Dr-1802

ANL-75-3

art III

170

11-25-75

ANL-75-3

Part III

RADIOLOGICAL AND ENVIRONMENTAL RESEARCH DIVISION ANNUAL REPORT

Ecology

January—December 1974

MASTER

U of C-AUA-USERDA

ARGONNE NATIONAL LABORATORY, ARGONNE, ILLINOIS

Prepared for the U. S. ENERGY RESEARCH
AND DEVELOPMENT ADMINISTRATION
under Contract W-31-109-Eng-38

The facilities of Argonne National Laboratory are owned by the United States Government. Under the terms of a contract (W-31-109-Eng-38) between the U. S. Energy Research and Development Administration, Argonne Universities Association and The University of Chicago, the University employs the staff and operates the Laboratory in accordance with policies and programs formulated, approved and reviewed by the Association.

MEMBERS OF ARGONNE UNIVERSITIES ASSOCIATION

The University of Arizona
Carnegie-Mellon University
Case Western Reserve University
The University of Chicago
University of Cincinnati
Illinois Institute of Technology
University of Illinois
Indiana University
Iowa State University
The University of Iowa
Kansas State University
The University of Kansas
Loyola University
Marquette University
Michigan State University
The University of Michigan
University of Minnesota
University of Missouri
Northwestern University
University of Notre Dame
The Ohio State University
Ohio University
The Pennsylvania State University
Purdue University
Saint Louis University
Southern Illinois University
The University of Texas at Austin
Washington University
Wayne State University
The University of Wisconsin

NOTICE

This report was prepared as an account of work sponsored by the United States Government. Neither the United States nor the United States Energy Research and Development Administration, nor any of their employees, nor any of their contractors, subcontractors, or their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness or usefulness of any information, apparatus, product or process disclosed, or represents that its use would not infringe privately-owned rights. Mention of commercial products, their manufacturers, or their suppliers in this publication does not imply or connote approval or disapproval of the product by Argonne National Laboratory or the U. S. Energy Research and Development Administration.

Printed in the United States of America
Available from
National Technical Information Service
U. S. Department of Commerce
5285 Port Royal Road
Springfield, Virginia 22161
Price: Printed Copy $7.60; Microfiche $2.25

Distribution Category:
Environmental Control Technology
and Earth Sciences (UC-11)

ANL-75-3
Part III

ARGONNE NATIONAL LABORATORY
9700 South Cass Avenue
Argonne, Illinois 60439

RADIOLOGICAL AND ENVIRONMENTAL RESEARCH DIVISION ANNUAL REPORT

Ecology

January through December 1974

R. E. Rowland, Division Director
J. S. Marshall, Section Head

Preceding Report: ANL-8060, Part III, January-December 1973

FOREWORD

This was an eventful year for the Ecology Section. Sixteen new staff members were hired, and two new programs — both the offspring of our studies of fallout plutonium in the Great Lakes — were initiated. The purpose of the larger of the new programs is to assess the behavior of plutonium in a watershed that has received plutonium from a nuclear facility as well as from fallout. The smaller program was initiated to determine the chemical and physical forms in which transuranic elements exist in natural waters.

The ongoing Great Lakes Radioecology and Thermal Effects programs both expanded modestly in scope during 1974, and two new Great Lakes studies have been initiated. The first is an investigation of the role of phytoplankton and zooplankton in the processes of transport and removal of energy-related pollutants in the Great Lakes. The other, undertaken to complement our ongoing field studies, is a laboratory study of the behavioral responses of Great Lakes fish to thermal and related stimuli associated with once-through cooling systems.

Preliminary studies of the effects of sulfur dioxide on crop plants were completed. Further work along this line will be continued as a part of the program on the Impact of Fossil Fuel Utilization on Terrestrial Ecosystems.

Highlights of our research accomplishments during 1974 include encouraging preliminary results from the use of sediment traps at different depths in the water column in Lake Michigan. Material collected in the traps indicates that phyto- and zoodetritus are important components in vertical transport. Zooplankton fecal pellets contain high concentrations of the prevailing diatom species and accelerate the downward transport of phytodetritus. However, it is estimated that less than 5% of the annual diatom production accumulates in the permanent sediments. Results of initial studies of ^{238}Pu behavior in the Miami River watershed in Ohio have established spatial and temporal variations of ^{238}Pu in water, suspended sediment, and biota of the Great Miami River. A pronounced discrimination against ^{238}Pu was found in the aquatic food chain, similar to that reported for ^{239}Pu in the Great Lakes. Three types of fish tag (identification, temperature-sensitive, and radio transmitter) have provided new information on the migratory behavior of large Lake Michigan salmonids and on their temperature selection and their residence times in a power-plant discharge. These findings have been related to growth rate, ^{137}Cs uptake, and rate of change of body temperature. The details of these and other results of research by the Ecology Section during 1974 are given in the body of this report. Publications by the staff of the Ecology Section during 1974 are listed at the end.

TABLE OF CONTENTS

NON-NUCLEAR STUDIES

NUCLEAR STUDIES

THERMAL STUDIES

THIS PAGE

WAS INTENTIONALLY

LEFT BLANK

ROLE OF COPEPOD FECAL PELLETS IN THE VERTICAL TRANSPORT OF FRESHWATER DIATOMS

J. G. Ferrante, J. I. Parker, and J. S. Marshall

Introduction

Recent studies on material transport systems in the ocean indicated the potential importance of planktonic crustacean fecal pellets as a downward transport mechanism.(1,2) However, little information is available from the freshwater environment.

Schrader(3) observed diatom frustules in fecal pellets collected at various depths in the Baltic Sea. He also proposed using the diatom frustule ornamentation as an indicator of dissolution of free settling diatoms. The presence of whole and fragmented diatom frustules in zooplankton fecal pellets and the accelerated sinking rate of the pellets relative to the individual phytoplankton cells(4,5) may account for the rapid removal of pelagic diatoms from the surface water in lakes.

The present study was initiated to evaluate the significance of zooplankton fecal pellets in the sedimentation and dissolution of freshwater diatoms. The study was conducted as part of a continuing investigation of biological transport processes in Lake Michigan.

Methods

Water for the collection of fecal pellets was pumped from the top of the epilimnion, from the metalimnion, and from the hypolimnion. A minimum of 200 liters of water was filtered through 35 μ netting, and material collected on the net was placed in sample bottles. Additional samples were collected in a 30-cm closing net (35 μ). A glutaraldehyde sodium cacodylate solution was added to the samples so that the final concentration of glutaraldehyde was approximately 2% by volume. The preserved samples were refrigerated and returned to the laboratory for analysis.

In the laboratory, the pellets were separated from the samples with a micropipette, and 5 to 10 specimens were placed on a 13-mm Nuclepore

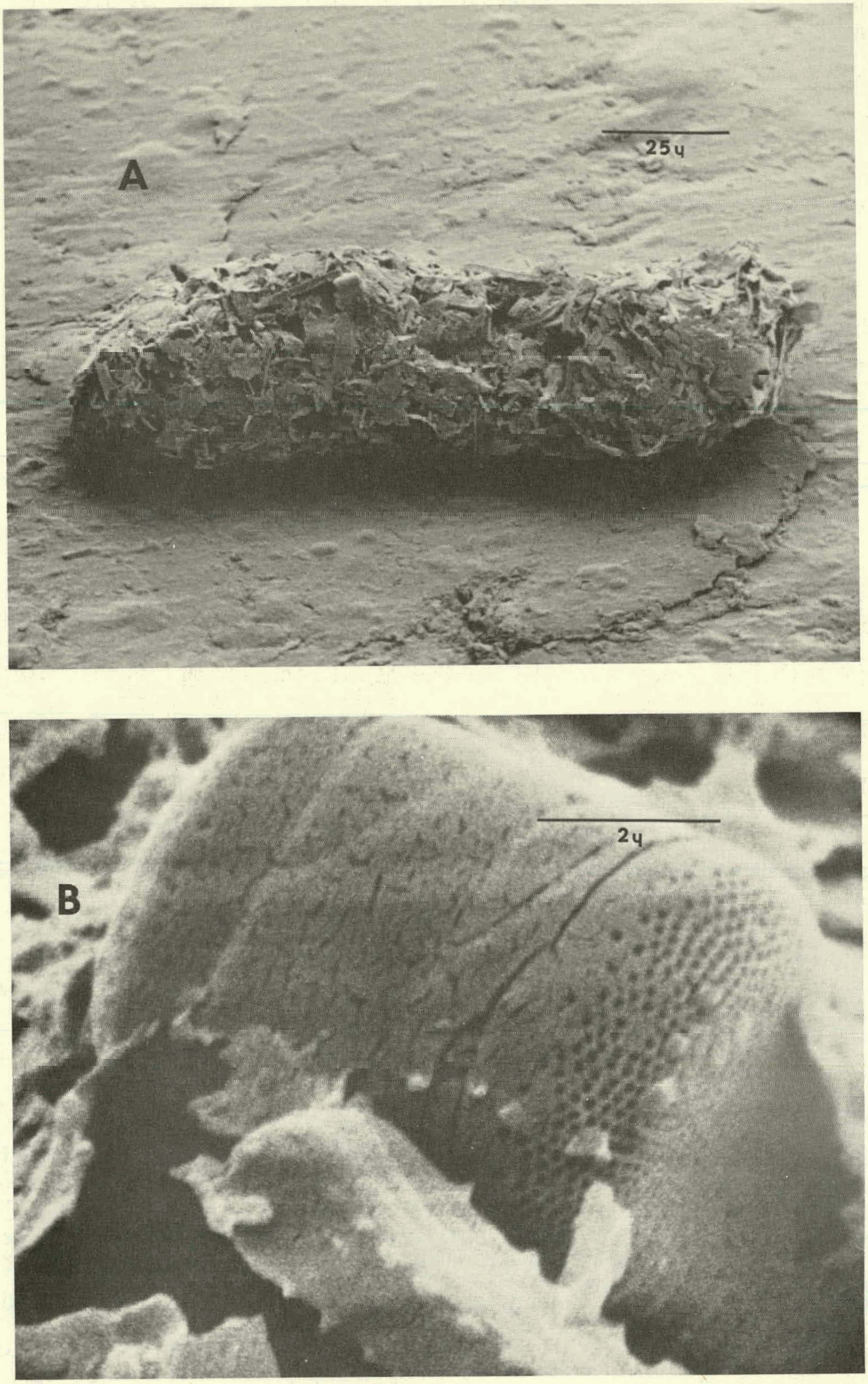


FIG. 1.--A. Calanoid fecal pellet from surface water of Lake Michigan. Peritrophic membrane removed by ashing, exposing diatom fragments within the pellet. B. Enlarged section of Fig. 1A, showing fragments of the diatom *Tabellaria* and *Asterionella* sp.

