963; Tyuryukanova et al., 1964), although these investigators did use soil with higher clay contents. Molchanova (1968) found that aqueous leachates from tree leaves increased the mobility of cerium in soil. Formation of radiocolloids by the rare earths is a common phenomenon that might account for the downward movement encountered here (Brown, Franklin, and Miller, 1969). Movement of radiocolloids would be governed more by filtration and surface adsorption than by ion exchange. No doubt a combination of physical and chemical processes accounted for the observed rates.

Regardless of the difference in rate of penetration, the organic layer and upper 9 cm of mineral soil retained all the detectable ^{144}Ce and ^{60}Co. The small standard errors about the mean rates of movement in this limited study indicate that neither element is likely to migrate rapidly through this silt loam. The significance of this, of course, is that these elements will not escape from the biologically active zone in the soil–vegetation–litter nutrient cycle.

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REFERENCES

Brown, R. E., R. E. Franklin, and R. H. Miller, 1969, Reactions of ^{144}Ce in Solution and Suspensions of Soil Humic Acid and Bentonite, *Soil Sci. Soc. Amer. Proc.*, **33**: 677-681.

Jones, G. B., D. S. Riceman, and J. O. McKenzie, 1957, The Movement of Cobalt and Zinc in Soils as Indicated by Radioactive Isotopes, *Aust. J. Agr. Res.*, **8**: 190-201.

Kulikov, N. V., N. M. Korobitsyn, 1968, Effect of Plant Cover on the Vertical Migration of Cerium-144 in Soil (in Russian), *Tr. Inst. Ekol. Rast. Zhivotn., Ural. Filial, Akad. Nauk SSSR*, **61**: 47-54 (*Chem. Abst.*, **70**: 17393y; *Biol. Abst.*, **51**: 80756).

Lomenick, T. F., and D. A. Gardiner, 1965, The Occurrence and Retention of Radionuclides in the Sediments of White Oak Lake, *Health Phys.*, **11**: 567-577.

Ichanova, I. V., 1968, Behavior of Cerium in Different Types of Soil (in Russian), *Tr. Inst. Ekol. Rast. Zhivotn., Ural. Filial, Akad. Nauk SSSR*, **61**: 4-11 (*Chem. Abst.*, **70**: 56746k; *Nucl. Sci. Abst.*, **24**: 7772).

Mortensen, J. L., 1963, Complexing of Metals by Soil Organic Matter, *Soil Sci. Soc. Amer. Proc.*, **27**: 179-186.

Nishita, H., and E. H. Essington, 1967, Effect of Chelating Agents on the Movement of Fission Products in Soils, *Soil Sci.*, **103**: 168-176.

Peters, L. N., D. F. Grigal, J. W. Curlin, and W. J. Selvidge, 1970, Walker Branch Watershed Project: Chemical, Physical, and Morphological Properties of the Soils of Walker Branch Watershed, USAEC Report ORNL-TM-2968, Oak Ridge National Laboratory.

Prokhorov, V. M., and Ch'ai Tien-in, 1963, Diffusion of Cerium-144 in the Soil, *Sov. Soil Sci. (Engl. Transl.)* **1963**: 706-707.

Thomas, W. A., 1973, Accumulation of ^{144}Ce by Hickory and ^{60}Co by Black Gum Seedlings, in Radionuclides in Ecosystems, Proceedings of the Third National Symposium on Radioecology, May 10, 1971, D. J. Nelson (Ed.), pp. 187-189, USAEC Report CONF-710501 (Vol. 1).

Tiller, K. G., J. F. Hodgson, and M. Peech, 1963, Specific Sorption of Cobalt by Soil Clays, *Soil Sci.*, **95**: 392-399.

Tyuryukanova, T. B., F. I. Pavlotskaya, A. N. Tyuryukanov, L. N. Zatsepina, T. V. Babicheva, and L. M. Rodionova, 1964, Movement and Distribution of Strontium-90 and Cerium-144 in the Soils of the Moscow Oblast, *Sov. Soil Sci. (Engl. Transl.)*, **1964**: 1063-1068.

LEACHING OF NUTRIENTS FROM LEAVES OF SELECTED TREE SPECIES IN NEW HAMPSHIRE

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ABSTRACT

Leaching of Ca^{2+}, Mg^{2+}, K^{+}, Na^{+}, and total N from foliage of sugar maple, yellow birch, and beech was measured experimentally by placing leaves in containers of water under controlled conditions. The greatest leaching occurred in sugar maple, followed by yellow birch and beech, respectively. In early summer, sun leaves leached at a faster rate than shade leaves. With increasing leaf maturity this difference became less pronounced and was insignificant after abscission. The rate of leaching for all species and for all elements except sodium, as well as the total amount leached, increased with leaf maturity to a maximum after abscission. The rate of nutrient removal in all three species was similar: K > Mg > Ca > N > Na. The loss of sodium from the leaves was negligible. The agreement of these results with field studies identifies this experiment as a simple and reliable procedure for evaluating the relative mobility of nutrients in leaf tissue subject to throughfall or decomposition processes.

Nutrients are returned to the forest floor from plants primarily through leaching from living tissue and decomposition of plant parts (litter). Leaching from green leaves occurs throughout the growing season. The quantity of some nutrients leached before abscission may be similar to or larger than the amount contained in falling leaves (Ruhland, 1958; Eaton, Likens, and Bormann, 1973). Many comparative information is available on the nutrient content of precipitation under the forest canopy (throughfall and stem flow) and in the open, which gives an indirect measure of leaching (Carlisle, Brown, and White, 1967; Mina, 1965; Eaton, Likens, and Bormann, 1973; Attiwill, 1966). Analyses of throughfall and stem flow give the magnitude of the leaching process, but they do little to help us understand the processes involved or to explain the

differences that exist among nutrients and species. Few investigators have made intensive quantitative measurements of nutrients leached from sun and shade leaves of different species at various stages of maturity. Information of this nature is essential in quantifying the role of different species and leaf types in nutrient cycles of ecological systems.

The Hubbard Brook Study is designed to elucidate the structure and functions of natural, forested watershed ecosystems. Leaching from plants is a very important process in these systems, but its role is not well understood. The complexity of the plant community and environmental interactions makes field work difficult to interpret. Therefore our objective was to provide information on the amount and rate of leaching which occurs from leaves of different species, leaf type, and maturity under controlled laboratory conditions.

STUDY AREA

The Hubbard Brook Experimental Forest, a facility of the Northeastern Forest Experiment Station, Forest Service, U. S. Department of Agriculture, is located in the White Mountains of New Hampshire. The terrain is rugged, ranging from an altitude of 229 to 1006 m, and is covered by unbroken forest of uneven-aged, well-stocked, second-growth northern hardwoods. The primary species are sugar maple, *Acer saccharum* March.; beech, *Fagus grandifolia* Ehrh.; and yellow birch, *Betula alleghaniensis* Britt., with some red spruce, *Picea rubens* Sarg., and balsam fir, *Abies balsamea* L. The growing season for these species begins about May 15, with budbreak at lower elevations occurring several days earlier than at higher elevations (Bormann et al., 1970). Among the deciduous species sugar maple buds break first, followed by beech and yellow birch. Leaf fall begins in September and reaches a maximum about October 20. A detailed report of the hydrology, climate, and geology of this area can be found in Likens et al. (1967).

METHODS AND PROCEDURES

Concentration alone is insufficient to describe amounts of nutrients in leaves since changes in dry weight during the season cause fluctuations in concentration (see Guha and Mitchell, 1966). Thus we report here both concentration and absolute amount. Concentrations are expressed as milligrams of element per 100 g of dry leaf tissue and absolute amounts as milligrams of element per square meter of leaf surface. The leaf-surface area was the sum of both upper and lower leaf surfaces. We felt this was a more accurate measure of leaf surface because both upper and lower leaf surfaces can participate in the leaching process.

Leaf collections were made during the summers of 1965 and 1966. Three species of leaves were used in the leaching experiments: sugar maple, beech, and yellow birch. The experimental design differed slightly each year and each is reported separately.

1965

Four leaf collections were made during the summer and fall of 1965: July 12, August 23, September 20, and October 25. On each of the collection dates, shade and sun leaves were collected from each species. Sun leaves were designated as exposed leaves near the top of the crown. Shade leaves were low interior crown leaves. On July 12 the leaves were collected randomly from a tower extending into the crown canopy. All subsequent collections of leaves of each species were made from the crown of a single, identified tree. Shortly before leaf fall 13-mm mesh nylon bags were placed over leaf-bearing branches. On October 25, after leaf fall, the leaves were recovered from the bagged branches.

The leaf-surface area (two sides) and fresh weight were recorded for individual leaves during the July, August, and September collections. Leaf-surface areas were measured with a photoelectric device originally developed at Brookhaven National Laboratory and then modified and constructed by us. Early calibration curves for the leaf-area meter appeared in error. Therefore area measurements for the various July collections were estimated from leaf dry-weight measurements in July and weight–area regression equations obtained from comparable samples of the August collection. Similarly, the condition of the leaves in the October collection allowed only fresh-weight measurements, and regression equations from the September collection were used with October leaf dry weights to estimate leaf areas in October. These regression equations were highly significant ($P < 0.01$) and should correctly estimate leaf areas during July and October.

Using plastic gloves and stainless-steel tongs, we dipped each leaf from a collection once into demineralized water and allowed the excess water to drip off. A sample of leaves from each species leaf type (sun or shade) was oven-dried at 104°C, and a dry-weight measurement was made on individual leaves. We then randomly selected sets of three leaves from each species and leaf type. Each set was placed into individual polyethylene containers with 500 ml demineralized water. The containers were closed to minimize evaporation. Subsamples of the demineralized water were analyzed for cation content. All sample containers were placed in a growth chamber at 20°C under lighted conditions. One week and then one month after each collection date, subsamples from each container were analyzed for Ca^{2+}, Mg^{2+}, Na^{+}, and K^{+} concentrations. After 1 month the leached sun- and shade-leaf tissues for each species were combined, oven-dried, and analyzed for cation content.

1966

Two collections were made during 1966: July 26 and October 25. On each of these dates, leaves from the upper, middle, and lower thirds of the crown of a single tree were collected from each of the three species. Leaf-bearing branches were bagged as in 1965 to make the October 25 collection. Leaf-surface area (two sides) and fresh weights of the July collection and fresh weights of the October collection were recorded. The October dry weights were used with July regression equations to estimate leaf areas for the October collection. The leaves were not washed in any manner.

Ten randomly selected leaves from each crown position per species were placed in a polyethylene container with 1500 ml of demineralized water and sealed. These containers were placed in a growth chamber at 20°C under lighted conditions. Another 10 randomly selected leaves of each sample were oven-dried at 104°C for 24 hr to obtain dry weight. After intervals of 1 and 5 weeks, 100 ml of solution was removed and analyzed for Ca^{2+}, Mg^{2+}, Na^{+}, K^{+}, and total N. After the leaching period the leaf tissue was oven-dried, weighed, and chemically analyzed.

Cation determinations were made on the solutions by atomic absorption spectrophotometry. A lanthanum solution was used to prevent interference with the calcium and magnesium determinations (Likens et al., 1967). Total nitrogen of the leachate was obtained by digestion and distillation (McKenzie and Wallace, 1954) followed by Nesslerization (Rainwater and Thatcher, 1960).

Plant tissue was analyzed for cations according to the procedure described by Likens and Bormann (1970). Total nitrogen of the tissue was analyzed by the micro-Kjeldahl procedure of McKenzie and Wallace (1954).

RESULTS AND DISCUSSION

Initial Leaf Nutrient Content

The seasonal patterns of leaf development and nutrient content shown in this study follow previous work (Hoyle, 1965; Ruhland, 1958). Nutrients are constantly cycling in living leaf tissue; however, at certain times during the growing season, a maximum accumulation is reached.

Sun leaves, because of their greater weight per leaf or weight per unit area, generally had higher absolute nutrient content (Table 1). However, shade leaves frequently had a higher concentration of an element, i.e., higher sample percent (milligram element/100 g of dry weight is used for convenience, Table 2). Initial calcium content in the sun and shade leaves of maple during 1965 increased in absolute amount from July to September, then decreased in October (Tables 1 and 2). Birch sun and shade leaves showed a decrease in calcium during both September and October. Beech leaves decreased in both concentration and absolute amount of calcium during August and September, followed by an

increase in October. The reason for this decrease of calcium in the mid-season months is not known. The 1966 collections of all species showed an increase in calcium from July to October (Table 3).

Initial magnesium contents for all three species generally showed slight increases from June to August and September 1965, followed by decreases in October (Tables 1 and 2). The collections of October 25 for both years were made after leaf abscission, and, since magnesium and calcium accumulate up to the time of abscission (Ruhland, 1958), the most probable cause of this decrease in amount after September was direct leaching by rain before the collection was made. The 1966 collections showed a slight increase in amount of magnesi

TABLE 1

INITIAL AND FINAL NUTRIENT CONTENT OF LEAVES DURING A 4-WEEK LEACHING PERIOD*

	Leaf collection date, 1965							
	July 12†		Aug. 23†		Sept. 20†		Oct. 25†	
Leaf type	I	F	I	F	I	F	I	F
	Calcium, mg/m²							
Sugar maple sun	344	341	409	362	424	354	313	216
Sugar maple shade	282	282	315	242	334	254	298	198
Yellow birch sun	381	349	974	930	651	547	557	497
Yellow birch shade	466	457	780		454	410	389	350
Beech sun	266	266	226		205	198	284	187
Beech shade	221	221	172		159	149	207	178
	Magnesium, mg/m²							
Sugar maple sun	58	45	72	54	59	40	43	19
Sugar maple shade	46	46	61	36	61	33	51	21
Yellow birch sun	84	68	119	99	158	96	103	58
Yellow birch shade	93	92	97	92	98	76	66	43
Beech sun	65	65	57		49	42	18	11
Beech shade	44	44	44		38	31	32	21
	Potassium, mg/m²							
Sugar maple sun	527	201	500	59	354	75	133	16
Sugar maple shade	301	269	347	43	340	51	211	15
Yellow birch sun	461	450	394	241	381	98	230	14
Yellow birch shade	416	385	317	263	310	268	83	11
Beech sun	540	523	339	331	375	119	161	40
Beech shade	270	267	196	186	195	124	244	20

*Collections made on four dates.
†I, initial; F, final.

TABLE 2

INITIAL AND FINAL NUTRIENT CONTENT OF LEAVES DURING A 4-WEEK LEACHING PERIOD*

Leaf type	Leaf collection date, 1965							
	July 12†		Aug. 23†		Sept. 20†		Oct. 25†	
	I	F	I	F	I	F	I	F
	Calcium, mg/100 g tissue							
Sugar maple sun	537	470	620	548	902	753	681	469
Sugar maple shade	627	620	684	526	711	541	566	388
Yellow birch sun	811	744	1948	1860	1183	995	1072	957
Yellow birch shade	1166	1144	1951		1196	1079	1144	1030
Beech sun	567	567	580		501	483	747	492
Beech shade	691	691	574		549	515	740	635
	Magnesium, mg/100 g tissue							
Sugar maple sun	90	69	109	81	125	84	94	42
Sugar maple shade	102	101	133	79	130	70	100	41
Yellow birch sun	178	145	238	199	287	174	198	112
Yellow birch shade	233	231	243	230	258	199	194	126
Beech sun	139	138	145	145	119	102	47	30
Beech shade	138	138	148	148	132	108	115	74
	Potassium, mg/100 g tissue							
Sugar maple sun	823	356	758	89	753	160	289	22
Sugar maple shade	668	597	755	94	723	109	413	30
Yellow birch sun	981	532	788	481	692	179	443	28
Yellow birch shade	1041	964	793	561	817	708	243	33
Beech sun	1149	1112	870	850	914	290	425	106
Beech shade	844	835	653	618	674	428	872	72
	Sodium, mg/100 g tissue							
Sugar maple	1.9	1.9	1.1	1.1	3.1	3.1	2.4	2.4
Yellow birch	3.8	3.8	2.0	2.0	9.8	9.8	9.3	9.3
Beech	1.2	1.2	3.5	3.5	3.6	3.6	4.4	4.4

*Collections made on four dates.

†I, initial; F, final.

TABLE 3

INITIAL AND FINAL NUTRIENT CONTENT OF LEAVES DURING A 5-WEEK LEACHING PERIOD

	Leaf collection date, 1966							
	July 26*		Oct 25*		July 26*		Oct. 25*	
	I	F	I	F	I	F	I	F
	Calcium, mg/m²				Calcium, mg/100 g			
Maple								
Upper	163	129	350	280	485	385	1043	833
Middle	217	169	457	337	540	420	1109	819
Lower	224	178	296	240	725	575	1007	817
Birch								
Upper	317	270	407	362	1072	912	1604	1424
Middle	321	272	405	360	1121	951	1596	1416
Lower	252	224	327	288	1297	1157	2070	1820
Beech								
Upper	156	147	179	170	492	462	797	757
Middle	135	133	173	162	637	627	938	878
Lower	164	162	139	124	941	931	817	727
	Magnesium, mg/m²				Magnesium, mg/100 g			
Maple								
Upper	51	28	60	27	88	48	179	79
Middle	47	27	71	30	117	67	173	73
Lower	42	23	59	33	135	75	201	111
Birch								
Upper	59	33	89	59	200	110	351	231
Middle	69	38	76	45	243	133	299	179
Lower	52	36	52	30	268	188	328	188
Beech								
Upper	34	27	40	28	106	86	177	127
Middle	34	33	28	19	160	155	154	104
Lower	34	33	26	16	193	187	152	92
	Potassium, mg/m²				Potassium, mg/100 g			
Maple								
Upper	366	56	140	15	626	96	384	44
Middle	341	59	130	11	848	148	316	26
Lower	277	60	144	12	892	192	490	40
Birch								
Upper	311	26	108	16	1049	89	424	64
Middle	342	36	72	16	1196	126	284	64
Lower	261	32	84	8	1344	164	531	51
Beech								
Upper	245	29	79	19	771	91	353	83
Middle	177	107	83	18	836	506	450	100
Lower	173	119	69	20	994	684	406	116

	Leaf collection date, 1966							
	July 26*		Oct 25*		July 26*		Oct. 25*	
	I	F	I	F	I	F	I	F
	Nitrogen, mg/m²				Nitrogen, mg/100 g			
Maple								
Upper	787	730	135	111	1346	1248	401	331
Middle	525	476	217	190	1305	1185	526	461
Lower	517	485	244	215	1667	1564	831	731
rch								
Upper	837	800	256	244	2829	2702	1009	961
Middle	814	787	264	244	2845	2751	1038	960
Lower	520	494			2681	2547		
Beech								
Upper	854	833	155	147	2685	2618	693	657
Middle	496	483	122	115	2340	2277	661	623
Lower	427	421	152	145	2454	2417	892	855
					Sodium, mg/100 g			
Maple					1.6	1.6	1.4	1.4
Birch					2.0	2.0	2.4	2.4
Beech					1.5	1.5	2.1	2.1

*I, initial; F, final.

from July to October. Because a September collection was not taken in 1966, the highest accumulation of calcium and magnesium may not have been shown, and any decrease in the October leaves was not apparent. A storm on October 22 and 23, 1965, produced 1.9 cm of precipitation on the area. From October 19 to 21, 1966, a total of 5.38 cm of precipitation fell. Nutrients appear to be leached rapidly from senescent leaves even while on the tree (Gosz, Likens, and Bormann, 1972), and this amount of precipitation could have caused the lower initial content of calcium and magnesium in the October leaves.

Potassium content was highest in the July leaves of all three species. The amount decreased throughout the period with accelerated losses from July to August for beech and from August and September to October for sugar maple birch (Tables 1 and 2). Because potassium is translocated to the stem before cission, it is difficult to partition the amount of reduction in the leaves due to translocation and that due to leaching from rain. Both undoubtedly played a role.

Nitrogen was analyzed only on the July and October collections of 1966. Significantly less nitrogen was found in the October leaves. Nitrogen is very readily translocated, and as our results show, it was difficult to leach. Therefore the primary cause of the reduction in leaf tissue before leaf fall appears to be translocation to the stem.

Of the elements studied, sodium was present in the smallest quantity in leaf tissue (Table 2). The amount of sodium increased through the summer, with a slight decrease after September for sugar maple and yellow birch. However, beech did not decrease in October (Table 2). Sodium was not leached to any extent from the leaves of any of the three species (Tables 2 and 3), therefore translocation may explain the October decrease.

Experimental Leaching Results

Each of the elements behaved differently, depending on the species, maturity of the leaf, and length of leaching period. Early in the summer nutrients were leached very sparingly from leaves. However, during this period a significant difference was apparent between sun and shade leaves for sugar maple and yellow birch. Early sun leaves of these species lost a larger amount of an element and at a faster rate by leaching (Tables 1 and 2). By August and September the rate of leaching of shade leaves increased to that of sun leaves. Sun and shade leaves of beech showed similar leaching patterns throughout the summer.

Much of the difference between sun and shade leaves appears to be a result of the physical state of the cuticle and epidermal cells (Watson, 1942a). In leaves developed in full daylight, both the cuticle and the epidermal cell walls rapidly become hardened. In light shade the cell walls and cuticle hardened less rapidly, whereas in deep shade the cuticle hardened slowly and the radial and tangential walls of epidermal cells remained very delicate and plastic for a still longer period. This hardening of the cuticle upon exposure to the sun renders it susceptible to cracking, exposing the pectins and cellulose of the primary cell walls. These morphological differences may explain why sun leaves lose more material more rapidly than shade leaves in the early summer.

The effects of acid rain also may be important here (Likens and Bormann, 1974). The mean monthly pH of rain during the summer months at Hubbard Brook Experimental Forest varies between 3.8 and 4.1, however, individual storms may have rain with a pH of 3.0 or less. This acidic solution could be a factor in eroding or "cracking" the cuticle. Since there appears to be a gradient from low pH of incident rainfall to higher pH of throughfall (Eaton, Likens, and Bormann, 1973), the effect of the acid would presumably be greatest on the upper, or sun, leaves of the canopy.

Young or rapidly growing leaves are very difficult to leach, but increasing age causes physical changes and increased leachability (Tukey, 1970). In our experiment, nutrients in mature leaves were generally leached both at a faster rate and more completely. The maximum rates of loss and the maximum amount leached occurred in leaves collected after abscission. Changes in the physical state of the cuticle and epidermal cells also may explain these results. One such physical change is the hardening of the cuticle. Schieferstein and Loomis (1959) reported the water permeability of cuticular membranes

significantly increased with age because of cracking and exposure of underlying tissues. Another change is physical weathering and damage by insects, both of which may make the leaves more permeable. Older leaves do not have as great a demand on the nutrients as young, physiologically active tissue, therefore the active breakdown and lower rates of reassimilation may release more nutrients for leaching. Such differences in developmental patterns between sun and shade leaves could also influence their leaching differences. There is evidence that sun leaves are initiated sooner or mature more rapidly than shade leaves (Watson, 1942b). As the season progresses, shade leaves catch up in maturity characteris- and likewise have similar leaching patterns (September and October). A parallel to this is the damage suffered by the leaves. As early as June 15, exposed sun leaves at the Hubbard Brook forest showed more damage from wind and insects than shade leaves. As the growing season progressed, shade leaves became increasingly damaged.

The results from upper, middle, and lower crown collections of 1966 agree with the 1965 sun- and shade-leaf data (Table 3). The upper crown leaves, presumably containing more sun leaves, had higher amounts of nutrients per square meter of leaf surface and faster initial leaching rates than lower crown leaves. The lower crown leaves frequently showed higher amounts of nutrients per 100 g of leaves caused by higher concentrations. The October leaves were capable of losing a larger percentage of an element and at a faster rate than the July leaves.

Sugar maple generally had the highest total nutrient loss followed by yellow birch and beech, respectively. In some cases, however, yellow birch lost as much or slightly more of an element than maple. These results support field studies on the Hubbard Brook forest which identify sugar maple foliage as losing the largest amounts of total nutrients (Eaton, Likens, and Bormann, 1973). Since the forest has a high percentage of sugar maple foliage (52% of leaf fall, Gosz, Likens, and Bormann, 1972), this species plays a prominent role in the throughfall process.

Potassium was removed faster and more completely followed by Mg^{2+}, Ca^{2+}, N, and Na^{+}, respectively, from all three species (Tables 1 to 3). These results support field studies of nutrient release from decomposing leaf tissue on the Hubbard Brook forest (Gosz, Likens, and Bormann, 1973). In the leaching periment 80 to 90% of the potassium content of the October leaves was hed out in 1 week, and it appears that this same amount may have been leached out much sooner. In contrast, the loss of Na^{+} from the leaves was negligible. Tamm (1953) reported the Na^{+} in precipitation under the crowns of eight species of trees to be 1.5 to 2.5 times the Na^{+} content of precipitation collected in the open. Throughfall studies at Hubbard Brook forest also showed relatively high levels of Na^{+} (Eaton, Likens, and Bormann, 1973). Since our laboratory studies and field-decomposition studies indicate that Na^{+} is not readily leached from leaves, the increased Na^{+} content of throughfall may reflect aerosol impaction and accumulation on leaf surfaces. The presence of relatively

large amounts of Cl^- and SO_4^{2-} in the throughfall supports this view (Eaton, Likens, and Bormann, 1973).

The agreement of field and laboratory results identifies the laboratory experiment as a simple and reliable procedure for evaluating the relative mobility of nutrients in leaf tissue subject to throughfall or decomposition processes.

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REFERENCES

Attiwill, P. M., 1966, The Chemical Composition of Rainwater in Relation to Cycling of Nutrients in Mature Eucalyptus Forest, *Plant Soil*, **24**: 390-406.

Bormann, F. H., T. G. Siccama, G. E. Likens, and R. H. Whittaker, 1970, The Hubbard Brook Ecosystem Study: Composition and Dynamics of the Tree Vegetation, *Ecol. Monogr.*, **40**: 373-388.

Carlisle, A., A. H. G. Brown, and E. J. White, 1967, The Nutrient Content of Rainfall and Its Role in the Forest Nutrient Cycle, in *14th Congress of International Union of Forestry Research Organizations, Munich*, Pt. II, Sec. 21, 145-158.

Eaton, J. S., G. E. Likens, and F. H. Bormann, 1973, Throughfall and Stem Flow Chemistry in a Northern Hardwood Forest, *J. Ecol.*, **61**: 495-508.

Gosz, J. R., G. E. Likens, and F. H. Bormann, 1973, Nutrient Release from Decomposing Leaf and Branch Litter in the Hubbard Brook Forest, New Hampshire, *Ecol. Monogr.*, **43**: 173-191.

___, G. E. Likens, and F. H. Bormann, 1972, Nutrient Content of Litterfall on the Hubbard Brook Experimental Forest, New Hampshire, *Ecology*, **53**: 769-784.

Guha, M. M., and R. L. Mitchell, 1966, The Trace and Major Element Composition of the Leaves of Some Deciduous Trees. II. Seasonal Changes, *Plant Soil*, **24**(1): 90-112.

Hoyle, M. C., 1965, Variation in Foliage Composition and Diameter Growth of Yellow Birch with Season, Soil, and Tree Size, *Soil Sci. Soc. Amer. Proc.*, **29**(4): 475-480.

Likens, G. E., and F. H. Bormann, 1974, Acid Rain: A Serious Regional Environmental Problem, *Science*, 184: 1176-1179.

___, and F. H. Bormann, 1970, *Chemical Analysis of Plant Tissue from the Hubbard Brook Ecosystem in New Hampshire*, Yale University, School of Forestry, Bulletin No. 79.

___, F. H. Bormann, N. M. Johnson, and R. S. Pierce, 1967, The Calcium, Magnesium, Potassium, and Sodium Budgets for a Small Forested Ecosystem, *Ecology*, **48**(5): 772-785.

McKenzie, H. A., and H. S. Wallace, 1954, The Kjeldahl Determination of Nitrogen: A Critical Study of Digestion Conditions—Temperature, Catalyst, and Oxidizing Agent, *Aust. J. Chem.*, **7**: 55-70.

Mina, V. N., 1965, Leaching of Certain Substances from Woody Plants by Rain, and Its Importance in the Biological Cycle, *Pocvovedenic*, **6**: 7-17; taken from *Forest. Abstr.*, **27**: 42.

Rainwater, F. H., and L. L. Thatcher, 1960, *Methods for Collection and Analysis of Water Samples,* U. S. Geological Survey, Water Supply Paper No. 1454.

Ruhland, W. (Ed.), 1958, *Mineral Nutrition of Plants,* Encyclopedia of Plant Physiology, Vol. 4, Springer-Verlag, New York.

Scheiferstein, R. H., and W. E. Loomis, 1959, Development of the Cuticular Layers in Angiosperm Leaves, *Amer. J. Bot.*, 46(9): 625-635.

Tamm, C. O., 1953, Growth, Yield, and Nutrition in Carpets of a Forest Moss (*Hylocomium splendens*), *Medd. Statens Skogsforskningsinst.*, 43(1): 1-40.

Tukey, H. B., Jr., 1970, The Leaching of Substances from Plants, *Ann. Rev. Plant Phys.*, 21: 305-324.

[illegible]an, R. W., 1942a, The Effect of Cuticular Hardening on the Form of Epidermal Cells, *New Phytol.*, 41: 223-229.

——, 1942b, The Mechanism of Elongation in Palisade Cells, *New Phytol.*, 41: 206-221.

PHOSPHORUS CYCLING IN A MARYLAND DECIDUOUS FOREST SUBJECTED TO VARIOUS LEVELS OF MINERAL-NUTRIENT LOADING

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ABSTRACT

Phosphorus loading of the leaf-litter zone was varied from the natural level (3 to 12 mg P m^{-2} day^{-1}) to 430 mg P m^{-2} day^{-1} above the natural level. Phosphorus-32 was used to measure transfer rates and to determine pathways of phosphorus cycling. Kinetics of phosphorus flux in leaf litter, in various depth zones of soil, in horizontal transects, and in tree leaves was estimated from the rates of change in specific and total activities. Phosphorus fractions [orthophosphate, acid-labile phosphorus (ALP), and acid-stable phosphorus (ASP)], which are metabolically meaningful, were used to interpret the biological pathways and mechanisms. Upon increased loading, the phosphorus content of the litter increased fourfold and then stabilized. When this loading was discontinued, the phosphorus content of the litter declined to the original level within 4 months. Phosphorus not assimilated by the leaf litter moved rapidly through the soil both vertically and horizontally. Forest trees obtained most of their phosphorus from the litter zone.

Phosphorus is an essential element for all forms of life (Bould, 1963; Jarvis and Jarvis, 1972). Since phosphorus in most terrestrial ecosystems or communities is derived only by such slow processes as immigration of biota or the washing in by rain of colloidal phosphorus-containing matter (Jarvis and Jarvis, 1972; Hobbie and Likens, 1973), these systems have evolved to efficiently retain and recycle phosphorus (Pomeroy, 1970).

In a forest ecosystem a large part of the biomass, and therefore of the biologically contained phosphorus, is in the form of trees (Luse, 1970; Marks and Bormann, 1972). These trees drop a large amount of litter, especially leaves, and this litter contains phosphorus. The litter zone thus becomes an obvious

interface across which the flux of phosphorus can be studied. The subsequent mineralization of the litter phosphorus and its recycling by microorganisms and higher plant feeder roots also can be studied here. Rainfall leaches phosphorus from the forest canopy and understory, depositing it in the litter as throughfall and stem flow (Carlisle, Brown, and White, 1966a, 1966b, 1967; Hobbie and Likens, 1973). A number of investigators have measured the phosphorus composition of various components of forest ecosystems, but only a few have used radiophosphorus to trace phosphorus movements in forest trees and soil (Luse, 1970; Kilian, 1974). None of these investigators has utilized the analysis of the kinetics of change in both the location and the specific activities of chemical fractions of phosphorus.

We performed our research to learn more about the phosphorus cycle in a deciduous temperate forest. Using a radioisotope of phosphorus allowed us to measure overall phosphorus flux rates and pathways of the phosphorus cycle. Experiments with carrier-free ^{32}P examined the system under currently normal levels of nutrient loading, where the main source of loading was from rainfall. We also made experiments on the effects of greatly increased, but defined, nutrient loading. We anticipated that these perturbations of the mineral cycles would aid in the analysis of phosphorus cycling and flux in forests subjected to normal rates of nutrient loading as well as those subjected to land disposal of effluents from sewage-treatment facilities.

We used a dual analytical approach. Samples were analyzed for the time course of change in both their total radioactivity and their specific radioactivity. These two parameters were used to calculate transfer of phosphorus, respectively, from and into the originally labeled samples. This approach has not been frequently applied to the in situ measurement of mineral cycling in ecological studies of natural populations. An example of the recognition of the value of this approach was presented at this symposium by Vanderploeg, Booth, and Clark.

All samples were also chemically fractionated, and the time course of change in the specific radioactivities and the total radioactivities of orthophosphate, acid-labile phosphorus, and acid-stable phosphorus were determined. This was done because orthophosphate is the only form of phosphorus which can be directly assimilated by an organism (Bould, 1963; Bieleski and Johnson, 1972; Rigler et al., 1972), and acid-labile phosphorus is a fraction of compounds whose common feature is the presence of high-energy bonds. High-energy bonds are used in the transfer of energy in biological systems (Atkinson and Morton, 1960), and, if they are not protected within a cell, they are rapidly hydrolyzed by extracellular enzymes present in the soil (Voight, 1971). Thus acid-labile phosphorus can be used as an index of what the biota are doing in such complex communities as are found in the soil. Although radiophosphorus studies in forest soils have been reported elsewhere (Luse, 1970; Kilian, 1974), none have used the overall approach reported here.

STUDY AREA

The experimental site was located on a forested portion of the property of the Smithsonian's Chesapeake Bay Center for Environmental Studies near Edgewater, Md. (approximately 38°53'20" north latitude and 76°33'20" west longitude). This property was first farmed about 1650 and was completely cleared by 1700. It was farmed almost entirely in tobacco until 1750 and then was planted with more diversified crops (i.e., corn, flax, tobacco, marijuana, wheat, oats, rye, and barley as well as cattle pastures) until 1800. By then the soils were so eroded and depleted that farming declined. In the period 1820 to 1840, fertilizers and contour plowing were introduced. After the civil war this area was allowed to develop into forest land again. It is now a mature deciduous forest dominated by American beech (*Fagus grandifolia* Ehrh.), northern red oak (*Quercus rubra* L.), white oak (*Quercus alba* L.), hornbeam (*Carpinus caroliniana* Walt.), and tulip (*Liriodendron tulipifera* L.). The soils are very low in humus, and their mineral particles between 2 and 64 μm in size are composed of montmorillonite (40%), vermiculite (20%), kaolinite (15%), quartz (10%), chlorite (5%), muscovite (5%), gibbsite (3%), K-spar (1%), and plagioclase (1%).

MATERIALS AND METHODS

The experimental plots consisted of two square areas 2.4 m on a side surrounded by square transects at various distances from the outer edges of the plots. At the beginning of an isotope experiment 10 mCi of carrier-free ^{32}P-orthophosphate was mixed with 10 liters of creek water, and the solution was sprinkled evenly over the plots prior to increased mineral nutrient loading.

Six experiments were conducted. These were begun in the spring and fall. Some were carried out under natural mineral-loading conditions; others were done while increased mineral-loading rates were artificially maintained. Data are reported for two time periods. (March–July and September–January). These correspond roughly with periods of high and low metabolic activity, respectively, especially by the roots of the vascular forest plants.

The experimental sites were sampled at 2-week intervals for 4 months. Composite samples were taken of (1) young beech leaves from seedlings whose roots were entirely within the labeled plot, (2) leaf litter from the surface of the forest floor, and (3) soil cores taken vertically to a depth of up to 30 cm with soil coring tubes with an inside diameter of 1.4 cm. Samples were composited from a number of samples (3 to 6) taken either scattered within the labeled plot for the determination of vertical gradients or along transect lines parallel to the outer edges of the plot for the determination of horizontal gradients.

In the experiments with increased nutrient loading, an area of 80 m^2 (including the labeled plot) was sprinkled with 1 liter of nutrients per square

meter each Monday, Wednesday, and Friday. The nutrient solution contained NH_4NO_3 and $(NH_4)H_2PO_4$ such that the molar ratio of ammonium ion to nitrate ion was 2 and the nitrogen to phosphate ratio was 2.7 by weight (atomic ratio of N/P = 6.0).

Samples were counted in a liquid scintillation spectrometer. The scintillation cocktail was composed of 5.5 g of 2,5-diphenyloxazole and 0.5 g of *p*-bis-[2-(4-methyl-5-phenyloxazoyl)] benzene dissolved in 800 ml of toluene and 200 ml of Triton X-100.

Dry weights were determined by bringing samples to a constant weight at . Monthly leaf-litter standing-crop estimates were made by throwing a wooden frame into the woods and collecting all leaf litter within its borders (1 dm^2). Leaf litter was defined as particulate matter recognizable as deriving from leaves, twigs, and material large enough to pick up with your fingers.

Samples were homogenized in distilled water, and a 5-ml aliquot was transferred to a tared 10-ml beaker for dry-weight determination. For orthophosphate determination a 10-ml aliquot was brought to 1*N* with concentrated hydrochloric acid and was added to 10-ml 88% phenol. Then the mixture was shaken vigorously. After the mixture was centrifuged, the upper aqueous layer was drawn off and saved. To the lower phenol layer was added 10 ml of water, and the sample was shaken and centrifuged again. The upper layer was combined with the first aqueous extract and diluted to 25 ml with water. For Δ_7-P determinations (Δ_7-P is the fraction of phosphorus which is released as orthophosphate when heated at 100°C with 1*N* HCl for 7 min), a 5-ml aliquot was brought to 10 ml with 2*N* HCl and was placed in a vigorously boiling water bath for 7 min, then cooled rapidly in an ice bath. Sample preparation then proceeded as for orthophosphate.

For total phosphorus determinations, a 5-ml aliquot was placed in a 30-ml micro-Kjeldahl flask. One drop of concentrated nitric acid and 2 ml of 72% perchloric acid were added. The sample was carefully boiled in a fume hood behind a safety shield on a micro-Kjeldahl digestion rack until the sample became colorless or pale yellow. After cooling, the sample was rinsed into a 25-ml graduate and was diluted to 25 ml with water. Appropriate subaliquots of the prepared orthophosphate, Δ_7-P, and total phosphorus samples were then colorimetrically analyzed for phosphate. The overall procedure for total phorus is a modification of the method of King (1932). A total phosphorus aliquot plus 4 ml of 72% perchloric acid was diluted to 25 ml with water, and 4 ml of 5% ammonium molybdate in water was added and mixed. Then 4 ml of sulfonic acid reagent was added, and a timer was started. After 5 min 20 ml of isobutanol was added, and the sample was shaken vigorously. The isobutanol phase was separated and adjusted to 25 ml with ethanol. The absorbance was read in the far-red region of the spectrum (700 to 750 nm). The absorbance was read within 20 min of the end of color development. An orthophosphate, or Δ_7-P, sample subaliquot was diluted to 25 ml, and 2 ml of 2.5% acidified

ammonium molybdate (Fiske and Subbarow, 1925) was added and mixed. Next, 2 ml of sulfonic acid reagent was added. After 10 min isobutanol was added, and the analysis proceeded as for total phosphorus. Standard curves were constructed by processing various amounts of phosphorus standards in the same manner. In this paper acid-labile phosphorus (ALP) refers to (Δ_7-P) minus orthophosphate and acid-stable phosphorus (ASP) refers to (total-P) minus (Δ_7-P). Samples for counting (1 to 2 ml) were pipetted from the isobutanol–ethanol solutions to scintillation vials after colorimetric readings were completed.

Rainfall was measured with a weighing, recording rain gauge. Rainwater for phosphorus-composition analysis was collected with a special apparatus made of glass and polyethylene which was located above the tree canopy. This apparatus was acid washed frequently. Total phosphorus was measured after persulfate digestion by the stannous chloride procedure (American Public Health Association, 1971).

RESULTS

Since the ^{32}P-phosphate was applied to the leaf litter, its rate of disappearance from the leaf litter and its rate of dilution within the leaf litter with cold phosphorus can be analyzed kinetically. These rates are functions, respectively, of the phosphorus flux rates from and into the leaf litter. Some general equations used to calculate the results are as follow:

Rate of P movement into leaf litter [μg P(g dry weight)$^{-1}$ day^{-1}]

$$= \{[\Delta \ln \text{cpm } (\mu\text{g P})^{-1} \text{ day}^{-1}] - 0.0483\} [\mu\text{g P (g dry weight)}^{-1} \text{ day}^{-1}] \quad (1)$$

where 0.0483 is the decay rate for ^{32}P.

Rate of P loss from leaf litter [μg P (g dry weight)$^{-1}$ day^{-1}]

$$= \frac{\{[\Delta \ln \text{cpm (g dry weight)}^{-1} \text{ day}^{-1}] - 0.0483\} \text{ (initial cpm/g dry weight)}}{\text{initial cpm/}\mu\text{g P}} \quad (2)$$

Rate of P transfer from labeled leaf litter to another sample

$$[\mu\text{g P (g dry weight)}^{-1} \text{ day}^{-1}] = \frac{\text{decay corrected cpm/g dry weight}}{\text{(initial cpm/}\mu\text{g P) (days elapsed)}}$$

Total activity and specific activity data from four separate experiments were used to calculate log-linear least-squares regressions. The slopes and intercepts of these regressions were then used to calculate flux rates (Eqs. 1 and 2). The flux calculations also required phosphorus-composition data. For the conversion from units of phosphorus per gram of dry weight to phosphorus per surface area, dry-weight data were needed. These data are given in Table 1 for the two periods

TABLE 1

PHOSPHORUS COMPOSITION OF WOODLAND SOILS UNDER NATURAL LOADING CONDITIONS*

Sample	Season†	g dry wt. / dm²	T-P, mg/g dry wt.	ASP, mg/g dry wt.	ALP, mg/g dry wt.	Ortho-P, mg/g dry wt.	T-P, g/m²	ASP, g/m²	ALP, g/m²	Ortho-P, g/m²
Leaf litter	1	9.7 ± 2.9	1.25 ± 0.33	0.76 ± 0.22	0.27 ± 0.078	0.24 ± 0.11	1.22	0.74	0.26	0.23
	2	13.1 ± 0.46	1.39 ± 0.24	0.92 ± 0.20	0.20 ± 0.066	0.28 ± 0.088	1.82	1.20	0.26	0.37
Soil (0–3 cm)	1	285 ± 9.9	0.93 ± 0.37	0.44 ± 0.23	0.25 ± 0.10	0.24 ± 0.14	26.5	12.5	7.1	6.8
	2	211 ± 26	1.28 ± 0.28	0.83 ± 0.26	0.22 ± 0.084	0.23 ± 0.089	27.0	17.5	4.6	4.9
Soil (3–5 cm)	1	279 ± 24.2	0.86 ± 0.27	0.38 ± 0.12	0.23 ± 0.087	0.24 ± 0.16	24.0	10.6	6.4	6.7
	2	268 ± 16	1.07 ± 0.18	0.68 ± 0.16	0.15 ± 0.052	0.23 ± 0.091	28.7	18.2	4.0	6.2
Soil (5–8 cm)	1	377 ± 69.9	0.62 ± 0.15	0.33 ± 0.061	0.15 ± 0.075	0.14 ± 0.024	23.4	12.4	5.7	5.3
	2	418 ± 18	0.81 ± 0.26	0.54 ± 0.22	0.082 ± 0.011	0.19 ± 0.050	33.9	22.6	3.4	7.9
Soil (8–12 cm)	1	698 ± 28.8	0.87 ± 0.38	0.46 ± 0.26	0.20 ± 0.098	0.22 ± 0.14	60.7	32.1	14.0	15.4
	2	584 ± 3.6	1.39 ± 0.41	0.72 ± 0.30	0.22 ± 0.12	0.44 ± 0.23	81.2	42.0	12.8	25.7
Soil (12–18 cm)	1	1050 ‡	0.75 ± 0.23	0.41 ± 0.11	0.19 ± 0.12	0.18 ± 0.14	78.8	43.0	20.0	18.9
	2	828 ± 48	0.72 ± 0.23	0.43 ± 0.18	0.17 ± 0.058	0.12 ± 0.053	59.6	35.6	14.1	9.9
Soil (18–24 cm)	1	1050 ‡	0.68 ± 0.28	0.36 ± 0.093	0.18 ± 0.094	0.14 ± 0.11	71.4	37.8	18.9	14.7
	2	858 ± 48	1.00 ± 0.28	0.69 ± 0.23	0.18 ± 0.015	0.13 ± 0.040	85.8	59.2	15.4	11.2
Live beech leaves	1		2.34 ± 0.55	1.25 ± 0.16	0.155 ± 0.070	0.94 ± 0.33				
	2		1.98 ± 0.61	0.80 ± 0.08	0.093 ± 0.002	1.08 ± 0.58				

*Values are means ± one standard deviation. T-P is total phosphorus, ASP is acid-stable phosphorus, ALP is acid-labile phosphorus, and ortho-P is orthophosphate-P.

†Season 1, spring–summer (March through July); season 2, fall–winter (September through January).

‡Assumed a composition of 1.75 g dry weight/cm³.

of the year (spring–summer included March through July; fall–winter included September through January).

Rates of flux through the leaf-litter community under natural conditions during the spring–summer period were estimated to be 3.4 μg P (g dry weight)$^{-1}$ day^{-1} or 3.3 mg P m^{-2} day^{-1} into the litter and 14.5 μg P (g dry weight)$^{-1}$ day^{-1} or 14.1 mg P m^{-2} day^{-1} out of the litter. The correlation coefficient (r) for the specific activity slope was 0.99 and for the total activity slope 0.99. The r values for the net specific activity slope and net total activity slopes (actual data plus correction for isotopic decay) were 0.65 and 0.91, respectively. In another experiment at the same time of year under increased loading conditions (natural plus 43 mg P m^{-2} day^{-1}), the flux rates were estimated to be 13.3 μg P (g dry weight)$^{-1}$ day^{-1} or 12.9 mg P m^{-2} day^{-1} into the litter and 11.2 μg P (g dry weight)$^{-1}$ day^{-1}) or 10.9 mg P m^{-2} day^{-1} out of the litter. The r values for the gross specific activity and the total activity slopes were both 0.99. The r values for the net specific activity and the total activity slopes were both 0.94.

Rates of flux through the leaf-litter community under natural conditions during the fall–winter period were estimated to be 9.4 μg P (g dry weight)$^{-1}$ day^{-1} or 12.3 mg P m^{-2} day^{-1} into the litter and 15.0 μg P (g dry weight)$^{-1}$ day^{-1} or 19.6 mg P m^{-2} day^{-1} out of the litter. The r values for the gross specific activity and the total activity slopes were both 0.99. The r values for the net specific activity and the total activity slopes were 0.87 and 0.89, respectively. In another experiment at the same time of year under increased loading conditions (natural plus 430 mg P m^{-2} day^{-1}), the flux rates were estimated to be 168 μg P (g dry weight)$^{-1}$ day^{-1} or 220 mg P m^{-2} day^{-1} into the litter and 56 μg P (g dry weight)$^{-1}$ day^{-1} or 73 mg P m^{-2} day^{-1} out of the litter. The r values for the gross specific activity and the total activity slopes were 0.99 and 0.98, respectively. The r values for the net specific activity and the total activity slopes were 0.86 and 0.83, respectively.

In Table 2, data for the time course of alteration in leaf-litter phosphorus composition under heavy loading are given. The bulk of the phosphate applied during the first 2 weeks was retained in the leaf litter as orthophosphate. From then on the total phosphorus content of the leaf litter did not increase significantly. When loading ceased, the phosphorus level in the leaf litter declined to the original level within 4 months. Statistically significant increases in phosphorus content of the soil were not observed at any time.

The specific activities of the measured phosphorus fractions in a given sample often were not equal. This was especially true during the first few weeks after an experiment was begun and at locations near the boundaries of the radioactive zones. Examples of three-dimensional distribution patterns of specific radioactivities for chemical fractions of phosphorus are given for natural loading conditions (Fig. 1) and greatly increased loading conditions (Fig. 2). Orthophosphate had lower specific activities than acid-labile phosphorus near the boundaries of the zones. Since the radioactive phosphorus was applied as

TABLE 2

CHANGE IN PHOSPHORUS COMPOSITION IN WOODLAND LEAF LITTER AND SOIL LOADED WITH ORTHOPHOSPHATE AT THE RATE OF 430 mg P/m^2 *

Days elapsed	Leaf litter			Soil, 0 to 3 cm			Cumulative load, g/m^2
	T-P, mg/g dry wt.	Ortho-P, mg/g dry wt.	T-P, g/m^2	T-P, mg/g dry wt.	Ortho-P, mg/g dry wt.	T-P, g/m^2	
	1.45 ± 0.18	0.42 ± 0.036	1.9	1.88 ± 0.24	0.84 ± 0.13	39.7	0
14	5.46 ± 1.87	4.47 ± 1.67	7.15	1.86 ± 0.25	1.04 ± 0.28	39.2	6.0
29	5.31 ± 1.18	3.86 ± 1.58	6.95	2.34 ± 0.21	1.29 ± 0.28	49.4	12.5
43	6.32 ± 0.62	5.10 ± 0.3	8.28	1.97 ± 0.29	1.12 ± 0.33	41.5	19.5
†	2.02	0.42	2.65	2.14	1.14	45.2	31

*Values are means ± one standard deviation (N = 5). Experiment was initiated on July 30, 1973. Abbreviations are the same as for Table 1.

†Loading was continued for a total of 72 days, then samples were taken after an additional 121 days of natural loading.

orthophosphate, it is evident that the applied phosphorus was incorporated into organisms and metabolized in the leaf-litter community, and then some of it was transferred vertically and horizontally in the form of microbial cellular phosphorus. The specific radioactivities of chemical fractions within samples were also used to determine the source of phosphorus for new tree growth in the forest. The specific activities of the acid-labile phosphorus in new beech leaves in the spring were compared with the specific activities of the orthophosphate in leaf litter and in soil samples taken from various depths. With time the specific activities of new-leaf acid-labile phosphorus approached that of the leaf-litter orthophosphate. Soil orthophosphate specific activities and leaf orthophosphate specific activities were much lower. After 52 days of natural loading in the spring, specific activities (cpm/μg P) were: beech leaf ALP, 85; beech leaf ortho-P, 3.6; leaf-litter ortho-P, 139; soil ortho-P from 0 to 3 cm deep, 8.0; and soil ortho-P from 3 to 5 cm deep, 2.4. In another spring experiment, after 52 of natural plus 43 mg P m^{-2} day^{-1} loading, specific activities were beech leaf ALP, 77; beech leaf ortho-P, 9.5; leaf-litter ortho-P, 64; soil ortho-P from 0 to 3 cm deep, 4.4; soil ortho-P from 3 to 5 cm deep, 1.4; soil ortho-P from 5 to 8 cm deep, 1.1; and soil ortho-P from 8 to 12 cm deep, 0.41. In both experiments soil was sampled to a depth of 30 cm, and specific activities continued to decrease. Thus the beech trees were obtaining most of the phosphorus for synthesis of new leaf acid-labile phosphorus from the orthophosphate fraction of the leaf litter. Leaf orthophosphate and surface-soil orthophosphate specific activities were about an order of magnitude lower.

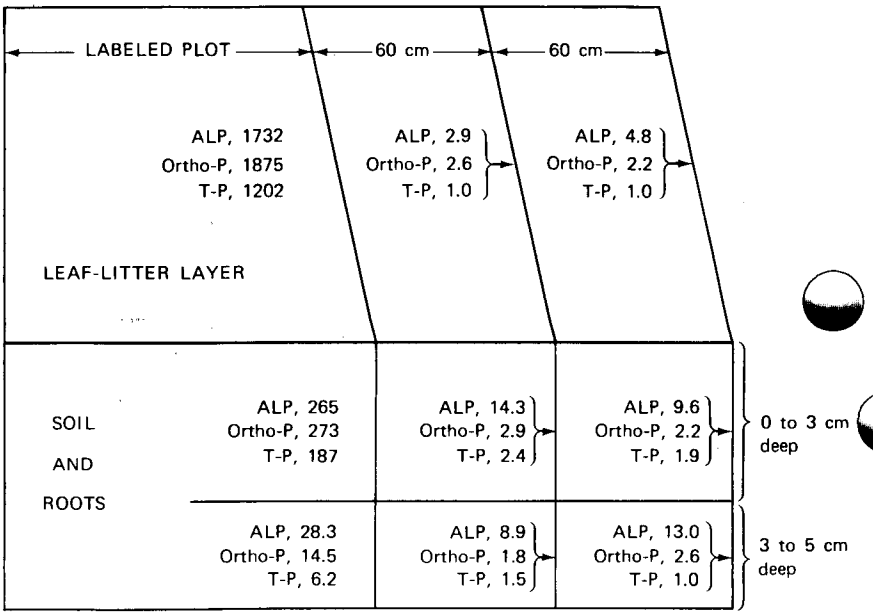

Fig. 1 Analysis of the chemical characteristics of the phosphorus that is moving out from the leaf litter by consideration of the specific activities of different phosphorus fractions under natural loading conditions. The specific activities given are for acid-labile phosphorus (ALP), orthophosphate (Ortho-P), and total phosphorus (T-P) at various locations along sampling transects 11 days after the experiment was initiated on Sept. 29, 1972.

Data on total radioactivities in soil zones beneath the plots and in leaf litter and soil at various distances from the plots were used to calculate (Eq. 3) rates and distances of phosphorus transfer vertically and horizontally (Table 3). Since the applied increased phosphorus loading in two experiments resulted in an effective isotope-chase experiment, these horizontal transfer rates were not tabulated. Table 3 shows that the vertical transfer of phosphorus under natural loading conditions is slow and only takes place in a very shallow zone (0 to 5 cm). When loading was increased, not only did vertical transfer increase amount but the distance moved was also greatly increased. Horizontal transfer of phosphorus under natural loading involved relatively small amounts of phosphorus but relatively great distances. Some selected phosphorus transfer rates (from leaf litter in the plots to the designated locations) are given in Table 4 for specific times in the four experiments. These rates were calculated from total radioactivity data. They illustrate data which led us to conclude that the main route of horizontal transfer from the leaf litter seems to be down into the soil (0 to 5 cm deep), lateral movement, then transfer vertically along the way. The

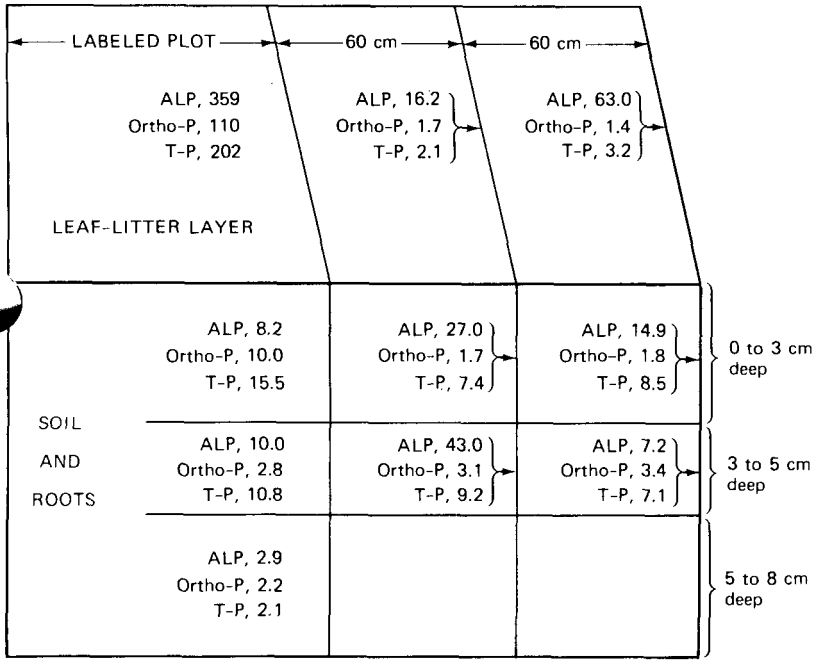

Fig. 2 Figure 2 is the same as Fig. 1, except that the experiment began on July 30, 1973, and the specific activities are for samples taken after 14 days. Loading was natural + 430 mg P m^{-2} day^{-1}.

specific activity patterns in Figs. 1 and 2 also show gradients along this pathway. At each step in the pathway, the high specific activities of the acid-labile phosphorus fractions indicate that this phosphorus is transferred in microbial cells. Increased phosphorus loading (Table 4) resulted in relatively more horizontal transfer in deeper soil layers than did natural loading conditions.

DISCUSSION

These studies of phosphorus flux and cycling took advantage of the ication of carrier-free radiophosphorus at a uniform rate per area to an terface community (leaf litter). Because the radiophosphorus was carrier free, the chemical level of phosphorus involved was insignificant. Because the metabolic rates in this community are so high, essentially all the radioisotopes were rapidly assimilated into cells. Little of the radioisotopes moved very far into the soil before assimilation. After 11 days (Fig. 1) the chemical fractions in the leaf litter were nearly uniformly labeled, and leaf-litter total-phosphorus specific activity was 200 times higher than soil total phosphorus at a depth of 3 to 5 cm. Since the plots were selected in locations that enclosed all the roots of

TABLE 3

DISTANCES AND RATES OF PHOSPHORUS TRANSFER FROM LEAF LITTER OF LABELED PLOT AS DETERMINED FROM TOTAL RADIOACTIVITY DATA*

		Vertical P flux			Horizontal P flux		
Period	P loading, Mg m^{-2} day^{-1}	Mg m^{-2} day^{-1}	Zone depth, cm	Mg cm^{-1} m^{-2} day^{-1}	Mg m^{-2} day^{-1}	Zone width, cm	Mg cm^{-1} m^{-2} day^{-1}
Spring–summer	Natural	12.3	(0–3)	25	6.0	(0–60)	1002
		1.6	(3–5)		4.3	(60–120)	
		13.9	(0–5)		2.9	(120–180)	
					13.2	(0–180)	
Spring–summer	Natural + 43	145	(0–3)	960			
		34	(3–5)				
		23	(5–8)				
		18	(8–12)				
		16	(12–18)				
		237	(0–18)				
Fall–winter	Natural	30.8	(0–3)	128	5.3	(0–60)	866
		8.4	(3–5)		3.7	(60–120)	
		3.8	(5–8)		2.5	(120–180)	
		43	(0–8)		11.5	(0–180)	
Fall–winter	Natural + 430	29.6	(0–3)	4830			
		32.2	(3–5)				
		50.9	(5–8)				
		137.1	(8–12)				
		52.4	(12–18)				
		103.4	(18–24				
		406	(0–24)				

*Horizontal transfer rates were calculated under conditions of increased loading the applied phosphorus acted as an isotope chaser. A faster-time-resolu would have been required under these conditions.

TABLE 4

PHOSPHORUS TRANSFER PATTERNS OF PHOSPHORUS DERIVED FROM LEAF LITTER OF LABELED PLOT*

Distance from plot edge and sample type	Spring–summer, after 38 days natural loading		Spring–summer, after 17 days natural + 43 mg P m^{-2} day^{-1}		Fall–winter, after 25 days natural loading		Fall–winter, after 14 days natural + 430 mg P m^{-2} day^{-1}	
	μg P (g dry weight)$^{-1}$ day^{-1}	μg P dm^{-2} day^{-1}	μg P (g dry weight)$^{-1}$ day^{-1}	μg P dm^{-2} day^{-1}	μg P (g dry weight)$^{-1}$ day^{-1}	μg P dm^{-2} day^{-1}	μg P (g dry weight)$^{-1}$ day^{-1}	μg P dm^{-2} day^{-1}
60 cm								
Leaf litter	0.56	5.4	0.38	3.7	0.52	6.8	0.42	5.5
Soil (0–3 cm)	0.055	15.7	0.24	68	0.083	17.5	0.84	177
Soil (3–5 cm)	0.040	11.2	0.14	39	0.043	11.5	1.16	311
120 cm								
Leaf litter	0.19†	1.8†	0.49	4.8	0.28	3.7	1.00	13.1
Soil (0–3 cm)	0.042†	12.0†	0.20	57	0.041	8.6	1.13	238
Soil (3–5 cm)	0.010†	2.8†	0.14	39	0.024	6.4	0.89	239

*Values were calculated from total radioactivity data.

†These values were taken 180 cm from the plot edge.

the beech trees sampled, quantitative conclusions as to the trees' source of phosphorus could be reached. Without the data on specific, metabolically meaningful chemical fractions, some of the conclusions, such as the source of beech tree phosphorus, still could not have been reached. Thus this study is a major advance over earlier forest phosphorus-cycling studies in that it has provided the data for quantitative calculations of rates, distances, relative source contributions, and the form in which the phosphorus is transferred. For example, in his study of tropical-forest phosphorus cycling, Luse (1970) applied ^{32}P to tree trunks. The results, although valuable, were limited by the lack of uniform distribution and the lack of known initial specific activity data. K[illegible] (1974) used ^{32}P to trace phosphorus movement from the surface down into the soil of a temperate forest under conditions of known increased phosphorus loading. He did not gather specific activity data, however, and thus his conclusions were limited.

The flux rates through the leaf-litter community reported here are not to be confused with recycling rates within this community. Recycling rates were too high to measure with data collected every 2 weeks. Uniform labeling was approached within the first 2 weeks (Fig. 1), while flux rates through the leaf litter under natural loading were only on the order of 1% of the total leaf-litter phosphorus per day.

Sufficient radioisotope was applied to enable accurate assays for six half-lives (about 3 months). Thus the rates measured were averaged over that amount of time. The raw data for the time courses of radioactivity changes fit log-linear least-squares regressions well (all associated r values were over 0.97). The net data (after correction for radioactive decay of ^{32}P) still had high correlation coefficients (all but one were over 0.8). The lowest correlation coefficient found was for the net change in specific activity under natural loading in the spring–summer period ($r = 0.65$) because the net slope was very small (Δ ln/half-life = 0.006). Thus the flux of phosphorus through the leaf litter can be properly classified as a case of pseudo first-order kinetics and Eqs. 1 and 2 can be used to calculate rate estimates. Under natural loading the rate out from leaf litter in the spring–summer period was 10.8 mg m^{-2} day^{-1} higher than the rate into leaf litter. This could be at least partly due to a rapid withdrawal of phosphorus from this layer by tree roots. If the difference were all due to this process, we might ask how much new tree growth it would be equivalent [illegible] From Table 1 we find that beech leaves contain about 2 mg P/g dry weigh[illegible] the fall. Thus we are asking, does this forest produce the equivalent of 5.4 g dry weight m^{-2} day^{-1} of beech leaves in the spring and summer? This would translate into about 700 g dry weight/m^2 during the spring–summer period involved. Although it may be a little high, this seems like a reasonable number since there is an increase of 400 g dry weight/m^2 of leaf litter from the spring–summer to the fall–winter period (Table 1). Annual biomass production ranges of 1200 to 1500 g m^{-2} $year^{-1}$ for temperate climax forests (including roots) have been

estimated (Marks and Bormann, 1972). Phosphorus loading due to rainfall was measured at the site and found for 1973 to be: spring–summer, 0.100 mg P m^{-2} day^{-1}; fall–winter, 0.090 P m^{-2} day^{-1}; and for the calendar year, 34.7 mg P/m^2 (Correll, 1974). This rate compares with an average rainfall loading rate of 0.13 mg P/m^{-2} day^{-1} measured for the eastern coastal United States by Pearson and Fisher (1971). These numbers are quite small when compared with flux rates in the leaf litter under natural conditions of 3 to 20 mg P m^{-2} day^{-1} and phosphorus levels of 1.2 to 1.8 g P/m^2 in the leaf litter and 285 to 316 g P/m^2 in the upper 24 cm of the soil (Table 1). Leaf fall alone has been estimated to be mg P/m^2 $year^{-1}$ at Hubbard Brook (Hobbie and Likens, 1973).

The importance of rainfall phosphorus loading to this forest is especially questionable because the leaf-litter and soil communities were apparently unable to retain higher levels of phosphorus than were present before increased loading was applied (Table 2). When increased phosphorus loading was applied, the increase in the estimated phosphorus flux into leaf litter was less than half as great (43 mg P m^{-2} day^{-1} loading vs. 9.6 mg P m^{-2} day^{-1} flux into litter in the spring–summer period; 430 mg P m^{-2} day^{-1} loading vs. 208 mg P m^{-2} day^{-1} flux into litter in the fall–winter period). This apparent problem may have been the result of some leakage of applied phosphorus into the surface few centimeters of soil before assimilation took place. The boundary between what was sampled as leaf litter and the humus layer beneath was rather arbitrary, and in reality a continuous gradient exists between leaves and soil. Since stepping up the loading rate resulted primarily in increased levels of orthophosphate in leaf litter (Table 2), we might assume that this was the result of physical and chemical binding. This was not the case. After 14 days leaf-litter orthophosphate had a lower specific activity than either ALP or total phosphorus fractions (Fig. 2). Thus the applied ^{32}P-phosphate was taken up by cells in the leaf litter and was metabolized (their phosphorus fractions approached uniform specific radioactivities). Then some of the cells were transported down into the first few centimeters of soil and laterally in the soil interstitial water. During this process the cells were still assimilating orthophosphate, but now it was cold orthophosphate. The results were the patterns of specific radioactivity shown in Figs. 1 and 2. Phosphorus that had been transported along this route was found preferentially in ALP at first, before cellular metabolism resulted in more uniform specific radioactivity patterns. The orthophosphate specific activity in the leaf litter (Fig. 2) was lower at 14 days owing to the isotope-chase effect of the cold orthophosphate that was applied during those 14 days.

Acid-labile phosphorus is a very useful phosphorus fraction to study for two reasons. (1) It is rapidly synthesized by all organisms and it is made from cellular orthophosphate. This is true whether the synthesis is driven by autotrophic or heterotrophic mechanisms (Atkinson and Morton, 1960). (2) This fraction of phosphorus is acid labile because it contains high-energy chemical bonds, and this leads us to the fact that these compounds are also very easily hydrolyzed

both chemically and enzymatically. Many extracellular enzymes are elaborated by soil and leaf-litter microorganisms (Voight, 1971). These enzymes assure a short survival for acid-labile compounds when they are released into this environment. These lines of reasoning guided our selection of the phosphorus fractions to be analyzed. We concluded from the relative specific activities of orthophosphate and ALP in samples taken in a three-dimensional pattern that most of the phosphorus was transferred vertically down into the soil and laterally within the soil inside microbial cells. Beech tree roots take up most of their phosphorus as orthophosphate from the leaf litter, translocate it to sites of new synthesis, and then form ALP compounds from it.

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REFERENCES

American Public Health Association, 1971, *Standard Methods for the Examination of Water and Waste Water,* 13th ed., American Public Health Association, New York.

Atkinson, M. R., and R. K. Morton, 1960, Free Energy and the Biosynthesis of Phosphates, in *Comparative Biochemistry,* Vol. II, pp. 1-96, M. Florkin and H. S. Mason (Eds.), Academic Press, Inc., New York.

Bieleski, R. L., and P. N. Johnson, 1972, External Location of Phosphatase Activity in Phosphorus-Deficient *Spirodela oligorrhiza, Aust. J. Biol. Sci.,* **25**: 707-720.

Bould, C., 1963, Mineral Nutrition of Plants in Soils, in *Plant Physiology, A Treatise,* Vol. III, pp. 15-96, F. C. Steward (Ed.), Academic Press, Inc., New York.

Carlisle, A., A. H. F. Brown, and E. J. White, 1967, The Nutrient Content of Tree Stem Flow and Ground Flora Leachates in a Sessile Oak (*Quercus petraea*) Woodland, *Ecol.,* **55**: 615-627.

——, A. H. F. Brown, and E. J. White, 1966a, The Litter Fall, Leaf Production, and Effects of Defoliation by *Tortrix vividana* in a Sessile Oak (*Quercus petraea*) Woodland, *J. Ecol.,* **54**: 65-85.

——, A. H. F. Brown, and E. J. White, 1966b, The Organic Matter and Nutrient Elements in the Precipitation Beneath a Sessile Oak (*Quercus petraea*) Canopy, *J. Ecol.,* **54**: 87-98.

Correll, D. L. (Ed.), 1974, *Environmental Monitoring and Baseline Data Report,* 1973, Vol. 1, Rhode River, Smithsonian Institution, Washington, D. C.

Fiske, C. H., and Y. Subbarow, 1925, The Colorimetric Determination of Phosphorus, *J. Biol. Chem.,* **66**: 375-400.

Fuhs, G. W., S. D. Demmerle, E. Canelli, and M. Chen, 1972, Characterization of Phosphorus-Limited Plankton Algae, in *Nutrients and Eutrophication; the Limiting Nutrient Controversy*, Special Symposium, Vol. 1, pp. 113-133, American Society of Limnology and Oceanography.

Hobbie, J. E., and G. E. Likens, 1973, Output of Phosphorus, Dissolved Organic Carbon, and Fine Particulate Carbon from Hubbard Brook Watersheds, *Limnol., Oceanogr.*, **18**: 734-742.

Jarvis, M. S., and P. G. Jarvis (Translators), 1972, *Staffelt's Plant Ecology*, John Wiley & Sons, Inc., New York.

Kilian, W., 1974, Tracer Experiments on the Vertical Translocation of Fertilizer Nutrients into Forest Soils, *Centralbl. Gesamte Forstwes.*, **91**: 41-51.

[illegible]g, E. J., 1932, The Colorimetric Determination of Phosphorus, *Biochem. J.*, **26**: 292-297.

Luse, R. A., 1970, The Phosphorus Cycle in a Tropical Rain Forest, in *A Tropical Rain Forest, A Study of Irradiation and Ecology at El Verde, Puerto Rico*, H. T. Odum and R. F. Pigeon (Eds.), pp. H-161-H-166, U. S. Atomic Energy Commission, TID-24270.

Marks, P. L., and F. H. Bormann, 1972, Revegetation Following Forest Cutting: Mechanisms for Return to Steady-State Nutrient Cycling, *Science*, **176**: 914-915.

Pearson, F. J., Jr., and D. W. Fisher, 1971, *Chemical Composition of Atmospheric Precipitation in the Northeastern United States*, U. S. Geological Survey, Water Supply Paper No. 1535-p.

Pomeroy, L. R., 1970, The Strategy of Mineral Cycling, *Annu. Rev. Ecol. Syst.*, **1**: 171-190.

Voight, G. K., 1971, Mycorrhizae and Nutrient Mobilization, in *Mycorrhizae*, pp. 122-131, Superintendent of Documents, U. S. Government Printing Office, Washington.

BASE-LINE DATA ON EVERGLADES SOIL-PLANT SYSTEMS: ELEMENTAL COMPOSITION, BIOMASS, AND SOIL DEPTH

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ABSTRACT

Plants and soils from plots in the Everglades Wildlife Management Area, Conservation Area 3, were examined. Chemical composition (N, P, K, Ca, Mg, Na, Cu, Fe, Mn, Zn, Co, Sr, Pb, Ni, Cr, Al, and Si) of most plant and soil digests was determined. *Cladium jamaicense* was the predominant plant species contributing to biomass in all plots except the wet prairie, where *Rhynchospora* sp. and *Panicum hemitomon* were most common. The biomass of dead *C. jamaicense* was greater than that of the living plants in unburned saw-grass plots. The burned saw grass, muck burn, and wet prairie were characterized by a large number of plant species per square meter but smaller average biomass production than the unburned saw-grass locations. Levels of Cu, Mn, Ca, Mg, K, and N in *C. jamaicense* differed significantly across locations. Highly significant differences in elemental composition existed between plant species. Concentrations of several elements (particularly Zn, Ca, Mg, P, and N) were low in live *C. jamaicense* compared with other plant species. Cesium-137 levels ranged from 670 to 3100 pCi/kg in sandy and in organic soils, respectively. *Polygonum* had a ^{137}Cs level of 11,600 pCi/kg. Dead *C. jamaicense* indicated a rapid leaching loss of ^{137}Cs from dead tissue.

The shallow Everglades basin is no longer a natural ecosystem but is rather a managed system that has suffered continued and severe alteration since the turn of the century (Alexander, 1971). Much of this basin is formed from limestone or marl originating in the Pliocene era (Davis, 1943; Jones, 1948). Organic soil (Histosols), ranging in depth from several centimeters to meters, cover most of the rock. Subsidence of these Histosols following drainage is well documented and has been occurring at the rate of 3 cm/year (Davis, 1946; Volk, 1973).

The physical features and vegetation of this freshwater marsh have been described by several investigators (Long and Lakela, 1971; Loveless, 1959a; 1959b). Saw-grass (*Cladium jamaicense*) ecosystems comprise about 70% of the total Everglades (Loveless, 1959b). Tree islands, aquatic sloughs, and wet-prairie

ecosystems are also present. Ecological changes from pure *C. jamaicense* communities to mixed systems have occurred primarily as a result of altered water systems (Davis, 1946; Loveless, 1959b). Recent water-management practices have replaced drainage priorities and have modified rates of ecosystem change (Alexander, 1971).

Since Everglades ecosystems will continue to be manipulated, we must have a thorough knowledge of interacting parameters if management is to follow natural ecological laws (Alexander, 1971). The effects of treated sewage water on plant communities in the conservation areas are being studied. Conservation of fresh water and the use of plants as nutrient filters are important considerations. A systems-analysis approach to the Everglades ecosystem was reported by Lugo et al. (1971). This extensive study showed the extreme complexity of an ecosystem and pointed out that many parameters must be estimated because of lack of data. Alexander (1971) also pointed out the dearth of basic knowledge on plant and soil factors comprising the saw-grass communities.

This paper proposes to provide base-line data on biomass production and elemental composition of plants from locations representative of Everglades saw-grass (*C. jamaicense*) communities (burned and unburned), a wet-prairie community, and a burned muck site of saw grass. The biomass and compositional analyses have been statistically compared by location or ecosystem, plant species, and relationship to soil composition and depth of soil. Fallout ^{137}Cs data are presented for soils and for four plant species.

METHODS AND MATERIALS

Location and Description of the Study Area

This study was conducted in the 293,000-ha Everglades Wildlife Management Area, Conservation Area 3 (Fig. 1). The six study plots were located on either side of the Miami Canal and north of Alligator Alley (State Road 84) in Broward County, Florida. The area and plot sites were selected as representative of the saw-grass Everglades.

The six fenced plots, each 91.5 m^2, were divided into 22 transects 3.7 m wide. Plot dimensions were selected to allow access by airboat and half-track vehicles for a vehicle-vegetation study (Schemnitz and Schortemeyer, 1973). Because of sampling problems, some soil and vegetation data are missing.

The individual plots were grouped on the basis of previous history or environmental conditions (Table 1). One location (plot E) had experienced a muck burn several years previously, and in two locations (plots A and B) the vegetation had burned approximately 1 year previously. One site (plot F) was categorized as a wet prairie, and two sites (plots C and D) had not burned within 5 years.

TABLE 1

PLANT BIOMASS (g/m^2) BY SPECIES AND LOCATION*

Species	Number of observations	Location						Mean and standard deviation	$LSD_{0.05}$ (locations)
		Burned saw grass		Unburned saw grass		Muck burn	Wet prairie		
		A	B	C	D	E	F		
Cladium jamaicense (saw grass, dead)	253	318	670	1548	954	51		812 ± 40	188
C. jamaicense (saw grass, live)	267	213	289	76	115	155		175 ± 10	52
Cephalanthus occidentalis (buttonbush)	11		161	59	66		1	68 ± 14	ns
Typha domingensis (cattail)	11				125	13		23 ± 11	39
Blechnum serrulatum (blechnum fern)	9			55				56 ± 13	
Cyperus haspan (nut sedge)	42	43	9		9	4	10	10 ± 2	ns
Panicum hemitomon (maiden cane)	81	32	46	4		20	29	30 ± 5	ns
Ludwigia sp.	16	29		12	2	79		38 ± 10	45
Ludwigia repens	4			13			5	7 ±3	ns
Eupatorium capillifolium (dog fennel)	46	27		16	15	38	5	32 ± 4	17
Pluchea foetida (marsh fleabane)	39	28		4	20	26		24 ± 3	ns
Gerardia purpurea	4	29		2		3		9 ± 7	13
Mikania scandens	16	18	7	3	10			8 ± 2	5
Sagittaria lancifolia (arrowhead)	83	12	40	4	10	19	2	23 ± 8	ns
Andropogon glomerat	2	21						21 ± 9	

Salix caroliniana (willow)	1				34			34 ± nd	
Crinum americanum (spider lily)	27		7	8	9		8	8 ± 2	ns
Diodia virginiana	2	7		1				4 ± 3	
Peltandra virginica	4		6					6 ± 2	5
Dryopteris thelypteris, Thylypteris palustris Schott var. *haleana*	3			8				8 ± 6	
Bacopa caroliniana (water hyssop)	31		4				3	3 ± 0.4	1
Myrica cerifera (wax myrtle)	1			4				4 ± nd	
Pontederia lanceolata (pickerelweed)	17		3					3 ± 0.5	
Polygonum sp. (smartweed)	19		5	1		25	1	18 ± 4	5
Amaranthus cannabinus Sauer (pigweed)	34					103		103 ± 18	
Rhynchospora sp. (beak rush)	51		2				37	31 ± 4	3
Eriocaulon compressum (pipewort)	16						11	11 ± 2	
Eleocharis sp. (spike rush)	27						11	11 ± 1	
Nymphoides aquatica	1						1	1 ± nd	
Solidago sp.	1						1	1 ± nd	
Mixed unidentified			30	4	6	13	87		
								$LSD_{0.05}$ (species)	121

*Abbreviations are $LSD_{0.05}$, least significant difference between two means which can be detected at the 0.05 level; ns, not significant; and nd, not determined.

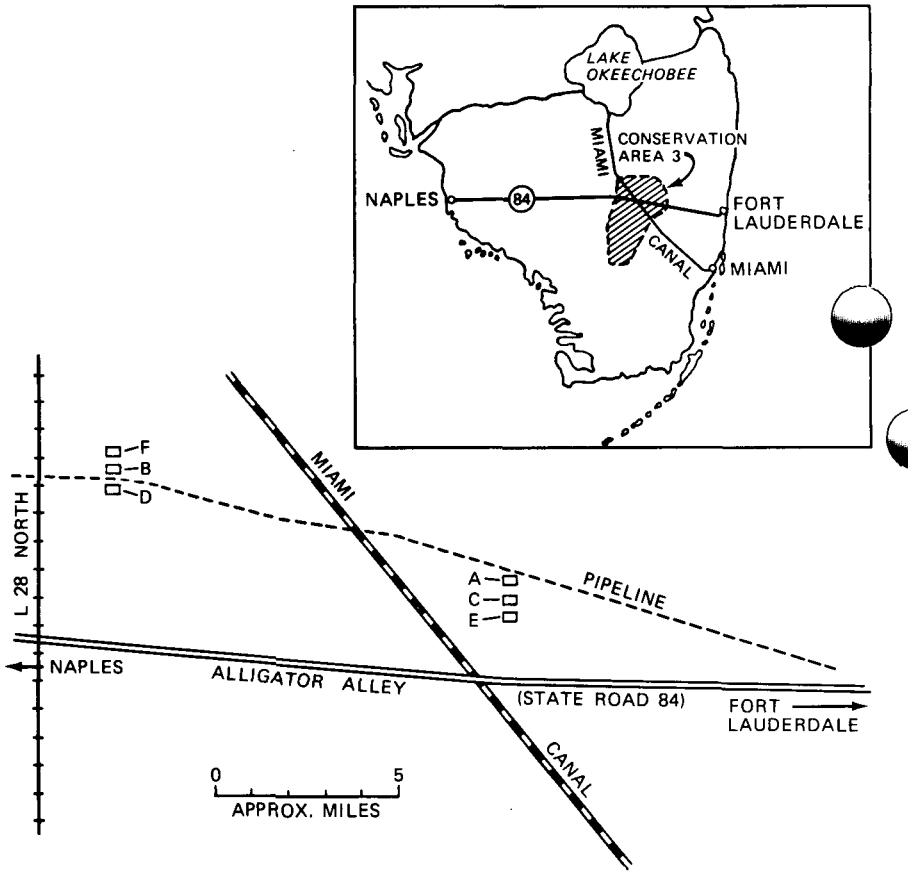

Fig. 1 Location of study plots (□), Conservation Area 3, Broward County, Florida.

Vegetation Sampling

Vegetation was clipped at ground or water level from one 3-m^2 subplot per transect. A welded-metal-rod frame was used to delineate the boundaries of the subplots (Loveless, 1957). Vegetation was segregated by species, and fresh we was recorded. Plants were placed in paper bags and oven-dried for 24 hr at 7 Dried plant tissue was ground in a stainless-steel mill to pass a 40-mesh stainless-steel screen and was stored in glass bottles. Plant nomenclature follows Long and Lakela (1971).

Soil Sampling

Surface soil samples (0 to 15 cm deep) were collected with a soil core sampler and placed in plastic bags. Nine samples per plot were collected, air

dried, thoroughly mixed, and subsampled for soil analysis. Soil ash content was determined by heating samples in a muffle furnace for 8 hr at 550°C. Soil depths on each plot were determined by inserting a $\frac{3}{8}$-in. diameter steel corner-marker rod into the soil to bedrock.

Chemical Analysis

Nitrogen determinations were made by the micro-Kjeldahl technique. Soil samples were dry-ashed at 450°C, and the residue was dissolved in 5*N* HCl, evaporated to dryness, redissolved in 1*N* HCl, and transferred to 50-ml volumetric flasks. Plant tissue was digested using the perchloric–nitric acid digestion procedure. The resulting plant and soil solutions were analyzed by atomic absorption spectrophotometry for Ca, Mg, Cu, Fe, Mn, Zn, Co, Sr, Pb, Ni, Cr, Al, and Si. Flame photometry was used for K and Na. Phosphorus in the solutions was measured by the chlorostannous-reduced molybodophosphoric blue method. All data are reported on an oven-dry basis. The soil pH was determined on a 1:2 soil–water mixture.

Cesium-137 Analysis

Gamma scans on unashed samples were performed using a 4- by 4-in. NaI(Th) crystal detector. Samples were packed to a uniform density in a 3.5-liter Maranelli beaker, and counts were made for 40 min and recorded on a 16-channel analyzer.

RESULTS AND DISCUSSION

Key factors influencing environmental conditions that affect marsh-plant growth rates are rainfall and water-table depth. The extreme drought conditions of the previous winter (1970-1971) had eased considerably during the year of this study. Total rainfall from June 1, 1971, to May 31, 1972, at Conservation Area 3 was 125, or 3.5 cm over the normal yearly rainfall of 121.5 cm. Water depths for plots west of the Miami Canal averaged 21.7 cm for the period from July to December 1971 and 4.4 cm for January to May 1972. Plots east of the Miami Canal were considerably drier, averaging 4.8 cm for July to December 1971 and less than 0.5 cm for January to May 1972. Inflow from Central and Southern Florida Flood Control District water structures also influenced water-table depths in the plot areas.

Approximately 30 species of plants occurred in the plots (Table 1). *Cladium jamaicense,* which occurred in 267 of 378 plots (71%), was the most abundant species identified. *Sagittaria lancifolia* (22%), *Panicum hemitomon* (21%), *Rhynchospora sp.* (13%), *Eupatorium capillifolium* (21%), *Cyperus haspan* (11%), and *Pluchea foetida* (10%) occurred with a frequency of >10% in the plots.

Because a large quantity of identifiable dead *C. jamaicense* was found on all sites, separate biomass and elemental determinations were performed on both living and dead plants of that species. Such dead material is one of the obvious precursors of organic soil. The biomass of each species averaged over all locations shows great variation (Table 1), but because there were many observations, biomass differed significantly between species [least significant difference that could be detected at the 0.05 level ($LSD_{0.05}$) was 121]. The biomass of *C. jamaicense, Rhynchospora* sp., *Typha domingensis, E. capillifolium, Ludwigia* sp., *Polygonum* sp., *Mikania scandens,* and *Gerardia purpurea* was significantly influenced by location.

The saw-grass plots were a *C. jamaicense–Cephalanthus occidentalis* community with 10 secondary species and another 10 members producing less biomass. There was a greater difference in species biomass between the two burned plots and the two unburned plots than between a burned and unburned plot (Table 1). *Cephalanthus occidentalis* appeared to be a codominant species but did not appear in one of the unburned plots. *Typha domingensis* occurs almost exclusively in the unburned plot D, and *Blechnum serrulatum* appears exclusively in unburned plot C.

The muck-burn plot contained biomass mostly from *C. jamaicense* and *Amaranthus cannabinus,* with *Ludwigia* sp. almost codominant in biomass production. Most of the secondary species in plot A appeared in a similar role in the muck-burn plot (E), except for *Polygonum* and *A. cannabinus,* which have almost an exclusive biomass production in the muck burn.

The wet prairie (F) was the most distinctive community, having lowest species number and biomass production. *Rhynchospora* was found here exclusively. *Panicum hemitomon* was codominant in biomass production. *Eriocaulon compressum* and *Eleocharis* sp. were also found only in the wet-prairie community.

The average numbers of plant species per square meter per plot were 7.1, 4.9, 8.3, and 7.3 for the burned saw-grass, unburned saw-grass, muck-burn, and wet-prairie locations, respectively. The low number of species in the unburned saw-grass location was expected since the accumulation of dead *C. jamaicense* would inhibit the growth of other species. The values for average biomass of all species were 471 and 236 g/m^2 for the unburned and burned saw-grass locations, respectively. Biomass values for the muck-burn and wet-prairie locations were 87 and 32 g/m^2, respectively, lower than the saw-grass locations. Significant differences ($LSD_{0.05}$ = 42) existed between locations and the average biomass of all species. The unburned saw grass showed the highest average (471 g) and the wet prairie without saw grass, the lowest (32 g).

Soil depths averaged 41 cm for the burned saw-grass location, 35 cm for the muck burn, and 21 cm for the unburned and wet-prairie locations. These depths were significantly correlated ($LSD_{0.05}$ = 2) with location; however, this correlation was most likely due to the geologic factors of gently rolling limestone

bedrock under the soil (Jones, 1948) rather than to location factors. If the limestone under the organic layer was level, frequent muck burns or burns in saw-grass areas would undoubtedly result in shallower soil because of a decrease in soil volume.

Levels of Cu, Mn, Ca, Mg, K, and N in live *C. jamaicense* differed significantly across locations (Table 2). In other species levels of micronutrients and/or nitrogen and phosphorus were significantly correlated with species location.

Highly significant differences in plant elemental composition existed between species. Concentrations of several elements (particularly Zn, Ca, Mg, P, and N) were low in live *C. jamaicense* as compared with other plant species. Low Mg, K, P, and N concentrations in dead *C. jamaicense* indicates the rapid loss of these elements from dead tissue. *Sagittaria lancifolia* contained notably high levels of potassium and phosphorus. A low iron level and high levels of potassium, phosphorus, and nitrogen characterize *T. domingensis. Pontederia lanceolata* contained low copper but high manganese, potassium, phosphorus, and nitrogen levels. Extremely high concentrations of calcium and magnesium were present in *A. cannabinus.* High levels of iron, manganese, and phosphorus were present in *E. compressum. Crinum americanum* was low in copper and manganese but high in calcium, magnesium, potassium, and phosphorus. The iron content of *Bacopa caroliniana* was the highest of any values reported here. Because of statistical interactions between data on plant species and location, inferences with regard to plant species must be related to a particular location.

A lack of published information on the chemical content of these species makes comparisons difficult. The limited data available (Boyd, 1970; Steward, 1973; and Loveless, 1959a) show similar elemental concentrations to our data, however. Nutritional data (on crude protein, crude fiber, ether extract, and nitrogen-free extract) from these species are published elsewhere (Schemnitz and Schortemeyer, 1972).

Analyses of soil collected from each location except the wet prairie are reported in Table 3. The percent of ash in soil shows that all soils except those at plot D would be classified as Histosols (soils from plot D are Entisols). Nitrogen concentrations were high, ranging from 1.16 to 3.29%. The copper content (3.5 to 10.1 ppm) was very similar to previously reported values for Everglades Histosols (Allison and Gaddum, 1940). Farmed Histosols of the Everglades have shown a great deficiency in copper for cultivated crops, and periodic additions of copper is necessary for good growth (Forsee, 1940). Manganese and zinc could also be limiting for optimum plant growth because of the relatively high soil pH (Forsee, 1940).

Levels of most elements were considered normal when compared with other Histosols, except for the relatively high concentrations of heavy metals. A direct comparison of our values with values reported in the literature has limitations because different soils were analyzed and different analytical techniques, such as

TABLE 2

DISTRIBUTION, ELEMENTAL CONCENTRATION, AND MEANS OF VARIOUS PLANT SPECIES AT DIFFERENT LOCATIONS*†

Location	Element										
	Cu, ppm	Fe, ppm	Mn, ppm	Zn, ppm	Al, ppm	Ca, ppm	Mg, ppm	K, ppm	Si, ppm	P, ppm	N, %
						Cladium jamaicense (live)					
A (22)	5.6 ± 1.0	83 ± 14	77 ± 7	10.2 ± 1.0	9.7 ± 2.6	2570 ± 131	594 ± 42	7810 ± 415	5800 ± nd	425 ± 50	0.85 ± 0.1
B (47)	11.4 ± 0.6	151 ± 21	99 ± 7	15.0 ± 0.7		2710 ± 148	480 ± 20	4340 ± 4933		392 ± 23	0.68 ± 0.02
C (16)	7.6 ± 1.4	171 ± 47	105 ± 16	12.6 ±1.2	6.3 ±2.9	2850 ± 133	426 ± 23	7260 ± 560		421 ± 42	0.75 ± 0.1
D(18)	11.4 ± 0.9	217 ± 50	114 ± 11	12.3 ± 1.9		2910 ± 145	460 ± 14	5700 ± 536		372 ± 32	0.71 ± 0.03
E (12)	8.9 ± 0.8	102 ± 31	77 ± 14	14.9 ± 1.4	33.3 ±16.7	5670 ± 1294	939 ± 115	6000 ± 892		573 ± 124	0.97± 0.15
Location mean	9.5 ± 0.4	146 ± 14	96 ± 5	13.3 ± 0.5	11.9 ± 2	3040 ± 170	540 ± 22	5767 ± 290	5800 ± nd	417 ± 20	0.76 ± 0.02
LSD	3.3	ns	23	ns	ns	1220	107	1581		ns	0.14
						Cladium jamaicense (dead)					
A (9)	13.4 ± 2.0	109 ± 7	90 ± 10	10.2 ± 0.9	18.8 ± 5.9	3270 ± 318	444 ± 40	1500 ± 197	5200 ± nd	132 ± 12	0.41 ± 0.4
B (40)	11.4 ± 0.6	1580 ± 213	220 ± 23	17.5 ± 1.0		5810 ± 683	392 ± 20	392 ± 20		254 ± 30	0.49 ± 0.02
C (19)	7.4 ± 1.0	569 ± 112	161 ± 18	11.8 ± 0.9	33.3 ± 7.0	3520 ± 270	358 ± 2.0	493 ± 91		239 ± 40	0.41 ± 0.03
D (14)	8.4 ± 0.8	1620 ± 442	222 ± 74	13.9 ± 1.6		6260 ± 651	379 ± 20	1090 ± 223		180 ± 33	0.50 ± 0.05
E (1)	17.5 ± nd	87 ± nd	81 ± nd	16.5 ± nd		3850 ± nd	550 ± nd	200 ± nd		140 ± nd	0.35 ± nd
F (3)	23.7 ± 1.6	1990 ± 723	453 ± 152	37.0 ± 5.1		5480 ± 628	683 ± 37	2430 ± 245		417 ± 24	1.09 ± 0.02
Location mean	10.8 ± 0.48	1171 ± 143	191 ± 18	14.8 ± 0.7	26 ± 6	5060 ± 628	390 ± 12	1221 ± 93	5200 ± nd	224 ± 18	0.46 ± 0.02
$LSD_{0.05}$	3.0	918	ns	5.0	ns	1191	108	368		ns	0.03
						Rhynchospora					
F (12)	23.5 ± 3.5	339 ± 47	135 ± 11	34.3 ± 3.3		3780 ± 100	936 ± 45	5300 ± 1282		618 ± 44	1.53 ± 0.11
						Blechnum serrulatum					
C(3)	6.2 ± 0.6	467 ± 136	112 ± 19	20.2 ± 1.2	37.5 ± 10.2	5460 ± 848	1720 ± 464	11440 ± 928		1130 ± 331	1.38 ± 0.29
						Sagittaria lancifolia					
A (2)	7.4 ± 0.4	110 ± 23	43 ± 1.4	23.1 ± 0.7		4960 ± 850	2010 ± 175	35000 ± 2800	500 ± nd	1580 ± 70	2.57 ± 0.05
B (16)	7.4 ± 0.7	261 ± 57	98 ± 7	36.1 ± 2.3		6300 ± 580	1550 ± 131	13490 ± 4640		1060 ± 105	2.08 ± 0.16
C (2)	7.9 ±	218 ± 88	97 ± 2	14.9 ± 2.9		8000 ± 3000	1810 ± 24	23130 ± 185		710 ± 10	0.24 ± 0.18
D(5)	3.9 ±	514 ± 116	104 ± 12	26.1 ± 2.3		8560 ± 3830	1800 ± 261	29140 ± 105		906 ± 116	1.19 ± 0.29

E (5)	6.5 ± 1.1	166 ± 59	91 ± 22	17.2 ± 1.2	18.8 ± 16.8	12060 ± 2330	1900 ± 187	18450 ± 8240		1300 ± 202	1.66 ± 0.24
F (3)	6.6 ± 2.7	637 ± 273	94 ± 27	29.2 ± 5.4	50.0 ± nd	10650 ± 2350	1360 ± 109	20370 ± 7970		583 ± 292	1.31 ± 0.09
Location mean	6.7 ± 0.5	307 ± 47	94 ± 6	29.0 ± 1.9	21.9 ± 1.9	7930 ± 634	1680 ± 85	19300 ± 3180	500 ± nd	1040 ± 77	1.74 ± 0.14
$LSD_{0.05}$	ns	ns	ns	ns	ns	ns	ns	ns		ns	ns
						Typha domingensis					
E (2)	7.3 ±1.3	119 ± 25	184 ± 35	28.5 ± 2.5	8.3 ± 10.2	14430 ± 3740	2000 ± 35	11140 ± 1560		1040 ± 444	2.16 ± 0.08
						Eupatorium capillifolium					
C (1)	5.0 ± nd	232 ± nd	66 ± nd	170 ± nd		4250 ± nd	800 ± nd	6250 ± nd	500 ± nd	444 ± nd	0.69 ± nd
D (1)	4.5 ± nd	1200 ± nd	90 ± nd	240 ± nd		4600 ± nd	510 ± nd	12000 ± nd		540 ± nd	1.19 ± nd
E(7)	3.6 ± 0.5	126 ± 13	30 ± 3	46.4 ± 2.8		18180 ± 1200	2430 ± 297	5910 ± 633		1030 ± 65	1.38 ± 0.04
F (2)	10.5 ± 2	2600 ± 1955	118 ± 7	30.3 ± 12.7		5730 ± 1180	700 ± nd	4940 ± 1060		818 ± 342	1.29 ± 0.54
Location mean	5.1 ± 0.92	682 ±400	55 ± 11	38.8 ± 4.2		13410 ± 2140	1900 ± 322	6320 ± 715	500 ± nd	896 ± 90	1.2 ± 0.1
$LSD_{0.05}$	2.3	130	34	ns		ns	ns	ns		ns	0.13
						Ludwigia sp.					
A (5)	6.8 ± 1.0	1110 ± 779	182 ± 81	38.4 ± 4.3	550 ± nd	19310 ± 2390	3320 ±326	8410 ± 1130	6500 ± nd	985 ± 135	1.19 ± 0.27
D (1)	4.5 ± nd	9050 ± nd	790 ± nd	43.0 ± nd		22500 ± nd	3100 ± nd	9500 ± nd		695 ± nd	0.70 ± nd
E (4)	7.0 ± 2.2	393 ± 303	122 ± 733	31.8 ± 11.1	213 ± 133	9160 ± 2280	2810 ± 703	3960 ± 796		1330 ± 623	0.49 ± 0.16
Location mean	6.5 ± 0.97	1620 ± 917	219 ± 79	36.2 ± 4.7	325 ± 85	15570 ± 2260	3090 ± 310	6740 ± 977	6500 ± nd	1110 ± 259	0.90 ± 0.18
$LSD_{0.05}$	ns	3472	ns	ns	ns	ns	ns	ns	ns	ns	ns
						Pontederia lanceolata					
B (2)	4.8 ± 0.8	381 ± 144	587 ± 242	27.3 ± 1.8		17250 ± 2750	1630 ± 325	31700 ± 28300	500 ± nd	1630 ± 70	1.90 ± nd
						Amaranthus cannabinus					
E (6)	8.3 ± 0.7	92 ± 5	38 ± 3	29.4 ± 2.0		87290 ± 4590	8290 ± 586	4930 ± 986		472 ± 52	0.91 ± 0.07
						Eriocaulon compressum					
F (5)	15.2 ± 2.4	4783 ± 1030	710 ± 98	35.9 ± 3.7		5750 ± 1710	888 ± 53	6870 ± 2560		535 ± 103	1.67 ± 0.26

Table 2 (Continued)

Location	Element										
	Cu, ppm	Fe, ppm	Mn, ppm	Zn, ppm	Al, ppm	Ca, ppm	Mg, ppm	K, ppm	Si, ppm	P, ppm	N, %
						Polygonum sp.					
A(1)	11.3 ± nd	500 ± nd	330 ± nd	38.8 ± nd	50 ± nd	10060 ± nd	3810 ± nd	5380 ± nd		675 ± nd	1.05 ± nd
B (7)	7.0 ± 0.6	4890 ± 1058	739 ± 112	48.3 ± 2.0		24610 ± 12630	1400 ± 91	7330 ± 1720		644 ± 91	0.71 ± 0.09
E (7)	16.7 ± 5.6	657 ± 237	348 ± 77	34.1 ± 1.8		48930 ± 4740	4000 ± 537	4960 ± 521		1100 ± 60	1.26 ± 0.06
Location mean	11.8 ± 2.8	2620 ± 746	542 ± 81	41.0 ± 2.2	50 ± nd	34990 ± 7030	2770 ± 422	6100 ± 863		860 ± 78	0.99 ± 0.09
$LSD_{0.05}$	ns	ns	ns	ns	ns	ns	1618	ns		363	0.47
						Crinum americanum					
C (2)	4.7 ± 1.6	203 ± 57	72 ± 17	27.0 ± 7.0	12.5 ± 12.5	21810 ± 10187	3590 ± 657	10750 ± 10500		813 ± 13	1.46 ± 0.22
F (2)	4.9 ± 1.3	588 ± 437	105 ± 25	29.8 ± 0.8	75.0 ± nd	19530 ± 469	2190 ± 91	12580 ± 8680		2550 ± 2450	1.27 ± 0.45
Location mean	4.8 ± 0.9	395 ± 212	88 ± 16	28.4 ± 3	33.3 ± 19	20670 ± 4220	2890 ± 489	11663 ± 5590		1680 ± 1120	1.36 ± 0.21
$LSD_{0.05}$	ns	ns	ns	ns	ns	ns	ns	225		ns	ns
						Eleocharis sp.					
F (13)	13.8 ± 1.4	930 ± 333	183 ± 42	23.5 ± 1.4	95.8 ± 41.9	3920 ± 586	888 ± 69	5740 ± 478	5500 ± nd	431 ± 51	1.03 ± 0.10
						Bacopa caroliniana					
D (1)	5.0 ± nd	15000 ± nd	815 ± nd	37.5 ± nd		25000 ± nd	1850 ± nd	10500 ± nd	5000 ± nd	630 ± nd	1.17 ± nd
F (7)	5.1 ± 1.0	6740 ± 980	692 ± 40	32.5 ± 2.0	283.3 ± 30.4	23280 ± 751	1690 ± 257	9460 ± 578		546 ± 88	1.19 ± 0.15
Location mean	5.1 ± 0.9	7770 ± 983	708 ± 38	33.1 ± 1.9	283 ± 28	23490 ± 686	1710 ± 223	9590 ± 518	5000 ± nd	556 ± 77	1.18 ± 0.13
						Peltandra virginica					
B (1)	4.0 ± nd	1000 ± nd	970 ± nd	32.0 ± nd		17500 ± nd	1500 ± nd	8750 ± nd		1400 ± nd	2.30 ± nd
						Panicum hemitomon					
A (5)	6.0 ± 1.4	117 ± 27	67.3 ± 12.3	107.1 ± 41.6		2870 ± 245	1340 ± 228	18340 ± 6000	14000 ± nd	1020 ± 354	1.82 ± 0.38
B (5)	26.4 ± 3.1	583 ± 275	140 ± 45	35.4 ± 3.0		2820 ± 946	608 ± 26	4930 ± 393		284 ± 27	0.64 ± 0.10
E (2)	20.3 ± 9.	109 ± 23	115 ± 11	26.5 ± 7.5	12.5 ± 12.5	3000 ± 950	1250 ± 500	7280 ± 248		2280 ± 1780	0.74 ± 0.10

Location mean	20.2 ± 2.6	436 ± 108	116 ± 15	43.4 ± 9.3	21.9 ± 5	2391 ± 331	893 ± 114	6987 ± 174	00 ± nd	683 ± 206	1.17 ± 0.17
$LSD_{0.05}$	7.0	ns	ns	ns	ns	ns	ns	ns		ns	ns
					Plucbea foetida						
C (1)	4.5 ± nd	423 ± nd	128 ± nd	35.0 ± nd	25.0 ± nd	12500 ± nd	1250 ± nd	8750 ± nd		533 ± nd	0.69 ± nd
D (1)	10.5 ± nd	375 ± nd	74 ± nd	58.5 ± nd		12500 ± nd	1500 ± nd	7450 ± nd		790 ± nd	1.29 ± nd
E (4)	4.0 ± 0.9	113 ± 33	53 ± 14	27.9 ± 4.2		10800 ± 2350	1280 ±188	4350 ± 568		732 ± 143	0.91 ± 0.04
Location mean	5.2 ± 1.20	208 ± 64	69 ± 15	34.2 ± 5.7	25 ± nd	11420 ± 1530	1310 ± 125	5600 ± 884		709 ± 97	0.94 ± 0.08
$LSD_{0.05}$	ns	ns	ns	ns	ns	ns	ns	ns		ns	ns
					Mikania scandens						
D (2)	10.8 ± 0.9	723 ± 127	123 ± 24	59.3 ± 15.8		16500 ± 4000	1760 ± 562	3850 ± 700		1030 ± 370	1.27 ± 0.18
					Andropogon glomeratus						
A (2)	10.5 ± 5.0	95.5 ± 5	35 ± 0.7	29.5 ± 3.5		5400 ± 2100	3540 ± 460	11680 ± 4430		673 ± 218	1.53 ± 0.11
					Cynoctonum sessilifolium						
B (1)	10.5 ± nd	4000 ± nd	968 ± nd	46.5 ± nd		21000 ± nd	2200 ± nd	5000 ± nd		53 ± nd	1.23 ± nd
Overall location Mean											
$LSD_{0.01}$	4.9	913	98	7.4	98	5640	394	5510		350	30

*Abbreviations are nd, not determined; LSD, least significant difference between two means which can be detected at a given level of significance (e.g., $LSD_{0.05}$ is at the 0.05 level); and ns, not significant.

†Single-location data also represent overall averages.

spectrographic analysis (Gammon et al., 1953), were used. Rogers et al. (1939) reported average levels of 10 ppm for chromium and nickel in the sandy soils of peninsular Florida. Allison and Gaddum (1940) reported the results of spectrographic analyses on organic soils showing a wide range of heavy element content. Levels of cobalt, lead, and strontium, average 1, 10, and 300 ppm, respectively, for soils in the United States (Vinogradov, 1959). Since most of the heavy elements in soil are related to the parent material from which the soil formed, it would be most interesting to analyze the heavy-metal content of the limestone under these Histosols. Such analyses would indicate whether the heavy metals present are from parent material or are transported in from atmospheric or fluvial sources.

As expected, the muck-burn site had greater concentrations of calcium and magnesium. The soil pH of the muck-burn site was also higher than that of other sites.

Although analyses for radioactive elements were not part of our original study plan, we were interested in the activity level of fallout ^{137}Cs because ^{137}Cs levels in milk from the area of Florida north of Lake Okeechobee are about 10 times the national average (80 to 8 pCi/liter) for the continental United States (Gamble, 1974). Studies indicate that ^{137}Cs is cycling from plants to the organic matter of the soil and back to plants with little loss. Data from pasture studies conducted in the 1960s, when corrected for radioactive decay, show that over 90% of the original ^{137}Cs activity is still present (Gamble, 1974). Highest ^{137}Cs levels in soils are found in the organic fraction of mineral soils (Gamble, 1971).

The range in ^{137}Cs levels for the Histosols in our study, which are 83 to 88% organic matter, was 2300 to 3100 pCi/kg. This corresponds closely to the level of 3200 pCi/kg found in the humus layer of a forest ecosystem (Gamble, 1971). The Entisol in our study (31% organic matter) contained 670 pCi/kg or about three times the level of 205 pCi/kg found in surface horizons of mineral soils containing 3 to 5% organic matter.

Live *C. jamaicense* and *P. hemitomon* contained 820 pCi/kg of ^{137}Cs, but dead *C. jamaicense* contained approximately one-fourth as much, (215 pCi/kg). Levels of ^{40}P were also much lower in the dead *C. jamaicense* than in other plants. These isotopes must be rapidly lost from dead plant tissue. *Sagittaria lancifolia* and *Polygonum* sp. contained much higher ^{137}Cs concentrations (2900 and 11,600 pCi/kg, respectively). Since these ^{137}Cs concentrations are the first reported for plants from the Everglade ecosystem, interpretations of results were not attempted.

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TABLE 3

ELEMENTAL CONCENTRATION (MEAN ± SD) OF SOILS FROM SAMPLING SITES

	Location				
	Burned saw-grass plot		Unburned saw-grass plot		Muck-burn plot
Element	A	B	C	D	E
N, %	3.29 ± 0.05	2.70 ± nd*	3.02 ± 0.01	1.16 ± 0.14	2.96 ± 0.08
Ca, %	30310 ± 598	31030 ± 394	34180 ± 1270	16800 ± 1370	47240 ± 1250
Mg, %	1400 ± 24	1080 ± 18	1420 ± 44	624 ± 46	1850 ± 36
K, %	368 ± 13	344 ± 18	327 ± 8	242 ± 16	349 ± 14
P, %	585 ± 8.4	463 ± 13	548 ± 15	374 ± 24	752 ± 25
Cu, %	10.1 ± 1.9	6.3 ± 0.4	5.5 ± 0.2	3.5 ±0.3	7.5 ± 0.3
Fe, %	6780 ± 90	9940 ± 975	5500 ± 276	7520 ±589	7790 ± 263
Mn, %	297 ± 21	147 ± 25	218 ± 5	97 ± 12	241 ± 10
Zn, %	12.4 ± 0.6	9.3 ± 0.9	12.4 ± 0.5	10.2 ± 2.3	12.7 ± 0.5
Na, %	428 ± 14	442 ± 29	322 ± 16	209 ± 19	584 ± 18
Al, ppm	2220 ± 169	6150 ± 204	2720 ± 270	4870 ± 410	2530 ± 105
Co, ppm	4.8 ± 0.1	5.5 ± 0.3	4.3 ± 0.1	2.9 ± 0.2	5.5 ± 0.2
Cr, ppm	4.6 ± 0.3	8.8 ± 0.3	5.0 ± 0.3	8.7 ± 0.6	5.0 ± 0.2
Ni, ppm	6.8 ± 0.1	9.1 ± 0.3	7.1 ± 0.3	6.3 ± 0.5	9.1 ± 0.2
Pb, ppm	27.5 ± 0.6	17.9 ± 0.7	21.1 ± 0.4	15.6 ± 1.2	25.3 ± 0.5
Sr, ppm	210 ± 4	114 ± 0.3	219 ± 8	55 ± 4.5	300 ± 1
Ash, %	11.9 ± 0.4	17.2 ± 0.6	13.2 ± 0.7	69.2 ± 3.3	14.0 ± 0.4
pH, moles/liter (1:2 soil–water)	6.7	6.2	6.2	6.2	7.0

*Abbreviation nd is not determined.

REFERENCES

Alexander, T. R., 1971, Sawgrass Biology Related to the Future of the Everglades Ecosystem, *Soil Crop Sci. Soc. Fla., Proc.*, **31**: 72-74.

Allison, R. V., and L. W. Gaddum, 1940, The Trace Element Content of Some Important Soils—A Comparison, *Soil Sci. Soc. Fla., Proc.*, **7**: 68-91.

Boyd, C. E., 1970, Chemical Analyses of Some Vascular Aquatic Plants, *Arch. Hydrobiol.*, 67(1): 78-85.

Davis, J. H., 1946, The Peat Deposits of Florida, Tallahassee Geological Bulletin No. 30, Florida Geological Survey, Tallahassee.

——, 1943, The Natural Features of Southern Florida, Geological Bulletin, No. 25, Florida Geological Survey, Tallahassee.

Forsee, W. T., 1940, Recent Plant Responses to Some of the Micro Elements on Everglades Peat, *Soil Sci. Soc. Fla., Proc.*, **7**: 53-58.

Hable, J. F., 1974, Botany Department, University of Florida, Gainesville, personal communication.

——, 1971, A Proposed Mechanism for the Recycling of Radiocesium in Florida Soil Plant Systems, in *Radionuclides in Ecosystems*, Proceedings of the Third National Symposium on Radioecology, D. J. Nelson (Ed.), USAEC Report CONF-710501-P1, pp. 133-139.

Gammon, N., Jr., J. R. Henderson, R. A. Carrigan, R. E. Caldwell, R. G. Leighty, and F. B. Smith, 1953, Physical, Spectrographic, and Chemical Analyses of Some Virgin Florida Soils, Agricultural Experiment Station Bulletin 524, University of Florida, Gainesville.

Jones, L. A. (Ed.), 1948, Soils, Geology, and Water Control in the Everglades Region, Agricultural Experiment Station Bulletin 442, University of Florida, Gainesville.

Long, R. W., and O. Lakela, 1971, *A Flora of Tropical Florida*, University of Miami Press, Coral Gables, Fla.

Loveless, C. M., 1959a, The Everglades Deer Herd Life History and Management, Technical Bulletin No. 6, Florida Game and Fresh Water Fish Commission, Tallahassee.

——, 1959b, A Study of the Vegetation in the Florida Everglades, *Ecology*, **40**(1): 1-9.

——, 1957, Clipping Study Techniques in Marsh Ecology Investigations, *Proc., Southeast. Assoc. Game Fish Comm.*, **11**: 119-124.

Lugo, A. E., S. C. Snedaker, S. Bayley, and H. T. Odum, 1971, Models for Planning and Research for the South Florida Environmental Study, Center for Aquatic Sciences, University of Florida, Gainesville.

Rogers, L. H., O. E. Gall, L. W. Gaddum, and R. M. Barnette, 1939, Distribution of Macro- and Micro-Elements in Some Soils of Peninsular Florida, Agricultural Experiment Station Bulletin 341, University of Florida, Gainesville.

Schemnitz, S. D., and J. L. Schortemeyer, 1973, The Impact of Half-Tracks and Airboats on the Florida Everglades Environment, in Proceedings of the Snowmobile and Off-the-Road Vehicle Symposium, Technical Report No. 9, pp. 86-117, Michigan State University, East Lansing.

——, 1972, The Influence of Vehicles on Florida Everglades Vegetation—A Preliminary Report, Florida Game and Fresh Water Fish Commission, July.

Steward, K. K., 1973, Agricultural Research Center, University of Florida, Fort Lauderdale, personal communication.

Vinogradov, A. P., 1959, *The Geochemistry of Rare and Dispersed Chemical Elements in Soils*, 2nd ed., translated from Russian, Consultants Bureau Enterprises, Inc., New York.

Volk, B. G., 1973, Everglades Histosol Subsidence. 1. CO_2 Evolution as Affected by Soil Type, Temperature, and Moisture, *Soil Crop Sci. Soc. Fla., Proc.*, **32**: 132-135.

EFFECTS OF CLEAR-CUTTING ON NUTRIENT LOSSES IN ASPEN FORESTS ON THREE SOIL TYPES IN MICHIGAN

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ABSTRACT

The effects of clear-cutting on NO_3^-, NH_4^+, PO_4^{3-}, K^+, Ca^{2+}, Na^+, Fe^{2+}, and Mg^{2+} losses were evaluated in three 60-year-old aspen stands in northern lower Michigan. Paired 0.5-ha sites (control and clear-cut) located on good, intermediate, and poor soils were compared for soil-nutrient leaching during the 1973 growing season. Preliminary analyses indicate that soil-nutrient leachate concentrations (NO_3^-, NH_4^+, PO_4^{3-}, K^+, Ca^{2+}, Na^+, Fe^{2+}, and Mg^{2+}) were not significantly higher ($P < 0.05$) on clear-cut plots than on paired control plots during the first growing season. Nitrate–nitrogen and ammonium–nitrogen leachate values were significantly less than seasonal precipitation input. Leachate concentrations reached maximum levels following spring thaw and then fluctuated through the growing season. Highest nutrient losses were generally found on the good soils, followed by the intermediate and then the poor soils. Groundwater accretion was estimated to be 12 cm per year higher on clear-cut plots. A preliminary nutrient budget was calculated from determinations of input (concentration x volume of precipitation) and output (leachate concentration x volume of groundwater flux). In the first-year data for carefully controlled clear-cuts, little evidence of increased nutrient losses was found for NO_3–N, NH_4–N, PO_4, Mg^{2+}, Na^+, K^+, and Fe^{2+} as a consequence of clear-cutting. Additional losses (leachate in excess of control losses) of Ca^{2+} and Mg^{2+} due to clear-cutting exceeded precipitation inputs only on the good soil. A definitive answer on nutrient losses cannot be determined until a complete nutrient and hydrologic budget is calculated over several seasons.

Quaking and bigtooth aspens (*Populus tremuloides* Michx. and *P. grandidentata* Michx., respectively) are among the dominant forest species in the Great Lake states of Michigan, Minnesota, and Wisconsin. Once considered a weed tree, aspen now contributes more than 45% (2 million cords) of the annual lake state pulpwood harvest (Leuschner, 1972). The aspen forests of the Great Lakes region today originated as sprout stands after the early logging and subsequent uncontrolled fires between 1870 and 1920 (Graham, Harrison, and Westel,

1963). Younger stands have been established over the past several decades by the practice of clear-cutting the older (50- to 80-year-old) aspen forests.

Increased clear-cutting of aspen because of pressures from the pulpwood industry and game management practices have made it essential to evaluate the consequences to soil and water regimes in the Great Lakes region in terms of both mineral cycling and productivity. This is especially true since the clear-cutting of forests has been brought under strong criticism (Connaughton, 1970; Davis, 1971). Economic and silvicultural motives are being reevaluated in consideration of possible aesthetic and environmental degradations resulting from the clear-cutting of forests. Much of the current criticism is a consequ of a study of vegetation removal in New Hampshire, in which it was found soil-nutrient losses were alarmingly accelerated from a watershed denuded of a northern hardwood forest (Likens et al., 1970).

Significant increases in erosion, runoff, nitrification, decomposition rates, and stream concentrations of cation and nitrate–nitrogen were also reported by Bormann et al. (1968) and Likens et al. (1967). In the New Hampshire study, cation losses can probably be attributed to a series of events resulting from deforestation on steep slopes and vegetation suppression with herbicidal treatments. We should note that this is an unrealistic treatment combination to use in evaluating the effects of commercial clear-cutting.

Functionally, a natural forest recycles nitrogen. Nitrogen uptake ceases with vegetation removal, and ammonium becomes available for production of nitrates. This process releases a large amount of hydrogen ions that in turn accelerate cation exchange with soil colloids; thus both cations and nitrates can be leached from the ecosystem by percolating rainwaters.

It is theorized that nutrient uptake will not be reduced significantly under clear-cut aspen because of rapid revegetation by aspen root sprouts. The mature root systems of harvested aspen trees remain alive and fully occupy the soil after clear-cutting. Within one year the site may support an aspen sprout stand that numbers 10,000 stems per acre and in two years up to nearly 28,000 stems per acre (Garrett and Zahner, 1964). This rapid development of shoots should permit absorption and recycling of nutrients from the soil solution and prevent their loss from the site. There are no scientific data to substantiate this, however, and there are no published studies of nutrient cycling in aspen-forest ecosystems. The purpose of this paper is to evaluate the first-year effects of clear-cutting on soil leaching in aspen forests on three soil types.

RESEARCH SITE AND METHODS

The effects of clear-cutting of aspen were studied at three sites on the forest land of the University of Michigan Biological Station near Pellston, Mich. (latitude 45°34′N). The three well-drained upland sandy soil sites chosen were considered representative of the moraine and glacial outwash typical of millions

of acres of aspen forests in the northern Great Lakes region. The soils of the research site were labeled good, intermediate, and poor on the basis of aspen production and are typical of areas where mature aspen stands (50 to 80 years old) have developed after logging and repeated fires. Two homogeneous study areas of approximately 1 ha each were located on each of the three soils. Homogeneity in terms of forest-species composition was determined by sampling all trees 5.00 cm (2.0 in.) and greater in diameter at breast height (dbh). Understory and ground cover were analyzed in 20 randomly placed 9- and 0.25-m^2 plots, respectively. Slopes on all sites range from 0 to 6%.

In the fall of 1972, paired 0.5-ha subplots established inside each 1-ha study area were utilized for treatment comparisons. One of the plots on each site was commercially clear-cut, and the slash material was left. The other site remained undisturbed as a control. A 25-m buffer strip separated the control from the clear-cut areas. The nutrient inputs and outputs of the control and clear-cut subplots were monitored in terms of bulk precipitation and soil leachate.

Precipitation (ppt) was measured with a network of six gages. Samples were collected immediately after rainfall and returned to the laboratory for chemical analysis. All analyses follow standard procedures (Environmental Protection Agency, 1971; Perkin–Elmer Corp., 1973).

Soil leachate from each of the sites was recovered with a series of pressure-vacuum lysimeters. The samplers consist of a one-bar entry value, porous, ceramic cup with a 1-μ size pore. The design and development of the lysimeter is described by Wagner (1962) and Parizek and Lane (1970). The control and clear-cut plots contain 20 and 30 lysimeters, respectively. Samplers were placed in pairs along five equidistant grid lines to uniformly divide the plots. Each lysimeter was placed in the upper portion of the C horizon (~90 cm deep). The lysimeters were installed at a 60° angle so that the porous ceramic tip would be positioned under an undisturbed profile.

Leachate was collected as soon as winter snow melt allowed. Samples were taken at monthly intervals or when sufficient leachate was available. All samples were frozen within 2 hr after collection, stored, and analyzed within 2 months. Cation analyses (Ca^{2+}, Mg^{2+}, K^{+}, and Na^{+}) were completed following standard procedures for atomic absorption spectrophotometry (Perkin–Elmer Corp., 1973). A Technicon Auto-Analyzer was used to analyze for NO_3, NH_3, PO_4, and Fe. Nitrate was analyzed for by the Greis–Ilsovay reaction and is reported as NO_3–N (Environmental Protection Agency, 1971). The Berphelot reaction was used to analyze for NH_4–N (Environmental Protection Agency, 1971). After manual digestion phosphorous was analyzed by the molybdate reaction and iron by the persulfate oxidation technique (Environmental Protection Agency, 1971).

A three-way layout was used to analyze the effects of time, site, and treatment on nutrient concentrations of soil leachate. All leachate values given are means of at least 15 replicates per treatment plot. Statistical analyses follow Sokal and Rohlf (1969).

RESULTS AND DISCUSSION

These results must be considered preliminary for two reasons. First, data from a single growing season are suggestive but not conclusive. Second, complete analysis of the effects of clear-cutting on the aspen ecosystem must await completion of total input–output nutrient and hydrological budgets for the system.

Site Description

Populus grandidentata Michx. is the dominant tree species on the treated sites, with a percent basal-area coverage ranging from a high of 88.8% on the good clear-cut site to a low of 51.6% on the poor control site (Table 1). The biotic homogeneity (species composition, basal area, number of stems per hectare, etc.) between each control and clear-cut site shows little variation (Table 1). The index of similarity (Phillips, 1959) between the control and clear-cut plots on the good, intermediate, and poor soils is 83, 80, and 93%, respectively.

The large differences in site quality indicated by Table 1 are further defined by a comparison of the physical characteristics of the soil at each site (Table 2). The good (Menominee) and intermediate (Emmet) site soils are distinguished by a thin clay lens in the upper portion of the C horizon. This substantially increases the water-holding capacity of the good and intermediate soils as compared with that of the poor soil. The poor soil (Rubicon sand) is a minimal podzol of relatively poor productivity (Table 1) and low water-holding capacity.

Chemical analyses also reveal significant differences in soil fertility between sites. Total nitrogen in the A horizon ranges from a high of 890 ppm in the good soil to a low of 230 ppm in the poor soil. Soil pH in the A horizon is 5.6, 5.4, and 5.2 on the good, intermediate, and poor soils, respectively.

Precipitation and Chemistry

Precipitation during the 1973 growing season (March to September) was 51.7 cm. The seasonal rainfall total of 82.9 cm was 3.5 cm greater than the 27-year average. Chemical analysis of rainfall includes dryfall contributions. The mean annual concentrations of cations were 0.97, 0.25, 0.14, and 0.44 ppm for Ca^{2+}, K^{+}, Mg^{2+}, and Na^{+}, respectively. Concentrations of NH_4–N ranged from 0.03 to 1.5 ppm, with a mean value of 0.49 ppm. The concentration of NO_3–N in precipitation ranged from 0.002 and 0.7 ppm, with most values being between 0.2 and 0.5 ppm. Phosphorous (PO_4–P) values averaged 0.02 ppm. Nutrient values for all chemicals appear to be near average nutrient concentrations reported in the literature (Likens et al., 1967; Pearson and Fisher, 1971; Pecor et al., 1973). Preliminary analyses indicate that precipitation chemistry is quite variable from month to month, however, and several years of values will be required to determine temporal trends.

TABLE 1

STAND COMPOSITION AND STRUCTURE* OF THREE 60-YEAR-OLD ASPEN STANDS ON GOOD, INTERMEDIATE, AND POOR SOILS AT THE UNIVERSITY OF MICHIGAN, BIOLOGICAL STATION, PELLSTON, MICH.

Treatment and species	Basal area, m^2/ha	Basal area, %	Stems per hectare	Stem number, %	Average height of aspen clones, m	S.D.
Good Soil						
Control						
Populus grandidentata	26.83	79.8	634	48.7	25.98	±2.2
Fagus grandifolia	3.78	11.2	460	35.4		
Acer rubrum	2.37	7.0	140	10.8		
Acer pensylvanicum	0.46	1.4	40	3.1		
Acer saccharum	0.15	0.5	20	1.5		
Prunus serotina	0.02	0.1	7	0.5		
Total	33.61	100.0	1301	100.0		
Clear-cut						
Populus grandidentata	28.49	88.8	720	62.1	25.91	±2.3
Acer saccharum	1.51	4.7	120	10.4		
Acer rubrum	1.12	3.5	107	9.2		
Acer pensylvanicum	0.82	2.6	173	14.9		
Fagus grandifolia	0.09	0.3	27	2.3		
Amelanchier sp.	0.04	0.1	13	1.1		
Total	32.07	100.0	1160	100.0		
Intermediate Soil						
Control						
Populus grandidentata	24.93	77.8	1207	67.3	20.65	±1.7
Acer rubrum	5.89	18.4	514	28.6		
Betula papyrifera	1.02	3.2	47	2.6		
Populus tremuloides	0.16	0.5	20	1.1		
Acer saccharum	0.01	0.1	7	0.4		
Total	32.01	100.0	1795	100.0		
Clear-cut						
Populus grandidentata	23.89	84.8	894	66.7	20.80	±2.5
[illegible]er rubrum	2.56	9.1	233	17.4		
[illegible]ulus tremuloides	1.68	5.9	193	14.4		
Betula papyrifera	0.04	0.1	13	1.0		
Quercus rubra	0.02	0.1	7	0.5		
Total	28.19	100.0	1340	100.0		
Poor Soil						
Control						
Populus grandidentata	10.99	51.6	660	45.0	15.01	±0.6
Quercus rubra	7.02	33.0	334	22.7		
Acer rubrum	1.96	9.2	314	21.4		

TABLE 1 (continued)

Treatment and species	Basal area, m^2/ha	Basal area, %	Stems per hectare	Stem number, %	Average height of aspen clones, m	S.D.
Betula papyrifera	0.80	3.8	100	6.8		
Pinus Strobus	0.48	2.2	47	3.2		
Pinus resinosa	0.03	0.1	7	0.5		
Fagus grandifolia	0.02	0.1	6	0.4		
Total	21.30	100.0	1468	100.0		
Clear-cut						
Populus grandidentata	10.88	57.5	747	57.2	14.17	2.5
Quercus rubra	5.98	31.6	247	18.9		
Acer rubrum	1.42	7.5	220	16.8		
Betula papyrifera	0.47	2.5	53	4.1		
Pinus Strobus	0.08	0.4	7	0.5		
Pinus resinosa	0.04	0.2	13	1.0		
Fagus grandifolia	0.04	0.2	13	1.0		
Populus tremuloides	0.02	0.1	7	0.5		
Total	18.93	100.0	1307	100.0		

*Only trees 5.0 cm dbh and greater are included here.

TABLE 2

PHYSICAL SOIL ANALYSES OF GOOD, INTERMEDIATE, AND POOR ASPEN SITES IN NORTHERN LOWER MICHIGAN

Horizon	Sand, %	Silt and clay, %	Depth, cm	Bulk density	Soil and series type	Physiography
			Good Soil			
A1	99.1	1.1	0–7	0.88	Menominee	Well-drained
A2	95.8	4.1	7–20	1.37	loamy sand	moraine
B	98.0	2.0	20–78	1.34		
C	85.0	15.0	78+	1.77		
			Intermediate Soil			
A1	96.9	3.1	0–5	0.62	Emmet	Well-drained
A2	94.8	5.2	5–20	1.47	loamy sand	outwash over
B	98.4	1.6	20–88	1.44		till
C	84.0	16.0	88+	1.83		
			Poor Soil			
A1	98.4	1.6	0–3	0.80	Rubicon	Well-drained
A2	98.2	1.8	3–10	1.51	sand	outwash
B	99.7	0.3	10–80	1.58		
C	99.8	0.2	80+	1.71		

Soil-Leachate Analysis

The mean concentrations of Ca^{2+}, Mg^{2+}, K^{+}, and Fe^{2+} in soil leachate for each site (control and clear-cut) during the 1973 growing season are given in Table 3. Considerable variation in leachate values among both treatment and control samplers at each site was found. A minimum of 15 and 20 individual replicate samplers were used per site during each month on the control and clear-cut plots, respectively. An analysis of variance showed no significant difference ($P < 0.05$) between the control and clear-cut plots for all nutrient-ate values. A statistically significant ($P < 0.05$) difference for month and site was found for all cations except sodium.

On the average, for the good and intermediate soils, the concentration of calcium leachate was 3 and 1.5 times as great, respectively, as that for the poor soil (Table 3). Iron leachate concentration was approximately 30% higher in the good soil than in the intermediate and poor soils (Table 3). The poor and intermediate soil leachate concentrations were only 25% of the Mg^{2+} leachate from the good soil (Table 3). Clear-cutting had no significant effect on phosphate leaching, but significant ($P < 0.05$) seasonal trends were found for PO_4–P (Fig. 1a).

Seasonal trends for leachate vary with each nutrient. Two general peaks in leachate concentration were noted in the April and July-to-August sampling periods. The first reflected spring thaw, and the second may be accounted for by the above average rainfall in July [Fig. 1 (a, b, and d) and Table 3].

In general, leachate concentrations did not closely follow precipitation patterns. This may be because lysimeters were not sampled after each rainfall; thus the leachate is a composite of several precipitation periods. It has also been reported that variation due to individual sampler intake rates, time between sampling periods, and microbial activity can modify leachate values considerably (Urie, 1974). To reduce variation in future seasons, we will sample a minimum of 20 lysimeters as soon as possible after each major rainfall.

Average monthly concentration values for NO_3–N, NH_4–N, and Na in control and clear-cut leachate on the good, intermediate, and poor soils is given in Fig. 1 (b, c, and d, respectively). Significant differences ($P < 0.05$) between sites were found for NO_3–N and K, Mg, Ca, and Fe. Seasonal differences were ...icant ($P < 0.05$) for all soil leachate ions except NO_3–N (Fig. 1 and ... 3).

Likens, Bormann, and Johnson (1969) have reported that nitrifier populations increase after clear-cutting. Our preliminary analysis of microbial populations in the litter indicate an increase from the poor to the good soil but show little difference between clear-cuts and controls. Further analysis on all sites will be required to substantiate the findings of Likens, Bormann, and Johnson.

Ammonium–nitrogen concentrations do not vary significantly among sites [Fig. 1(c)], but significant concentration differences ($P < 0.05$) are found among months [Fig. 1(c)]. During a few months on the good and intermediate

TABLE 3

MEAN* MONTHLY CONCENTRATIONS OF FOUR CATIONS IN SOIL LEACHATE FROM CONTROL AND CLEAR-CUT ASPEN PLOTS ON GOOD, INTERMEDIATE, AND POOR SOILS IN NORTHERN LOWER MICHIGAN

Site and treatment	March		April		May		June		July–August	
	$\bar{X}$	S.E.†	$\bar{X}$	S.E.†	$\bar{X}$	S.E.†	$\bar{X}$	S.E.†	$\bar{X}$	S.E.†
Calcium, ppm										
Good										
Control	6.62	0.50	10.42	9.23	9.17	1.76	9.93	1.97	13.56	2.72
Clear-cut	13.70	2.58	13.02	1.75	12.49	2.35	13.63	2.37	13.41	[illegible]
Intermediate										
Control	6.35	0.44	10.69	1.44	6.21	1.13	6.67	1.06	9.19	0.77
Clear-cut	5.99	0.53	9.27	0.77	6.37	1.13	5.62	0.97	6.94	0.80
Poor										
Control	6.06	0.59	6.65	0.53	3.45	0.41	3.35	0.47	5.21	0.50
Clear-cut	5.86	0.30	6.17	0.39	3.39	0.36	2.04	0.32	3.45	0.34
Magnesium, ppm										
Good										
Control	2.26	0.25	3.54	0.70	3.25	0.76	4.66	1.24	7.84	2.98
Clear-cut	5.65	1.64	3.83	0.58	4.72	1.11	4.23	1.03	7.44	2.21
Intermediate										
Control	1.31	0.09	2.43	0.41	1.58	0.31	2.03	0.26	2.09	0.30
Clear-cut	1.10	0.13	1.80	0.11	1.16	0.16	1.36	0.14	1.09	0.16
Poor										
Control	1.15	0.07	1.38	0.08	0.89	0.08	0.95	0.08	1.01	0.09
Clear-cut	1.14	0.07	1.42	0.06	0.85	0.06	1.05	0.06	0.61	0.07
Potassium, ppm										
Good										
Control	1.32	0.18	1.44	0.24	1.24	0.16	1.48	0.19	1.74	0.26
Clear-cut	1.78	0.21	3.83	0.45	1.57	0.19	1.85	0.31	2.09	0.28
Intermediate										
Control	1.57	0.11	2.44	0.28	1.72	0.20	1.91	0.17	2.23	0.14
Clear-cut	1.79	0.22	2.89	0.14	2.00	0.24	2.24	0.24	2.26	0.23
Poor										
Control	1.67	0.26	1.67	0.15	1.35	0.11	1.19	0.09	1.35	0.11
Clear-cut	1.40	0.10	2.00	0.10	1.20	0.13	1.09	0.10	0.94	0.08
Iron, ppb										
Good										
Control	59.68	4.70	63.41	6.12	96.84	15.23	47.09	9.86	69.76	[illegible]
Clear-cut	63.73	7.20	63.32	8.33	83.17	10.37	59.73	5.05	63.38	4.97
Intermediate										
Control	60.14	9.18	56.63	4.97	86.14	17.19	27.48	2.80	41.80	4.33
Clear-cut	56.41	5.10	57.73	6.44	67.62	9.49	37.48	2.91	51.96	5.70
Poor										
Control	53.69	8.52	50.38	4.54	93.89	8.78	29.38	3.45	39.09	2.78
Clear-cut	55.07	4.60	47.15	3.83	64.94	6.21	26.30	3.14	44.47	3.32

*A minimum of 15 replicates were used in each calculation.

†One standard error of the mean.

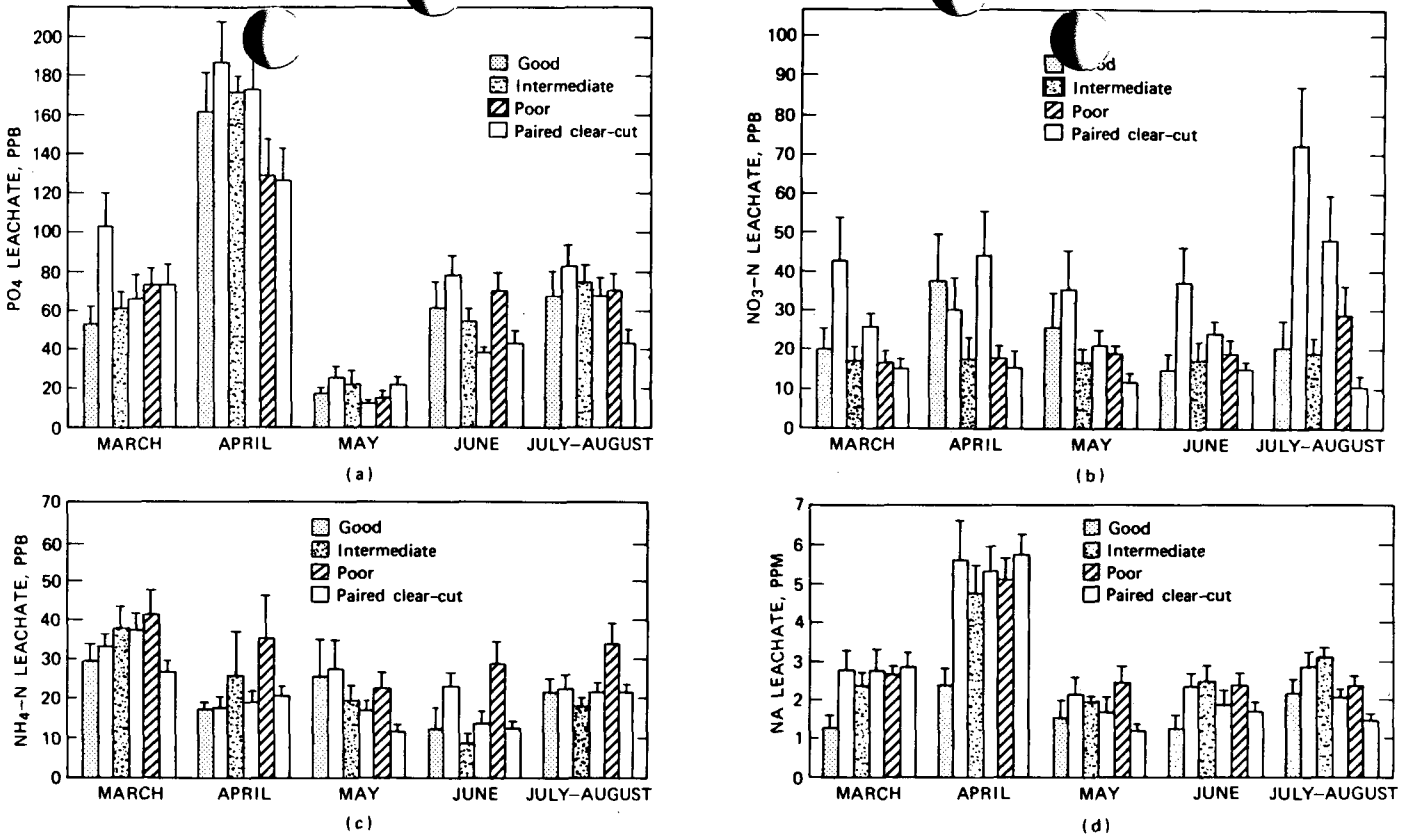

Fig. 1 Average monthly soil leachate concentrations for (a) PO_4, (b) NO_3–N, (c) NH_4–N, and (d) Na^+ in aspen plots on good, intermediate, and poor soils in northern lower Michigan. The error bars indicate one standard error of the mean.

soils and in all months on the poor soil, the control plots released a more concentrated NH_4—N leachate than the clear-cut plots. Biological activity and the amount of organic matter present play important roles here. The amounts of carbon in the A horizon of the poor control and poor clear-cut plots are 0.41 and 0.24%, respectively. Nitrogen (Kjeldahl) values average 230 ppm on both sites. The lower carbon-to-nitrogen ratio for the poor clear-cut area may be indicative of reduced ammonification and the resulting decrease in NH_4—N leachate concentration.

Preliminary Water and Nutrient Budget

Although few clear-cutting effects have been shown in terms of nutrient concentration losses, it is possible to fully estimate nutrient-enrichment effects or net losses in the ecosystem only when some indication of accompanying water fluxes are given.

Annual potential evapotranspiration was calculated to be 55.5 cm (Thornthwaite and Mather, 1957). Hendrickson and Doonan (1972) estimated evapotranspiration for the area to be 45.7 cm by subtracting the average annual runoff from the average annual precipitation. Since aspen stands reach their best development on sandy soils with high infiltration capacity, it is doubtful if any nutrients are added directly to streams via surface runoff.

Thus estimates of groundwater accretion range from a low of 27.5 to a high of 37.2 cm per year on the control plots. The higher accretion value (37.2 cm) was used in this study to calculate maximum potential losses of nutrients via groundwater leaching on control plots (ppt − evapotranspiration = groundwater accretion: 82.9 − 45.7 = 37.2 cm).

Evapotranspiration in aspen stands is estimated to be reduced 27% by the effects of clear-cutting (Johnston, 1970). Thus clear-cutting is estimated to result in an annual increase in groundwater yield of 12.3 cm. This estimate is close to the 10-cm values reported by Urie (1971) in a study estimating groundwater yield after strip cutting of pine on sandy soils in northern lower Michigan. The clear-cut plots are, thus, estimated to yield a maximum of 49.5 cm of water to groundwater during the first year after clear-cutting.

Table 4 summarizes available data on inputs, outputs, and treatment effects on the three aspen stands. The calculated losses on the clear-cut plots are generally considered to overestimate nutrient losses since increases in evapotranspiration due to aspen sucker regrowth was not included in this budget. Net losses from the system would also decrease if some estimate of nutrient addition via geologic weathering were included.

Nitrogen inputs in precipitation greatly exceed leachate losses on all sites. This, coupled with the extremely low but similar levels of NO_3—N and NH_4—N leachate on both the control and clear-cut sites, indicates little or no effect of clear-cutting on nitrogen losses. This finding is in contrast to the high nitrogen losses reported by both Bormann et al. (1968) in their study of clear-cut and

TABLE 4

PRELIMINARY NUTRIENT BUDGET COMPARING THE CONTROL AND CLEAR-CUT ASPEN PLOTS ON GOOD, INTERMEDIATE, AND POOR SOILS IN NORTHERN LOWER MICHIGAN*

Constituent (major form)	Input from precipitation	Output by good control plot	Output by good clear-cut plot	Δ,† kg/ha	Output by intermediate control plot	Output by intermediate clear-cut plot	Δ,† kg/ha	Output by poor control plot	Output by poor clear-cut plot	Δ,† kg/ha
NO_3–N	2.1	0.3	0.2	‡	0.1	0.2	0.1	0.1	0.1	0.0
NH_4–N	4.1	0.1	0.1	0.0	0.2	0.2	0.0	0.1	0.1	0.0
PO_4–P	0.2	0.3	0.5	0.2	0.3	0.4	0.1	0.3	0.3	0.0
Ca	8.3	38.8	65.2	26.4	28.6	36.2	7.6	19.4	19.8	0.4
Mg	1.7	17.7	26.6	8.9	7.0	6.6	‡	3.9	4.9	1.0
Na	3.3	6.7	15.3	8.6	10.6	14.2	3.6	11.2	12.0	0.8
K	2.5	7.6	9.6	2.0	7.4	11.2	3.8	5.3	7.6	2.3
Fe	§	0.3	0.4	‡	0.2	0.4	0.2	0.2	0.2	0.0

*The budget was calculated from determinations of input (nutrient concentrations x volume of precipitation) and output (nutrient concentrations x volume of groundwater accretion).

†Control losses minus clear-cut losses. Losses are based on a yearly maximum groundwater accretion of 37.2 and 49.5 cm for the control and clear-cut plots, respectively.

‡Clear-cut losses are less than control.

§Samples were not analyzed for this constituent.

herbicide treatment and Reinhart (1973) in his clear-cut study in New Hampshire.

The effects of clear-cutting on PO_4—P losses appear minimal since first-year leachate values are low and the additional losses (Δ = control losses − clear-cut losses, in kilograms per hectare) caused by clear-cutting did not exceed inputs (Table 4).

Significant losses as a result of clear-cutting were not found for potassium or iron. Only at the clear-cut site on good soil did additional (Δ = 8.6 kg/ha) sodium leachate losses greatly exceed ppt input (Table 4). This increase in leachate may be due to the higher levels of slash material left at this site. The importance of net losses of sodium from the site is reduced when the estimate of Johnson et al. (1967) for sodium inputs (4.6 ± 0.4 kg/ha) via chemical weathering for midlatitude glaciated regions is added to the ppt inputs for the system.

Calcium and magnesium losses on the control and clear-cut sites on good soil and calcium losses on control and clear-cut sites on intermediate soil exceed the range of losses reported by Cole and Gessel (1965), Likens et al. (1967), and Weetman and Webber (1972) for perturbated forest ecosystems. However, calcium losses from our system are within the range of values reported by Reinhart (1973). He calculated calcium losses to be 90 kg/ha (41 kg/ha for year 1 and 48 kg/ha for year 2) over a two-year period after the clear-cutting of a New Hampshire forest. The significance of calcium discharge from the New England clear-cut seems minimal since Reinhart (1973) estimated that calcium losses amounted to only 4% of the nutrient capital (organic matter and soil) available in the ecosystem.

The percent loss of nutrient capital of calcium and other cations from the aspen system may be very low also. A final evaluation of the importance of net cationic losses resulting from clear-cutting in the aspen forest will be possible only when a complete nutrient and hydrologic budget is completed through several seasons after sucker regrowth.

The implication of our first-year data is that, under carefully controlled clear-cuts on the three glacial soil types of our study areas, little evidence of increased nutrient loss was found for NO_3—N, NH_4—N, PO_4, K^+, Na^+, and Fe^{2+} as a consequence of clear-cutting. Additional leachate losses (above control values) of Ca^{2+} and Mg^{2+} due to clear-cutting exceeded ppt inputs only on the good soil. This seems to support the hypothesis of Marks and Bormann (1972) that dense stands of fast-growing successional species will regulate ecosystem function soon after perturbation.

Extrapolation from these data is valid only on the condition that aspen regrowth be allowed to develop naturally after clear-cutting. These data also do not address the practices of whole-tree harvesting, clear-cutting followed by burning, the optimum clear-cut size, or the rotation periods necessary to maintain a viable forest ecosystem on sandy soils in the Great Lake states. The

important issue of evaluating clear-cutting in the aspen forest obviously deserves more basic research.

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REFERENCES

Bormann, F. H., G. E. Likens, D. W. Fisher, and R. S. Pierce, 1968, Nutrient Loss Accelerated by Clearcutting of a Forest Ecosystem, *Science*, **159**: 882-884.

Cole, D. W., and S. P. Gessel, 1965, Movements of Elements Through a Forest Soil as Influenced by Tree Removal and Fertilizer Additions, in *Forest-Soil Relationships in North America*, Proceedings of the Second North American Forest Soils Conference, pp. 95-104, C. T. Youngberg (Ed.), Oregon State University Press, Corvallis.

Connaughton, C. A., 1970, The Revolt Against Clearcutting, *J. Forest.*, **68**: 264-265.

Davis, K. P., 1971, Hearings on Clearcutting, *J. Forest.*, **69**: 339-342.

Environmental Protection Agency, 1971, *Methods for Chemical Analysis of Water and Wastes*, National Environmental Research Center Publication 16020: 07-71, Cincinnati, Ohio.

Garrett, P. W., and R. Zahner, 1964, Clonal Variation in Suckering of Aspen Obscures Effect of Various Clearcutting Treatments, *J. Forest.*, **62**: 749-750.

Graham, S. A., R. P. Harrison, and C. E. Westel, 1963, *Aspens: Phoenix Trees of the Great Lakes Region*, The University of Michigan Press, Ann Arbor.

Hrickson, G. E., and C. J. Doonan, 1972, *Hydrology and Recreation on the Cold-Water Rivers of Michigan's Southern Peninsula*, Water Information Series Report No. 3, U. S. Geological Survey.

Johnson, N. M., G. E. Likens, F. H. Bormann, and R. S. Pierce, 1967, Rate of Chemical Weathering of Silicate Minerals in New Hampshire, *Geochim. Cosmochim. Acta.*, **32**: 531-545.

Johnston, R. S., 1970, Evapotranspiration from Bare, Herbaceous, and Aspen Plots: A Check on a Former Study, *Water Resour. Res.*, **7**(6): 324-327.

Leuschner, W. A., 1972, *Projecting the Aspen Resource in the Lake States*, Research Paper NC-81, North Central Forest Experiment Station, Forest Service, U. S. Department of Agriculture.

Likens, G. E., F. H. Bormann, and N. M. Johnson, 1969, Nitrification: Importance to Nutrient Losses from a Cutover Forested Ecosystem, *Science*, **163**: 1205-1206.

——, F. H. Bormann, N. M. Johnson, D. W. Fisher, and R. S. Pierce, 1970, The Effects of Forest Clearcutting and Herbicide Treatment on Nutrient Budgets in the Hubbard Brook Watershed Ecosystem, *Ecol. Monogr.*, **40**(1): 23-47.

——, F. H. Bormann, N. M. Johnson, and R. S. Pierce, 1967, The Calcium, Magnesium, Potassium and Sodium Budgets for a Small Forested Ecosystem, *Ecology*, **48**: 772-785.

Marks, P. L., and F. H. Bormann, 1972, Revegetation Following Forest Cutting: Mechanisms for Return to Steady-State Nutrient Cycling, *Science*, **176**: 914-915.

Parizek, R. R., and B. E. Lane, 1970, Soil-Water Sampling Using Pan and Deep Pressure-Vacuum Lysimeters, *J. Hydrol.*, **11**: 1-21.

Pearson, F. J., and D. W. Fisher, 1971, Chemical Composition of Atmospheric Precipit[illegible] in the Northeastern United States, Water-Supply Paper No. 1535-P, U. S. Geolo[illegible] Survey.

Pecor, C. H., J. R. Novy, K. E. Childs, and R. A. Powers, 1973, Houghton Lake Annual Nitrogen and Phosphorous Budgets, Technical Bulletin No. 73-6, Department of Natural Resources, Lansing, Mich.

Perkin–Elmer Corp., 1973, Analytical Methods for Atomic Absorption Spectrophotometry, No. 303-0152, Norwalk, Conn.

Phillips, E. A., 1959, *Methods of Vegetation Study*, Holt, Rinehart and Winston, Inc., New York.

Reinhart, K. G., 1973, Timber-Harvest Clearcutting and Nutrients in the Northeastern United States, Research Note NE-170, Northeastern Forest Experiment Station, Forest Service, U. S. Department of Agriculture.

Sokal, R. R., and F. J. Rohlf, 1969, *Biometry: The Principles and Practice of Statistics in Biological Research*, W. H. Freeman and Company, San Francisco.

Thornthwaite, C. W., and J. R. Mather, 1957, Instructions and Tables for Computing Potential Evapotranspiration and the Water Balance, *Climatology*, **10**(3): 185-311.

Urie, D. H., 1974, Forest Service, U. S. Department of Agriculture, Cadillac, Mich., personal communication.

——, 1971, Estimated Groundwater Yield Following Strip Cutting in Pine Plantations, *Water Resour. Res.*, **7**(6): 1497-1510.

Wagner, G. H., 1962, Use of Porous Ceramic Cups to Sample Soil Water Within the Profile, *Soil Sci.*, **94**: 379-386.

Weetman, G. F., and B. Webber, 1972, The Influence of Wood Harvesting on the Nutrient Status of Two Spruce Stands, *Can. J. Forest Res.*, **2**: 351-369.

MOBILIZATION OF NUTRIENTS IN SOIL BY ACIDS OF SULFUR AND CHELATING AGENTS

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ABSTRACT

A slightly acid soil (Yolo loam) was further acidified with sulfur to determine some of its effects on mobilization of soil minerals by test plants (*Glycine Max* L., soybean; and *Hordeum vulgare* L., barley). A liming treatment was included. All three soil treatments, which gave a pH gradient at the end of the test of 4.5, 6.0, and 7.5, were interacted with an ethylenediamine tetraacetic acid (EDTA) treatment as a model of an organic chelator in the soil system. Sulfur acidification increased plant accumulation of several elements, especially the element manganese. The high level of available manganese in the acidified soil sometimes decreased plant accumulation of some heavy metals. There were several metal chelate interactions at the various soil pH values. The results emphasized that soil acidification can have great (massive) effects on mineral cycling, particularly in poorly buffered soils, and that there can be interactions with organic constituents of the soil which chelate minerals.

The release of oxides of sulfur to the atmosphere from burning of fossil fuels is one means of hastening the acidification type of soil-forming process. World-wide release of sulfur dioxide is equivalent to 5×10^7 tons of sulfur, and almost one-third of this comes from the United States (Kellogg et al., 1972). Rain deposits the sulfur as sulfurous or sulfuric acid. Kellogg et al. (1972) and Altshuller (1973) estimated that as much as 80 kg of sulfur per hectare may be deposited in the United States, but the average may be between 3 and 10 kg/ha. This sulfur dioxide can result in soil acidification, depending on the type of soil. For example, near a smelter plant in Canada, the soil acidity produced from sulfur dioxide was sufficient to decrease soil pH to 2.6 within a few miles of the plant (Costescu and Hutchinson, 1970).

Fragile ecosystems associated with low soil pH and low soil cation-exchange capacity (often less than 2 meq/100 g soil) are common in the southeastern

states, and the burning of high-sulfur-containing fuels or the processing of ores high in pyrites could disrupt ecosystems in such areas if the fallout and rainout of sulfur products are too high.

If the average amount of sulfur released per hectare per year in the United States amounts to about 10 kg, that is sufficient to add about 0.05 meq H^+ per 100 g of soil to a depth of about 15 cm. Even though this is a small quantity per year, in 20 to 40 years it could result in complete H^+ saturation of some low-buffered soils with resulting loss of exchanged cations to groundwaters.

Kellogg et al. (1972) say that in industrial areas man is "overwhelming natural processes" with the amount of sulfur released into the atmosphere. Many southeastern soils do have low sulfur reserves and often there is yield response to sulfur so that its effects are not all deleterious (Bardsley, Suman, and Stewart, 1964).

The hypothesis that industrialization and urbanization result in greater release of sulfur than some southeastern ecosystems can tolerate can be tested by various means. Among these are studies of effects on ion uptake by plants of soil acidification with sulfur products and also effects of leaching of ions from soil under similar treatments. The present report describes an experiment that has bearing on this problem.

MATERIALS AND METHODS

Soybean and barley responses to sulfur acidification of soil were compared with the addition of excess lime to Yolo loam soil. This soil from the western United States has about 10 times the cation-exchange capacity of many eastern soils. It is a slightly acid soil of pH 6, with a cation-exchange capacity of 19 meq/100 g and a soil organic-matter content of 2.5%. Sulfur at the rate of 0.05 dry weight of soil was mixed with the soil in the dry state. This is sufficient to add 31 meq/100 g of H^+ when all the sulfur is oxidized. In comparison with 10 kg ha^{-1} $year^{-1}$ on a soil of 2 meq/100 g cation-exchange capacity, this is equivalent to a 60-year supply to the Yolo loam in one application. Lime ($CaCO_3$) was mixed with other quantities of the soil, and each amendment was equilibrated for a period of 1 month with soil moisture near $-\frac{1}{3}$ bar. This is sufficient time for *Thiobacillus* sp. to oxidize the sulfur. Two soybean seedlings 7 days old (PI54619-5-1, *Glycine Max* L.) were transplanted to each of different 500-g lots of each of the three soil treatments. Seedlings were used to overcome any effect due to germination differences. One-half of each of the three groups received 50 ppm ethylenediamine tetraacetic acid (EDTA) applied as the sodium salt, and all the groups received 100 ppm nitrogen as NH_4NO_3, all on the dry weight of soil basis. After 20 days the plant leaves were washed successively in 0.1*N* HCl and deionized water to eliminate contamination, then dried to constant weight. The samples were assayed for several mineral elements simultaneously by emission spectrography (Wallace, 1972b; Wallace, Romney, and Alexander, 1974). All data were subjected to analysis of variance.

After the soybean part of the experiment, 10 barley plants (*Hordeum vulgare* L.) were seeded into each pot, and the number of plants was thinned to 4 after germination. After 34 days the plants were handled in the same manner as the soybeans.

RESULTS AND DISCUSSION

Yields of soybeans were decreased by the sulfur, which caused considerable acidification during the period of incubation. Yields probably would have been even further decreased if all the sulfur applied had been oxidized and if the metals made soluble by the acidification had been leached into subsoils or to groundwaters rather than remaining available to plants in soluble form in the pots. The element most disrupted in the Yolo loam by the mild sulfur acidification was manganese, as reflected by the composition of soybean leaves (Table 1). In this particular study the 10-fold increase in plant manganese is probably partially responsible for the negative effects of acidification on the iron and zinc concentrations in the plants. In many of our studies, sulfur acidification has resulted in increased iron availability. The copper, cobalt, nickel, phosphorus, magnesium, and silver in the soil were also increased in availability because of the acidification as indicated by their concentrations in plants (magnesium was significantly different at the 0.05 level and all other elements were at the 0.01 level) (Table 1).

Although the H^+ produced replaced some of the exchangeable cations on the clay in the soil, only magnesium became more available to the plants.

Acidification decreased the availability of two elements to plants. The decrease in molybdenum is due to its decreased solubility at low soil pH (Evans, Purvis, and Bear, 1951). The large decrease in barium in the leaves is an obvious consequence of the insolubility of barium sulfate.

The lime can be expected to have an opposite effect to acidification. Actually, for the soil used it does not change characteristics greatly in that there is little natural acidity to neutralize. The most pronounced effect of lime was the greatly increased level of molybdenum in the plants because of increased solubility of molybdenum in soil (Evans, Purvis, and Bear, 1951).

The chelator used in the study had profound effects at each soil pH value and can be envisioned as a model for certain types of soil-forming and degrading processes. The chelator and sulfur were sometimes additive in their effects.

A most interesting iron–manganese interaction has been observed in relation to some chelating agents in certain soils (Knezek and Greinert, 1970). This experiment shows that the chelate-induced increase in iron accumulation in leaves at soil pH levels of 6.0 and 4.5 was associated with a simultaneous decrease in manganese accumulation. At pH 7.5, however, the chelator increased both manganese and iron accumulation by leaves. Metal chelates are more stable generally at pH 7.5 than at 6.0 and more stable at 6.0 than at 4.5 (Martell,

TABLE 1

SOME EFFECTS OF SULFUR ACIDIFICATION, LIMING, AND A CHELATOR ON YIELDS AND MINERAL COMPOSITION OF SOYBEANS (DRY-WEIGHT BASIS)

	6.0*	6.0†	4.5* (0.05% S)	4.5† (0.05% S)	7.5† (2% $CaCO_3$)	7.5† (2% $CaCO_3$)	F value	LSD¶ 0.05	LSD¶ 0.01
Leaf yield, mg/plant	668	568	453	428	556	549	12.2‡	34	45
Element, ppm									
Mn	53	20	497	440	86	98	165.7‡	45	59
Fe	79	134	68	94	46	55	80.3‡	8	11
Zn	65	75	56	44	64	110	88.5‡	7	9
Cu	5.0	6.3	9.0	9.3	6.1	10.5	96.6‡	0.6	0.8
Co	0.5	1.6	2.1	11.2	0.5	0.7	204.4‡	1.0	1.3
Ni	2.4	12.8	6.9	12.6	1.7	4.3	60.5‡	1.8	2.3
Ag	0.09	0.08	0.44	0.45	0.08	0.09	278.4‡	0.03	0.04
Al	8.9	8.9	10.0	10.5	7.6	9.4	2.6§	1.7	
B	181	206	152	126	79	82	49.3‡	21	27
Mo	1.4	1.2	0.5	0.6	7.2	7.7	127.4‡	0.6	0.8
Sr	60	57	61	66	43	46	26.4‡	4	6
Ba	57	60	10	10	22	22	83.0‡	3	5
Sn	1.6	1.7	2.1	2.1	1.5	1.6	17.6‡	0.2	0.3
Nickel leaf/ stem ratio	2.1	9.7	2.6	4.4	2.9	8.2	36.2	1.5	2.0
Element, %									
Si	0.34	0.37	0.43	0.39	0.17	0.16	133.6‡	0.03	0.04
P	0.252	0.259	0.362	0.359	0.163	0.167	139.9‡	0.021	0.027
K	3.17	3.34	2.93	2.90	2.70	2.77	4.9‡	0.20	0.26
Ca	1.46	1.53	1.52	1.50	1.46	1.53	1.8‡	NS**	NS
Mg	0.35	0.35	0.39	0.39	0.34	0.35	3.7§	0.03	NS

*No EDTA.
†EDTA added.
‡Denotes significance at the P = 0.01 level.
§Denotes significance at the P = 0.05 level.
¶LSD [illegible] significant difference.
**NS [illegible] gnificant.