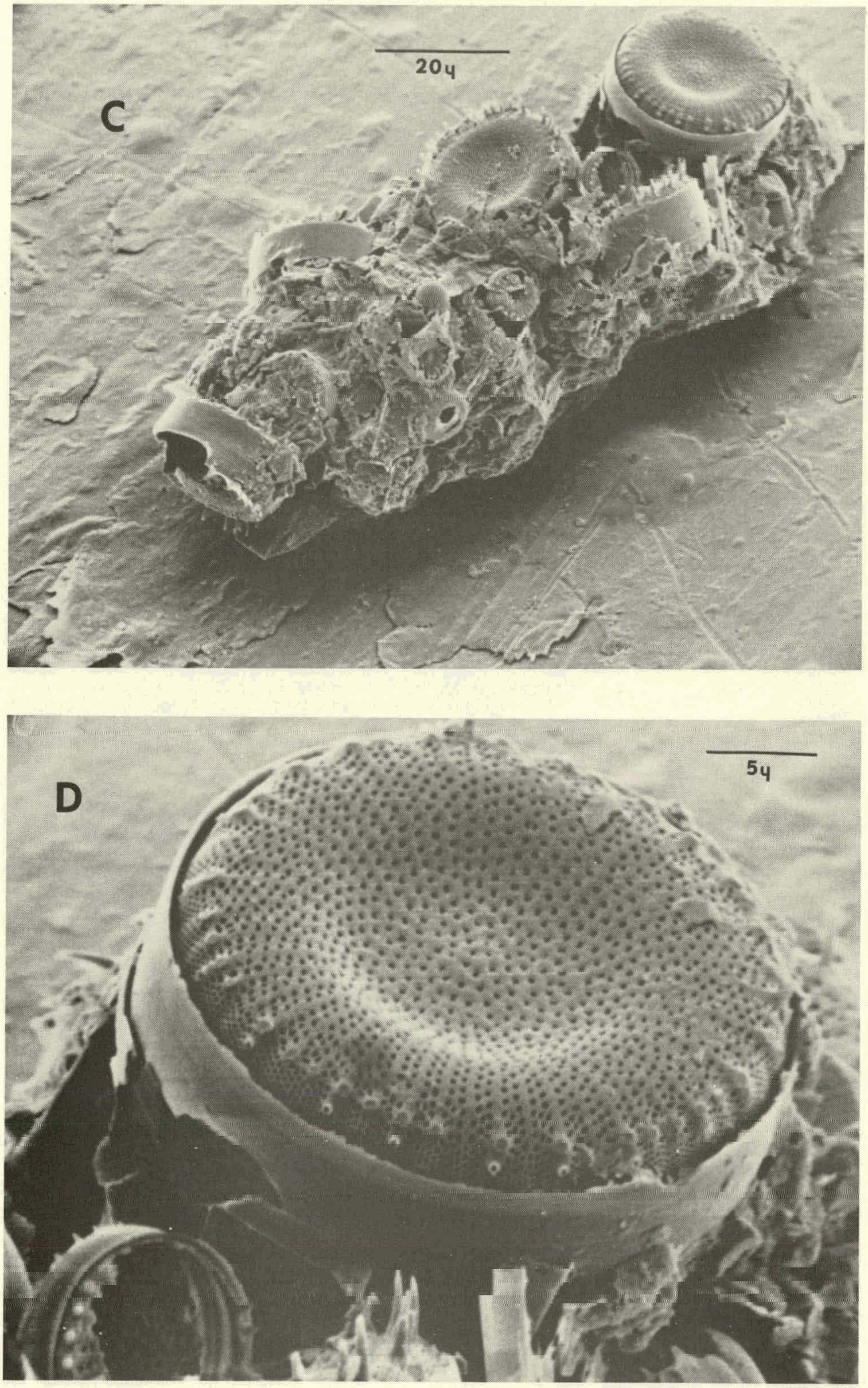


FIG. 1.--C. Calanoid pellet containing large fragments of the diatom <u>Stephanodiscus</u> (peritrophic membrane of pellet removed by ashing). D. Enlarged section from Fig. 1C of <u>Stephanodiscus</u>.

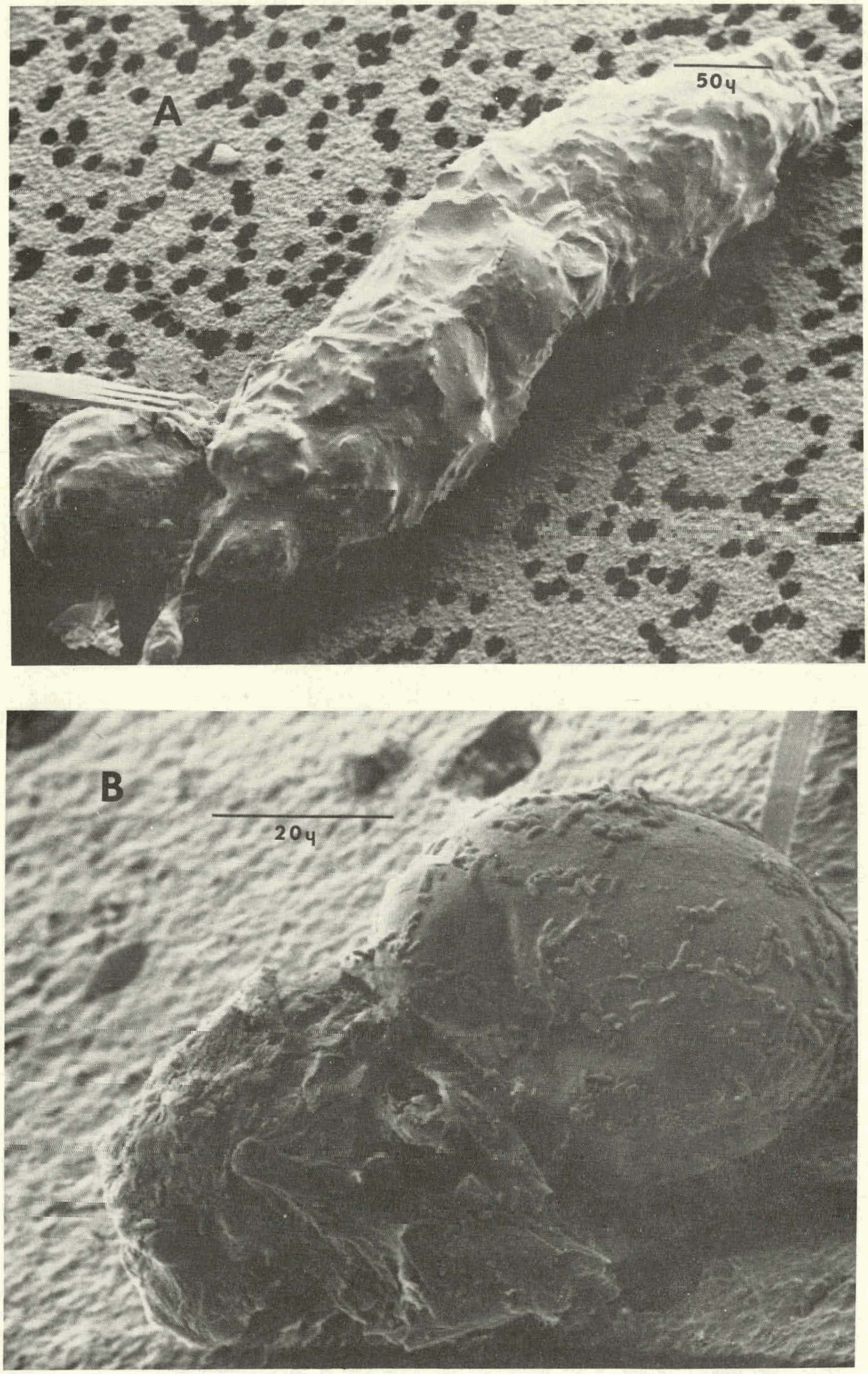


FIG. 2.--A. Intact peritrophic membrane on calanoid fecal pellet collected in vitro. B. Bacterial colonies attached to peritrophic membrane of pellet collected in situ at the epi-metalimnion interface.

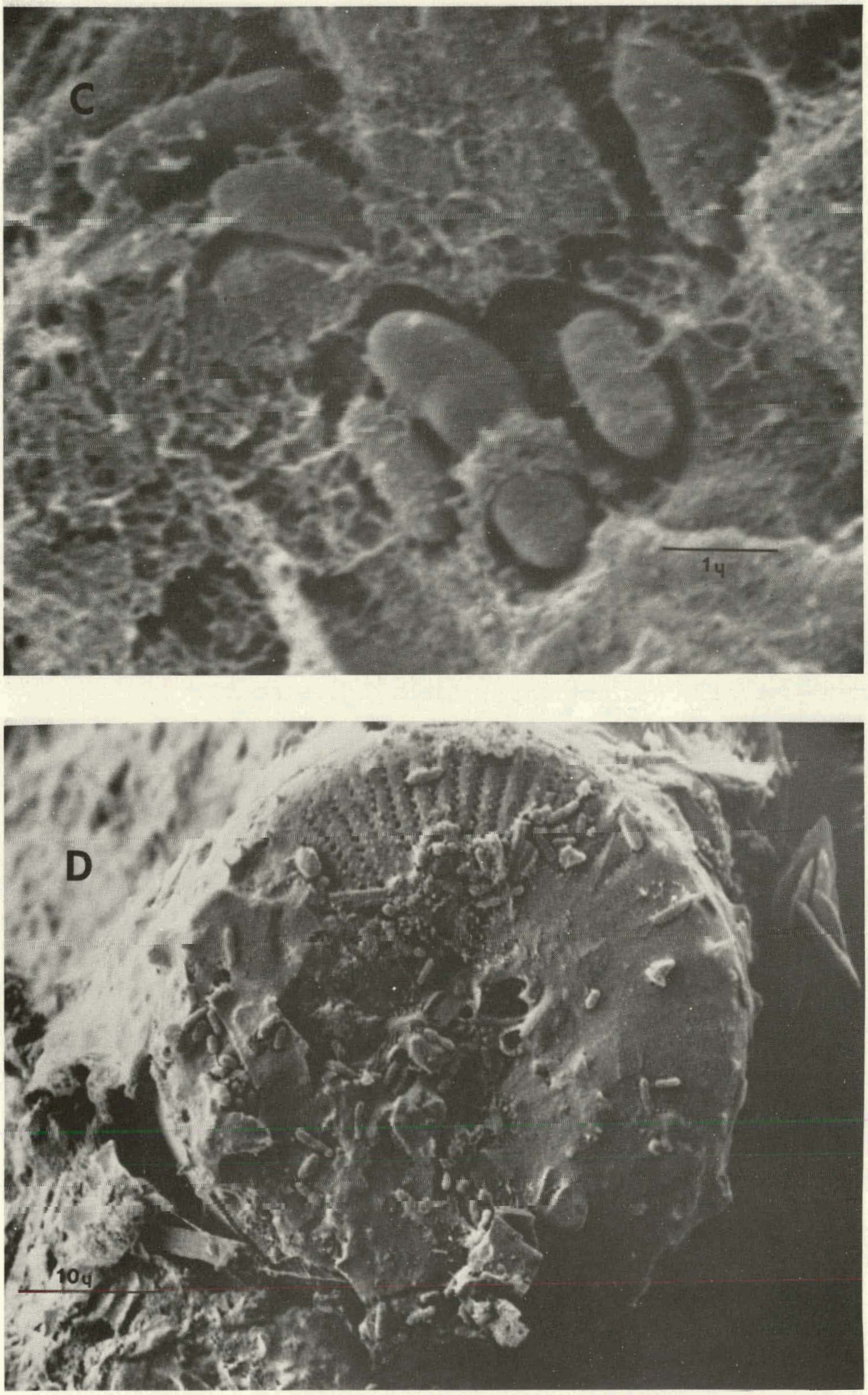


FIG. 2.--C. Bacterial decomposition of the peritrophic membrane. D. Bacterial removal of the membrane illustrating exposure of diatom frustule to dissolution.

membrane filter (3 μ). Each filter was stapled between two 24-mm Whatman filter papers and washed in two baths of sodium cacodylate (0.4 m) buffer and two baths of deionized water. The filters were then passed through an ethyl alcohol dehydration and Freon series, 25, 50, 75, 90, 100% and 20, 40, 60, 80, 100%, respectively. The filters were placed in a Bomar 900 critical point drying apparatus and dried in a Freon system.(6) Some specimens were transferred directly from field samples to specimen stubs and ashed for 40 min at 500° C to remove the peritrophic membrane. All specimens were coated with gold in a Kinney evaporator system and observed on a Cambridge Stereoscan Mark II scanning electron microscope (SEM).