1964). The iron chelate is more stable at each pH than is the manganese chelate, but at pH 7.5 manganese and zinc largely replace iron as the chelated form (Halvorson and Lindsay, 1972). Hence iron competes with manganese for root absorption more at pH 6 than at pH 7.5. The same general order applies for all metal chelates, with only the magnitude changing. These phenomena are of considerable consequence since organic compounds in soil interact with minerals in cycling processes.

The EDTA increased zinc and copper accumulation in leaves more at pH 7.5 than at pH 6.0 and not at all at pH 4.5. This, again, is in keeping with relative ility constants for the different pH values and implies that the chelated s were more available than nonchelated forms (Halvorson and Lindsay, 1972; Wallace, 1972a).

The effect of EDTA on cobalt and nickel accumulation, in contrast to copper and zinc, was more pronounced at pH 6.0 and 4.5 than at pH 7.5. Because this is reversed from the order of stability constants, it must be explained on the basis of the necessity for H^+-induced solution of certain soil minerals before these minerals can be chelated or accumulated. This implies a simultaneous effect of H^+ and chelating agent. The chelator was exceptionally effective in the acidified soil in promoting movement of cobalt into the plants (and also through the soil). The combination of acidification and chelation would be equally effective in promoting leaching from soil in cycling processes. Interestingly enough, the chelating agent, EDTA, as well as other similar agents (Wallace et al., 1974) resulted in considerably increased transport of nickel through the plant as indicated by leaf–stem ratios for it (Table 1).

The chelating agent had no apparent effect on plant accumulation of any other of the elements assayed.

Generally, in barley, as in soybeans, the sulfur acidification resulted in plant mobilization of increased manganese, cobalt, lithium, and aluminum (each significant at the 0.01 level) (Table 2). Simultaneous decreases in molybdenum, barium, phosphorus, potassium, and calcium were noted. Several of these are different for soybeans. Except for iron at the lower pH values, there was little interaction with the chelating agent in barley. Even though there was possible decomposition or leaching of the EDTA, resulting in lower amounts present than with the soybean, the differences between soybeans and barley are largely due to ies (Wallace and Mueller, 1969).

This study provides an example of how soil acidification caused by sulfur or sulfur dioxide can greatly change the solubility of soil minerals. The increased levels of many of the heavy metals in plants illustrate the increased solvency of them. The level of sulfur applied in the test, if all of it were oxidized, was roughly equivalent to about 60 years accumulation of the present industrial contribution to southeastern soils. A massive release to the atmosphere of sulfur dioxide will become a more and more serious factor in mineral cycling in southeastern ecosystems because the soils there are so fragile.

TABLE 2

SOME EFFECTS OF SULFUR ACIDIFICATION, LIMING, AND A CHELATOR ON YIELDS AND MINERAL COMPOSITION OF BARLEY (DRY-WEIGHT BASIS)

	Soil pH								
	6.0*	6.0†	4.5* (0.05% S)	4.5† (0.05% S)	7.5* (2% $CaCO_3$)	7.5† (2% $CaCO_3$)	F value	LSD¶ 0.05	LSD¶ 0.01
Shoot yield, mg/four plants	426	400	378	388	410	357	0.90	NS	NS
Element, ppm									
Mn	111	126	850	566	110	127	58.5‡	81	107
Fe	33	44	34	56	40	43	3.8§	8	NS
Zn	58	70	53	47	50	69	3.3§	10	NS
Cu	11.2	10.6	13.8	10.8	10.8	13.4	0.6	NS	NS
Co	Trace	Trace	2.4	4.0	Trace	Trace	60.1‡	1.0	1.3
Li	1.5	1.4	14.8	8.5	0.4	0.4	19.1‡	2.6	3.5
Al	8.4	8.5	26.0	22.2	11.6	14.4	10.3‡	4.5	5.9
Mo	8.9	15.6	0.7	0.7	33.0	51.4	35.2‡	6.6	8.8
Sr	43	52	44	37	51	50	2.2	NS	NS
Ba	44	58	2	2	22	27	72.7‡	7	10
Element, dry-weight, %									
Si	0.67	0.81	0.64	0.59	0.41	0.50	6.6‡	0.12	0.16
P	1.00	1.00	0.81	0.88	0.64	0.91	3.5§	0.14	NS
K	6.71	6.59	4.42	4.63	4.92	5.35	7.5‡	1.0	1.32
Ca	0.68	0.77	0.53	0.54	1.17	1.09	38.7‡	0.09	0.11
Mg	0.23	0.26	0.25	0.17	0.30	0.31	5.1§	0.04	NS

*No EDTA.
†EDTA added.
‡Denotes significance at the P = 0.01 level.
§Denotes significance at the P = 0.05 level.
¶LSD = least significant difference.

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REFERENCES

Muller, A. P., 1973, Atmospheric Sulfur Dioxide and Sulfate Distribution of Concentration at Urban and Nonurban Sites in the United States, *Environ. Sci. Technol.*, 7(8): 709-712.

Bardsley, C. E., R. F. Suman, and E. H. Stewart, 1964, *The Sulfur Status of South Carolina Crops and Soils*, South Carolina Agricultural Experiment Station Technical Bulletin 1013.

Costescu, L., and T. C. Hutchinson, 1970, Airborne Metallic Contamination of Soils in the Sudbury Area, Ontario, *Agronomy Abstracts*, Div. S-4, p. 117.

Evans, H. J., E. R. Purvis, and F. E. Bear, 1951, Effect of Soil Reaction on Availability of Molybdenum, *Soil Sci.*, 71: 117-124.

Halvorson, A. D., and W. L. Lindsay, 1972, Equilibrium Relationships of Metal Chelates in Hydroponic Solutions, *Soil Sci. Soc. Amer. Proc.*, 36(5): 755-761.

Kellogg, W. W., R. D. Cadle, E. R. Allen, A. L. Lazrus, and E. A. Martell, 1972, The Sulfur Cycle, *Science*, 175(4022): 587-596.

Knezek, E. D., and H. Greinert, 1970, Influence of Soil Iron and Manganese EDTA Interactions upon the Iron and Manganese Nutrition of Bean Plants, *Agronomy Abstracts*, Div. S-4, p. 123.

Martell, A. E., 1964, Stability Constants, in *Special Publication No. 17*, Sec. 11, *Organic Ligands*, The Chemical Society, London.

Wallace, A., R. T. Mueller, J. W. Cha, and E. V. Alexander, 1974, Soil pH and Excess Lime Concentrations of Microelements in Soybean Plants, *Agron. J.*, 66(5): 698-700.

—, E. M. Romney, and G. V. Alexander, 1974, Variations in the Simultaneous Analysis by Emission Spectrography of Twenty-Four Elements in Plant Material, *Commun. Soil Sci. and Plant Analysis*, 5: 45-50.

—, 1972a, Effect of Soil pH and Chelating Agent (DTPA) on Uptake by and Distribution of ^{241}Am in Plant Parts of Bush Beans, *Radiat. Bot.*, 12: 433-435.

—, 1972b, *Regulation of the Micronutrient Status of Plants by Chelating Agents and Other Factors*, pp. 1–4, A. Wallace (Editor and Publisher), Los Angeles.

—, and R. T. Mueller, 1969, Effect of Chelating Agents on the Availability to Plants of Carrier-Free ^{59}Fe and ^{65}Zn Added to Soil to Simulate Contamination from Fallout, *Soil Sci. Soc. Amer. Proc.*, 33(6): 912-914.

EFFECTS OF TREE SPECIES, TEMPERATURE, AND SOIL ON TRANSFER OF MANGANESE-54 FROM LITTER TO ROOTS IN A MICROCOSM

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ABSTRACT

A microcosm experiment illustrates the importance of microbial effects on movement of ^{54}Mn. It shows that soil microflora can accelerate as well as decelerate the downward movement of ^{54}Mn into the root zone and the subsequent uptake by tree seedlings. Root uptake of this element appears to be largely a function of microbial action on detritus and on mineral mobility and of the interaction between microbes and roots. These results indicate that, in contrast to the existing models of mineral transfer from detritus to roots, future models should specifically address the effects of microbial activity on such transfers.

About the least known transfers of the various models of mineral cycling in ecosystems are those leading from the debris of producers and consumers to the roots of the primary producers. Proposed models (Shugart et al., 1974; Sollins et al., 1974; Patterson et al., 1974; Dett et al., 1972) use four major forcing functions for mineral transfers from detritus to roots, namely, (1) rate, seasonality, and quality of mineral input by detritus to the forest floor; (2) distribution coefficient (K_d) for the various elements leaching through soil; (3) passive transport of minerals in leachate moving from litter to roots, sometimes combined with diffusion near roots when there is no mass transport; (4) rate of breakdown of the detritus as an indicator of solubilization of detritus minerals. Instead of the breakdown rate, such rate-controlling factors as temperature and moisture or such measures of decomposer activity as adenosine triphosph concentration, O_2 consumption, CO_2 evolution, or bacterial densities may used.

These models are quantitative approximations describing natural decomposition phenomena involving only one of the four driving forces to move nutrient or toxic elements from litter to soil. Data on the interactions between decomposability of litter, soil characteristics, and microbial action during

nuclide transfer from detritus to primary producers are not available in the literature, even though we recognize their importance in the transfer of elements between litter and plants. Therefore we designed an experiment to evaluate the relative importance of litter, soil, and microbial effects on the transfer of ^{54}Mn from litter into roots of the same species.

EXPERIMENTAL DESIGN

Transfer of ^{54}Mn was compared for two levels of litter decomposability, two contrasting local soils, and two levels of microbial activity. Materials and methods were chosen to correspond with local conditions (McBrayer et al., 1973). The tree species were black locust, which is a local pioneer along road banks and river banks and on poor hillsides, and loblolly pine, which is widely grown for pulp. The foliage litter of these species represent rapid and slow decomposition, respectively (Cromack et al., 1974).

The two contrasting soils were taken from directly under the litter on a dolomitic limestone ridge and on an adjacent parallel sandstone–shale ridge. The respective pH values for limestone and shale were 5.6 and 4.4. The affinity for ^{54}Mn of the dolomite soil was only slightly higher than that of the shale-derived soil. After the samples had been shaken for 18 hr, shale soil (1 g dry weight) taken from directly under the litter layer removed 74.9% of ^{54}Mn from solution (50 ml), and the dolomite limestone soil removed 89.5% of ^{54}Mn.

The two levels of microbial activity were induced by keeping half the detritus at 2°C, simulating winter conditions with little or no microbial breakdown, and half at 25°C to represent summer temperature and an active decomposer flora in the litter. Mass transport by water was not a variable. The water was provided by weekly additions of 2.5 cm of water, the approximate average rainfall in the area.

The experiment was a 2^3 factorial, with three replications. Leaves were tagged with ^{54}Mn through branch uptake. In one series 4 g dry weight of loblolly needles and in the other series a layer of the same thickness, 1.5 g dry weight, of locust leaves were put in round containers (50 cm^2) with about 2 cm of A_1 soil. All were incubated for 15 weeks. Leachates from soil were periodically analyzed for ^{54}Mn content and added to a similar box with 2 cm of same soil and 10 seedlings of the same species as the litter. The percent of ^{54}Mn originating from the litter that was found in the seedlings was taken as a measure of the external recycling of ^{54}Mn.

In general, ^{54}Mn behavior is influenced by pH. At pH $>$ 8, trivalent and tetravalent insoluble oxides impede manganese mobility and uptake. Below pH 5.5, manganese occurs mainly as divalent cation, and at a pH between 5.5 and 8 either form may occur, depending mainly on local biological control of pH and oxygen concentration (Dommergues and Mangenot, 1970). Root uptake is mainly in the form of Mn^{2+}, but this form is also easily complexed by plant and

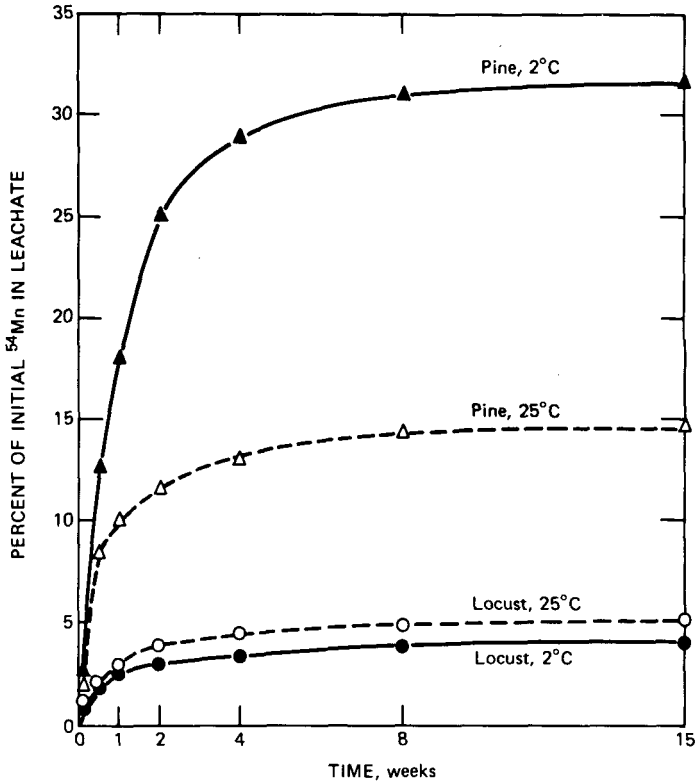

Fig. 1 Percent of initial ^{54}Mn added to pine and locust microcosms recovered in leachate following 1, 2, 4, 8, and 15 weeks of incubation at one of two temperatures.

microbial compounds and taken up by microorganisms (Bétrémieux and Hénin, 1965).

RESULTS

The cumulative curves of ^{54}Mn in leachate at 2-cm depth (Fig. 1) show more than half the ^{54}Mn loss from litter took place during the first week, indicating high leachability and mobility of ^{54}Mn. The percent of ^{54}Mn leaching from slowly decomposing pine litter is much greater than from rapidly decaying locust leaves. The results show that temperature has a greater effect on the rate of leaching of ^{54}Mn from pine needles than from locust leaves.

A tabulation of the significance of the variables on the final distribution of ^{54}Mn in the main compartments (Table 1) shows that litter species has a significant effect on ^{54}Mn remaining in litter, its downward percolation, and its

TABLE 1

FINAL DISTRIBUTION (%) OF ^{54}Mn FROM LITTER IN LITTER + TOPSOIL, BOTTOM SOIL, AND TREE SEEDLINGS FOR LOCUST VS. PINE LITTER, LITTER INCUBATION AT 2°C VS. 25°C, AND DOLOMITIC VS. SHALE-DERIVED SOIL SERIES (AVERAGES OF 12)*

	Litter + topsoil	Bottom soil	Tree seedlings
Locust	96	4.2	0.22
Pine	77†	22†	0.94†
2°C	82	17	0.76
25°C	90†	9.5†	0.41
Dolomitic soil	86	14	0.17
Shale-derived soil	86	13	1.00†

*Incubation time was 15 weeks.

†Averages differ significantly at 1% probability level as determined by analysis of variance.

subsequent uptake by the seedlings. The effect of rapid leaching from slowly decomposing needles and low losses from rapidly decaying leaves is the opposite of the accepted relationship between cycling and decomposition. A description of the decomposed locust leaves may give some insight as to why the ^{54}Mn remained in the top soil. The locust leachate is viscous and black. It has a pH of 8.4 and a high organic-compound content. After 7 days at 25°C, 18.2 X 10^6 bacteria/ml develop on nutrient agar. Adsorption of ^{54}Mn to the leached organics and microbial immobilization keep the ^{54}Mn in the top layer, and only about 0.2% of the initial leaf ^{54}Mn is taken up by seedlings. In contrast, pine needles show almost no visual decomposition. The acid leachate, pH 3.7, from the needles has the viscosity of water, is light yellow, and contains 1.1 X 10^6 bacteria/ml. The high acidity and low microbial immobilization may have enhanced transfer of ^{54}Mn from pine through soil. Complexing of cations by dark leachate from rapidly decomposing deciduous litter as compared to free ions in the acid leachate of slowly decomposing litter was reported earlier (Witkamp, 1969). During the periodic handling of the cultures, there was less visual evidence of organics infiltrating soil with the leachate and of the associated microbial bloom in the soil, suggesting less microbial immobilization in the topsoil under pine needle than under locust litter. Consequently as much as one-third of the ^{54}Mn from needles decomposing at 2°C leached through the topsoil (Fig. 1), and as much as 2.5% of the ^{54}Mn was taken up by the pine trees.

The effect of temperature was most evident in the ^{54}Mn content of the leachate from pine (Fig. 1). At 2°C there was no visible microbial growth on the

needles. As a result leaching of ^{54}Mn was unimpeded by microbial uptake. Clearly visible growth of mycelium in the 25°C cultures presumably immobilized the ^{54}Mn at the eventual expense of the seedlings. In contrast, loss of ^{54}Mn from locust litter and topsoil was affected by the temperature difference in the opposite way. Almost complete decay at 25°C apparently mineralized more ^{54}Mn from the litter than was immobilized by the microflora. Subsequent retention of the ^{54}Mn in the topsoil prevented much of the mineralized ^{54}Mn from reaching the leachate. At 2°C more ^{54}Mn remained in the locust litter even though decomposition of this litter after 15 weeks appeared to be much greater than that of pine needles at 25°C. Thus litter species and rate of microbial activity are dominating and statistically significant factors (Table 1) in external recycling of ^{54}Mn from detritus to plants.

The two contrasting soils did not have a significant overall effect on transfer of ^{54}Mn from litter and topsoil to bottom soil but did significantly affect ^{54}Mn uptake by trees. The greater (6 times) amount of ^{54}Mn in trees on dolomite than on shale was almost exclusively the result of the difference in ^{54}Mn in pine. The greater (12 times) ^{54}Mn uptake by pine on shale-derived soil than on dolomitic soil was presumed to be the result of observed extensive development of mycorrhizae on pine roots in shale. No mycorrhizae were seen in dolomite-derived soil (Skinner and Bowen, 1974). Concentrations of ^{54}Mn (Table 1), as well as the affinity for ^{54}Mn, in both soils were about equal and thus would not explain this large difference in uptake. Apparently here too the significant effect was microbial.

These results indicate that the significant differences in recycling from detritus to tree seedlings are associated with differences in microbial density (locust vs. pine), microbial activity (2°C vs. 25°C), or mycorrhizae formation (Skinner and Bowen, 1974) (pine on dolomite vs. shale). There is a possibility of manganese insolubilization at the high pH of locust litter, but, in view of the rapid transformation of this litter to a waterlogged amorphous mass and the high oxygen requirements by the highly active microflora manganese, immobilization by oxidation seems less likely than by microbial uptake. We therefore suggest that models for transfer of ^{54}Mn and probably other elements should take into account microbial action.

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REFERENCES

Bétrémieux, R., and S. Hénin, 1965, in *Experimental Pedology*, pp. 179-188, E. G. Hallsworth and D. V. Crawford (Eds.), Buttersworth & Co. (Publishers), Ltd., London.

Cromack, K., D. Sharpe, B. Ausmus, G. Henderson, R. Fogel, and C. Monk, 1974, A Regional Approach to Forest Decomposition Processes, in Proceedings of the Ecological Society of America Symposium on Decomposition and Mineral Cycling Processes in Forests, Tucson, Ariz., June 1974 (in press).

Dett, G. R., M. J. Shafee, and W. J. Moore, 1972, *Computer Simulation Model of Dynamic Biophysicochemical Processes in Soils*, Technical Bulletin 196, Agricultural Experiment Station, University of Arizona, Tucson.

Dommergues, Y., and F. Mangenot, 1970, *Ecologie Microbienne du Sol*, Masson et Cie S.A., Paris.

McBrayer, J. F., D. E. Reichle, and M. Witkamp, 1973, Energy Flow and Nutrient Cycling in a Cryptozoan Food Web, Report EDFB-IBP-73-8, Oak Ridge National Laboratory.

Patterson, M. R., J. K. Munro, D. E. Fields, R. D. Ellison, A. A. Brooks, and D. D. Huff, 1974, A User's Manual for the Fortran IV Version of the Wisconsin Hydrologic Transport Model, Report EDFB-IBP-74-9, Oak Ridge National Laboratory.

Shugart, H. H., R. A. Goldstein, R. V. O'Neill, and J. B. Mankin, 1974, TEEM: A Terrestrial Ecosystem Energy Model for Forests, *Oecol. Plant.*, 9(3): 231-264.

Skinner, N. F., and G. D. Bowen, 1974, The Uptake and Translocation of Phosphate by Mycelial Strands of Pine Mycorrhizas, *Soil Biol. Biochem.*, 6: 53-56.

Sollins, P., G. Swartzman, D. Johnson, K. Cromack, C. Grier, R. Fogl, and F. Glenn, Modeling the Nutrient Cycles of a Temperate Coniferous Forest, Proceedings of the Ecological Society of America Symposium on Decomposition and Mineral Cycling Processes in Forests, Tucson, Ariz., June 1974 (in press).

Witkamp, M., 1969, Environmental Effects on Microbial Turnover of Some Mineral Elements, II. Biotic Factors, *Soil Biol. Biochem.*, 1: 177-184.

ASPECTS OF MINERAL-NUTRIENT CYCLING IN A SOUTHERN MIXED-HARDWOOD FOREST IN NORTH CENTRAL FLORIDA

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ABSTRACT

Analyses of water collected from stemflow, throughfall, and rainfall samples over a 2-year period provided estimates of mineral nutrient inputs (phosphorus, calcium, magnesium, and potassium) to the forest floor. Total nutrient inputs from these sources (in kilograms per hectare per year) were phosphorus, 3.2; potassium, 24.7; calcium, 29.7; and magnesium, 8.1. Unusually high concentrations in the rainfall contributed to these values. The presence of evergreen species in the forest also appears to play an important role in making these values higher than corresponding values in other temperate hardwood forests. Particular attention is paid to the similarity in the patterns of concentration of potassium and ^{137}Cs. As demonstrated by samples taken from lysimeters and from groundwater pits, the concentration of both elements drops considerably as the water passes through the root zone in the soil. A mycorrhizal uptake mechanism is implicated.

The study of mineral cycles is a basic approach to analysis of the structure and function of ecosystems. Determining the behavior of certain elements within an ecosystem often makes it possible to predict the response of the ecosystem to changes that may affect it. One such change was the introduction in the 1960s of atmospheric fallout of radionuclides from nuclear weapons testing. Sampling programs in agricultural areas were begun at that time to locate possible radionuclide concentrations in various compartments of the ecosystem. In Florida the continuation of above-average activity of radiocesium in both plant and animal biomass long after aboveground testing had ceased is well documented in managed ecosystems. This is particularly true in pastures; very high levels of cesium activity have been found in milk (Roessler, Roessler, and Dunavent, 1969).

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This phenomenon was investigated in a series of studies. The primary goal of the project was to determine whether ^{137}Cs accumulates in a natural system and, if so, whether it accumulates in a compartment with a counterpart in a managed system. In the part of the project discussed here, mineral cycles in a relatively undisturbed ecosystem were investigated, with special attention to pathways that might affect the distribution of cesium in the ecosystem.

Base-line ecological studies have been conducted in a mixed-hardwood forest at the Horticultural Unit of the University of Florida, 8 miles northwest of Gainesville (Lugo, Snedaker, and Gamble, 1971). This forest is an example of a successional stage of the hardwood forest that once covered a large part of the state. The mixed-hardwood community is probably the most diverse and complex terrestrial ecosystem type in the State of Florida. It differs from more temperate forests in having several species of evergreen hardwoods as canopy dominants (e.g., *Magnolia grandiflora* and *Quercus laurifolia*). Consequently, there is less seasonal change in this forest than in more decidous forests.

One of the principal nutrient inputs to a terrestrial ecosystem is rainfall, which may bring in appreciable quantities of certain elements. The rainfall over a forest reaches the ground primarily as throughfall, either falling directly through forest openings or dripping off leaves. Another pathway that rainfall follows is that of stemflow; i.e., water passes over leaves and bark and then runs down the trunks of trees. The chemical composition of rainwater is altered as it becomes throughfall and stemflow, and various elements and compounds are either leached from the tree and from the epiphytes on leaves and bark or are taken up directly by these plant tissues. Presented here are the results obtained from seasonal analysis of rainfall as its composition is affected by different components of the ecosystem encountered as the water travels to the forest floor and then leaches through the soil system to groundwater.

METHODS

A 1-ha study plot was marked off in a stand of mixed hardwoods located near the experimental fields of the University of Florida's Horticultural Unit. Near this plot in the same stand, a 100-m^2 section containing 12 trees (six different species) was demarcated as a stemflow study area.

Amounts of rainfall, throughfall, and stemflow at the study area were monitored from July 1971 to June 1973. There are effectively two seasons in the study area; summer (March to October), when all the trees are in full leaf; and winter (November to February), when the deciduous trees have lost their leaves. Loss of leaves from deciduous species in the fall and their regrowth in the spring occur in a fairly short period of time.

Rainfall was measured with an intensity-recording rain gauge placed about 25 m from one corner of the plot, just outside the forest next to a pasture. An open plastic collector was placed near the gauge to collect rainwater for the

analyses. The original purpose of the plastic collector was to provide a sample for chemical analysis that would not be contaminated by the galvanized funnel of the rain gauge. A comparison of results obtained from the bucket with those from the rain gauge showed that the amount of rainfall collected in the bucket agreed closely and consistently with the rain gauge except on occasions when the rain exceeded 50 mm; then there was some loss from the plastic bucket by splashing. The regression equation relating millimeters of rainfall in the bucket (Y) to rainfall in the gauge (X) is

$$Y = 0.99X - 1.01 \qquad (r = 0.97)$$

This double check on rainfall was of value when the rain gauge yielded a short series of erratic recordings in the latter part of the study.

Throughfall was sampled within the forest by a series of 30 plastic buckets, 15 cm in diameter and 20 cm high, placed at approximately 5-m intervals along one of the diagonals of the 1-ha plot. Throughfall collections were made after each rainfall. The buckets were wiped dry after being emptied and were kept clean of litter and grass between rains. Water samples from the first 15 collectors were pooled and subsampled for chemical analysis; the same was done for the second 15 collectors. If a sample appeared to be contaminated with droppings or had a suspicious color, the volume of that sample was noted, and its contents were analyzed separately. No gross differences were ever found, however.

Stemflow collars were placed on each of the 12 trees located within the 100-m^2 stemflow plot. Each collar consisted of a 10-cm strip of polyethylene wrapped around a strip of foam rubber that encircled the smoothed bark at breast height. The resulting trough, 2.5 cm wide by 4 cm deep, was lined with wax and sealed with acrylic caulking cement. Each trough was connected by plastic tubing to a separate covered 25-gal plastic barrel. The collar design was suggested by Clements and Colon (1970).

The volume of each sample was recorded after each rainfall, and a subsample was taken for chemical analysis. Because of problems with leakage and overflow (the original collectors were 10-gal containers), only 21 complete collections were obtained for analysis between August 1971 and April 1973. An additional 14 collections were not analyzed.

Four soil pits dug during the early months of the study were used to obtain groundwater samples and leachates from zero-tension lysimeters. Duplicate lysimeters were located in each pit immediately below the litter, 10 cm deep (in the middle of the A horizon), 45 cm deep (in the middle of the B horizon), and, in two of the pits, 90 cm deep.

The total number of collections of leachates from the lysimeters (19)—particularly from lysimeters placed below 10 cm in the soil profile—was restricted because the water table remained within 1 m of the surface

throughout much of the 3-year study period and collectors had been set at the bottom of the pits.

Groundwater was also collected periodically. The pits were pumped out and cleaned, and incoming water was sampled for analysis. Thirty-two groundwater collections were analyzed.

Chemical analyses were performed at the Analytical Research Laboratory at the University of Florida. Calcium and magnesium were analyzed by atomic absorption spectrophotometry; potassium was analyzed by flame photometry; and phosphorus was determined colorimetrically using the molybdenum blue method (Truog and Meyer, 1929).

RESULTS

Rainfall

Summer and winter rainfalls were found to differ significantly (at the 5% level) only in the average lengths of the storms. Data from 84 summer rainfalls showed that the average length of a storm was 3.8 hr, but the average length per storm for 26 winter rainfalls was 6.5 hr. Of the summer rainfalls, which were primarily afternoon thundershowers, 82% lasted less than 6 hr. Only 50% of the winter rainfalls, which were caused primarily by frontal activity, lasted less than 6 hr. Total rainfall during 1972, the only complete calendar year included within the sampling period, was 1175 mm. Of this total 742 mm fell during the 7-month summer season and 433 mm fell during the 5-month winter season. Average summer rainfall per storm was 23.2 mm, and the average winter rainfall per storm was 26.3 mm. Roughly two-thirds of both winter and summer rainfalls were less than 25 mm, and all the winter rainfalls and 94% of the summer rainfalls had an intensity of less than 20 mm/hr.

Both rainfall and throughfall amounts were recorded for 107 storms during the 3-year study period, 79 during the summer months and 28 during the winter months. Some of the throughfall containers consistently yielded larger samples than the rest. The extent of canopy closure over each throughfall collector was therefore measured in July with a spherical densiometer. Considerable variation was found; the 30 readings averaged 90.7% cover, with a range from 78.1 to 96.4%. Both the densiometer readings and the variation among the throughfall collectors indicate a localized funneling effect. Total estimated throughfall exceeded rainfall in 1 of the 26 winter storms and in 8 of the 78 summer storms for which both throughfall and rainfall data were collected during the study period. Some of these instances could be explained by the very spotty distribution of the thundershowers. In one or two of the summer storms, the study area itself may have actually received more rain than did the rain gauge.

Throughfall

During 1972 total throughfall recorded in the summer months was 672 mm; throughfall in the winter was 349 mm. The average throughfall per storm was

89% of the rainfall in the summer, a value not significantly different from the average of 87% for the winter storms.

Linear regression equations relating rainfall (P) to throughfall (T) were calculated for 78 summer storms and 26 winter storms:

$$\text{Summer: } T = 0.89P + 0.24 \qquad (r = 0.99)$$

$$\text{Winter: } T = 0.94P - 1.11 \qquad (r = 0.99)$$

Amounts of throughfall and rainfall are expressed in millimeters.

Stemflow

Stemflow samples were collected for individual trees, and the total amount of stemflow for the 100-m^2 stemflow plot was calculated from these figures. This value was then used with the measurements of rainfall and throughfall to estimate the total quantity of water reaching the forest floor.

The complete record of stemflow for the study period was not available because of difficulties encountered with the collecting apparatus. However, linear regression equations using data from 17 summer storms and 18 winter storms were calculated to determine the relationship between stemflow (S) and rainfall (P) in both winter and summer:

$$\text{Summer: } S = 0.06P - 0.32 \qquad (r = 0.86)$$

$$\text{Winter: } S = 0.07P - 0.42 \qquad (r = 0.87)$$

Using these equations, we calculated the total summer stemflow on the stemflow plot in 1972 to be 44.2 mm, and the winter stemflow to be 29.9 mm.

Once again, seasonal differences in amounts were not significant. In the summer 3% of the rainfall became stemflow in each of the storms, and in the winter 5% of the rainfall became stemflow.

To test the validity of extrapolating from the 35 rain events for which stemflow data were available, we performed a Student's t-test to compare the average amounts of rainfall in these storms with those in the complete set of 110 storms. The difference was not significant. Therefore the data presented here are believed to comprise a representative sample of all the stemflow amounts during the study period.

Although our main purpose was to summarize total water and nutrient inputs to the forest floor, it became obvious during the study that differences in the yield of stemflow per storm among the trees on the plot were significant. An analysis of variance for a randomized complete block design was performed on the average yield of stemflow for each tree on the plot, each tree representing a treatment and each storm representing a block. The differences between the trees were significant at the 5% level; Duncan's new multiple-range test separated

them into three fairly distinct categories according to the relative amount of stemflow per storm. The results of this test and the percentage of the total seasonal stemflow contributed by each tree are outlined in Table 1. Three groups of trees appear to be differentiated by the test: those yielding a considerable amount, a moderate amount, and only a small amount of stemflow.

Nutrient Inputs

Rainfall, throughfall, and stemflow samples from a series of rain events between July 1971 and April 1973 were analyzed for calcium, magnesium, phosphorus, and potassium. Data on amounts of rainfall were collected over the entire period, but, because of equipment failure, contamination by bird droppings, or analytical error, complete sets of data for each rain event were not obtained. Analyses from 21 to 27 winter storms and 41 to 70 summer storms provided the basis for estimating the input of each nutrient from rainfall. Throughfall estimates were obtained from 20 to 26 winter storms and 38 to 69 summer storms, and stemflow estimates were based on 9 to 12 winter storms and 12 to 13 summer storms.

Comparisons in Table 2 of the average concentrations of nutrients in rainfall, throughfall, and stemflow suggest different behavior patterns for each element. All elements except phosphorus, for instance, are present in significantly greater concentrations in rainfall in winter than in summer. Calcium and phosphorus are leached at significantly higher concentrations in throughfall in winter. None of the differences in stemflow were significant.

To summarize the nutrient inputs on a 1-year basis, we used the following procedure. Nutrient inputs from each rainfall event were first summed for all the available summer rainfalls and then for all the available winter rainfalls. The seasonal totals were then used to calculate factors that could be used, in turn, to calculate the input associated with the rainfall for a given season. For instance, a total of 0.5 kg/ha of phosphorus was introduced with 524.8 mm of rain in 21 winter storms in the period from 1971 through 1973. The winter rain for 1972 totaled 433 mm, which, assuming linearity, would have contained 0.4 kg/ha of phosphorus. Similarly, the 1050.4 mm of rainfall from 41 summer rains totaled 0.7 kg/ha, which corresponds to 0.6 kg/ha of phosphorus for the 742 mm of rain that fell during the summer of 1972. Thus the total phosphorus input from rain in 1972 was calculated to be 1.2 kg/ha.

The total nutrients introduced with the throughfall were calculated similarly. An amount attributable to the rainfall was subtracted so that the estimate is the net quantity that actually leached or was washed from the vegetation. The regression equations calculated earlier were used to estimate total stemflow. As with throughfall, the amount of each nutrient attributable to rainfall was subtracted from the stemflow total.

The total nutrient input for each season is shown in Table 3. Although there was less rainfall during the 5-month winter season, winter inputs are still higher

TABLE 1

RELATIVE STEMFLOW YIELDS FOR 12 TREES IN A SOUTHERN MIXED-HARDWOOD FOREST

Tree species	Total height, m	Crown diameter, m	Percent of total stemflow in summer*	Percent of total stemflow in winter†	Yield category
Water oak‡ (*Quercus nigra* L.)	20.0	5.5	16.0	14.3	Heavy
Water oak	18.5	6.4	14.3	13.9	Heavy
Water oak	18.0	8.2	12.7	13.4	Heavy
Laurel oak‡ (*Q. laurifolia* Michx.)	26.5	7.6	12.8	11.2	Heavy
Laurel oak	19.0	9.3	12.4	14.9	Heavy
Hickory [*Carya glabra* (Mill.) Sweet]	20.5	3.6	9.4	6.5	Moderate
Loblolly pine‡ (*Pinus taeda* L.)	24.5	6.2	7.8	8.1	Moderate
Hop hornbeam [*Ostrya virginiana* (Mill.) K. Koch]	14.5	6.0	7.5	8.7	Moderate
Hop hornbeam	10.5	3.2	2.5	1.9	Light
Hop hornbeam	9.0	2.7	2.1	3.3	Light
Hop hornbeam	7.5	4.1	1.7	2.9	Light
Sweet gum (*Liquidambar styraciflua* L.)	8.5	3.4	0.7	0.6	Light

*For 17 summer rainfalls, 1394 events of stemflow were collected.
†For 19 winter rainfalls, 1862 events of stemflow were recorded.
‡Evergreen species.

TABLE 2

AVERAGE SEASONAL CONCENTRATIONS OF NUTRIENTS IN RAINFALL, THROUGHFALL, AND STEMFLOW

	Average concentrations of nutrients, mg/liter					
	Rainfall		Throughfall		Stemflow	
Nutrient	Summer	Winter	Summer	Winter	Summer	Winter
[illegible]m	0.96*	2.92	1.87†	4.04	4.42	10.14
[illegible]sium	0.26*	0.53	0.97	1.25	1.21	1.03
Phosphorus	0.08	0.12	0.15†	0.54	0.47	1.38
Potassium	0.80*	1.25	2.67	2.63	10.28	12.49

*Student's t-test indicates a significant difference between summer and winter at the 0.05 level.

†Student's t-test indicates a significant difference between summer and winter at the 0.01 level.

TABLE 3

TOTAL SEASONAL NUTRIENT INPUTS CONTRIBUTED BY RAINFALL, THROUGHFALL, AND STEMFLOW

	Nutrient inputs, kg ha^{-1} $season^{-1}$					
	Rainfall		Throughfall		Stemflow	
Nutrient	Summer	Winter	Summer	Winter	Summer	Winter
Calcium	5.2	14.1	5.1	3.4	1.5	0.4
Magnesium	1.7	1.2	2.8	2.2	0.1	0.1
Phosphorus	0.5	0.4	0.8	1.2	0.1	0.2
Potassium	4.3	3.9	7.9	3.9	3.4	1.3

than summer inputs for calcium in rainfall and for phosphorus in throughfall and stemflow.

[illegible]ients in Soil Water

Thirty-two analyses of nutrient concentrations in the groundwater pits were obtained over a period extending from July 1970 through July 1973. In addition, 19 analyses were performed on samples taken from lysimeters located just below the litter layer and in the middle of the A, B, and C horizons during the period from July 1970 to August 1971. The averages of these values are shown in Fig. 1, along with the average composition of the water reaching the forest floor, i.e., the throughfall and stemflow.

No significance tests were performed on the data presented in Fig. 1 since each mean was derived somewhat differently. The average concentrations in the throughfall and stemflow reaching the forest floor came from the 22 storms for which complete analyses were obtained. The mean concentrations of nutrients in

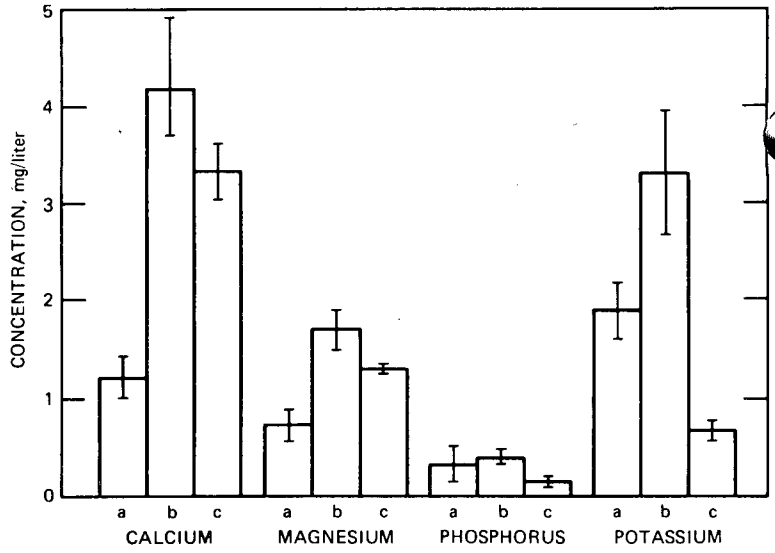

Fig. 1 Concentrations of four elements at three points in the process of percolation through the ecosystem to the groundwater. (a) Water reaching the forest floor (i.e., throughfall and stemflow). (b) Water below the litter layer. (c) Groundwater.

the water percolating through the litter layer were obtained by averaging the concentrations of nutrients obtained from one to four lysimeters located just beneath the litter layer on 19 days from July 1970 through August 1971. Mean concentrations of nutrients in the groundwater were similarly calculated by averaging the concentrations of nutrients in water obtained from some or all four soil pits in the study area. The standard error of the mean is indicated.

DISCUSSION

The main difference between the mixed-hardwood ecosystem in Florida and more-northern temperate hardwood forests lies in the degree of evergreenness. The impact of this feature on nutrient cycling is not entirely clear, however. In some respects the Florida ecosystem behaves very much like other systems but differs in other respects.

Water Inputs

The linear regression equations derived in our study are similar to those derived by Helvey and Patric (1965) from a large number of values reported in studies of mature mixed-hardwood forests in the eastern United States. For the relationship between throughfall (T) and rainfall (P) (in millimeters), their equations are:

Summer: $T = 0.90P - 0.76$ (n = 12 equations)

Winter: $T = 0.91P - 0.51$ (n = 7 equations)

When rainfall data from our study are substituted into these equations, the amount of throughfall predicted is virtually the same as that from the equations derived for Florida. The evergreenness, therefore, has not caused major changes in the overall interception of rainfall by the canopy.

Equations expressing the relationship between rainfall (P) and stemflow (S) were also developed by Helvey and Patric (1965). The equation they derived for the winter months is a function of the equation for the growing season since so few data were available for the winter in temperate areas. Their equations (values in millimeters) are:

Summer: $S = 0.04P - 0.25$ (n = 13 equations)

Winter: $S = 0.06P - 0.25$ (estimated as described in text)

Both these equations predict less stemflow per storm than the Florida equations. Either a greater density of stems or a higher leaf-area index in southern forests might account for this difference since, after the surfaces have been wetted and rain is falling steadily, the more extensive surface area might trap more water and funnel it to the trunk as stemflow. Unfortunately, the few data available do not support this hypothesis.

Differences between trees in contributing varying amounts to the stemflow yield are apparent The trees in the canopy have the largest crown diameters and intercept the greatest amount of water. Of the 12 trees sampled, all 5 oaks, representing two species, and the hickory consistently yielded the largest amount of stemflow; the pine and 1 hop hornbeam yielded an intermediate amount; and the 3 remaining hop hornbeams and the sweet gum yielded the smallest amount. All the oaks were found in the top layer of the canopy, and the tallest of the hop hornbeams yielded the most stemflow of the trees of that species.

Hamilton and Rowe (1949) found that the largest proportion of the rainfall was trapped by trees with smooth upright stems and the smallest amount by trees with spreading branches and rough bark. In our study, however, the height of the tree and the size of the crown seemed to be the important features, but

there were not enough trees to distinguish clearly between the effects of size and roughness. The largest amounts of stemflow came from the trees with the largest crowns and the smallest amounts from the shortest trees. The pine had the roughest bark and yielded a moderate amount of stemflow; the smooth-barked hop hornbeams yielded only a small amount. The tallest hop hornbeam yielded considerably more water than the other three hop hornbeams.

Nutrient Inputs

The total mineral nutrient inputs of four elements to the study are shown in Table 4, along with values from other studies. An examination of rainfall values shows that, with the exception of magnesium, our values are at the upper end of the range shown in this table, and our values for phosphorus are higher than any of the others reported. It is not clear why our phosphorus values should be high. Both fertilizer application and dolomite mining upwind from the study area may have an influence, but no studies have been performed to substantiate this.

The total phosphorus input in the throughfall is again considerably higher for the Florida hardwoods than for the other ecosystems reported in Table 4, and the value for calcium is slightly higher also. The continued leaching of appreciable concentrations of these elements into the throughfall during the winter accounts for this increase. Phosphorus and potassium inputs in the stemflow are higher than in other areas. The concentrations of these elements, as shown in Table 2, are higher in the winter, but not significantly so.

Monk (1966) documented the degree of evergreenness in several plant communities in north central Florida and supported Harper's (1914) suggestion that nutrient availability is an important factor in the distribution of evergreen species. Our data support Monk's suggestion that continual leaching from vegetation all year may be a significant factor in allowing the ecosystem to continue production in winter despite the naturally low fertility of the soil. Since the nutrients in the stemflow are concentrated around the bases of the trees rather than spread out over the plot, the contribution by stemflow may be especially significant. Data presented earlier (Lugo, Snedaker, and Gamble, 1971) show high rates of litterfall throughout the year, except during the summer months when daily thunderstorms provide a constant nutrient input from throughfall and stemflow.

Nutrient Outflows

Considering the fate of the nutrients once they reach the forest floor brings out additional features of importance to the functioning of this ecosystem. The soils in the study area are less than 2% clay and less than 4% organic matter. They are very low in cation-exchange capacity (less than 10 meq/100 g), and nutrients reaching the mineral soil would be expected to pass through the root zone and into the water table.

TABLE 4

ANNUAL NUTRIENT INPUTS DETERMINED IN EIGHT DIFFERENT STUDIES IN TEMPERATE DECIDUOUS FORESTS

Source and element	Nutrient input, kg ha^{-1} $year^{-1}$							
	Florida mixed hardwoods	North Carolina hardwoods*	Hubbard Brook†	Belgian hardwoods‡	Belgian mixed oakwoods¶	French spruce §	Great Britain**	Temperate regions in general††
Rainfall								
P	0.9	0.28				0.04	4	0.2–0.6
K	8.2	0.88	1.1	4	5	5–10	3	1–10
Ca	19.3	3.42	2.6	15	19		11	3–19
Mg	2.9	0.62	0.7		5.8	2–3	4	4–11
Throughfall								
P	2.0	0.61		0	0.6	0.21		
K	11.8	17.48		22	16	11–16		
Ca	8.5	0.61		9	6.2			
Mg	5.0	3.75		7	5.6	0–1		
Stemflow								
P	0.3	0		0	0	0		
K	4.7	0.65		2	0.8	0		
Ca	1.9	2.02		2	0.9			
Mg	0.2	0.24		0	0.6	0		

*Strain, 1971.
†Likens and Bormann, 1971.
‡Duvigneaud, 1968; Duvigneaud and Denaeyer-DeSmet, 1968.
¶Duvigneaud and Denaeyer-DeSmet, 1970.
§Aussenac, Bonneau, and LeTacon, 1972.
**Carlisle, Brown, and White, 1966.
††Ovington, 1968.

The pattern of leaching shown by calcium and magnesium in Fig. 1 is typical, with an increase in concentration as the solution passes through the decomposing litter. Since some of the nutrients are then absorbed in the root zone, concentration in groundwater is somewhat less than that in the water emerging from the litter zone. Both phosphorus and potassium behave atypically. The mild to strongly acid sands of the area generally have a very active alumino–silica anionic complex that acts as a sink for soluble phosphates (Fiskell and Ballard, 1973), and phosphate concentration in groundwater is less (though perhaps not significantly) than in the water reaching the forest floor.

Potassium, the most soluble and mobile of the elements studied, would be expected to pass out of the root zone with little or no retention in the mineral soil. Instead the data show a marked decrease in concentration, to 25% of the original value, between the litter layer and the groundwater. It is possible that potassium is being tied up in an organic complex in the upper root zone. A direct recycling mechanism may be implicated, however; otherwise the potassium would be lost with further decomposition. Evidence of the direct recycling of potassium has been found in fertilization studies of local forests (Pritchett and Smith, 1974). It has long been known that slash pine does not show a response from potassium fertilizer although soil extracts show little potassium. No potassium minerals, such as feldspars, are present in the sand, and clay minerals are rare.

Implications for Cycling of ^{137}Cs in the Ecosystem

A potassium–cesium congener relationship has never been so well demonstrated as the calcium–strontium relationship. In this instance, however, the potassium movement closely follows the pattern of ^{137}Cs reported by Gamble (1971). The concentration of ^{137}Cs was shown to be 1700 pCi/kg in the fresh litter, 3200 pCi/kg in the fermentation layer, 375 pCi/kg in the first 2 cm of mineral soil, and 0.09 pCi/kg in groundwater (about the same concentration as in the incoming rain). The same recycling mechanism that is removing potassium from the root zone may also be responsible for the continued high levels of ^{137}Cs after fallout levels had decreased. It has been hypothesized that mycorrhizal fungi perform this function (Gamble, 1971); the fruiting bodies of mushrooms show levels of ^{137}Cs of 10 to 50,000 pCi/kg and levels of potassium exceeding 12%.

The need for mycorrhizal fungi in the associative microorganism complex of pine plantations has long been established. The evidence for their having a similar effect in the hardwood ecosystem, however, is still largely inferential, but there are over 200 species of ectomycorrhizal fungi as well as several endomycorrhizal types in the study area. Mechanisms have been invoked in similar ecosystems to explain the slowness of the loss of nutrients through leaching from the soil. Stark (1973), for instance, discusses the effects of rhizomorph tissues from several kinds of soils in North, Central, and South

America on nutrient uptake, with different tissues showing different characteristics.

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REFERENCES

Aussenac, G., M. Bonneau, and F. LeTacon, 1972, Restitution des éléments minéraux au sol par l'intermédiaire de la litière et des précipitations dans quatre peuplements forestiers de l'est de la France, *Oecol. Plant.*, 7: 1-21.

Carlisle, A., A. H. F. Brown, and E. J. White, 1966, The Organic Matter and Nutrient Elements in the Precipitation Beneath a Sessile Oak Canopy, *J. Ecol.*, 54: 87-98.

Clements, R. G., and J. A. Colon, 1970, A Versatile Stemflow Collar for Interception Studies, in The Rain Forest Project, Annual Report, USAEC Report PRNC-147, pp. 7-9, Puerto Rico Nuclear Center.

Duvigneaud, P., 1968, Recherches sur l'écosysteme forêt. La Chênair—Frênaie à Coudrier du Bois de Weve, Aperçu sur la biomasse, la productivité et le cycle des éléments biogenes, *Bull. Soc. Roy. Bot. Belg.*, 101: 111-127.

___, and S. Denaeyer-DeSmet, 1970, Biological Cycling of Minerals in Temperate Deciduous Forests, in *Analysis of Temperate Forest Ecosystems*, D. E. Reichle (Ed.), pp. 199-225, Springer-Verlag, New York.

—, and S. Denaeyer-DeSmet, 1968, Biomass, Productivity and Mineral Cycling in Deciduous Mixed Forests in Belgium, in *Symposium on Primary Productivity and Mineral Cycling in Natural Ecosystems*, H. E. Young (Ed.), pp. 167-186, University of Maine Press, Orono.

Fiskell, J. G. A., and R. Ballard, 1973, Prediction of Phosphate Retention and Mobility in Florida Soils, in *Landspreading Municipal Effluent and Sludge in Florida*, Workshop, pp. 152-169, Institute of Food and Agricultural Sciences, University of Florida.

Gamble, J. F., 1971, A Proposed Mechanism for the Recycling of Radiocesium in Florida Soil Plant Systems, in *Radionuclides in Ecosystems*, Proceedings of the Third National Symposium on Radioecology, May 10-12, 1971, Oak Ridge, Tenn., D. J. Nelson (Ed.), USAEC Report CONF-710501-P1, pp. 133-139.

Hamilton, E. L., and P. B. Rowe, 1949, Rainfall Interception by Chaparral in California, California Department of Natural Resources, Division of Forestry, Sacramento.

[illegible]r, R. M., 1914, The "Pocosin" of Pike County, Alabama, and Its Bearing on Certain Problems of Succession, *Bull. Torrey Bot. Club*, 41: 209-220.

Helvey, J. D., and J. H. Patric, 1965, Canopy and Litter Interception of Rainfall by Hardwoods of Eastern United States, *Water Resour. Res.*, 1: 193-206.

Likens, G. E., and F. H. Bormann, 1971, Nutrient Cycling in Ecosystems, in *Ecosystem Structure and Function*, J. A. Wiens (Ed.), Proceedings of the 1970 Biology Colloquium, pp. 25-65, Oregon State University Press, Corvallis.

Lugo, A. E., S. C. Snedaker, and J. F Gamble, 1971, Models of Matter Flow in a Southern Mixed Hardwood Forest in Florida: Preliminary Results, in *Radionuclides in Ecosystems*, Proceedings of the Third National Symposium on Radioecology, May 10-12,

1971, Oak Ridge, Tenn., D. J. Nelson (Ed.), USAEC Report CONF-710501-P2, pp. 929-935.

Monk, C. D., 1966, An Ecological Significance of Evergreenness, *Ecology*, **47**: 504-505.

Ovington, J. D., 1968, Some Factors Affecting Nutrient Distribution Within Ecosystems, *UNESCO Natur. Resour. Res.*, **5**: 95-105.

Pritchett, W. L., and W H. Smith, 1974, Management of Wet Savanna Forest Soils for Pine Production, Technical Bulletin 762, Agricultural Experiment Station, University of Florida, Gainesville.

Roessler, C. E., G. S. Roessler, and B. G. Dunavent, 1969, Unusual Behavior of Cesium in the Florida Biosphere, *Quart. J., Fla. Acad. Sci.*, **32**: 1-11.

Stark, N., 1973, Nutrient Cycling in a Jeffrey Pine Forest Ecosystem, Clerical Depart University of Montana, Missoula.

Strain, B. R., 1971, Triangle Research Site Progress Report, 1970-1971, Eastern Deciduous Forest Biome Memo Report 71-93, U. S. International Biological Program.

Troug, E., and A. H. Meyer, 1929, Improvements in the Denige's Colorimetric Method for Phosphorus and Arsenic, *Ind. Eng. Chem., Anal. Ed.*, **1**: 136-139.

THE QUANTITY AND DISTRIBUTION OF FOUR NUTRIENT ELEMENTS IN HIGH-ELEVATION FOREST ECOSYSTEMS, BALSAM MOUNTAINS, NORTH CAROLINA

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ABSTRACT

The quantities and distribution patterns of four nutrients (Ca, K, Mg, and P) were determined in immature red spruce–Fraser fir, immature yellow birch, and mature yellow birch ecosystems. Relative quantities in these ecosystems decreased in the order Ca > K > Mg > P. Except for quantities of phosphorus which differentiated the immature ecosystems, the ecosystems could not be distinguished by the magnitude of nutrient pools. Nutrient sinks in decreasing order were, for calcium, vegetation ≈ forest floor > soil; for magnesium, phosphorus, and potassium in the spruce–fir ecosystem, forest floor > vegetation > soil; for potassium in the yellow birch ecosystem, vegetation ≈ forest floor ≈ soil. Proportional distributions of nutrients varied sufficiently within these general patterns to differentiate these ecosystems. Trees and shrubs ≥2.54 cm in diameter at breast height contained most of the nutrients in the vegetational compartment. Within this stratum, most of the nutrients were in boles in the spruce–fir ecosystem. Branches were of equal or greater importance than boles in yellow birch ecosystems. Mosses and herbs were important nutrient sinks in stands where habitats were suitable for their development. Within the forest floor, the largest quantities of calcium and magnesium were in the O1 horizon, and the largest quantities of potassium and phosphorus were in the O2 horizon, although intersystem variations occurred. The relative distribution of dry matter among compartments was not a reliable indicator of nutrient distributions within these ecosystems.

In this study the quantities and distribution patterns of Ca, K, Mg, and P were estimated and compared in adjacent red spruce (*Picea rubens* Sarg.)–Fraser fir [*Abies Fraseri* (Pursh) Poiret] and yellow birch (*Betula lutea* Michaux f.) ecosystems. Differences in the distribution of dry matter within these ecosystems (Weaver and DeSelm, 1973) and variations in nutrient concentrations of species (Scott, 1955; Likens and Bormann, 1970) suggested that each ecosystem might be further characterized by the magnitudes and locations of nutrient pools. These patterns might also provide useful insights concerning

functional processes and possible impact of perturbations, such as fire or timber harvesting, on the ecosystems.

THE STUDY AREA

The study area was between elevations of 1524 and 1954 m in the Balsam Mountains, Haywood and Jackson Counties, North Carolina. Cool summers, cold winters (Dickson, 1959), and a mean annual precipitation of 193 cm/year (Tennessee Valley Authority, 1970) characterize the climate. The area is within the southern section of the Blue Ridge province of the Appalachian highlands (Fenneman, 1938). Sandy loam Inceptisols (Sols Bruns Acides) derived from mica gneiss and mica schist residuum (Hadley and Goldsmith, 1963) predominate.

The original forests were northern hardwoods on protected sites, northern red oak on open slopes, and red spruce–Fraser fir at higher elevations (Holmes, 1911; Braun, 1950). A wide variety of successional types make up the present vegetation (Remseur, 1960). The current vegetational mosaic apparently reflects the past history of logging and burning, which were extensive between 1911 and 1930 (Korstian, 1937). Forty- to sixty-year-old stands of Fraser fir and red spruce occur at higher elevations in parts of the study area where either seed trees remained or burning was not intensive after logging (Korstian, 1937). Nearly pure and often extensive immature yellow birch stands of similar age are interspersed with spruce–fir stands. These occur where large quantities of logging slash accumulated, where spruce or fir seed trees were absent, or on previously burned sites (Korstian, 1937). Red spruce has not regenerated as successfully as Fraser fir, which now predominates in most of the coniferous stands. Occasional small stands of mature yellow birch, aged 100 years or more, persist in steep boulder-filled coves at the lower elevations of the study area.

METHODS

After a reconnaissance survey of forests in the study area, stands were stratified according to density and basal area of canopy dominants and by aspect factors. Fourteen spruce–fir, four immature yellow birch, and two mature yellow birch stands that represent the range of conditions encountered were selected for intensive study.

Most vegetational parameters of each stand were estimated by use of a set of concentric circular plots as follows: trees and tall shrubs, $\geqslant$2.54 cm in diameter at breast height (dbh), one 0.04-ha plot; saplings and low shrubs, $<$2.54 cm dbh and $\geqslant$0.46 m tall, one 0.009-ha plot; woody regeneration, $<$0.46 m tall, and herbs, three 0.0001-ha plots. Mosses were sampled by five 100-cm^2 quadrats randomly located within the perimeter of each 0.04-ha plot.

Total nutrient contents (kg/ha) in aboveground vegetation and forest floor were estimated from component nutrient concentrations and dry weights. Calcium, potassium, and magnesium concentrations were determined by flame emission spectrophotometry, and phosphorus concentrations were determined by the vanadomolybdophosphoric yellow method, after wet digestion by HNO_3-HClO_4-HCl (Freeman, 1965). Dry weights of woody strata $\geq$0.46 m tall were estimated by the every-tree-summation method (Shanks and Clebsch, 1962). Weights of components of these strata were estimated from stem diameters using regression equations developed from dimension analysis of trees shrubs harvested in the study area. Aboveground weights of other getational strata were estimated from clip samples from appropriate plots. Forest-floor detritis [O1 and O2 horizons (Soil Conservation Service, 1962)] weight was estimated as the sum of weights of dead, down boles and branches $\geq$2.54 cm in diameter, all other O1 horizon components, and the O2 horizon. The first group was sampled by harvesting boles and branches from four randomly selected 1- by 3-m quadrats.

Bulk soil samples collected from each horizon of one or two pits excavated within each plot were leached with 1*N* ammonium acetate (Jackson, 1958). Exchangeable calcium, magnesium, and potassium were determined by atomic absorption spectrophotometry. Acid-soluble phosphorus in these samples was determined by dilute acid–fluoride extraction and a molybdophosphoric blue method (Jackson, 1958, pp. 148-151, 159-161). These procedures, which are more sensitive than those used for plant and forest-floor samples, were selected because of anticipated low concentrations of phosphorus in these soils. Weights of nutrients in the soil fraction $\leq$2 mm in diameter in the A1 to B2 horizons were estimated by applying nutrient concentrations to estimates of soil weight. Nutrients in lower horizons were not included because roots were rarely encountered below B2.

RESULTS

Calcium

The amounts and distribution of calcium, which was present in the largest antities of the four nutrients, are given in Table 1 for each ecosystem. though some differences between totals in the ecosystems were indicated, variations among stands were large and ranges for ecosystems broadly overlapped; differences were not significant ($P < 0.10$). In each ecosystem the most important sinks were vegetation and the forest floor.

Ninety-one percent or more of the vegetational calcium was contained by the tree–tall shrub stratum. Mosses were the most important understory stratum, especially in the mature yellow birch ecosystem. Woody regeneration contained very small proportions of the calcium. In the tree–tall shrub stratum,

TABLE 1

QUANTITIES AND DISTRIBUTION OF CALCIUM IN THREE ECOSYSTEMS

Compartment	Spruce–fir		Immature yellow birch		Mature yellow birch	
	Mean*	SEE†	Mean*	SEE†	Mean*	SEE†
All compartments, kg/ha	768.5	81.4	931.5	145.7	755.4	147.4
Vegetation, %	51.0	4.6	42.6	8.6	43.6	8.4
Forest floor, %	39.8	4.0	42.6	3.6	48.8	
Soil, %	9.2	2.8	14.8	6.7	7.6	
Vegetation, aboveground, kg/ha	360.0	23.4	375.7	79.5	316.9	0.9
Trees and tall shrubs, %	98.4	0.4	96.9	1.4	91.0	2.1
Saplings and low shrubs, %	0.16	0.05	0.4	0.2	0.7	0.4
Woody regeneration, %	0.05	0.03	0.06	0.05	0.01	0.01
Herbs, %	0.26	0.06	0.6	0.4	0.4	0.1
Mosses, %	1.20	0.35	1.9	1.2	8.0	2.4
Forest floor, kg/ha	328.0	66.6	407.8	91.8	381.0	138.7
O1 horizon						
Boles and branches, %	25.2	4.5	33.4	11.4	0.4	0.3
Other components, %	47.5	4.3	39.5	6.6	47.7	0.6
O2 horizon, %	27.3	3.1	27.1	5.2	51.9	0.2
Soil, A1 to B2 horizons, kg/ha	80.7	26.4	148.0	88.6	57.4	7.8

*Means in compartments calculated from distributions within each sample plot.
†SEE = $S/\sqrt{n}$.

boles contained most of the calcium in the spruce–fir and mature yellow birch ecosystems (Table 2). Branches contained large proportions in yellow birch ecosystems and exceeded the proportions contained by boles in immature stands.

About 73% of the calcium in the forest floor in the spruce–fir and immature yellow birch ecosystems occurred in the O1 horizon (Table 1); however, calcium was distributed about equally between O1 and O2 horizons in the mature yellow birch ecosystem. This was due in part to the very small amount of calcium bole and branch litter in the mature ecosystem, but it also reflected a greater accumulation in the O2 horizon in this ecosystem. In each of the immature systems, similar proportions of forest-floor calcium were distributed between bole and branch and O2 components.

About 70% of the calcium in the soil, which contained the smallest quantity of any compartment, was in the A horizon in the spruce–fir and immature yellow birch ecosystems. In the mature yellow birch ecosystem, calcium was about evenly divided between the A and B horizons.

TABLE 2

DISTRIBUTION OF FOUR NUTRIENT ELEMENTS AMONG ABOVEGROUND COMPONENTS OF TREES AND TALL SHRUBS

Nutrient and component	Spruce–fir		Immature yellow birch		Mature yellow birch	
	Mean	SEE*	Mean	SEE*	Mean	SEE*
Calcium						
Boles, %	59.4	2.2	36.8	2.8	55.5	0.6
Branches, %	23.8	1.8	49.2	2.3	35.4	0.5
Foliage, %	16.8	0.7	14.0	0.8	9.1	0.1
Potassium						
Boles, %	54.6	1.7	40.4	3.0	61.5	0.1
Branches, %	20.1	0.9	34.7	1.8	23.7	0.1
Foliage, %	25.3	1.0	24.8	1.8	14.8	0.2
Magnesium						
Boles, %	62.8	0.9	33.0	2.4	44.5	0.6
Branches, %	20.3	0.6	44.6	1.8	37.4	0.3
Foliage, %	16.8	0.5	22.4	0.8	18.0	0.3
Phosphorus						
Boles, %	66.4	2.4	39.7	1.2	50.8	2.0
Branches, %	17.1	0.4	42.7	1.4	37.8	2.5
Foliage, %	16.5	2.3	17.6	1.2	11.4	0.4

*SEE = $S/\sqrt{n}$.

Potassium

Potassium, generally the second most abundant of the four elements, varied widely in quantities among stands within ecosystems. The average total amounts (Table 3) did not vary significantly ($P < 0.10$) between either spruce–fir and immature yellow birch or immature and mature yellow birch ecosystems. Rather large differences in distributional patterns distinguished spruce–fir and yellow birch ecosystems, however; the forest floor was the major potassium sink, and soil was the minor sink in the spruce–fir ecosystem. The distribution of potassium among the compartments was more nearly balanced in yellow birch ecosystems.

The major proportions of the potassium in the vegetational compartment were in the tree–tall shrub stratum although understory strata were more important sinks for potassium than for calcium. Herbs and mosses were especially important in the yellow birch ecosystems. Within the tree–tall shrub stratum, large proportions of the potassium were in boles in the spruce–fir and mature yellow birch ecosystem (Table 2). Branches contained the second largest amounts in the yellow birch ecosystems, but exact proportions varied between the two.

TABLE 3

QUANTITIES AND DISTRIBUTION OF POTASSIUM IN THREE ECOSYSTEMS

Compartment	Spruce–fir		Immature yellow birch		Mature yellow birch	
	Mean*	SEE†	Mean*	SEE†	Mean*	SEE†
All compartments, kg/ha	555.3	57.9	488.1	125.0	361.8	35.1
Vegetation, %	36.6	3.4	31.6	10.6	29.7	3.0
Forest floor, %	50.4	4.4	32.0	4.6	39.8	
Soil, %	13.0	4.5	36.4	14.5	30.5	
Vegetation, aboveground, kg/ha	187.2	13.8	119.5	17.6	106.4	0.6
Trees and tall shrubs, %	94.7	1.3	86.1	5.4	78.7	5.0
Saplings and low shrubs, %	0.40	0.11	1.1	0.5	1.0	0.6
Woody regeneration, %	0.14	0.08	0.3	0.2	0.03	0.03
Herbs, %	1.86	0.64	7.5	4.1	4.5	0.4
Mosses, %	2.95	0.88	5.0	3.1	15.7	2.4
Forest floor, kg/ha	287.9	48.5	139.4	14.0	143.6	11.4
O1 horizon						
Boles and branches, %	4.3	1.0	17.6	8.3	0.2	0.1
Other components, %	38.4	3.7	21.9	2.2	18.1	2.5
O2 horizon, %	57.3	3.7	60.4	7.6	81.6	2.8
Soil, A1 to B2 horizons, kg/ha	80.1	22.5	229.2	128.4	111.8	24.3

*Means in compartments calculated from distributions within each sample plot.
†SEE = $S/\sqrt{n}$.

Most of the potassium in the forest floor was in the O2 horizon, but exact proportions varied according to the ecosystem (Table 3). Potassium was about equally distributed between the components of the O1 horizon in the immature yellow birch ecosystems. In each of the other ecosystems, bole and branch litter contained only very small amounts. About 60% of soil potassium was in the A horizon of the spruce–fir and immature yellow birch ecosystems. In contrast, the B horizon contained two-thirds of the soil potassium in the mature ecosystem.

Magnesium

Magnesium was the third most abundant of the four elements in each ecosystem. Differences between total amounts in spruce–fir and immature yellow birch and between totals in immature and mature yellow birch ecosystems (Table 4) were not significant ($P < 0.10$). Quantities contained within individual compartments also did not vary significantly. Within each ecosystem, however, the forest floor was the major magnesium sink. The

TABLE 4

QUANTITIES AND DISTRIBUTIONS OF MAGNESIUM IN THREE ECOSYSTEMS

Compartment	Spruce–fir		Immature yellow birch		Mature yellow birch	
	Mean*	SEE†	Mean*	SEE†	Mean*	SEE†
All compartments, kg/ha	317.7	34.0	289.1	72.7	212.4	40.9
Vegetation, %	27.2	2.9	25.8	6.0	27.9	6.4
Forest floor, %	63.3	4.0	55.4	3.8	60.0	7.1
Soil, %	9.5	2.9	18.8	7.2	12.1	0.7
Vegetation, aboveground, kg/ha	76.9	3.9	62.8	10.8	56.4	2.4
Trees and tall shrubs, %	93.81	1.9	88.4	5.0	66.4	5.5
Saplings and low shrubs, %	0.42	0.13	1.8	0.6	0.9	0.6
Woody regeneration, %	0.61	0.12	0.3	0.2	0.04	0.04
Herbs, %	1.61	0.62	2.8	1.7	1.9	0.3
Mosses, %	4.82	1.51	7.2	4.3	30.8	6.4
Forest floor, kg/ha	210.7	31.6	161.8	43.2	130.4	39.8
O1 horizon						
Boles and branches, %	27.5	5.0	37.3	10.6	0.6	0.4
Other components, %	36.1	3.9	30.3	7.1	43.9	3.5
O2 horizon, %	36.4	4.6	32.3	5.5	55.5	4.0
Soil, A1 to B2 horizons, kg/ha	30.1	9.0	64.5	38.2	25.6	3.5

*Means in compartments calculated from distribution within each sample plot.
†SEE = $S/\sqrt{n}$.

smallest proportions were usually in the soil compartment, but in yellow birch ecosystems differences in contents of vegetation and soils were reduced.

Trees and tall shrubs contained the largest amounts of vegetational magnesium. The proportional content of magnesium was not as great in this stratum in the mature yellow birch as in the other systems, however. In the mature ecosystem, mosses contained nearly 31% of the vegetational magnesium. Within the tree–tall shrub stratum of the spruce–fir ecosystem, most of the magnesium was contained in boles (Table 2). Branches were particularly important as sinks in yellow birch ecosystems.

Nearly two-thirds of the magnesium in the forest floor was contained in the O1 horizon in the spruce–fir and immature yellow birch ecosystems (Table 4). Of the total in this horizon, a significant proportion was contained in boles and branches. These components contained a very small proportion of the forest-floor magnesium in the mature yellow birch ecosystem. More than one-half of the soil magnesium was in A horizon of the immature yellow birch and spruce–fir ecosystems. In the mature yellow birch ecosystem, only about 40% was in the A horizon.

Phosphorus

Phosphorus was the least abundant of the four nutrients and least variable among stands within ecosystems. The average quantity (Table 5) in the immature yellow birch ecosystem was significantly lower than in either the spruce–fir ($P < 0.05$) or the mature yellow birch ($P < 0.10$) ecosystems. These differences were primarily due to smaller quantities of phosphorus in the forest floor in the immature yellow birch ecosystem. In each ecosystem, however, the forest floor was the major phosphorus sink (Table 5). The relative proportions in vegetation and soil varied between ecosystems.

The largest fraction of vegetational phosphorus was contained in the tree–tall shrub stratum, but mosses contained 20% of the ecosystem total in the mature yellow birch ecosystem. In the spruce–fir ecosystem, about two-thirds of the phosphorus in the tree–tall shrub stratum was in boles, and the remainder was equally divided between branches and foliage (Table 2). Both boles and branches contained relatively large proportions of phosphorus in the yellow birch ecosystems, but some intersystem differences were suggested.

TABLE 5

QUANTITIES AND DISTRIBUTION OF PHOSPHORUS IN THREE ECOSYSTEMS

Compartment	Spruce–fir		Immature yellow birch		Mature yellow birch	
	Mean*	SEE†	Mean*	SEE†	Mean*	SEE†
All compartments, kg/ha	142.1	11.7	104.9	8.8	126.0	2.3
Vegetation, %	29.4	2.4	30.7	4.4	21.3	0.6
Forest floor, %	63.7	2.8	47.8	5.1	59.5	4.5
Soil, %	6.9	0.8	21.5	4.8	19.2	5.2
Vegetation, kg/ha	39.1	2.4	32.2	5.2	26.8	0.3
Trees and tall shrubs, %	93.98	1.90	90.4	2.4	77.4	6.9
Saplings and low shrubs, %	0.30	0.80	1.6	1.0	1.0	0.6
Woody regeneration, %	0.13	0.09	0.2	0.2	0.04	0.04
Herbs, %	0.88	0.30	2.4	1.4	1.9	0.[illegible]
Mosses, %	4.89	1.64	5.5	3.3	19.7	7.[illegible]
Forest floor, kg/ha	93.6	10.5	49.2	3.5	74.8	4.4
O1 horizon						
Boles and branches, %	1.9	0.4	11.9	6.8	0.1	0.07
Other components, %	44.5	3.3	26.3	0.3	14.5	3.2
O2 horizon, %	53.6	3.3	61.2	7.1	85.4	3.3
Soil, A1 to B2 horizons, kg/ha	9.4	1.3	23.5	7.0	24.4	7.0

*Means in compartments calculated from distributions within each sample plot.
†SEE = $S/\sqrt{n}$.

The distribution of phosphorus was relatively uniform between O1 and O2 horizons of the spruce–fir forest floor, but, in both yellow birch ecosystems, phosphorus was strongly concentrated in the O2 horizon. Proportions in bole and branch components were especially small in the spruce–fir and mature yellow birch ecosystems. Soil phosphorus was about evenly distributed between A and B horizons in soils of the spruce–fir and immature yellow birch ecosystems. In the mature yellow birch ecosystem, 77% of the soil phosphorus was in the B1 and B2 horizons.

DISCUSSION

The nutrient contents of these ecosystems undoubtedly were underestimated because faunal and root components were omitted from consideration. Although the nutrient contents of the faunal components are probably small on an area basis (Grimshaw et al., 1958), roots may contain between 5 and 15% of the total nutrients in forest ecosystems (Rennie, 1955; Ovington, 1962).

Accurate determination of nutrient amounts in the biosphere, i.e., included within nutrient cycles, is particularly difficult because of inadequate knowledge of the forms in which soil nutrients are available to trees. Estimates of soil nutrient pools have been based on analyses of total nutrients (Weetman and Webber, 1972) or on exchangeable or easily soluble nutrients, as in this and other studies (Weetman and Webber, 1972). Although using total nutrients probably gives overestimates of nutrient pools, using exchangeable nutrients surely gives underestimates (Kramer and Kozlowski, 1960). Potassium is apparently available to trees through direct uptake from biotite (Voigt, 1965), which occurs in soils in the study area (Hadley and Goldsmith, 1963). It is also likely that supplies of undetermined magnitude of each nutrient are mobilized from geologic substrates by mycorrhizae (Voigt, 1971), but the processes are poorly understood (Bowen, 1973). To properly characterize these ecosystems on the basis of compartmental nutrient pools and to evaluate the impact of such perturbations as fire and timber harvesting, we must determine the availability of nutrients from these sources.

The amounts of Ca, K, Mg, and P relative to one another were similar to those reported for several other coniferous and temperate deciduous forests (Rennie, 1955; Shanks, Clebsch, and DeSelm, 1961; Ovington, 1962; Rodin and Bazilevich, 1968; Weetman and Webber, 1972). Absolute quantities of each were large in comparison with levels in Canadian spruce–fir ecosystems in which total pool sizes were estimated (Weetman and Webber, 1972). Compared with other ecosystems for which pool size estimates are available for one or two compartments (Rennie, 1955; Ovington, 1962; Rodin and Bazilevich, 1968; Weetman and Timmer, 1967; Gessel and Balci, 1965; Wooldridge, 1970; Damman, 1971), forest-floor pools tend to be large, soil pools small (except for

potassium), and vegetational pools typical in the study-area ecosystems. The quantities of soil potassium may reflect the presence of biotite in the soils.

Differences among quantities of nutrients were not sufficient to distinguish between ecosystems, except for phosphorus pool sizes. Large stand-to-stand variations in pool sizes seem to characterize each of these ecosystems, but quantities of phosphorus seemed to be less variable among stands than quantities of the other nutrients. More intensive sampling, especially of forest-floor and soil compartments, than was possible in this study is needed to adequately evaluate apparent similarities of pool sizes in these ecosystems.

There was sufficient variation (differences significant at $P < 0.10$) f general distribution patterns of some nutrients to differentiate between th ecosystems. Spruce–fir and yellow birch ecosystems were distinguished by the smaller soil nutrient pools and by larger accumulations of potassium, magnesium, and phosphorus in the forest floor in the spruce–fir. Comparisons also indicated that the forest floor in the mature yellow birch ecosystem contained proportionately larger quantities of magnesium and phosphorus than that in the immature yellow birch ecosystem. Within the forest floor, there was a greater accumulation of nutrients in the O2 horizon in the mature as compared with either the immature yellow birch or spruce–fir ecosystems. Larger proportions of nutrients in O1 bole and branch components, which differentiated immature yellow birch ecosystems, reflect a large accumulation of these components due to intensive natural thinning that is occurring in these stands. The larger nutrient content of branches in each yellow birch ecosystem, as compared with the spruce–fir ecosystem, is attributed to the proportionately larger biomass (Weaver and DeSelm, 1973) and greater nutrient concentrations (Weaver, 1973) in branches in these ecosystems.

A major role for mosses and herbs, including ferns, in nutrient storage in these ecosystems is indicated. Because of high nutrient concentrations in herbs (Weaver, 1973) the proportion of total ecosystem organic matter in herbaceous strata is a poor indicator of the importance of these strata in ecosystem nutrient dynamics. Although the dominant species varied between ecosystems and with respect to nutrients (Weaver, 1973), these strata were important in stands where site conditions were favorable for their development. The importance of mosses was greatest in the mature yellow birch ecosystem where a relatively large biomass could be supported because of th presence of boulder fields that provide favorable habitats. Ferns and herbace angiosperms were most important in spruce–fir and immature yellow birch ecosystems, respectively.

Differences between distributional patterns within the forest floor may be related to relative nutrient mobility. Since calcium, a structural component (Kramer and Kozlowski, 1960), is not as readily leached from decomposing litter as potassium and magnesium are (Gosz, Likens, and Bormann, 1973), its retention in the O1 horizon would be expected. The differences between forest-floor horizons should be further accentuated by rapid leaching of any mineralized

calcium that reaches the acid O2 horizons occurring in these ecosystems (Weaver, 1973).

Potassium, which is highly susceptible to leaching from decomposing litter (Gosz, Likens, and Bormann, 1973), was easily removed from O1 components. The proportionately large quantities in the O2 horizon may indicate fixation by expanding-layer silicates that may be present in this stratum (Wolfe, 1967) and by potassium released from soil mineral material during digestion of samples. The O2 horizon, which is not always easily delineated from the A1 horizon of these soils, contained as much as 53% incorporated mineral material (Weaver, 1973).