Results

Fecal pellets ranged from 80 to 120 μ in length, and from 30 to 50 μ in width. The size and shape of the pellets examined from in situ samples correspond with calanoid copepod pellets collected in vitro.

Photomicrographs of fecal pellets illustrated the abundance of centric and pennate diatoms (Fig. 1B and 1D) in the diet of pelagic zooplankton in Lake Michigan (Fig. 1A). Fragments of Melosira spp., Stephanodiscus spp., Cyclotella spp., Tabellaria spp., Asterionella spp., Synedra spp., and Fragilaria spp., have been observed in fecal pellets. Some pellets contained slightly damaged frustules, but the majority of frustules showed signs of extensive mechanical damage (Fig. 1C).

The peritrophic membrane, found on all calanoid copepod pellets observed, is secreted by the epithelium of the posterior half of the mid gut.(7) Bacteria were not observed on the peritrophic membrane of pellets collected in vitro (Fig. 2A). However, pellets collected in situ had bacterial colonies on the membrane (Fig. 2B). This suggests that these bacteria originate from the environment rather than from the gut. Bacteria appear to attach themselves to the membrane after the pellet is expelled into the water. Pellets collected from the metalimnion and hypolimnion had large colonies of bacteria growing on the membrane surface and showed extensive bacterial degradation of the membrane (Figs. 2C and 2D).

Discussion

Copepod fecal pellets have a relatively impermeable peritrophic membrane, which retards the rate of dissolution of diatom fragments as the pellets rapidly sink. SEM photomicrographs indicated that bacterial decomposition of this membrane exposes the frustules to dissolution and suggests eventual dispersion in the water column.

The significance of copepod fecal pellets as a vertical transport mechanism for pelagic diatoms has been postulated by Schrader.(3) He suggests that intact pellets may reach the surficial sediment in the Baltic Sea. Parker and Edgington(8) observed no fecal pellets in surficial sediment samples from Lake Michigan. They suggest that less than 1% of the estimated annual diatom crop settles to the sediment.

We conclude that zooplankton fecal pellets are an important mechanism for accelerated transport of diatom frustules from the epilimnion of Lake Michigan. However, most of the fecal pellets do not become incorporated intact in the permanent sediments. Zooplankton grazing fractures most ingested diatom frustules, and subsequent bacterial degradation of the peritrophic membrane exposes the fragments to dissolution within the water column.

The importance of fecal pellets produced by hypolimnetic zooplankton in accelerating transport of detritus in the hypolimnion is being investigated.

References

1. Lowman, F. G., T. P. Rice, and F. A. Richards. Accumulation and redistribution of radionuclides by marine organisms. Radioactivity in the Marine Environment, Nat. Acad. Sci. U.S., Washington, D.C., 1971, Chap. 7, pp. 161–199.
2. Osterberg, C., A. Cary, and H. Curl. Acceleration of sinking rates of radionuclides in the ocean. Nature 200, 1276–1277 (1963).
3. Schrader, H. J. Fecal pellets in sedimentation of pelagic diatoms. Science 174, 55–57 (1971).
4. Smayda, T. Some measurements of the sinking rate of fecal pellets. Limnol. Oceanogr. 14, 621–625 (1969).
5. Smayda, T. The suspension and sinking of phytoplankton in the sea. Oceanogr. Mar. Biol. Ann. Rev. 8, 353–414 (1970).
6. Cohen, A. L., D. P. Marlow, and G. E. Garner. A rapid critical point method using fluorocarbons (Freons) as intermediate and transitional fluids. J. Microscopie 7, 331–342 (1968).

7. Gould, T. D. A peritrophic membrane in calanoid copepods. Nature 179, 325–326 (1957).
8. Parker, J. I. and D. N. Edgington. Distribution of diatom frustules in Lake Michigan sediment cores. This report.

VERTICAL TRANSPORT OF PARTICULATE MATERIAL IN LAKE MICHIGAN BY THE LORICA OF CODONELLA CRATERA

J. I. Parker and J. G. Ferrante

Surveys of protozoa in the Laurentian Great Lakes report the abundance of Codonella cratera, a ciliate of the order Tintinnida. Leach(1) observed 25 to 38 per liter in the Ontario waters of Lake St. Clair, and Davis(2) reported a maximum of 8.8 per liter in the east basin of Lake Erie during October. We have observed Codonella cratera Vorce(3) in both the water column and sediment of Lake Michigan. However, the scant information on their abundance reveals little about their significance to the plankton community.

Codonella has a vase-shaped lorica, which is divided into a collar and basal portion. A crown of perioral cilia, membranelles, and ciliary membrane form a feeding apparatus, which protrudes beyond the aperture at the oral end of the lorica. The lorica is composed of secreted organic material (xanthoproteins), which is discharged through the gullet after cell division and shaped by the oral apparatus.(4) The surface of the lorica is frequently covered with material referred to by Hall as "foreign particles." Mackinnon and Hawes(5) describe the coating of foreign particles as arenaceous or "sandy" material. However, this coating has not been extensively described. The objective of this investigation is to describe the particulate matter of the lorica, to illustrate the abundance of Codonella, and to discuss their possible significance in Lake Michigan.

A 30-cm diameter closing net with a mesh size of 35μ was hauled twice, once from 30 to 0 m and again from 75 to 55 m before closing. Specimens were removed from the samples with a micropipette, preserved in 2.0% glutaraldehyde solution buffered with sodium cacodylate, and air dried on aluminum SEM stubs. Specimens were coated with gold in a Kinney evaporator and observed on a Cambridge Stereoscan Mark II scanning electron microscope. Abundance was measured by counting aliquots of the net samples with an inverted Zeiss microscope.

The lorica ranges from 50 to 65μ long and was approximately 40μ wide. The organic matrix of the lorica is approximately 3 to 5μ thick, and foreign particles are attached to and imbedded within the matrix. Particle size ranged from less than 1.0μ to a maximum size of 10.0μ in broadest dimension. The upper limit of particle size in all lorica observed was uniform. This may suggest that application of the particles to the lorica is an active process by the animals and not a random process of adhesion by local particulate matter. Perhaps the oral apparatus is capable of manipulating particles of a particular size range.

Mineral fragments were the major group of particles; both granular and flat clay-like material was observed (Fig. 1B). Whole diatom frustules and fragments of frustules constituted the second category. Whole specimens of the species of small diatom (less than 8.0μ in diameter) Cyclotella pseudostelligera Hust. were observed (Fig. 1A). Gold(6) suggests that some species of tintinnids attach only specific species of diatoms to their lorica. Unidentified fragments of other diatoms were also observed. Hall(4) describes the diet of Codonella as organic detritus and bacteria, but perhaps the smaller species of diatoms are also consumed. Gold(7) reported ingestion of algal nannoplankton by a marine tintinnid.

Particles of uncertain origin were also observed. Distinctive small spheres that ranged from 1.0 to 4.0μ in diameter were seen on some lorica (Fig. 1C). Similar spheres are frequently observed in other plankton samples from Lake Michigan, but their origin is unknown.

Initial estimates of concentration and distribution range from 16 organisms per liter in surface waters to 6 organisms per liter in the deeper sample collected in the central portion of Lake Michigan during January. In contrast, approximately 3.0 zooplankton crustaceans per liter were observed in the same surface water sample. Although Codonella are smaller than most zooplankton their greater numerical abundance during certain seasons suggests their importance in the plankton community. Occurrence of the diatom-containing lorica in sediment illustrates that Codonella remove diatoms from the water column. In addition, the particulate material on the lorica may be important

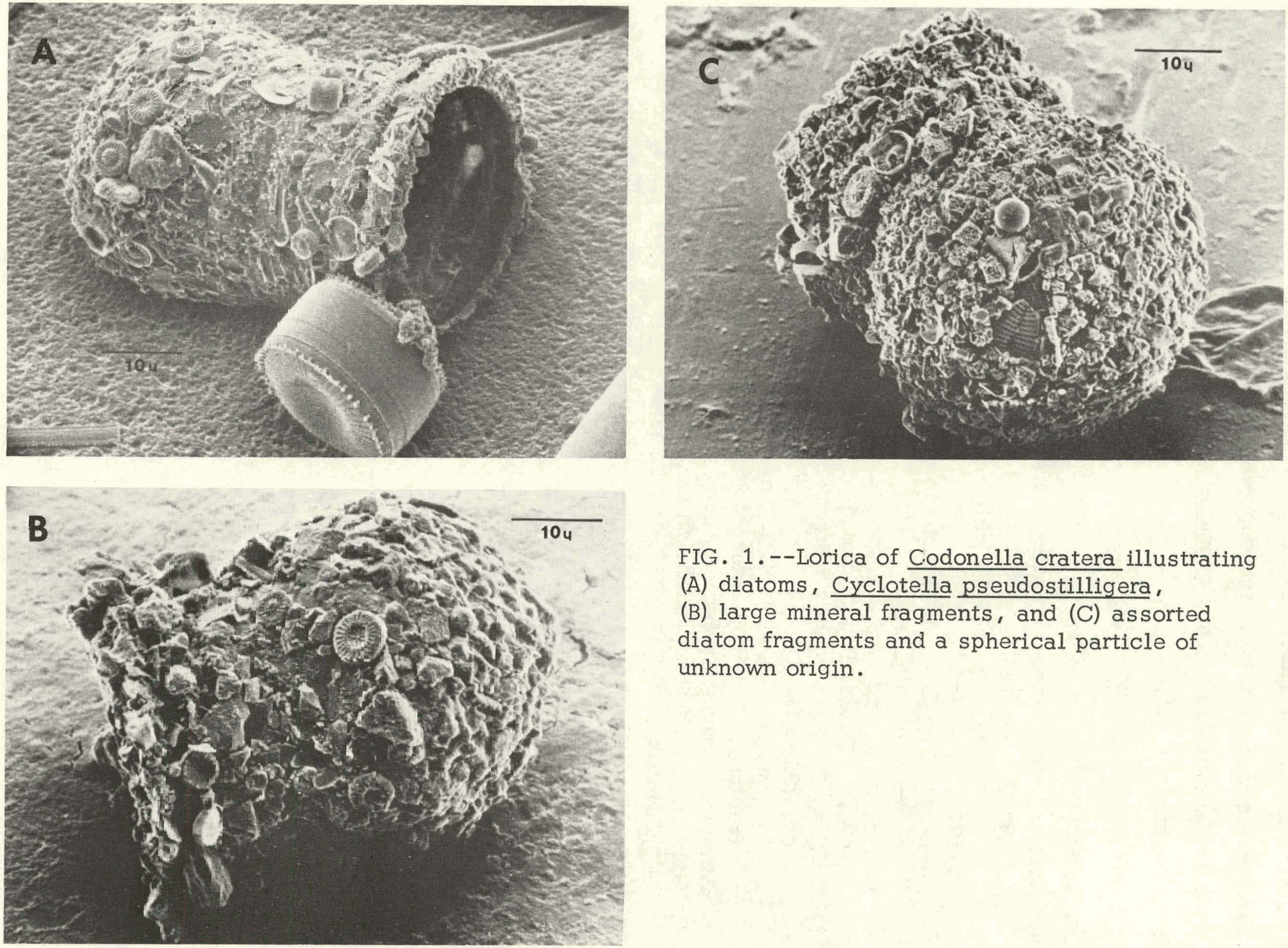


FIG. 1.--Lorica of Codonella cratera illustrating (A) diatoms, Cyclotella pseudostilligera, (B) large mineral fragments, and (C) assorted diatom fragments and a spherical particle of unknown origin.

as sorptive sites for transport of toxic materials from the surface water. Continued investigation of their abundance and feeding habits will be required to evaluate the significance of Codonella cratera as a transport mechanism in Lake Michigan.