Some removal of phosphorus from litter by leaching would be expected (Attiwill, 1967), but low concentrations in bole and branch components seemed to be the principal factor contributing to the small contents in the O1 horizon. The low phosphorus concentrations were due to the loss of bark which, as compared with wood, contained much of the phosphorus in bole and branch components (Weaver, unpublished data).

The relatively large amount of phosphorus in the O2 horizon suggests immobilization of both organic and inorganic forms. Plant residues contain phytin, which is one of the compounds in which organic phosphorus occurs in humus (Stevenson, 1964). As decomposition proceeds insoluble iron and aluminum phytates, which are not readily metabolized by microbes, form. Furthermore, any inorganic phosphates that are present are probably fixed by double decomposition reactions involving iron and aluminum which predominate under the low hydroxyl ion concentrations (Kardos, 1964; Wolfe, 1967) characteristic of most O2 horizons in the study area.

Magnesium leached from decomposing litter (Gosz, Likens, and Bormann, 1973) might be expected to accumulate in the O2 horizon and have a distributional pattern similar to that of other mobile nutrients. Its distributional pattern was actually similar to that of calcium, however. This suggests either that magnesium is less mobile in these ecosystems as compared with others or that mechanisms for immobilizing magnesium, which are comparable to those postulated for potassium and phosphorus, are less efficient in the O2 horizon. If so, then mineralized magnesium could be rapidly leached or reabsorbed by plants, and the proportion in the O2 horizon would remain small. The small proportions of each nutrient in boles and branches in the mature yellow birch ecosystem primarily reflect the small standing crop of these components characteristic of this ecosystem.

This study also indicated that the distribution of most nutrients among compartments differed significantly from the distribution of dry matter (Weaver and DeSelm, 1973). The proportion of ecosystem nutrients contained in the vegetation was usually larger than the corresponding proportion of organic matter. The forest floor was much more important as a sink for nutrients than was organic matter in each ecosystem. The soil, which contained very small proportions of ecosystem nutrients (except potassium in certain cases),

contained as much as 73% of the organic matter estimated for these systems. Intensive leaching of absorbed ions from these acid soils is suggested.

This study suggests that the effects of such perturbations as timber harvesting and fire on nutrient pools would vary both among nutrients and ecosystems. Harvesting trees, for example, should affect the nutrient pools in yellow birch ecosystems less than in the spruce–fir ecosystem because of the higher importance of bryophytes and herbs in the yellow birch ecosystems. Fire and/or timber harvesting, which would diminish the forest floor (Wright, 1957), could affect magnesium and phosphorus pools more than potassium and calcium pools. Differences between the distribution of nutrients in O1 and O2 horiz suggest that effects on nutrient pools could also vary with the intensity of f Depletion of the forest floor by extensive burning in parts of the Balsam Mountains (Korstian, 1937) and subsequent loss of nutrients through leaching and erosion may partially explain the slow redevelopment of forests which seems to characterize certain sections of the area (Ramseur, 1960).

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REFERENCES

Attiwill, P. M., 1967, The Loss of Elements from Decomposing Litter, *Ecology*, 4 142-145.

Bowen, G. D., 1973, Mineral Nutrition of Ectomycorrhizae, in *Ectomycorrhizae*, G. Marks and T. T. Kozlowski (Eds.), pp. 151-205, Academic Press, Inc., New York.

Braun, E. L., 1950, *Deciduous Forests of Eastern North America*, Blakiston Company, Philadelphia.

Damman, A. W. H., 1971, Effect of Vegetation Changes on the Fertility of a Newfoundland Forest Site, *Ecol. Monogr.*, 41: 253-270.

Dickson, R. R., 1959, Some Climate–Altitude Relationships in the Southern Appalachian Mountain Region, *Bull. Amer. Meteorol. Soc.*, 40: 352-359.

Fenneman, N. M., 1938, *Physiography of Eastern United States*, McGraw-Hill Book Company, New York.

Freeman, C. E., 1965, The Effect of Potassium Fertility Levels on the Uptake and Utilization of Potassium, Calcium, and Magnesium by Corn Inbreds and Hybrids, Master's Thesis, The University of Tennessee, Knoxville.

Gessel, S. P., and A. N. Balci, 1965, Amount and Composition of Forest Floors Under Washington Coniferous Forests, in *Forest-Soil Relationships in North America*, Proceedings of the Second North American Forest Soils Conference, C. T. Youngberg (Ed.), pp. 11-23, Oregon State University Press, Corvallis, Ore.

Gosz, J. A., G. E. Likens, and F. H. Bormann, 1973, Nutrient Release from Decomposing Leaf and Branch Litter in the Hubbard Brook Forest, New Hampshire, *Ecol. Monogr.*, **43**: 173-191.

Ingshaw, H. M., J. D. Ovington, M. M. Betts, and J. A. Gibb, 1958, The Mineral Content of Birds and Insects in a Plantation of *Pinus sylvestris* L., *Oikos*, 9: 26.

Hadley, J. B., and R. Goldsmith, 1963, Geology of Eastern Great Smoky Mountains, North Carolina and Tennessee, *U. S., Geol. Surv., Prof. Pap.*, **349-B**: B1-B118.

Holmes, J. S., 1911, Forest Conditions in Western North Carolina, The North Carolina Geological and Economic Survey, Bulletin No. 23.

Jackson, M. L., 1958, *Soil Chemical Analysis*, Prentice-Hall, Inc., Englewood Cliffs, N. J.

Kardos, L. T., 1964, Soil Fixation of Plant Nutrients, in *Chemistry of the Soil*, F. E. Bear (Ed.), 2nd ed., pp. 369-394, Reinhold Publishing Corporation, New York.

Korstian, C. F., 1937, Perpetuation of Spruce on Cut-Over and Burned Lands in the Higher Southern Appalachian Mountains, *Ecol. Monogr.*, **7**: 125-167.

Kramer, P. J., and T. T. Kozlowski, 1960, *Physiology of Trees*, McGraw-Hill Book Company, New York.

Likens, G. E., and F. H. Bormann, 1970, Chemical Analysis of Plant Tissues from the Hubbard Brook Ecosystem in New Hampshire, Yale University School of Forestry, Bulletin No. 79.

Ovington, J. D., 1962, Quantitative Ecology and the Woodland Ecosystem Concept, *Advan. Ecol. Res.*, **1**: 103-203.

Ramseur, G. S., 1960, The Vascular Flora of High Mountain Communities of the Southern Appalachians, *J. Elisha Mitchell Sci., Soc.*, **76**: 82-112.

Rennie, P. J., 1955, The Uptake of Nutrients by Mature Forest Growth, *Plant Soil*, **7**: 49-95.

Rodin, L. E., and N. I. Bazilevich, 1968, *Production and Mineral Cycling in Terrestrial Vegetation*, translated by G. E. Fogg, Oliver and Boyd, Ltd., London.

Scott, D. R. M., 1955, Amount and Chemical Composition of the Organic Matter Contributed by Overstory and Understory Vegetation to Forest Soil, Yale University School of Forestry, Bulletin No. 62.

Shanks, R. E., and E. E. C. Clebsch, 1962, Computer Programs for the Estimation of Forest Stand Weight and Mineral Pool, *Ecology*, **43**: 339-341.

——, E. E. C. Clebsch, and H. R. DeSelm, 1961, Estimates of Standing Crop and Cycling Rate of Minerals in Appalachian Ecosystems, paper presented at the Symposium on Cycles of Biologically Important Elements in Ecological Systems, American Institute of Biological Sciences meetings, Purdue University, Lafayette, Ind., mimeographed.

Soil Conservation Service, 1962, Supplement to Soil Survey Manual (Agriculture Handbook No. 18), U. S. Department of Agriculture.

Stevenson, I. L., 1964, Biochemistry of Soil, in *Chemistry of the Soil*, F. E. Bear (Ed.), 2nd ed., pp. 242-291, Reinhold Publishing Corporation, New York.

Tennessee Valley Authority, 1970, Precipitation in Tennessee River Basin, Annual Report No. 0-243.

Voigt, G. K., 1971, Mycorrhizae and Nutrient Mobilization, in Mycorrhizae, Proceedings of the First North American Conference on Mycorrhizae, April 1969, E. Hacskaylo (Ed.),

pp. 122-131, U. S. Department of Agriculture, Forest Service, Miscellaneous Publication No. 1189.

——, 1965, Biological Mobilization of Potassium from Primary Minerals, in *Forest-Soil Relationships in North America,* Proceedings of the Second North American Forest Soils Conference, C. T. Youngberg (Ed.), pp. 33-46, Oregon State University Press, Corvallis, Ore.

Weaver, G. T., 1973, Biomass and Nutrient Pools in Herbaceous Strata in Contrasting Ecosystems, in Proceedings of the International Geobotany Conference, Mar. 2-4, 1973, Knoxville, Tenn.

——, and H. R. DeSelm, 1973, Biomass Distributional Patterns in Adjacent Coniferous and Deciduous Forest Ecosystems, in *Biomass Studies,* pp. 415-427, International Union Forest Research Organizations, Working Party on the Mensuration of Forest Biom College of Life Sciences and Agriculture, University of Maine, Orono.

Weetman, G. F., and V. Timmer, 1967, Feather Moss Growth and Nutrient Content Under Upland Black Spruce, Woodland Research Index No. 183, Pulp and Paper Research Institute of Canada.

——, and B. Webber, 1972, The Influence of Wood Harvesting on the Nutrient Status of Two Spruce Stands, *Can. J. Forest Res.,* **2**: 351-369.

Wolfe, J. A., 1967, Forest Soil Characteristics as Influenced by Vegetation and Bedrock in the Spruce–Fir Zone of the Great Smoky Mountains, Ph. D. Thesis, The University of Tennessee, Knoxville.

Wooldridge, D. D., 1970, Chemical and Physical Properties of Forest Litter Layers in Central Washington, in *Tree Growth and Forest Soils,* Proceedings of the Third North American Forest Soils Conference, C. T. Youngberg and C. B. Davey (Eds.), pp. 327-337, Oregon State University Press, Corvallis, Ore.

Wright, T. W., 1957, Some Effects of Thinning on the Soil of a Norway Spruce Plantation, *Forestry,* **30**: 123-133.

SIGNIFICANCE OF BIOLOGICAL NITROGEN FIXATION AND DENITRIFICATION IN A DECIDUOUS FOREST ECOSYSTEM

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ABSTRACT

Gaseous transformations of nitrogen were quantified in relation to other components of the nitrogen cycle of a mixed deciduous forest ecosystem at the Coweeta Hydrologic Laboratory, North Carolina. Rates and total annual amounts of nitrogen fixation and potential denitrification were measured for several components of the litter–soil subsystem (decaying logs, woody and leaf litter, and general soil layers) of a mature oak–hickory forest. Highest rates of both processes were observed in leaf and woody litter, but highest totals occurred in the soil. Of the total nitrogen input, including that via bulk precipitation, biological fixation accounted for 75%. Potential denitrification losses exceeded stream-water losses by 200 times. Our results show that consideration must be given to both levels of activity and total fluxes in any examination of the forest nitrogen cycle and that existing pools of nitrogen may not indicate the magnitude of gaseous transformations that are occurring.

Evidence is continuing to accumulate which emphasizes the importance of biological nitrogen transformations to the functioning of forest ecosystems. Especially important are the gaseous processes of nitrogen fixation and denitrification. Yet our knowledge of these processes, especially of their magnitudes in relation to other nitrogen transfers, such as meteorologic inputs and outputs, is incomplete. As part of our investigations of nutrient circulation in southern Appalachian forested ecosystems, we have measured nitrogen gains and losses via nitrogen fixation and denitrification for various components of the litter–soil subsystem of a deciduous forest ecosystem (Todd, 1971, 1973; Cornaby and Waide, 1972, 1973). In this paper we report mean rates and total annual nitrogen transfers for these two processes for several forest-floor components and compare the magnitudes of the gaseous inputs and outputs with those of bulk precipitation and stream water.

METHODS

The experimental area is a gauged 12.4-ha mature hardwood watershed (WS18) at the Coweeta Hydrologic Laboratory, Franklin, N.C. This watershed is one of the intensive study areas of the Coweeta site of the Eastern Deciduous Forest Biome, U. S. International Biological Program. A description of the Coweeta basin and of the experimental watershed is given by Johnson and Swank (1973).

The components of the litter–soil subsystem sampled are decaying twigs, decaying branches and logs (less and more decayed), leaf litter (L and H layers), and soil (depths of 0 to 10, 10 to 20, and 20 to 40 cm). Methods of sampling woody litter and the criteria for separating this material into more and less decayed are given in Cornaby and Waide (1973). A description of the litter- and soil-sampling procedures followed appear in Todd (1971). Data compared in this paper represent mean values determined for each substrate at several time intervals throughout 1 year.

Nitrogen-fixation rates were quantified using the acetylene–ethylene method described by Hardy et al. (1968, 1973). Samples were collected in 140- or 220-ml glass jars with lids fitted with rubber serum stoppers. After being transported back to the laboratory, each container received an atmosphere of 20% acetylene. Following incubation at 18°C for 18 to 24 hr, 1 ml of the atmosphere was removed, and the ethylene–acetylene content was determined by gas chromatography by comparisons to standard gas atmospheres. Ethylene production was linear up to 24 hr. A Varian Aerograph Series 1400 gas chromatograph connected to a Varian A-25 strip-chart recorder was used for these analyses. The column (10 ft by ¼ in.) was filled with Porapak R (80 to 100 mesh) and operated at 50°C. Injection temperature was set at 75°C, and detector (flame ionization) temperature, at 110°C. Concentrations of ethylene were identified by comparison to a gas standard (Fisher Scientific, Atlanta). Dry weight of each sample was determined following analysis by drying to constant weight at 75°C. Activity is expressed on a dry weight per 24-hr basis.

Denitrification rates were measured with the N_2O incubation method (Barbaree and Payne, 1967; Payne, 1973; Todd and Nuner, 1973). The samples, again contained in 140- or 220-ml screw-top jars with lids fitted with serum stoppers, were flushed with N_2O for 10 min. After incubation at 18°C for 18 to 24 hr, 0.2 or 0.5 ml of the gas atmosphere over each sample was removed and injected into an F and M Model 700 gas chromatograph connected to an Infotronics integrator and Honeywell strip-chart recorder. The column (19.5-ft by ⅛-in. stainless steel packed with Porapak Q) was operated at ambient temperature. Nitrogen was detected by a thermal conductivity detector operating at 250°C and 150 mA. Activity is expressed on a dry-weight basis per 24-hr period.

RESULTS AND DISCUSSION

The techniques used to quantify rates of nitrogen fixation and denitrification in this study yield estimates of relative activity. This is especially true of the denitrification measurements since N_2O represents an intermediate substrate common to several pathways in the nitrogen cycle and because the samples were assayed under optimum incubation conditions. However, we do feel confident that our estimates are reasonably accurate and that the estimate of nitrogen fixation may be a conservative one.

Measured mean rates and estimated annual fluxes for nitrogen fixation and denitrification are shown in Table 1. These data show that the highest activities for both nitrogen fixation and denitrification were obtained in woody and leaf litter, with measured rates being generally an order of magnitude higher than rates in the soil. However, when considered on a surface-area basis over an annual cycle, the largest nitrogen transformation within this watershed occur in the soil owing to the greater mass of soil. These results indicate that consideration must be given to levels of activity as well as to total fluxes in any

TABLE 1

NITROGEN FIXATION AND POTENTIAL DENITRIFICATION IN THE FOREST-FLOOR PROFILE OF A MIXED HARDWOOD WATERSHED (WATERSHED 18) AT COWEETA

	Nitrogen fixation		Denitrification	
Substrate	nmoles N g^{-1} day^{-1}	kg N ha^{-1} $year^{-1}$	nmoles N g^{-1} day^{-1}	kg N ha^{-1} $year^{-1}$
Twigs	21.24	0.27	Nd*	Nd*
Branches				
Less decayed	5.40	0.08	12.24	0.17
More decayed	13.06	0.09	6.78	0.05
Logs				
Less decayed	4.67	0.30	25.01	1.61
More decayed	14.34	0.92	25.55	1.63
Litter				
L layer	1.53	0.03	Nd*	Nd*
H layer	7.90	0.63	9.63	0.08
Soils				
0 to 10 cm	0.36	4.04	25.69	11.90
10 to 20 cm	0.17	1.77	2.42	2.47
20 to 40 cm	0.13	2.72	0.13	0.25
Total		10.85		18.16

*Not determined.

TABLE 2

MEASUREMENT OF BIOLOGICAL NITROGEN FIXATION IN SOILS USING THE ACETYLENE REDUCTION TECHNIQUE

Soil	Nitrogen fixed, kg N ha^{-1} $year^{-1}$	Reference
Agricultural		
California	2 to 5	Steyn and Delwiche (1970)
Pennsylvania	0.7 to 30	Hardy et al. (1968, 1971)
Sweden (algal mat)	15 to 51	Henriksson (1971)
Rice paddy	10.0	Rinando et al. (1971)
Grassland		
Canada		
(virgin)	0.2 to 3.4	Paul et al. (1971)
(cultivated)	0.0 to 0.1	Vlassak et al. (1973)
Colorado	<0.2	Copley and Reuss (1972)
Desert		
Arizona		
(algal mat)	26 to 35	MacGregor and Johnson (1971)
Sand dune	0.1 to 0.9	Akkermans cited by Hardy et al. (1973)
Saline soil	0.0	Hauke-Pacewiczowa et al. (1970)
Coniferous forest		
Douglas fir	6.9 to 13.8	Jones (1970)
Mixed conifers	0.38 to 24.5	Silvester and Bennett (1973)
Loblolly pine	0.03 to 0.9	Jorgensen and Wells (1971)
Tropical rain forest	88.0	Edmisten (1970)
Deciduous forest		
Mixed hardwood	4.7 to 14.1	This study

examination of the forest nitrogen cycle. Further, our data suggest that existing pools of nitrogen may not indicate the magnitude of gaseous transformations that are occurring and that rates of nitrogen transformations are related to the carbon content of the substrate.

These estimates of annual amounts of nitrogen fixation and denitrification are quite large, suggesting that gaseous transformations represent major inputs and outputs of nitrogen for the forest-floor subsystem. Nitrogen input in bu[illegible] precipitation averaged 3.4 kg ha^{-1} $year^{-1}$ (Swank and Henderson, 1974), outp[illegible] in stream water 0.08 kg ha^{-1} $year^{-1}$ (Waide and Swank, 1974), and output in sediments, 0.23 kg ha^{-1} $year^{-1}$ (Monk, this volume) for the same watershed. Of the total nitrogen input to this watershed, approximately 75% appears to enter via biological fixation within the forest floor, whereas potential denitrification losses could exceed stream-water losses by about 200 times. Thus gaseous inputs and outputs of nitrogen represent major components of the forest nitrogen cycle and appear to dominate total gains and losses.

Total nitrogen input to the forest ecosystem considered in this study is about 14 kg ha^{-1} $year^{-1}$, whereas total output averages about 18 kg ha^{-1} $year^{-1}$. These data suggest that this watershed may be slowly losing nitrogen. However, we have not yet quantified rates of epiphytic nitrogen fixation in the aboveground vegetation. Additionally, estimates of nitrogen input in bulk precipitation may be low since particulate organic inputs of nitrogen have been ignored (Swank and Henderson, 1974). Further, our measurements of denitrification activity have the potential of being an overestimate. Data of the type obtained in extended studies of this nature currently under way may yield estimates of nitrogen inputs and outputs which show closer agreement.

Estimates of nitrogen fixation obtained in this study (soil only) are compared in Table 2 with similar values for a number of other ecosystems. To our knowledge, annual values of nitrogen fixation have not been previously reported for a deciduous forest ecosystem. However, values determined in the current study compare favorably with estimates for coniferous forests. Of the three types of natural ecosystems considered (desert, grassland, and forest), the data in Table 2 suggest that nitrogen fixation may represent a significant nitrogen input only for forests. Although the value given for the desert algal mat is high, its areal extent is small. However, West (1974) reported a value of 16 kg ha^{-1} $year^{-1}$ for nitrogen fixation in a desert ecosystem, most of which could be attributed to a blue–green algal crust covering the soil surface. It is also apparent from Table 2 that values reported for forests are not that much smaller than for agricultural systems. Further studies are needed to substantiate these trends.

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REFERENCES

Daree, J. M., and W. J. Payne, 1967, Products of Denitrification by a Marine Bacterium as Revealed by Gas Chromatography, *Mar. Biol.*, 1: 136-139.

Copley, P. W., and J. O. Reuss, 1972, Evaluation of Biological N_2 Fixation in a Grassland Ecosystem, Grassland Biome, Technical Report No. 152, U. S. International Biological Report Program.

Cornaby, B. W., and J. B. Waide, 1973, Nitrogen Fixation in Decaying Chestnut Logs, *Plant Soil*, 39: 445-448.

——, and J. B. Waide, 1972, Nitrogen Fixation, Nutrient Contents, and Microbial Densities of Decaying Chestnut Logs in a Temperate Forest Ecosystem, Eastern Deciduous Forest Biome Memo Report No. 72-54, U. S. International Biological Program.

Edmisten, J. A., 1970, Preliminary Studies of the Nitrogen Budget of a Tropical Rain Forest, in A Tropical Rain Forest, H. T. Odum and R. F. Pigeon (Eds.), USAEC Report Tid-24270, Book 3, Chap. H-21, pp. H211-H215.

Hardy, R. W. F., R. C. Burns, R. R. Herbert, R. D. Holsten, and E. K. Jackson, 1971, Biological Nitrogen Fixation: A Key to World Protein, in *Biological Nitrogen Fixation in Natural and Agricultural Habitats,* T. A. Lie and E. G. Mulder (Eds.), pp. 561-590, a special volume of *Plant and Soil,* the Hague.

——, R. C. Burns, and R. D. Holsten, 1973, Applications of the Acetylene–Ethylene Assay for Measurement of Nitrogen Fixation, *Soil Biol. Biochem.,* 5: 47-81.

——, R. D. Holsten, E. K. Jackson, and R. C. Burns, 1968, The Acetylene–Ethylene Assay of N_2 Fixation: Laboratory and Field Evaluation, *Plant Physiol.,* 43: 1185-1207.

Hauke-Pacewiczowa, T., J. Balendreau, and Y. Dommergues, 1970, Fixation Microbienne l'Azote dans un Sol Salinin Tunisien, *Soil Biol. Biochem.,* 2: 47-53.

Henriksson, E., 1971, Algal Nitrogen Fixation in Temperate Soils, in *Biological Nitrogen Fixation in Natural and Agricultural Habitats,* T. A. Lie and E. G. Mulder (Eds.), pp. 475-479, a special volume of *Plant and Soil,* the Hague.

Johnson, P. L., and W. T. Swank, 1973, Studies of Cation Budgets in the Southern Appalachians on Four Experimental Watersheds with Contrasting Vegetation, *Ecology,* 54: 70-80.

Jones, K., 1970, Nitrogen Fixation in the Phyllosphere of Douglas Fir, *Ann. Bot. (London),* 34: 239-244.

Jorgensen, J. R., and C. G. Wells, 1971, Apparent Nitrogen Fixation in Soil Influenced by Prescribed Burning, *Soil Sci. Soc. Amer. Proc.,* 35: 806-810.

MacGregor, A. N., and D. E. Johnson, 1971, Capacity of Desert Algal Crusts to Fix Atmospheric Nitrogen, *Soil Sci. Soc. Amer. Proc.,* 35: 843-844.

Paul, E. A., R. J. Myers, and W. A. Rice, 1971, Nitrogen Fixation in Grasslands and Associated Cultivated Ecosystems, in *Biological Nitrogen Fixation in Natural and Agricultural Habitats,* T. A. Lie and E. G. Mulder (Eds.), pp. 495-507, a special volume of *Plant and Soil,* the Hague.

Payne, W. J., 1973, The Use of Gas Chromatography for Studies of Denitrification in Ecosystems, *Bull. Ecol. Res. Comm., NFR,* 17: 263-268.

Rinando, R., J. Balandreau, and Y. Dommergues, 1971, Algal and Material Nonsymbiotic Nitrogen Fixation in Paddy Soils, in *Biological Nitrogen Fixation in Natural and Agricultural Habitats,* T. A. Lie and E. G. Mulder (Eds.), pp. 471-479, a special volume of *Plant and Soil,* the Hague.

Silvester, W. B., and K. H. Bennett, 1973, Acetylene Reduction by Roots and Associated Soil by New Zealand Conifers, *Soil Biol. Biochem.,* 5: 171-179.

Steyn, P. L, and C. C. Delwiche, 1970, Nitrogen Fixation by Nonsymbiotic Microorganisms in Some Southern California Soils, *Environ. Sci. Technol.,* 4: 1122-1128.

Swank, W. T., and G. S. Henderson, 1974, Atmospheric Input of Some Cations and Anions to Forest Ecosystems in North Carolina and Tennessee, paper presented at the Symposium on Chemistry of Atmospheric Precipitation, 55th Annual Meeting, American Geophysical Union, Washington, D. C., April 1974.

Todd, R. L., 1973, Microbial Dynamics of Nitrogen in Forested Ecosystems, Agronomy Abstracts, p. 95.

——, 1971, Microbial Transformations of Nitrogen in Natural and Manipulated Watersheds at Coweeta, Eastern Deciduous Forest Biome, Memo Report No. 71-133, U. S. International Biological Program.

——, and J. H. Nuner, 1973, Comparison of Two Techniques for Assessing Denitrification in Terrestrial Ecosystems, *Bull. Ecol. Res. Comm., NFR,* 17: 277-278.

Vlassak, K., E. A. Paul, and R. E. Harris, 1973, Assessment of Biological Nitrogen Fixation in Grassland and Associated Sites, *Plant Soil,* 38: 637-649.

Waide, J. B., and W. T. Swank, 1974, Comparative Studies of Nutrient Cycling in Watershed Ecosystems in the Southern Appalachians, paper presented at the Symposium on Metabolism of Terrestrial and Freshwater Ecosystems, American Institute of Biological Sciences Meetings, Tempe, Ariz., June 16–21, 1974.

West, N. E., 1974, Nitrogen Cycles in Desert Ecosystems, paper presented at the Symposium on Metabolism of Terrestrial and Freshwater Ecosystems, American Institute of Biological Sciences Meetings, Tempe, Ariz., June 16–21, 1974.

MINERAL CYCLING STRATEGIES OF TWO DECIDUOUS AND TWO EVERGREEN TREE SPECIES ON A SOUTHERN APPALACHIAN WATERSHED

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ABSTRACT

Variations in strategies of resource usage should be apparent in variations in growth form. In the present study conducted at Coweeta Hydrologic Laboratory, Franklin, N. C., four tree species were compared in relation to biomass, production, and nutrient standing crops. The four species included a deciduous canopy tree (*Quercus prinus*), a deciduous subcanopy tree (*Cornus florida*), an evergreen canopy tree (*Tsuga canadensis*), and an evergreen subcanopy tree (*Rhododendron maximum*). The largest total standing crop of nutrients was in *Q. prinus* owing to its large biomass, but the greatest proportion of calcium and magnesium in leaves was in *Rhododendron*. *Cornus* is important in the annual nutrient cycle because *Cornus* has a high proportion of nutrient-rich leaves. *Quercus prinus* is important in the annual cycle and in a long-term nutrient cycle. *Rhododendron* is important in a cycle of intermediate length because the turnover time for *Rhododendron* leaves is about 7 years. Thus mineral-cycling strategies of individual species mesh together to form a network of cycles of varying lengths.

Although the deciduous forest presents a uniform physiognomy to the casual observer, it is, in fact, a mosaic of form, structure, and function. If it is a mature forest, it supports maximum biomass, is maximally complex, and its inhabitants manifest variations to maximize utilization of available resources (Odum, 1969). An attempt to distinguish between woody plants in a community might differentiate between canopy and subcanopy species as well as between evergreen and deciduous species. We would intuitively suspect that variations in strategies of resource usage would be apparent in variations of growth form.

In this paper we examine and compare one aspect of niche development—the mineral-cycling strategies of two canopy species (one

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deciduous and one evergreen) and two subcanopy species (one deciduous and one evergreen). The data were obtained from studies conducted on watershed 18 at Coweeta Hydrologic Laboratory, a facility of the U. S. Forest Service, located in Macon County, N. C. This is a control watershed dominated by a hardwood forest and selected for investigation because it approached maturity more closely than other available sites. Although there was some logging and burning in the area long ago, there have been no disturbances on the watershed in over half a century, with the major exception of the chestnut blight that was discovered at Coweeta in 1925. Detailed descriptions of the study area are in papers by Liming (1955), Nelson (1955), Dils (1957), and Day and Monk (1974).

The species selected for comparison were *Quercus prinus,* a canopy deciduous tree; *Tsuga canadensis,* a canopy-level evergreen tree; *Cornus florida,* a subcanopy deciduous tree; and *Rhododendron maximum,* a subcanopy evergreen.

METHODS

Standing-crop biomass estimates for *Q. prinus, Tsuga,* and *Cornus* were based on regressions on stem-diameter measurements taken in 1970 (where log dry weight = A + B log dbh). One set of equations estimating leaf, stem, and branch dry weights was used with *Q. prinus* and *Cornus,* and another set of equations was used with *Tsuga.* These equations have been reported by Day and Monk (1974). Values for *Rhododendron* were obtained by harvesting whole plants.

Vernier tree bands (Liming, 1957) were used to measure diameter increase of *Q. prinus, Tsuga,* and *Cornus* over a 2-year period, after which new biomass estimates were calculated using the same regression equations. The difference between the first and second estimates was taken to be net primary production. *Rhododendron* net production was based on mean biomass increase in plants of various ages. Details of the methodologies can be found in McGinty (1972) and Day (1974).

Subsamples were taken of wood, bark, current twigs, and leaves for determination of nutrient concentrations. Ten trees each of *Q. prinus* and *Cornus* were subsampled monthly, and 45 branches on about 20 *Rhododendron* trees were harvested monthly. The *Tsuga* data are based on a sample of 20 trees (Santee, unpublished). Samples for analysis were oven-dried and ground. Leaves and twigs were analyzed for phosphorus, potassium, calcium, and magnesium by spark-emission spectroscopy (Jones and Warner, 1969) and for nitrogen by a micro-Kjeldahl method. Bark and wood samples were wet ashed and analyzed for potassium, calcium, and magnesium on an atomic absorption spectrophotometer. Nutrient standing crops were calculated as the product of standing-crop biomass and nutrient concentration in a given plant component. Most of the "other species" reported in Tables 1 and 2 were sampled and analyzed individually in the above-mentioned manner (Day, 1974).

TABLE 1

ABOVEGROUND STANDING CROP BIOMASS AND NET PRIMARY PRODUCTION ON A HARDWOOD FOREST WATERSHED AT COWEETA

Species	Bark	Wood	Twigs	Leaves	Total
			Biomass, kg/ha		
Quercus prinus	5,931.6	25,583.9	32.0	845.9	32,393.1
Cornus florida	583.8	2,465.8	5.0	175.5	3,230.1
Rhododendron maximum	773.3	5,717.7	23.9	1160.4	7,[illegible]
Tsuga canadensis	254.3	1,447.5	3.1	91.6	1,79[illegible]
Other species	16,641.8	73,767.9	119.6	2888.7	93,418.0
Total	24,184.8	108,982.8	183.6	5162.1	138,513.0
			Production, kg ha^{-1} $year^{-1}$		
Quercus prinus	124.1	552.0	32.0	845.9	1554.0
Cornus florida	16.7	72.7	5.0	175.5	269.9
Rhododendron maximum	96.7	292.5	23.9	263.4	676.5
Tsuga canadensis	4.3	33.5	3.1	23.8	64.7
Other species	438.4	1956.0	119.6	2886.2	5400.2
Total	680.2	2906.7	183.6	4194.8	7965.3

RESULTS AND DISCUSSION

A comparison of the four species on the basis of standing-crop biomass demonstrates the importance of each species on the watershed (Table 1). *Quercus prinus* had the largest total biomass (32, 393.4 kg/ha) because of its size and abundance, but *Rhododendron* had the largest leaf biomass (1160.4 kg/ha compared to 845.9 kg/ha of *Q. prinus* leaves). The large standing biomass of *Rhododendron* leaves may be attributed to the high density of stems (887/ha) and to the persistent leaves that increase in biomass until their fifth growing season (McGinty, 1972). Since leaves have relatively high concentrations nutrients, the large *Rhododendron* leaf biomass could have considerab importance in the watershed nutrient cycle. A comparison of primary production values reveals that leaf production for *Rhododendron* (263.4 kg ha^{-1} $year^{-1}$) was considerably less than for *Q. prinus* (845.9 kg ha^{-1} $year^{-1}$). Therefore, even though *Rhododendron* had a large leaf biomass, a relatively small portion of that biomass pool is recycled annually to the forest floor.

The largest total standing crop of nutrients in a given species was in *Q. prinus* because it had the largest biomass on the watershed. The largest standing crop of

TABLE 2

NUTRIENT STANDING CROPS IN THE ABOVEGROUND VEGETATION*

Species	Bark	Wood	Twigs	Leaves	Total
			Potassium, kg/ha		
Quercus prinus	7.7(12%)	46.1(71%)	0.1(<1%)	10.7(17%)	64.6(100%)
Cornus florida	2.0(22%)	4.4(49%)	0.04(<1%)	2.5(28%)	8.9(100%)
[illegible]dendron [illegible]imum	1.2(8%)	8.4(52%)	0.4(2%)	6.0(38%)	16.0(100%)
Tsuga canadensis	0.6(19%)	2.0(62%)	0.01(<1%)	0.6(19%)	3.2(100%)
Other species	26.0(19%)	83.7(61%)	0.7(<1%)	26.8(20%)	137.2(100%)
Total	37.5(16%)	144.6(62%)	1.2(1%)	46.6(20%)	229.9(100%)
			Calcium, kg/ha		
Quercus prinus	74.1(73%)	23.0(23%)	0.2(<1%)	4.9(5%)	102.2(100%)
Cornus florida	13.8(70%)	2.7(14%)	0.04(<1%)	3.2(16%)	19.7(100%)
Rhododendron maximum	3.7(17%)	4.1(19%)	0.2(1%)	13.9(63%)	1.9(100%)
Tsuga canadensis	1.7(58%)	0.7(24%)	0.01(<1%)	0.5(18%)	2.9(100%)
Other species	329.4(82%)	48.7(11%)	1.2(<1%)	24.2(6%)	403.5(100%)
Total	422.7(77%)	79.2(14%)	1.6(<1%)	46.7(9%)	550.2(100%)
			Magnesium, kg/ha		
Quercus prinus	4.2(53%)	2.6(32%)	0.03(<1%)	1.2(15%)	8.0(100%)
Cornus florida	1.1(38%)	1.0(36%)	0.01(<1%)	0.7(27%)	2.8(100%)
Rhododendron maximum	0.1(5%)	0.5(17%)	0.04(1%)	2.2(77%)	2.8(100%)
Tsuga canadensis	0.03(13%)	0.04(23%)	0.0001(<1%)	0.1(64%)	0.2(100%)
Other species	11.9(35%)	13.4(40%)	0.1(<1%)	8.4(25%)	33.8(100%)
Total	17.3(36%)	17.8(37%)	0.2(<1%)	12.6(26%)	48.0(100%)

Species	Twigs	Leaves	Twigs	Leaves
	Nitrogen, kg/ha		Phosphorus, kg/ha	
Quercus prinus	0.1	19.5	0.05	1.4
Cornus florida	0.01	3.7	0.01	0.3
Rhododendron maximum	0.2	14.5	0.01	1.5
Tsuga canadensis	0.02	1.2	0.003	0.2
Other species	0.7	56.1	0.19	4.7
Total	1.0	95.0	0.2	8.1

*Numbers in parentheses represent percentages of row totals; i.e., percent allocation of nutrients to a given component in a given species.

potassium was in *Q. prinus* wood (46.1 kg/ha), and the largest standing crops of calcium and magnesium were in *Q. prinus* bark (74.1 kg/ha and 4.2 kg/ha, respectively) (Table 2). Since nutrients in the wood and bark are immobilized, *Q. prinus* is very important in the long-term nutrient cycle on the watershed, these compartments having the longest turnover time. Even though *Q. prinus* had a larger twig biomass than *Rhododendron, Rhododendron* had the highest concentration and the highest nutrient standing crops of nitrogen, calcium, magnesium, and potassium in the twig compartment.

Most significant was the standing crop of nutrients in the leaf compartment which has the shortest turnover time. *Q. prinus* had the largest standing crop of nitrogen and potassium in the leaf compartment (19.5 kg/ha and 10.7 kg/ha), but *Rhododendron* had the highest standing crops of calcium and magnesium in the leaves (13.9 kg/ha and 2.2 kg/ha). Since *Rhododendron* is evergreen, much of this large calcium and magnesium pool in the leaves is recycled slowly instead of being returned to the forest floor in 1 year. Nitrogen and phosphorus concentrations were higher in *Q. prinus* leaves; whereas, calcium and magnesium concentrations were higher in *Rhododendron* leaves (Table 3). Leaves in *Cornus* concentrate over three times as much calcium per unit leaf biomass as *Q. prinus,* and one and one-half times as much per unit biomass as *Rhododendron.* The amount of calcium cycled annually by leaves of *Cornus* is about 66% of that cycled by *Q. prinus* leaves and about 150% of that cycled by *Rhododendron.* Therefore *Cornus* is probably more important in the annual nutrient cycle than might be apparent from dry weight of leaves. Thomas (1969) has suggested that *Cornus* may function as a nutrient reservoir in some forest stands.

The proportion of potassium in the different plant components did not differ greatly by species. For all four species, the greatest percentage of total potassium in the tree was in the wood. Concentrations in the wood were low, but wood represented a large portion of the standing-crop biomass. The wood component has the slowest turnover and the highest proportion of potassium standing crop in the tree; therefore the wood is important in the long-term cycle of potassium on the watershed. The leaves are more important in the short-term cycle of potassium than might appear from the percent contribution by the leaves to the total standing crop of potassium. Potassium is very leachable since it is not bound in structural components of the plant, and a considerable amount of potassium will leach out of the leaves during the year.

The greatest proportion of the total calcium standing crop in the tree was in the bark in *Q. prinus, Cornus,* and *Tsuga* and in the leaves of *Rhododendron. Rhododendron* had a high concentration of calcium in the leaves and a low concentration in the bark; whereas the other three species had the reverse situation. Thus in *Q. prinus, Cornus,* and *Tsuga,* the bark, which also has a slow turnover, is important in the long-term cycle of calcium on the watershed. *Rhododendron* leaves are important in a shorter term nutrient cycle but do not contribute greatly to the annual cycle. *Rhododendron* leaves persist as long as 7

TABLE 3

MEAN NUTRIENT CONCENTRATIONS IN THE VEGETATION*

Species	Bark	Wood	Twigs	Leaves
		Potassium, % dry weight		
Quercus prinus	0.13 ± 0.04	0.18 ± 0.04	0.39 ± 0.03	1.26 ± 0.06
Cornus florida	0.34 ± 0.06	0.18 ± 0.02	0.72 ± 0.04	1.44 ± 0.11
Rhododendron maximum	0.13 ± 0.06	0.24 ± 0.04	1.55 ± 0.77	0.52 ± 0.26
Tsuga canadensis†	0.24	0.14	0.19	0.67
		Calcium, % dry weight		
Quercus prinus	1.25 ± 0.17	0.09 ± 0.01	0.68 ± 0.06	0.58 ± 0.07
Cornus florida	2.36 ± 0.26	0.11 ± 0.01	0.80 ± 0.06	1.85 ± 0.11
Rhododendron maximum	0.30 ± 0.10	0.07 ± 0.31	0.99 ± 0.24	1.20 ± 0.29
Tsuga canadensis†	0.68	0.05	0.37	0.58
		Magnesium, % dry weight		
Quercus prinus	0.07 ± 0.01	0.01 ± 0.001	0.08 ± 0.02	0.14 ± 0.01
Cornus florida	0.18 ± 0.03	0.04 ± 0.01	0.13 ± 0.01	0.42 ± 0.03
Rhododendron maximum	0.02 ± 0.02	0.01 ± 0.01	0.15 ± 0.05	0.19 ± 0.06
Tsuga canadensis†	0.01	0.003	0.002	0.13

Species	Twigs	Leaves	Twigs	Leaves
	Nitrogen, % dry weight		Phosphorus, % dry weight	
Quercus prinus	0.43 ± 0.04	2.30 ± 0.06	0.15 ± 0.01	0.16 ± 0.004
Cornus florida	0.22 ± 0.02	2.11 ± 0.06	0.10 ± 0.002	0.16 ± 0.01
Rhododendron maximum	1.01 ±0.14	1.25 ± 1.47	0.21 ± 0.04	0.13 ± 0.02
Tsuga canadensis†	0.50	1.34	0.10	0.17

*Error terms are ±1 standard error.
†W. Santee (unpublished data).

s, thus their turnover of calcium is not as rapid as in a deciduous species. Calcium is not as readily leached as potassium since it is found primarily as calcium pectate in the middle lamella of cell walls.

The greatest percentage of the magnesium standing crop in the tree was in the bark in the two deciduous species and in the leaves in the two evergreen species. The bark of the deciduous species would be more important in the long-term magnesium cycle on the watershed. The leaves of the evergreen species would be more important in a shorter term magnesium cycle, but, again, they

would not be so important in the annual cycle since the leaves remain on the tree for several years. Leaching is not an important source of magnesium recycling either since most magnesium in the leaves is bound in chlorophyll.

A deciduous understory species such as *Cornus* is especially important in the annual nutrient cycle because *Cornus* has a large proportion of leaves to wood and high nutrient concentrations in the leaves. Such canopy species as *Q. prinus* are also very important in the annual cycle owing to their large leaf biomass, but they are also important in the long-term nutrient cycle because they have a large woody biomass as well. This large store of nutrients in the wood is recycled slowly as individual trees die. An evergreen understory species such as *Rhododendron* is especially important in a cycle of intermediate length since there is a considerable store of nutrients in the persistent leaves Nutrients in *Rhododendron* leaves are turned over in about 7 years. Thus, in a mature forest, nutrients are stored in the vegetation and recycled at various time intervals ranging from a year to several hundred years, depending on the plant component. Individual species may be more important in one or more phases of this cycling scheme, depending on the growth habits of the species.

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REFERENCES

Day, F. P., 1974, Primary Production and Nutrient Pools in the Vegetation on a Southern Appalachian Watershed, Ph. D. Dissertation, University of Georgia.

——, and C. D. Monk, 1974, Vegetation Patterns on a Southern Appalachian Watershed, *Ecology*, 55: 1064-1074.

Dils, R. E., 1957, *A Guide to the Coweeta Hydrologic Laboratory,* Southeastern F Experiment Station, Forest Service, U. S. Department of Agriculture.

Jones, J. B., and M. H. Warner, 1969, Analysis of Plant—Ash Solutions by Spark-Emission Spectroscopy, in *Developments in Applied Spectroscopy,* Vol. 7a, Plenum Publishing Corporation, New York.

Kovner, J. L., 1955, Changes in Streamflow and Vegetation Characteristics of a Southern Appalachian Mountain Watershed, Ph. D. Dissertation, State University of New York.

Liming, F. G., 1957, Homemade Dendrometers, *J. Forest.*, 55: 575-577.

McGinty, D. T., 1972, The Ecological Roles of *Kalmia latifolia* and *Rhododendron maximum* in the Hardwood Forest at Coweeta, Master's Thesis, University of Georgia.

Nelson, T. C., 1955, Chestnut Replacement in the Southern Highlands, *Ecology*, **36**: 352-353.

Odum, E. P., 1969, Strategy of Ecosystem Development, *Science*, **164**: 262-270.

Thomas, W. A., 1969, Accumulation and Cycling of Calcium by Dogwood Trees, *Ecol. Monogr.*, **39**: 101-120.

THE EFFECT OF NONREMOVAL CLEAR-CUTTING AND PINE REFORESTATION ON THE CATION COMPOSITION OF A HARDWOOD FOREST SOIL

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ABSTRACT

Soil studies were conducted at Coweeta Hydrologic Laboratory, N. C., in a deciduous hardwood forest and in a white pine plantation established after clear-cutting and decay of all previous vegetation. These studies demonstrate that the soil under the pine forest, which was planted 14 years after clear-cutting and was 15 years old at the time of the study, differs from the control hardwood forest in the opposite direction to that expected based on relative nutrient demands of young pine forests and mature hardwood forests. The principal difference is a high calcium concentration in the pine soil compared with the control and, related to that, a higher pH than that of the control. Not only is cation exchange capacity significantly higher in the pine-plantation soil but percent base saturation is also higher. The latter characteristics produce a buffering effect, as evidenced by a less variable pH in the pine-plantation soil. These apparent anomalies are attributed to the cations (principally calcium) incorporated into the soil from the entire above- and belowground plant biomass of the former hardwood forest.

It has long been recognized (Lutz and Chandler, 1946; Remezov, 1961) that the development of a soil from parent material and the development of the associated vegetation are mutually dependent processes. In mature ecosystems there is often a concentration of nutrient elements in the upper soil horizons considerably above that found in the parent material, tending toward a composition that reflects the nutrient needs of the associated biota (Remezov and Pogrebynak, 1969). The forest soil and forest floor thereby become major reservoirs for most of the elements required for ecosystem metabolism and structural maintenance (Witkamp, 1971).

At the Coweeta Hydrologic Laboratory, operated by the Forest Service, U. S. Department of Agriculture and located in western North Carolina in the southern Appalachians, the movement of water through the forest floor and soil, along with hydrologic input and output from gaged watersheds, has been studied and monitored since the early 1930s. These studies include watersheds

with native mature hardwood vegetation as well as those in which the vegetation has been modified to estimate water loss through evapotranspiration (Fig. 1). Since 1968 the University of Georgia Institute of Ecology has been carrying out a program of research on the ecological structure, productivity, and biogeo-

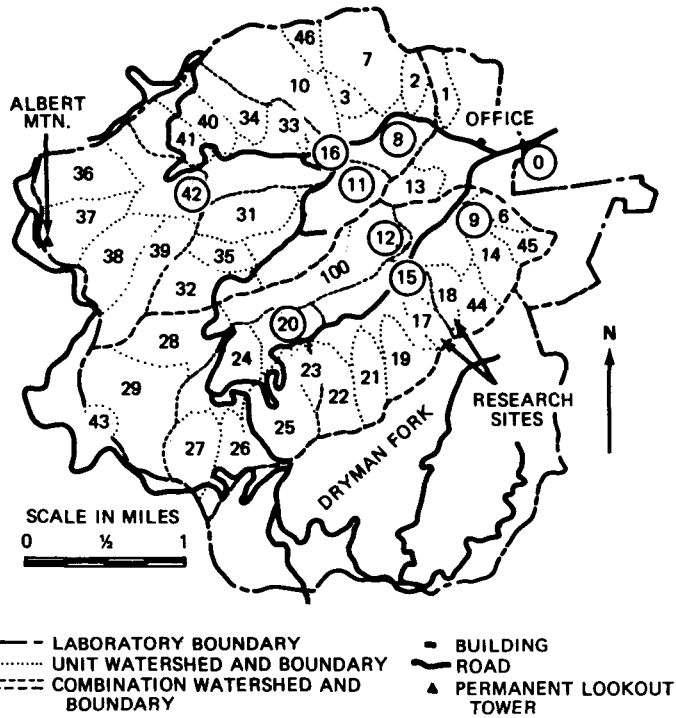

Fig. 1 Coweeta Hydrologic Laboratory, North Carolina, showing watershed boundaries and numbers.

chemical cycling pathways in several of these watersheds in cooperation with the Coweeta Laboratory staff. Since 1970 this facility has been a research site of the ern Deciduous Forest Biome, U. S. Analysis of Ecosystems Program, rnational Biological Program (IBP).

One of the watershed ecosystems in the IBP study is a mature deciduous hardwood forest comprising 12.46 ha (Coweeta watershed 18). Immediately adjacent is a uniform white pine (*Pinus strobus* L.) plantation comprising 13.48 ha (Coweeta watershed 17). The hardwood watershed has been undisturbed by man since at least 1924 (Johnson and Swank, 1973). Before that there was a limited, but otherwise undetermined, amount of hardwood cutting and periodic burning of the herb- and shrub-layer vegetation by early settlers and Indians. The major disturbance of this watershed was the complete elimination

of American chestnut (*Castanea dentata*) as a dominant canopy species by the chestnut blight of the early 1930s. Chestnut is now a minor understory species.

The history of the white-pine-plantation watershed was the same as that of the hardwood until January 1942, when, as part of an experiment designed to measure the effect of evapotranspiration on stream flow, all vegetation was cut and left in place to decay. The soil was essentially undisturbed. Annual sprout growth was cut back in most years between 1943 and 1955, during which time a low herbaceous and shrub cover developed. In 1956 researchers planted eastern white pine seedlings to compare water use by pine and by the original hardwood forest.

Therefore two major stresses or manipulations have been applied to this ecosystem, both of which might be expected to influence the soil compartment. Both changes would affect the soil by changing the nature of the forest floor, or litter layer, i.e., the ecosystem compartment from which the upper soil receives its major direct input of materials. The soil as a whole, of course, also receives an input of materials from bedrock and parent material weathering. For the upper soil, however, this is an indirect input through plant uptake and deposition to the forest floor.

The effects on soil structure and physical properties of the nonremoval clear-cutting and annual cutting of sprout growth was investigated by Freeland (1956). In his study watershed 18, the hardwood watershed, also served as the control. After 10 years the only changes he was able to detect were a slight deterioration in the stability of large aggregates in the surface soil layers and a slight trend toward higher soil-moisture content during the growing season. The former change he attributed to the reduced surface litter, which after 10 years was much less than that in the control hardwood watershed. The higher soil-moisture content was attributed to reduced water loss via evapotranspiration during the growing season.

The results of my study show the combined effects on the soil of (1) the input of the entire above- and belowground plant biomass and its accumulated nutrient capital; (2) the passage of 14 years in which the soil had a herbaceous and shrub cover, reduced evapotranspirational loss, and an increased flow of water through the soil mantle; and (3) the abrupt substitution of a completely different tree cover with different nutrient requirements, greater evapotranspiration loss (Swank and Miner, 1968), and a different litter type.

In removal clear-cutting, followed by establishment of a pine plantation, we could hypothesize a gradual decay, or loss, of the basic elements from the soil until a new steady-state condition was established which reflected the lower basic element demand of a pine forest. An opportunity existed here to examine as part of a total watershed study the effects of a transfer of materials from one major ecosystem compartment, the primary producers, to another, the soil (i.e., the decomposition and reservoir compartment). Although its effect is not precisely known, the 14-year gap between clear-cutting and pine planting probably served chiefly to incorporate the large amount of litter into the soil.

METHODS AND MATERIALS

Two sample transects were established in each of the two watersheds. Each transect led from the stream channel to a point 60 m up on both facing slopes. The layout of the transects was affected by the watershed topography. In the hardwood watershed (18), transects were at midwatershed level on each of two stream channels. In the white pine watershed (17), the transects were across the lower and upper thirds of the single channel. These transects were selected in areas with the following vegetation growth forms: (1) broad-leaved deciduous deciduous understory, (2) broad-leaved deciduous with broad-leaved evergreen understory (*Kalmia* and *Rhododendron*), and (3) needle-leaved evergreen (white pine).

Two plots (2 by 15 m each) were established on each slope of a transect as near as practical to the stream and 60 m upslope. There was a total of 16 plots, 8 per watershed. Every two months, triplicate soil samples from A1 and A2 horizons were taken from the center of each of three randomly selected 0.25-m^2 quadrats. Litter was also sampled (for the results of this study, see Yount, this volume).

Soil samples were air dried and submitted to the University of Georgia Soil Testing and Plant Analysis Laboratory for chemical analysis. The following is a brief summary of the analytical procedures employed by the laboratory (Jones and Isaac, 1971).

Calcium, magnesium, sodium, and potassium were extracted by means of a mixed-acid extracting solution consisting of 0.05*N* HCl and 0.025*N* H_2SO_4, which, because of the conditions of the test, gives results quite similar to ammonium acetate extraction. Sodium was analyzed by atomic absorption spectrophotometry. Calcium, magnesium, and potassium were determined with a Technicon Auto-Analyzer. Soil pH was determined on a 1 : 1 (w/w) mixture of soil and water. Exchangeable acidity was determined by the extent of pH lowering in a mixture of standard buffer solution and soil (Adams and Evans, 1962).

Cation-exchange capacity (CEC) in milliequivalents per 100 grams of soil (meq/100 g) was calculated from the sum of exchangeable acidity and acid-extractable cations. Percent base saturation (PBS) was calculated from the sum of the cations in meq/100 g divided by the CEC.

The high between-plot variability of the soil chemical properties did not permit any analysis of possible trends within a watershed. Since significant differences between plots could not be demonstrated, the data for each parameter were combined by watershed and considered as one sample. When this was done, significant differences between means often resulted, both as a function of watershed and of time.

Freeland (1956) determined the bulk density of the A1 and A2 horizons to be approximately 1.0 g/cm^3. This value was used as the best estimate for

calculating area weights of elements. At each sampling point the depth of the A1 horizon was measured. The means of these measurements varied slightly from one sampling time to another, but all were close to 5 cm, which was set as the lower boundary of the A1 horizon. A straightforward conversion then yields a value of 500 tonnes/ha for the weight of the A1 horizon. Similarly the weight of the A2 horizon (from 5- to 30-cm depth) is 2500 tonnes/ha. The area weights of the elements were calculated from these figures and the concentration data. For a more detailed discussion of methods and a detailed data tabulation, see the IBP report by Yount (1972).

RESULTS AND DISCUSSION

As hypothesized previously, removal of native hardwood vegetation and replacement with white pine should eventually result in a soil with a lower steady-state nutrient composition. This was expected for at least two reasons: (1) the higher net productivity of the young pine forest, which results in relatively high nutrient demands on the soil; and (2) the lower nutrient requirements of pines in general, which results in a lower nutrient input to the soil by litterfall recycling.

The most obvious indication that the pine-plantation soil does not conform to this expectation is its comparatively high pH, averaging 5.8 throughout most of the year and varying only ±0.1 pH unit (Fig. 2). This soil is evidently very well buffered. The hardwood-forest soil, by contrast, is considerably more acid, frequently below pH 5.0 and falling as low as 4.7. Two pH peaks occur in the hardwood soil, around September (5.4) and again around March (5.2). The hardwood-forest soil is evidently less well buffered than the pine-forest soil.

This difference in soil buffering capacity can be partially explained by the comparative percent base saturation of the two soils (Fig. 2). The pine-forest soil CEC is 60 to 70% saturated, whereas the hardwood-forest soil varies between 40 and 55% saturated. The higher PBS in the pine soil occurs despite a higher total CEC (around 12 meq/100 g compared with around 7.5 meq/100 g for the native-hardwood-forest soil).

Sodium levels are very similar in the soils of both watersheds in both the A1 and A2 horizons; all levels are quite low, less than 25 kg/ha in the A1 horizon (Fig. 3). Potassium levels are 40 to 100 kg/ha in the A1 horizon and are generally higher in the hardwood-forest soil than in the pine-forest soil.

The divalent cations, calcium and magnesium, do not behave like the monovalent cations. Levels of both elements are higher in the pine-forest soil over most of the year (Fig. 3). The contrast is particularly striking in the case of calcium. Calcium levels in both the A1 and A2 horizons (to a depth of 30 cm) are about twice as high in the pine soil as in the hardwood soil. Calcium alone takes up from one-third to one-half the total cation-exchange capacity of the pine soil.

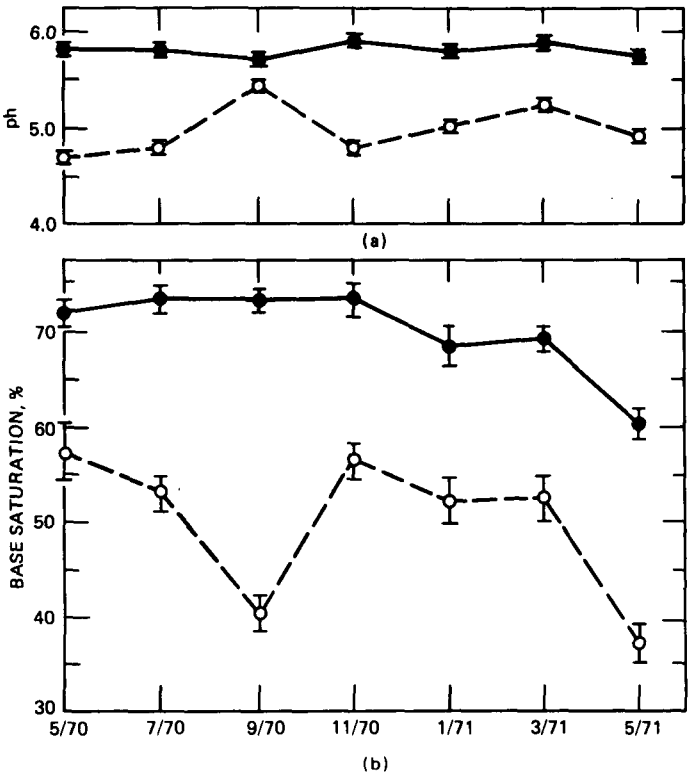

Fig. 2 Soil pH (a) and base saturation (b), A1 horizon. —●—, pine. - -○- -, hardwood. Vertical lines denote ±1 SE (N = 24).

Since no fertilizer or lime has been applied to the soil in the pine watershed, the only conceivable source of the additional calcium and magnesium is the accumulated nutrient capital of the entire above- and belowground plant biomass incorporated into the soil after the original hardwood vegetation was cut and left in place to decay.

By comparison and contrast, in the Virelles mixed-oak forest in Belgium (Duvigneaud and Danaeyer-De Smet, 1970), calcium and magnesium in the total vegetation (aerial and underground) were 1248 and 102 kg/ha, respectively, compared with 13,600 and 151 kg/ha in the soil. The soil in the Belgian forest is calcareous, however; whereas that at Coweeta is derived from acidic metamorphic bedrock.

At Coweeta in the native-hardwood-forest soil, total calcium to a depth of 30 cm varies between 170 and 500 kg/ha and total magnesium between 130 and 270 kg/ha considering seasonal variation. In the pine soil total exchangeable calcium varies between approximately 600 and 1200 kg/ha and total exchangeable magnesium between 160 and 500 kg/ha (Table 1). Thus there is between

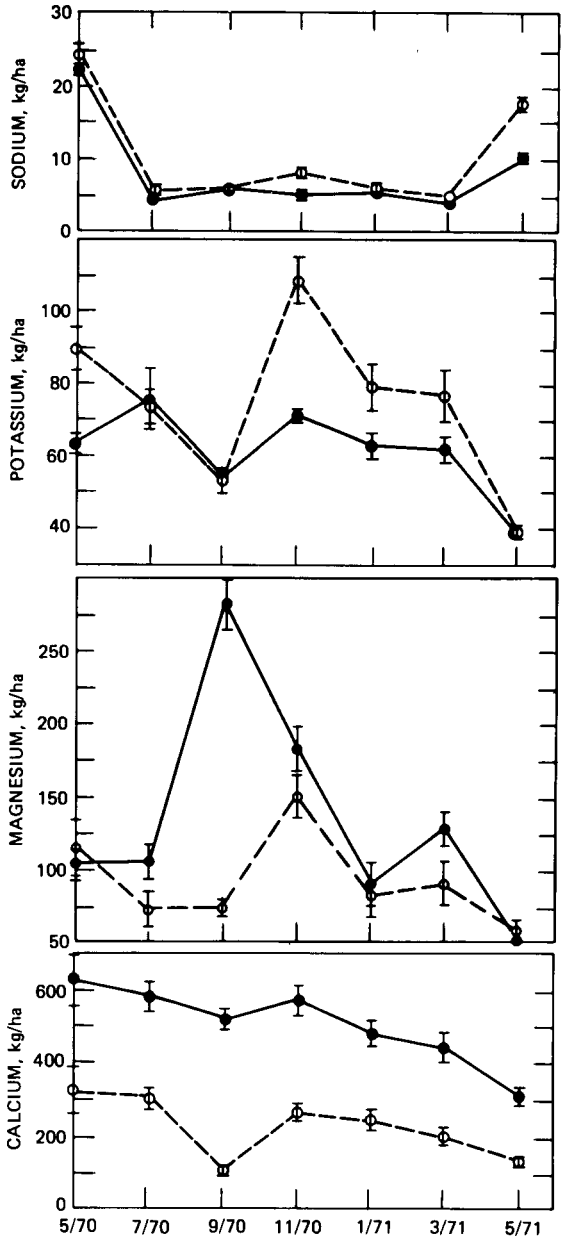

Fig. 3 Soil cations, A1 horizon to 5-cm depth. —●—, pine. --○--, hardwood. Vertical lines denote ±1 SE (N = 24).

TABLE 1

TOTAL CALCIUM AND MAGNESIUM IN HARDWOOD-FOREST AND WHITE-PINE-PLANTATION SOILS TO 30-cm DEPTH (kg/ha)

Watershed	5/70	7/70	9/70	11/70	1/71	3/71	5/71
				Calcium			
White pine	1176	1231	874	982	901	771	627
Hardwood	457	499	170	418	367	353	188
Excess in pine soil	719	732	704	564	534	418	439
				Magnesium			
White pine	224	244	505	405	160	214	161
Hardwood	198	145	239	273	160	224	130
Excess in pine soil	26	99	266	132	0	−10	31

418 and 732 kg/ha excess calcium and between 0 and 266 kg/ha excess magnesium in the pine-plantation soil.

Day (1974) determined the total aboveground nutrient standing crops in the native hardwood watershed. Total aboveground calcium is 551 kg/ha, and total aboveground magnesium is 48 kg/ha. Data for root nutrient standing crops are not yet available, but an estimate can be made using the Virelles mixed-oak-forest data (Duvigneaud and Danaeyer-De Smet, 1970). Multiplying the Coweeta aboveground data by the ratio of total to aboveground calcium (1.44) and magnesium (1.26) in the Virelles forest, we obtain an estimate of 793 kg/ha for the input of calcium into the white-pine-forest soil from the total above- and belowground vegetation. For magnesium the corresponding estimate is 61 kg/ha. By this estimate there appears to be sufficient calcium in the hardwood watershed vegetation to account for the excess calcium in the pine-forest soil. Magnesium, however, does not exhibit such a clear and consistent excess nor such good agreement with estimated plant-biomass pools. Perhaps further research will show that excess magnesium, if any, is in some other ecosystem compartment for part of the year.

The other principal soil cations, potassium and sodium, do not exhibit any consistent differences in amount between these two watersheds (Table 2). For these two elements, Day (1974) found aboveground plant pools of 233 kg/ha for potassium and 48 kg/ha for sodium. Converting the potassium figures to total above- and belowground plant-biomass pools, as we did for calcium and magnesium, we obtain an estimate of 326 kg/ha. Data for sodium in the Virelles forest were not given.

TABLE 2

TOTAL POTASSIUM AND SODIUM IN HARDWOOD-FOREST AND WHITE-PINE-PLANTATION SOILS TO 30-cm DEPTH (kg/ha)

Watershed	5/70	7/70	9/70	11/70	1/71	3/71	5/71
			Potassium				
White pine	225	260	176	225	210	173	153
Hardwood	241	200	163	219	206	193	135
Excess in pine soil	−16	60	13	6	4	−20	18
			Sodium				
White pine	143	20	27	22	26	21	61
Hardwood	125	24	29	28	24	21	71
Excess in pine soil	18	−4	−2	−6	2	0	−10

It seems reasonable to attribute the difference in calcium, pH, and base saturation between the soils of these two ecosystems primarily to an input of calcium from the clear-cutting and decay of the plant biomass in what is now a white-pine-plantation forest ecosystem.

Thus we can expect the calcium level in the soil of the white-pine-plantation watershed to decrease over a number of years (with a corresponding decrease in soil pH and base saturation) to a lower steady-state level. In fact, the approach to a new steady-state may have been accelerated by the unusually wet spring in 1971 (see Yount, this volume). The level of calcium, as well as that of all other soil cations measured, was considerably lower in May 1971 than in May 1970.

ACKNOWLEDGMENT

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REFERENCES

Adams, F., and C. E. Evans, 1962, A Rapid Method for Measuring Lime Requirements of Red-Yellow Podzolic Soils, *Soil Sci. Soc. Amer., Proc.*, 26: 355-357.

Day, Frank, 1974, Botany Department, University of Georgia, unpublished.

Duvigneaud, P., and S. Danaeyer-De Smet, 1970, Biological Cycling of Minerals in Temperate Deciduous Forests, in *Analysis of Temperate Forest Ecosystems*, pp. 199-225, D. E. Reichle (Ed.), Springer-Verlag, New York.

Freeland, F. D., 1956, The Effects of a Complete Cutting of Forest Vegetation and Subsequent Annual Cutting of Regrowth upon Some Pedologic and Hydrologic Characteristics of a Watershed in the Southern Appalachians, Ph. D. Thesis, Michigan State University, East Lansing.

Johnson, P. L., and W. T. Swank, 1973, Studies of Cation Budgets in the Southern Appalachians on Four Experimental Watersheds with Contrasting Vegetation, *Ecology*, **54**: 70-80.

Jones, J. B., and R. Isaac, 1971, Laboratory Procedures for the Analysis of Soils, Feed, Water and Plant Tissue, Soil Testing and Plant Analysis Laboratory, University of Georgia, Athens.

...itz, H. J., and R. F. Chandler, Jr., 1946, *Forest Soils*, John Wiley & Sons, Inc., New York.

...mezov, N. P., 1961, Decomposition of Forest Litter and the Cycle of Elements in an Oak Forest, *Sov. Soil Sci. (Engl. Transl.)*, **1961**: 703-711.

——, and P. S. Pogrebnyak, 1969, *Forest Soil Science*, Translated by A. Gourevitch, Y. Haver (Ed.), Israel Program for Scientific Translations, Ltd., Jerusalem. Published pursuant to agreement with the U. S. Department of Agriculture and the National Science Foundation, Washington, D. C.

Swank, W. T., and N. H. Miner, 1968, Conversion of Hardwood Covered Watersheds to White Pine Reduces Water Yield, *Water Resour. Res.*, **4**: 947-954.

Witkamp, M., 1971, Soils as Components of Ecosystems. *Annu. Rev. Ecol. Systemat.*, **2**: 85-110.

Yount, J. D., 1972, Soil and Forest Floor Chemical Dynamics in Two Contrasting Watershed Ecosystems, Eastern Deciduous Forest Biome, Memo Report No. 72-53, U. S. International Biological Program.

SOME EFFECTS OF FERTILIZATION ON MINERAL CYCLING IN LOBLOLLY PINE

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ABSTRACT

Nitrogen, phosphorus, and potassium applied at rates of 226, 60, and 136 kg/ha as ammonium nitrate, triple superphosphate, and muriate of potash, respectively, were not immobilized in the forest floor. Part of the NO_3–N leached to the 120-cm depth in the soil in concentrations up to 7 ppm at some sample points, but the concentration had declined to an average of 0.5 ppm 3 years after application. Even with increased losses from fertilization, the loss of NO_3–N below 120 cm would be approximately balanced by precipitation input. Increased mineral elements in litterfall and throughfall the first year after fertilization account for about 5% of the nitrogen and 10% of the potassium applied. During the second year after fertilization, increased litterfall and increased concentrations in litterfall and throughfall amounted to 10% of the nitrogen and potassium applied. As determined by measurement of the difference between fertilized and nonfertilized plots, about 25% of the nitrogen applied was in the forest floor 2 years after fertilization, but litterfall rather than immobilization of the nitrogen applied appeared to be the major source of the additional nitrogen.

Since loblolly pine (*Pinus taeda* L.) is considered the most important forest tree species in the South, it will be a prime candidate for fertilization as the demand for wood increases. Knowledge of mineral cycling is essential for development of wise and economical fertilization programs. This paper reports the effect of nutrients in the litterfall and throughfall, on mineral accumulation in the forest floor, and on minerals in soil water of nitrogen, phosphorus, and potassium fertilization of a 14-year-old loblolly pine plantation. Data were taken for the first 3 years after fertilization—the time during which treatment has the greatest effect on the mineral cycle.

The information presented here should help to develop and validate models of fertilization effects. The mineral cycle is visualized as a number of mineral pools in ecosystem components or compartments (mineral soil, stem, branches, forest floor) connected by transfer paths. When we consider the processes controlling components and transfer paths, the mineral cycle, even in the simplest ecosystem, is extremely complex in quantitative terms. Cycling investigations for loblolly pine are not sufficiently complete for budgeting nutrients on any site or stand of trees.

A number of general soil–tree relationships have been established for mineral cycling in loblolly pine systems without fertilization. Mineral transfer and accumulation rates vary widely with soil but are greatest in the early years of stand development and decline as competition between trees becomes severe (Switzer and Nelson, 1972). About 50% of the nitrogen, phosphorus, and potassium transfers from the needles to the trees just before needle abscission (Wells and Metz, 1963). Minerals accumulate rapidly in the forest floor at the time of canopy closure and immediately thereafter and approach an equilibrium as the stand matures (Switzer, Nelson, and Smith, 1968; Wells and Jorgensen, 1974).

Mineral nutrient content of the mineral soil declines during canopy closure and stand development and then tends to reach an equilibrium, at least in the A horizon. Tree harvest removes significant but varying quantities of nutrients depending on the management program. Precipitation removed more potassium from the needles by throughfall leachate and stemflow than is in litterfall (Wells, Whigham, and Lieth, 1972). Precipitation adds significant quantities of nutrients, especially nitrogen, to the forest over long periods. Loss of nutrients from loblolly pine sites is considered low and probably does not exceed input from rainfall on most soils; however, data on losses in water and erosion are needed. The information available on loblolly pine provides guides to forestry practices and is now being used in a simulation model of the nitrogen cycle (Penning de Vries et al., this volume).

METHODS

Site

This study was initiated in April 1971 in a well-stocked 14-year-old loblolly pine plantation on the Triangle Site of the Eastern Deciduous Forest Biome, International Biological Program (Ralston, 1973). The trees were originally spaced on 2- by 2-m plots and at the time of the study averaged 11 m tall and 19 cm in diameter. The sparse undergrowth of mostly eastern red cedar was removed. The soil was Appling sandy loam, a Typic Hapludults.

Treatments, Sampling, and Analyses

Data were collected from six 0.1-ha plots. Two plots served as controls, two plots were fertilized in April 1971, and two plots were fertilized in April 1972. One of the two control plots was selected to supplement another study, and treatments were randomly assigned to the other five plots. The fertilization rate was nitrogen, 226 kg/ha; phosphorus, 60 kg/ha; and potassium, 136 kg/ha, as ammonium nitrate, triple superphosphate, and muriate of potash, respectively.

The forest floor was sampled in April 1971 and April 1973. Twenty sample points were located randomly on each plot inside two rows of border trees. The points were marked for collection of paired samples in April 1971 before fertilization and in April 1973. At each sample point, a 0.093-m^2 sample of forest floor was collected by L and F layers.

Litter was removed monthly from five 1-m^2 screen traps randomly located in each plot and was dried at 70°C and weighed. Samples were then ground and stored in polyethylene containers for chemical analysis.

Precipitation and throughfall water were collected after each storm or storm period in polypropylene bottles with 17-cm polyethylene funnels. Six bottles were randomly placed between the second and third rows from the border of each plot, and three bottles were in an adjacent open area. A plug of glass wool was placed in each funnel to remove the fine litter, and the needles were removed from the funnels at each collection.

Soil water was collected monthly in porous cup samplers when there was sufficient moisture for extraction. Sample tubes were installed on each plot at depths of 30, 60, and 120 cm—a total of four sample tubes for each treatment at each depth. The 30-cm depth corresponds closely with the A2 horizon boundary.

Total nitrogen was determined by Kjeldahl procedures; NH_4, NO_3, S, and P were determined by autoanalyzer; and K, Ca, Mg, Mn, Zn, Cu, Fe, and Al were determined by atomic absorption.

RESULTS

Fertilization increased average needle length from 15.3 to 17.4 cm, weight per fascicle from 0.112 to 0.139 g, and proportion of fascicles with greater than three needles from 0.5 to 14.8%. Maki (1962) also reported a greater proportion of four-needle fascicles and a greater litterfall after fertilization. Needle fascicles produced both the first and second years after fertilization were about 28% heavier than those on control plots. Since total needlefall was increased about 28% by fertilization, it follows that fertilization increased the number of needles per fascicle and the length of needles but not the number of fascicles in the plantation. Increases in needle length, weight, and number per fascicle are not expected to influence notably the decomposition and release of elements from the forest floor.

Litterfall

Fertilization increased the concentration of nitrogen in needles that fell the year the fertilizer was applied (Table 1). A small increase was also indicated for phosphorus and potassium concentrations in the litterfall, but greater increases occurred in throughfall (Table 2). This shows that fertilizer elements are rapidly distributed within the system. In the second year after fertilization, needlefall per hectare on the fertilized plots contained 60% more nitrogen and 45% more phosphorus than that on control plots. The greater nitrogen and phosphorus contents resulted from a 28% increase in needle weight and increased concentration of the elements in the needles. That manganese in needlefall increased by 57%, sodium by 75%, and magnesium by 40% indicates increased concentrations in the needles. Since fertilization increased potassium and aluminum in needlefall by only 2%, potassium and aluminum concentrations in needles decreased after fertilization as a result of greater needle mass and a dilution effect.

Although not related to treatment, the branch portion of litterfall was about twice as great the second year of the study as the first year. The trash of litterfall, the fine bark and insect frass, increased in quantity and content of N, P, K, Ca, Mg, and Mn as a result of fertilization.

Throughfall

Most of the nitrogen leached from the canopy by throughfall was organic (O–N); a small part was NO_3–N (Table 2). The lesser amount of NH_4–N in throughfall in comparison with that in precipitation in the open may be a result of biological activity in the sample before analysis. An exchange is probably active across the leaf surface during precipitation, however, and the amount leached is the net effect. Analysis of specific rain storms indicated that both NH_4 and NO_3 were removed from precipitation by the canopy. It is not possible on the basis of these data to determine quantitatively the source of the elements leached from the canopy.

A large proportion of the potassium in throughfall was leached from the trees, and fertilization increased such leaching by about 5 kg ha^{-1} $year^{-1}$ (Table 3). The total potassium content of needles on a similar plantation was 48 kg/ha (Wells and Jorgensen, 1974). Since the amount leached from this plantation was from 10 to 16 kg ha^{-1} $year^{-1}$, 20 to 30% of potassium in needles may be leached annually. On nonfertilized plots about 3.5% of the nitrogen, 2.5% of the phosphorus, 12% of the calcium, and 14% of the magnesium in throughfall was leached from the needles. Fertilization almost doubled these percentages for nitrogen and phosphorus.

Minerals in Soil Water

Within a few months after fertilization, the NH_4 and NO_3 ion concentration in soil water at the 120-cm depth increased (Table 4). The NH_4–N concentra-

TABLE 1

TOTAL LITTERFALL BIOMASS AND MINERAL QUANTITY, GIVEN BY FERTILIZER TREATMENT (kg ha^{-1} $year^{-1}$)

Treatment and material sampled	Biomass	N	P	K	Ca	Mg	Mn	Zn	Fe	Cu	Na	Al
						June 1971 to May 1972						
Control												
Needles	4750	26.81	3.05	4.92	4.75	3.52	1.89	0.206	0.478	0.014	0.224	3.04
Branches	572	1.72	0.10	0.15	1.31	0.11	0.05	0.014	0.077	0.002	0.010	0.21
Trash	240	1.92	0.15	0.23	0.50	0.11	0.04	0.018	0.092	0.001	0.011	0.13
Fertilized 1972												
Needles	4446	27.84	3.10	5.24	5.12	3.29	1.88	0.193	0.386	0.014	0.211	2.85
Branches	324	1.12	0.05	0.08	0.90	0.06	0.04	0.007	0.044	0.001	0.006	0.11
Trash	250	2.09	0.16	0.27	0.52	0.12	0.05	0.008	0.107	0.001	0.012	0.16
Fertilized 1971												
Needles	4784	40.52	3.53	5.66	5.89	3.81	2.00	0.204	0.364	0.016	0.244	3.02
Branches	262	0.94	0.06	0.11	0.81	0.06	0.03	0.008	0.0[illegible]	0.001	0.006	0.12
Trash	313	3.15	0.23	0.43	0.76	0.16	0.06	0.017	0.1[illegible]	0.002	0.015	0.16

June 1972 to May 1973

Control												
Needles	5136	30.74	3.19	5.46	6.38	3.28	2.44	0.213	0.352	0.020	0.178	3.44
Branches	1118	4.02	0.26	0.41	2.16	2.06	0.09	0.029	0.177	0.002	0.023	0.05
Trash	372	2.85	0.21	0.38	0.78	0.16	0.06	0.022	0.139	0.001	0.012	0.26
Fertilized 1972												
Needles	5042	36.66	3.72	6.24	5.56	3.46	2.40	0.186	0.321	0.023	0.249	2.89
Branches	1097	4.02	0.22	0.29	2.33	0.21	0.10	0.028	0.159	0.002	0.019	0.51
Trash	396	3.66	0.23	0.48	0.95	0.18	0.08	0.014	0.112	0.002	0.013	0.27
Fertilized 1961												
Needles	6589	49.31	4.62	5.57	7.28	4.60	3.82	0.281	0.505	0.026	0.311	3.52
Branches	1316	4.99	0.32	0.56	3.02	0.40	0.15	0.037	0.170	0.003	0.028	0.66
Trash	466	4.54	0.31	0.56	1.03	0.22	0.11	0.022	0.120	0.002	0.014	0.31

tion reached a high of 0.79 ppm and averaged less than 0.1 ppm at all depths for the 3 years after fertilization.

In the winter of 1971 after ammonium nitrate had been applied the previous spring, NO_3—N reached highs of 36 ppm for one sample at the 60-cm depth and 7 ppm at the 120-cm depth. The highs for NO_3—N were 12 and 76 ppm at the 30- and 60-cm depths for another set of plots fertilized in 1972. The greatest annual average NO_3—N concentrations were 5.6, 7.8, and 2.1 ppm for the 30-, 60-, and 120-cm depths.

Analyses of selected samples showed that potassium at the 120-cm depth was 0.8 ppm in the control and 1.5 ppm on the fertilized plots the first after treatment. The concentration of potassium in the fertilized plots dec to the level of the control by the third year. The concentration of calcium at 120 cm was 3.6 ppm in fertilized plots and 1.0 ppm in the control the first year after fertilization. Content in fertilized plots declined to about 0.9 ppm by the third year.

The loss of all elements to groundwater was estimated to be small. For example, if 20 cm of water per year is assumed to move through the 120-cm depth and out of the root zone, soil-water analyses indicate that NO_3—N losses would be 4.2, 2.4, and 1.1 kg/ha in the first, second, and third years, respectively, after fertilization. Control-plot losses would be 0.41, 0.63, and 0.51 kg/ha for the corresponding years.

Effect of Fertilization on the Forest Floor

The forest floor was extremely variable because litter accumulated between ridges left from prior agricultural use. For all treatments biomass accumulation in the forest floor was less than 1000 kg ha^{-1} $year^{-1}$ (Table 5). A plantation similar in productivity on Creedmore sandy loam accumulated nearly 4000 kg of biomass per hectare per year in the forest floor between tree ages of 13 and 16 years (Wells and Jorgensen, 1974).

During the 2 years after fertilization, 30 kg ha^{-1} $year^{-1}$ more nitrogen accumulated in the forest floor of the fertilized plots than in that of control plots. Fertilization increased nitrogen, phosphorus, and potassium in the forest floor in amounts approximately equal to the increased annual input of these elements from litterfall (Table 3). Although the processes involved cannot be evaluated, the results indicate that the fertilizers applied moved through forest floor and the small net increases in nitrogen, phosphorus, and potassi in the forest floor came from the increased content of these elements in litterfall.

The fate of fertilizer elements and the influence of fertilization on element flows can only be estimated from total tree and soil analyses. Quantitative investigations, such as our study of litterfall, throughfall, forest floor, and soil water, are useful for evaluating nutrient-cycle simulation models. Elements applied as fertilizers moved through the forest floor and were reflected in

TABLE 2

MINERALS IN PRECIPITATION IN THE OPEN AND IN THROUGHFALL, GIVEN BY FERTILIZER TREATMENT (kg ha^{-1} $year^{-1}$)

Treatment	NH_4–N	NO_3–N	O–N	Total N	P	K	Ca	Mg	S
				June 1971 to May 1972					
Open	1.37	2.02	1.73	5.12	0.20	1.89	2.96	0.74	7.89
Control	1.49	2.47	4.65	8.60	0.48	11.24	4.90	1.85	9.89
Fertilized 1972	0.88	2.38	4.99	8.24	0.42	13.89	4.65	2.38	10.06
Fertilized 1971	1.34	2.70	5.63	9.68	0.60	16.54	4.83	2.31	10.52
				June 1972 to May 1973					
Open	2.02	2.62	1.65	6.29	0.29	2.03	2.06	0.66	9.59
Control	0.74	2.45	5.28	8.48	0.52	10.06	4.10	1.76	12.70
Fertilized 1972	1.14	2.68	5.58	9.40	0.72	14.92	4.01	1.48	11.92
Fertilized 1971	1.10	3.28	6.84	11.22	0.78	15.13	4.23	2.65	12.30

TABLE 3

MINERAL ELEMENTS LEACHED FROM THE CANOPY OF CONTROL PLOTS AND NET INCREASE IN CONTENT OF THROUGHFALL (TF) AND LITTERFALL (LF) AS A RESULT OF FERTILIZATION (kg ha^{-1} $year^{-1}$)

Sample	Biomass	NH_4–N	NO_3–N	O–N	Total N	P	K	Ca	Mg	S
Leached*		−0.58	0.14	3.28	2.84	0.25	8.69	1.99	1.10	2.56
Year 1†										
TF		0.12	0.23	0.64	1.0	0.30	5.08	−0.08	0.09	0.12
LF	−147				10.4	0.52	0.83	0.23	0.68	
Total					11.4	0.82	5.91	0.15	0.77	
Year 2†										
TF		0.36	0.83	1.56	2.7	0.26	5.07	0.13	0.89	−0.40
LF	1745				21.2	1.59	0.44	2.01	0.28	
Total					23.9	1.85	5.51	2.14	1.17	

*Net increase in content of throughfall compared with precipitation in the open.

†Net increase in throughfall and litterfall content of fertilized plots compared with control plots.

TABLE 4

RANGE AND AVERAGE NH_4–N AND NO_3–N CONCENTRATIONS (ppm) IN SOIL WATER, GIVEN BY FERTILIZER TREATMENT AND SOIL DEPTH

Treatment	Depth, cm	May 1971–April 1972			May 1972–April 1973			May 1973–April 1974		
		No.*	Range	Av.	No.*	Range	Av.	No.*	Range	Av.
					NH_4–N					
Control	30	7	0.000–0.095	0.026	7	0.004–0.091	0.022	0		
	60	14	0.006–0.062	0.021	28	0.000–0.085	0.026	21	0.000–0.045	0.014
	120	13	0.005–0.142	0.054	14	0.000–0.077	0.022	16	0.003–0.055	0.021
Fertilized	30	7	0.008–0.040	0.020	7	0.008–0.138	0.062	3	0.010–0.093	0.047
1972	60	15	0.004–0.054	0.019	25	0.000–0.117	0.025	21	0.006–0.195	0.030
	120	14	0.005–0.058	0.022	22	0.004–0.240	0.052	23	0.005–0.150	0.042
Fertilized	30	10	0.018–0.275	0.094	10	0.001–0.138	0.030	3	0.030–0.140	0.070
1971	60	12	0.013–0.108	0.038	18	0.001–0.190	0.035	12	0.000–0.075	0.021
	120	16	0.005–0.238	0.074	21	0.000–0.792	0.084	15	0.000–0.075	0.025
					NO_3–N					
Control	30	8	0.000–0.075	0.022	8	0.000–0.028	0.010	0		
	60	15	0.001–0.150	0.029	31	0.000–0.118	0.020	21	0.000–1.800	0.095
	120	13	0.002–0.805	0.204	17	0.001–0.900	0.318	16	0.000–0.740	0.253
Fertilized	30	8	0.010–0.140	0.056	7	0.420–12.450	4.171	3	3.100–6.900	5.613
1972	60	15	0.001–0.025	0.008	30	0.000–76.200	5.944	21	0.000–4.180	1.403
	120	14	0.001–0.340	0.084	24	0.000–11.935	1.873	23	0.000–6.875	1.318
Fertilized	30	10	0.050–9.400	1.782	11	0.018–0.515	0.084	3	0.035–0.340	0.145
1971	60	12	0.022–36.400	7.783	22	0.778–14.120	3.114	12	0.430–1.400	0.855
	120	15	0.080–7.050	2.093	25	0.215–3.600	1.118	16	0.010–1.865	0.544

*Number of samples

TABLE 5

COMBUSTIBLE BIOMASS AND N, P, K, Ca, AND Mg LEVELS OVER A 2-YEAR PERIOD (kg/ha) IN THE FOREST FLOOR

Treatment*	Biomass	N	P	K	Ca	Mg
Control						
1971	15,512	182	11.4	10.3	77.0	11.4
1973	15,002	176	11.8	11.1	53.3	10.9
Δ	−502	−6	0.4	0.8	−23.7	−0.5
tilized 1972						
1971	14,234	158	10.4	10.5	61.5	11.3
1973	16,454	204	13.7	12.3	67.9	11.3
Δ	2,220	46	3.3	1.8	6.4	0.0
Fertilized 1971						
1971	15,621	164	10.7	9.2	85.0	11.1
1973	17,114	223	14.7	13.8	72.8	14.0
Δ	1,493	59	4.0	4.6	−12.2	2.9

*Fertilization significantly increased nitrogen and phosphorus at the 5% level, potassium at the 10% level, and biomass at the 15% level.

increased quantities in the litterfall, throughfall, and soil water. Any effect that can be considered a disturbance or an imbalance had largely reverted to the nonfertilized level after 2 or 3 years.

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REFERENCES

Maki, T. E., 1962, Some Effects of Fertilization on Loblolly Pine, in *Transactions of the 7th International Congress of Soil Science,* Madison, Wis., 1960, pp. 363-375, American Elsevier Publishing Co., Inc., New York.

Ralston, C. W., 1973, Annual Primary Productivity in a Loblolly Pine Plantation, in *International Union of Forestry Research Organizations, Biomass Studies,* H. E. Young, (Ed.), pp.105-117, College of Life Sciences and Agriculture, University of Maine, Orono.

Switzer, G. L., and L. E. Nelson, 1972, Nutrient Accumulation and Cycling in Loblolly Pine (*Pinus taeda* L.) Plantation Ecosystems: The First Twenty Years, *Soil Sci. Soc. Amer., Proc.,* 36: 143-147.

——, L. E. Nelson, and W. H. Smith, 1968, The Mineral Cycle in Forest Stands, in *Forest Fertilization—Theory and Practice,* pp. 1-9, Tennessee Valley Authority, Knoxville, Tenn.

Wells, C. G., and J. R. Jorgensen, 1974, Nutrient Cycling in Loblolly Pine Plantations, in *Proceedings of the Fourth North American Forestry Soils Conference,* Laval University, Quebec, Canada, in press.

——, D. Whigham, and H. Lieth, 1972, Investigation of Mineral Nutrient Cycling in an Upland Piedmont Forest, *J. Elisha Mitchell Sci. Soc.,* **88**: 66-78.

——, and L. J. Metz, 1963, Variation in Nutrient Content of Loblolly Pine Needles with Season, Age, Soil, and Position on the Crown, *Soil Sci. Soc. Amer., Proc.,* **27**: 90-93.

INFLUENCE OF NUTRIENT AVAILABILITY ON ECOSYSTEM STRUCTURE

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ABSTRACT

Studies of granite outcrop soils identified well-defined gradients in nutrient availability which can be correlated with species distribution patterns. Comparisons of nutrient availability and species nutrient uptake in these systems showed that soil nutrients become limiting to the growth and distribution of the dominant plants, *Sedum smallii*, *Minuartia uniflora*, and *Viguiera porteri*. The availability of calcium, magnesium, and nitrogen, as well as interspecific competition for these elements, most significantly limit species growth and distribution during periods when moisture availability is no longer limiting.

Studies of plant succession on exposed rock substrates have correlated the successive formation of early seral states with the accumulation of soil and availability of water (Cooper, 1913; Whitehouse, 1933; Keever, Oosting, and Anderson, 1951; Burbanck and Platt, 1964). Extensive field and laboratory studies of granite outcrop communities in similar seral states described species responses to soil depth and moisture gradients (Lugo, 1969; Sharitz and McCormick, 1973). The herbaceous-annual ecosystems (Burbanck and Platt, 1964) of many southeastern granite outcrops are dominated by three plant species, *Sedum smallii* (Britt.) Ahles, *Minuartia uniflora* (Walt.) Mattf., and *Viguiera porteri* (A. Gray) Blake. Each of these species occupies a distinct habitat easily defined by soil depth (Sharitz and McCormick, 1973). Braun (1971) correlated outcrop-species distribution patterns with soil-nutrient gradients, while Lammers (1959) suggested that nutrients may act as limiting factors in such ecosystems. These facts may be significant with respect to the zonation patterns of outcrop species since nutrient availability has been shown to

influence population distribution in other terrestrial ecosystems (Snaydon, 1962; Willis, 1963; Faye and Brown, 1964; Jeffries and Willis, 1974; Loach, 1968; Goodman, 1968; McCown and Williams, 1968; Snaydon and Bradshaw, 1969). It is proposed that nutrient availability functions as a second-order limiting factor influencing ecosystem structure since previous studies (Lugo, 1969; Sharitz and McCormick, 1973) have shown that moisture availability is primarily limiting.

Granite outcrops of the southeastern United States are isolated rock exposures located in a band approximately 120 miles wide to the north and west of the intersection of the Coastal Plain and Piedmont between North Carol[illegible] and Alabama (McVaugh, 1943). Rock types found are granite or granitic gn[illegible] composed principally of quartz and feldspar (Hermann, 1954). Isolated, elliptical, shallow depressions on these rock surfaces accumulate soil and support plant populations that are rigidly zoned in habitats of varying soil depth. Extensive field and laboratory studies of granite-outcrop communities have related ecosystem structure to soil depth and moisture gradients (Lugo, 1969; Sharitz and McCormick, 1973). Species adaptations to the rigorous environmental conditions that prevail on the outcrops have been described (McCormick and Platt, 1964; Lugo, 1969; Sharitz and McCormick, 1973; Mellinger, 1972). Three distinct vegetation zones have been identified in these herbaceous–annual ecosystems (Sharitz and McCormick, 1973). The most shallow habitat around the periphery of the ecosystem is dominated by *Sedum smallii.* The next innermost habitat of intermediate soil depth is dominated by *Minuartia uniflora.* The interior of the ecosystem contains *Viguiera porteri* along with several perennial species. These three plant species are endemic to rock outcrops of the southeastern United States (McVaugh, 1943; McCormick, Bozeman, and Spongberg, 1971).

Previous research on structural and functional relationships in these outcrop communities (Sharitz and McCormick, 1973; Mellinger, 1972) and the unique features of the ecosystems make them ideal for studying effects of nutrients on ecosystem structure. Specifically, (1) clear-cut nutrient gradients exist; (2) ecosystem boundaries are distinct; and (3) natural selection, resulting from nutrient limitation and other environmental factors, is an annually occurring event.

This study included (1) an analysis of ecosystem structure, including population distribution, density, and biomass; and (2) determination of nutrie[illegible] availability in soils of each species habitat, including contributions from rain, groundflow, soil pools, mineralization of soil organic matter, and leaching from dead vegetation. Estimates of nutrient uptake were obtained for *S. smallii, M. uniflora,* and *V. porteri* populations at various times during their life cycles. Comparisons of nutrient availability in different habitats with nutrient levels required by populations of species dominating each habitat led to the development of the hypothesis that the population distribution of these three

species in the outcrop ecosystem is influenced by nutrient availability and/or competition for available nutrients. An experiment incorporating a modified random block design was conducted to test this hypothesis.

MATERIALS AND METHODS

Ten island ecosystems of the annual–perennial herb type (Burbanck and Platt, 1964) were selected on Mt. Arabia, a large granitic gneiss dome 25 km southeast of Atlanta, Ga. The island ecosystems are circular–elliptical in outline, from 5 to 10 m in diameter, and do not exceed 25 cm in depth. Each habitat in seven island ecosystems was sampled to determine if nutrient concentrations differed as a function of soil depth and species habitat. Nine soil cores were collected per habitat. Each core was subdivided into samples from 0 to 2 and 2 to 4 cm increments in the *Sedum* habitat, 0 to 2, 2 to 4, and 4 to 8 cm increments in the *Minuartia* habitat, and 0 to 6, 6 to 12, and 12 to 18 cm increments in the *Viguiera* habitat. Standard chemical analyses were run on each sample.

Rainfall was collected in 8-in. rain gauges, modified with Parafilm, polyethylene tubing, and polyethylene containers. Analyses of organic nitrogen, nitrate, ammonia, phosphorus, cations, and pH of rainwater were conducted following summer storms. Groundwater nutrient concentrations were determined by collecting samples of inflow and outflow from each of four ecosystems three times during the year.

Groundwater inflow was determined for a relatively isolated ecosystem near the summit of the dome. Except for a small ecosystem located directly above the study site, the water flow was entirely from the surrounding rock surface. The watershed of this area was estimated by determining flow patterns at 0.3-m intervals of 18 compass azimuths radiating from the center of the main ecosystem. Drainage divides were plotted, graphically connected with a boundary line, and the watershed size was calculated through planimetry. Influx of water to the larger ecosystem was then determined by measuring rainfall and performing some simple mathematics based on watershed size. A correction factor for water retention by the other ecosystem in the watershed was also applied. Loss of groundwater from the watershed was determined by collecting all the groundflow from it via a conduit extending from a small dam constructed across its base. Nutrient fluxes were determined from measurements made on water samples collected at this site.

Living and dead biomass from *S. smallii, M. uniflora,* and *V. porteri* populations were collected at monthly intervals throughout the year from 1 dm^2 areas in the respective species habitats of 10 designated ecosystems.

Soil-particle size was measured by the Bouyoucos hydrometer method (Bouyoucos, 1927, 1936). Soil organic matter, pH, and cation-exchange capacity were determined by the Soil Testing Division of the North Carolina Department

of Agriculture. Soil-nutrient extracts were prepared following the procedure of Reid and Copeland (1969), and copper, manganese, zinc, calcium, magnesium, and potassium concentrations were determined by atomic absorption spectrophotometry. Total nitrogen and mineralized nitrogen were determined with a macro-Kjeldahl apparatus (Black, 1965). Concentrations of phosphorus, nitrate, and ammonia in rainwater, groundflow, and in soil extracts were measured with a Technicon autoanalyzer (Environmental Protection Agency, 1971). Plant phosphorus concentration was analyzed using a molybdo-vanadate method (Gillam and Stryker, 1970).

Nitrogen mineralization rates were determined in a laboratory incuba experiment. Sample aliquots of potassium chloride extract steam distilled w magnesium oxide and Devarda alloy were incubated for 14 days and then analyzed for NO_3, NH, and total nitrogen (Black, 1965; Meyer, 1972).

Soil samples were similarly prepared for phosphorus mineralization determinations and subjected to the same environmental parameters as those in the earlier experiment. At the end of the incubation period, 10 ml of triple-distilled water was added to each sample, and the samples were allowed to equilibrate for 30 min. The samples were vacuum filtered and analyzed following the procedure of Ng (1970). Ground oven-dried plant material was ashed at 500°C. Sample preparation for analysis followed the techniques of Gilliam and Stryker (1970) and Wells (1971).

Chemical analysis of rainwater and groundflow samples included the determination of calcium, magnesium, potassium, nitrate, ammonia, and organic nitrogen. Samples were refrigerated following collection and frozen until preparation for analysis. Cation and phosphorus concentrations were determined for 100-ml sample aliquots that had been evaporated to dryness, treated with 2 ml of 30% hydrogen peroxide, dried again, and rediluted with a 10-ml solution of 0.4*N* HCl : 0.25% La_2O_3. Nitrate and ammonia analyses were determined for unconcentrated samples. Organic nitrogen was determined for 25-ml samples digested with a potassium sulfate catalyst mixture (Black, 1965).

A modified random-block experimental design was used in the laboratory to test responses of each species to variations in soil-nutrient availability and competition for available nutrients. Tests included competition experiments with mixed populations of *S. smallii* and *M. uniflora* grown on soils characteristic of the habitat of each species. Mixed populations of *M. uniflora* and *V. por* were grown on soils collected from the *Minuartia* habitat. Soil depth, soil moisture, and population density were eliminated as variables through the selection of sets of conditions under which successful species growth had previously been demonstrated (Sharitz and McCormick, 1973; Mellinger, 1972). Simulation of natural profiles was achieved by layering surface soils above the subsoil. All pots were watered every 24 to 36 hr to attain a water-to-soil ratio (w/w) of 10%. Laboratory equilibration studies confirmed determinations by Sharitz and McCormick (1973) that this condition approximates field capacity.

The sizes of seed cohorts sown were based on earlier studies to minimize the effects of crowding (Sharitz and McCormick, 1973; Mellinger, 1972). The *S. smallii* and *M. uniflora* populations were subjected to a programmed environment simulating temperature and light conditions on the outcrops between the months of October and May, while *V. porteri* populations were subjected to an environment simulating outcrop conditions between January and September. Each treatment combination was replicated five times. Aboveground, oven-dried biomass was measured shortly after flowering ceased.

A nutrient-addition experiment was designed to determine which nutrients ...t limit species growth. Seeds of each of these species were sown on soils of ... respective habitats. To each pot the following single-element additions were made: nitrogen (50, 100 ppm), phosphorus (50, 100 ppm), potassium (39, 78 ppm), calcium (100 ppm), and magnesium (25, 50 ppm). Multiple-element additions were also made to assess species response to nutrient interactions. Initiating a series of nutrient additions with phosphorus, one element was added to each treatment, resulting in the sequence P (100 ppm), P + N (100 ppm N), P + N + K (78 ppm K), P + N + K + Ca (300 ppm Ca), P + N + K + Ca + Mg (25 ppm Mg). Soil depth, soil moisture, and seed cohort levels sown were identical to those used in the former experiment. Two replicates of each treatment combination were run per species. Assessment of results included the determination of available nutrients (magnesium, potassium, calcium, PO_4, NO_3, NH_3) at the outset of the study, total nutrient uptake by each species per treatment, and oven-dry biomass production.

Analysis of variance was used to determine the statistical significance of the results of the nutrient-addition study. Biomass production per single-nutrient-addition treatment was compared to the control, while biomass produced as a result of multiple-nutrient additions was compared to that resulting from the immediately previous treatment in the experimental sequence. Biomass data from other experiments were calculated as individual means ± 1 standard error (SE).

RESULTS

Soils underlying each habitat consist of greater than 85% sand. The mean soil ...k density in four ecosystems is 1.33 g/cm^3. In surface soils, organic matter increases from 1.75 to 8.21% from the periphery of the ecosystem to the center (Table 1). Cation-exchange capacity paralleled this gradient, ranging from 3.20 to 6.60 meq/100 g soil.

With the exception of phosphorus, surface soil-nutrient concentrations increased across the soil depth gradient (Table 1). Thus higher concentrations of elements were found in the *Viguiera* habitat than in the *Sedum* habitat. Calcium is the most abundant element with a concentration of 60.12 ppm. Surface soil trace-element concentrations also paralleled the soil depth gradient, ranging from

TABLE 1

PHYSICAL AND CHEMICAL CHARACTERISTICS OF OUTCROP ECOSYSTEMS*

Habitat	Soil depth, cm	Organic matter, %	Cation-exchange capacity, meq/100 g soil	Nutrients, ppm			
				Ca	Mg	K	P
Sedum smallii	0–2	1.75 ± 0.23	3.20 ± 0.31	15.6 ± 0.7	2.9 ± 0.2	19.6 ± 1.2	14.7 ± 1.0
	2–4	1.51 ± 0.35	3.13 ± 0.53	12.7 ± 0.6	1.9 ± 0.1	13.8 ± 0.6	25.0 ± 1.8
Minuartia uniflora	0–2	4.96 ± 0.79	4.53 ± 0.59	20.7 ± 1.5	4.7 ± 0.3	24.3 ± 1.5	23.9 ± 1.5
	2–4	2.33 ± 0.45	4.03 ± 0.59	13.5 ± 1.1	2.4 ± 0.2	15.0 ± 1.2	23.2 ± 1.8
	4–8	1.77 ± 1.10	3.91 ± 0.53	8.5 ± 0.7	2.0 ± 0.2	12.8 ± 1.0	23.6 ± 2.6
Viguiera porteri	0–6	8.21 ± 1.02	6.60 ± 1.30	60.1 ± 5.1	8.6 ± 0.4	29.5 ± 2.4	8.6 ± 0.4
	6–12	3.63 ± 0.48	4.85 ± 0.33	8.7 ± 0.5	3.2 ± 0.1	14.4 ± 0.9	6.8 ± 0.4
	12–18	2.48 ± 0.24	4.22 ± 1.31	6.5 ± 0.5	2.2 ± 0.1	10.2 ± 0.9	13.6 ± 0.6

*All values are arithmetic means of nine soil cores per habitat removed from each of seven outcrop ecosystems ±1 SE.

0.36 to 0.56 ppm for copper, 0.31 to 3.56 ppm for zinc, and 0.24 to 4.30 ppm for manganese.

Mean pH of rain samples was 4.86 with little variability. Nitrate (0.10 to 0.13 ppm) and ammonia (0.13 to 20 ppm) concentrations were generally greater than that of other elements (calcium, 0.09 to 0.15; magnesium, 0.03 to 0.05; potassium, 0.06; phosphorus, 0.001 ppm).

Calculation of the nutrient flux resulting from rainfall, for one ecosystem, included determinations of rain volume, the surface area drained by the ecosystem, and the chemical concentration of dissolved nutrients in groundwater flowing into and out of the system. Nutrient inputs and outputs for a 1.2-cm rainfall (615.5 liters of water) were, respectively: calcium, 40.95 and 40.90 mg; magnesium, 17.84 and 17.73 mg; potassium, 33.60 and 33.40 mg; phosphorus, 0.12 and 0.09 mg; and NH_4, 1.86 and 0.85 mg. The annual nutrient budget resulting from rainfall and throughflow for the ecosystem is shown in Table 2.

Losses of nutrients from dead biomass of *S. smallii*, *M. uniflora*, and *V. porteri* vary with season and by species. Rates of nutrient loss and percentage nutrient depletion were highest in populations of *M. uniflora* (Meyer, 1972). Nutrient losses in the first 4 months following the death of each species ranged from 70 mg Mg/m^2 to 583 mg N/m^2 in *S. smallii* populations, from 0.105 mg P/m^2 to 1051 mg N/m^2 in *M. uniflora* populations, and from 153 mg Mg/m^2 to 1815 mg N/m^2 in *V. porteri* populations (Table 2).

Factors contributing to nutrient availability include soil nutrient content, additions from rainfall and groundflow, additions from leaching of dead biomass, and additions from mineralization. Coupling these components and multiplying them by the respective surface areas of each habitat provided an estimate of total nutrient availability per habitat for the ecosystem (Table 2) as well as an estimate of nutrient availability for the entire system. With the exception of phosphorus, nutrient availability per habitat parallels the soil depth gradient. The total nutrient availability for one island ecosystem was calcium, 23.86 g, magnesium, 6.53 g, potassium, 25.21 g, phosphorus, 29.63 g, and nitrogen, 27.90 g.

Seasonal biomass distribution and seasonal variation in nutrient content for species populations of *S. smallii*, *M. uniflora*, and *V. porteri* are shown in Table 3. Maximum biomass for these respective populations was 0.77 g/dm^2 in March, 0.72 g/dm^2 in April, and 2.61 g/dm^2 in September. Nitrogen, potassium, and calcium ranked first, second, and third in relative abundance within each species population at maturity.

Populations of *S. smallii* and *V. porteri* achieved maximum biomass production in soils characteristic of their native habitat (Fig. 1), while biomass production by *M. uniflora* was not significantly influenced by soil type. Competition with *M. uniflora* greatly inhibited biomass production (Fig. 2) and nutrient uptake in *S. smallii*. When grown in the presence of *M. uniflora*, nutrient uptake by *S. smallii* dropped, relative to control populations, as

TABLE 2

FACTORS CONTRIBUTING TO NUTRIENT AVAILABILITY IN THREE HABITATS OF AN ISLAND ECOSYSTEM*

Habitat	Ca	Mg	K	P	NO_3–N	NH_4–N	N
				Nutrients in the Soil, g/m²			
Sedum	0.884	0.178	1.036	1.530	0.051	0.028	0.078
Minuartia	0.877	0.283	1.587	2.709	0.011	0.137	0.149
Viguiera	3.259	0.899	3.992	1.494	0.210	0.092	[illegible]3
				Addition from Leaching of Dead Vegetation, g/m²			
Sedum	0.221	0.070	0.306	0.079			0.583
Minuartia	0.140	0.128	0.430	0.105			1.05[illegible]
Viguiera	1.010	0.153	1.549	0.167			1.8[illegible]
				Addition from Nitrogen and Phosphorus Mineralization, g/m²			
Sedum				0.005			1.246
Minuartia				0.006			1.043
Viguiera				0.008			0.886
				Addition from Rainwater and Throughflow, g/m²			
Sedum	0.002	0.003	0.002	0.0		0.001	
Minuartia	0.004	0.005	0.004	0.0		0.001	
Viguiera	0.006	0.008	0.007	0.0		0.002	
				Annual Nutrient Availability, g/m²			
Sedum	1.106	0.250	1.328	1.614			1.907
Minuartia	1.021	0.416	2.028	2.820			2.243
Viguiera	4.285	1.060	5.548	1.669			2.815
				Annual Nutrient Availability, g/habitat			
Sedum	4.958	1.121	6.023	7.209			8.5[illegible]
Minuartia	4.493	1.833	8.890	12.381			9.873
Viguiera	14.408	3.573	18.697	5.624			9.487

*Annual nutrient availability in each habitat is estimated by the sum of the contributions of each factor. Where numerical values are not reported, no chemical a[illegible]s was performed.

follows: calcium, 0.26 to 0.10 mg/dm^2; magnesium, 0.80 to 0.20 mg/dm^2; potassium, 0.55 to 0.15 mg/dm^2; phosphorus, 0.35 to 0.15 mg/dm^2; and nitrogen, 0.68 to 0.19 mg/dm^2.

Minuartia uniflora, however, was relatively unaffected by competition with *S. smallii.* Biomass production in *M. uniflora* populations was significantly reduced by competition with *V. porteri.* These results are in accord with the field observations and competition studies of Sharitz and McCormick (1973).

TABLE 3

SEASONAL DISTRIBUTION OF NUTRIENTS AND BIOMASS IN THREE DOMINANT OUTCROP PLANT SPECIES*

	Biomass, g/m²			Nutrient content, g/m²													
				Ca			Mg			K			P			N		
Month	S	M	V	S	M	V	S	M	V	S	M	V	S	M	V	S	M	V
Feb.	52	34	6	0.19	0.05	0.01	0.07	0.08	0.003	0.09	0.13	0.004	0.11	0.10	0.01	0.67	0.86	
Mar.	77	52	22	0.29	0.11	0.17	0.07	0.09	0.08	0.29	0.31	0.24	0.11	0.18	0.04	0.97	0.79	
Apr.	66	72	40	0.25	0.16	0.31	0.06	0.13	0.15	0.25	0.43	0.44	0.09	0.11	0.07	0.83	1.09	1.51
May	59	54	58	0.25	0.11	0.43	0.07	0.06	0.21	0.18	0.13	0.70	0.10	0.03	0.14	0.60	0.51	1.71
June	54	35	98	0.21	0.06	0.69	0.02	0.01	0.23	0.03	0.02	1.28	0.09	0.02	0.20	0.61	0.28	2.59
July	50	18	150	0.15	0.02	1.05	0.03	0.0	0.24	0.06	0.01	1.04	0.07	0.01	0.20	0.68	0.15	2.46
Aug.	48	4	214	0.07	0.0	1.06	0.01	0.0	0.22	0.02	0.0	1.23	0.03	0.0	0.21	0.65	0.03	2.23
Sept.	46		261	0.06		1.18	0.02		0.26	0.03		1.83	0.04		0.24	0.50	0.0	2.77

**Sedum smallii,* S; *Minuarta uniflora,* M; and *Viguiera porteri,* V.

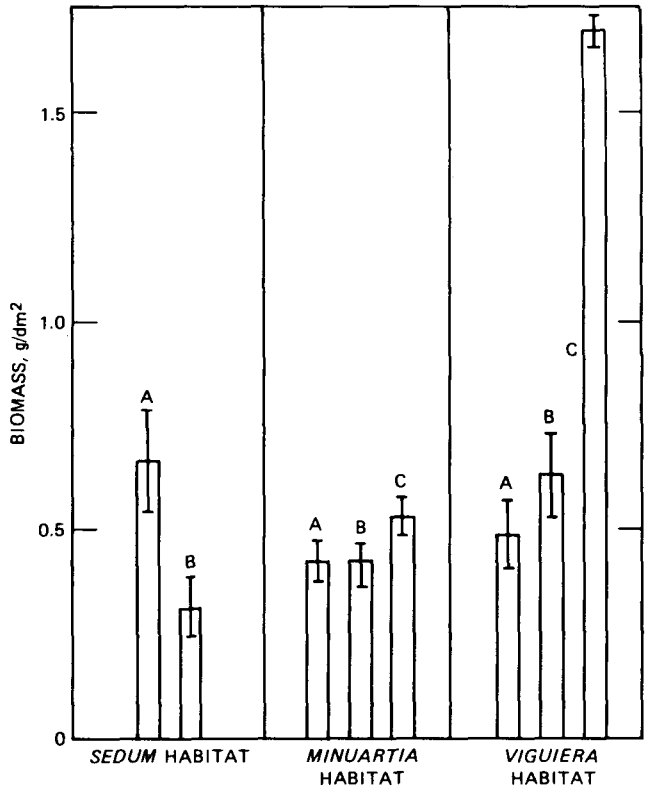

Fig. 1 Species growth of soil from three outcrop habitats. Biomass production is shown by A, *Sedum smallii*; B, *Minuartia uniflora*; and C, *Viguiera porteri* on soils of the habitat shown. All values are arithmetic means ± 1 SE.

Significant biomass increases resulted from N and N + P treatments in *S. smallii* from Ca + N, N + P + K, N + P + K + Mg, and total treatments in *M. uniflora*; and from N + P, N + P + K + Mg, and total nutrient additions in *V. porteri* (Table 4).

DISCUSSION

Well-defined gradients of pH, soil organic matter, cation-exchange capacity, and nutrients exist within granite-outcrop island ecosystems (Table 1). In *Sedum, Minuartia,* and *Viguiera* habitats, these shallow sandy soils with low pH are relatively infertile. This condition is partly offset by a high organic-matter content, particularly in the surface soils of the *Viguiera* habitat. Soil organic matter, cation-exchange capacity, and soil nutrients (with the exception of phosphorus) all increase toward the center of the ecosystem. For instance,

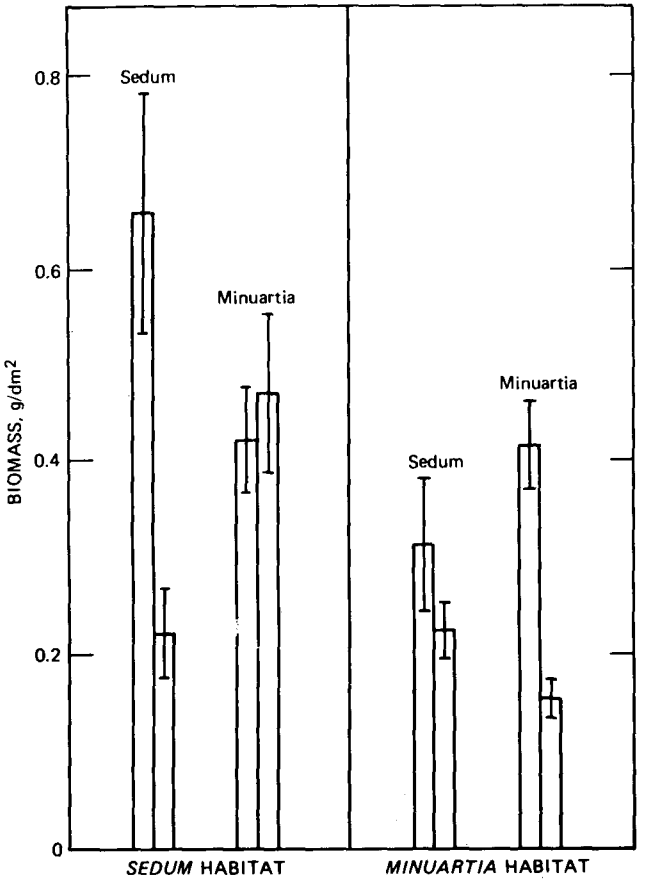

Fig. 2 Competition effects between populations of *Sedum smallii* and *Minuartia uniflora*. Biomass produced in competition-free soils is represented by the left-most bar of each group; biomass produced during competition is represented by the second bar. *Sedum smallii* and *M. uniflora* were competitors except in the last group, where *Minuartia* competed with *Viguiera porteri* All values are arithmetic means ±1 SE.

cium concentration across the soil depth gradient was 15.6 ppm in the *Sedum* habitat, 20.7 ppm in the *Minuartia* habitat, and 60 ppm in the *Viguiera* habitat (Table 1).

Comparisons of nutrient uptake for populations of *S. smallii*, *M. uniflora*, and *V. porteri* (Table 3) with the estimated annual nutrient availability (Table 2) in the three respective habitats show the potentiality for growth of a species in zones outside that of its natural occurrence. For example, since calcium availability in all habitats exceeds the 0.29 g Ca/m^2 required by *S. smallii* populations, *Sedum* should not be restricted to any particular zone by this

TABLE 4

BIOMASS PRODUCTION, g/dm^2, IN THREE OUTCROP SPECIES FOLLOWING NUTRIENT ADDITIONS TO OUTCROP SOILS*

	Sedum smallii	*Minuartia uniflora*	*Viguiera porteri*
Control	0.96	0.45	0.82
Mg	1.31	0.58	1.05
Mg+	0.93	0.31	0.95
K	0.71	0.45	0.83
K+	0.71	0.20	0.93
N	1.65†	0.37	0.99
Ca	0.74	0.28	0.89
Ca + N	0.73	0.57‡	1.80
P	0.80	0.49	0.76
P+	1.03	0.35	0.87
N + P	1.91‡	0.48	3.11†
N + P + K	2.01	0.70‡	4.81
N + P + K + Mg	2.46	2.16‡	7.08‡
Total	2.67	3.03‡	10.74‡

*Each species was grown on soils collected from its native habitat. Levels of nutrient concentrations (ppm) in single element additions are N = 50, P = 50, K = 39, Ca = 300, and Mg = 25. Values followed by a plus indicate concentrations twice as high as the foregoing. Levels of nutrient concentrations in multiple element additions are P = 100, N = 100, K = 78, Ca = 300, and Mg = 25. In multiple-element additions, statistical comparisons are with the prior treatment, while in single-element additions, statistical comparisons are with the control.

†Significant at the 10% level.

‡Significant at the 5% level.

element. Similar comparisons for other elements indicate that neither *S. smallii* nor *M. uniflora* is limited by nutrients in any habitat when growing in competition-free environment. When in competition with each other, however, they tend to be limited by insufficient nitrogen (Tables 2 and 3). Such comparisons also showed that *V. porteri* populations are severely limited by calcium and nitrogen deficiencies in shallow-depth soils. It was therefore hypothesized that nutrient availability can influence species growth and distribution and thus affect the structure of outcrop ecosystems.

Experimental studies substantiate this hypothesis by showing the limiting effect of soil nutrients on the growth and distribution of the dominant plant

species. In *S. smallii* populations, greatest biomass was produced in competition-free soil of the shallowest soil zones (Fig. 1), and biomass was reduced in competition-free soil from the adjacent habitats. Since Sharitz and McCormick (1973) showed that *S. smallii* thrived in deep outcrop soils in relatively competition-free environments, these results suggest differences in nutrient levels and moisture-holding capacity in soil from the different habitats.

Factors controlling the distribution of *S. smallii* populations are soil depth and available water (Sharitz and McCormick, 1973), insufficient nitrogen resulting from lower mineralization rates in relatively deeper island soils (Table 2), and the inability of *Sedum* to compete with *M. uniflora* for nitrogen as well as for magnesium and potassium. Soil depth is an important factor controlling water availability and acting as a pool for nutrients.

The differences between soil-nutrient availability and nutrient concentrations in mature plant tissue indicate nutrient stress in soils 1 cm deep in the *S. smallii* habitat. As the soil depth increases to 4 cm, a four-fold increase in nutrient availability eliminates this stress. This is substantiated by the fact that maximum population development of the species occurs in soils 2 to 10 cm deep (Sharitz and McCormick, 1973). Field studies showed the availability of all nutrients in the *Minuartia* habitat to be adequate for growth of *S. smallii* or *M. uniflora* populations. Since all elements except nitrogen are sufficiently available for growth of mixed populations of these species (Tables 2 and 3), it may be assumed that decreased growth of *S. smallii* populations in *Minuartia* habitats is due to the inability of *Sedum* to compete for nitrogen. The sum of nitrogen in plant tissue from these two species is 2.06 g N/m^2, while only 1.91 g N/m^2 is available under optimum soil conditions where these species naturally overlap. Thus competition for this element may occur, as indicated by the substantial reduction in biomass production in *S. smallii* under competition (Fig. 2). Decreased uptake of nitrogen, magnesium, and potassium in *S. smallii* also occurs under competition. Lower nitrogen mineralization rates in the *Minuartia* habitat (Table 2) may also explain the reduction in biomass which occurs when *S. smallii* populations grow on soils of the *Minuartia* habitat (Fig. 1). Supporting evidence from controlled laboratory experiments (Table 4) show that *S. smallii* populations are limited primarily by nitrogen and to a lesser extent by phosphorus. Similar results were reported by Lammers (1959) in granite-outcrop communities and by McCown and Williams (1968) who suggested that insufficient nitrogen and other nutrients are responsible for species distribution patterns in grassland ecosystems.

The distribution of *M. uniflora* is influenced by water availability (Sharitz and McCormick, 1973) and competition for nitrogen with *V. porteri*. Competition determines the inner boundary of *M. uniflora* populations. Combined nitrogen uptake of *M. uniflora* and *V. porteri* populations, which overlap in March, varies between 2.08 and 2.59 g N/m^2, while the total nitrogen availability under most optimal conditions is only 2.24 g/m^2, (Table 2). In

addition, biomass of *M. uniflora* grown in competition with *V. porteri* is reduced (Fig. 2). Shading by *Polytrichum commune* populations probably further restricts *M. uniflora* populations to shallow soils where *Polytrichum* is not commonly found (Meyer, 1972).

The growth and distribution of *V. porteri* is limited by inadequate soil moisture (Lugo, 1969; Mellinger, 1972) and nutrients. Normal development of this species requires a minimum of 100 drought-free days during the growing season (Lugo, 1969; McCormick, Lugo, and Sharitz, 1974). Furthermore, this 100-day period cannot be interrupted by more than 14 days of consecutive drought stress. It is important to determine if nutrients become limiting during this favorable moisture period because stunted *V. porteri* plants are relatively more susceptible to drought stress (Mellinger, 1972). Comparisons of nutrient uptake by natural populations of this species (Table 3) with estimated nutrient availability in the different habitats (Table 2) indicates that nitrogen limits *V. porteri* growth in shallow zone soils, while cation availability is secondarily limiting. Thus decreased nutrient availability in shallow soils causes stunting and thereby limits the distribution of this species to the deep-soil habitat.

ACKNOWLEDGMENTS

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REFERENCES

Black, C. A., et al., 1965, *Methods of Soil Analysis,* Vol. 2, American Society of Agronomy, Madison, Wisc.

Bouyoucos, E. J., 1936, Direction for Making Mechanical Analysis of Soils by the Hydrometer Method, *Soil Sci.,* 42: 225-230.

——, 1927, The Hydrometer Method for Studying Soils, *Soil Sci.,* 25: 365-369.

Braun, D., 1971, Studies of Outcrops on Mt. Panola, Georgia, Emory University, Atlanta, Ga., unpublished.

Burbanck, M. P., and R. B. Platt, 1964, Granite Outcrop Communities of the Piedmont Plateau in Georgia, *Ecology,* 45: 292-305.

Cooper, W. S., 1913, The Climax Forest of Isle Royale, Lake Superior, and Development, *Bot. Gaz. (Chicago),* 55: 1-44.

Environmental Protection Agency, 1971, *Methods for Chemical Analysis of Water and Wastes,* Water Quality Office, Cincinnati, Ohio.

Faye, C. C., and J. C. Brown, 1964, Toxic Factors in Acid Soils. II. Differential Aluminum Tolerance of Plant Species, *Soil Sci. Soc. Amer., Proc.,* 28: 27-32.

Gilliam, J., and R. Stryker, 1970, *Plant Analysis Procedures of the Analytical Service Laboratory of the Soil Science Department,* North Carolina State University, Raleigh N. C.

Goodman, G. T., 1968, The Role of Mineral Nutrients in *Eriophorium* Communities: Effects of Added Limestone on Availability and Uptake of Inorganic Elements, *J. Ecol.*, **56**: 545-564.

Hermann, L. A., 1954, *Geology of the Stone Mountain–Lithonia District*, Georgia Geological Bulletin No. 61, Georgia State Division of Conservation.

Jeffries, R. L., and A. J. Willis, 1964, Studies on Calcicole–Calcifuge Habitat, *J. Ecol.*, **52**: 121-138.

Keever, C., H. J. Oosting, and L. Anderson, 1951, Plant Succession on Exposed Granite of Rocky Face Mountain, Alexander County, N. C., *Bull. Torrey Bot. Club*, **78**: 401-421.

Lammers, W., 1959, A Study of Certain Environmental and Physical Factors Influencing the Adaptation of Three Granite Outcrop Endemics, Ph. D. Dissertation, Emory University, Atlanta, Ga.

Loach, K., 1968, Relations Between Soil Nutrients and Vegetation in Wet Heaths, *J. Ecol.*, **56**: 117-127.

Lugo, A., 1969, Carbon, Water, and Energy Budgets of a Natural Community, Ph. D. Dissertation, University of North Carolina, Chapel Hill, N. C.

McCormick, J. F., J. R. Bozeman, and S. Spongberg, 1971, A Taxonomic Revision of Granite Outcrop Species of *Minuartia (Arenaria)*, *Brittonia*, **23**: 149-160.

——, A. Lugo, and R. R. Sharitz, 1974, Experimental Analysis of Ecosystems, *Handbook of Vegetation Science*. Part VI. Vegetation and Environment, W. Junk, Publishers, The Hague.

——, and R. B. Platt, 1964, Ecotypic Differentiation in *Diamorpha cymosa*, *Bot. Gaz. (Chicago)*, **125**: 271-279.

McCown, R. L., and W. A. Williams, 1968, Competition for Nutrients and Light Between Annual Grassland Species, *Ecology*, **49**: 981-990.

McVaugh, K., 1943, The Vegetation of the Granite Flat-Rocks of the Southeastern United States, *Ecol. Monogr.*, **13**: 120-166.

Mellinger, A. C., 1972, Ecological Life Cycle of *Viguiera porteri*, Ph. D. Dissertation, University of North Carolina, Chapel Hill, N. C.

Meyer, K. A., 1972, Influence of Nutrient Availability and Nutrient Cycles Upon Ecosystem Structure and Stability, Ph. D. Dissertation, University of North Carolina, Chapel Hill, N. C.

Ng, S. K., 1970, Automated Determination of Phosphate Content of Soils Under Rubber Cultivation, *J. Sci. Food Agr.*, **21**: 275-278.

Reid, P., and C. Copeland, 1969, *Analytical Methods Used by the Soil Testing Division*, North Carolina Department Agriculture, Raleigh, N. C.

Sharitz, R. R., and J. F. McCormick, 1973, Population Dynamics of Two Competing Annual Plant Species, *Ecology*, **54**(4): 723-740.

Snaydon, R. W., 1962, Microdistribution of *Trifolium repens* L. and Its Relation to Soil Factors, *J. Ecol.*, **50**: 133-143.

——, and A. Bradshaw, 1969, Difference Between Natural Population of *Trifolium repens* in Response to Mineral Nutrients: Ca, Mg, and K, *J. Appl. Ecol.*, **6**: 185-202.

Wells, C., 1971, U. S. Forest Service, Research Triangle Park, North Carolina, personal communication.

Whitehouse, E., 1933, Plant Succession on Central Texas Granite, *Ecology*, **14**: 391-405.

Willis, A. J., 1963, Braunton Burrows: The Effects on the Vegetation of the Addition of Mineral Nutrients to the Dune Soils, *J. Ecol.*, **51**: 353-374.

NUTRIENT BUDGETS FOR UNDISTURBED ECOSYSTEMS ALONG AN ELEVATIONAL GRADIENT IN NEW MEXICO

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ABSTRACT

The Tesuque watersheds in the Sangre de Cristo Mountains of New Mexico were studied to compare the nutrient flux of ecosystems from different zones and biomes along an elevational gradient and on a common bedrock. Nutrient budgets for Ca, Mg, Na, and K are presented for 1972 and 1973 for watershed ecosystems with vegetation ranging from piñon–juniper to spruce–fir and alpine tundra. Nutrient inputs varied over elevation as a result of large quantities of precipitation at high elevations and of dust at low elevations. The seasonal quantity and distribution of precipitation affected the relationship between nutrient inputs from dust and precipitation. Stream chemistry and nutrient output (dissolved loss) also varied over the elevational gradient. A number of factors appear to be involved: evapotranspiration, nutrient uptake, throughfall, discharge volume, CO_2 production in soil, and soil chemistry. The nutrient budgets for the watersheds showed that the smallest loss or maximum accumulation generally occurred on intermediate elevations having mixed conifer vegetation. This vegetation zone has the greatest plant and animal diversity, and the high actual evapotranspiration rate of this zone suggests that it has the highest rate of primary production. These data support the hypothesis that a high efficiency of nutrient cycling (nutrient conservation) is associated with high productivity and community complexity.

Recent research has identified the efficiency with which undisturbed ecosystems cycle their nutrient capital. Studies at Hubbard Brook in New Hampshire have shown that the nutrients lost annually comprise a very small percentage of the nutrients cycling within the system (Likens and Bormann, 1971; Gosz, Likens, and Bormann, 1972; 1973; 1974). Much of the annual net loss for some nutrients can be explained by weathering of the bedrock. Other nutrients, e.g., nitrogen and phosphorus, demonstrated an annual net accumulation. Studies of undisturbed hardwood forests in North Carolina substantiate many of these results (Johnson and Swank, 1973). Although the effectiveness of undisturbed

hardwood forest ecosystems has been demonstrated, there is a dearth of literature identifying the relative nutrient-cycling efficiencies of undisturbed ecosystems from different vegetation zones or biomes. How efficient is the cycling process for ecosystems differing in productivity, biomass, and diversity? A major difficulty with this research is that the variation in bedrock composition of different areas significantly affects losses of dissolved nutrients (Hem, 1970). The mountainous regions of the Southwest provide an area where this type of research can be performed. Relatively large elevational changes can be found over a short distance. This causes a steep gradient of moisture and temperature thus allows the presence of a number of vegetational zones and biomes in a tively small area, often with a common bedrock. The Tesuque watersheds in the Sangre de Cristo Mountains of New Mexico provide such a study area. The objective of this paper is to report on the nutrient budgets for Ca, Mg, Na, and K of a number of undisturbed communities ranging from piñon–juniper to spruce–fir and alpine tundra. The nutrient budgets will be related to the hydrological cycle and biological parameters of each community.

TESUQUE WATERSHED ECOSYSTEMS

The small watershed approach has been shown to facilitate the study of nutrient cycles because it is advantageous in evaluating interrelationships between the biota, nutrient cycles, hydrologic cycle, and energy flow in a single ecosystem (Bormann and Likens, 1967). This approach allows us to quantify inputs to the ecosystem (by precipitation and sedimentation) and output from the system (by stream transportation) and, hence, allows us a comprehensive view of the dynamic status of the ecosystem. The nutrient flux obtained by this approach indicates the ability of the ecosystem to retain or accumulate nutrient capital.

A survey was made of a number of forested watersheds in New Mexico for use in ecosystem studies. Three criteria were used in the selection process; each watershed must (1) have a uniform geological formation that is watertight; (2) be on federally owned land to allow controlled long-term studies; and (3) be accessible at all times of the year. The Tesuque watersheds in the Sangre de Cristo Mountains best fit these requirements. They are located about 15 km theast of Santa Fe in the Santa Fe National Forest.

The Sangre de Cristo Mountain range is oriented in a north–south direction. The topography of the study watersheds ranges from narrow, steep canyons to steep, complex mountainside slopes. There is some evidence of glaciation at the highest elevations. The majority of the watersheds are typified by slopes greater than 40%. The elevation of the study area ranges from 2408 m (8000 ft) to 3750 m (12,300 ft). The bedrock of the area is Embudo granite (Miller, 1961) and is watertight (Cobb and Dien, 1974). During the period from 1961 to 1964, gaging stations having either 90° or 120° V-notch weirs were constructed on seven watersheds (Fig. 1). Construction of these weirs was a joint effort of the

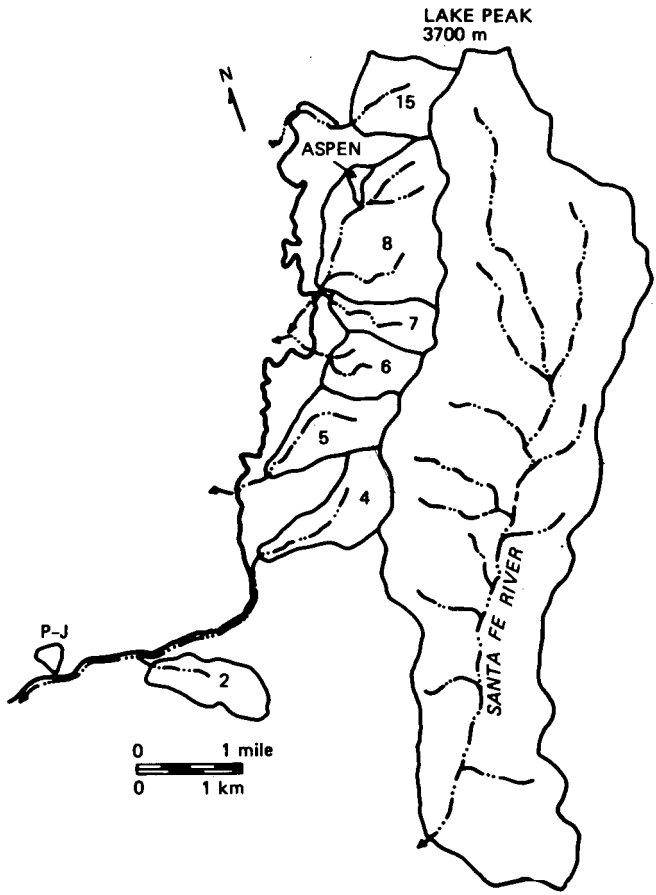

Fig. 1 Tesuque watershed study area, showing the various watershed sampling stations (P–J, piñon–juniper).

U. S. Geological Survey, Interstate Stream Commission, and the U. S. Forest Service. During 1973 an eighth weir (22½° V notch) was constructed on a small aspen watershed (3.4 ha) within one of the larger watersheds. This watershed is currently being used for intensive studies of intrasystem cycling. A surfaced road allowing access to the gaging stations is maintained throughout the year. A secondary gravel road, which is closed to the public, allows access to the crest of the mountain range during the snow-free months. This road passes through two of the study watersheds (7 and 8), and its effect on their nutrient budgets will be discussed.

In addition, the Santa Fe municipal watershed is used to verify some of the results from the Tesuque watersheds. The Santa Fe watershed is very large

(3250 ha) and covers the same elevational range and vegetation associations found in the Tesuque study area. The bedrock is also the same, Embudo granite. This large watershed has no roads and has been completely closed to the public since the 1940s. Its undisturbed condition allows us to evaluate changes in cation concentrations in the main stream as affected by nutrient output from smaller watersheds of different vegetational composition and elevation.

A number of vegetational zones or biomes exist in the study area (Table 1). At the lower elevations the piñon–juniper [*Pinus edulis* Engelm.–*Juniperus monosperma* (Engelm.) Sarg] community predominates. Ponderosa pine (*Pinus ponderosa* Laws.), mixed conifer [*P. ponderosa* Laws., *P. flexilis* James, *Abies concolor* Lindl., *Pseudosuga menziesii* Franco, *Picea engelmannii* Parry, and *Abies lasiocarpa* var. *arizonica* (Merriam) Lemm.], trembling aspen (*Populus tremuloides* Michx.), and spruce–fir [*Picea engelmannii* Parry–*Abies lasiocarpa* var. *arizonica* (Meriam) Lemm.] communities occur at successively higher elevation zones. Subalpine grassland and alpine tundra occur at the highest elevations. In 1886 a severe fire occurred which removed a portion of the climax spruce–fir forest in two of the watersheds (7 and 8). This area now has aspen vegetation (up to 3355 m) or subalpine grassland. The large watersheds range

TABLE 1

CHARACTERISTICS OF THE TESUQUE WATERSHEDS

Item characteristic	Watershed						
	2	4	5	6	7	8	15
Runoff,* cm							
1963	1.12		8.89	16.05	21.06	28.78	
1964	0.76		7.21	14.78	19.05	26.95	39.78
1965	0.89	7.75	14.38	27.28	36.80	46.46	65.93
1966	1.12	6.71	13.34	26.67	34.01	42.60	47.96
1967	0.23	1.70	4.37	10.06	11.63	17.58	28.07
1968	0.64	7.52	10.41	20.17	27.81	36.04	44.40
Average	0.79	5.92	9.78	19.18	25.07	33.07	45.24
Elevation, m							
Maximum	2850	3383	3444	3520	3490	3658	3734
Minimum	2423	2621	2804	2972	2987	2941	3231
Vegetation, ha							
Piñon–juniper	10	0	0	0	0	0	0
Pine	106	0	11	0	0	0	0
Mixed conifer	0	100	18	0	0	0	0
Spruce–fir	0	80	112	103	64	45	123
Aspen	0	0	23	19	13	203	0
Nontimbered	0	0	0	0	23	166	40
Total	116	180	164	122	100	414	163

*Per water year.

from 100 to 415 ha and have a mixture of vegetational types because of their size and aspect variations.

The orientation and altitude of the mountain ranges and its interior continental location give the Santa Fe region a semiarid climate. The two major source areas for precipitable moisture are the Pacific Ocean to the west and the Gulf of Mexico to the southeast. Several high mountain chains (the Sierra Nevada and Cascade ranges) and plateaus (Colorado plateau and smaller plateaus within the Basin and Range province) modify and dry out the air masses from the Pacific Ocean. Air masses from the Gulf of Mexico are not so highly modified but still are relatively dry. These two air masses are seasonal in their dominance. The summer precipitation originates from the Gulf of Mexico, and winter moisture arrives from the Pacific Ocean. The Gulf of Mexico air masses produce about 70% of the total precipitation for the Santa Fe area (Trewartha, 1968). The westward thrusts of Gulf air masses plus orographic lifting caused by the Sangre de Cristo Mountains are responsible for nearly all the summer precipitation in the study area. Most of this precipitation is from thunderstorms. Moisture that produces winter precipitation is brought into the Southwest by eastward-moving low-pressure cells that originate in the northern Pacific. Precipitation from both orographic and frontal lifting occurs during the winter.

These climatic conditions cause monthly and yearly precipitation to be unpredictable, with the predictability of summer precipitation being less than that of winter precipitation. Table 2 shows the monthly average, range, and maximum storm (24-hr period) for rain and snow at Santa Fe. The data emphasize the variability of precipitation and the fact that a single storm can exceed the long-term precipitation average for almost any month of the year.

All gaged watersheds contain perennial streams with the exception of the lowest watersheds during very dry summers. The elevational range covered by the watersheds causes a wide range in annual discharge volumes (Table 1). A progressive snow-melt peak typically ranges from April at the lower watersheds to June at the upper watersheds. Summer thunderstorms cause peak flows in August for all watersheds.

METHODS AND PROCEDURES

Quantification of precipitation, streamflow, and the concentrations of nutrients entering and leaving the watershed allows us to calculate nutrient flux for individual watersheds. Although a number of cations and anions are under investigation, we will only report on calcium, magnesium, sodium, and potassium in this paper.

Precipitation was recorded by a combination of standard and recording rain gages. During the study period reported here (October 1971 to September 1973), three precipitation stations, at 2377, 2987, and 3292 m elevation, were in service. Currently, seven precipitation stations are in service over the

TABLE 2

LONG-TERM PRECIPITATION RECORDS*
FOR SANTA FE, NEW MEXICO, 1850 TO 1970

Month	Total precipitation, cm			Snowfall, cm	
	Monthly average	Range	Maximum during 24-hr period	Monthly average	Maximum during 24-hr period
Jan.	1.7	0–7.7	3.1	18.8	69.3
Feb.	1.9	0–13.2	2.1	16.8	47.5
Mar.	2.1	0–6.6	3.1	12.7	46.2
Apr.	2.4	0–12.2	3.5	6.1	33.5
May	3.4	0–14.2	6.3	1.3	12.4
Jun.	2.7	0–11.1	5.5	0.0	0.0
Jul.	6.2	1.0–18.9	7.2	0.0	0.0
Aug.	5.8	0.9–20.0	4.2	0.0	0.0
Sept.	3.8	0–13.7	7.2	0.5	10.2
Oct.	2.9	0–10.6	4.6	0.5	32.5
Nov.	1.7	0–9.0	3.3	7.9	37.6
Dec.	1.9	0–5.8	2.4	16.0	50.8
Annual	36.5	12.8–63.0		80.6	

*Data from Kelly, 1973.

elevational gradient at approximately 300-m intervals. Regressions of precipitation on elevation were calculated for annual precipitation and applied to individual watersheds to estimate the weighted areal precipitation. Rainfall samples for chemical analysis were collected weekly from polyethylene collectors described by Likens et al. (1967). The design of these collectors eliminates the concentration of solutes by evaporation. Snowfall was collected in large plastic garbage cans lined with clean plastic bags and placed about 2 m above the ground. The bags were removed and closed to prevent contamination during transit to the laboratory. Since the precipitation samples contained chemicals from dry fallout, the analyses estimate bulk precipitation. Samples contaminated by bird droppings, etc., were disregarded. The product of precipitation volume and chemical concentration estimates the nutrient input of the four cations under study.

Streamflow was measured continuously at the base of each gaged watershed. During winter months the weirs were heated to prevent the V notches from icing up. Samples of stream water were collected weekly from each gaged watershed for chemical analysis. During periods of high discharge more frequent sampling occurred. The samples were collected above the weir in 500-ml acid-washed polyethylene bottles. Weekly stream samples also were collected from a piñon–juniper watershed (P–J, Fig. 1), which is not gaged. At the collection site bottles were rinsed twice with stream water before collection. Samples collected

before Nov. 1, 1972, were returned to the laboratory within 6 hr of collection and frozen until analysis. Later experiments demonstrated that the freezing process causes precipitation of a portion of the dissolved salts. The amount of precipitate formed was directly related to the concentration of dissolved salts. In our procedure samples are not filtered and are well shaken before analysis. Thus the concentration values reported for samples collected before November 1972 are expected to be similar to actual values but may be more variable because the amount of precipitate in the portion taken for analysis varied. Subsequent experiments have shown that concentration values for frozen samples range from within ±5% of those for fresh samples at watershed 15 to within ±13% at P–J watershed. The averages of values for fresh and frozen samples were not significantly different ($P < 0.05$). All samples collected after Nov. 1, 1972, were returned to the laboratory within 6 hr and refrigerated at 2°C until they were analyzed. Analyses occurred within 2 to 3 days of collection.

Chemical analyses were performed on an atomic absorption spectrophotometer. Sodium and K^+ were analyzed directly from sample bottles, but Ca^{2+} and Mg^{2+} analyses were made after pretreatment with a lanthanum–HCl buffer to avoid interferences (Slavin, Sprague, and Manning, 1963). The product of stream flow volume and chemical concentration gives estimates of nutrient output from a watershed. It was necessary to use the water year (October to September) because of significant snowfall during October to December which covers the watersheds until the following spring.

RESULTS AND DISCUSSION

Hydrology

The monthly and yearly variability of precipitation in the Santa Fe region has been documented. The hydrology on the study watersheds during the 1972 and 1973 water years further evidences the variability. Regressions of annual precipitation over elevation during 1972 and 1973 were significant at the 0.10 and 0.01 significance levels, respectively. Although there were only three precipitation stations, the regression equations accounted for 98% and 99% of the variability. Thus, although annual precipitation is difficult to predict, its distribution over the elevational gradient is easily expressed. The distribution of annual precipitation over the elevational gradient (2408 to 3750 m) ranged from 48.0 to 64.6 cm in 1972 and 49.5 to 104.5 cm in 1973. This substantiates the importance of the orographic effect in this region. The differences between moist and dry years is magnified as elevation increases (Table 3). Although these two years appear very different in annual precipitation, they fall within the range of annual precipitation measured at these stations during the period from 1965 to 1973.

The relationship between precipitation, runoff, and evapotranspiration also differs significantly because of seasonal variation in these factors (Table 4). In

TABLE 3

MONTHLY PRECIPITATION (CM) AT THREE ELEVATIONS ON THE TESUQUE WATERSHED STUDY AREA DURING 1972 AND 1973 WATER YEARS

Month	1971-1972*			1972-1973†		
	2377 m	2987 m	3292 m	2377 m	2987 m	3292 m
Oct.	6.8	8.1	9.8	8.2	11.4	15.6
Nov.	6.6	7.8	8.6	4.4	6.8	7.4
Dec.	3.6	5.9	6.7	3.5	4.9	6.4
Jan.	0.4	0.5	0.5	3.1	4.4	5.7
Feb.	0.3	0.6	0.7	2.2	2.8	3.5
Mar.	0.4	0.6	0.8	7.8	13.3	14.2
Apr.	0.3	0.7	0.8	3.5	4.7	4.1
May	2.0	3.2	3.5	2.8	3.8	5.0
Jun.	3.0	4.2	3.2	1.9	1.8	2.6
Jul.	11.9	8.3	7.2	5.1	6.7	6.2
Aug.	7.1	8.3	10.9	2.0	3.5	5.6
Sept.	5.6	5.5	6.4	4.1	4.5	4.5
Annual	48.0	53.7	59.1	48.6	68.6	80.8

*log ppt (cm) = 1.450 + 0.000096 (elev); r^2 = 0.98 (r^2 x 100 = % of variation).
†log ppt (cm) = 1.112 + 0.000242 (elev); r^2 = 0.995 (r^2 x 100 = % of variation).

TABLE 4

WEIGHTED AREAL PRECIPITATION (P), MEASURED RUNOFF (R), AND EVAPOTRANSPIRATION* (E) FOR THE TESUQUE WATERSHEDS IN CENTIMETERS OF WATER

Watershed	1971-1972			1972-1973		
	P	R	E	P	R	E
15	61.2	28.3	32.9 (53.8%)	91.4	86.9	4.5 (4.9%)
8	58.6	20.6	38.0 (64.8%)	82.1	72.6	9.5 (11.6%)
7	58.5	17.5	41.0 (70.1%)	81.8	69.2	12.6 (15.4%)
6	57.7	10.4	47.3 (82.0%)	78.8	42.9	35.9 (45.6%)
5	56.5	4.8	51.7 (91.5%)	75.0	29.5	45.5 (60.7%)
4	55.0	2.5	52.5 (95.5%)	70.1	25.9	44.2 (63.1%)
2	50.9	0.6	50.3 (98.9%)	57.5	9.3	48.2 (83.8%)
P–J	48.8	0.5	43.8 (99.0%)	51.6	8.0	43.6 (84.5%)

*Evapotranspiration was calculated as the difference between P and R. Runoff for the P–J watershed was estimated from discharge patterns on watershed 2.

the 1971 to 1972 period most of the precipitation fell during the summer months; this increased the significance of the evapotranspiration factor. Although significantly more precipitation occurred in the 1972 to 1973 period, most of it came during the winter months. This increased the importance of the runoff factor (spring melt). Elevation also plays an important role because of the increased amounts of precipitation at higher elevations. During 1972-1973 the higher elevations had proportionally more snow than the lower elevations; this increased the significance of the runoff factor at the upper elevations. The relationship between evapotranspiration and runoff also appears to vary as a result of the vegetational community and its soil development. The maximum quantity of evapotranspiration (in centimeters) occurred in watersheds having large proportions of the mixed conifer and pine vegetation (Tables 1 and 5). Although the quantities of precipitation and runoff differed substantially between the 1971-1972 and 1972-1973 periods for all watersheds, the lower watersheds of mixed conifer and pine vegetation showed similar evapotranspiration quantities. This suggests that these communities are best able to modify the hydrological cycle (i.e., the relationship between precipitation and runoff). The quantity of evapotranspiration from the mixed conifer and pine zones was similar to that of the northern hardwood forest at Hubbard Brook (Likens et al., 1967) and to that of cold deciduous forests of central Europe, Northeast Asia, and the southern Andes (Stanhill, 1970). The amount of evapotranspiration decreased in the piñon–juniper zone below the pine, probably because of decreased precipitation, smaller soil volume to hold moisture, and lower biomass and

TABLE 5

WEIGHTED MONTHLY AVERAGE CONCENTRATIONS (MG/LITER) OF Ca^{2+}, Mg^{2+}, Na^{+}, AND K^{+} IN BULK PRECIPITATION AT THE 2377-m COLLECTION STATION

	Ca^{2+}		Mg^{2+}		Na^{+}		K^{+}	
Month	1972	1973	1972	1973	1972	1973	1972	1973
Jan.	0.11	1.09	0.01	0.05	0.54	0.34	0.01	0.06
Feb.	1.31	0.29	0.07	0.01	0.69	0.27	0.11	0.04
Mar.	2.83	1.49	0.20	0.11	0.01	0.11	0.12	0.04
Apr.		1.71		0.14		0.13		0.07
May	2.15	1.63	0.19	0.13	0.13	0.09	0.19	0.16
Jun.	1.01	0.80	0.07	0.05	0.04	0.18	0.09	0.19
Jul.	1.98	0.86	0.09	0.06	0.06	0.04	0.12	0.22
Aug.	1.42	0.86	0.08	0.11	0.05	0.08	0.09	0.13
Sept.	0.53	0.73	0.02	0.04	0.01	0.02	0.03	0.04
Oct.	1.45	0.54	0.09	0.03	0.01	0.07	0.01	0.03
Nov.	2.49	0.72	0.06	0.05	0.05	0.06	0.13	0.12
Dec.	1.78	1.28	0.09	0.09	0.79	1.04	0.11	0.51

productivity, which would transpire the water. Above the mixed conifer zone the amount of evapotranspiration also decreased, perhaps as a result of decreased soil volumes and the increased importance of snowfall and runoff during spring melt before the biologically active season. Shorter growing seasons, lower average temperatures, and lower productivity rates also reduce the quantity of evapotranspiration. Rosenzweig (1968) reports that net primary productivity is directly associated with actual evapotranspiration. This suggests that the mixed conifer and pine zones have the highest net primary productivity of the communities in the study area. Differences in the hydrological cycle and rates of production among communities could affect nutrient fluxes, as discussed later.

Precipitation Chemistry

The concentrations of cations in precipitation reported in this study are estimates of bulk precipitation (i.e., dry fallout plus precipitation). We expect that our results underestimate the actual dry fallout since the efficiency of precipitation collectors for this material is no doubt less than 100%.

In contrast to studies in eastern deciduous forests (Likens et al., 1967; Johnson and Swank, 1973), dry fallout is a significant factor in our study area. The major source of aerosols in the study area is from the arid region to the west and southwest. The months with the highest average wind velocity are March to June, and the prevailing wind direction is from the southwest (Rivera, 1940). Maximum wind velocities for the year often occur during these months. This period of high wind velocities coincides with a relatively dry period before the summer rains and after the winter precipitation. Thus surface soils southwest of the study area are dry and easily airborne. These soils are high in base salts (Buckman and Brady, 1969). The weighted monthly cation concentrations in precipitation show this effect, with high concentrations of Ca^{2+} and Mg^{2+} occurring during the spring months (Table 5). They also indicate the differences between the two years of study since the winter and spring precipitation was much lower during 1971-1972 than during 1972-1973. The combination of more precipitation (dilution) and a reduced input of dust during 1972-1973 resulted in lower Ca^{2+} and Mg^{2+} concentrations.

The concentrations of Na^{+} show a more complex pattern. Concentrations during the spring months show the effect of inputs of aerosols, but high concentrations also occurred during the winter months; these were associated with precipitation from Pacific regions to the northwest. This pattern is difficult to interpret; however, Junge (1963) showed relatively high Na^{+} values in precipitation extending from the northwest coast into the Basin and Range region of Idaho, Nevada, and Utah. Perhaps the Basin and Range region may be a source of Na^{+} for New Mexico, or perhaps winter storms are able to carry Na^{+} salts into New Mexico from the northern Pacific.

We are not able to interpret the monthly variation in K^{+} concentrations. It appears to be a complex relationship between aerosol input during spring

months, inputs associated with winter precipitation, and biological activity. Precipitation collections near the aspen vegetation tend to have higher K^+ concentrations.

Concentrations of cations in precipitation vary over the elevational gradient of the study area because of higher precipitation at upper elevations (dilution) and higher quantities of aerosols being deposited at lower elevations (Junge, 1963). This generally causes higher concentrations of cations in precipitation at lower elevations, but the actual input of cations in kilograms per hectare over the elevational gradient is affected by the seasonal distribution of precipitation. This is discussed later.

Stream-Water Chemistry

Stream chemistry varies over the elevational gradient, with all cations becoming more concentrated at lower elevations (Table 6). This trend was very consistent throughout the study period, but streams at lower elevations were much more variable. Analyses of stream water taken over the entire length of the Santa Fe River in the Santa Fe municipal watershed confirm patterns found in the Tesuque watersheds. Nutrient concentrations in the main stream increased progressively as the stream dropped in elevation. This was largely the result of higher concentrations of cations in feeder streams at lower elevations. The pattern remained the same throughout the year, but the values in the main stream changed seasonally. Early in the spring the majority of snow melt occurred at the low elevations, and the higher concentrations in streams from these elevations caused cation concentrations of the main stream to be relatively high at the base of the watershed. Later in the spring the discharge was a result of snow melt at upper elevations, and cation concentrations at the base of the

TABLE 6

MEAN CONCENTRATION (MG/LITER) AND STANDARD ERROR OF CATIONS IN WEEKLY STREAM-WATER COLLECTIONS FOR THE PERIOD OCTOBER 1971 TO SEPTEMBER 1972

Watershed	Calcium	Magnesium	Sodium	Potassium
15	2.96 (0.04)	0.61 (0.01)	2.05 (0.03)	0.57 (0.02)
8	2.82 (0.03)	0.84 (0.01)	2.34 (0.03)	0.76 (0.02)
7	3.49 (0.03)	1.08 (0.01)	2.41 (0.03)	1.02 (0.01)
6	3.27 (0.07)	1.13 (0.01)	2.70 (0.03)	0.68 (0.01)
5	4.31 (0.11)	1.60 (0.03)	3.47 (0.06)	1.11 (0.02)
4	6.93 (0.46)	2.74 (0.11)	5.05 (0.13)	1.33 (0.04)
2	33.98 (3.60)	11.10 (0.30)	11.55 (0.46)	1.19 (0.05)
Aspen	3.72 (0.07)	1.04 (0.04)	3.14 (0.03)	0.78 (0.03)
P–J	78.60 (5.09)	34.37 (1.12)	15.85 (0.82)	2.16 (0.07)

watershed were relatively low. The bedrock is reported to be similar for all the study watersheds; this suggests that the patterns are a result of different vegetation associations and soils. Local variations in bedrock mineralogy do occur, however, with bedrock ranging from amphibolite to granite (Graustein, 1974), but we are not certain whether variations occur uniformly throughout all the watersheds.

A number of physical and biological variables that could affect the stream chemistry from different vegetational zones appear to exist. Since our data on these factors are preliminary at this point, we can only suggest relationships. Present research is attempting to ascertain the relative importance of each of the factors and of their interactions.

Evapotranspiration varies significantly over the elevational gradient, and this concentration effect could be responsible for higher concentrations at lower elevations. There are notable exceptions, however. The cation concentrations in stream water of the lowest elevations (watersheds 2 and P–J) are higher than can be explained by evapotranspiration, and concentrations at intermediate elevations are lower than expected. In addition to increased concentrations at lower elevations, there also are changes in the relative proportions of several elements. The Mg^{2+}-to-Na^{+} ratio of concentrations has a relatively low value at upper elevations. This relationship reverses with a decrease in elevation to a situation where Mg^{2+} is more prominent than Na^{+} (Table 6). This appears similar to the natural softening effect described for groundwater (Grover, 1925). The base elements of groundwater (e.g., magnesium) are exchanged for Na^{+} in Na^{+}-bearing silicates. The extent of the exchange depends on the amount of silicate minerals available (volume of soil), the Na^{+} exchange capacity of the silicates, and the length of time groundwater is in contact (watershed residence time). Current studies show that there is an analogous pattern for the SO_4^{2-}-to-HCO_3^{-} ratio over elevation. The value for the ratio is low at upper elevations and high at lower elevations.

The soils are very different over this elevational gradient. The primary soil at upper elevations is a Dystric Cryocrept (Nambe cobbly loam) with a pH of 5 to 6 (Carleton and Gass, 1972). The relatively large amounts of organic matter in this soil and its low base saturation make it a well-buffered soil and may account for the relatively constant cation concentrations (see Table 6). At lower elevations the soil is a Typic Ustorthent (Mirabal gravelly sandy loam) with a pH of 6.8 to 7.0. The lower organic matter content and high base saturation of this soil cause it to have a relatively low buffering capacity. The dominance of evapotranspiration over runoff at these low elevations causes base salts to be precipitated out in the subsoil. The presence of this material may account for a portion of the variability of cation concentrations in runoff.

The analyses of groundwater from well points on the study watersheds show that the pH increases after the water comes in contact with the atmosphere (Graustein, 1974). The reason appears to be a high level of HCO_3^{-} in groundwater (supersaturated) resulting from the production of CO_2 by roots

and decomposition. This lowers the pH, and this, in turn, can cause more weathering or replacement of other cations on exchange sites. After emerging from the ground, the water rapidly loses CO_2 and comes to equilibrium with atmospheric concentrations of CO_2. Our data also suggest that there is a variable level of CO_2 in groundwater within and between watersheds, and this varies the importance of this factor.

Because stream discharge varies significantly more over the year than cation concentrations, total cation output in kilograms per hectare is affected by total discharge, but cation concentrations are not well related to discharge. For example, element concentrations were not correlated with stream discharge in watershed 8 during the period from October 1971 to September 1972 (Fig. 2). Relatively low discharge during the summer months had much higher concentra-

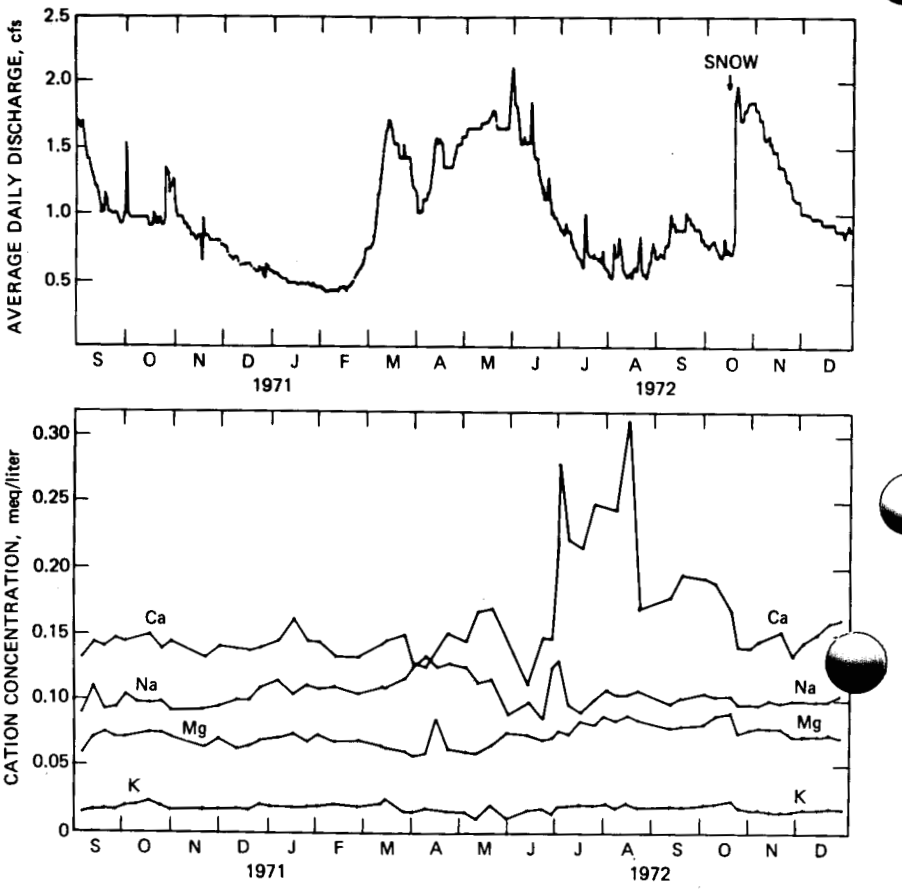

Fig. 2 Cation concentrations in weekly collections of stream water and average daily discharge for watershed 8.

tions of some cations than the same discharge during winter months. Only during the period from June to August were there significant correlations (negative) between Ca^{2+} and discharge and Mg^{2+} and discharge.