References

1. Leach, J. H. Seasonal distribution, composition, and abundance of zooplankton in Ontario waters of Lake St. Clair. Proc. 16th Conf. Great Lakes Res., Int. Assoc. Great Lakes Res., Ann Arbor, Michigan, 1973, pp. 54–64.
2. Davis, C. C. Seasonal distribution, constitution, and abundance of zooplankton in Lake Erie. J. Fish. Res. Bd. Canada 26, 2459–2476 (1969).
3. Kofoid, C. A. and A. S. Campbell. Conspectus, Tintinnopsis. Univ. Calif., Davis, Publ. Zool. 34, 1 (1929).
4. Hall. R. P. Protozoology. Prentice-Hall, Inc., New York, 1953, pp. 391–393.
5. Mackinnon, D. L. and R. S. J. Hawes. An Introduction to the Study of Protozoa. Oxford University Press, London, 1961, pp. 360–363.
6. Gold, K. Personal communication.
7. Gold, K. Some observations on the biology of Tintinnopsis sp. J. Protozool. 15 (1), 193–194 (1968).

DISTRIBUTION OF DIATOM FRUSTULES IN LAKE MICHIGAN SEDIMENT CORES

J. I. Parker and D. N. Edgington

Introduction

Schelske and Stoermer(1) suggest increased phosphorus input in Lake Michigan has stimulated diatom production. The average algal standing crop (primarily diatoms) at the Chicago Water Filtration Plant has changed from 850 cells/ml in 1926(2) to 2000 cells/ml in 1972.(3) Recent changes in species composition show a reduction in the proportion of diatoms due to increased concentrations of less desirable green and blue-green algal species.(1) Decreasing dominance of diatoms appears to be the result of enhanced dissolved silica utilization with a resulting decline in dissolved silica.(4) Powers and Ayers(5) have shown decreasing silica levels for Lake Michigan in data from the past 40 years, but the reasons for the reduction have not been explained. A possible explanation for the silica reduction may be loss through sedimentation of siliceous diatom frustules or recent changes in the silica-sediment recycling mechanism.

Evaluation of diatom frustules in sediment cores has provided some insight into the changes in the trophic nature of other large lakes. Stockner and Benson(6) investigated diatom remains in Lake Washington sediment and found a strong correlation between changes in diatom composition and cultural eutrophication. Similar data were shown by Duthie and Sreenivasa(7) from Lake Ontario cores. However, little or no information is available on the distribution or concentration of diatom frustules in Lake Michigan sediment or their relation to silica recycling and eutrophication. The objectives of this investigation were to measure the concentration of diatom frustules in Lake Michigan sediment cores and to consider their role in silica recycling.

Methods

We measured the concentration of diatom frustules as a function of depth in 14 selected sediment cores (Fig. 1). The cores (sectioned at 0.5- to 2.0-cm intervals) had previously been dated by the ^{210}Pb and ^{137}Cs technique.(8)

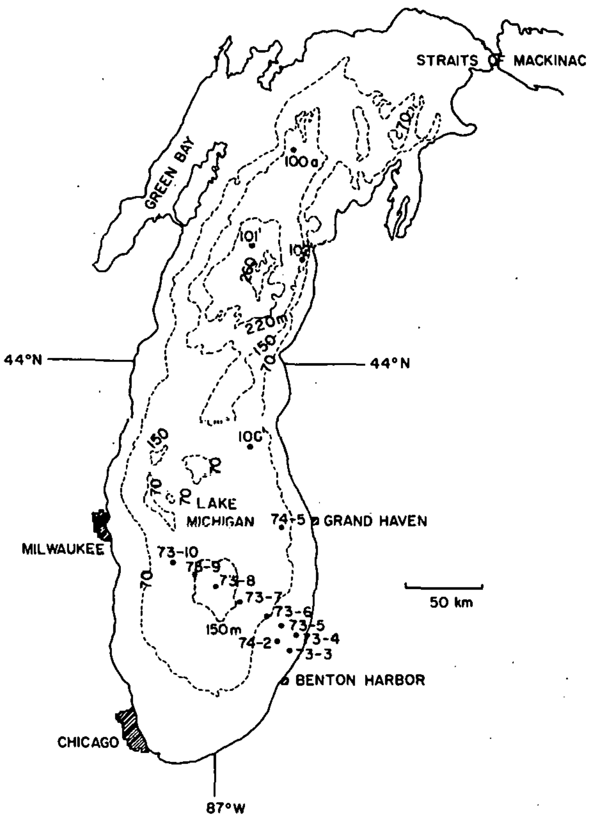


FIG. 1.--Core sample locations in Lake Michigan (ANL Neg. 149-6617)

Subsamples of oven-dried sections were weighed, resuspended in water, and counted at 780 X with a Zeiss inverted microscope. Frustules equal to or greater than one-half of a whole diatom were counted.(9)

Ten preweighed samples of ashed Lake Michigan phytoplankton were counted to determine the average number of frustules per gram. Weight percent of frustules per dry gram of sediment were calculated. The annual deposition of frustules was calculated from weight of frustules per unit weight of sediment deposited in one year.

The estimated annual diatom crop potentially available for settling to the sediment was calculated as described by Honjo.(10) The average annual standing crop of 1000 cells/ml was estimated from values presented by Damann,(2) Stoermer and Kopczynska,(11) Stoermer, Schelske, and Feldt,(12) and Ayers and Kopczynska.(13) The yearly turnover rate (185 to 365 times per year) and the mean settling velocity (1.0 to 5.0 m/day) were estimated from values given by Hutchinson(14) and Smayda,(15) respectively.

Results and Discussion

The concentration of frustules in surficial sediment varied between 6.31×10^5 and 3.71×10^7 g^{-1} dry weight (0.08 to 4.95%) in nearshore and offshore samples, respectively (Table 1 and Fig. 1). Increasing concentrations of frustules per gram sediment in offshore samples reflect less dilution with allochthonous material from rivers and shore erosion. The highest concentrations of frustules were found at stations where the water depth was greatest

TABLE 1. Concentration and Percent Dry Weight of Diatom Frustules in the Upper Centimeter of Sediment, and Mass Sedimentation Rate (R) at Different Locations in Lake Michigah

Station number	Number of frustules per dry gram	Weight % (dry) frustules	R $g/cm^2/yr$
72 - 100a	1.05×10^7	1.40	0.0295
72 - 101'	3.71×10^7	4.95	0.0140
72 - 102'	6.31×10^5	0.08	0.0111
72 - 106'	1.32×10^6	0.18	0.0083
73 - 3	4.90×10^6	0.65	0.0879
73 - 4	3.72×10^6	0.50	0.0415
73 - 5	7.41×10^6	0.99	0.0404
73 - 6	5.13×10^6	0.68	0.0460
73 - 7	1.62×10^7	2.20	0.0321
73 - 8	2.45×10^7	3.30	0.0145
73 - 9	8.51×10^6	1.10	0.0200
73 - 10	1.58×10^6	0.21	0.0146
74 - 2	2.88×10^6	0.38	--
74 - 5	3.72×10^6	0.50	0.0420

in the northern and southern basins.

The concentration of frustules decreased by at least two orders of magnitude with a depth in each core equivalent to 80 to 100 years BP (Fig. 2). This may suggest an increase in diatom production over the last 100 years. However, an increase of two orders of magnitude over this period of time is quite unlikely since historical data on diatom populations in Lake Michigan clearly do not illustrate an increase of this magnitude. Danforth(3) has found at the Chicago Water Filtration Plant that the average diatom concentration was 2000 cells/ml from 1968 to 1972, which is only double the concentration observed in 1926.

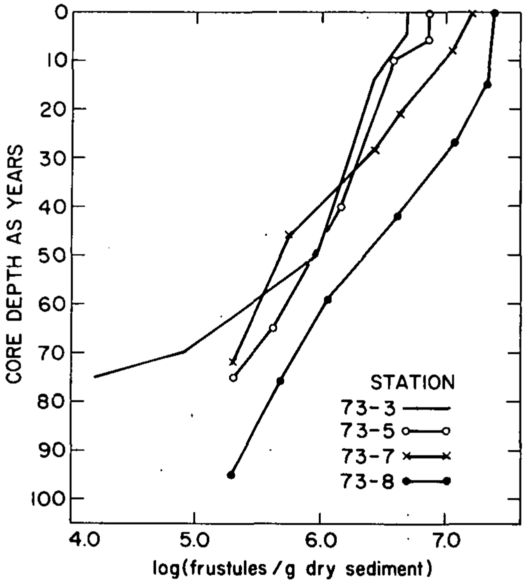


FIG. 2.--Reduction in the concentration of diatom frustules per gram dry sediment as a function of core depth in year (ANL Neg. 149-6618)

Scanning electron micrographs confirm the degradation of diatom frustules in the sediment cores. The frustule walls become thinner and pore size larger with increasing depth in the cores. Schrader(16) has shown similar results for frustules from the Baltic sea sediments. In some cores, the concentration of frustules diminished to undetectable levels at 150 years BP. The proportion of fragments to whole frustules did not appear to increase with core depth.

These data, together with chemical analyses for dissolved silica in the interstitial water of the sediment,(17) strongly suggest that diatom frustules are dissolved within the sediment of Lake Michigan. The slope of the profiles show an average half-life for dissolution of approximately 12 to 15 years.

Approximately 12 genera are listed as dominant phytoplankton diatoms in Lake Michigan; Melosira spp. and Tabellaria spp. are the most abundant.(18) Four genera contributed 90 to 100% of the diatom frustules observed in the sediment . These were, in decreasing order of abundance, Melosira spp., Tabellarea spp., Cyclotella spp., and Stephanodiscus spp. Melosira spp. was dominant in surficial sediment, but its relative abundance decreased with depth, while that of Tabellaria spp. increased. Cyclotella spp. increased with depth in the core and became dominant at lowest levels examined. Apparently some genera are more resistant to complete degradation and dissolution than others. Other major plankton genera, Fragilaria spp., Asterionella spp., Rhizosolenia spp., and Synedra spp. were very rarely observed in the sediment.

The annual deposition of frustules ranged from 2.3×10^4 to 5.3×10^5 cm^2 yr^{-1}. This is less than 5% of the estimated annual diatom crop potentially available for settling to the sediment and suggests that most of the annual crop is degraded within the water column before reaching the sediment surface. The degradation process is probably aided by zooplankton grazing, which fractures the frustules and enhances dissolution.(19)

It does not appear that floristic changes in sediment frustules can be used as an indicator of developmental trends or changes in trophic status for Lake Michigan over the last 100 years. The similar vertical profiles of diatom concentrations at all stations suggest that an active silica dissolution process has been occurring in both the water column and the sediment for at least the last 100 years. Reduced dissolved silica concentrations in the surface water of Lake Michigan may be the result of increased diatom standing crop, which retains more silica in the phytoplankton biomass of the water column. The sediment does not appear to be an effective sink for amorphous silica in the form of diatom frustules. Investigation of the processes of diagenesis and concentration of silica in interstitial water are in progress to further define silica cycling and its relation to eutrophication trends in Lake Michigan.