Watershed 8 is relatively large (415 ha), and the elevational gradient within the watershed may have been responsible for some of our results. For example, since more precipitation falls on the upper elevations, there would be more water with lower concentrations of elements. The relatively large volume of water from the upper elevations would dilute concentrations at lower elevations and give negative correlations between concentration and discharge. In an attempt to avoid this problem, we gaged a small aspen watershed (3.4 ha) within watershed 8 during the summer of 1973. Analyses of stream water from this watershed have been made since 1971, and the data show even more variability than that from the larger watershed (Fig. 3). The greater stream discharge that occurs on a large watershed appears to dampen the chemical variability. Sufficient discharge data are not yet available for the small aspen watershed to allow correlations with concentration.

Element concentrations in stream water of the aspen watershed show their lowest values in the spring months at the time of snow melt (Fig. 3). Dilution may be a factor, but this also is the time when significant quantities of nutrients can be taken up by the tree vegetation or metabolized by soil organisms. The condition of warm days and freezing nights appears to be responsible for large increases in sap ascent in trees (Kramer and Kozlowski, 1960), which is accompanied by the uptake of nutrients. This may occur many weeks before buds start to expand. The spring period of lower element concentrations in stream water also shows a change in relative abundance. Calcium and Mg^{2+} were reduced proportionately more than Na^{+} in the spring of 1972; this suggests that differential uptake may have been occurring. In the spring months of 1973, the reverse occurred (Fig. 3). The much higher stream discharge during the spring of 1973 may have hidden patterns due to uptake by trees and metabolism by soil organisms.

Significant quantities of some nutrients are leached from foliage. During the summer of 1973, stream chemistry in the small aspen watershed showed Ca^{2+} and Mg^{2+} peaks correlating well with throughfall values for this watershed. Potassium was an important exception. Concentrations of K^{+} in milliequivalents per liter in stream water were relatively constant despite the large quantity of K^{+} leached from the vegetation. This suggests either rapid uptake by vegetation or a clay mineralogy that rapidly fixes K^{+}.

Nutrient Budgets

The nutrient budget for each of the Tesuque watersheds was determined from the difference between nutrient input in bulk precipitation and output in drainage water (Table 7). These budgets are for dissolved substances only and

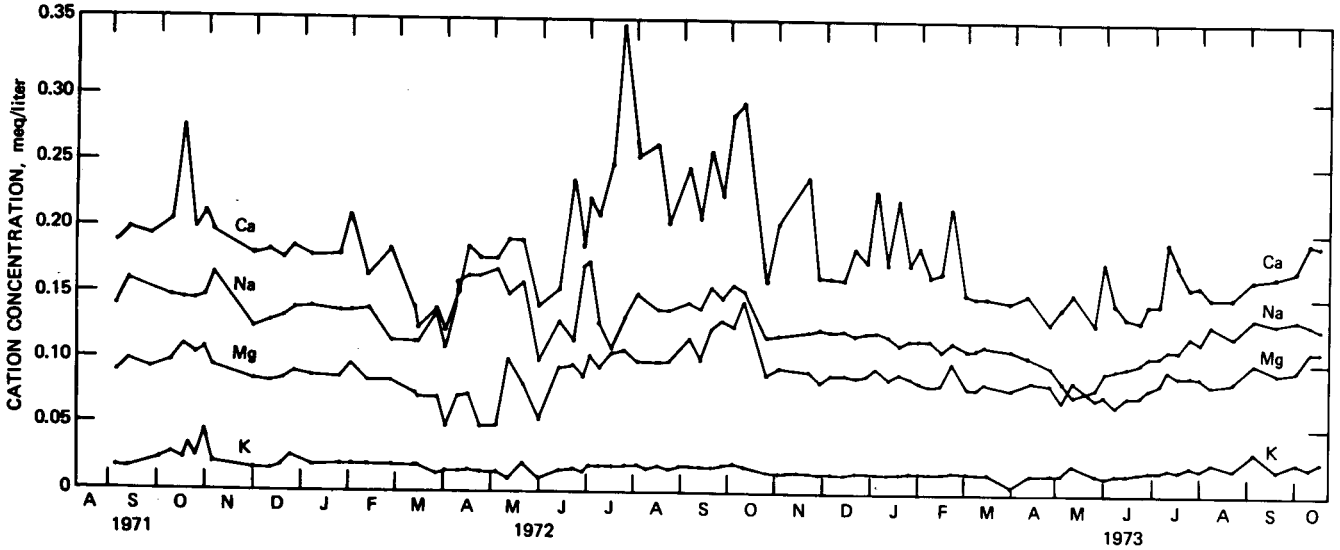

Fig. 3 Cation concentrations in weekly collections of stream water from the aspen watershed, located within watershed 8.

TABLE 7

CATION INPUT (I), OUTPUT (O), AND FLUX* (F) FOR THE TESUQUE WATERSHEDS EXPRESSED AS KILOGRAMS PER HECTARE

Watershed	Ca^{2+}			Mg^{2+}			Na^{+}			K^{+}		
	I	O	F	I	O	F	I	O	F	I	O	F
October 1971 to September 1972												
[illegible]	7.4	9.4	−2.0	0.4	1.8	−1.4	0.2	6.3	−6.1	0.2	1.5	−1.3
[illegible]	7.2	6.9	+0.3	0.4	1.7	−1.3	0.3	4.9	−4.6	0.5	1.4	−0.9
[illegible]	7.2	6.7	+0.5	0.4	1.9	−1.5	0.3	4.3	−4.0	0.4	1.7	−1.3
6	7.5	4.2	+3.3	0.4	1.2	−0.8	0.4	2.8	−2.4	0.3	0.7	−0.4
5	7.7	2.2	+5.5	0.4	0.8	−0.4	0.4	1.7	−1.3	0.3	0.5	−0.2
4	7.9	1.5	+6.4	0.4	0.6	−0.2	0.4	1.2	−0.8	0.4	0.3	+0.1
2	8.0	3.7	+4.3	0.4	1.0	−0.6	0.4	1.2	−0.8	0.4	0.2	+0.2
P–J	8.0	4.4	+3.6	0.4	1.8	−1.4	0.4	1.5	−1.1	0.4	0.3	+0.1
October 1972 to September 1973												
15	7.2	24.5	−17.3	0.6	5.0	−4.4	1.0	13.6	−12.6	2.1	4.3	−2.2
8	7.2	19.6	−12.4	0.6	5.9	−5.3	1.0	13.9	−12.9	1.7	5.1	−3.4
7	7.2	24.0	−16.8	0.6	8.2	−7.6	1.0	14.0	−13.0	1.5	6.8	−5.3
6	7.1	14.5	−7.4	0.5	5.3	−4.8	0.7	10.5	−9.8	1.5	3.0	−1.5
5	6.1	14.3	−8.2	0.5	5.3	−4.8	0.6	9.3	−8.7	1.5	3.2	−1.7
4	6.1	17.3	−11.2	0.5	7.3	−6.8	0.6	11.3	−10.7	1.5	4.0	−2.5
2	6.1	17.8	−11.7	0.5	6.8	−6.3	0.6	7.8	−7.2	1.5	1.0	+0.5
P–J	6.1	54.8	−48.7	0.5	26.7	−26.2	0.6	13.6	−13.0	1.5	1.5	+0.0

*Negative or positive flux values indicate net cation loss or accumulation, respectively.

could be affected if analyses of particulate-matter loss were considered. This is addressed later in this section.

The results show that nutrient inputs differed slightly during the two-year period and that the pattern of distribution varied over the elevational gradient. As a result of low winter and spring precipitation in 1971-1972, significant [illegible]antities of dust entered the study area, being deposited primarily at the lower [illegible]ations. This pattern was most pronounced for Ca^{2+} and Na^{+}. Potassium also showed this pattern, except for watersheds 7 and 8, which had a higher input of K^{+} than was expected. These watersheds have significant quantities of aspen vegetation. Throughfall studies show that K^{+} is readily leached from aspen vegetation; thus the higher values for K^{+} in precipitation on watersheds 7 and 8 may have come from K^{+} originating within the watersheds. The input of Mg^{2+} did not vary over the elevational gradient. The heavy winter and spring precipitation in 1972-1973 reduced the amount of dust generated in the arid regions west of the study area. Since the cation inputs appeared to be related to

the quantity of precipitation received, there were greater inputs at high elevations. This pattern was seen for all four cations, with Mg^{2+} again showing the least variation.

The nutrient outputs for these watersheds differed significantly during the two-year period as a result of significant differences in discharge. The 1972-1973 watershed discharge ranged from 3 (watershed 15) to 16 (watershed 2) times higher than that of 1971-1972. Nutrient output was not entirely governed by discharge volume, however. The highest nutrient losses (in kilograms per hectare) generally occurred from the highest and the lowest elevations. In fact, 1972-1973 the highest losses of Ca^{2+} and Mg^{2+} occurred from the piñon–juni watershed, which had the lowest discharge volume. In general, the lowest nutrient output occurred from intermediate elevations. In 1971-1972 the smallest losses generally occurred from watersheds 2, 4, and 5, which are characterized by pine and mixed conifer communities. During 1972-1973 the smallest losses of Ca^{2+} and Mg^{2+} occurred from watersheds 5 and 6, which are characterized by mixed conifer and low-elevation spruce–fir communities. An exception to this pattern (which we are not able to explain at this time) was exhibited by K^{+}, which showed very small losses in the piñon–juniper watershed and in watershed 2. The output of Na^{+} from watershed 6 was similar to that from watersheds 4 and 5 during 1972-1973.

One of the watersheds (7) showed relatively large dissolved cation losses compared with adjacent watersheds during 1972-1973 (Table 7). The causal factor appears to be an unimproved road at the higher elevations of the watershed. A short portion of the road curves through steep terrain, and there has been significant erosion that caused an excessive output of particulate matter as well as dissolved material. The effect of the road was much more apparent during the wet year (high runoff) than during the dry year. The road also passes through an adjacent watershed (8) but is relatively stable there, and less erosion has occurred. Although dissolved losses from watershed 8 were less than those from watershed 7 in 1972-1973, they were larger than those from watershed 15 for several elements.

The dominance of nutrient output caused nutrient fluxes to follow patterns similar to those of output (Table 7). This suggests that, in addition to dampening storm activity, the mixed conifers at intermediate elevations are best able to accumulate nutrients or to prevent their loss. This characteristic generally is associated with a diverse or complex community with high productivity and biomass (Odum, 1969) and extensive buffering capacity of the soil (Likens et al., 1967). Of the vegetation zones and biomes in the southern Rocky Mountains, the mixed conifer zone has been shown to be the most complex community in terms of the diversity of plants (Mackay, 1970), avifauna (Carothers, Haldeman, and Balda, 1973), vertebrate fauna (Findley, 1974), and invertebrates (Hoff, 1962). In addition, the mixed conifer zone is the most diverse structurally, having more foliage layers (Carothers, Haldeman, and Balda, 1973). The high

actual evapotranspiration of this community (Table 4) may mean that it has the highest primary productivity (Rosenzweig, 1968), but this needs further verification. Of significant interest is the fact that the greatest nutrient conservation (especially of Ca^{2+} and Mg^{2+}) occurred in watersheds 2, 4, and 5 during 1971-1972 and watersheds 5 and 6 during 1972-1973. This suggests that nutrient conservation was greatest in the pine and mixed conifer communities during a dry year (1971-1972) and greatest in mixed conifer and low-elevation spruce–fir communities during a wet year (1972-1973). It is not yet known whether this elevational shift was an artifact or a true response. The buffering capacity of the soil in a pine community may be relatively small because of lower concentrations of organic matter and reduced soil volume. Thus an increased runoff can more easily remove nutrients from this community. During a dry year there is very little runoff from this zone (Table 4). If the biological cycling of nutrients is a dominant factor in nutrient conservation, however, then increased moisture might be expected to reduce nutrient loss in the pine community because of increased productivity and nutrient uptake. During a dry year the more mesic mixed conifer and low-elevation spruce–fir communities would be more productive because of somewhat warmer temperatures and sufficient available moisture. A seasonal analysis of precipitation shows that, although the annual 1971-1972 precipitation was low, it occurred primarily during the growing season (Table 3). The high precipitation during 1972-1973 was largely the result of snow; the summer was quite dry. The data support the suggestion that the elevational shift in nutrient conservation during 1971-1973 is associated with a shift of optimum growing conditions during that period. Additional study of years of nutrient flux and productivity are needed to verify these results.

The nutrient outputs reported here are of dissolved cations only. Thus we must consider whether the budgets for the undisturbed watersheds would be different if particulate losses were accounted for. Studies at the Hubbard Brook and Coweeta watersheds show very small particulate output for undisturbed forests (Likens et al., 1967; Johnson and Swank, 1973). As a result Ca^{2+}, Mg^{2+}, Na^{+}, and K^{+} outputs in particulate matter were a small percentage of the total output (<1% at Coweeta). Particulate-mass loss is directly related to the volume of water leaving a watershed (i.e., to discharge) and indirectly related to the amount of vegetative biomass and organic debris in a watershed (Bormann, Likens, and Eaton, 1969). Thus in the Tesuque watersheds the high-elevation (i.e., high-discharge) and the low-elevation (i.e., low surface cover and biomass) watersheds should have relatively more particulate output than the watersheds at intermediate elevations with mixed conifer vegetation. The high evapotranspiration of mixed conifer vegetation (Table 4) may be an important factor in reducing storm runoff and particulate output (Bormann, Likens, and Eaton, 1969). Thus, although particulate output is expected to vary over the elevational range of the study area, the patterns of nutrient loss from particulate output are expected to reinforce the patterns shown by dissolved losses.

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REFERENCES

Bormann, F. H., and G. E. Likens, 1967, Nutrient Cycling, *Science*, **155**: 424-429.

—, G. E. Likens, and J. S. Eaton, 1969, Biotic Regulation of Particulate and Solution Losses from a Forest Ecosystem, *Bioscience*, **19**: 600-610.

Buckman, H. O., and N. C. Brady, 1969, *The Nature and Properties of Soils*, 7th ed., The Macmillan Company, New York.

Carleton, J. O., and J. M. Gass, 1972, Soils Report for Tesuque Watersheds, Santa Fe National Forest, Southwestern Region, Forest Service, U. S. Department of Agriculture.

Carothers, S. W., J. R. Haldeman, and R. P. Balda, 1973, *Breeding Birds of the San Francisco Mountain Area and the White Mountains, Arizona*, Museum of Northern Arizona Technical Series, No. 12, Northern Arizona Society of Science and Art, Inc., Flagstaff.

Cobb, E., and W. Dien, 1974, U.S. Geological Survey, personal communication.

Findley, J., 1974, University of New Mexico, personal communication.

Gosz, J. R., G. E. Likens, and F. H. Bormann, 1974, Organic Matter and Nutrient Dynamics of the Forest Floor in the Hubbard Brook Forest, in *The Below Ground Ecosystem*, Proceedings of the U. S. International Biological Program Symposium, J. Marshall (Ed.), Colorado State University, Fort Collins, in press.

—, G. E. Likens, and F. H. Bormann, 1973, Nutrient Release from Decomposing Leaf and Branch Litter in the Hubbard Brook Forest, New Hampshire, *Ecol. Monogr.*, **43**: 173-191.

—, G. E. Likens, and F. H. Bormann, 1972, Nutrient Content of Litter Fall on the Hubbard Brook Experimental Forest, New Hampshire, *Ecology*, **53**: 769-784.

Graustein, W., 1974, Yale University, personal communication.

Grover, N. C., 1925, *Contributions to the Hydrology of the United States*, Water-Supply Paper No. 520, U. S. Geological Survey.

Hem, J. D., 1970, *Study and Interpretation of the Chemical Characteristics of Natural Water*, 2nd ed., Water-Supply Paper No. 1473, U.S. Geological Survey.

Hoff, C. C., 1962, Some Terrestrial Gastropoda from New Mexico, *Southwest. Natur.*, **7**: 51-63.

Johnson, P. L., and W. T. Swank, 1973, Studies of Cation Budgets in the Southern Appalachians on Four Experimental Watersheds with Contrasting Vegetation, *Ecology*, **54**: 70-80.

Junge, C. E., 1963, *Air Chemistry and Radioactivity*, Academic Press, Inc., New York.

Kelly, N. E., 1973, Ecology of the Arroyo Hondo Pueblo Site, M.S. Thesis, University of New Mexico, Albuquerque.

Kramer, P. J., and T. T. Kozlowski, 1960, *Physiology of Trees*, McGraw-Hill Book Company, New York.

Likens, G. E., and F. H. Bormann, 1971, Nutrient Cycling in Ecosystems, in *Ecosystem Structure and Function,* Proceedings of the 1970 Biology Colloquium, pp. 25-67, J. A. Wiens (Ed.), Oregon State University Press, Corvallis.

——, F. H. Bormann, N. M. Johnson, and R. S. Pierce, 1967, The Calcium, Magnesium, Potassium, and Sodium Budgets for a Small Forested Ecosystem, *Ecology,* **48**: 772-785.

Mackay, H. A., 1970, A Comparative Floristic Study of the Rio Hondo Canyon—Lake Fork—Wheeler Peak Locale, New Mexico, and the Huerfano River—Blanca Peak Locale, Colorado, Ph. D. Thesis, University of New Mexico, Albuquerque.

Miller, J. P., 1961, *Solutes in Small Streams Draining Single Rock Types, Sangre de Cristo Range, New Mexico,* Water-Supply Paper No. 1535-F, U. S. Geological Survey.

[illegible], E. P., 1969, The Strategy of Ecosystem Development, *Science,* 164: 262-270.

[illegible]a, J. A., 1940, Annual Meteorological Summary with Comparative Data, 1940, Santa Fe, New Mexico, U. S. Weather Bureau, Reno, Nev.

Rosenzweig, M. L., 1968, Net Primary Productivity of Terrestrial Communities: Prediction from Climatological Data, *Amer. Natur.,* **102**: 67-74.

Slavin, W., S. Sprague, and D. C. Manning, 1963, The Determination of Calcium by Atomic Absorption Spectrophotometry, *At. Absorption Newslett.,* **15**: 1-8.

Stanhill, G., 1970, The Water Flux in Temperate Forests: Precipitation and Evapotranspiration, in *Analysis of Temperate Forest Ecosystems,* pp. 247-256, D. E. Reichle (Ed.), Springer-Verlag, New York.

Trewartha, G. T., 1968, *An Introduction to Climate,* 4th ed., McGraw-Hill Book Company, New York.

NUTRIENT RETURN IN THE STEMFLOW AND THROUGHFALL OF INDIVIDUAL TREES IN THE PIEDMONT DECIDUOUS FOREST

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ABSTRACT

Stemflow and throughfall were collected under mature trees of six species: *Fagus grandifolia, Carya tomentosa, Liriodendron tulipifera, Pinus echinata, Pinus taeda,* and *Quercus alba.* Chemical analysis of stemflow and throughfall revealed that calcium and potassium were returned to the soil in the greatest amounts, followed by magnesium and manganese. Concentrations were always higher in stemflow than in throughfall. On a crown-area basis, *Fagus* contributed the least calcium and potassium. *Pinus taeda* returned the most calcium, and *Carya* returned the most potassium. The pH of stemflow and throughfall from the two pine species was the lowest; *Carya* stemflow and throughfall had the highest pH. With several of the species, soil nutrient patterns near the trees could be related to the distribution and nutrient content of stemflow.

Gross rainfall over a forest stand can be divided into three components: throughfall, stemflow, and interception loss. Throughfall is the portion of gross rainfall which reaches the forest floor through openings in the canopy and by dripping off leaves, branches, and stems. Stemflow is the portion of gross rainfall which is caught by the tree crowns and runs down the stems to the forest floor. Interception loss is the difference between gross rainfall and the sum of throughfall and stemflow. Both throughfall and stemflow differ from rainwater in their chemical composition as a result of contact with the leaves and bark. This study evaluated both quantitative and qualitative aspects of the stemflow and throughfall of individual trees in an oak–hickory forest in North Carolina. The influence of stemflow on certain soil chemical characteristics was also investigated.

Numerous studies within the past century have dealt with the quantitative aspects of stemflow and throughfall. Helvey and Patric (1965) summarized the

studies of rainfall interception in hardwood forests of the eastern United States and provided linear regression equations for stemflow and throughfall estimates in forest stands. In general, throughfall in forest stands accounts for 70 to 90% of the gross rainfall, while stemflow, if projected over the entire area covered by the crowns, is usually less than 5% of gross rainfall. Voigt (1960b) has shown, however, that stemflow is concentrated near the base of the trunk. For such smooth-barked trees as American beech, this concentration of stemflow may result in 5 to 10 times as much precipitation in the area near the trunk as is recorded in the open. Gersper (1970) reported that the greatest influence of beech stemflow in concentrating fallout radioisotopes is limited to a sphere of influence extending 30 cm from the trunk and to a depth of 30 to 45 cm. Because of its concentration near the trunks of trees, stemflow has a localized influence on soil properties. Soil leaching by stemflow water may result in lower nutrient concentrations in the soil near the trunk (Gersper and Holowaychuk, 1970b; Patterson, 1970). Soil pH may also be influenced by stemflow (Mina, 1967; Gersper and Holowaychuk, 1971).

The chemical enrichment of rainwater that contacts the leaves and bark of trees as throughfall or stemflow has been reported for a number of forest trees (Tamm, 1951; Madgwick and Ovington, 1959; Voigt, 1960a; Carlisle, Brown, and White, 1967). This enrichment occurs through both the leaching of metabolites from the plant tissue and the washoff of atmospheric particulate matter that has been deposited on the plant surfaces. The pH of rainwater is also altered as it passes over plant surfaces (Eaton, Likens, and Bormann, 1973).

The relatively high concentrations of inorganic nutrients in stemflow and throughfall suggest that these two precipitation components may be of importance in the nutrient cycle of forest stands. Will (1959) found that throughfall in a Douglas fir forest in New Zealand accounted for twice as much potassium and an equal amount of phosphorus as did litterfall. Eaton, Likens, and Bormann (1973) calculated the total contribution of several elements in throughfall and stemflow for June through October in a northern hardwood forest in New Hampshire. During that period 6.73 kg Ca/ha, 2.00 kg Mg/ha, 30.08 kg K/ha, 9.92 kg total N/ha, and 0.68 kg PO_4—P/ha were returned as throughfall and stemflow. For a similar site the total annual return in litterfall was 45.2 kg Ca/ha, 6.4 kg Mg/ha, 21.1 kg K/ha, 55.8 kg total N/ha, and 3.7 kg PO_4—P/ha. Again, as in Will's study, the return of potassium was higher in stemflow and throughfall than in litterfall. The ready leachability of potassium probably accounts for its rapid cycling in stemflow and throughfall. Since nutrients returned in stemflow and throughfall are in soluble forms, they should be readily available for plant uptake in the soil, and the decomposition process involved in freeing organically complexed nutrients returned in the litter may be bypassed. Witherspoon (1964) found that understory plants absorbed radiocesium from white-oak throughfall directly through their foliage. This could result in even more rapid cycling of elements in forest stands.

MATERIALS AND METHODS

Thirteen mature trees—two American beeches (*Fagus grandifolia*), two mockernut hickories (*Carya tomentosa*), two yellow poplars (*Liriodendron tulipifera*), three shortleaf pines (*Pinus echinata*), two loblolly pines (*Pinus taeda*), and two white oaks (*Quercus alba*)—were selected for the stemflow and throughfall measurements. The trees were in an oak–hickory forest at the Duke University botany experimental plot in Durham County, N. C. The soil was White Store sandy loam. The diameter at breast height (DBH), basal area, crown area, and height of each of the 13 trees are shown in Table 1.

TABLE 1

DESCRIPTION OF TREES FROM WHICH STEMFLOW AND THROUGHFALL WERE COLLECTED

Tree No.	Species	Height, m	DBH, cm	Basal area, m^2	Crown area, m^2
FG-1	*Fagus grandifolia*	29.5	43.7	0.150	159
FG-2	*F. grandifolia*	24	39.6	0.124	117
CT-1	*Carya tomentosa*	26	43.9	0.151	142
CT-2	*C. tomentosa*	32	54.6	0.234	111
LT-1	*Lirodendron tulipifera*	30	49.5	0.193	86
LT-2	*L. tulipifera*	30	48.3	0.183	43
PE-1	*Pinus echinata*	32.5	73.7	0.425	115
PE-2	*P. echinata*	27	29.0	0.066	29
PE-3	*P. echinata*	27.5	35.6	0.100	43
PT-1	*Pinus taeda*	27	28.5	0.064	20
PT-2	*P. taeda*	29	46.7	0.171	55
QA-1	*Quercus alba*	26.5	61.0	0.292	141
QA-2	*Q. alba*	27	62.2	0.304	201

Gross rainfall (GRF) was measured with a standard Weather Bureau rain gauge and four No. 10 cans located in an open area near the study site. A recording rain gauge was used to determine the duration of each storm. Rain to be chemically analyzed was collected in No. 10 cans lined with plastic bags. Stemflow was collected with aluminum-foil gutters attached in a spiral around the tree trunk. The gutter was connected to the collection vessel with plastic tubing. Stemflow was measured after each storm. Storms were defined as distinct periods of precipitation separated by at least 24 hr. Throughfall under each tree was collected in four No. 10 cans located at the four cardinal

directions midway between the trunk and the edge of the crown. When collections were to be made for analysis, the cans were lined with plastic bags. Stemflow and throughfall were measured from 36 storms between Apr. 5, 1969, and Mar. 22, 1970. These storms ranged from 0.30 cm to 6.48 cm, with an average of 2.29 cm. For nine of the storms, ranging from 0.51 cm to 6.48 cm, with an average of 2.85 cm, stemflow and throughfall were collected for chemical analysis.

Mineral soil samples (0 to 10 cm in depth) for chemical analysis were collected under nine trees (two each of *Carya tomentosa, Fagus grandifolia,* *dendron tulipifera,* and *Quercus alba* and one *Pinus echinata.* All the sampled trees were located on the study site and were similar in size to those used in the collection of stemflow and throughfall. Soil samples were taken from two areas under each tree: the zone of stemflow absorption near the trunk and a second area near the edge of the crown. These sample zones were chosen to determine the influence of stemflow on the soil near the trunk compared to an area that received no stemflow. Chemical analyses of the soil and water samples were made by the Soil Testing Laboratory of the North Carolina Department of Agriculture, using analytic procedures of Reid and Copeland (1969).

RESULTS

Quantitative Aspects of Stemflow and Throughfall

The average amounts of stemflow in liters per storm produced by each of the 13 trees varied by more than a factor of 150 (Table 2). Of the six species, beech produced the most stemflow. The stemflow from FG-1 during the 1969 growing season ranged from 3.7 liters during a storm of 0.30 cm to 486 liters during a storm of 5.28 cm. After leaf fall, FG-1 produced 683 liters of stemflow during a storm of 5.28 cm. The two hickories were next in the production of stemflow. Stemflow from CT-1 during the growing season ranged from 0.1 liter for a storm of 0.38 cm to 278 liters for storms of 5.28 and 6.48 cm. After leaf fall, CT-1 produced 295 liters of stemflow from a storm of 5.28 cm. Stemflow from the other four species rarely exceeded 20 liters except in storms greater than 3 cm. analysis of variance indicated that the beeches produced significantly more stemflow than any of the other trees ($P = 0.05$). The hickories produced the next largest amounts, and the other nine trees did not differ significantly in the average amount of stemflow produced. The stemflow characteristics of the individual trees are reflected in the linear regression equations that express stemflow (SF) in liters as a function of gross rainfall (GRF) in centimeters (Table 3). Confidence intervals calculated for the slopes of the regression lines (Table 3) indicated three classes of stemflow producers (the beeches > the hickories > the other nine trees), confirming the differences established above.

TABLE 2

AVERAGE AMOUNTS OF STEMFLOW AND THROUGHFALL*

Tree No.	GRF, cm	SF, liters	SF (BA), %	SF(CA), %	TF (CA), %	IL (CA), %
FG-1	2.04	167	5100	4.8	77	18
FG-2	2.09	145	5150	5.5	75	20
CT-1	2.16	66	1390	1.5	90	9
CT-2	2.21	49	533	1.1	80	19
LT-1	2.17	6.4	95	0.2	88	12
LT-2	2.21	7.4	122	0.5	90	10
PE-1	2.21	8.0	55	0.2	77	23
PE-2	2.21	2.1	100	0.2	88	11
PE-3	2.21	1.4	50	0.1	87	13
PT-1	2.21	2.5	128	0.4	87	13
PT-2	2.21	4.5	82	0.3	92	8
QA-1	2.13	14	119	0.2	86	14
QA-2	2.16	1.2	12	0.02	80	20
		S.(37)†	S.(343)†	S.(0.46)†	S.(7)†	S.(7)†

*GRF, average gross rainfall; SF, stemflow; BA, basal area; CA, crown area; TF, throughfall; IL, interception loss.

†S. indicates a significant F value at the 0.05 level from analyses of variance, and numbers in parentheses are least significant difference.

The amount of gross rainfall required for the initiation of stemflow was estimated by setting SF equal to zero. These values, expressed as centimeters of rainfall, are shown in Table 3 as GRF_0. Only 0.10 to 0.20 cm of rain was required for the initiation of stemflow from the two beeches. For the other trees, at least 0.7 cm was required.

The precipitation budgets of the individual trees can be compared by computing the average throughfall and stemflow expressed as a percentage of gross rainfall. This requires that stemflow be projected over the entire crown area so that it may be converted to depth in centimeters. The sum of the average throughfall and stemflow as percent of gross rainfall subtracted from 100 gives the average interception loss as a percent of gross rainfall (Table 2). Interception loss was highest under the two beeches, one of the hickories, and the large shortleaf pine and lowest under the smaller shortleaf and loblolly pines. Only under hickory and beech did stemflow account for more than a fraction of a percent of the water reaching the forest floor.

Qualitative Aspects of Stemflow and Throughfall

The average pH and the average concentrations of calcium, magnesium, potassium, and manganese in rainwater, throughfall, and stemflow for nine

TABLE 3

LINEAR REGRESSION EQUATIONS FOR STEMFLOW (SF) IN LITERS AS A FUNCTION OF GROSS RAINFALL (GRF) IN CENTIMETERS

Tree No.	Regression equation	Confidence limits for slope*	R†	GRF_0 ‡
FG-1	SF = 85.5 (GRF) − 9.87	±35.6	0.944	0.12
FG-2	SF = 71.8 (GRF) − 11.93	±20.3	0.972	0.17
[illegible]T-1	SF = 51.3 (GRF) − 41.95	±22.4	0.954	0.82
[illegible]T-2	SF = 40.7 (GRF) − 40.19	±39.6	0.813	0.99
LT-1	SF = 5.06 (GRF) − 4.17	±3.6	0.861	0.82
LT-2	SF = 5.22 (GRF) − 3.56	±5.9	0.719	0.68
PE-1	SF = 9.47 (GRF) − 9.46	±7.4	0.836	1.00
PE-2	SF = 1.70 (GRF) − 1.39	±1.1	0.880	0.82
PE-3	SF = 1.11 (GRF) − 0.85	±0.7	0.877	0.76
PT-1	SF = 1.83 (GRF) − 1.35	±0.7	0.954	0.74
PT-2	SF = 4.53 (GRF) − 4.20	±3.2	0.853	0.93
QA-1	SF = 13.5 (GRF) − 13.19	±6.9	0.921	0.98
QA-2	SF = 0.92 (GRF) − 0.73	±0.8	0.817	0.79

*Confidence limits (0.05 level) are for coefficient of GRF (slope of regression line).

†R, correlation coefficient.

‡GRF_0 = gross rainfall in centimeters required for initiation of stemflow.

storms on Apr. 5, Apr. 16, June 9, July 26–29, and Oct. 2, 1969, and Feb. 25, Mar. 4, Mar. 12, and Mar. 18–22, 1970, were calculated (Table 4). The average concentrations of calcium and magnesium in throughfall were 1.5 to 2 times greater than those in rainfall during this period. Potassium concentrations were 3 to 4 times greater, and manganese concentrations were 4 to 10 times greater. There were no significant differences in nutrient concentrations or pH in throughfall among the 13 trees. The average stemflow produced per storm ranged from only 1.9 liters for QA-2 to 224 liters for FG-1. Pine stemflow was much more acid (pH 3.2 to 3.9) than hardwood stemflow, although stemflow from the two beeches was also relatively acid (pH 4.4 and 4.7). The stemflow from the hickories and white oaks had the highest pH (6.3 to 6.8). Among the hardwoods, the beeches had the lowest concentrations of calcium, magnesium, and potassium in stemflow. The hickories had the lowest manganese concentrations and the two white oaks had the highest calcium and potassium concentrations. These differences in ion concentrations in hardwood stemflow are a function of the amounts of stemflow produced as well as the relative susceptibilities to leaching of the different trees. The five pines, although they produced small amounts of stemflow, tended to have relatively low concentrations of calcium, magnesium, potassium, and manganese in the stemflow.

TABLE 4

AVERAGE pH AND AVERAGE CONCENTRATIONS OF Ca, Mg, K, AND Mn IN THROUGHFALL AND STEMFLOW FOR NINE STORMS*

Tree No.	TF, cm SF, liters	pH	Ca	Mg, mg/liter	K	Mn
FG-1	2.16(0.24)	4.9(0.8)	4.3(2)	0.30(0.2)	1.3(0.4)	0.14(
	224(136)	4.7(0.9)	4.6(1.9)	0.31(0.2)	4.7(4)	0.18(0.2)
FG-2	2.11(0.27)	5.0(0.8)	4.3(1.3)	0.38(0.3)	1.5(0.4)	0.13(0.1)
	190(136)	4.4(0.8)	4.4(2.1)	0.28(0.2)	3.7(1.6)	0.20(0.2)
CT-1	2.79(0.28)	5.2(0.9)	4.0(1.2)	0.31(0.3)	1.8(1)	0.14(0.2)
	109(102)	6.4(0.4)	19.7(15)	1.37(1.3)	5.8(2.6)	0.09(0.2)
CT-2	3.01(0.42)	5.7(0.8)	3.6(1.5)	0.30(0.2)	2.6(2)	0.13(0.2)
	98(45)	6.8(0.4)	27.3(11)	1.97(0.7)	11.8(3.5)	0.05(0.1)
LT-1	3.15(0.27)	5.5(0.9)	5.0(1.1)	0.43(0.3)	2.2(0.9)	0.13(0.1)
	20(17)	5.4(0.4)	22.3(13)	2.10(1.2)	19.4(8.2)	0.73(0.8)
LT-2	3.22(0.35)	5.5(0.9)	4.0(1.3)	0.33(0.2)	2.2(0.9)	0.13(0.1)
	20(17)	5.4(0.4)	22.3(13)	2.10(1.2)	19.4(8.2)	0.73(0.8)
PE-1	2.78(0.57)	4.5(0.8)	5.7(2)	0.47(0.2)	2.1(0.8)	0.17(0.1)
	24(25)	3.6(0.3)	18.7(11)	2.47(1.3)	5.6(1.6)	1.42(0.9)
PE-2	3.17(0.40)	4.9(0.8)	4.3(2)	0.40(0.2)	1.4(0.9)	0.08(0.1)
	4.5(4.8)	3.7(0.2)	16.3(7.7)	1.93(0.9)	5.8(1.3)	0.85(0.5)
PE-3	3.13(0.42)	4.5(0.8)	5.0(2.1)	0.33(0.2)	1.6(0.5)	0.08(0.1)
	2.7(2.7)	3.9(0.2)	12.7(5.3)	1.47(0.6)	5.0(0.9)	0.73(0.3)
PT-1	3.13(0.35)	5.1(1.1)	5.0(1.7)	0.53(0.3)	1.9(0.9)	0.10(0.1)
	5.2(4.0)	3.4(0.3)	7.3(3)	1.00(0.4)	4.4(1.2)	0.40(0.2)
PT-2	3.32(0.46)	4.6(0.8)	4.7(1.6)	0.42(0.2)	1.7(0.7)	0.13(0.1)
	13(15)	3.2(0.3)	9.0(4.7)	1.50(0.8)	7.0(2.6)	0.57(0.4)
QA-1	3.08(0.33)	5.0(0.7)	5.0(2.1)	0.37(0.2)	1.6(0.6)	0.12(0.1)
	36(31)	6.3(0.5)	38.7(20)	1.80(0.9)	37.4(13)	1.45(1.7)
QA-2	2.88(0.34)	5.4(0.6)	5.0(2.1)	0.33(0.2)	2.1(0.8)	0.20(0.1)
	1.9(1.7)	6.7(0.3)	53.7(28)	0.22(0.2)	79.2(20)	2.18(2.1)
Open		4.9(0.9)	2.7(0.9)	0.22(0.2)	0.5(0.2)	0.03(0.02)
	TF†	N.S.	N.S.	N.S.	N.S.	N.S.
	SF†‡	S.(0.55)	S.(13.5)	S.(1.05)	S.(8.0)	S.(0.92)

*Throughfall values are given on the first line; stemflow values on the second line. Th standard deviation is given in parentheses.

†From the analysis of variance, N.S. indicates a nonsignificant and S. a significant F value at the 0.05 level.

‡The values in parentheses for stemflow indicate the least significant difference.

Since the amounts of stemflow and throughfall varied among the 13 trees, a better picture of the relative mineral cycling efficiencies is obtained by calculating the average amounts of nutrients returned by stemflow and throughfall from the different trees. The amounts of nutrients returned in stemflow can be expressed in two ways. First, for a comparison of stemflow inputs and throughfall inputs, it is useful to project the stemflow over the entire crown area. Second, since stemflow is concentrated in the soil near the trunk, it is of interest to compute the amounts of nutrients returned per square meter of basal area.

The average amounts of calcium, magnesium, potassium, and manganese returned in stemflow and throughfall from three storms during the 1969 growing season were calculated as milligrams per square meter of crown area (Table 5). The largest returns were of calcium and potassium. On an areal basis, about 1.5 to 2 times as much calcium, 2 to 4 times as much magnesium and manganese, and 3 to 8 times as much potassium were returned in throughfall compared to the returns in gross rainfall in the open. The analysis of variance indicated no significant difference ($P = 0.05$) among the 13 trees in the amounts of nutrients returned in throughfall. When projected over the entire crown area, the amounts of calcium, magnesium, potassium, and manganese returned in stemflow were small, usually amounting to 10% or less of the totals returned in both stemflow and throughfall. The beeches and hickories and one of the white oaks generally returned significantly greater amounts of calcium and potassium in stemflow than the other trees. There were no significant differences in the returns of manganese, but the two hickories generally returned significantly higher amounts of magnesium. The localized impact of stemflow is shown in the amounts of nutrients returned per square meter of basal area (Table 5). The amounts of calcium and potassium returned by beech and hickory and one of the white oaks ranged from 2 to 10 g per square meter of basal area. The contributions of magnesium and manganese were considerably lower but were still large when projected over the small zone of stemflow influence. Beech and hickory generally returned significantly greater amounts of calcium and potassium per square meter of basal area than the other trees.

Influence of Stemflow on Chemical Characteristics of the Soil

When the soil properties in the zone of stemflow absorption are compared with those under the edge of the crown, several trends are apparent (Table 6). Under all the hardwoods, the concentrations of potassium were higher in the stemflow zone than under the crown edge. Under the two white oaks and the two hickories, the calcium concentrations were markedly higher in the zone of stemflow absorption than under the crown edge. Under both yellow poplars and both beeches, the concentrations of calcium, magnesium, and manganese were

TABLE 5

AVERAGE AMOUNTS OF Ca, Mg, K, AND Mn RETURNED FROM THREE STORMS IN THROUGHFALL AND STEMFLOW*

Tree No.		Ca, mg/m²	Mg, mg/m²	K, mg/m²	Mn mg/m²
	TFCA	108.1	11.5	49.3	4.7
FG-1	SFCA	6.5	0.40	8.6	0.11
	SFBA	6860	427	9156	115
	TFCA	105.0	18.9	65.1	5.4
FG-2	SFCA	10.2	0.56	9.0	0.30
	SFBA	9650	530	8726	358
	TFCA	139.1	19.4	136.9	4.9
CT-1	SFCA	10.8	0.73	5.7	0.06
	SFBA	10159	684	6258	54
	TFCA	108.0	13.7	107.8	4.3
CT-2	SFCA	14.1	0.99	7.3	0.04
	SFBA	6702	472	2256	18
	TFCA	212.7	25.4	119.9	7.4
LT-1	SFCA	3.2	0.31	3.3	0.09
	SFBA	1437	138	1475	40
	TFCA	123.6	13.7	93.7	2.9
LT-2	SFCA	4.9	0.68	6.0	0.08
	SFBA	1142	160	1404	18
	TFCA	157.2	15.9	97.4	4.6
PE-1	SFCA	2.3	0.34	1.1	0.16
	SFBA	619	92	289	44
	TFCA	128.4	14.0	61.6	3.5
PE-2	SFCA	1.7	0.23	0.99	0.09
	SFBA	747	99	434	39
	TFCA	139.3	10.7	58.0	3.4
PE-3	SFCA	0.4	0.08	0.41	0.03
	SFBA	172	10	175	14
	TFCA	197.9	28.3	114.4	4.2
PT-1	SFCA	1.3	0.16	1.0	0.06
	SFBA	417	51	318	18
	TFCA	172.7	17.1	79.8	5.7
PT-2	SFCA	1.3	0.27	1.6	0.10
	SFBA	429	86	523	32
	TFCA	162.3	12.1	65.6	3.4
QA-1	SFCA	6.5	0.19	8.6	0.13
	SFBA	3139	91	4140	62
	TFCA	158.7	13.3	102.5	7.2
QA-2	SFCA	0.2	0.01	0.59	0.005
	SFBA	135	8	387	3
Open		88	7.1	15.8	2.2
	TFCA†	N.S.	N.S.	N.S.	N.S.
	SFCA†‡	S.(4.3)	S.(0.47)	S.(6.1)	N.S.
	SFBA†‡	S.(2828)	S.(361)	S.(5262)	S.(93)

*Returns in throughfall are milligrams per square meter of crown area (TFCA); returns in stemflow are milligrams per square meter of crown area (SFCA) and milligrams per square meter of basal area (SFBA).

†From the analysis of variance, N.S. indicates a nonsignificant and S. indicates a significant F value at the 0.05 level.

‡Numbers in parentheses represent the least significant difference.

TABLE 6

SOIL pH AND Ca, Mg, K, AND Mn CONCENTRATIONS UNDER NINE TREES

Tree	Area sampled*	pH	Parts per million			
			Ca	Mg	K	Mn
Hickory-1	S	5.8	1600	92	87	54
	C	5.2	436	56	46	43
Hickory-2	S	6.2	972	67	66	46
	C	5.2	464	55	31	37
Beech-1	S	4.4	48	11	41	9
	C	4.5	96	15	20	19
Beech-2	S	4.6	112	21	79	22
	C	5.0	272	89	28	31
Yellow Poplar-1	S	4.8	384	57	74	29
	C	5.7	728	72	38	50
Yellow Poplar-2	S	4.1	208	31	41	11
	C	5.0	320	53	38	21
Shortleaf Pine	S	3.9	240	31	30	6
	C	4.8	368	45	32	23
White Oak-1	S	6.5	1960	37	110	84
	C	4.9	256	45	46	24
White Oak-2	S	5.9	1960	29	117	64
	C	4.8	208	37	33	37

*S, near the trunk; C, under the edge of the crown.

greater under the crown edge than in the stemflow zone. Under both hickories the magnesium and manganese concentrations were greater in the stemflow zone. With white oak the magnesium concentration was higher in the stemflow zone, but the manganese concentration was higher under the crown edge. Under the shortleaf pine, calcium, magnesium, and manganese concentrations were higher under the crown edge. There was little difference in the potassium concentration. Under yellow poplar and shortleaf pine, soil pH was higher under the crown edge, but under white oak and hickory, the pH was higher in the stemflow zone.

DISCUSSION

The six species studied differed considerably in their stemflow characteristics because of their branching patterns and bark characteristics. The trees with relatively smooth nonabsorbent bark produced larger amounts of stemflow than those with rough or scaly absorbent bark. Among the hardwoods, the bark of white oak is the roughest and hence the most absorbent; yellow poplar is less so,

followed by hickory and then beech. Beech bark is almost paper smooth and appears to have very low water-absorption capacity. Hickory bark is furrowed, but its surface is hard and absorbs little water. The water-storage capacity of hickory bark is relatively high, however, because of the furrowed surface. The bark of yellow poplar resembles that of hickory in the upper parts of the tree, but the bark of the lower trunk of poplar is rougher and more absorbent. Billings and Drew (1938) reported that yellow-poplar bark had a water-holding capacity of 173% on an oven-dry weight basis, compared to 64% for beech. White-oak bark often forms large, rather loose plates and appears to be highly absorbent. White oak probably produces a good bit of bark drip. The branching habit and crown size of a tree also influence its production of stemflow (Geiger, 1966). All the hardwoods examined in this study have deliquescent branching patterns except for yellow poplar, which has more of an excurrent pattern. The major branches of beech and hickory are more vertically oriented than those of white oak and thus tend to collect more stemflow.

These characteristics help to explain the differences in stemflow production among the different species. Thus beech, with smooth bark and vertically oriented branches, produced the most stemflow and required the least amount of rain for the initiation of stemflow. Hickory, with a branching habit similar to beech but with furrowed bark, was next in the production of stemflow. The higher storage capacity of hickory bark was indicated by the greater amount of rainfall required for the initiation of stemflow. Yellow poplar and white oak produced the least stemflow among the hardwoods—poplar because of its small crown and excurrent branching and white oak because of its absorbent bark and less vertically oriented main branches. Four of the five pines measured produced, on the average, small amounts of stemflow, probably because of their excurrent branching pattern and small crowns (Table 1). The exception was PE-1, the large shortleaf pine. During a rain of 5.28 cm, PE-1 produced 40 liters of stemflow.

As was to be expected, in view of the differences in amounts of stemflow produced, there were marked differences in amounts of the various elements returned to the soil in stemflow. The amounts of calcium and potassium returned by the beeches and hickories were considerably greater than those returned by any of the other trees with the exception of one of the white oaks, QA-1. The return of manganese in hickory stemflow was surprisingly low considering the quantities of the other elements returned. The white oaks returned very little magnesium, compared to most of the other trees. In general, the pines returned smaller amounts of calcium, magnesium, potassium, and manganese than the hardwoods; calcium and potassium returns were especially low.

Throughfall is less enriched chemically than is stemflow, but total nutrient returns are much greater in throughfall because of the larger volume of water that reaches the soil as throughfall. For all the 13 trees, throughfall during the growing season accounted for about 98% of the water that reached the forest

floor. Throughfall returned 96% of the calcium, 97% of the magnesium, 95% of the potassium, and 98% of the manganese which reached the forest floor in precipitation.

Stemflow assumes more of a role in amounts of water and nutrients returned when we consider its limited zone of influence. For example, when the average 154 liters of stemflow per storm for FG-1 was projected over its basal area (0.15 m^2), this amounted to some 50 times the depth of gross rainfall received in an equal area in the open. This basal area received, on the average, over 600 times as much potassium, 86 times as much calcium, 60 times as much magnesium, and 105 times as much manganese as an equal area in the open.

The stemflow of beech has been shown by Gersper and Holowaychuk (1970a and b) to affect the morphological and physical properties of soil as well as soil chemistry in the zone of stemflow influence. In the present study, soil samples collected under nine trees near the base of the trunk and under the edge of the crown provided further evidence of the effect of stemflow and throughfall on the soil. The trends in surface-soil pH under most of the sampled trees seemed to be correlated with the pH of the stemflow and throughfall of each species. Under hickory and white oak, soil pH tended to be highest in the zone of stemflow absorption and to decrease with increasing distance from the trunk. This tendency was consistent with the differences in the pH of stemflow and throughfall in both species. In beech and shortleaf pine, stemflow pH was lower than throughfall pH, and these differences were reflected in the soil pH. Under both beech and shortleaf pine, the soil pH was lowest near the trunk and tended to increase with increasing distance from the trunk.

Soil potassium content (0 to 10 cm in depth) under all the hardwoods sampled was higher in the zone of stemflow absorption than under the edge of the crown. Under hickory and white oak, the soil calcium content tended to be markedly higher near the trunk than under the edge of the crown, but this difference may be related to patterns of litter deposition rather than stemflow. Gersper and Holowaychuk (1971) found that soil potassium was generally highest near the trunks of several hardwoods, even some that produced large volumes of stemflow. They attributed this pattern of potassium concentration near the trunk to the low leaching potential of stemflow for soil potassium. That is, the ratio of stemflow potassium to soil exchangeable potassium was much higher than the ratio of stemflow calcium to soil exchangeable calcium. This differential leaching potential may help to account for the patterns of concentration of other soil nutrients as well.

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REFERENCES

Billings, W. D., and W. B. Drew, 1938, Bark Factors Affecting the Distribution of Corticolous Bryophytic Communities, *Amer. Midland Natur.*, **20**: 302-330.

Carlisle, A., A. H. F. Brown, and E. J. White, 1967, The Nutrient Content of Tree Stemflow and Ground Flora Litter and Leachates in a Sessile Oak (*Quercus petraea*) Woodland, *Ecol.*, **56**: 615-627.

Eaton, J. S., G. E. Likens, and F. H. Bormann, 1973, Throughfall and Stemflow Chemistry in a Northern Hardwood Forest, *J. Ecol.*, **61**: 495-508.

Geiger, R., 1966, *The Climate near the Ground*, Harvard University Press, Cambridge, Mass.

Gersper, P. L., 1970, Effect of American Beech Trees on the Gamma Radioactivity of Soils, *Soil Sci. Soc. Amer., Proc.*, **34**: 318-323.

——, and N. Holowaychuk, 1971, Some Effects of Stemflow from Forest Canopy Trees on Chemical Properties of Soils, *Ecology*, **52**: 691-702.

——, and N. Holowaychuk, 1970a, Effects of Stemflow Water on a Miami Soil Under a Beech Tree: I. Morphological and Physical Properties, *Soil Sci. Soc. Amer., Proc.*, **34**: 779-786.

——, and N. Holowaychuk, 1970b, Effects of Stemflow Water on a Miami Soil Under a Beech Tree: II. Chemical Properties, *Soil Sci. Soc. Amer. Proc.*, **34**: 786-794.

Helvey, J. D., and J. H. Patric, 1965, Canopy and Litter Interception of Rainfall by Hardwoods of Eastern United States, *Water Resour. Res.*, **1**: 193-206.

Madgwick, H. A. I., and J. D. Ovington, 1959, The Chemical Composition of Precipitation in Adjacent Forest and Open Plots, *Forestry*, **32**: 14-22.

Mina, V. N., 1967, Influence of Stemflow on Soil, *Sov. Soil Sci. (Engl. Transl.)*, **1967**: 1321-1329.

Patterson, D. T., 1970, Chemical and Volumetric Characteristics of Stemflow and Throughfall in the Carolina Piedmont Forest, MA Thesis, Duke University, Durham, N. C.

Reid, P. H., and C. Copeland, 1969, *Analytical Methods used by the Soil Testing Division*, North Carolina Department of Agriculture, Raleigh, N. C.

Tamm, C. O., 1951, Removal of Plant Nutrients from Tree Crowns by Rain, *Physiol. Plant.*, **4**: 184-188.

Voight, G. K., 1960a, Alteration of the Composition of Rainwater by Trees, *Amer. Midland Natur.*, **63**: 321-326.

——, 1960b, Distribution of Rainfall Under Forest Stands, *Forest. Sci.*, **6**: 2-10.

Will, G. M., 1959, Nutrient Return in Litter and Rainfall Under Some Exotic Conifer Stands in New Zealand, *N. Z. J. Agr. Res.*, **2**: 719-734.

Witherspoon, J. P., Jr., 1964, Cycling of Cesium-134 in White Oak Trees, *Ecol. Monogr.*, **34**: 403-420.

THE RAINFALL INTERCEPTION PROCESS AND MINERAL CYCLING IN A MONTANE RAIN FOREST IN EASTERN PUERTO RICO

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ABSTRACT

A comprehensive interception study was carried out in a montane rain forest in eastern Puerto Rico. Results indicate that the factors of intensity, duration, and overall distribution of storms by storm size must be taken into consideration when determining the fate of isotopes that reach the forest via rainfall. The relationships rainfall–throughfall and rainfall–stemflow are best described by linear equations. However, neither is a constant percentage of rainfall but varies with storm size. The predictive equation for throughfall is $Y = 0.954P - 0.028$, and for stemflow it is $Y = 0.088P - 0.037$. Although small storms contribute very little to the total annual rainfall, their impact on the chemical inputs to this tropical ecosystem is major.

Input budgets for calcium, magnesium, sodium, and potassium are estimated at 115.2, 79.1, 415.8, and 98.7 kg ha^{-1} $year^{-1}$. Throughfall is the major contributor of magnesium, sodium, and potassium to the soil system, accounting for 60, 60, and 80%, respectively, of the estimated inputs of these elements. Leaf fall provides 71% of the calcium input and throughfall accounts for 22%.

The contamination of terrestrial systems with radionuclides may occur either by particulate fallout or by isotopes associated with rainfall. Foliar absorption of isotopes by plants has been demonstrated. The actual uptake of isotopes from rainfall is a function of the intensity, duration, storm size, and the length of time the water is in contact with the absorbing surfaces. A review of rainfall distribution at El Verde from 1964 through May 1966 showed that approximately 70% of the daily rain events were 12.7 mm (0.5 in.) or less. There has never been sufficient emphasis on the importance of the small storm and its role in the uptake of radionuclides.

Fassig (1916) studied the duration, frequency, and intensity of tropical rains in Puerto Rico. He reported that, at the Caguas station, out of an annual frequency of 262 rain days, 160 rain days had rains between 0.25 and 2.54 mm

(0.01 and 0.10 in.). On the western end of the island, the highest frequency occurred between 5.1 and 7.6 mm (0.20 and 0.30 in.). His data suggested that, for the Luquillo area, approximately 89% of the rains were 12.7 mm (0.5 in.) or less. Odum, Drewry, and Kline (1970) reported that light rains between 0.25 and 2.5 mm/hr (0.01 to 0.10 in./hr) accounted for 82% of the rains at El Verde. According to Libby (1956), cleansing of the atmosphere of particulate matter in a zone of precipitation is assumed to be fairly complete with 2.5 mm (0.1 in.) of rain.

For some time foliar applications have been used to correct minor element deficiencies in plants. Radioisotope studies have confirmed that materials applied to leaves can be absorbed, translocated, and used by plants. Studies on the absorption of radioisotopes from dilute solutions have indicated that the greatest uptake occurs in the first 24 hr after application (Biddulph, 1960; Bukovac and Wittwer, 1960). Bukovac and Wittwer (1960) also showed that the amounts of ^{32}P absorbed vary with the moisture conditions of the leaf surface. Wittwer and Teubner (1959) have shown that ^{42}K, ^{55}Fe, ^{65}Zn, ^{32}P, and ^{35}S can be absorbed by the bark of fruit trees and contribute to the nutrition of the underlying areas. Thus the deposition and subsequent absorption of radionuclides by light rains just sufficient to wet the leaves can be compared to foliar absorption.

Much work has been done on rainfall and interception in the hardwood forests of the eastern United States. Helvey and Patric (1965) summarized what was available. They had to conduct their own experiments to estimate interception since the applicability of the data reported in the literature was restricted by sampling and/or methods of measurement. However, they did find that the published data on regression equations were fairly uniform. Reanalysis of these data led to the development of generalized equations for predicting the quantity of throughfall and stemflow from gross rainfall in eastern hardwood forests. The two equations derived were

$$T = 0.901P - 0.031$$

$$S = 0.041P - 0.005$$

where T and S are the amount of throughfall and stemflow, respectively, and P is gross rainfall.

Similar work in tropical areas is scarce. Mohr and Van Baren (1954) presented data on the amount of rainfall retained by the canopy in Surinam. They reported that with a rain of 0.10 mm (0.04 in.) 80% was retained and that this percentage decreased to 19.5% with a rain of 35.56 mm (1.4 in.). Jordan (1968) initiated a series of studies on the water budget of the El Verde forest. In this study stemflow was measured on 27 trees ranging from 4.1 to 78 cm (1.6 to 30.7 in.) in diameter at breast height (dbh). Throughfall was collected and measured in 12 trough-type gauges located at various sites in the

forest. He found stemflow to be almost a constant percentage of gross rainfall, ranging between 17.5 and 22% depending on storm size. Throughfall was approximately 70% of gross rainfall. Regression equations of the form $Y = a + bx$ were developed for each dbh class between 5.1 and 76.2 cm (2 and 30 in.). Intermediate size trees yielded the largest amounts of stemflow from a given storm. These equations were then combined with data on the number of trees per hectare and the dbh distribution of trees to estimate the contribution of stemflow to the water budget.

In their discussion Helvey and Patric (1965) cited two important points. First, a complete interception study including litter interception has never been reported, and, second, stemflow has not been well documented on an areal basis. Traditionally stemflow has been measured on individual trees, and the results have been extrapolated to an areal basis as represented by the work of Jordan (1968). Hydrologic studies quite often have been too restricted in scope and have not considered the full importance of the interrelationships that occur on an areal basis. However, this approach has been restricted because of the lack of adequate techniques, especially in the area of stemflow measurements. Helvey and Patric (1965) pointed out that the paucity of stemflow data was no doubt due to the high cost and hard work involved in this type of study. Thus, if interception studies are to be initiated on an areal basis, the question of stemflow collar and measurements must be solved. A simple, inexpensive, inert, and easily installed collar was developed to permit an areal study of stemflow (Clements and Colon, 1970). With this development a comprehensive interception study was designed. The interception study had the following objectives:

1. First, to determine the quantitative relationships between gross rainfall measured above the canopy and the parameters of throughfall and stemflow yield, litter interception and evaporation, and soil-moisture changes.

2. To determine the chemistry of each parameter and define the chemical changes that take place as rainfall is intercepted and redistributed as throughfall and stemflow. The elements to be determined are calcium, potassium, sodium, and magnesium.

3. To develop predictive equations through correlation–regression analysis on the relationships between gross rainfall and the associated interception parameters which will include both quantity and chemistry.

Procedure

An 80-m by 80-m section of forest at the El Verde forest site in close proximity to the 21.9-m (72-ft) walk-up tower was selected and subdivided into 16 smaller plots of 20 m by 20 m. Five plots were randomly selected for the studies. A grid of 1 m^2 was laid down in each of the five plots; the location of each tree was recorded, and notes were made regarding its bark characteristics, leaf size, presence or absences of epiphytes and vines, and whether it was erect

or inclined. Each tree was classified according to its interception potential as follows:

1. Primary interceptor: those trees occupying a canopy position and receiving direct rainfall.

2. Secondary interceptor: those trees occupying a subcanopy position and receiving throughfall from a primary interceptor.

3. Tertiary interceptor: those trees occupying a subcanopy position and receiving throughfall from a secondary interceptor.

One plot, from the five set aside, was randomly selected to initiate the interception study. All trees in the plot having a dbh of 7.62 cm (3 in.) or larger were fitted with a stemflow collar. Of the 45 trees fitted with collars, 15 were classified as primary interceptors, 14 as secondary interceptors, and 16 as tertiary interceptors.

Six troughs, 20.3 cm (8 in.) wide by 7.32 cm (24 ft) long, were fabricated from galvanized metal to collect throughfall. Each trough was lined with polyethylene sheeting. The troughs were given a 10% slope to facilitate rapid drainage of water. Throughfall was collected in covered 76-liter (20-gal) plastic containers, and quantities were determined by measuring with a calibrated stick. The effective collecting area of each trough, after adjusting for slope, was 13,696 cm^2. Therefore, 1 in. of throughfall would yield 34,789 ml of water, thus allowing the measurement of small quantities of throughfall. The troughs were selected over other means of gauging because of the interest in the chemistry of the water. In this way the troughs integrated the throughfall and gave a more representative sample of the area than would spot sampling.

Gross rainfall measurements were measured from a 1-m^2 stainless-steel collector located on top of a 21.9-m (72 ft) tower. With an effective collecting surface of 10,000 cm^2, a 1-in. rain would yield 25,400 ml, thus giving a sensitivity of 0.001 in.

Previous evaluation of rainfall in the El Verde area indicated that most storms were less than 1.27 cm (0.5 in.), were of light intensity and short duration, and generally occurred during the morning hours. Therefore measurements of gross rainfall, throughfall, and stemflow were made after each rain event during daytime. These measurements were classified as "timed" events since the onset and end on each event was recorded. Rain events that occurred during the nighttime or on weekends were measured at the beginning of each day and labeled as "nontimed" events. The purpose of this classification was to evaluate the rainfall–throughfall and stemflow relationships on an individual storm basis and collectively on a day basis.

Water samples for chemical analysis were taken for each rain event for each of the six throughfall collectors and for stemflow for each of the 45 trees. The elements determined were calcium, magnesium, sodium, and potassium.

Results and Discussion

Throughfall

The relationship between gross rainfall and throughfall is based on the correlation–regression analysis of 137 rain events over a 12-month period. The timed and nontimed events were analyzed separately and then combined for a separate analysis. Regression analysis shows the best fit to be a straight line (see Fig. 1). The coefficients of determination along with the predictive equations are summarized in Table 1. The importance of "timed" observations in the evaluation of the rainfall–throughfall relationship becomes apparent on comparison of the predictive equations. "Nontimed" observations (the usual method in interception studies) were shown in this study to underestimate throughfall by approximately 10%. Throughfall was not a constant percentage of rainfall but varied from 67% at 2.54 mm (0.1 in.) of rain to 92.5% at 25.4 mm (1.0 in.) of

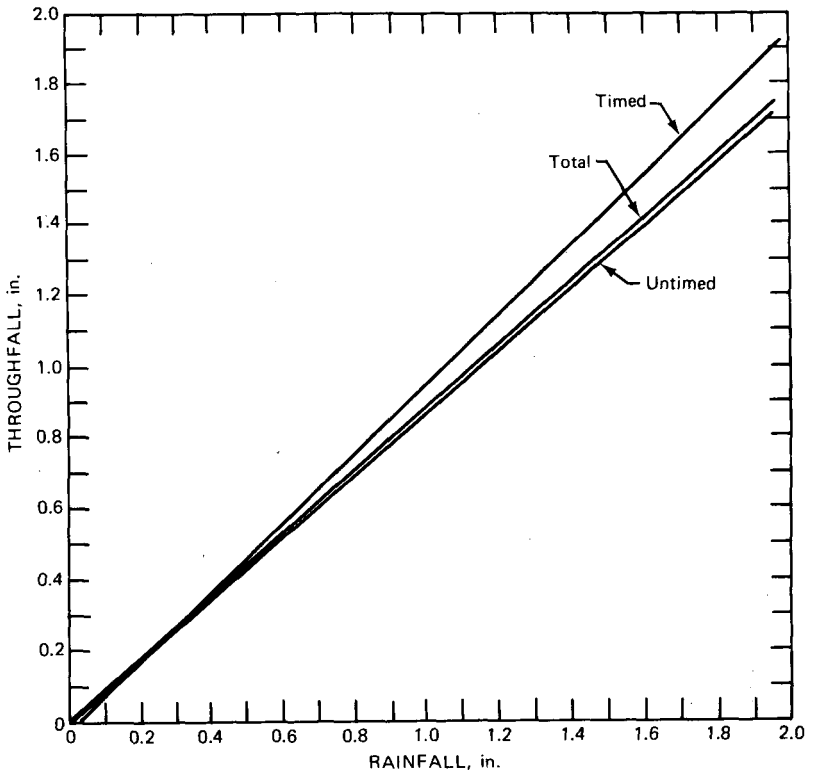

Fig. 1 Linear relationship between gross rainfall and throughfall on a whole-plot basis for timed and nontimed observations.

TABLE 1

PREDICTIVE EQUATIONS AND COEFFICIENTS OF DETERMINATION (IN PARENTHESES) FOR RAINFALL, THROUGHFALL, AND STEMFLOW RELATIONSHIPS

Parameter	Observation*		
	Timed	Nontimed	Total
Throughfall	0.954P − 0.028 (0.982)	0.874P − 0.032 (0.968)	0.884P − 0.024 (0.973)
Stemflow			
Whole plot	0.088P − 0.037 (0.878)	0.072P − 0.044 (0.851)	0.077P − 0.038 (0.882)
Primary interceptors	0.050P − 0.021 (0.827)	0.040P − 0.024 (0.820)	0.043P − 0.021 (0.836)
Secondary interceptors	0.029P − 0.011 (0.966)	0.023P − 0.011 (0.866)	0.025P − 0.011 (0.933)
Tertiary interceptors	0.009P − 0.004 (0.795)	0.009P − 0.006 (0.850)	0.009P − 0.005 (0.857)

*Timed observations = 85; nontimed observations = 52; and total observations = 137.

rain. On the average approximately 0.76 mm (0.03 in.) of rain is required to saturate the forest canopy and produce throughfall. This value will vary between 0.0 and 1.27 mm (0.0 and 0.05 in.) depending on the moisture status of the leaf surfaces at the onset of a rain event. This value, along with the intensity, duration, and storm size, will determine the fate of radionuclides in rainfall.

By using a community approach rather than an individualistic one, we feel that some of the questions raised by Helvey and Patric (1965) have been answered. The predictive equation developed in this study supports their conclusions on the use of general equations to estimate throughfall and stemflow in the mature hardwood forest of the eastern United States. We would like to further suggest that where mature forest conditions exist, such as in the eastern hardwoods or tropical forests, the equations derived in this study are applicable.

Stemflow

Although stemflow constituted a small percentage of the total water reaching the forest soil, it cannot be considered insignificant on a whole-plot basis. Individual trees yielded stemflow at lower values; however, the average value of rainfall on a whole-plot basis (400 m^2) required to yield measurable stemflow was 10.67 mm (0.42 in.). Stemflow as a percentage of rainfall varied between 1.4% with a 12.7-mm (0.5-in.) rain and 5.1% with a 25.4-mm (1-in.) rain. Stemflow is important in the fate of nuclides because the trees funnel a large quantity of water and deposit it over a small area at the base of each tree. The extreme yield of stemflow by an individual tree during this study was

180 liters as a result of 48.3 mm (1.9 in.) of rain in a 2-hr period. The overall relationship for rainfall and stemflow on a whole-plot basis is given in Fig. 2.

Storm-Size Distribution

Storm-size distribution is important to an understanding of the fate of nuclides associated with rainfall. Initially it was reported by Clements (1969) that 70% of all storms at the El Verde site were 12.7 mm (0.5 in.) or less. The results of our study showed this value to be 89%. The number of storms between 15.24 and 25.4 mm (0.6 and 1.0 in.) accounted for approximately 6% of the total, and the number of storms greater than 25.4 mm (1.0 in.) accounted for approximately 5%. Thus in this area the larger storms must be treated as the exception rather than the rule, and the fate of isotopes in rainfall would be controlled primarily by the smaller storms. This becomes more evident when considering that in our study 69% of all storms fell in the rain class 1.52 mm to 3.81 mm (0.06 to 0.15 in.). The use of a class mean of 2.54 mm in the regression equation indicates that roughly one-third of the incoming rain was intercepted and retained by the canopy. This information, along with the studies on epiphylls associated with the leaves, is now thought to explain the levels of radioactivity found by Kline (1968) at El Verde.

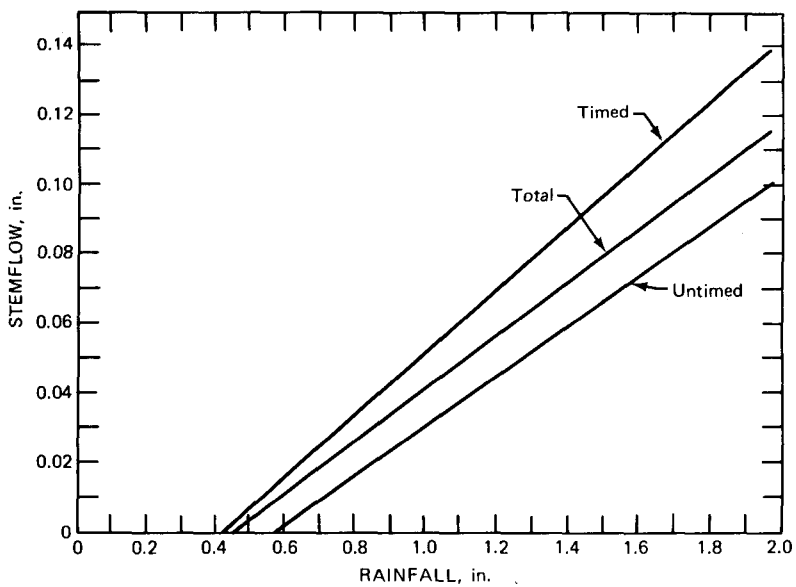

Fig. 2 Linear relationship between gross rainfall and stemflow on a whole-plot basis for timed and nontimed observations.

Duration and Intensity

The duration and intensity of storms also play an important role in the fate of nuclides associated with rainfall.

Rains of light intensity and short duration would be conducive to foliar absorption, whereas rains of heavy intensity would result in a transfer of isotopes to the forest floor. A frequency distribution of storm duration showed that 78% of the storms lasted 1 hr or less and 33% lasted 20 min or less. Analysis of storm intensity showed 91.2% of the storms were 12.7 mm/hr (0.5 in./hr) or less. The results show that frequency of storms and the interval between storms affected not only the throughfall and stemflow yields but also the chemistry of throughfall and stemflow water. The position of a tree with respect to canopy, subcanopy, or understory and nearest neighbor affected the yield and chemistry of stemflow water.

A preliminary investigation into the chemistry of rainfall by 0.25-mm (0.01-in.) fractions provided an additional insight into the interception process and mineral cycling. For a total of 45 rain events the incoming rain was sampled by 0.25-mm (0.1-in.) units, and each fraction was analyzed for sodium, potassium, calcium, and magnesium. The data suggest that the concentration of the four elements follows a normal dilution curve with incoming rainfall, with the highest concentration of the elements occurring in the first four to five fractions, 1.02 to 1.27 mm (0.04 to 0.05 in.). This amount of rainfall coincides with the quantity of rainfall required to saturate the forest canopy and produce throughfall. The data for calcium and magnesium, along with throughfall expressed as a percent of rain, are shown in Fig. 3. The area between 0.0 to 0.75 mm (0 to 0.03 in.) of rain has been labeled the zone of maximum foliar absorption because where frequent rain events yielding 0.76 to 1.02 mm (0.03 to 0.05 in.) occur there would be maximum foliar absorption and a significant input of elements into the forest. This would be of special importance with respect to radionuclides in rainfall.

Chemical Budgets

Although certain aspects of the study are incomplete, it is possible to prepare a tentative budget of the inputs and outputs in this system not including the soil. The average concentrations of calcium, magnesium, sodium, and potassium in rain, throughfall, and stemflow for the period studied are shown in Table 2. In the comparison of rainfall with throughfall, removal by leaching is emphasized. As rainfall passed through the forest canopy, calcium, magnesium, sodium, and potassium concentrations were increased by factors of 4.4, 2.6, 1.8, and 9.6, respectively. The chemistry of stemflow reflects a similar increase, but not to the same level as throughfall. It is possible that as water flows over the limbs and trunks some cation exchange takes place owing to the large surface area exposed along with mosses, lichens, and other plant life

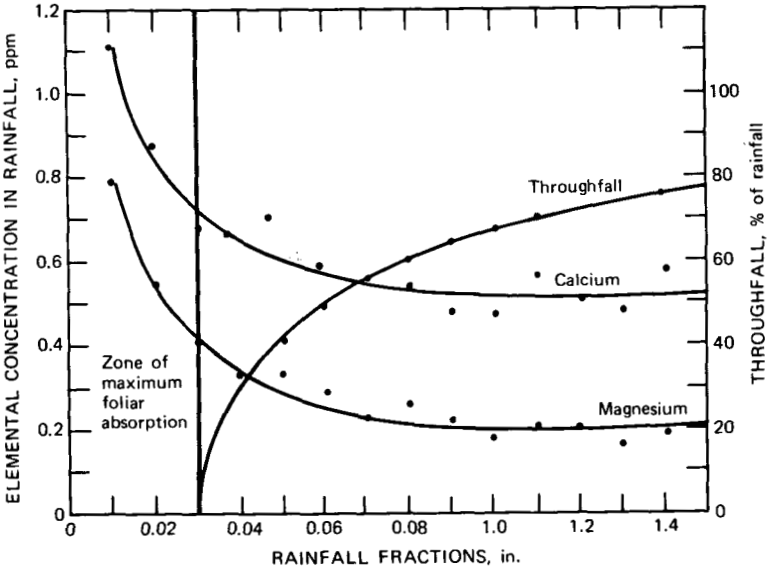

Fig. 3 Chemistry of rainfall as a function of rainfall fractions.

TABLE 2

AVERAGE CHEMICAL CONTENT OF RAIN, THROUGHFALL, AND STEMFLOW

	Parts per million			
Parameter	**Ca**	**Mg**	**Na**	**K**
Rain	0.25	0.78	6.0	0.35
Throughfall	1.10	2.02	10.6	3.36
Stemflow				
Whole plot	0.91	1.22	7.14	2.91
Primary interceptors	0.91	1.07	7.50	3.13
Secondary interceptors	1.01	1.50	6.64	2.59
Tertiary interceptors	0.75	1.05	7.37	3.06

associated with the bark surfaces. The total input–output budget for any given year will depend on the total annual rainfall. Since available records for the El Verde site show annual rainfall to vary between approximately 1780 mm (70 in.) to over 3800 (150 in.) per year, an annual budget was estimated on the basis of 2540 mm (100 in.) per year. This budget, along with the estimated turnover of elements from leaf fall based on 3 years of record, is shown in Table 3.

TABLE 3

ESTIMATED INPUT OF Ca, Mg, Na, AND K IN MONTANE RAIN FOREST BASED ON ANNUAL RAINFALL OF 2540 mm

Parameter	Input, kg ha^{-1} $year^{-1}$			
	Ca	Mg	Na	K
Rainfall	6.4	19.8	152.4	8.9
Throughfall	25.8	47.5	249.0	79.0
Stemflow	1.2	1.6	9.3	3.8
Litterfall	81.8	10.2	5.1	7.0
Total	115.2	79.1	415.8	98.7

The total elemental inputs to the soil system in terms of calcium, magnesium, sodium, and potassium were 115.2, 79.1, 415.8, and 98.7 kg/ha, respectively. With the exception of calcium, throughfall accounts for the largest contribution to the soil; rainfall is the second largest contributor. Leaf fall and throughfall accounted for approximately 93% of the estimated annual total of calcium with leaf fall accounting for 71% and throughfall for 22.4%.

A comparison of the rainfall input budget with that reported by Likens et al. (1967) for a temperate forest shows that the inputs for the tropical area are considerably higher for calcium, magnesium, sodium, and potassium by factors of approximately 1.4, 14.4, 66, and 2.8, respectively.

ACKNOWLEDGMENT

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REFERENCES

Biddulph, O., 1960, Radioisotopes in Plants: Foliar Entry and Distribution, in *Radioisotopes in the Biosphere*, pp. 73-85, R. E. Caldecott and L. A. Synder (Eds.), Printing Department, University of Minnesota, Minneapolis.

Bukovac, M. J., and S. H. Wittwer, 1960, Absorption and Distribution of Foliar Applied Mineral Nutrients as Determined with Radioisotopes, in *Plant Analysis and Fertilizer Problems*, pp. 215-230, W. Reuther (Ed.), American Institute of Biological Sciences, Washington, D. C.

Clements, R. G., 1969, Annual Report on Terrestrial Ecology, in Puerto Rico Nuclear Center Annual Report, USAEC Report PRNC-140, pp. 115-121, Puerto Rico Nuclear Center.

——, and José A. Colón, 1970, A Versatile Stemflow Collar for Interception Studies, in The Rain Forest Project Annual Report, USAEC Report PRNC–147, pp. 7-9, Puerto Rico Nuclear Center.

Fassig, Oliver L., 1916, Tropical Rains: Their Duration, Frequency and Intensity, *Mon. Weather Rev.*, **44**: 329-337.

Helvey, J. O., and J. P. Patric, 1965, Canopy and Litter Interception of Rainfall by Hardwoods of Eastern United States, *Water Resour. Res.*, **1** (2): 193-206.

Kline, J. R., 1968, Fallout Radionuclide Distribution in Vegetation of Puerto Rico, in the Rain Forest Project Annual Report, USAEC Report PRNC–119, pp. 61-69, Puerto Rico Nuclear Center.

___, C. F. Jordan, and G. E. Drewry, 1968, The Rain Forest Project Annual Report, USAEC Report PRNC–119, Puerto Rico Nuclear Center.

Libby, W. F., 1956, Radioactive Fallout and Radioactive Strontium, *Science*, **123**: 657-660.

Likens, G. E., F. H. Bormann, N. M. Johnson, and R. S. Pierce, 1967, The Calcium, Magnesium, Potassium, and Sodium Budgets for a Small Forested Ecosystem, *Ecology*, **48** (5): 772-784.

Mohr, E. C. J., and F. A. Van Baren, 1954, *Tropical Soils*, pp. 17-99, Interscience Publishers, Inc., New York.