References

1. Schelske, C. L. and E. F. Stoermer. Phosphorus, silica, and eutrophication of Lake Michigan. Nutrients and Eutrophication: The Limiting Nutrient Controversy, Ed. G. E. Likens. Special Symp. No.1, Am. Soc. Limnol. Oceanogr., 1972, pp. 157–171.
2. Damann, K. E. Plankton Studies of Lake Michigan. Pub. No. 15, Great Lakes Res. Div., Univ. Michigan, Ann Arbor, 1966, pp. 9–17.
3. Danforth, W. Illinois Institute of Technology, Chicago, Illinois. Personal communication (1974).
4. Lund, J. W. G. Phytoplankton. Eutrophication: Causes, consequences, correctives. Pub. 1700, Nat. Acad. Sci., Nat. Res. Council, Washington, D.C., 1969, pp. 306–330.
5. Powers, C. F. and J. C. Ayers. Water quality and eturophication trends in southern Lake Michigan. Studies on the Environment and Eutrophication of Lake Michigan, Spec. Report No. 30, Univ. Michigan, Great Lakes Res. Div., Ann Arbor, 1967, pp. 142–178.
6. Stockner, J. G. and W. W. Benson. The succession of diatom assemblages in the recent sediments of Lake Washington. Limnol. Oceanogr. 12, 513–532 (1967).
7. Duthie, H. C. and M. R. Sreenivasa. Evidence for the Eutrophication of Lake Ontario from the Sedimentary Diatom Succession. Proc. 14th Conf. Great Lakes Res., Int. Assoc. Great Lakes Res., Ann Arbor, Mich., 1971, pp. 1–13.
8. Robbins, J. A. and D. N. Edgington. Determination of recent sedimentation rates in Lake Michigan using Pb^{210} and Cs^{137}. Geochim. Cosmochim. Acta 39, (1975).
9. Johnson, T. C. The dissolution of siliceous microfossils in surface sediments of the eastern tropical Pacific. Deep-Sea Res. 21, 851–864 (1974).
10. Honjo, S. Dissolution of Suspended Coccoliths in the Deep-Sea Water Column and Sedimentation of Coccolith Ooze. Contrib. No. 3436, Woods Hole Oceanographic Inst., 1974.
11. Stoermer, E. F. and E. E. Kopczynska. Phytoplankton populations in the extreme southern basin of Lake Michigan, 1962–1963. Proc. 10th Conf. Great Lakes Res., Int. Assoc. Great Lakes Res., Ann Arbor, Mich., 1967, pp. 88–106.
12. Stoermer, E. F., C. L. Schelske, and L. E. Feldt. Physoplankton assemblage differences at inshore versus offshore stations in Lake Michigan, and their effects on nutrient enrichment experiments. Proc. 14th Conf. Great Lakes Res., Int. Assoc. Great Lakes Res., Ann Arbor, Mich., 1971, pp. 114–118.

13. Ayers, J. C. and E. E. Kopczynska. The Phytoplankton of 1973. Special Report No. 51, Great Lakes Res. Div., Univ. Michigan, Ann Arbor, Mich., 1974, pp. 139–173.
14. Hutchinson, G. E. A Treatise on Limnology, Vol. II, Introduction to Lake Biology and the Limnoplankton. John Wiley and Sons, Inc., New York, 1967.
15. Smayda, T. J. The suspension and sinking of phytoplankton in the sea. Oceanogr. Mar. Biol. Ann. Rev. 8, 353–414 (1970).
16. Schrader, H. Fecal pellets: Role in sedimentation of pelagic diatoms. Science 174, 55–57 (1971).
17. Edgington, D. N. Unpublished data.
18. Stoermer, E. F. and J. J. Yang. Distribution and Relative Abundance of Dominant Plankton Diatoms in Lake Michigan. Publ. No. 16, Univ. Michigan, Great Lakes Res. Div., 1969.

DISTRIBUTION OF AMORPHOUS, DIATOM FRUSTULE, AND DISSOLVED SILICA IN A LEAD-210 DATED CORE FROM SOUTHERN LAKE MICHIGAN

J. A. Robbins,* D. N. Edgington, and J. I. Parker

Within approximately the upper ten centimeters of fine-grained sediments from Lake Michigan, the concentration of diatom frustules increases toward the sediment-water interface by over two orders of magnitude.(1) As shown by ^{210}Pb dating, this dramatic increase occurs mainly within the period of significant cultural eutrophication. But since the diatom population has only doubled within the last 45 years,(1) the sediment frustule concentration profile can be related at best only indirectly to eutrophic changes in overlying water. More likely, the nearly exponential profiles result from dissolution of frustules on burial. As these diatom remains contain about 86% SiO_2 by weight and comprise up to about 1/2% of the total sediment weight, their dissolution may contribute measurably to interstitial silica concentrations.

To assess the effect and significance of dissolution of frustule silica, and more generally to compare regeneration of interstitial silica from biogenic phases with contributions from solution of clay minerals, we have measured ^{210}Pb and amorphous, diatom, and dissolved silica in the same sediment core. ✓

We obtained the core (ANL-5) from the fine-grained organic rich clayey silt deposits approximately 5 miles offshore southwest of Grand Haven, Michigan in October, 1974. The core was kept cooled (6° C) and under purified nitrogen both during sectioning and hydraulic squeezing. About 10 ml of pore water from each centimeter section passed in line successively through Whatman 41 and 0.45-μ Millipore filters and were immediately frozen. In the laboratory, pore water samples were allowed to stand for several hours to depolymerize silica(2) prior to analysis with conventional colorimetric methods.(3) Amorphous silica was extracted from freeze-dried pore-water-depleted sediment cakes with diluted sodium carbonate solution. The extraction method is described elsewhere.(4) Diatom frustule concentrations were determined with

---

*University of Michigan.

an optical microscope. Frustules equal to or greater than one-half an intact diatom were counted. Lead-210 and ^{137}Cs measurements were made using previously reported methods.(5) The data are shown in Fig. 1 and summarized in Table 1.

The lead-210 data (Fig. 1) indicate an unsupported level of about 0.9 pCi/g and some flattening of the activity within the upper 2.5 cm, suggesting mixing of the sediment solids. Some inconsistency in this interpretation is apparent from examination of the frustule silica distribution in Fig. 1, which shows no comparable flattening within this interval. In most cases in which the ^{210}Pb curve is flat, profiles of other components associated with sediment solids, such as ^{137}Cs, Pb, or the plutonium isotopes,(6) are also constant over the same interval. In this core, the ^{137}Cs and ^{239}Pu (not shown) are indeed flat. Since the frustule concentration decreases by about a factor of three over this interval, either the mixing model developed previously is wrong, or it is not applicable to frustules. In view of the success of the model, we are inclined to believe that mixing has occurred in this core but

TABLE 1. Data for Lake Michigan Core ANL-5 (1974).

Sediment Interval (cm)	Porosity	Total Lead-210 (pCi/g)	Silica (SiO_2)		
			Amorphous (wt %)	Diatom (wt %)(a)	Dissolved (μg/ml)(b)
0-1	0.93	7.80	--	0.41	18.4, 29.6
1-2	0.88	7.63	3.75	0.21	39, 43
2-3	0.86	7.28	3.1	0.17	44
3-4	0.85	5.48	3.45	0.14	45
4-5	0.84	5.73	3.1	--	45
5-6	0.83	4.41	3.1	0.080	43
6-7	0.83	3.59	2.8	0.074	43
7-8	0.82	2.37	2.45	0.057	43, 44
8-9	0.81	1.60	2.25	--	38, 40, 44
9-10	0.82	1.11		--	38, 43
10-12	0.80	1.06	1.65	0.022	43(c)
12-14	0.78	0.95	1.35		45(c)

(a) Wt % values based on count of frustules plus all fragments greater than approximately 1/2 cell.

(b) Additional values derived from analysis of separate cores.

(c) Last two values correspond to 10-11 and 11-12 cm.

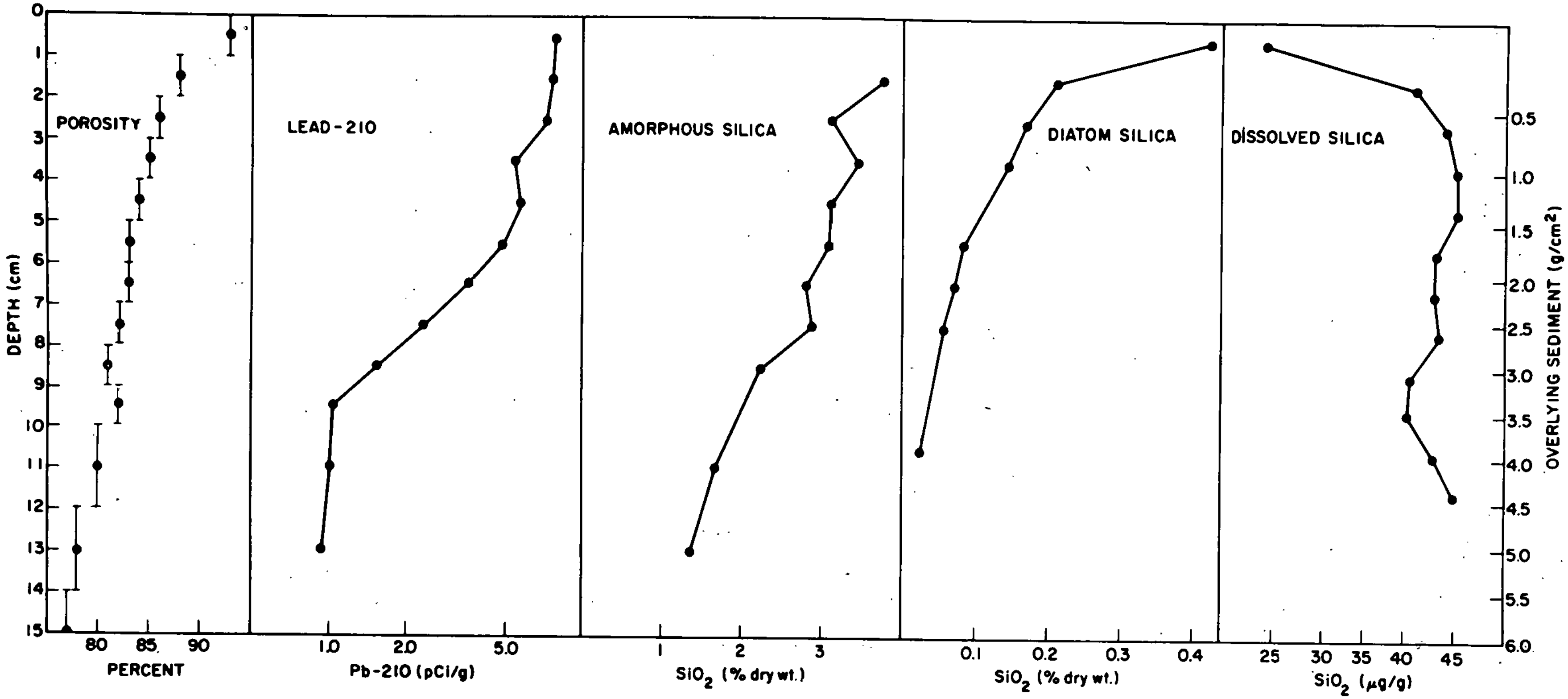


FIG. 1.--Distribution of porosity, total lead-210 and amorphous, diatom frustule, and dissolved silica in core ANL-5.

that frustules are partially immune to its effects. In some way they are preferentially sorted by processes responsible for redistribution of sediment grains. The application of the mixing model to the unsupported lead-210 data is shown in Fig. 2. The results are not as impressive as they are in most cases, but the least-squares derived sedimentation parameters of 0.55 g/cm^2 or 2.5 cm for the mixing depth(s) and 0.045 g/cm^2/yr for the sedimentation rate are acceptable for the present purpose.

The concentration of frustules is shown in terms of weight percent SiO_2. Conversion from raw counts was made by taking the average number of frustules per dry gram (7.5×10^8) and the SiO_2 concentration as 85.7% by weight.(1) The distribution is approximately exponential, decreasing by a factor of 20 from the surface to a 10-cm depth. Parker and Edgington observed progressive frustule degradation with depth, but the proportion of fragments to whole frustules did not appear to increase with depth.(1)

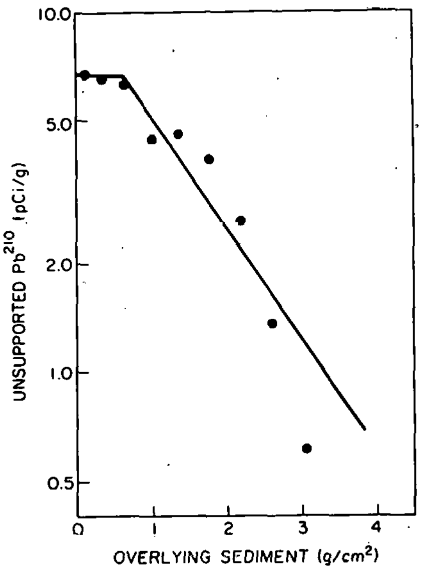


FIG. 2.--Unsupported lead-210 and the mixing model distribution for a sedimentation rate of 0.045 g/cm^2/yr and mixing depth of 0.55 g/cm^2 in core ANL-5.

Fragmentation might be expected if dissolution were responsible for the reduction in frustule numbers with depth. However, the dissolution rate in the diffusion-limited case is inversely proportional to fragment size.(7) Rapid dissolution and disappearance of small diatom fragments could conceivably explain the predominance of degraded but intact frustules at all sediment depths. In such a case a crude quantitative model can be set forth for frustule dissolution which treats them as spheres depositing at a uniform rate at the sediment surface. Diffusion-limited dissolution of a single sphere of radius R is given by(7)

$$\frac{dR}{dt} = \frac{vD_s(C_s - C_\infty)}{R} , \qquad (1)$$

where t is the time elapsed since deposition, v is the molar volume, D_a is the diffusion coefficient of silica in bulk sediment, C_∞ is the dissolved silica concentration at distances much greater than R and C_s in the concentration at the frustule surface. If the initial radius is R_0, then

$$R^2(t) = R_0^2 - \int_0^t vD_s(C_s - C_\infty)\,dt \,. \tag{2}$$

Since C_∞ is nearly constant at depths greater than two centimeters, treating the integral as constant we obtain

$$R(t) = \left(R_0^2 - 2\,vD_s(C_s - C_\infty)t\right)^{\frac{1}{2}} \,. \tag{3}$$

The fraction of dry weight of silica associated with loss as a function of time by uniformly dissolving spheres is

$$f(t) = f_0\,(R/R_0)^3 \,, \tag{4}$$

where f_0 is the fraction at t = 0. Therefore, substituting Eq. (4) in Eq. (3)

$$f^{2/3} = f_0^{2/3}\left(1 - \frac{2vD_s(C_s - C_\infty)t}{R_0^2}\right) = \alpha - \beta t \,. \tag{5}$$

Thus, there should be a linear relationship between the 2/3 power of the dry weight of the diatom silica fraction and the elapsed time. In Fig. 3 we have shown this relationship using dates derived from the lead-210 sedimentation rate of 0.045 g/cm^2/yr. With the exception of the first point, the fit is excellent. A similar relationship holds for amorphous silica. It should be emphasized that the data do not really allow a least-squares determination of the 2/3 exponent value. A wide range of exponents will give equally acceptable fits. In fact, the best fit is obtained for an exponent of zero. Thus, it can only be said that the model is consistent with the observed distribution. The ratio

$$\beta/a = 2vD_s(C_s - C_\infty)/R_0^2 \,,$$

which is independent of f_0, depends only on the properties of the environment of the dissolving grains. To the extent that v and C are the same for diatom and amorphous silica

$$(\beta/\alpha)\ \text{diatom}/(\beta/\alpha)\ \text{amorphous} = (R_0\ \text{diatom}/R_0\ \text{amorphous}) = 3.33 \,. \tag{6}$$

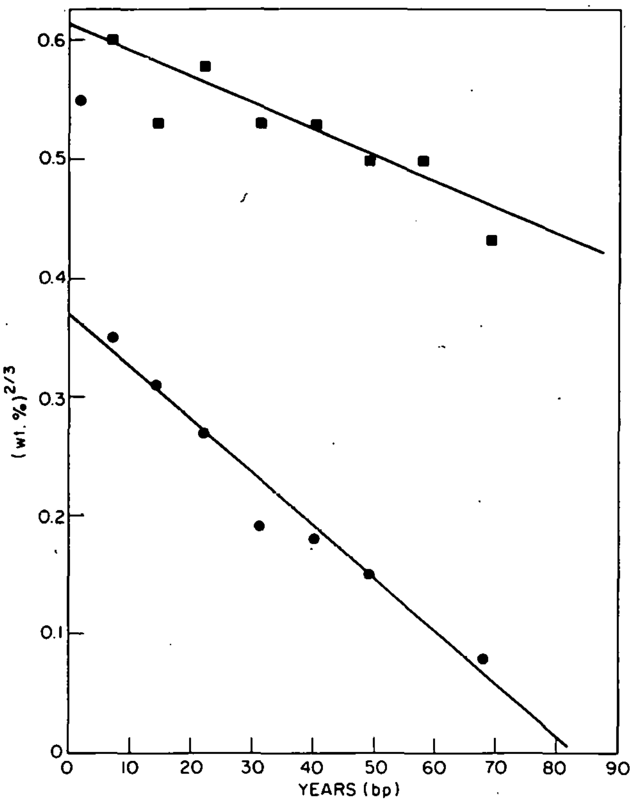


FIG. 3.--(Weight percent silica)$^{2/3}$ versus year based on the ^{210}Pb sedimentation rate in core ANL-5. A linear relationship is expected for a collection of identical spheres dissolving under diffusion-limited conditions. ■ , amorphous silica × $\frac{1}{4}$; ●, diatom silica.

In this case, the slower rate of dissolution might be attributed to a mean particle size which is larger by a factor of 2 in the amorphous silica phase. Validity of this approach might be confirmed by determination of frustule distributions for several species having very different initial sizes. It is likely, however, that chemical factors, and not simple diffusion, control the dissolution of amorphous and frustule silica in freshwater sediments as they do in marine sediments.(4) In that case, Eq. (1) would not be applicable.

The dissolved silica distribution shown in Fig. 1 is typical of distributions both in marine sediments and in freshwater sediments of the Great Lakes.(8,9) Within several centimeters below the sediment surface, concentrations rise by roughly a hundredfold over concentrations of a few tenths ppm SiO_2 in overlying water. Computation of fluxes of silica across the sediment interface cannot be reliably calculated when so drastic a change occurs within so small an interval of sediment. Loss of a few centimeters of sediment or slight mixing of surface sediments resulting from coring can have very serious and opposite effects. Loss of top sediment would tend to produce artificially high values of the computed gradients, while experimenter-induced mixing would broaden the profile and give erroneously low calculated gradients. It is evident that accurate measurement of silica gradients and concentration profiles in the fine-grained sediments requires very careful methods of sampling and analysis. Values of parameters derived from the application of mathematical models of reaction and diffusion must be treated with caution as the following discussion shows.

Interstitial silica concentrations are maintained by interaction of clay minerals with silica produced by the dissolution of frustules or tests(10) and by diffusion. The relative importance of biogenic silica and clay minerals in controlling levels of dissolved silica is related to the productivity of overlying waters.(11) In regions of low productivity, clay minerals regulate silica concentrations, while in areas of high productivity, dissolution of frustules will saturate the exchange capacity of clay minerals and give rise to very high interstitial silica concentrations. The correspondence between productivity of overlying water and interstitial silica concentrations is clearly shown by Schink et al.(12) They concluded that levels of dissolved silica in surface sediments must originate primarily from dissolution of biogenic amorphous silica rather than from clay minerals. On the other hand, Hurd concluded that in sediments from the central Equatorial Pacific Ocean, silicate minerals, as well as biogenic amorphous silica, are important in regulating dissolved silica concentrations.(4) Although some of his cores were as high as 30% biogenic opal by weight, the interstitial waters remained undersaturated with respect to this phase, presumably because of the consumption of dissolved silica by other silicate minerals.

As the concentration of diatom and amorphous silica in this sediment core are comparatively low, we may expect dissolved silica levels to be controlled mainly by clay mineral solution equilibria. Weiler found interstitial silica concentrations in Lake Ontario sediments of around 25 ppm. Corrected for the effects of squeezing at temperatures above those in situ, the recomputed value of 17 ppm compares well with 14 ppm expected from clay mineral equilibrium calculations.(9) Our high value of around 45 ppm is probably not due to frustule dissolution as can be seen from application of the diffusion equation.

The diffusion and reaction of dissolved silica can be described by a single one-dimensional steady-state diffusion equation(13)

$$\frac{\partial}{\partial z}\left(\phi D_s \frac{\partial c}{\partial z}\right) - \frac{\partial}{\partial z}(\phi vc) + \phi Q = 0 \ , \tag{7}$$

where

z = sediment depth (cm)
c = silica concentration ($\mu g/cm^3$)
ϕ = sediment porosity
D_s = the bulk diffusion coefficient (cm^2/yr)
V = velocity of pore water flow relative to the sediment-water interface
Q = rate of addition and/or removal of silica due to slow reactions.

It is assumed that rapid exchange reactions (sorption and desorption) of dissolved silica with solids is negligible. To model the observed profile we shall solve a differential equation which is simplified by additional approximations. We take both D_s and ϕ as constant. The bulk diffusion coefficient, D_s, actually depends on sediment porosity. Hurd used an empirical relationship derived from measurements in clays, between D_s and the diffusion coefficient of substances in free solution, D_0,

$$\log (D_s/D_0) = 1.6\ (\phi - 1) \tag{8}$$

and he argued that this formula also gives the proper correction for tortuosity in terms of porosity.(4) As ϕ varies from 0.93 to 0.76 over the upper 15 cm, the corresponding variation in the ratio (D_s/D_0) is from 0.77 to 0.40, or about 60% decrease with depth. However, because of the large uncertainties in the experimental results, the model is developed primarily for illustrative purposes; examination of the effects of nonconstant diffusion coefficients is premature. Taking the mean porosity as $\phi = 0.85$, the ratio D_s/D_0 is 0.57. The self-diffusion coefficient of dissolved silica in seawater at 25° C is 1.0×10^{-5} cm^2/sec.(14) At the sediment temperature (6° C) in situ this value should be approximately halved, that is, 6×10^{-6} cm^2/sec.(15) Since the value for D_0 in freshwater should be comparable, the best estimate for D_s is 3.4×10^{-6} cm^2/sec or roughly 100 cm^2/yr.