Odum, H. T., G. E. Drewry, and J. R. Kline, 1970, Climate at El Verde, 1963–1966, in *A Tropical Rain Forest*, H. T. Odum (Ed.), pp. B-347-B-418, U. S. Atomic Energy Commission, TID–24270.

Wittwer, S. H., and F. G. Teubner, 1959, Foliar Absorption of Mineral Nutrients, *Annu. Rev. Plant Physiol.*, **10**: 13-32.

NITROGEN FIXATION BY LICHENS OF THE NORTHERN PIEDMONT

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ABSTRACT

Nitrogen fixation by lichens containing blue-green algae phycobionts was measured using the acetylene-reduction method. Collection sites were restricted to the mature forests of the Northern Piedmont of North Carolina. Species sampled included lichens containing blue-green algae as their primary phycobionts (*Leptogium cyanescens, Leptogium corticola, Collema subfurvum, Collema conglomeratum,* and *Sticta weigelii*), and lichens containing blue-green algae in cephalodia (*Lobaria pulmonaria* and *Lobaria quercizans*). Fixation rates measured in the presence of light and high moisture were compared with nitrogen content and surface area of the thallus. Lichens with blue-green algae as their primary phycobiont tended to fix nitrogen at a faster rate than those with the algae in cephalodia. Fixation rates were not adequate to account for a total replacement of the thallus nitrogen each year but, in view of the slow growth of lichens, appeared to be adequate to account for the thallus nitrogen.

It has been known since the end of the nineteenth century that blue-green algae have the ability to fix atmospheric nitrogen (Fogg, 1947; Stewart, 1966). Subsequent studies have shown that their nitrogen contribution is particularly significant in certain tropical areas, such as far-eastern rice paddies (Fogg, 1947), and in the arctic tundra (Alexander and Schell, 1973; Schell and Alexander, 1973). Fogg (1947) suggested that blue-green algae also fix nitrogen when they are in a symbiotic relationship and that nitrogen fixation could occur in lichens that contain blue-green algae.

It can be determined from information presented by Ahmadjian (1967) a by Hale and Culberson (1970) that lichens containing blue-green algae represent from 5 to 10% of all lichens in the continental United States and Canada. These

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lichens can be divided into two groups: (1) those having blue-green algae as their primary and most often only phycobiont and (2) those having green algae as their primary phycobiont and blue-green algae as their secondary or less frequently their tertiary phycobiont. Among the first group are the gelatinous lichens *Leptogium* and *Collema* and the nongelatinous lichens *Pannaria, Heppia,* and *Coccocarpia.* Lichens of the second group have the blue-green algae in cephalodia (or packets) either externally, as in *Peltigera* and *Stereocaulon,* or internally, as in the *Lobaria.*

Schollhorn and Burris (1966) and Dilworth (1966) discovered that nitrogenase, the enzyme responsible for the reduction of atmospheric nitrogen, also reduces acetylene (C_2H_2) to ethylene (C_2H_4). This discovery had a very significant impact on nitrogen-fixation research (Bergersen, 1970; Hardy, Burns, and Holsten, 1973; Stewart, Fitzgerald, and Burris, 1967). The production of ethylene can be measured by gas chromatography methods, and the amount of ethylene produced is proportional to the amount of nitrogen that would be produced under similar conditions. The commonly accepted reduction ratio of three acetylene molecules to each nitrogen molecule is used in nitrogen-fixation calculations (Hardy, Burns, and Holsten, 1973). The acetylene-reduction method has greatly facilitated the investigation of nitrogen fixation in lichens and enables investigators to study the effect of ecological and physiological parameters on nitrogen-fixation rates.

Studies on species of *Peltigera* and *Lobaria* (Kershaw and Millbank, 1970; Millbank, 1972; Millbank and Kershaw, 1969; Millbank and Kershaw, 1970) have shown that the rate of nitrogen fixation by the intact lichen, *Peltigera canina,* with a *Nostoc* phycobiont, was higher than that of a free-living blue-green alga (*Nostoc* species) and that almost all the fixed nitrogen is utilized by the fungal component. Henriksson and Simu (1971), measuring nitrogen-fixation rates of *Collema tuniforme* and *Peltigera rufescens* and comparing specimens recently removed from the substrate with specimens that were dried and stored for as much as 30 weeks, found good recovery of fixation in the desiccated specimens. In a report on the amount of reduced nitrogen contributed by lichens to an Oregon forest, Denison (1973) estimated that *Lobaria oregana,* a lichen found on Douglas fir trees, contributed from 1.8 to 10 lb of nitrogen per acre per year (2 to 11 kg ha^{-1} $year^{-1}$).

The most comprehensive study on nitrogen fixation in lichens to date was conducted by Hitch and Stewart (1973). Thirty-six species of lichens were collected and examined for nitrogen fixation. Those which fixed nitrogen were of the genera *Collema, Lichina, Peltigera,* and *Placopsis.* It was shown that desiccation was the most important factor affecting fixation in the field.

The purpose of our research was to examine the rates of nitrogen fixation by lichens in the North Carolina Piedmont area by the acetylene-reduction method. From this information, we will calculate the amount of reduced nitrogen contributed by these lichens to their ecosystem.

MATERIALS AND METHODS

Seven different species of four genera of lichens were collected from areas in the North Carolina Piedmont. Collection sites were located in the city of Winston-Salem and on Sauratown Mountain at elevations of 275 and 600 m, respectively. All were removed from the bark of trees found in relatively closed forested areas. The two species of *Lobaria* have blue-green algae in cephalodia; the rest have blue-green algae as the primary phycobiont.

A grid prepared by lacing fishing line through a metal frame was used to measure the surface area of the lichens on the tree. Measurements were taken from two-dimensional perspective; overlapping in portions of the thallus or vertical displacements, such as on bark, were not considered. After determining the surface area, we either removed the lichens directly from the substrate in the field or returned them to the laboratory and removed them with the aid of a binocular microscope. Dry weights of these samples were measured as previously described (Hitch and Stewart, 1973).

Lichen samples used in the nitrogen-fixation studies were placed in a covered petri dish containing two pieces of filter paper saturated with tap water. The lichens were incubated in this condition for 12 hr in a growth chamber with constant light at 2000 lux, as measured with a quantum photometer, and at a temperature between 22 and 25°C. At the end of the incubation period, the lichens were removed, and the wet weight was determined. Then nitrogen fixation was determined by the acetylene-reduction method (Hardy, Burns, and Holsten, 1973). Each sample was placed in a 70-ml serum bottle; the ambient air was replaced with an atmosphere of 80% argon and 20% oxygen; and acetylene was added to a level of 0.1 atm. The bottles were placed into the growth chamber, and the production of ethylene was measured at time intervals up to 12 hr. Ethylene production rates were determined from the initial and linear portions of the incubation periods. Aliquots of 0.05 cm were removed, and ethylene levels were measured with a gas chromatograph equipped with a flame ionization detector. The aluminum gas chromatography column (3.2 mm by 3.05 m) was packed with Porapak-R, 100 to 120 mesh. The carrier gas was helium at a flow rate of 30 ml/min. The temperatures of the column oven, injection port, and flame detector were 60, 100, and 250°C, respectively. Nitrogen-fixation rates were determined from the theoretical ratio of 1.5 atoms of nitrogen reduced per molecule of ethylene formed (Hardy, Burns, and Holsten, 1973), and the change in weight was recorded as loss in moisture. Nitrogen-fixation rates in the field were measured in 15-cm^3 serum bottles after 0.1 atmosphere was replaced with acetylene. Gaseous samples were taken with Vacutainers as previously described (Schell and Alexander, 1970).

The total nitrogen of each sample was measured commercially by a macro-Kjeldahl method by Southern Testing and Research Laboratory, Inc., Wilson, North Carolina. Meteorological data were obtained from the Weather Bureau at the Greensboro–Winston-Salem–High Point airport.

RESULTS

Species of lichens collected, number of samples, collection sites and tree substrates are shown in Table 1. All the trees were relatively mature deciduous hardwoods; none were less than 20 cm in diameter. The tree species and diameters and the distribution of the lichens on the tree trunks are described in the table. Lichens were growing low on the trunks, very seldom more than 1.5 m from the ground, and appeared to be randomly distributed. Mosses were often interspersed among the lichens. This is indicative of a moist environment. Subsequent data, whenever possible, will be accompanied with one standard deviation value.

From visual observations in the field, we determined that approximately 0.5 cm of rainfall was required to penetrate the forest canopy to the level of nitrogen-fixing lichens. Since the amount of nitrogen fixation in the field taken with *Collema subfurvum* and *Leptogium corticola* was barely detectable at rainfall levels of 0.46 to 0.63 cm, this was taken as the minimum amount of rainfall necessary for fixation. Also at these rainfall levels the wet-to-dry-weight

TABLE 1

LICHEN SPECIES COLLECTED AND COLLECTION SITES

Species and number of samples	Site	Substrate*	Location on tree trunk
Leptogium cyanescens (Ach.) Körb., 4	City†	Red maple (*Acer rubrum* L.), 2 trunks: 39.6, 29.1 cm	Ground to 2.5 m all around
L. cyanescens, 2	Mountain‡	Chestnut oak (*Quercus prinus* L.), 51.7 cm	Ground to 35.6 cm east half
L. corticola (Tayl.) Tuck., 2	City§	Black oak (*Quercus velutina* Lam.), 26.7 cm	Ground to 12.7 cm northeast
Collema subfurvum (Müll. Arg.) Degel., 4	City†	Black oak, 48.5 cm	Ground to 25.4 cm west half
C. subfurvum, 2	Mountain‡	Chestnut oak, 35.6 cm	Ground to 2.3 m west
C. conglomeratum Hoffm., 4	City†	Black oak, 2 trunks: 62.3, 36.4 cm	Ground to 1.4 m southeast
baria pulmonaria (L.) Hoffm., 8	Mountain‡	Chestnut oak, 39.6 cm	Ground to 1.4 m north
L. quercizans Michx., 3	Mountain‡	Chestnut oak, 25.9 cm	10.2 to 38.1 cm west
Sticta weigelii (Isert ex Ach.) Vain., 2	Mountain‡	Chestnut oak, 53.4 cm	Ground to 12.7 cm all around

*Values given in centimeters are diameters of tree trunks at 1.5 m.
†Wooded acreage at the end of Fred's Road, Winston-Salem, Forsyth County, N. C.
‡Mountain Top Youth Camp, Sauratown Mountain, Stokes County, N. C.
§Woods across from Faculty Apartments, Wake Forest Campus, Winston-Salem, N. C.

ratio for seven samples of *Collema subfurvum* was 3.48 ± 0.64 and for four samples of *Leptogium corticola* was 4.98 ± 0.64. This corresponds to ratios of 9.40 ± 2.03 and 7.70 ± 0.50 for the respective species under the laboratory conditions of this investigation. Also, from temperature profiles for *Leptogium cyanescens, Sticta weigelii, Lobaria pulmonaria,* and *Collema subfurvum* (Kelly, 1974) it was determined that fixation rates were very low below 15°C.

TABLE 2

HOURLY AND YEARLY NITROGEN-FIXATION RATES BASED ON DRY WEIGHT AND NITROGEN CONTENT*

Species and number of samples	Nitrogen,† nm g^{-1} hr^{-1}	Nitrogen,† mg g^{-1} $year^{-1}$	Nitrogen content, mg/g
Leptogium cyanescens, 6	2638 ± 747	14.6 ± 4.1	56
L. corticola, 2	840 ± 456	4.6 ± 2.5	44
Collema subfurvum, 6	2852 ± 861	15.8 ± 4.8	43
C. conglomeratum, 4	650 ± 97	3.6 ± 0.5	37
Lobaria pulmonaria, 8	453 ± 161	2.5 ± 0.9	27
L. quercizans, 3	694 ± 165	3.8 ± 0.9	30
Sticta weigelii, 2	2607 ± 99	14.4 ± 0.5	44

*Dry weight was determined after drying the samples to a constant weight at 100° C. See text for discussion of methods for determining fixation rates and nitrogen content.

†Values are mean ± standard deviation.

A compilation of meteorological data for 1969 through 1973 on days with a mean temperature above 15°C and rainfall levels of 0.5 cm and above yielded an average of 33 fixation days each year for the lichens. We should emphasize that moisture has been reported to be the greatest limiting factor for nitrogen fixation by lichens (Hitch and Stewart, 1973). Also, since nitrogen-fixation rates have been shown to decrease dramatically toward evening (Hitch and Stewart, 1973), the average day length was considered to be 12 hr.

A comparison of the fixation rates of the lichens is shown in Table 2. These values are computed from measurements of fixation rates taken under constant light, high moisture, and temperature conditions as described previously. Yearly fixation rates are based upon 33 fixation days each year. Total nitrogen was determined by Southern Testing and Research Laboratory, Inc. With the exception of *Collema conglomeratum,* the mean fixation rates of the lichens with blue-green algae as the primary phycobiont exceeded the packeted *Lobaria* species. Yearly fixation rates were always considerably below the nitrogen content of the sample.

The data presented in Table 3 are computed on a surface-area basis. Nitrogen contents range from 0.31 to 0.62 mg/cm^2. Lichens with a leathery thallus or

TABLE 3

NITROGEN-FIXATION RATES AND TOTAL NITROGEN BASED ON SURFACE AREA* (CM^2)

Species and number of samples	Nitrogen, mg/cm^2	Nitrogen, mg(fixed) cm^{-2} $year^{-1}$
Leptogium cyanescens, 6	0.34 ± 0.09	0.09
L. corticola, 2	0.22 ± 0.01	0.02
Collema subfurvum, 6	0.31 ± 0.08	0.11
Lobaria pulmonaria, 8	0.52 ± 0.13	0.05
L. quercizans, 3	0.69 ± 0.17	0.09
Sticta weiglii, 2	0.80 ± 0.27	0.26

*See text for discussion of methods for determining surface area and fixation rates.

densely packed lobes exhibited a higher nitrogen content per unit surface area. Lichens that initially fixed nitrogen at a high rate (Table 2) also fixed at a high rate per unit surface area. From the data in Tables 2 and 3, we cannot say conclusively that lichens with blue-green algae as the primary phycobiont fix nitrogen at a higher rate than lichens with blue-green algae in cephalodia. However, the lichens with the higher rates of fixation, *Leptogium cyanescens, Collema subfurvum,* and *Sticta weigelii,* all have blue-green algae as the primary phycobiont. As in Table 2, nitrogen-fixation rates were always lower than the nitrogen content of the thallus; this indicates that a complete yearly replacement of thallus nitrogen is not possible.

DISCUSSION

The fixation rates and percentages of total nitrogen of these lichens compare favorably with rates and percentages of other lichens of the same genera reported in the literature. Denison (1973) gave a figure of 200 nmoles of nitrogen fixed per gram of dry weight per hour for *Lobaria oregana;* this is somewhat lower than our results for *Lobaria* (Table 2). Henrikkson and Simu (1971) reported a rate of 30 ng per milligram of dry weight per hour for *Collema uniforme.* This converts to 2140 ng g^{-1} hr^{-1} and compares with our values of 2852 and 650 ng g^{-1} hr^{-1} for *Collema subfurvum* and *Collema conglomeratum,* respectively (Table 2). Hitch and Stewart (1973) showed a rate of 820 nmoles of nitrogen fixed per gram of dry weight per hour for *Collema crispum.*

Goas and Bernard (1967) gave a total nitrogen content for *Lobaria pulmonaria* (2.2%), *Lobaria laetevirens* (2.7%), and *Sticta sylvatica* (4.0%). Masse (1966) reported nitrogen percentages for several species from each of the four genera of this report: *Leptogium* (5.9%), *Collema* (5 to 6%), *Lobaria*

(4.2%), and *Sticta* (4.8%). All these figures are similar to the data of Table 2. In general, the values for nitrogen content determined by Masse (1966) are higher and those by Goas and Bernard (1967) are lower than the values in Table 2. Lichens with blue-green algae as primary phycobionts had a higher nitrogen content than the *Lobaria* species, and this could be the result of a generally higher fixation rate. The *Collema conglomeratum* species, which had a lower nitrogen content, also had a lower fixation rate and was covered with apothecia.

The results reported here, except for *Leptogium corticola* and *Collema conglomeratum,* tend to support the general idea that lichens with blue-green algae as primary phycobionts fix nitrogen at a higher rate than lichens w blue-green algae in cephalodia, but further experimentation is required to pro the point. Hitch and Stewart (1973) found that a fruiting thallus of *Peltigera rufescens* fixed nitrogen at a lower rate than a vegetative thallus of the same species. This information could help explain why *Leptogium corticola* and *Collema conglomeratum* have a lower rate than *Leptogium cyanescens* and *Collema subfurvum;* both of the former have ample fruiting structures, or apothecia, but both of the latter rarely have any. Fruiting structures could add to the weight of *Leptogium corticola* and *Collema conglomeratum* but would decrease the fixation rate per gram of lichen.

The nitrogen contents per unit surface area are less variable than the fixation data and appear to be related to the thickness of the thallus or the compactness of the lobes. *Sticta weigelii* has a thick leathery thallus, uniformly distributed blue-green algae, and a high nitrogen content per unit area. The remaining species tend to be less dense or, in the case of *Lobaria,* e.g., have the blue-green algae in cephalodia. Lichens with either large numbers of apothecia or blue-green algae in cephalodia tend to have lower fixation rates per unit surface area (see Table 3). *Leptogium cyanescens* and *Sticta weigelii* lack fruiting structures, have uniformly distributed blue-green algae, and have high fixation rates. A curious, apparent, and unexplained exception to much of this is that, although *Lobaria quercizans* has ample apothecia and *Lobaria pulmonaria* has none, the former has a higher fixation rate and higher total nitrogen.

In estimating annual fixation rates, we must consider that lichens do not fix nitrogen throughout the year, because of limiting temperature and moisture conditions. Light may also be a factor, but it appears to be less limiting than temperature and moisture (Hitch and Stewart, 1973). Since nitrogen fixation d decrease toward darkness, fixation was considered to occur mostly during t daytime. Taking these factors into consideration, we calculated an annual average of 33 fixation days of 12-hr duration. It is likely that fixation will occur longer on days when rainfall is heavy; however, this would probably be balanced by shorter fixation days when rainfall was close to 0.5 cm.

Considering the slow growth rates of lichens (Hale, 1973), it is highly likely that fixation rates could account for the amount of reduced nitrogen in the thallus (Tables 2 and 3). Growth rates for *Lobaria pulmonaria* and *Lobaria*

quercizans were reported as 4.82 and 5.62 mm of radial distance per year (Hale, 1973). These were the only species reported on which corresponded to those of our investigation, and they were among the fastest growing lichens. More-representative rates would be in the vicinity of from 1 to 2 mm/year. Both *Lobaria* species have a large thallus, and it is likely that fixation rates would be adequate to account for both total nitrogen content (Table 2) and growth rates.

Finally, the lichens we studied appear to fix an adequate amount of nitrogen to account for their own total nitrogen. It is not possible at present to deduce whether a significant amount of reduced nitrogen is lost by leaching from the thallus. In any case, if the fixation rate is only equivalent to the amount of nitrogen in the thallus, when the lichen dies, the amount of reduced nitrogen will be added to the ecosystem.

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REFERENCES

Ahmadjian, V., 1967, *The Lichen Symbiosis*, Blaisdell Publishing Company, Waltham, Mass.

Alexander, V., and D. M. Schell, 1973, Seasonal and Spatial Variation of Nitrogen Fixation in the Barrow, Alaska, Tundra, *Arctic Alpine Res. (Boulder, Colo.)*, **5**: 77-88.

Bergersen, F. J., 1970, The Quantitative Relationship Between Nitrogen Fixation and the Acetylene-Reduction Assay, *Aust. J. Biol. Sci.*, **23**: 1015-1025.

Denison, C. C., 1973, Life in Tall Trees, *Sci. Amer.*, **228**(6): 75-80.

Dilworth, M., 1966, Acetylene Reduction by Nitrogen-Fixing Preparations from *Clostridium pasteurianum*, *Biochem. Biophys. Acta*, **127**: 285-294.

Fogg, G. E., 1947, Nitrogen Fixation by Blue-Green Algae, *Endeavour*, **6**: 172-175.

Goas, G., and T. Bernard, 1967, Contribution à l'étude du métabolisme azoté des Lichens: les différentes formes d'azote de quelques espèces de la famille des Stictacées, *C. R. Hebd. Séances, Ser. D, Sci. Natur. (Paris)*, **265**: 1187-1190.

Hale, M. E., 1973, Growth, in *The Lichens*, V. Ahmadjian and M. E. Hale (Eds.), pp. 473-492, Academic Press, Inc., New York.

, and W. L. Culberson, 1970, A Fourth Checklist of the Lichens of the Continental United States and Canada, *Bryologist*, **73**: 499-543.

Hardy, R. W. F., R. C. Burns, and R. D. Holsten, 1973, Applications of the Acetylene–Ethylene Method of Nitrogen Fixation, *Soil Biol. Biochem.*, **5**: 47-81.

Henriksson, E., and B. Simu, 1971, Nitrogen Fixation by Lichens, *Oikos*, **22**: 119-121.

Hitch, C. J. B., and W. D. P. Stewart, 1973, Nitrogen Fixation by Lichens in Scotland, *New Phytol.*, **72**: 509-524.

Kelly, B. B., 1974, Effects of Temperature, Light Intensity, and Moisture on Nitrogen Fixation in *Lobaria pulmonaria*, *Sticta weigelii*, *Leptogium cyanescens*, and *Collema subfurvum*, unpublished M. S. Thesis, Wake Forest University, Winston-Salem, N. C.

Kershaw, K. A., and J. W. Millbank, 1970, Nitrogen Metabolism in Lichens. II: The Partition of Cephalodial-Fixed Nitrogen Between the Mycobiont and Phycobionts of *Peltigera aphthosa, New Phytol.*, **69**: 75-79.

Masse, L., 1966, Etude comparée des teneurs en azoté total des lichens et de leur substrat: les espèces à gonidies Cyanophycées, *C. R. Hebd. Séances, Ser. D, Sci. Natur. (Paris)*, **263**: 781-784.

Millbank, J. W., 1972, Nitrogen Metabolism in Lichens. IV: The Nitrogenase Activity of the *Nostoc* Phycobiont in *Peltigera canina, New Phytol.*, **71**: 1-10.

——, and K. A. Kershaw, 1970, Nitrogen Metabolism in Lichens. III: Nitrogen Fixation by Internal Cephalodia in *Lobaria pulmonaria, New Phytol.*, **69**: 595-597.

——, and K. A. Kershaw, 1969, Nitrogen Metabolism in Lichens. I. Nitrogen Fixation in the Cephalodia of *Peltigera aphthosa, New Phytol.*, **68**: 721-729.

Schell, D. M., and V. Alexander, 1973, Nitrogen Fixation in Arctic Coastal Tundra in Relation to Vegetation and Micro-Relief, *Arctic*, **26**: 130-137.

——, and V. Alexander, 1970, Improved Incubation and Gas Sampling Techniques for Nitrogen Fixation Studies, *Limnol. Oceanogr.* **15**: 961-962.

Schollhorn, R., and R. H. Burris, 1966, Study of Intermediates in Nitrogen Fixation, *Fed. Proc.*, **24**: 710.

Stewart, W. D. P., 1966, *Nitrogen Fixation in Plants*, The Athlone Press, University of London, London.

——, G. P. Fitzgerald, and R. H. Burris, 1967, *In situ* Studies on N_2 Fixation Using the Acetylene Reduction Technique, *Proc. Nat. Acad. Sci. U. S. A.*, **58**: 2071-2078.

EFFECTS OF FOREST FIRES ON ATMOSPHERIC LOADS OF SOLUBLE NUTRIENTS

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ABSTRACT

Combustion of litter in pine forests was reproduced under controlled conditions by enclosing fire and smoke in an airtight chamber sufficiently large to prevent oxygen starvation. A known proportion of the air was pumped out of the chamber after the fire and passed through triplicate water columns designed to extract water-soluble substances released by the fire. Combustion of light litter did not produce significant amounts of airborne cations or sulfur compounds but did produce significant amounts of soluble organic compounds and inorganic nitrogen compounds. Mean nitrogen content of unburned litter was 0.95%. About one-third of this, 72 kg/ha, was released by fire. Although the bulk of the nitrogen was not recoverable as fixed inorganic nitrogen, significant amounts of nitrite and ammonia were present in the combustion products. The amounts of nitrite were unexpectedly high, and nitrate was not produced at all. Total release of nitrite and ammonia from these light litter fires was approximately equal to two-thirds of the yearly input of fixed nitrogen in rain. The implications of these findings for the atmospheric links in the nitrogen cycle are discussed.

Fire is a potent environmental catalyst capable of abruptly altering the distribution and flux of nutrients in grasslands and forests. The significance of fire in mineral cycling is actually dual, since combustion can be expected to affect the flow of nutrients across ecosystem boundaries as well as between ecosystem compartments. Both inter- and intrasystem effects are of great ecological interest, but the focus of this paper is on the transfer of materials across ecosystem boundaries.

Fire promotes the movement of nutrients across ecosystem boundaries by three principal mechanisms. (1) Fire destroys the structural matrix of organic matter so that salts can be leached in large amounts from the litter and can pass into aquatic systems via runoff, and to a lesser extent into groundwater. (2) Fire produces ash, which is moved more readily by wind than unburned litter, and

simultaneously opens the understory to wind. (3) Fire produces volatile and fine particulate material that can be returned to terrestrial or aquatic systems by rain or dry fallout. Loss of nutrients in water or wind can be considerable or slight depending on the conditions of combustion. For example, great increases in solubility of ions in litter will in some cases be offset by low runoff or high soil adsorption capacities. Factors that control the output of volatile and fine particulate material due to fire are much less obvious, as is the general significance of fire in the atmospheric links of various nutrient cycles. The experimental work described here was formulated to help clarify the role of fire in promoting the atmospheric transport of nutrients.

There is, of course, a large body of information dealing with the combustion products of fossil fuels, and some of this information is relevant to this study. Much air-pollution study is focussed on substances that are actually or potentially hazardous to human health. Since the point of interest here is instead the transport of materials that are potentially of general ecological significance, the scope of the investigation can be simplified in several ways. First, materials that are not soluble in water will be considered nutritionally irrelevant on the supposition that they are not readily returned to the soil and are quickly diluted to insignificance by the atmosphere, despite the possibility that they may be sufficiently concentrated at the site of a fire to constitute a short-term human health hazard. For example, hydrocarbons are produced both by controlled (i.e., industrial, domestic) combustion (Butcher and Charlson, 1972) and by combustion of agricultural and forest materials (Darley et al., 1966; Gerstle and Kemnitz, 1967; Fritschen, Bovee, and Buethner, 1970). Since most of these compounds are highly insoluble, they are more likely to be photochemically degraded than scrubbed out by rain. Similarly, much emphasis has been directed toward carbon monoxide as a combustion product, but CO is not likely to perturb normal carbon cycling. Although CO is produced by combustion in amounts sufficient to create a local hazard, its general abundance is certain to be much lower than that of CO_2 because it is converted to CO_2 at a steady rate in air (Dimitriades and Whisman, 1971) and probably at soil surfaces as well (Inman, Ingersoll, and Levy, 1971).

Substances of direct nutritional significance which could be liberated by open fires include the major inorganic salts, fixed nitrogen compounds, and soluble organic matter. The mechanisms of release include true volatilization and particulate emission. This study attempts to quantify the total output of soluble substances from litter fires by both mechanisms. The only litter type considered here is that of a mature longleaf pine (*Pinus palustris* Mill.) forest; it should be emphasized that the general combustion properties of other litter types may be considerably different. Some tree species, including longleaf and other pines as well as eucalyptus species, produce an especially combustible litter that apparently evolved as an adaptive mechanism favoring fire, which confers a competitive advantage on these species (Mutch, 1970). Other litter types may

burn more slowly and give off different amounts of volatile and particulate materials.

METHODS

Experimental fires were ignited inside an airtight combustion chamber made of Plexiglas (1.8 by 1.3 by 1.3 m). The walls of the chamber were provided with gas bladders to accommodate the expansion of air during combustion. After combustion and a brief settling period (5 to 10 min), air from the chamber was pumped at a known rate (1 m^3/hr) through a series of three glass extraction columns containing 5 liters each of distilled water. The gas bladders on the chamber collapsed as a predetermined portion of the volatile and fine particulate materials was pumped from the combustion chamber. The water from each of the three extraction columns was then analyzed separately. The efficiency of extraction for each substance was computed from the decrease in its concentration between columns. Retention of materials on chamber walls was assumed to be insignificant.

The conditions of combustion were fixed in that the chamber was closed to outside air currents and the fuels were not sloped. Convection currents caused by the rapid heating of air circulated oxygen over the flame at what was considered to be a realistic rate of airflow for calm weather. Oxygen was, of course, consumed by the flame, but the amount of fuel was always small compared to the total air capacity of the chamber. The amount of fuel was adjusted so that the decrease in dry weight caused by combustion did not exceed 30 g. Calorimetric energy values for pine straw may vary slightly between species, but they average very near 5000 cal/g (Hough, 1969). Thus each fire produced at most 150 kcal of heat. Complete combustion of average biological hydrocarbons (glucose) produces heat at a rate of 114 kcal per mole of O_2 consumed. The amount of oxygen required to burn 30 g of pine straw at STP is that in 29.5 liters of air, which is equivalent at 25°C to 0.15 m^3 of air. Since the capacity of the chamber plus bladders is almost 20 times this figure, oxygen starvation, other than that which would ordinarily occur in the deeper, more poorly ventilated portions of the litter, is not likely.

All chemical determinations on the water from the extraction columns were matched by control runs during which the chamber was flushed of smoke, resealed, and partially emptied into the gas train in a manner analogous to the experimental procedure except that there was no fire. Values reported here are the differences between these control values and the fire treatments, unless otherwise indicated.

Water analysis was initiated immediately after extraction. All samples were filtered onto glass fiber paper that had been ignited in a muffle furnace to remove organics and nitrogen compounds. The samples were analyzed for pH, conductance, Ca^{2+}, Mg^{2+}, K^+, Na^+, SO_4^{2-}, PO_4^{3-}, silicate, NO_3^-, NO_2^-, NH_4^+, and

absorbance spectrum (200 to 900 nm). Cations were measured by atomic absorption, sulfate by the barium turbidometric method (Golterman and Clymo, 1969), and phosphate by an ascorbic acid–molybdate method (Murphy and Riley, 1962). Silicate tests were done by the method of Armstrong and Butler (1962) on unfiltered samples. Nitrate was determined as nitrite after reduction in a cadmium–copper couple (Wood, Armstrong, and Richards, 1967). Ammonia analysis followed a phenolhypochlorite method (Solorzano, 1969). Absorbances were measured in a spectrophotometer with a 10-cm cell.

The composition of burned and unburned litter samples was determined by arc spectrograph for the first 14 elements shown in Table 1, by Kjeldahl digestion for nitrogen, and by sulfur analysis for total sulfur following the method of Jones and Isaac (1972). Dry weights were determined by desiccation in a forced-draft oven (80°C).

TABLE 1

COMPOSITION OF LITTER SAMPLES FROM THE STUDY AREA*

Fraction of dry weight, ppm									
Na	Sr	Ba	B	Al	Mo	Mn	Fe	Cu	Zn
71	15	18	9	1700	8	283	510	9	28

Fraction of dry weight, %					
Ca	Mg	K	P	N	S
0.36	0.23	†	0.10	0.95	0.08

*Each value is the mean of nine determinations.
†Below detection limit.

Litter samples were taken from a mature (~30-year-old) stand of South Carolina longleaf pine. The litter in the collection area was composed almost exclusively of pine needles in various stages of decomposition. The litter was readily separable from a matted duff over the mineral soil. The water content of the litter averaged 20.5% (SD, 8.1%). The dry weight of litter in the collection area was 2.2 kg/m^2 (SD, 0.30 kg/m^2).

The principal set of experiments was conducted on intact soil–litter blocks that were transferred from the field site to the combustion chamber. The blocks were carefully removed after an incision had been made around a square of litter surface measuring about 15 by 15 cm. Exact measurements of block size were made after combustion. Whenever sampling followed a heavy rain, the blocks were allowed to dry in the laboratory for from 1 to 4 days. At the time of an

experiment, a soil–litter block was placed in the center of the chamber and ignited at one point on its surface.

RESULTS AND DISCUSSION

The average composition of the dry litter is indicated in Table 1, and the percent change in its composition due to combustion is shown in Fig. 1. The uppermost needles were completely reduced to ash during combustion, but lower portions of the litter, which were both wetter and less adequately ventilated, burned incompletely. Reduction of litter weight by combustion averaged 38.5% for the soil–litter blocks. Reliable figures for reduction in weight of litter caused by prescribed fire under field conditions range between 75% (Sweeney and Biswell, 1961) and 26% (Wells, 1971) for pine forests. Percentages may be considerably higher for wildfires. Prescribed winter fire in a pine forest near the site of litter collection reduced the litter weight by 33%

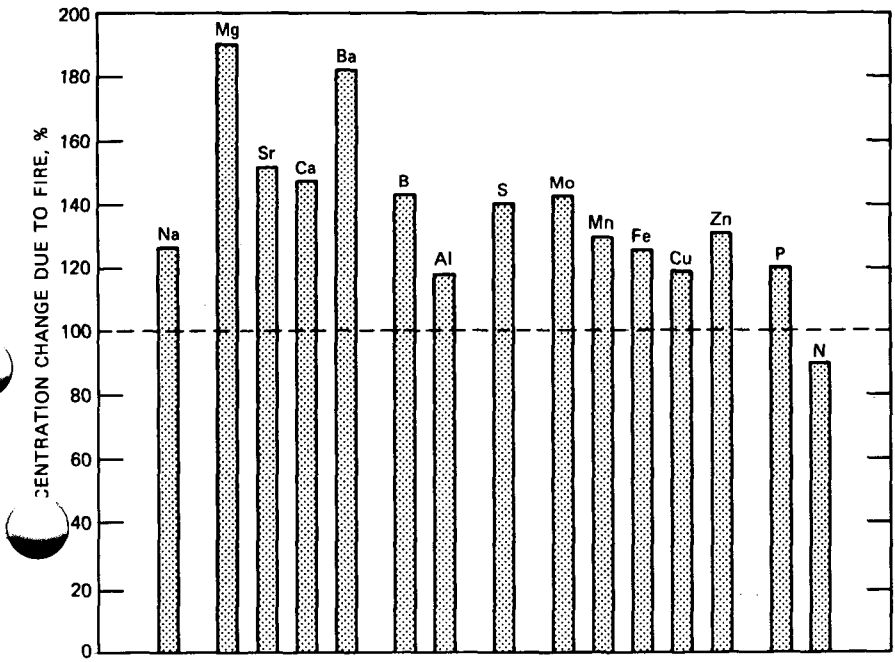

Fig. 1 Changes in elemental composition of the litter due to an experimental fire consuming approximately one-third of the litter. Change is expressed as the ratio of the postfire concentration to the prefire concentration of the elements times 100 (%).

(Lewis, 1974). The reduction in litter weight under experimental conditions therefore conforms with the reduction anticipated for light fires under field conditions.

Figure 1 gives no evidence of gross volatile loss for any element except nitrogen. Apparent concentrations of magnesium and barium are greater than anticipated, probably because of methodological inaccuracies. Pairwise statistical comparison of change in nitrogen with changes in other elements indicates that the decrease in nitrogen concentration due to fire is significant at $\alpha_i = 0.05$ (nonparametric sign test, $n = 9$, Sokal and Rohlf, 1969). Other elements are concentrated in the postfire litter by an amount approximately equal to the inverse of litter weight loss due to burning. Thus it is clear that the only elements volatilized in amounts that are large compared with the amounts present in litter are C, H, O, and N. Volatile release of small amounts of salts or release of small amounts of soluble compounds attached to particulates cannot be deduced from the litter-composition data but should be detectable in the water extractions.

The effect of combustion products on the pH and conductance of water in the extraction columns is shown in Table 2. The use of three columns proved unnecessary since the extraction of soluble substances was essentially complete

TABLE 2

EXTRACTION DATA AND EFFECT OF COMBUSTION PRODUCTS ON pH AND CONDUCTANCE OF WATER IN EXTRACTION COLUMNS*

	Treatment		Control	
	Col. 1	Col. 2	Col. 1	Col. 2
Ca^{2+}, ppb	8	8	0	8
Mg^{2+}, ppb	12	10	9	9
Na^{2+}, ppb	17	10	7	39
K^{+}, ppb	31	10	19	10
SO_4^{2-}, ppb	380	144	252	116
PO_4^{3-}, ppb	113	37	77	3
Silicate, ppb	80	150	40	100
pH	4.64	5.29	5.46	6.02
CV† for pH, %	1.1	1.0	2.2	1.7
Conductance, μmho/cm	13.38	4.17	3.06	2.08
CV† for conductance, %	9.6	13.7	13.9	10.0

*The amount of air pumped from chamber into columns was 1 m^3; all columns contained 5 liters of water.

†Coefficient of variation.

in the first two columns. Table 2 shows that combustion products markedly lowered the pH of the first treatment column. This effect is attributable to CO_2 produced by combustion and to inorganic acids. The pH of the first control column is also depressed below that of the second control column because of the presence of soluble substances, primarily CO_2, in untreated air, but the effect is much less pronounced than in the treatment columns. Conductance follows the same patterns. Initial conductance of the distilled water was 1.3 to 1.6 μmho/cm.

or Cations, Sulfate, Phosphate, and Silicate

The extraction data on major cations, sulfate, orthophosphate, and reactive silicate are summarized in Table 2. There is no statistical difference in the concentration of these substances between treatments and controls.

Given the detection limits of the analytical techniques, the amount of litter burned, and the percentage of volatile materials that were passed through the extraction columns, we can calculate the maximum amount of each of the major cations that could have been produced without showing up in Table 2. For calcium, an output of 38 ppm Ca^{2+} from the burned litter is the detection threshold. This is 1.1% of the calcium available in the litter (Table 1). Thus, if inorganic calcium was released in volatile or fine particulate form, it did not exceed 38 ppm of the burned material or 1.1% of the calcium available in the litter. Comparable figures for magnesium are 5 ppm (0.2%), and for sodium, 6 ppm (8.4%). The exact amount of potassium in the litter is known only to be less than 100 ppm. The amounts in fresh litter are ordinarily higher than this, but potassium is leached rapidly from litter (Gosz, Likens, and Bormann, 1973). For present purposes the amount of potassium can be conservatively approximated as 80 ppm. The escape of potassium to air must be less than 24 ppm or, using the approximation, 30% of the available potassium.

The complete absence of detectable levels of cations is somewhat surprising. Measurable cation output has been reported in at least one account of low-temperature combustion (Allen, 1964). Allen gives evidence that measurable amounts of all major cations are lost in smoke from heather fires burning at temperatures that would be within the same general range expected in the fires my study (550 to 650°C). Since Allen's fires were much more confined than pine-litter fires described here, he may have included some of the larger particulate material that was allowed to settle in my study. The losses reported by Allen for Ca^{2+} (0.1%) and K^+ (1.4%) would have gone undetected in the pine-litter study, but a release of Mg^{2+} equivalent to that observed by him (0.4%) should have been detected. The exact conditions of combustion may prove to be important.

It can be shown from the data at hand that amounts of major cations released by light litter fires cannot be significant in comparison with the amounts of ions normally present in rain. The amount of ionic calcium in

continental rain is approximately 0.25 to 0.75 ppm (Gorham, 1961; Gambell and Fisher, 1966; Wells, Whigham, and Lieth, 1972), hence the amount delivered in rain over a year in the South Carolina area averages about 6 kg ha^{-1} $year^{-1}$. This approximation is confirmed by measurements near the study site for the year 1969, during which calcium input by rain was 6.3 kg ha^{-1} $year^{-1}$ (Polisini, Boyd, and Didgeon, 1970). Thus the amount of calcium delivered in rain over a year is about seven times the maximum amount that could have been liberated in the experimental fires. Additional normal delivery of calcium in fallout renders this estimate even more conservative. For magnesium the annual rain input is only about 10% as much as for calcium, or 0.6 kg ha^{-1} $year^{-1}$ (Pol[illegible] et al. found 0.9 kg ha^{-1} $year^{-1}$). This is six times the maximum possible release due to light fire. Sodium input is highly variable according to proximity of the sea, but it can be approximated as 0.5 ppm, or 6.0 kg ha^{-1} $year^{-1}$ (Polisini et al. found 3.7 kg ha^{-1} $year^{-1}$). This is 44 times the maximum possible release of sodium. Potassium concentration in rain is roughly 0.2 ppm, which amounts to 2.0 kg ha^{-1} $year^{-1}$ (Polisini et al. found 3.0 kg ha^{-1} $year^{-1}$). This is four times the maximum amount that could have been released under the experimental conditions of this study. Since the annual input of all major cations in rain is considerably above the maximum possible release due to the litter fires, fires of this type are not likely to produce ecologically significant amounts of atmospheric cations.

The small amount of detectable sulfate in the extraction is not surprising considering the rather small amounts of sulfur in pine litter (Table 1). Combustion may have produced some SO_2, which would not necessarily have been detected by the analytical method used. There was an excess of sulfate in the treatments, but the amounts are not quite statistically separable from the controls. If further study validates the amounts reported in Table 2, the total yield of SO_4^{2-} due to fire would be about 20 mg/m^2 or 0.20 kg/ha for conditions similar to the experimental ones. This is far below the annual rain input, which is near 25 kg ha^{-1} $year^{-1}$, or two orders of magnitude greater (Gambell and Fisher, 1966). Amounts such as those recovered from the treatments are not likely to be significant considering the industrial output of sulfur and the amount of sulfur in rain (Johnson, Reynolds, and Likens, 1972).

The presence of detectable orthophosphate is in apparent agreement with the findings of Allen (1964), who reported loss of phosphorus in heather f[illegible] The present data indicate that the amount of phosphorus lost as phosphate is about 0.96 kg/ha, but this figure is not statistically significant. If this proves to be a good estimate, release of phosphorus by litter fires may be ecologically interesting. Very small amounts of phosphorus are delivered in rain, hence any source of atmospheric phosphorus could significantly increase the input from this source. Annual phosphorus delivery in rain, reported by Wells, Whigham, and Lieth, (1972), is 0.28 kg ha^{-1} $year^{-1}$ and, by Polisini, Boyd, and Didgeon (1970), is 0.29 kg ha^{-1} $year^{-1}$. Hence a release of the type obtained in this study

could be equivalent to a 3- to 4-year input by rain. Phosphorous may, of course, have been released in other forms, such as organic complexes, which would not have been detected by the ascorbic acid–molybdate test, and any output by such mechanisms would augment the ecological significance of phosphorus release.

Volatilization of silicate was not expected at all, but it was considered possible that particulate material from fires might give up silicate in measurable amounts. This did not prove to be the case, as indicated in Table 2. The amount of soluble reactive silicate released in fires is no doubt insignificant in view of the concentrations of this substance in surface water and interstitial groundwater.

Nitrogen Compounds

The total amounts of nitrate, nitrite, and ammonia produced by the litter fires are indicated in Table 3. The extraction efficiency for all these compounds was quite high. Averages of 74% of the ammonia, 86% of the nitrite, and 84% of the nitrate were found in the first extraction column.

Combustion of litter under field conditions associated with prescribed burning of pine forests is known to release large amounts of nitrogen, ordinarily comprising some one-fourth to one-half of the total nitrogen in the litter, or 100 to 300 kg/ha of nitrogen (Knight, 1964; Wells, 1971). Knight (1966) has also shown by use of a muffle furnace that volatile loss of nitrogen begins at about 300°C and increases to about 60% at 700°C. It has been generally assumed, largely because of lack of contrary evidence, that most of the nitrogen is released as N_2. DeBell and Ralston (1970), looking for nitrate and ammonia in smoke from pine litter burned in the laboratory, found a small amount of NO_x (0.3%

TABLE 3

TOTAL YIELD OF INORGANIC FIXED NITROGEN FROM COMBUSTION OF PINE LITTER*

	NH_4^+–N	NO_2^-–N	NO_3^-–N	Total N (fixed inorganic)
Released/ha†	0.27	1.20	0.00	1.47
% burned litter	0.0032	0.0144	0.0000	0.0176
% burned litter N	0.33	1.50	0.00	1.83
CV,‡ %	19	27		18

*All values are significantly different from controls at $\alpha = 0.05$ (nonparametric signs test), except nitrate.

†The yield per hectare is computed on the basis of 2.2 kg/m² of litter and 38.5% combustion.

‡The coefficient of variation (CV) indicates the experimental variability of release.

of nitrogen released) and no ammonia. Fixed nitrogen was therefore considered to be an insignificant by-product of fires.

The results of the present study differ in several important respects from those of DeBell and Ralston. Substantial ammonia was routinely detected in the treatment runs. It seems likely that the ammonia was volatilized at relatively low temperatures in the upper mineral soil or duff, where it would not decompose in the flame, and subsequently escaped into the atmosphere. This could not have happened in the DeBell and Ralston experiments since uniform fuels rather than the soil–litter complex were used. The large amounts of nitrite in the extraction water were also unexpected. Since nitrite and nitrate are lumped by analytical methods used by DeBell and Ralston, no comparison is possible. That nitrite is, in fact, the principal soluble nitrogen byproduct of the experimental fires in my study is interesting in view of the scarcity of information on nitrite in rain. It is probably possible for nitrite to be converted to nitrate in air (Georgii, 1963).

The nitrate and nitrite released by the fire must be to a large degree derived from the volatile nitrogen oxides known to be produced in varying amounts by the combustion of organic matter. Of the three major oxides (N_2O, NO, NO_2), nitrous oxide (N_2O) is not likely to be involved in nitrate and nitrite production because it is quite inert even in the atmosphere (Robinson and Robbins, 1970).

Both NO and NO_2 are probably produced by litter fires although the relative amounts are not known. The NO produces NO_2 in air at a rate that is markedly dependent on the amount of NO present (Hardison, 1970). Nitrogen dioxide then combines with water in an autoredox reaction that produces equal amounts of nitric and nitrous acids (Hutchinson, 1954). If fixed nitrogen were produced by this mechanism during the experimental fires, we would expect nitrate as well as nitrite to occur in the leach water. Since nitrite was recovered in great amounts and nitrate not at all, it appears that either a more complex set of reactions, leading to nitrite accumulation, occurs in the tubes or that other mechanisms of nitrogen release are involved.

The behavior of the nitrogen oxides in air would presumably be quite different from that in the extraction tubes, although some of the oxides would undoubtedly be scrubbed out by rain. Since the dominant photochemical reactions of the oxides all lead ultimately to the formation of nitrate, nitric ammonia, the nitrogen recovered in the experiments (Table 3) is assumed to be destined for biological use. It is possible that, with the exception of the ammonia, some or all of this fixed nitrogen is "new" in the sense that it may be derived from combination of N_2 with O_2 in the flame rather than from the organic matter itself.

The fixed nitrogen recovered from the litter fire is of ecological significance in view of the limiting effect of nitrogen in many habitats. Although values vary considerably, the average input of ammonia, nitrate, and nitrite in rain in rural

areas is very likely to be less than 10 kg ha^{-1} $year^{-1}$ as nitrogen (Eriksson, 1952). Survey values for the continental United States indicate that the average is, in fact, considerably lower. The data given by Junge (1958) suggest a rainfall input of NH_4–N of about 0.2 kg ha^{-1} $year^{-1}$ in the South Carolina region and of NO_3^-–N plus NO_2^-–N of 0.6 kg ha^{-1} $year^{-1}$, for a total of about 0.8 kg ha^{-1} $year^{-1}$. The data summarized by Wells, Whigham, and Leith (1971) suggest a somewhat higher figure, perhaps nearer 2.0 kg ha^{-1} $year^{-1}$, and the value reported by Polisini, Boyd, and Didgeon (1970) is still higher, 5.7 kg ha^{-1} $year^{-1}$. Given the intermediate value of 2.0 kg ha^{-1} $year^{-1}$, the total amount of nitrogen [illegible]t to the atmosphere in the experimental litter fires is approximately [illegible]uivalent to a 40-year rain input of nitrogen. The amount of fixed nitrogen, which is a small portion of the total released in these fires, is equivalent to about two-thirds of the annual rain input.

Because field fires consume more fuel and burn hotter than the experimental fires, it is not unreasonable to expect volatile output of fixed nitrogen to reach 10 times the amount reported here in some cases. Forest fires must therefore be considered a significant element in producing regional and probably global supplies of fixed nitrogen in the atmosphere, but it hardly seems possible from the data at hand that fires can be the dominant atmospheric source of these compounds.

Soluble Hydrocarbons

The water from the first extraction column in the treatment series always showed a marked light absorbance at short wavelengths, principally in the near ultraviolet range. It was concluded that the compounds responsible for this effect must be highly soluble since the effect was barely detectable in the second column of the series. The absorbance spectra of the water from the first treatment and first control columns are shown in Fig. 2. The only potential cause for the absorbance other than organic matter is nitrite. Laboratory tests with solutions of 100 ppb NO_2^- gave an absorbance due to nitrite of 0.021 at 300 nm (10-cm cell). Considering the concentrations of nitrite present in the first treatment column, we would predict an average absorbance of 0.032 at 300 nm, but the observed absorbance is actually about triple this amount [illegible]ig. 2). It is evident from these data that organic matter is responsible for most [illegible]f the absorbance in the water of the first treatment column.

The organic compounds causing absorbance have not yet been identified, but they are probably of low molecular weight since the larger compounds known to be produced by combustion of plant matter (e.g., terpenoids) are for the most part insoluble. The compounds produced during combustion may prove to be insignificant in comparison with the amounts of organics routinely released by plants (Went, 1960), or they may be significant as carriers of limiting nutrients, such as phosphorus or nitrogen.

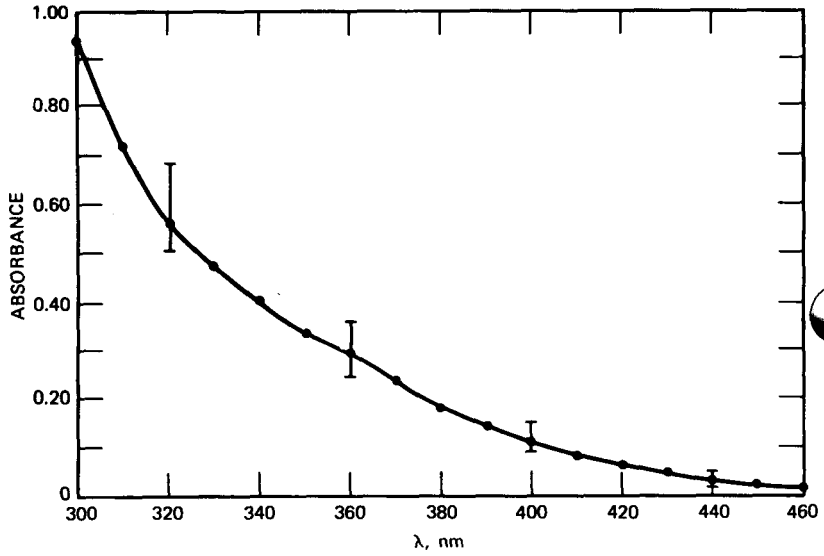

Fig. 2 Absorbance spectra (10-cm cell) of water from the first treatment extraction columns. The range of values is indicated for selected points along the curve (N = 4). Absorbance of control columns over the same range was effectively zero (<0.05).

CONCLUSIONS

Fires of the type described here are not significant ecological sources of major cations or sulfate in air. The atmospheric links of the nitrogen cycle and possibly of the phosphorous cycle as well are affected by open burning of forest materials, however. Thus forest fires may be a prehistoric and modern source of atmospheric nutrients. Although the delivery of nutrients in rain over a year is, in general, far exceeded by the total inventory of nutrients in the standing crop, the steady supply via rainfall can, over long time spans, play an important role in determining the nutrient inventory of the standing crop. Since the mobility of numerous nutrients is being radically changed by man, it is presently of great interest to determine which nutrient supply factors are most important in b natural and altered systems, and fire would seem to deserve more consideratio in this context.

ACKNOWLEDGMENT

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REFERENCES

Allen, S. E., 1964, Chemical Aspects of Heather Burning, *J. Appl. Ecol.*, **1**: 347-367.

Armstrong, F. A. J., and E. I. Butler, 1962, Chemical Changes in the Sea Water off Plymouth During 1960, *J. Mar. Biol. Ass. U.K.*, **42**: 253-258.

Butcher, S. S., and R. J. Charlson, 1972, *An Introduction to Air Chemistry*, Academic Press, Inc., New York.

Darley, E. F., F. R. Burleson, E. H. Mateer, J. T. Middleton, and V. P. Osterli, 1966, Contribution of Burning of Agricultural Wastes to Photochemical Air Pollution, *J. Air Pollut. Contr. Ass.*, **11**: 685-690.

Bell, D. S., and C. W. Ralston, 1970, Release of Nitrogen by Burning Light Forest Fuels, *Soil Sci. Soc. Amer., Proc.*, **34**: 936-938.

Dimitriades, B., and M. Whisman, 1971, Carbon Monoxide in Lower Atmosphere Reactions, *Environ. Sci. Technol.*, **5**: 219-222.

Eriksson, E., 1952, Composition of Atmospheric Precipitation. I. Nitrogen Compounds, *Tellus*, **3**: 215-232.

Fritschen, L., H. Bovee, and K. Buethner, 1970, Slash Fire and Atmospheric Pollution, Research Paper PNW-97, Pacific Northwest Forest and Range Experiment Station, Forest Service, U. S. Department of Agriculture.

Gambell, A. W., and D. W. Fisher, 1966, Chemical Composition of Rainfall in Eastern North Carolina and Southeastern Virginia, Water-Supply Paper 1535-K, U. S. Geological Survey.

Georgii, H. W., 1963, Oxides of Nitrogen and Ammonia in the Atmosphere, *J. Geophys. Res.*, **68**: 3963-3971.

Gerstle, R. W., and D. A. Kemnitz, 1967, Atmospheric Emissions from Open Burning, *J. Air Pollut. Contr. Ass.*, **17**: 324-327.

Golterman, H. L., and R. S. Clymo, (Eds.), 1969, *Methods for Chemical Analysis of Fresh Waters*, International Biological Program Handbook No. 8, Blackwell Scientific Publications, Oxford.

Gorham, E., 1961, Factors Influencing Supply of Major Ions to Inland Waters, with Special Reference to the Atmosphere, *Geol. Soc. Amer., Bull.*, **72**: 795-840.

Gosz, J. R., G. E. Likens, and F. H. Bormann, 1973, Nutrient Release from Decomposing Leaf and Branch Litter in the Hubbard Brook Forest, New Hampshire, *Ecol. Monogr.*, **43**: 173-191.

Hardison, L. C., 1970, Techniques for Controlling the Oxides of Nitrogen, *J. Air Pollut. Contr. Ass.*, **20**: 377-382.

Hough, W. A., 1969, Caloric Value of Some Forest Fuels of the Southern United States, Research Note SE-120, Southeastern Forest Experiment Station, Forest Service, U. S. Department of Agriculture.

Hutchinson, G. E., 1954, The Biochemistry of the Terrestrial Atmosphere, in *The Earth as a Planet*, The Solar System Series, Vol. 2, G. P. Kuiper (Ed.), pp. 371-433, University of Chicago Press, Chicago.

Inman, R. E., R. B. Ingersoll, and E. A. Levy, 1971, Soil: A Natural Sink for Carbon Monoxide, *Science*, **172**: 1229-1231.

Johnson, N. M., R. C. Reynolds, and G. E. Likens, 1972, Atmospheric Sulfur: Its Effect on the Chemical Weathering of New England, *Science*, **177**: 514-516.

Jones, J. B., and R. A. Isaac, 1972, Determination of Sulfur in Plant Material with a Leco Sulfur Analyzer, *J. Agr. Food Chem.*, **20**: 1292-1294.

Junge, C. E., 1958, The Distribution of Ammonia and Nitrate in Rain Water over the United States, *Trans. Amer. Geophys. Union*, **39**: 241-248.

Knight, H. A. W., 1966, Loss of Nitrogen from the Forest Floor by Burning, *Forest. Chron.*, **42**: 149-152.

——, 1964, Some Effects of Slash Burning and Clearcut Logging on Soil Properties and Initial Tree Growth, Ph. D. Thesis, University of Washington, Seattle.

Lewis, W. M., Jr., 1974, Effects of Fire on Nutrient Movement in a South Carolina Pine Forest, *Ecology*, **55**: 1120-1127.

Murphy, J., and J. P. Riley, 1962, A Modified Single Solution Method for the Determination of Phosphate in Natural Waters, *Anal. Chim. Acta*, **27**: 31-36.

Mutch, R. W., 1970, Wildland Fires and Ecosystems—A Hypothesis, *Ecology*, **51**: 1046-1051.

Polisini, J. M., C. E. Boyd, and B. Didgeon, 1970, Nutrient Limiting Factors in an Oligotrophic South Carolina Pond, *Oikos*, **21**: 344-347.

Robinson, E. and R. C. Robbins, 1970, Gaseous Nitrogen Compound Pollutants from Urb and Natural Sources, *J. Air Pollut. Contr. Ass.*, **20**: 303-306.

Solorzano, L., 1969, Determination of Ammonia in Natural Waters by the Phenolhyp chlorite Method, *Limnol. Oceanogr.*, **14**: 799-801.

Sokal, R. R., and F. J. Rohlf, 1969, *Biometry*, the Principals and Practice of Statistics in Biological Research, W. H. Freeman and Company, San Francisco.

Sweeney, J. R., and H. H. Biswell, 1961, Quantitative Studies of the Removal of Litter and Duff by Fire Under Controlled Conditions, *Ecology*, **42**: 572-575.

Wells, C. G., 1971, Effects of Prescribed Burning on Soil Chemical Properties and Nutrient Availability, Prescribed Burning Symposium Proceedings, pp. 86-97, Southeastern Forest Experiment Station, Asheville, N. C., Forest Service, U. S. Department of Agriculture.

Wells, C. G., D. Whigham, and H. Lieth, 1972, Investigation of Mineral Nutrient Cycling in an Upland Piedmont Forest, *J. Elisha Mitchell Sci. Soc.*, **88**: 66-78.

Went, F. W., 1960, Blue Hazes in the Atmosphere, *Nature*, **187**: 641-643.

Wood, E. D., F. A. J. Armstrong, and F. A. Richards, 1967, Determination of Nitrate in Sea Water by Cadmium–Copper Reduction to Nitrite, *J. Mar. Biol. Ass. U.K.*, **47**: 23-31.

CATION FLUX IN HARDWOOD AND WHITE PINE WATERSHEDS

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ABSTRACT

The nutrient content of precipitation input, throughfall, litter flow through, soil percolation, and stream discharge was measured in a hardwood and in a white pine watershed. Amounts of water passing through various levels of the forest ecosystems changed markedly from input to output, and leaching of cations from vegetation exhibited pronounced seasonal changes. Leaching of potassium, calcium, and magnesium was least during dormant winter months but increased with commencement of spring growth. Most potassium was leached from the leaves before leaf fall, but most calcium and magnesium losses occurred after leaf fall. A reduction of sodium in throughfall during the summer months was evident in white pines. The total leachate loss from vegetation was greatest for potassium and least for sodium; magnesium and calcium losses were intermediate. Once the water became streamflow discharge, the cation load was similar to its original input level, giving evidence of the ability of the ecosystem to minimize external loss while maintaining a large internal flux.

The two major sources of cation input to a terrestrial first-order watershed ecosystem are (1) atmospheric input and (2) weathering of bedrock material. Atmospheric input may enter the system in the form of snow, sleet, rain, hail, or dry precipitation. When we consider nutrient cycles, we assume that any loss from a stable ecosystem which is not re-supplied by atmospheric input is restocked by rock weathering (Johnson et al., 1968). Rock weathering releases some elements that become bound on exchangeable sites in secondary minerals and others that are made available to the ecosystem in the form of soluble ions.

Atmospheric input of most cations shows seasonal, or slightly seasonal, variations. The seasonal aspect of input derives from the release, in the form of dust, of the free cations by agricultural practices; this yields concentrations high in the summer and low in the winter (Gambell and Fisher, 1966; Fisher, 1968).

Cation input by rain is also a function of the origin and movement of storm systems (Burnett, 1965; Gambell and Fisher, 1966). As storm systems move over the land, varying amounts of cations are added to the storm by dust, industrial pollution, agricultural practices, and forest aerosols. The amounts contributed depend on the length of time the storm spends over the land and the season during which it occurs.

Factors affecting nutrient leaching from the canopy are plant species, leaf maturity, leaf condition, ionic concentration, and duration of rainfall. Stenlid (1958) suggested that wettability increases at high temperatures, causing salts to be dissolved more readily. Since young leaves are hydrophobic, they absorb l water and lose fewer nutrients through leaching than older leaves d Hydrophobia of leaves decreases with maturity (Stenlid, 1958; Tukey and Tukey, 1959; Tukey, 1970). Old or damaged leaves tend to lose more nutrients than do young, healthy leaves. Rainwater causes greater cation loss through diffusion than does a similar amount of distilled water (Bahn, Wallace, and Lunt, 1959).

Mineral leaching from the canopy may serve to increase nutrient availability by redistributing the elements in the forest floor and upper soil layers, thus making them more accessible for root uptake. Since calcium and magnesium movement in plants is polar, cyclic patterns of movement by mass flow to leaves and subsequent leaching of unbound calcium and magnesium may circumvent basipetal immobility of these elements (Wittwer and Teubner, 1959; Tukey, 1970).

Our main objective in this study was to follow the flux of selected dissolved cations (K, Na, Ca, and Mg) through various levels of a forest from input of ions in rainfall to output of ions from the watershed in stream discharge in two communities, a mature hardwood forest and an eastern white pine (*Pinus strobus* L.) plantation. Nutrient concentrations were measured in precipitation input (bulk precipitation, including both wet and dry precipitation), throughfall, litter flow through, soil percolation, and stream discharge. Nutrient flux was calculated from measurements of concentration and volume. The results obtained at Coweeta are discussed and compared with similar studies in other forests.

STUDY SITE

The Coweeta Hydrologic Laboratory is located in the Blue Ridge Province of the Southern Appalachian Highlands of southwestern North Carolina, approximately 15 miles southwest of Franklin. Dils (1957) and Johnson and Swank (1973) gave a detailed description of the laboratory.

The hardwood-forest watershed (12.46 ha) has served as a control since the establishment of the laboratory in 1924. Canopy species in this mixed hardwood forest are predominantly oaks and, less importantly, hickories, with red maple

and black gum being the principal subcanopy species. Mountain laurel and rhododendron are important understory species, and dogwood and witch hazel are somewhat less important. Density of stems over 1 in. in diameter at breast height (dbh) is approximately 3032 stems/ha, representing a basal area of 25.6 m^2/ha (Day and Monk, 1974).

All shrub and hardwood-forest vegetation was cut without removal of timber products from the eastern white pine watershed (13.48 ha) in 1942 (Dils, 1957; Hoover, 1944). Annual sprout growth was cut back in most years between 1943 and 1955, and a low herbaceous and shrub cover developed. Eastern white pines were planted in 1956. Since that time the sprouting hardwood understory has been cut periodically to suppress competition. A survey of the watershed in 1969 indicated 1668 pine stems per hectare, with a total basal area of 15.3 m^2/ha (Johnson and Swank, 1973).

METHODS

Bulk precipitation (wet plus dry) samples were collected in ½-gal polyethylene jugs fitted with polyethylene funnels 15 cm in diameter. Glass wool was used in the funnels to prevent deposition of large particles in the jugs. All incident rainfall gauges in both watersheds were distributed in open areas near U. S. Forest Service standard rain gauges.

Helvey and Patric (1966) developed criteria for estimating throughfall and stemflow. Selection of the Forest Service standard 8-in. rain gauges for throughfall studies requires that a large number of gauges be located and moved randomly throughout the study to insure a small possibility of error (Coffay, 1962). Their method for selecting the number of gauges has merit, however. Kimmins (1973) presented valid arguments favoring a large number of throughfall collectors when throughfall chemistry is desired but failed to consider the importance of increasing the sampling area of the throughfall collectors. To integrate canopy drip over a large area and to reduce the number of gauges needed, we used aluminum troughs measuring 15 by 200 cm (3000 cm^2) to collect throughfall. The throughfall gauges were placed approximately 75 cm above the ground. Twenty troughs were placed in each watershed and were moved randomly after each 2-month sampling period. The water collected by each trough drained into a 5-gal polyethylene jug. The inside trough was lined with aluminum screen to exclude leaf and insect material. The screen was cleaned after each sampling.

Tension-free lysimeters (Jordan, 1968) were used to collect litter flow through and soil percolate. Lysimeters for measuring leachate passing through the litter were placed at the soil–litter interface. Lysimeters for measuring soil percolate were inserted into the bank of the soil in the manner described by Jordan (1968). The soil lysimeters were placed at a depth of 25 cm. Four soil and four litter lysimeters were installed in the hardwood watershed, and three of each were stationed in the white-pine watershed.

Incident rainfall, throughfall, and stream-discharge samples were collected at weekly or bimonthly intervals from October 1969 to November 1970. Lysimeter samples were collected monthly.

All samples were filtered through acid-washed filter paper and stored at 4°C until analysis. Cation concentration was determined by atomic absorption spectrophotometry. To avoid interference with the determination of calcium and magnesium by the atomic absorption method, we added appropriate amounts of lanthanum chloride to the samples (Likens et al., 1967).

RESULTS

Cation concentrations in water from the time it entered the forest ecosystems until it left the systems as streamflow discharge were not static (Table 1). Passage through the vegetation layer caused a marked enrichment of water with ions. The total flux from the vegetation was greatest for potassium and least for sodium; magnesium and calcium fluxes were intermediate. In most cases there were further enrichments to the water after it passed through the litter layer. The element that increased most in water movement through the litter layer was calcium. By the time the water became streamflow discharge, the cation load was nearly back to its original input levels. The amount of nutrients removed from water as it moved through the soil (litter flow through minus stream discharge) was considerable. On an annual basis about 28 kg/ha of potassium, 17.7 kg/ha of calcium, and 3.7 kg/ha of magnesium were removed.

These dynamic cation fluxes are more striking when we consider that less water passes through each successive level (Table 1). On a yearly basis, about 75% of the rainfall in both watersheds reached the forest floor as throughfall. The remaining 25% was either retained on plant surfaces or moved through the canopy to soil as stemflow. About 15 to 20% of the throughfall water was retained by the litter layer. On an annual basis, about 52% of the rainfall in the hardwood forest left the system as streamflow discharge. This was in contrast to 37% loss from the white pine plantation. The 15% difference was attributable in part to greater evapotranspiration in the white pine system plus the possibility of greater losses by deep seepage. Loss of water through streamflow was much less during the growing season. Streamflow losses from June to November ranged from about 20% in the white-pine plantation to about 30% in the hardwood forest.

The dynamic nature of cation leaching is illustrated by an examination of concentration and magnitude of change from one level to another rather than by amounts since change is not so dependent on the quantity of water. The annual weighted concentrations and the ratios of change of the four cations from one position to another in the forests are given in Table 2. Potassium concentrations were enhanced the greatest in the throughfall water of both systems. The magnitude of concentration increase for potassium in throughfall was over

eightfold. Magnesium concentration increased three- to fivefold, calcium twofold, and sodium less than twofold. In all cases cation concentrations increased as the water moved through the litter layer; however, the four cations were leached at different rates. The calcium concentration increased fourfold over the throughfall concentration; magnesium increased about threefold and potassium and sodium less than twofold. Thus the order of leaching from the vegetation was $K > Mg > Ca > Na$, and the order of leaching from the litter was $Ca > Mg > K > Na$.

The leaching of cations from vegetation exhibited pronounced seasonal changes in both watersheds (Fig. 1). Potassium, calcium, and magnesium responded in a similar manner, i.e., less leaching during the dormant winter months followed by an increase with the commencement of growth in the spring. At this time the two forests differed. The cation leachate was at its maximum just before leaf fall in the hardwood system; whereas cation leachate in throughfall water in the pine plantation peaked in late spring and early summer and then declined in late summer and early fall.

The seasonal trend of sodium concentrations in the throughfall water was variable. During the summer months there was more sodium in rainfall than in throughfall under the white pines (Fig. 1). The trend followed precipitation patterns more closely than biological features of the forests.

Leaching of cations from the litter occurred throughout the year. There was a slight seasonal tendency regarding the leaching of potassium, calcium, and magnesium for both watersheds with greater amounts passing through the litter during the growing season. Sodium leached slightly more in the spring months.

DISCUSSION

Cation concentrations in rain at Coweeta were generally similar to those reported earlier (Tamm, 1951; Voigt, 1960; Kaul and Billings, 1965; Gambell and Fisher, 1966; Likens et al., 1967; 1970; Fisher, 1968; Johnson and Swank, 1973). Differences in cation concentrations were attributed to differences in sampling methods, storm size and duration, location, season, and source of air masses.

Potassium input from the atmosphere was relatively constant throughout the year, with slightly larger amounts occurring in the spring and summer months. This agrees with the pattern found by Likens et al. (1967). The increase was concomitant with agricultural activities and indicated soil dust as a significant contributor of potassium (Gambell and Fisher, 1966). There was no relationship between rainfall amounts and potassium amounts ($r = -0.28$, p = N.S.). The pattern of sodium input from the atmosphere in this study was slightly correlated with rainfall amounts ($r = 0.66$, $p < 0.5$), but a seasonal pattern was also evident. Since rainfall sources were relatively constant throughout the year,

TABLE 1

QUARTERLY AND YEARLY MOVEMENT OF WATER AND SELECTED CATIONS THROUGH WHITE PINE AND HARDWOOD WATERSHEDS

Level	Hardwood watershed (18)					White pine watershed (17)				
	Water, mm	K, kg/ha	Na, kg/ha	Ca, kg/ha	Mg, kg/ha	Water, mm	K, kg/ha	Na, kg/ha	Ca, kg/ha	Mg, kg/ha
Winter										
Rainfall	330	0.2	0.8	0.9	0.1	352	0.3	1.0	0.9	0.1
Throughfall	260	1.4	1.4	1.0	0.3	266	1.9	1.5	1.0	0.2
Litter flow through	224	5.1	1.7	3.8	0.8	216	3.3	1.5	2.0	0.5
Soil percolate	64	0.4	0.6	0.6	0.1	96	1.9	1.2	1.2	0.2
Stream discharge	295	1.1	2.3	1.5	0.7	233	0.8	1.4	0.9	0.4
Net gain (+) or loss (−)	+35	−0.9	−1.5	−0.6	−0.6	+119	−0.5	−0.4	0.0	−0.3
Spring										
Rainfall	384	1.6	2.0	1.5	0.3	405	1.6	2.1	1.6	0.3
Throughfall	298	5.9	2.4	2.1	0.7	291	7.0	2.0	1.9	0.5
Litter flow through	196	5.7	2.1	4.7	1.3	232	8.0	3.3	5.3	1.4
Soil percolate	34	0.8	0.3	0.5	0.1	36	0.3	0.3	0.6	0.2
Stream discharge	280	1.2	2.5	1.8	0.8	212	0.8	1.6	1.1	0.5
Net gain (+) or loss (−)	104	+0.4	−0.5	−0.3	−0.5	+193	+0.8	0.5	+0.5	−0.2

Summer										
Rainfall	513	1.7	2.1	1.0	0.2	501	1.8	2.2	1.0	0.2
Throughfall	415	7.2	2.4	2.3	0.7	380	10.6	1.7	2.1	0.8
Litter flow through	270	10.9	2.4	8.5	2.2	335	15.7	3.2	8.5	1.7
Soil percolate	35	0.3	0.3	0.4	0.1	39	1.0	0.5	1.0	0.2
Stream discharge	156	1.0	1.6	1.3	0.5	97	0.6	0.9	0.6	0.2
Net gain (+) or loss (−)	+357	+0.7	+0.5	−0.3	−0.3	+404	+1.2	+1.3	+0.4	0.0
Fall										
Rainfall	477	1.2	1.4	0.8	0.2	502	1.2	1.5	0.9	0.2
Throughfall	407	16.0	2.5	2.7	1.4	391	11.0	2.0	1.3	0.5
Litter flow	216	10.0	2.3	6.4	1.6	262	7.0	2.2	5.1	1.8
Soil percolate	39	0.6	0.7	0.4	0.3	44	0.9	0.6	0.8	0.3
Stream discharge	162	0.9	1.4	1.1	0.5	115	0.6	0.8	0.6	0.3
Net gain (+) or loss (−)	+315	+0.3	0.0	−0.3	−0.3	+387	+0.6	+0.7	+0.3	−0.1
Yearly										
Rainfall	1704	4.7	6.3	4.2	0.8	1760	4.9	6.8	4.4	0.8
Throughfall	1380	30.5	8.6	8.1	3.1	1328	30.5	7.2	6.3	2.0
Litter flow through	906	31.7	8.5	23.4	5.9	1045	34.0	10.2	20.9	5.4
Soil percolate	172	2.1	1.9	1.9	0.6	215	4.1	2.6	3.6	0.9
Stream discharge	893	4.2	7.8	5.7	2.5	657	2.8	4.7	3.2	1.4
Net gain (+) or loss (−)	+811	+0.5	−1.5	−1.5	−1.7	+1103	+2.1	+2.1	+1.2	−0.6

TABLE 2

AVERAGE WEIGHTED CONCENTRATION (ppb) OF SELECTED CATIONS IN WATER PASSING THROUGH VARIOUS LEVELS OF A WHITE PINE AND A HARDWOOD-FOREST WATERSHED AT COWEETA*

Level	Hardwood-forest watershed				White pine watershed			
	K	Na	Ca	Mg	K	Na	Ca	Mg
Rainfall	276	369	246	47	278	386	250	45
Throughfall	2210(8.0)	623(1.7)	587(2.4)	225(4.8)	2297(8.3)	542(1.4)	474(1.9)	145(3.2)
Litter flow through	3499(1.5)	938(1.4)	2583(4.1)	651(2.7)	3254(1.4)	976(1.8)	2000(4.2)	517(3.6)
Soil percolate	1221(0.3)	1105(1.2)	1105(0.4)	349(0.5)	1907(0.6)	1290(1.2)	1674(0.8)	419(0.8)
Stream discharge	470(0.4)	873(0.8)	368(0.3)	280(0.8)	426(0.2)	715(0.6)	487(0.3)	213(0.5)

*The numbers in parentheses represent the change in concentration of the cations at that level in reference to the concentration in the level immediately above.

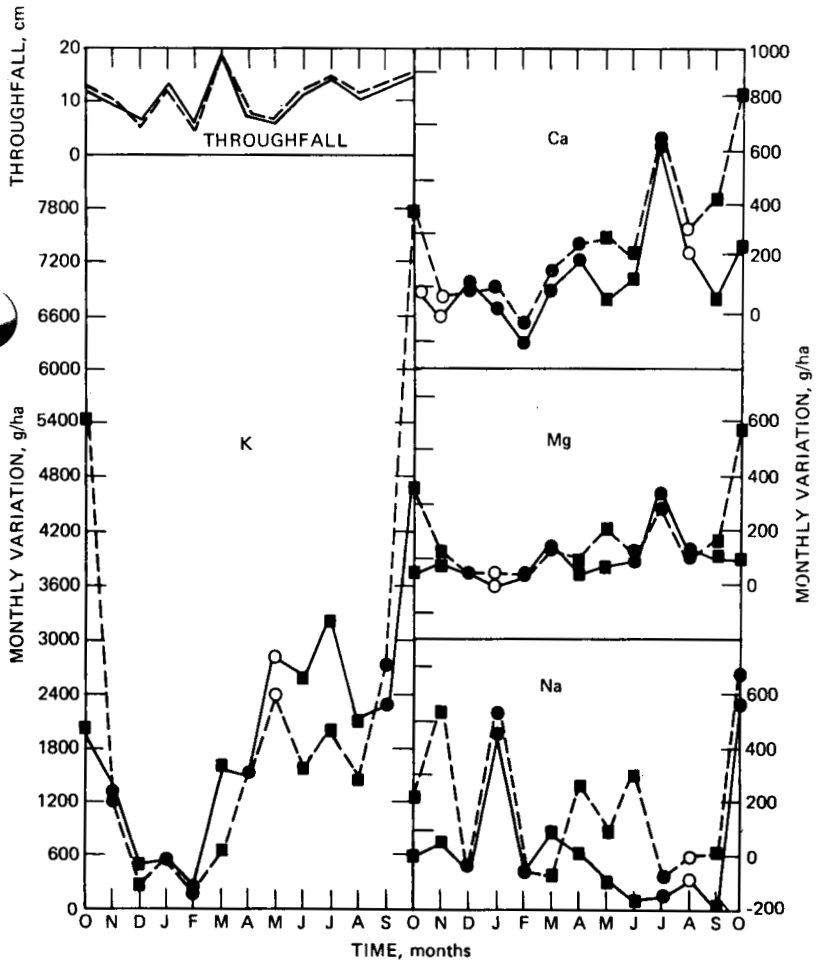

Fig. 1 Monthly variation in cations (g/ha) in absolute throughfall (throughfall minus rainfall) in a hardwood and a white pine watershed. - - - -, hardwood; —, pine; ●, no significant difference between the watersheds; ○, significantly different at $p < 0.05$; ■, significantly different at $p < 0.01$.

the increased sodium during the summer was probably also a result of increased agricultural activity, stirring the soil and releasing sodium to the atmosphere as soil dust. Calcium input from rainwater was relatively constant throughout the year, with very little calcium being supplied to these watersheds from the atmosphere. Except for the unusually high amount of calcium present in rainwater in February and March, the pattern of calcium input was similar to

that of sodium. Like that of calcium, magnesium input from rainfall was relatively stable throughout the year, with no apparent seasonal pattern and only slight correlation with rainfall patterns (Ca: $r = 0.64$, $p < 0.05$; Mg: $r = 0.60$, $P < 0.05$). The quantity of calcium, magnesium, and sodium in rainwater generally depended on individual storm size. Magnesium showed the greatest stability with regard to season and amount of rainfall. Although sodium, as well as magnesium, increased with an increase in rainfall, sodium was much more variable, showing a greater dependence on the volume of each storm.

Throughfall values in the hardwood forest (81.0% of gross precipitation) and in the eastern white pines (75.4% of gross precipitation) generally agreed with those reported in the literature (Semago and Nash, 1962; Helvey, 1964; 1967; Helvey and Patric, 1966; Lawson, 1967; Nihlgard, 1970). The results indicate that varying amounts of cations were leached from trees in relation to leaf maturity (season) and to volume of rainwater. Sodium leaching was mainly a function of the rainfall volume. Calcium and magnesium were leached with little respect to the rainfall amount; the leaching of potassium seemed to be strictly dependent on leaf maturity.