We also neglect the advection term. Its effect is nil, as can be seen from the scale length parameter ($D_s/v \cong 10^3$ cm.$^{(16)}$ Compared to the scale over which significant changes in concentration occur (< 10 cm), diffusional processes are clearly dominant. With the foregoing approximations incorporated, the resulting equation is

$$D_s \frac{\partial^2 C}{\partial z^2} + R = 0 \ . \qquad (9)$$

For clay mineral equilibrium control, Anikouchine suggested that the reaction term R should be of the form

$$R = k_1 (C_f - C) \ , \qquad (10)$$

where k_1 is the first order rate constant and C_f if the equilibrium silica concentration.$^{(17)}$ The solution of Eq. (1) is then

$$C = C_f (1 - e^{-\beta z}) \ , \qquad (11)$$

where $\beta = (k_1/D_s)^{\frac{1}{2}}$.

The distributions of silica in cores studied by Anikouchine$^{(17)}$ and Hurd$^{(4)}$ are well described by this solution. Typical rate constants obtained by Hurd were 0.4 yr^{-1}. The least squares fit to our data gives a value of $k_1 = 230\ yr^{-1}$ and $C_f = 45$ ppm SiO_2. It is difficult to reconcile these vastly different rates. Laboratory measurements of standard clay mineral dissolution in seawater$^{(18)}$ give constants in the range of 2 to 20 yr^{-1}, much closer to the values of Hurd. We could expect to get high values if the upper parts of the core were lost or if the gradient extended beyond the sediment-water interface. Morse suggested that computed fluxes may be in error owing to the presence of a stagnant boundary layer up to a centimeter thick above the sediment-water interface.$^{(19)}$ To illustrate the sensitivity of calculated gradients and values of k_1, consider the case in which the top centimeter of sediment is lost on coring. The calculated value of k_1 is given by

$$k_1 = D_s \frac{1}{C_f} \left(\frac{dC}{dz}\right)^2_{z=0} \ . \qquad (12)$$

Thus, k_1 depends on the square of the gradient which is about $24/0.5 = 48\ g \cdot cm^3/cm$. If the origin is displaced upward by 1 cm, the computed gradient is

$24/1.5 \cong 16$ g/cm^3/cm, a factor of 3 smaller. The estimated value of k_1 changes by nearly a factor of 10.

Where appreciable quantities of a given phase are dissolving incongruently throughout the length of the core, Eq. (10), for the reaction term must be modified. Robbins and Callender have suggested that when a solid phase concentration profile is at steady state, a first order term must be included in the expression for R.(20) They show that the rate of dissolution of a substance into interstitial water is given by

$$k_0(z) \equiv \frac{dC}{dt} = -\frac{1}{\phi}\,\frac{dC_v}{dt} = -\frac{r}{\phi}\,\frac{dC_s}{dz} \;, \tag{13}$$

where k_0 is the zero order rate term (µg/cm^3/yr), C_v is the concentration of the dissolving (or growing) phase in µg/volume of bulk sediment, and C_s is the concentration in terms of µg/g dry sediment; r is the sedimentation rate in g/cm^2/yr; k_0 is the net rate at which silica is being transferred from frustules or amorphous silica into interstitial water. The first order term must still be retained since it represents the rate at which other silicate minerals consume (or add) silica from the dissolving amorphous phase. For ease of computation, the amorphous (or frustule) silica can be represented by an exponential term

$$C_s = C_0 e^{-\gamma z} \;. \tag{14}$$

Then the diffusion reaction equation is

$$D_s \frac{\partial C^2}{\partial z^2} + k_1(C_f - C) + \frac{C_0 r\gamma e^{-\gamma z}}{\phi} = 0 \;, \tag{15}$$

and the solution is

$$C = C_f + \Gamma e^{-\gamma z} - (C_f + \Gamma)e^{-\beta z}$$

$$\Gamma = C_0 r\gamma/\phi\,(k_1 - D_s\beta^2) \;. \tag{16}$$

For amorphous silica $r = 0.092$ cm^{-1} and $C_0 = 5 \times 10^4$ µg SiO/g (0.5 wt %). The maximum rate of dissolution of amorphous silica is then

$$C_0 r\gamma/\phi = 240 \text{ µg } SiO_2/cm^3/yr \;. \tag{17}$$

This rate compares favorably with dissolution rates ranging up to 120 $\mu g/cm^3/yr$ measured by Hurd$^{(4)}$ and with the results obtained by Lerman et al.$^{(18)}$ of around 110 $\mu g/cm^3/yr$ for standard clay minerals. It is significant that our dissolution rate, which is not related to interstitial water measurements, tends to agree with measurements of others, while our first order rate constants, which depend on details of the dissolved silica concentration, are dissimilar.

The set of curves shown in Fig. 4 are calculated from Eq. (16) for various values of the initial weight percent of amorphous silica. Because both k_1 and D_s are large, the level of dissolved silica is not appreciably raised by the dissolution of the amorphous phase. The large amount dissolving per unit volume is effectively removed by diffusion and by reaction with other silicate minerals. If the initial concentration was unrealistically large (50%) then there would be a detectable effect. With the exception of the last two data points, which are not averages, there appears to be a maximum SiO_2 concentration around 4 cm with a gradual decrease to a depth of 10 cm. These features could be reproduced by the mathematical model for realistic values of C_0, provided an appreciably smaller value of k_1 could be used. As previously stated, this would be the case either if some of the uppermost sediment were not recovered or if the gradient extended beyond the sediment-water interface. In either case, the proper

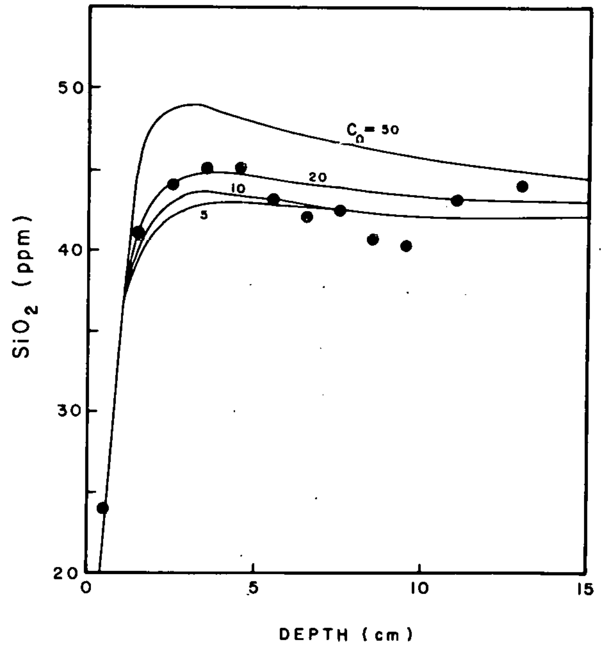


FIG. 4.--Dissolved silica data and diffusion-reaction model distributions for various choices of the initial weight percent amorphous silica, C_0. The effect of amorphous silica dissolution on interstitial silica concentration is small because of the high values of k_1 required to reproduce the gradient around $z = 0$. Diffusion reaction parameters are $D_s = 100\ cm^2 = 100\ cm^2/yr$ and $k = 230\ yr^{-1}$.

model fit with lower values of k_1 would require an appreciably lower value of C_f, more in accord with probable concentrations of dissolved silica in equilibrium with clay minerals. Careful sampling and analysis of many additional sediment cores are necessary before further progress can be made in the application of such diffusion reaction models and in our understanding of processes controlling the distribution of silica among sedimentary components.

References

1. Parker, J. I. and D. N. Edgington. Distribution of diatom frustules in Lake Michigan sediment cores. To be published.
2. Burton, J. D. and T. M. Leatherland. The reactivity of dissolved silicon in some natural waters. Limnol. Oceanogr. 15, 473–476 (1970).
3. Strickland, J. D. H. and T. R. Parsons. A Practical Handbook of Seawater Analysis. Fish Res. Board Can., Bull. 167 (1968).
4. Hurd, D. C. Interactions of biogenic opal, sediment and seawater in the Central Equatorial Pacific. Geochim. Cosmochim. Acta 37, 2257–2282 (1973).
5. Robbins, J. A. and D. N. Edgington. Determination of recent sediment rates in Lake Michigan using ^{210}Pb and ^{137}Cs. Geochim. Cosmochim. Acta 39, 285–304 (1975).
6. Edgington, D. N. and J. A. Robbins. Records of lead deposition in Lake Michigan sediments since 1800. To be published.
7. Berner, R. A. Principles of Chemical Sedimentology. McGray-Hill, New York (1971).
8. Sutherland, J. C., J. R. Karmer, L. Nichols, and T. D. Kurtz. Mineral-water equilibria Great Lakes: Silica and phosphorous. Great Lakes Res., University of Michigan, Ann Arbor, Michigan, Publication No. 15, 1966.
9. Weiler, R. R. The interstitial water composition in sediments of the Great Lakes. I. Western Lake Ontario. Limnol. Oceanogr. 18, 918–931 (1973).
10. Bischoff, J. L. and T. L. Ku. Pore fluids of recent marine sediments. I. Oxidizing sediments of 20° N, continental rise to mid-Atlantic Ridge. J. Sed. Petrol. 40, 960–972 (1970).
11. Fanning, K. A. and D. K. Schink. Interaction of marine sediments with dissolved silica. Limnol. Oceanogr. 14, 59–58 (1969).
12. Schink, D. R., K. A. Fanning, and M. E. Q. Pilson. Dissolved silica in the upper pore-waters of the Atlantic Ocean floor. J. Geophys. Res. 79, 2243–2250 (1974).
13. Berner, R. A. Diagenetic models of dissolved species in the interstitial waters of compacting sediments. Am. J. Sci. 275, 88–96 (1975).

14. Wollast, R. and R. M. Garrels. Diffusion coefficient of silica in seawater. Nature (Phys. Sci) 229, 94 (1971).
15. Li, Y. G. and S. Gregory. Diffusion of ions in seawater and in deep-sea sediments. Geochim. Cosmochim. Acta 38, 703–714 (1974).
16. Tzur, Y. Interstitial diffusion and advection of solute in accumulating sediments. J. Geophy. Res. 76, 4208–4211 (1971).
17. Anikouchine, W. A. Dissolved chemical substances in compacting marine sediments. J. Geophys. Res. 72, 505–509 (1967).
18. Lerman, A., F. T. Mackenzie, and O. P. Bricker. Rates of dissolution of aluminosilicates in seawater. Earth Planet. Sci. Lett. 25, 82–88 (1975).
19. Morse, J. W. Calculation of diffusion fluxes acrodd the sediment-water interface. J. Geophys. Res. 79, 5045–5048 (1974).
20. Robbins, J. A. and E. C. Callender. Diagenesis of manganese in Lake Michigan sediments. Am. J. Sci. 275, 512–533 (1975).

STABLE LEAD GEOCHRONOLOGY OF FINE-GRAINED SEDIMENTS IN SOUTHERN LAKE MICHIGAN

J. A. Robbins* and D. N. Edgington

In a previous article,(1) we showed that the vertical distribution of stable lead in the fine-grained sediments of Lake Michigan reflects the history of cultural lead inputs. We found that the lead distributions in dated cores are quantitatively described by a universal time-dependent loading or source function which is a linear combination of estimated annual inputs of atmospheric lead derived from the combustion of leaded gasoline and the burning of coal in and around Chicago since about 1800.(2)

The existence of such a source function for lead implies that stable lead itself may be used to date sediment cores. The idea of using cultural heavy metal horizons for the determination of recent sedimentation rates has been examined by Walters and Wolery.(3) They found that the mercury depth profiles in western Lake Erie sediments showed several horizons which correspond to the development of local industrial use of mercury over the past forty years or so. The construction of the lead source function for Lake Michigan sediments was based on only four lead-210 dated cores. To establish the validity of the source function concept, we now have examined its application to the distribution of lead determined by others in many cores from southern Lake Michigan.