We found that tree species was also a factor determining the degree of cation leaching; this agrees with the results reported by Tarrant et al. (1968) and Nihlgard (1970). The yearly cation loss from white pines was only slightly less than the loss from the hardwood forest (Table 1); however, there were months during the growing season when the mineral loss from the canopies of the two forests differed significantly (Fig. 1). This suggests the possibility of species difference in susceptibility to leaching.

A greater loss of nutrients from mature stands of evergreens than from stands of hardwoods was reported by Nihlgard (1970), but Madgwick and Ovington (1959) reported similar losses occurring from stands of pines and hardwoods. Because the white pine stand in our study was young (12 to 13 years of age) and was undergoing vigorous growth, we expected greater nutrient utilization there than in the hardwoods. Since there was no significant difference between throughfall concentration of the white pine canopy and the hardwood canopy (Table 2), this greater nutrient utilization was not realized. The apparent net gain of elements by the white pines (Table 1) was probably a result of less water loss by stream discharge rather than greater mineral utilization.

One of the most significant periods of material loss from a tree is the leaf-fall period, as shown in Fig. 1 by the considerable leaching of potassium, calcium, and magnesium before leaf fall. The large amount of leachable nutrients lost from leaves between the formation of the abscission layer and actual leaf fall may account for the high nutrient loss from the canopy which occurred during October. Since white pines lose needles throughout the year, the fall peak in leaching was not as pronounced in this watershed. Another peak in throughfall cations occurred at the onset of increased activity of the canopy. In the

hardwoods this increase corresponded closely with an increase in meristematic activity in the buds in late March and April, with the initial peak being reached at the time of bud break and leaf expansion. This pattern of canopy leaching was especially evident from the potassium data. Leaching of potassium was drastically reduced by the demand created by the young, vigorously growing leaves. As the leaves approached senescence, potassium release increased. A maximum in potassium release from the canopy became evident soon after the formation of the abscission layer. After leaf fall a substantial amount of potassium was leached from the twigs and branches of the hardwoods.

The pattern of potassium loss from each forest canopy differed significantly throughout the growing season (Fig. 1), yet the yearly potassium loss was similar, with about 25 kg ha^{-1} $year^{-1}$ (throughfall minus input) leached from the canopy of each forest. Monk (1966) stressed the major ecological role of deciduous and evergreen species in mineral conservation. Apparently there is a more closed potassium cycle in the white-pine watershed. The comparatively high potassium loss occurred during the growing season when potassium demand by the biota was high, thereby reducing soil leaching loss. There was a significantly lower loss in the fall when greater soil leaching would be expected.

On several occasions throughfall sodium in the hardwood forest was less than sodium in the incoming rainfall (Fig. 1). This was true for much of the year in the pine plantation (Fig. 1). Foliar absorption of nutrients has been shown by a number of authors (Ingham, 1950; Tukey, Tukey, and Wittwer, 1958; Tukey and Tukey, 1959; Wittwer and Teubner, 1959; Tukey, 1969). The reduction of sodium in throughfall may be the result of sodium uptake by plant parts across a diffusion gradient.

Throughfall calcium had an initial peak at the onset of the growing season in both watersheds. This high amount of leachate corresponded to the increase in activity of the buds and newly forming leaves of the hardwoods and to a stimulation of growth activity in the white pines. A sustained amount of calcium leached from the canopy probably resulted from the transpiration stream's moving an excessive amount to the leaves (Stenlid, 1958), where it became available for leaching. This mass flow of calcium may have occurred if all exchangeable sites were occupied by ions that were not displaced by calcium (Thomas, 1967).

An autumn maximum and a spring minimum of calcium in throughfall waters were observed (Fig. 1). An additional peak was observed in July for the white pines and in October for the hardwoods. The October peak for the hardwoods is easily explained since a substantial amount of cations was leached from leaves just before leaf fall. A reason for the July peak of leached calcium from the white pines is not evident, although a dry period in June and July, combined with the completion of growth by the pines, may have created an excess of nutrients in the transpiration stream.

If the nutrient reservoir in the forest floor of each watershed was stable, although not in a static state, then the loss of nutrients from the forest floor should have equaled the loss of decomposing litter plus throughfall. Of the downward movement of calcium, 8.1 kg ha^{-1} $year^{-1}$ (35%) and 6.3 kg ha^{-1} $year^{-1}$ (30%) occurred as throughfall from the hardwoods and white pines, respectively, with the remaining downward movement occurring as leaf fall. These amounts are in general agreement with those reported by Stenlid (1958), Mecklenburg and Tukey (1964), and Carlisle, Brown, and White (1967).

Throughfall of magnesium followed the same general pattern as that of calcium. There is no corresponding use for magnesium in the buds as was evid for potassium and calcium, but an increase in magnesium in the transpirati stream in early spring was probably the result of an increase in the demand for magnesium for chlorophyll synthesis in new leaves. The amount of magnesium in throughfall and below the litter (see Table 1) offers support for the suggestion by Carlisle, Brown, and White (1967) that leaves account for about 69% of the magnesium movement.

The litter layer constitutes a reservoir of cations within the watershed system. Shortly after leaf fall the remaining leachable cations are lost rapidly. Subsequently, microbial breakdown of the leaves releases nutrients that were formerly tied up in leaf structures.

That the white pine foliage tended to retain a greater hold on potassium and sodium before leaf fall than did the hardwood is evident in the amounts of these elements leached from the litter (Table 1). The movement of calcium through the litter corresponded closely with throughfall amounts, supporting the suggestion that about 65% of the calcium was released by litter decomposition and the remainder occurred as throughfall. There was an increase in magnesium from 3.1 kg ha^{-1} $year^{-1}$ in throughfall to 5.9 kg ha^{-1} $year^{-1}$ in the litter discharge in the hardwoods and from 2.0 kg ha^{-1} $year^{-1}$ in throughfall to 5.4 kg ha^{-1} $year^{-1}$ in litter flow through in the white pines; i.e., about 50 to 60% of magnesium recycling in the watershed occurs after leaf fall.

Greater amounts of nutrients moved through the soil lysimeters in the white pine watershed than in the hardwood watershed (Table 1). This indicates that the foliage of the white pines retained a greater hold on nutrients until leaf drop, whereupon the nutrients were released into the upper layers of the soil. The differences in cation release from the two watersheds may, in fact, ha been similar since a greater concentration of cations was found in the discharg waters of the hardwood watershed than in those of the white pine watershed. The results suggest that substantial amounts of cations were removed from decomposing litter and stored in the soil. According to Johnson et al. (1968), soil and rock weathering may contribute substantial amounts of exchangeable cations to the watershed; this indicates that stream discharge may, in fact, release a greater amount of nutrients than would pass through the upper layer of the soil (see Table 1; compare results of soil lysimeters to stream output). Soil

lysimeter results revealed that the soil acted as a buffer against excessive loss of nutrients from the system by not releasing nutrients from the soil in accordance with the release from the litter. Part of this buffering process of the soil may be related to a high degree of uptake of cations by the plant roots, as well as to an incorporation on the exchange sites of the soil and organic particles. Since cations in the litter and upper layers of the soil are released slowly and are stored in the upper soil layers, they are more accessible to recycling and thereby constitute a form of biological conservation or buffering capacity.

The greatest apparent stability of cations occurred in stream discharge. The consistency of nutrient content in the discharge water in this study gives strong support to the suggestion by Johnson et al. (1968) for a steady-state release of chemicals by rock weathering. This steady-state release "implies that some continuous and self-perpetuating buffering process is in effect."

Although similar amounts of nutrients were leached from the canopies of both hardwoods and white pines, the pattern of release was different. An abrupt pulse of nutrients, evident in the hardwood forest, created an overflow of nutrients in the storage compartment, allowing a greater drain of nutrients from the system. The period of estival release may also have been a factor related to total nutrient discharge from the system. The peaks of magnesium and calcium release from the white-pine canopy occurred at a period when a demand for nutrients may have still existed. The evergreenness of the white pines was probably the most dominant factor causing the retention of cations within the watershed system by creating an ever present, although fluctuating, demand for cations.

Potassium movement within the two forest types was similar except for stream discharge. A greater potassium loss in stream discharge occurred in the hardwood watershed; this was probably a result of the greater water loss caused by decreased interception and evapotranspiration from the foliageless trees during the winter months (Johnson and Swank, 1973). More calcium was discharged from the hardwood watershed than from the white pine watershed (see Table 1). Since the pattern of calcium discharge from the watersheds was similar, the larger amounts lost from the hardwood watershed were probably related to the greater amount of water passing out of the system. Also, the release of leachate from the hardwoods corresponded to a period of low biologic activity in the litter and soil. There was probably less demand for nutrients by the ground flora during October and November, when calcium was released from the hardwood canopy, than during the late summer months, when the calcium was released from the white pine canopy. Because of this lull in the need for calcium, a greater amount was discharged from the hardwood watershed rather than being incorporated into biologic components of litter and soil. There was a greater net loss of magnesium than of any other cation from the watersheds. Stream discharge of magnesium closely resembles the water discharge from the watersheds.

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REFERENCES

Bhan, K. C., A. Wallace, and O. R. Lunt, 1959, Some Mineral Losses from Leaves by Leaching, *Proc. Amer. Soc. Hort. Sci.*, **73**: 289-293.

Burnett, C. R., 1965, Anomalous Abundance of Upper Atmosphere Sodium, 1964, *Science*, **147**: 736-737.

Carlisle, A., A. H. F. Brown, and E. J. White, 1967, The Nutrient Content of Tree Stem Flow and Ground Flora Litter and Leachates in a Sessile Oak (*Quercus petraea*) Woodland, *J. Ecol.*, **55**: 615-627.

Coffay, E. W., 1962, Throughfall in a Forest, *Int. Assoc. Sci. Hydrol. Bull.*, **7**: 10-16.

Day, F. P., and C. D. Monk, 1974, Vegetation Patterns on a Southern Appalachian Watershed, *Ecology*, **55**: 1064-1074.

Dils, R. E., 1957, A Guide to the Coweeta Hydrologic Laboratory, Miscellaneous Publication, Southeastern Forest Experiment Station, Forest Service, U. S. Department of Agriculture.

Fisher, D. W., 1968, Annual Variations in Chemical Composition of Atmospheric Precipitation, Eastern North Carolina and Southeastern Virginia, Water-Supply Paper 1535-M, U. S. Geological Survey.

Gambell, A. W., and D. W. Fisher, 1966, Chemical Composition of Rainfall, Eastern North Carolina and Southeastern Virginia, Water-Supply Paper 1535-K; U. S. Geological Survey.

Helvey, J. D., 1967, Interception by Eastern White Pine, *Water Resour. Res.*, **3**: 723-729.

——, 1964, Rainfall Interception by Hardwood Forest Litter in the Southern Appalachians, Research Paper SE-8, Southeastern Forest Experiment Station, Forest Service, U. S. Department of Agriculture.

——, and J. H. Patric, 1966, Design Criteria for Interception Studies, *Int. Assoc. Sci. Hydrol., Bull.*, **67**: 131-137.

Hoover, M. D., 1944, Effect of Removal of Forest Vegetation upon Water Yields, *Trans. Amer. Geophys. Union*, **6**: 969-975.

Ingham, G., 1950, Effects of Materials Absorbed from the Atmosphere in Maintaining Soil Fertility, *Soil Sci.*, **70**: 205-212.

Johnson, N. M., G. E. Likens, F. H. Bormann, and R. S. Pierce, 1968, Rate of Chemical Weathering of Silica to Minerals in New Hampshire, *Geochim. Cosmochim. Acta*, **32**: 531-545.

Johnson, P. L., and W. T. Swank, 1973, Studies of Cation Budgets in the Southern Appalachians on Four Experimental Watersheds with Contrasting Vegetation, *Ecology*, **54**: 70-80.

Jordan, C. F., 1968, A Simple Tension Free Lysimeter, *Soil Sci.*, **105**: 81-86.

Kaul, O. N., and W. D. Billings, 1965, Cation Content of Stemflow in Some Forest Trees in North Carolina, *Indian For.*, **91**: 367-370.

Kimmins, J. P., 1973, Some Statistical Aspects of Sampling Throughfall Precipitation in Nutrient Cycling Studies in British Colombian Coastal Forests, *Ecology*, **54**: 1008-1019.

Lawson, E. R., 1967, Throughfall and Stemflow in a Pine–Hardwood Stand in the Quachita Mountains of Arkansas, *Water Resour. Res.*, **3**: 731-735.

Likens, F. F., F. H. Bormann, N. M. Johnson, and R. S. Pierce, 1967, The Calcium, Magnesium, Potassium and Sodium Budgets for a Small Forested Ecosystem, *Ecology*, **48**: 772-785.

——, F. H. Borman, N. M. Johnson, R. S. Pierce, and D. W. Fisher, 1970, Effects of Forest Cutting and Herbicide Treatment on Nutrient Budgets in the Hubbard Brook Watershed Ecosystem, *Ecol. Monogr.*, **40**: 23-47.

Madgwick, H. A. I., and J. D. Ovington, 1959, The Chemical Composition of Precipitation in Adjacent Forest and Open Plots, *Forestry*, **32**: 14-22.

Mecklenburg, R. A., and H. B. Tukey, Jr., 1964, Influence of Foliar Leaching on Root Uptake and Translocation of Calcium-45 to the Stems and Foliage of *Phaseolus vulgaris*, *Plant Physiol.*, **39**: 533-536.

Monk, C. D., 1966, An Ecological Significance of Evergreenness, *Ecology*, **47**: 504-505.

Nihlgard, B., 1970, Precipitation, Its Chemical Composition and Effect on Soil Water in a Beech and a Spruce Forest in South Sweden, *Oikos*, **21**: 208-217.

Semago, W. T., and A. J. Nash, 1962, Interception of Precipitation by a Hardwood Forest Floor in the Missouri Ozarks, Resources Bulletin No. 796, University of Missouri Agricultural Experiment Station.

Stenlid, G., 1958, Salt Losses and Redistribution of Salts in Higher Plants, *Encyclopedia of Plant Physiology*, **4**: 615-637.

Tamm, C. O., 1951, Removal of Plant Nutrients from Tree Crowns by Rain, *Physiol. Plant.*, **4**: 184-188.

Tarrant, R. F., K. C. Lu, W. B. Bollen, and C. S. Chen, 1968, Nutrient Cycling by Throughfall and Stemflow Precipitation in Three Coastal Oregon Forest Types, Research Paper PNW-54, Pacific Northwest Forest and Range Experiment Station, Forest Service, U. S. Department of Agriculture.

Thomas, W. A., 1967, Dye and Calcium Ascent in Dogwood Trees, *Plant Physiol.*, **42**: 1800-1802.

Tukey, H. B., and H. B. Tukey, Jr., 1959, Practical Implications of Nutrient Losses from Plant Foliage by Leaching, *Proc. Amer. Soc. Hort. Sci.*, **74**: 671-676.

Tukey, H. B., Jr., 1970, The Leaching of Substances from Plants, *Annu. Rev. Plant Physiol.*, **21**: 305-324.

——, 1969, Implications of Allelopathy in Agricultural Plant Science, *Bot. Rev.*, **35**: 1-16.

——, H. B. Tukey, and S. H. Wittwer, 1958, Loss of Nutrients by Foliar Leaching as Determined by Radioisotopes, *Proc. Amer. Soc. Hort. Sci.*, **71**: 496-506.

Voigt, G. K., 1960, Distribution of Rainfall Under Forest Stands, *Forest Sci.*, **6**: 2-10.

Wittwer, S. H., and F. G. Teubner, 1959, Foliar Absorption of Mineral Nutrients, *Annu. Rev. Plant Physiol.*, **10**: 13-32.

NUTRIENT LOSSES IN PARTICULATE FORM AS WEIR POND SEDIMENTS FROM FOUR UNIT WATERSHEDS IN THE SOUTHERN APPALACHIANS

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ABSTRACT

Weir-pond sediments were collected at 3-month intervals for a period of 2 years from four watersheds with contrasting vegetation. Annual sediment losses for the four watersheds were 283 kg/ha from the coppice hardwoods, 176 kg/ha from the old field, 76 kg/ha from the pine plantation, and 30 kg/ha from the mature hardwoods. Greater losses occurred during the winter season. The composition of the sediments from the old field, coppice hardwoods, and pine plantation were similar (sand, 77.4%; silt, 13.6%; clay, 9.0%; and organic matter, 7.6%). By contrast, the values for the mature hardwoods were 49.9, 17.6, 32.5, and 21.9%. Nutrient concentrations varied from watershed to watershed and in some instances seasonally. The order of concentration from high to low was nitrogen, calcium, magnesium, potassium, sodium, and phosphorus. Nutrient loss as weir-pond sediments accounts for no more than 1% of the total loss.

Much has been written in the past decade of the effects of clear-cutting of small watersheds on water quantity and quality. Aubertin and Patric (1974) pointed out that water yield is increased following clear-cutting (approximately 4.5 per year per percent reduction in forest cover) and that with reforestation water yield is diminished. The effects of clear-cutting on water quality are not as straightforward and may be related in part to supplemental treatment accompanying the clear-cut. Following an experimental clear-cut with no harvest and a precut herbicide treatment to prevent revegetation, water quality was adversely affected (Hubbard Brook; Likens et al., 1967). A more conventional clear-cut was performed at Fernow, W. Va., simulating a more realistic silvicultural practice [merchantable timber and pulpwood harvested and remaining trees felled and left in place, thus permitting the establishment of an even-aged forest (Aubertin and Patric, 1974)]. Water yield was increased 20 cm the first year following the clear-cut and 6.4 cm the second year. Water quality was affected only slightly.

Brown, Gahler, and Marston (1973) monitored nutrient losses for 2 years in three small watersheds in the Oregon Coast Range prior to two logging treatments (patch cut and clear-cut–slash burned) and for 2 years following logging. No changes in concentration or yield were noted on the patch-cut watershed for nitrate nitrogen, phosphorus, or potassium. On the clear-cut–slash-burned watershed, nitrate nitrogen yield was increased from 4.94 to 15.66 kg/ha the first year following treatment. The data suggest a return to pretreatment levels within 6 years. Potassium concentration increased markedly with burning but returned to pretreatment level within 2 months. Concentration phosphorus was unchanged. Similar treatment responses have been reported r the coast Douglas fir region by Fredriksen (1971).

The loss of nutrients from unit watersheds via the stream may be grossly categorized into (1) dissolved fraction, (2) suspended particulate fraction, and (3) erosional fraction that is rolled along the streambed. The concentrations and amounts of nutrients found in these fractions may be affected by land-management practices as is the actual weight of the erosional fraction (weir-pond sediment load).

There have been a number of clear-cut experiments of unit watersheds at the Coweeta Hydrologic Laboratory, Franklin, N. C., over the past 30 years. Posttreatment management has varied. The weight and nutrient losses in the erosional fraction from four watersheds, each under a different management practice, are given in this paper.

METHODS

Watershed 6 (old field, 8.86 ha) was clear-cut in 1958, and all merchantable timber was removed. It was then planted with Kentucky 31 fescue. In 1959, 6.7 metric tons of dolomitic limestone was applied to each hectare of the watershed along with 2.2 metric tons of 2–12–12 fertilizer. In 1966 the grass cover was killed with herbicides. No further treatment has been applied to the watershed since spring 1968. Watershed 13 (coppice, 16.11 ha) was clear-cut during 1939–1940. Sprouts were permitted to grow until 1962, when they were again cut. No treatment has been applied to the watershed since. Watershed 17 (white pine, 13.48 ha) was clear-cut in 1942, and annual sprout growth was cut ost years until 1955. It was then planted with white pine in 1956. Watershed 18 (mature hardwood forest, 12.46 ha) serves as a control watershed. For a more detailed treatment history of these four watersheds see Johnson and Swank (1973).

Weir-pond sediments were collected at 3-month intervals for 2 years beginning in September 1969. The streams were sandbagged above the weir pond, and water was diverted over the weir. The water in the pond was siphoned, then the sediments were removed to plywood boxes. After a period of drainage, three samples of known volumes were collected and dried, and the

weight was estimated. The samples were analyzed for particle size (Bouyouuos method), organic matter (ashing if >10% and potassium dicromate digestion if <10%), nitrogen (Kjeldahl), calcium, magnesium, potassium, phosphorus (Technicon Autoanalyzer), and sodium (atomic absorption). The percent sand, silt, and clay values reported were adjusted for the organic-matter content of the sediment.

RESULTS AND DISCUSSION

The organic and inorganic content of the weir-pond sediments are given Table 1, along with the particle-size distribution of the inorganic fraction. The

TABLE 1

EROSIONAL LOSSES* (IN PARTICULATE FORM AS WEIR SEDIMENTS) FROM FOUR WATERSHEDS (SEPT. 69–SEPT. 70, 368 DAYS)† (SEPT. 70–SEPT. 71, 352 DAYS)‡

Watershed	Inorganic, kg/ha		Organic, kg/ha	Sand, %	Silt, %	Clay, %
	<2 mm	>2 mm				
Old field	16†	139.7	12.3	73.6 ± 1.6	15.2 ± 1.9	11.2 ± 0.5
(WS 6)	16‡	181.0	15.6			
Coppice	26†	242.5	15.5	80.2 ± 1.3	12.7 ± 1.0	7.1 ± 0.6
(WS 13)	31‡	266.0	17.0			
White pine	8†	74.0	7.0	78.5 ± 1.4	12.9 ± 0.8	8.6 ± 0.7
(WS 17)	6‡	64.9	6.1			
Mature hardwood	5†	26.9	7.2	49.9 ± 2.9	17.6 ± 1.2	32.5 ± 2.0
(WS 18)	2‡	26.6	7.4			

*Percentages represent averages of eight quarterly collections ±1 SE.
†Data taken September 1969 to September 1970, 368 days.
‡Data taken September 1970 to September 1971, 352 days.

sediment loss followed a general seasonal trend, with peak losses normally coming during the winter quarter. If we consider the old field watershe coppice forest, pine plantation, and mature hardwood forest to form a general succession sequence, then it is clear that young successional stages have more erosion than older ones. The larger inorganic sediment loss from the coppice forest has two possible explanations: (1) longer stream channel and (2) part of the stream is underground, and erosion is enhanced by freeze–thaw action during the winter.

Sediment losses in the <2-mm fraction show good agreement for the 2 years. Annual losses of inorganic sediments (<2 mm) averaged 160.3 kg/ha from WS 6,

254.2 kg/ha from WS 13, 69.4 kg/ha from WS 17, and 26.7 kg/ha from WS 18. The larger sediment fraction (>2 mm) exhibited the same trend as the smaller fraction; however, its weight was generally 10-fold less. The annual rates of inorganic erosion (grams/hectare/day) were 483 (WS 6), 774 (WS 13), 209 (WS 17), and 83 (WS 18).

The amount of organic matter followed the same trend between the four watersheds as the inorganic fraction (Table 1); however, its percentage contribution to the weir-pond sediment did not. The percentages of organic matter in the sediments coming from the four watersheds were 8.1 (WS 6), 6.0 (WS 13), 8.6 (WS 17), and 21.0 (WS 18).

The composition of the sediments coming from the old field, coppice hardwood forest, and the pine-plantation watersheds was similar [averaging 77.4% sand, 13.6% silt, 9.0% clay, and 7.6% organic matter (Table 1)]. By contrast, the same values for the mature hardwood forest were 49.9, 17.6, 32.5, and 21.9%. The most obvious difference in the nonorganic sediment losses from the four watersheds other than amounts was the greatest proportion of clay and lesser amounts of sand coming from the hardwood forest.

The amount of inorganic sediments leaving the mature hardwood at Coweeta annually is higher than for a northern hardwood forest at Hubbard Brook (Bormann, Likens, and Eaton, 1969). The 2-year average of weir-pond sediments from the northern hardwood forest was 9.42 kg ha^{-1} water $year^{-1}$ as inorganics. The corresponding value for the hardwood forest at Coweeta was 30.25. Perhaps the main factors contributing to these differences are (1) the difference in slope; 26% at Hubbard Brook vs. 52% at Coweeta, (2) approximately 7 cm more precipitation per year at Coweeta, and (3) differences in soil characteristics. Organic losses were the same for the two systems; 7.8 kg ha^{-1} $year^{-1}$ at Hubbard Brook and 7.3 kg ha^{-1} $year^{-1}$ at Coweeta.

The concentration of calcium, magnesium, potassium, and phosphorus showed no regular seasonal pattern. In general, the concentrations were less in the sediments coming from the coppice forest; a fact probably related to the greater erosional losses. Nitrogen and sodium concentrations exhibited seasonal changes, with greatest concentrations occurring in the winter. For nitrogen this trend is undoubtedly related to the pattern of organic-matter losses, which was also higher during the winter months. No explanation can be made of the higher sodium concentrations during the winter.

The annual average concentrations of six elements are given in Table 2. There are several items worthy of notice. First is the consistently lower concentration of all elements in sediments from the coppice watershed. This fact is probably related to the larger erosional losses from the watershed. Second, the higher nitrogen concentrations in sediments coming from the hardwood-forest watershed are surely related to the higher organic matter losses. Third, the higher calcium and magnesium losses from the pine plantation and the hardwood forest are probably related to the large calcium and magnesium pool in the litter layer

TABLE 2

CONCENTRATION AND ANNUAL LOSS (<2-MM FRACTION) OF SELECTED ELEMENTS IN WEIR-POND SEDIMENTS FROM FOUR WATERSHEDS

Watershed	Phosphorus		Nitrogen		Sodium		Potassium		Calcium		Magnesium	
	ppm	kg/ha	ppm	kg/ha	ppm	kg/ha	ppm	kg/ha	ppm	kg/ha	ppm	kg/ha
Old field (WS 6)	9*	0.001	3077	0.49	24	0.004	60	0.009	977	0.15	143	0.02
	7†		3341		29		32		720		111	
Coppice (WS 13)	5*	0.001	1917	0.52	15	0.004	21	0.005	479	0.12	66	0.02
	4†		2275		30		18		497		57	
White pine (WS 17)	9*	0.001	2450	0.20	23	0.002	36	0.003	822	0.07	106	0.009
	7†		3066		37		30		887		89	
Mature hardwood (WS 18)	10*	0.000	6450	0.23	41	0.001	58	0.002	1883	0.06	170	0.005
	7†		8433		31		40		1127		140	

*Data taken from September 1969 to September 1970, 368 days.
†Data taken from September 1970 to September 1971, 352 days.

(Yount, this volume), and the high concentration of calcium and magnesium coming from the old-field watershed may be related to the dolomitic limestone application of 1959 (Best and Monk, this volume).

The adjusting concentration of nutrient loss to reflect total weight loss will give some idea of the importance of erosion on nutrient depletion of watersheds. The annual losses of the six elements are given in Table 2. The total losses are very small, actually less than 1% of the dissolved fraction (Johnson and Swank, 1973).

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REFERENCES

Aubertin, G. M., and J. H. Patric, 1974, Water Quality After Clear-Cutting a Small Watershed in West Virginia, *J. Environ. Qual.*, 3: 243-249.

Bormann, F. H., G. E. Likens, and J. S. Eaton, 1969, Biotic Regulation of Particulate and Solution Losses from a Forest Ecosystem, *Bioscience*, 19: 600-610.

Brown, G. W., A. R. Gahler, and R. B. Marston, 1973, Nutrient Losses After Clear-Cut Logging and Slash Burning in the Oregon Coast Range, *Water Resour. Res.*, 9: 1450-1453.

Fredriksen, R. L., 1971, Comparative Water Quality—Natural and Disturbed Streams, in *Forest Land Uses and Stream Environment*, Symposium Proceedings, pp. 125-137, Oregon State University Press, Corvallis.

Johnson, P. L., and W. T. Swank, 1973, Studies of Cation Budgets in the Southern Appalachians on Four Experimental Watersheds with Contrasting Vegetation, *Ecology*, 54: 70-80.

Likens, G. H., F. H. Bormann, N. M. Johnson, and R. S. Pierce, 1967, The Calcium, Magnesium, Potassium, and Sodium Budgets for Small Forested Watersheds, *Ecology*, 48: 772-785.

THE EFFECT OF URBAN LAND USE ON NUTRIENT AND SUSPENDED-SOLIDS EXPORT FROM NORTH FLORIDA WATERSHEDS

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ABSTRACT

Two watersheds of similar size, geomorphology, and pedology representing forested–agricultural and residential–commercial (urban) land use were hydrologically instrumented to obtain comparative nutrient and suspended-solids export data. Constituents measured included suspended solids, total dissolved solids, dissolved silicon, and dissolved nutrients (nitrogen and phosphorus).

Intensive hydrochemical analysis of runoff from 13 storms in the urban watershed and 8 storms in the forested watershed demonstrated a strong contrast in the magnitude and temporal distribution of nutrient and suspended-solids concentrations and exports. Suspended-solids concentration and export were directly dependent on stream discharge. Although concentrations of dissolved constituents were generally inversely dependent on stream discharge, export of dissolved constituents was directly dependent on stream discharge. Higher cumulative stream discharge in the urban watershed thus exported higher total storm loads of all constituents except dissolved silicon. Exports of suspended solids, total dissolved solids, and all the dissolved nitrogen species from the urban watershed were higher than the higher volume of stream discharge in this watershed might otherwise indicate, suggesting significant additional sources of these constituents in the urban watershed. Exports of dissolved phosphorus from the urban watershed were also higher but near what the higher volume of stream discharge might indicate. Exports of dissolved silicon from the urban watershed were lower than from the forested watershed despite the higher volume of stream discharge in the urban watershed. Observed differences in exports were related to the changes in hydrology associated with urban development, i.e., in streamflow rate, total volume of stream discharge, and the relative significance of various pathways of water movement, as well as to increased diffuse anthropogenic inputs in the urban watershed. Comparison of material loads exported by storm flow and low flow in each watershed suggested increased significance of storm events in materials export in the urban watershed.

Understanding the responses of a watershed ecosystem to various disturbances by man is frequently limited by a lack of appropriate background data on the

ecosystem prior to disturbance. Rarely is a watershed ecosystem sufficiently studied prior to disturbance, such as those at the Hubbard Brook Experimental Forest (Likens et al., 1970) and at the Coweeta Hydrologic Laboratory (Johnson and Swank, 1973), to permit accurate assessment of the impact of the disturbance. With the increasing demand for better watershed management strategies, particularly in culturally developing watersheds, there is a pressing need to be able to predict the impact of alternative development schemes on watershed and receiving aquatic ecosystems. Calibration of a watershed prior to disturbance is obviously the most desirable approach to understanding the effects of various disturbances, but this is typically a long-term undertaking and not the only approach that can yield meaningful results. Adjoining watersheds, one of which is undisturbed, or relatively so, may often be used with some success provided they otherwise have similar climate, geology, hydrology, and topography. We report early findings on the export of water, suspended solids, and dissolved nutrients from two adjacent watersheds in north Florida, one of which is being rapidly urbanized.

Although there are some data available on the quality of urban runoff (Sylvester, 1961; Weibel, Anderson, and Woodward, 1964; Pravoshinsky and Gatillo, 1969; AVCO, 1970; Bryan, 1972, Sartor and Boyd, 1972; Wells et al., 1973; Whipple, Hunter, and Yu, 1974; Kluesener and Lee, 1974; Pitt and Amy, 1973), these are not readily comparable to adjacent undisturbed systems. Thus, although increased concentrations of nutrients and suspended solids have been recorded from urban runoff, the magnitude of the increase over preurban conditions has not been clearly established. In addition, many of the published data on urban water quality include combined storm and domestic sewage flow. Finally, very few reported studies have attempted to identify the geologic, meteorologic, and land-use factors that ultimately control urban runoff quantity and quality (Pravoshinsky and Gatillo, 1969; AVCO, 1970; Wells et al., 1973).

This study has three major objectives related to the impact of urbanization on a north Florida watershed:

1. Quantification of changes in runoff-water chemistry.
2. Quantification of changes in the export of selected constituents of runoff.
3. Identification and evaluation of the relative significance of the geologic, meteorologic, and land-use factors that control the quality of urban runoff and export of runoff constituents.

These objectives are especially timely in this case because the receiving aquatic ecosystem, a large (1960 ha) freshwater lake, is still largely undamaged by the rapid urban encroachment into its watershed.

THE STUDY AREA

Lake Jackson and its watershed (11,190 ha) are located just north of Tallahassee in north Florida. Two subbasins of the Lake Jackson drainage area

were selected for intensive comparative study to quantify changes in water quality and geochemical exports resulting from the increased urbanization of one subbasin. These watersheds are reasonably similar in size, geomorphology, and pedology but are strikingly dissimilar with respect to type and extent of cultural development.

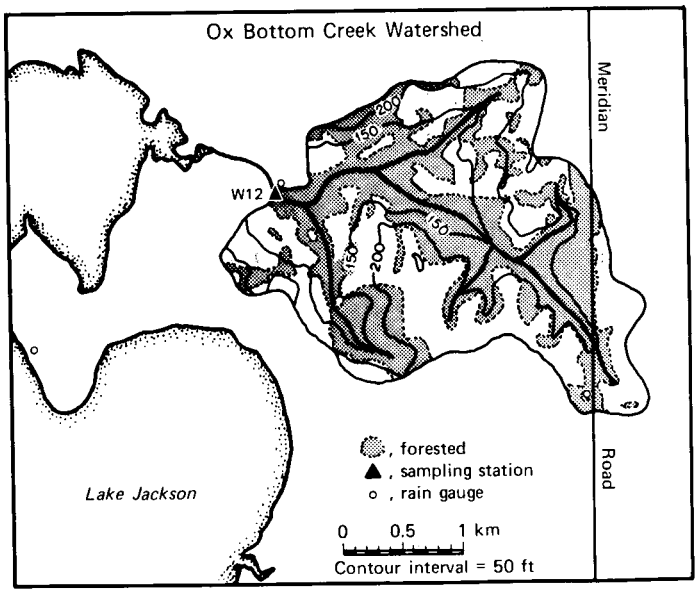
Ox Bottom Creek (Fig. 1), which enters the northern end of Lake Jackson, drains part of a large private estate with limited public access. Over 50% of this 633-ha watershed is forested, and the remainder is in old field and light agricultural use. Most of the forested portion (mixed pine and hardwoods) is located along the stream channel; the farmland is on the higher land toward the periphery of the basin. Soils are well-drained sandy loams over loamy subsoils and include mainly the Dothan–Orangeburg and Faceville–Tifton–Greenville associations. Average ground slope is 4.4%. For purposes of identification this watershed will be referred to in the remainder of the paper as the forested watershed.

The Meginniss Arm watershed (Fig. 1) at the southern end of Lake Jackson has undergone rapid urban development in the past 20 years and is now about 80% urban. Most of the 721-ha urban watershed is composed of low-density single-family housing, but several apartment complexes, office parks, commercial areas (including two large shopping malls), and two schools are included. Sanitary-sewer facilities export wastes from this watershed to the watershed of an adjacent lake. Thus sanitary effluents are never deliberately a component of streamflow. Soils in this watershed are well-drained sandy soils over loamy subsoils and include mainly the Dothan–Orangeburg association. Average ground slope is 4.2%. For purposes of identification, this watershed will hereafter be referred to as the urban watershed.

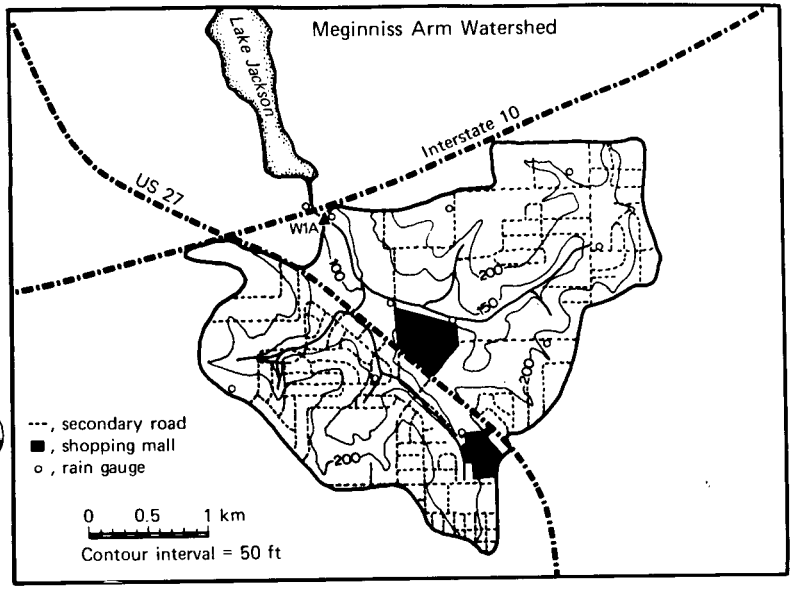
Rainfall in the study area varies widely over the basin on a storm-by-storm basis but averages 146 cm per year. There are summer and winter wet seasons, April–May and October–November being dry periods. Average annual temperature is 19.4°C, with an average high of 27.2°C in July and an average low of 12°C in January (Hendry and Sproul, 1966). The streams draining each study watershed typically have low-flow discharges of less than 0.02 m^3/sec and are sometimes dry between rainfalls.

METHODS AND MATERIALS

Because of the often intermittent nature of streamflow in these watersheds, major emphasis was placed on sampling storm flow. Automatic water samplers (Sigmamotor Model WM-4-24) were installed at suitable downstream sites to adequately sample runoff from storms. These samplers were either activated manually prior to the start of a storm or preset to activate automatically with a rise in the stream water level. Generally, it was preferable to activate the samplers manually to obtain a prestorm sample and to ensure proper operation of the sampler. Automatic activation was used primarily to sample storms that



(a)



(b)

Fig. 1 Maps of Ox Bottom Creek (forested) and Meginniss Arm (urban) watersheds.

might have been missed if only manual activation were used. Discrete 500-ml samples were taken over entire storm hydroperiods at preset time intervals (20 or 30 min on the urban and 1-hr on the forested watershed). The sampler normally required 10 to 12 min to pump 500 ml, thus samples were actually time integrated. Storm hydroperiods generally encompassed less than 8 hr at the urban watershed and often as long as 48 hr at the forested watershed.

Turbidity and conductivity of each sample were determined within 24 hr of collection. Samples were composited on the basis of these measurements and stream discharge at the time of collection. A (Hach model 2100A) turbidimeter and (Barnstead model PM-70CB) conductivity bridge were used for the turbidity and conductivity measurements, respectively.

Base-flow, or low-flow, samples were collected weekly or more frequently and processed without compositing in the same manner as storm-flow samples.

Sample aliquots for dissolved constituent analyses were filtered through prewashed 0.45-μm Millipore membrane filters and preserved with $HgCl_2$. These samples were analyzed on an autoanalyzer system using the following Technicon Industrial Methodologies:

Ammonia—nitrogen (indophenol method)	154-71W
Nitrate + nitrite – nitrogen (Cd reduction and diazotization)	158-71W
Nitrite—nitrogen (diazotization)	161-71W
Ortho phosphate—phosphorus (molybdate reactive phosphorus, MRP)	155-71W
Dissolved silicon (molybdate reactive)	186-72W

Total dissolved phosphorus was determined on filtered (0.45 μm) sample aliquots by H_2SO_4—$HClO_4$ digestion followed by analysis for molybdate reactive phosphorus. Analytical quality control was checked regularly using Environmental Protection Agency (EPA) nutrient reference samples.

Suspended solids (nonfiltrable residue) and dissolved solids (filtrable residue) were determined according to sections 224-C and 224-E of *Standard Methods for the Examination of Water and Wastewater* (American Public Health Association, 1971). It should be noted that dissolved solids as used in this study may include some suspended solids since the glass-fiber filters used in the determination had a pore size too large (1 to 3 μm) to exclude all the smaller suspended solids.

Discharge of the streams was determined from ratings and stage-height recordings (15-min intervals) supplied by the U. S. Geological Survey (USGS) as part of a cooperative study. Both intensity and total quantity of rainfall were also recorded continuously in each watershed by the USGS; these data were supplemented by data from a network of plastic rain gauges distributed throughout the watersheds.

Instantaneous and total constituent exports were calculated using stream discharge and constituent concentration. Because samples collected during storms were often out of phase with discharge records, it was necessary to determine stream discharge at the midpoint of the sampling interval by linear interpolation. Since stream discharge was recorded at 15-min intervals and sampling was integrated over 10 to 12 min, interpolation in this manner probably introduced little error. Constituent discharges were calculated at 15-min intervals using interpolated concentrations where actual concentrations were unavailable. This interpolation was justified because samples collected near streamflow or during periods of rapid change in streamflow were rarely composited and reasonably defined the critical areas of the discharge curves. Total water and constituent exports were calculated using the trapezoidal rule of numerical integration. Data presented in this paper were statistically treated using programs BMD02D and BMD02R of the *BMD: Biomedical Computer Programs* series (Dixon, 1973).

The period of study reported was from August 1973 to April 1974 and includes, in addition to regular low-flow sampling, intensive sampling of 13 storms at the urban watershed, and 8 storms at the forested watershed. The storms sampled represent a series encompassing considerable range in total rainfall, rainfall intensity, and length of antecedent dry period.

RESULTS AND DISCUSSION

Stream-Water Composition and Flow Relations

A comparison of the average composition (mean) and variability [standard deviation (SD) and range] in composition of the streams draining the two study watersheds at low- (base flow) and high- (storm flow) flow conditions between August 1973 and April 1974 is presented in Table 1. The primary differences in stream-water composition under all flow conditions between the forested and urban watersheds were in the concentrations of suspended solids, total dissolved solids (TDS), and dissolved silicon. The forested drainage exhibited consistently lower dissolved silicon concentrations under all flow conditions, whereas TDS was consistently higher in the urban drainage. The concentration of suspended solids exhibited a reversal as a function of flow conditions, with higher concentrations in the forested drainage at low flow but considerably higher concentrations in the urban drainage at high stream flow. At low streamflow all the dissolved nutrients exhibited overlapping concentration ranges in the two watersheds. Interestingly, the mean nitrate concentration at low flow was higher in urban drainage but mean ortho and dissolved phosphorus concentrations were higher in the forested drainage.

TABLE 1

COMPARISON OF MEAN CONCENTRATIONS OF STREAM-WATER CONSTITUENTS BETWEEN THE URBAN AND FORESTED WATERSHEDS UNDER STORM-FLOW AND BASE-FLOW CONDITIONS

Constituents	Urban watershed concentrations, mg/liter			Forested watershed concentrations, mg/liter		
	Mean	±SD	Range	Mean	±SD	Range
			Storm flow			
Suspended solids	299	378	7–2094	34	25	7–129
Dissolved solids	161	181	10–1627	58	25	14–153
Silicon	1.72	0.74	0.52–3.06	3.57	0.48	2.38–4.32
NO_3–N	0.115	0.104	0.01–0.82	0.063	0.025	0.01–0.13
NO_2–N	0.014	0.020	0.001–0.09	0.002	0.002	0.001–0.01
NH_3–N	0.156	0.229	0.004–2.04	0.055	0.022	0.01–0.18
Ortho PO_4–P	0.123	0.131	0.001–0.69	0.103	0.059	0.004–0.38
			Base flow			
Suspended solids	2.8	2.7	0.5–9	14.0	5.7	7–25
Dissolved solids	73.3	20.8	50–120	48.8	8.1	34–60
Silicon	2.46	0.40	1.92–3.80	3.88	0.57	2.66–4.60
NO_3–N	0.104	0.054	0.021–0.180	0.055	0.030	0.001–0.100
NO_2–N	0.010	0.013	0.001–0.059	0.012	0.026	0.001–0.095*
NH_3–N	0.050	0.063	0.012–0.276	0.046	0.012	0.022–0.068
Ortho PO_4–P	0.068	0.034	0.024–0.149	0.111	0.052	0.036–0.220
Total dissolved P	0.078	0.062	0.040–0.225	0.118	0.085	0.055–0.270

[redacted]ree NO_2–N values in January 1974 appeared atypical for this watershed but w[redacted]cluded in th[redacted]mary.

The higher mean nitrate concentrations in the urban drainage at low flow is consistent with findings in other experimentally disturbed and urban watersheds (Likens et al., 1970; Symons, 1970), but the higher concentrations of ortho and dissolved phosphorus in the forested drainage at low flow is in sharp contrast to findings by others (reviewed by Ryden, Syers, and Harris, 1972). Several possible explanations for this observation include: (1) groundwater concentrations of phosphorus are higher in the forested watershed because the soils in that watershed contain more mineralized phosphorus, either natural or agriculturally derived, (2) algal primary productivity in the largely unshaded urban stream is high enough to significantly reduce dissolved levels of phosphorus in low-flow runoff, (3) although the urban stream carries a smaller quantity of suspended solids at low flow, these solids have higher adsorptive capacity for dissolved phosphorus than those carried by the forested stream at low flow. Further work is in progress to determine which, if any, of these explanations is operative.

Concentrations of all constituents in the urban drainage exhibited considerable variability under storm-flow conditions as indicated by the high standard deviations and ranges given in Table 1. In contrast, concentrations of all constituents in the forested drainage under storm-flow conditions exhibited much less variability, and their mean concentrations were not markedly different from those observed for low-flow conditions.

Figure 2 further illustrates the variability in selected constituent concentration during typical storm-flow conditions and demonstrates the obvious dependence on stream discharge in both watersheds. The storm event illustrated was characterized by two peaks in rainfall intensity and similar total amounts of rainfall in both watersheds. The shape of the urban hydrograph accurately depicts the rainfall intensity curve for this storm. To best illustrate concentration–discharge relations in each watershed, we have plotted stream discharge, constituent concentrations, and time in this figure on scales that differ between the watersheds.

The expected direct relation between the concentration of suspended solids and stream discharge in both watersheds is well illustrated. The much higher stream discharge in the urban watershed was, as expected, associated with much higher suspended-solids concentrations. The dissolved constituents, of which iron and ortho phosphorous are shown in Fig. 2, demonstrated an inverse relation with stream discharge in both watersheds. The peak in ortho phosphorus concentration prior to peak stream discharge in the forested watershed is a frequently recurring feature in both watersheds, and is probably related to the first flushing of accumulating surfaces and soil moisture. Fredriksen (1972) noted higher concentrations of dissolved organic nitrogen on the rising limb of a storm hydrograph than on the falling limb and also attributed this initial rise in concentration to flushing of available sources within the vegetation, soil, and atmosphere.

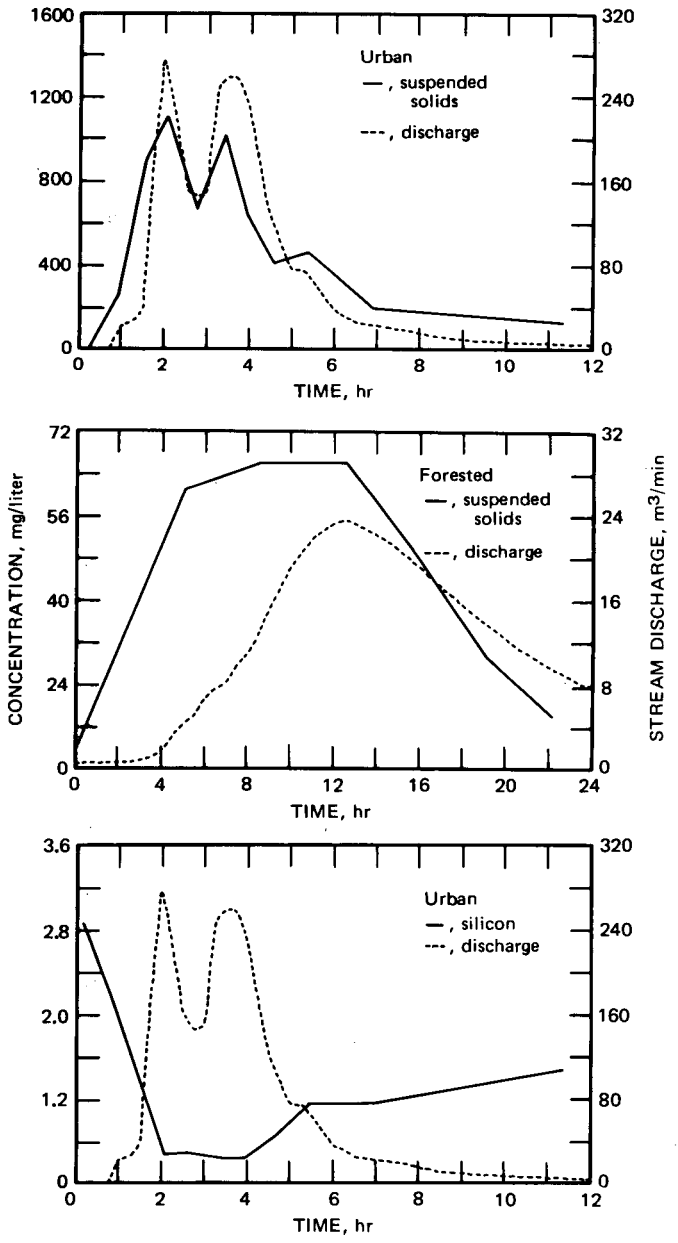


Fig. 2 Comparison of stream discharge and concentrations of suspended solids, silicon, and ortho phosphate–phosphorus vs. time in the two experimental watersheds for the storm of Nov. 21, 1973. Note variations in horizontal (time) and vertical (discharge and concentration) scales between watersheds.

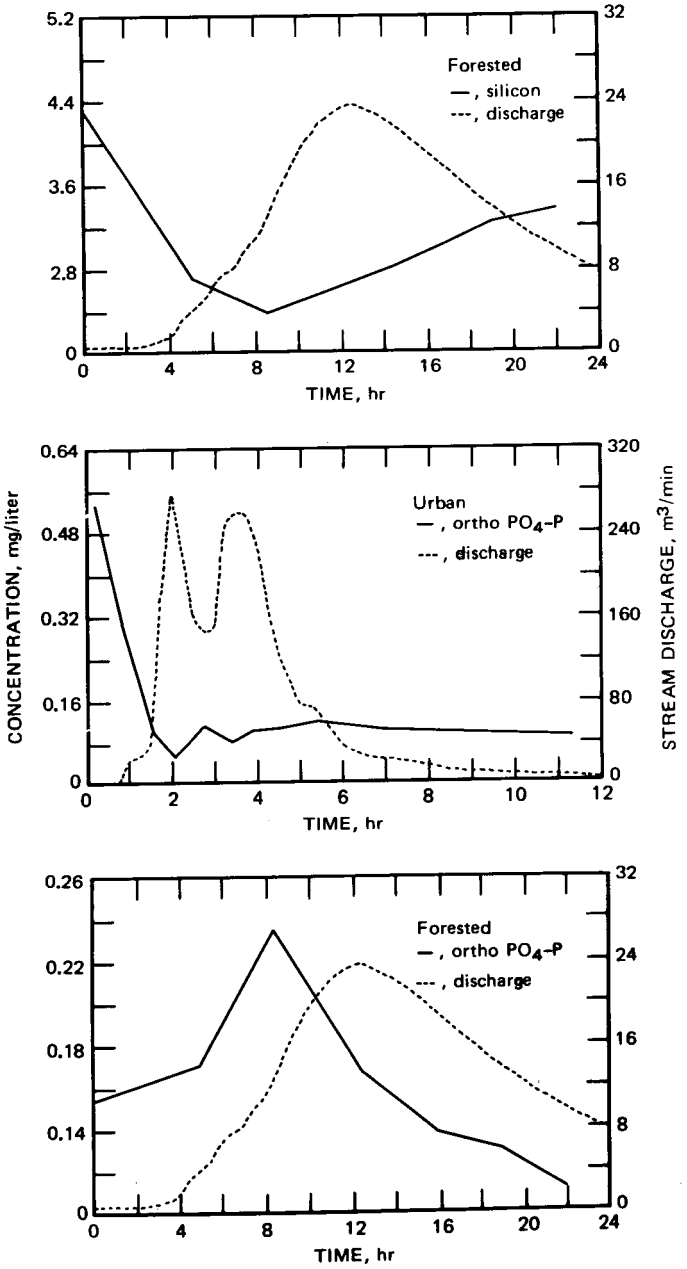


Fig. 2 Continued.

Stream and Constituent Discharge Relations

A comparison of stream and constituent discharge as a function of time, for the same storm as shown in Fig. 2, for the streams draining the two study watersheds is given in Fig. 3. In Fig. 3, stream and constituent discharge have been normalized by expressing quantities transported in 15-min intervals as percentages of the total storm load and plotting the percentages against time. This method permitted convenient comparison of stream and constituent discharge within a watershed and also provided a convenient means of comparing the two watersheds with respect to the relative magnitude and temporal distribution of both stream and constituent discharge.

Figure 3 clearly demonstrates that, although concentrations of dissolved constituents were generally *inversely* related to stream discharge, export of dissolved materials was *directly* related to stream discharge. Thus, although the lowest concentrations of dissolved constituents occurred near peak stream discharge, the maximum discharge of any dissolved constituent very closely corresponded to the maximum stream discharge in both watersheds. Stream discharge was thus the overwhelming factor governing export. Related to this observation, Taylor, Edwards, and Simpson (1971) and Ryden, Syers, and Harris (1972) found that the export of selected dissolved substances (phosphorus and nitrogen) from watersheds was more dependent on streamflow than on variations in concentrations. Figure 3 also illustrates the striking contrast in the relative magnitude and temporal distribution of both stream and constituent discharge between the two watersheds. Much greater proportions of the total storm loads of water and all constituents were transported during the near-peak intervals in the urban watershed. Since the peak stream and constituent discharges were higher and more flashy in the urban watershed, the period of storm flow began sooner and was considerably shorter in duration. Kluesener and Lee (1974) reported very similar characteristics for urban storm discharge in Madison, Wis.

Comparison of Cumulative Loads

Table 2 statistically summarizes water and cumulative constituent loads for the storm events sampled in this study. Although the standard deviations and ranges in this table indicate considerable variability within each watershed and overlap between watersheds, the mean loads rather accurately express observed relative differences in cumulative storm loads on an individual storm basis. With the exception of silicon, the mean cumulative loads of all constituents, particularly suspended solids and TDS, were much greater in the urban watershed.

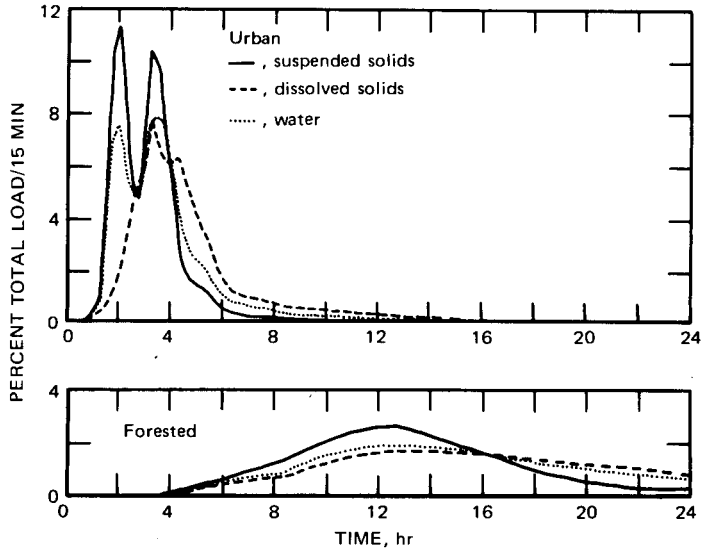
Total storm loads of suspended solids and dissolved silicon were highly correlated (Table 3) with total volume of storm flow, and equivalent loads of water always exported higher loads of dissolved silicon in the forested watershed

TABLE 2

COMPARISON OF CUMULATIVE STORM LOADS FOR THE URBAN AND FORESTED WATERSHEDS

Parameter	Load, urban (N = 13)*			Load, forested (N = 8)*			Mean urban load/ Mean forested load
	Mean	SD	Range	Mean	SD	Range	
Discharge, 10^3 liters	18,880	16,482	459–49,252	7482	5387	2360–18,100	2.52
Suspended solids, kg	11,655	11,781	23–34,479	288	292	59–890	40.47
Dissolved solids, kg	4,107	4,722	59–16,469	316	170	142–580	13.00
Silicon, kg	18.48	14.50	1.152–42.133	24.02	14.95	9.17–52.16	0.77
NO_3–N, kg	1.98	2.32	0.028–7.607	0.41	0.23	0.107–0.734	4.83
NO_2–N, kg	0.14	0.22	0.002–0.759	0.017	0.017	0.005–0.053	8.24
NH_3–N, kg	1.46	1.27	0.034–4.01	0.47	0.40	0.085–1.236	3.11
Ortho PO_4–P, kg	1.22	1.43	0.31–4.78	0.74	0.95	0.156–2.88	1.65
Dissolved P, kg	1.77	1.79	0.048–5.56	0.98	1.00	0.34–2.98	1.81

*N = number of storm events included.



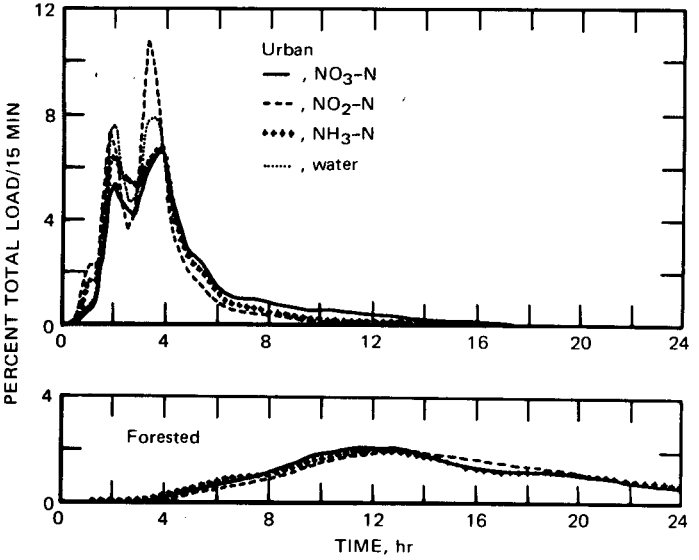


Fig. 3 Comparison of the percent total loads of water, suspended and dissolved solids, dissolved inorganic nitrogen species, dissolved silicon, and dissolved phosphorus transported in 15 min vs. time for the two experimental watersheds for storm of Nov. 21, 1973.

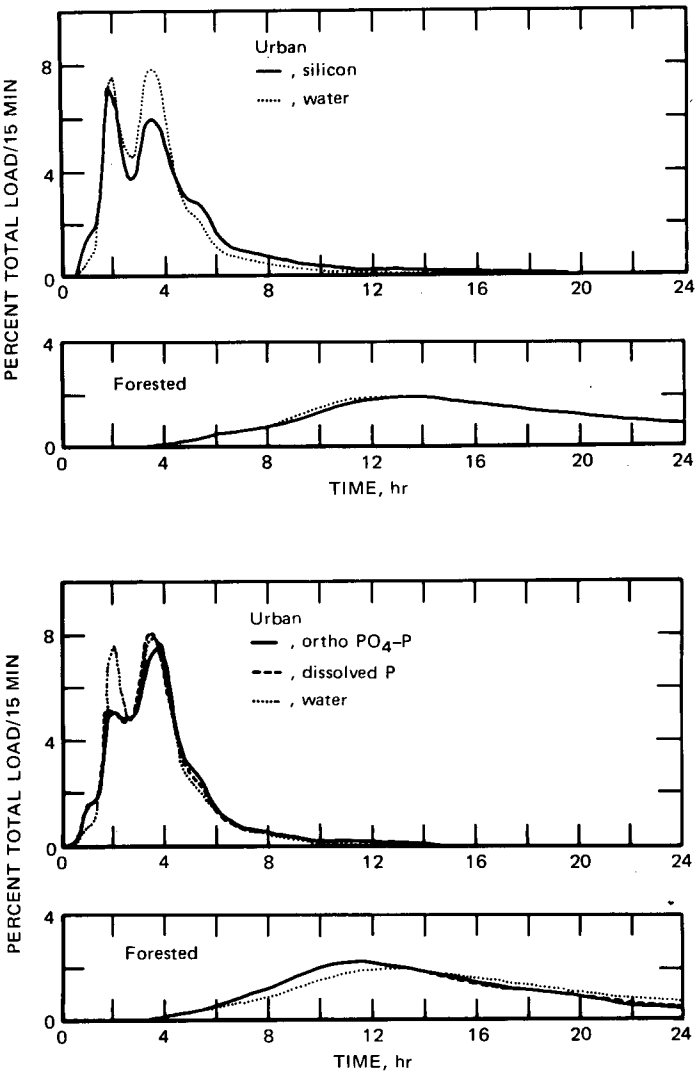


Fig. 3 Continued.

TABLE 3

CORRELATION MATRICES* FOR SELECTED HYDROLOGIC AND METEOROLOGIC FACTORS AND TOTAL STORM LOADS OF SELECTED CONSTITUENTS FOR THE URBAN (LOWER LEFT, N = 13) AND FORESTED (UPPER RIGHT, N = 8) WATERSHEDS

	Vol. of stream discharge	Peak discharge	Amount of rain	Intensity of rain	Duration of rain	Days since last rain	Suspended solids	Dissolved solids	Silicon	NO_3-N	NO_2-N	NH_3-N	Ortho PO_4-P
Vol. of stream discharge		[0.99]	[0.88]	0.57	0.24	0.38	[0.91]	[0.90]	[0.99]	[0.84]	0.18	[0.92]	[0.90]
Peak discharge	[0.79]		[0.91]	0.54	0.35	0.33	[0.88]	[0.91]	[0.99]	[0.90]	0.30	[0.96]	[0.91]
Amount of rain	[0.88]	[0.71]		0.75	0.23	0.45	[0.85]	0.78	[0.87]	0.71	0.18	[0.89]	[0.99]
Intensity of rain	0.37	0.63	0.53		−0.41	0.41	0.72	0.33	0.51	0.17	−0.30	0.47	0.77
Duration of rain	0.62	0.31	0.65	−0.25		−0.31	−0.08	0.46	0.32	0.69	[0.91]	0.49	0.15
Days since last rain	0.16	0.17	0.18	0.18	0.00		0.62	0.17	0.30	0.06	−0.52	0.29	0.53
Suspended solids	[0.95]	[0.77]	[0.82]	0.35	0.56	0.36		0.67	[0.86]	0.63	−0.10	0.82	[0.90]
Dissolved solids	[0.70]	[0.78]	0.50	0.57	0.07	0.16	[0.72]		[0.94]	[0.83]	0.30	0.81	0.75
Silicon	[0.96]	[0.87]	[0.85]	0.41	0.59	0.04	[0.90]	[0.72]		[0.87]	0.25	[0.92]	[0.87]
NO_3-N	[0.84]	[0.69]	0.59	0.42	0.25	−0.01	[0.77]	[0.89]	[0.82]		0.66	[0.93]	0.69
NO_2-N	−0.01	0.21	−0.26	−0.11	−0.18	−0.33	−0.05	0.01	0.02	0.04		0.48	0.10
NH_3-N	[0.93]	[0.75]	[0.76]	0.41	0.43	0.37	[0.93]	[0.69]	[0.82]	[0.79]	0.13		[0.89]
Ortho PO_4-P	[0.74]	0.42	[0.74]	−0.03	[0.78]	0.40	[0.77]	0.15	0.62	0.30	−0.07	[0.73]	

*Correlation coefficients significant at the 0.01 level are shown in brackets.

and higher loads of suspended solids in the urban watershed. For example, the slopes of regression lines forced through origin of the form $Y = mX$, where Y = load of silicon or suspended solids and X = load of water, suggested that for equivalent quantities of water approximately 3 times as much dissolved silicon was exported from the forested watershed as from the urban watershed and about 14 times as much suspended solids was exported from the urban watershed as from the forested watershed.

Since stream discharge was the transport agent, it was reasonable to consider whether the observed higher storm loads in the urban watershed could be accounted for simply by the observed higher cumulative stream discharge. If this explanation were the explanation, the ratios of cumulative loads of specific constituents from the two watersheds should closely approximate the corresponding ratio of cumulative stream discharge. Higher values of the ratio would suggest additional, or better sustained, sources of specific constituents in the urban watershed. Alternately, ratios less than that of stream discharge but greater than unity would suggest diminished sources of specific constituents in the urban watershed. Finally, a ratio less than unity would obviously indicate higher cumulative loads in the forested watershed and suggest sources of that constituent in the forested watershed, or unique biogeochemical processes, sufficient to overcome the stream discharge discrepancy between the watersheds. The load ratios given in Table 2 suggest that suspended solids, TDS, nitrate, nitrite, and ammonia have additional, or better sustained, sources in the urban watershed, that ortho and dissolved phosphorus have diminished sources in the urban watershed, and finally that silicon has sources in the forested watershed sufficient to produce higher cumulative loads in spite of the lower cumulative stream discharge.

Two factors clearly contribute to the large ratio of mean storm loads of suspended solids: (1) the capacity of streams to erode and transport particulate matter increases with increasing stream velocity (Leopold, Wolman, and Miller, 1964) and (2) the land-clearing and earth-moving activity associated with urbanization markedly increases the erodability of soils (Wolman and Schick, 1967; Rickert and Spieker, 1971). In this urban watershed natural stream channels have been locally modified to increase flow velocities, are generally underfit to handle the increased peak flows, and drain substantial areas where soils have been rendered unstable, often permanently, by urban construction.

We suggest, in relation to dissolved constituents, that differences between the two watersheds in the rates and major pathways of water movement are largely responsible for the higher cumulative load of silicon in the forested watershed and apparent diminished loads of ortho and dissolved phosphorus in the urban watershed. Since there are no point sources of these constituents, such as sanitary sewage outfalls in either watershed, dissolved phosphorus and silicon in stream waters are probably derived largely from dissolution of soil minerals and decomposition of organic detritus, with locally significant but diffuse

anthropogenic sources possible in the urban watershed. The increased overland flow of water associated with such cultural improvements as forest clearing and impervious paving reduces the quantity of water that passes through the litter and soil profile before entering surface streams and thus diminishes the intimate contact necessary for the dissolution of silicon- and phosphorus-containing minerals and detritus. Water that does pass through the soil profiles may do so at an accelerated rate and without having interacted with an organic litter layer, which is likely to be absent in urban watersheds. Gburek and Heald (1974) proposed similar explanations for observed fluctuations in phosphorus output from an agricultural watershed during storm hydroperiods.

Clearly atmospheric and diffuse anthropogenic sources may supply quantities of dissolved constituents sufficient to balance, or exceed, the diminished detritus–soil sources. The higher load ratios for all the dissolved nitrogen species (Table 2) suggests that atmospheric and/or anthropogenic sources have become significant in the urban watershed. Considering that rainfall and dry fallout were shown to be significant sources of dissolved nitrogen compounds (Brezonik et al., 1969; Junge and Werby, 1958), the higher ratios for these constituents suggest a possible diminished function of vegetative cover and soils in the urban watershed in controlling stream-water concentrations. In view of the reported compositions and quantities of substances swept and washed from typical urban streets (Sartor and Boyd, 1972), there is little doubt that anthropogenic sources can make significant contributions to the dissolved load of storm runoff in the urban watershed. Also, higher dissolved loads have been reported from lawns in residential areas (Beers, 1973).

Meteorologic and Hydrologic Factors Affecting Cumulative Storm Loads

As a first step toward identifying the meteorologic and hydrologic factors that may affect cumulative storm loads in each watershed, we computed correlation matrices for selected hydrologic and meteorologic factors and cumulative storm loads for each watershed (Table 3). Recognizing that the correlation coefficient measures only the strength of linear relations between variables and that many of the functional relations between these variables may be nonlinear, we did not expect this approach to be revealing of all interrelations. In particular, we were interested in discovering whether similar interrelations existed in both watersheds. Some of the statistically significant correlations that emerged from this analysis appeared to be functionally significant as well. These included the excellent correlations in both watersheds between volume of stream discharge and peak discharge, amount of rain, suspended solids, and all the dissolved constituents except nitrite; between peak discharge and amount of rain, suspended solids, and all the dissolved constituents except nitrite; and, finally, between several of the constituents. Correlations between dissolved loads (TDS, silicon, and nutrients) and the

hydrologic factors (volume and peak) were notably stronger in the forested watershed, suggesting that dissolved loads exported from this watershed are more closely regulated by hydrology.

It was surprising, in view of the findings of Pravoshinsky and Gatillo (1969) and Sartor and Boyd (1972), that "days since last rain," or antecedent conditions, did not show a significant correlation with any constituent load in the urban watershed. This correlation may be statistically insignificant in this case because: (1) the functional relation, if any exists, is nonlinear; (2) the urban watershed used in this study is not sufficiently urbanized to provide enough relative area of impervious surfaces on which to accumulate pollutants between rainfall events; and (3) the variability in total amount of rainfall, and thus volume of stream discharge, in this small population of storm events obscures the expected functional relation.

Significance of Storm Events in Materials Export

Storm flow has been shown by others (Leopold, Wolman, and Miller, 1964; Fredriksen, 1972; Bormann et al., 1974; Henderson and Harris, 1974) to be significant in the annual streamflow export of materials from watersheds. To assess the significance of storm flow in our experimental watersheds, we computed the number of days required to export equivalent amounts of selected constituents from each of our watersheds at base flow as are transported by an average storm (Table 4). The discharge of each constituent integrated over total storm hydroperiods was divided by the average daily load exported by base flow. Although only an approximation of the relative significance of storm flow in

TABLE 4

DAYS REQUIRED TO TRANSPORT EQUIVALENT AMOUNTS OF SELECTED CONSTITUENTS AT BASE FLOW AS ARE TRANSPORTED BY AN AVERAGE STORM

Constituent	Urban watershed	Forested watershed
Water	19.3	6.2
Suspended solids	4254 (11.6 years)	17
Dissolved solids	57.2	5.4
Silicon	7.7	5.1
NO_3–N	19.0	6.2
NO_2–N	14.0	1.2
NH_3–N	29.8	8.4
Ortho PO_4–P	18.2	5.5
Dissolved P	28.3	6.8

materials export from these watersheds, this table strongly suggests that urbanization has increased the relative importance of storm flow in the materials loading of the receiving aquatic system (Lake Jackson). If consideration is given to the seasonality in the frequency of storm events in these watersheds, the wetter summer and winter months represent periods of probable maximum influence of storm flow on materials export, particularly from the urban watershed.

CONCLUSIONS

This study has demonstrated some of the ways that urban development in a watershed may result in changes in the quantity and quality of stream runoff, in the total export of both suspended and dissolved constituents, and in the temporal distribution of exports. Assuming that the two watersheds used in this study are truly comparable in all respects except land use, several conclusions related to effects of urban development in one of them are apparent. Urbanization has:

1. Increased peak stream discharge.
2. Increased total volume of stream discharge.
3. Increased mean concentrations of dissolved solids (TDS), nitrate, and ammonia under all streamflow conditions.
4. Decreased mean concentrations of dissolved silicon under all streamflow conditions.
5. Decreased mean concentrations of suspended solids, ortho phosphorus, and total dissolved phosphorus under low streamflow conditions.
6. Increased mean concentrations of suspended solids, dissolved solids, nitrate–N, nitrite–N, ammonia–N, and ortho phosphorus under storm-flow conditions.
7. Increased variability in the composition of stream waters under all flow conditions.
8. Increased export rates of all dissolved and suspended constituents during storm events.
9. Increased total storm export of all dissolved and suspended constituents except dissolved silicon.
10. Increased relative significance of storms as transport mechanisms.

The study suggested that changes in hydrology associated with urban development, i.e., in streamflow rate, total volume of streamflow, and relative significance of various pathways of water movement, as well as increases in diffuse anthropogenic inputs, were responsible for observed differences in export of suspended solids and dissolved nutrients.

Results in this paper have important implications for watershed management. First, water-quality criteria for urban runoff should be based on both loading rates and concentrations, particularly where there is no outlet to the receiving aquatic system, such as with many lakes. Second, water-quality

monitoring systems in urban areas should always include provisions for sampling complete storm hydrographs because of the potentially increased importance of storm water in total export of substances in urban watersheds. Third, plans for beneficial uses of storm water (Mallory, 1973) may have to include differential collecting systems (i.e., roof runoff vs. street runoff) to be effective. Runoff from an entire urban watershed may often be too degraded and of such variable quality to be completely compatible with certain uses. Finally, techniques for management of storm-water quality are urgently needed to prevent undesirable changes in downstream ecosystems as a result of hydrochemical changes in runoff from urban watersheds.

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REFERENCES

American Public Health Association, 1971, *Standard Methods for the Examination of Water and Wastewater,* 13th ed., APHA, Washington, D. C.

AVCO Corporation, 1970, *Storm-Water Pollution from Urban Land Activity,* U. S. Department of the Interior, Federal Water Quality Administration, Superintendent of Documents, U. S. Government Printing Office, Washington.

Beers, G. D., 1973, *Management of Storm Water Runoff in Suburban Environments,* Project Completion Report, Office of Water Resources Research, Title II, Project No. C-2079, Engineering-Science Inc., Cincinnati, Ohio.

Bormann, F. H., G. E. Likens, T. G. Siccama, R. S. Pierce, and J. S. Eaton, 1974, The Export of Nutrients and Recovery of Stable Conditions Following Deforestation at Hubbard Brook, *Ecol. Monogr.*, 44: 255-277.

Brezonik, P. L., W. H. Morgan, E. E. Shannon, and H. D. Putnam, 1969, *Eutrophication Factors in North Central Florida Lakes,* University of Florida Industrial Engineering Experimental Station, Bulletin, Serial No. 134, Gainesville, Fla.

Bryan, E. H., 1972, Quality of Stormwater Drainage from Urban Land, *Water Res. Bull.*, 8: 578-588.

Dixon, W. J., 1973, *BMD: Biomedical Computer Programs,* University of California Publications in Automatic Computation: No. 2, University of California Press, Berkeley, Calif.

Fredriksen, R. L., 1972, Nutrient Budget of a Douglas Fir Forest on an Experimental Watershed in Western Oregon, in *Research on Coniferous Forest Ecosystems—A Symposium,* J. F. Franklin, L. J. Dempster, and R. H. Waring (Eds.), pp. 115-131, Pacific Northwest Forest and Range Experiment Station, Portland, Ore.

Gburek, W. J., and W. R. Heald, 1974, Soluble Phosphate Output of an Agricultural Watershed in Pennsylvania, *Water Resour. Res.*, 10: 113-118.

Henderson, G. S., and W. F. Harris, 1974, An Ecosystem Approach to Characterization of the Nitrogen Cycle in a Deciduous Forest Watershed, in *Proceedings of the 4th North American Forest Soils Conference,* Quebec, Canada, August 1973, in press.

Hendry, C. W., Jr., and C. R. Sproul, 1966, *Geology and Groundwater Resources of Leon County, Florida,* Florida Geological Survey, Bulletin No. 47.

Johnson, P. L., and W. T. Swank, 1973, Studies of Cation Budgets in the Southern Appalachians on Four Experimental Watersheds with Contrasting Vegetation, *Ecology,* 54: 70-80.

Junge, C. E., and R. T. Werby, 1958, The Concentration of Chloride, Sodium, Potassium, Calcium, and Sulfate in Rainwater Over the United States, *J. Meteorol.*, 15: 417-425.

Kluesener, J. W., and G. F. Lee, 1974, Nutrient Loading from a Separate Storm Sewer Madison, Wisconsin, *J. Water Pollut. Contr. Fed.*, 46: 923.

Leopold, L. B., M. G. Wolman, and J. P. Miller, 1964, *Fluvial Processes in Geomorphology,* W. H. Freeman and Co., San Francisco.

Likens, G. E., F. H. Bormann, N. M. Johnson, D. W. Fisher, and R. S. Pierce, 1970, Effects of Forest Cutting and Herbicide Treatment on Nutrient Budgets in the Hubbard Brook Watershed Ecosystem, *Ecol. Monogr.*, 40: 23-47.

Mallory, C. W., 1973, *The Beneficial Use of Storm Water,* U. S. Environmental Protection Agency Research Report EPA-R2-73-139, Washington, D. C.

Pitt, R. E., and G. Amy, 1973, *Toxic Materials Analysis of Street Surface Contaminants,* U. S. Environmental Protection Agency, Research Report EPA-R2-73-283, Washington, D. C.

Pravoshinsky, N. A., and P. D. Gatillo, 1969, Determination of the Pollutional Effect of Surface Runoff, in *Advances in Water Pollution Research,* Proceedings of the 4th International Conference, pp. 187-195, Prague, S. H. Jenkins (Ed.), Pergamon Press, Inc., New York.

Rickert, D. A., and A. M. Spieker, 1971, *Real Estate Lakes,* U. S. Geological Survey, Circular No. 601-G.

Ryden, J. C., J. K. Syers, and R. F. Harris, 1972, *Nutrient Enrichment Potential of Urban Soils in the City of Madison,* Wisconsin Water Resources Center Technical Report.

Sartor, J. D., and G. B. Boyd, 1972, *Water Pollution Aspects of Street Surface Contaminants,* U. S. Environmental Protection Agency, Research Report EPA-R2-72-081, Washington, D. C.

Sylvester, R. O., 1961, Nutrient Content of Drainage Water from Forested, Urban, and Agricultural Areas, in *Algae and Metropolitan Wastes,* pp. 8-87, U. S. Public Health Transcript of 1960 Seminar, Taft Sanitary Engineering Publication No. SEC-TR-W61-3.

Symons, J. M., 1970, Urban Sources of Nitrate, in *Proceedings of the 12th Sanitary Engineering Conference,* University of Illinois Press, Urbana, Feb. 11–12, 1970, pp. 78-83.

Taylor, A. W., W. M. Edwards, and E. C. Simpson, 1971, Nutrients in Streams Draining Woodland and Farmland Near Coshocton, Ohio, *Water Resour. Res.*, 7: 81-89.

Weibel, S. R., R. J. Anderson, and R. L. Woodward, 1964, Urban Land Runoff as a Factor in Stream Pollution, *J. Water Pollut. Contr. Fed.*, 36: 914-924.

Wells, D. M., J. F. Anderson, R. M. Sweazy, and B. J. Claborn, 1973, *Variation of Urban Runoff Quality with Duration and Intensity of Storms: Phase II,* Office of Water Resources Research, Project No. B-104-TEX, Completion Report, Lubbock, Texas.

Whipple, W., J. V. Hunter, and S. L. Yu, 1974, Unrecorded Pollution from Urban Runoff, *J. Water Pollut. Contr. Fed.*, 46: 873.

Wolman, M. G., and Schick, A. P., 1967, Effects of Construction on Fluvial Sediment, Urban and Suburban areas of Maryland, *Water Resour. Res.*, 3: 451-464.

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