Source Function Model

We assume that lead has a negligible residence time in the water(4) and negligible postdepositional chemical or diffusional mobility. Since Winchester and Nifong showed that 95% of atmospheric lead emissions around Chicago and Gary, Indiana originate from coal and gasoline combustion, we consider only these sources.(5) In addition, since atmospheric inputs may well be the major source of cultural lead in the sediments, we shall assume that

---

*The University of Michigan.

other sources (river and direct discharges) are proportional to the atmospheric inputs. Let the time parameter t arbitrarily be set equal to zero at some convenient preindustrial date, say 1700. If $J_a^g(t)$ is the rate of atmospheric emissions for coal-derived lead and $J_a^c(t)$ is the rate for gasoline-derived lead, then the total cultural lead input is

$$J(t) \propto [J_a^g(t) + kJ_a^c(t)] \ , \tag{1}$$

where k is the proportion of coal-derived lead before about 1960.(1) That is, $k = 1$ for $260 \leqq t \leqq 272$, and $k \geqq 1$ for $t \leqq 260$.

If this source function j(t) (Eq. 1) is "universal," then the space-time variables are separable so that the concentration of lead in a sediment core is described by

$$C(t) = f(x,y) \cdot J(t) + C_0 \ , \tag{2}$$

where f is the spatially dependent part describing the relative efficiency of transfer of lead to a given location in the lake; C_0 is the precultural lead concentration. If R is the sedimentation rate (cm/yr), then at depth z the concentration of lead will be

$$C(z) = f \cdot J\left(\frac{272 \cdot R - z}{R}\right) + C_0 \ . \tag{3}$$

When there is vertical mixing(6) Eq. (3) must be modified. We derive here a more convenient form of the mathematical model expressed previously in terms of a finite sum.(6) Let S(cm) be the thickness of the mixing zone at the top of the sedimentary column. At time t (yr) the concentration (μg/g) within this zone is $C_m(t)$. At time $t + \delta t$ new sediment having concentration $C(t + \delta t)$ is added at the top of the core. This material is assumed to be instantly distributed throughout the mixing zone, which has moved upward by an amount $R\delta t$. The new concentration within the zone is then

$$C_m(t + \delta t) = \frac{C(t + \delta t) \cdot R\delta t + C_m(t) \cdot (S - R\delta t)}{S} \ ; \tag{4}$$

the rate of change of C_s is then

$$\frac{\delta C_m}{\delta t} = \frac{C_m(t + \delta t) - C_m(t)}{\delta t} = \gamma \, [C(t + \delta t) - C_m(t)] \ . \tag{5}$$

Passing to the limit as $\delta t \rightarrow 0$ and integrating, the solution is(7)

$$C_m(t) = \gamma \int_0^t e^{\gamma(\tau - t)} \, C(\tau)\, d\tau \quad , \tag{6}$$

where $\gamma = R/S$.

Thus the concentration of lead will be

$$C_{Pb}^{mix'}(t) = f\gamma \int_0^t e^{\gamma(\tau + t)} \, J(\tau)\, d\tau + C_0 \tag{7a}$$

and $t \leqq 1/\gamma$; and

$$C_{Pb}^{mix'}(t) = C_{Pb}(1/\gamma) \text{ for } t \geqq 1/\gamma \ . \tag{7b}$$

At time t the base of the mixing zone will be located at $R(272 - t) + S$ centimeters. So, for $z > s$

$$C_{Pb}^{mix}(z) = C_{Pb}^{mix'} \left(\frac{272 -)z - s)}{R} \right) \tag{8a}$$

and for $z < s$

$$C_{Pb}^{mix}(z) = C_{Pb}^{mix'}\,(272) \ . \tag{8b}$$

The effect of sectioning the cores in finite intervals is included by integrating Eq. (8) over the appropriate depth interval. Compaction effects are treated as described in Robbins and Edgington.(6)

Application to the IGS Cores

To obtain the least squares fits to the lead distributions in the four dated cores, R and S were known and held fixed while f, k, and C_0 were allowed to vary. The best fit value for k was 1.5 ± 0.1. The resulting source function J(t) is shown in Fig. 1. With the value of k established, we can now use the model to infer the sedimentation rate and mixing depth in undated sediments where the distribution of lead is known.

Shimp et al. have measured the distribution of lead in a series of cores (IGS) in southern Lake Michigan at locations shown in Fig. 2.(8) In Fig. 3, selected distributions and model fits are shown. In each case k was held fixed at 1.5 while R, S, and f were allowed to vary. The best fit values for both the IGS cores and our lead-210 dated UMAN cores are given in Table 1,

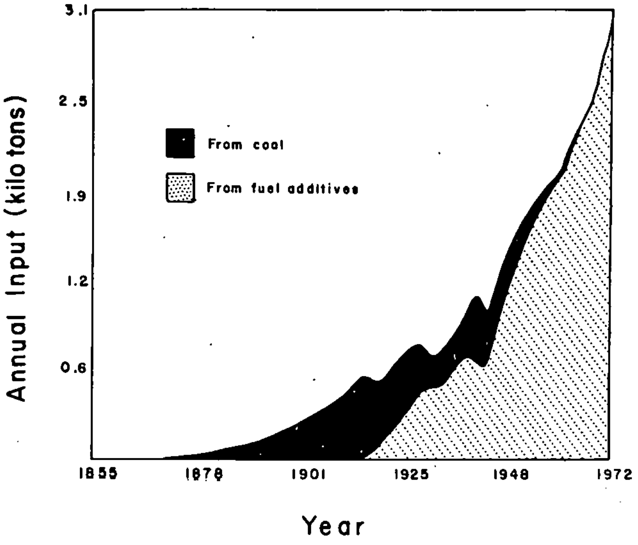


FIG. 1.--The lead source function. A linear combination of coal and gasoline-derived lead emissions to which the annual input of lead to the sediments is proportional.

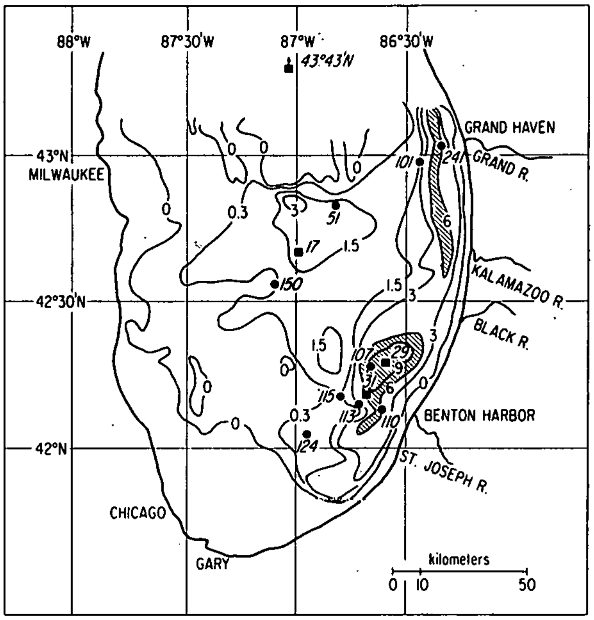


FIG. 2.--Study area in southern Lake Michigan. The contours (in meters) indicate the thickness of the Waukegan member.[9] ■, UMAN stations, this study; ●, IGS (Illinois Geological Survey) stations (Shimp et al.)[8] (ANL Neg. No. 149-6656)

TABLE 1. Model-derived sedimentation parameters

Core	Sedimentation Rate $\bar{R}$ (cm/yr)	Sedimentation Rate $\bar{\omega}$ (mg/cm^2/yr)	Mixing Depth S (cm)	1972 Cultural Lead Concentration (µg/g)	1972 Cultural Lead Flux (µg/cm^2/yr)
UMAN					
LM-12-17	0.06	12	0	145	2
29	0.15	94	4	266	25
31	0.04	18	2	271	5
105	0.07	15	0	200	3
IGS* 51-3	0.12	29	4	294	9
101-3	0.12	29	0	182	5
107-2	0.32	78	0	197	15
110-3	0.15	36	5	112	4
113-3	0.18	44	0	154	7
115-3	0.07	17	0	197	3
124-3	0.04	10	0	283	3
150-3	0.20	49	0	140	7
241-3	0.15	36	0	119	4

* For all IGS cores the porosity ϕ_o is taken as 0.9 and the mean density of sediment solids ρ_s as 2.45 g/cm^3. The mass sedimentation rate $\omega = R\rho_s (1-\phi) \approx \bar{R}\rho_s (1-\phi_o)$.

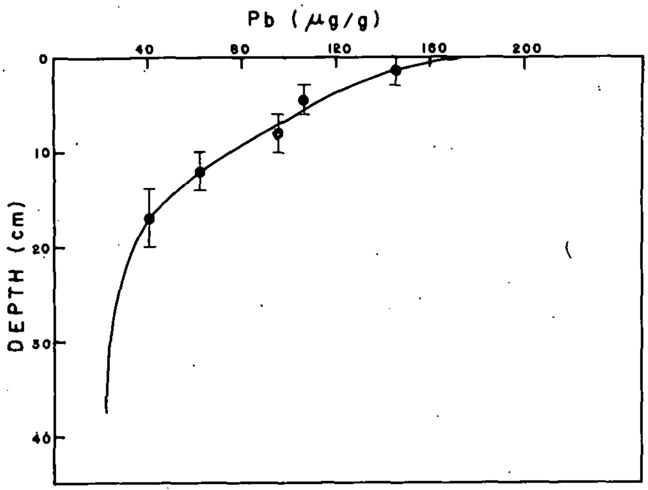


FIG. 3.--The model fit to several lead distributions in undated sediment cores (Shimp et al.)(8) using the lead source function shown in Fig. 1. In these cases the mean sedimentation rate, mixing depth, and factor f were allowed to vary.

along with extrapolated 1972 lead fluxes. The fits to the IGS lead distributions are quite good in every case, but the uncertainties in derived values of R and S are appreciable at least for two reasons. First, the porosity vs. depth was not known and was assumed to be 0.9 and constant for purposes of calculating the mass sedimentation rate. Second, the intervals of sediment analyzed were usually broad in comparison with the extent of the cultural lead distribution. The mean values of ω given in Table 1 for the UMAN cores are derived for purposes of comparison by allowing R as well as k and f to vary and not making compaction corrections.

As in the case of our ^{210}Pb dated cores, the IGS lead distributions sometimes possess a "tail" which is not adequately reproduced by the model unless contributions of coal-derived lead are included. However, in the undated cores, it often is possible to obtain reasonable fits using gasoline-derived lead only ($J_a^c = 0$) and larger values for the sedimentation rate. This demonstrates the difficulty in determining the source function parameters without an independent geochronology.

The relation between the estimated Waukegan member thickness,(9) and the mean mass sedimentation rate is shown in Fig. 4. The sedimentation rate values shown for ^{137}Cs are averages of rates derived from ^{137}Cs distributions in cores located within a specified Waukegan member depth contour interval.(10) While there is a fair amount of scatter in the data, there is a clear correlation between modern sedimentation values and postglacial accumulation of fine-

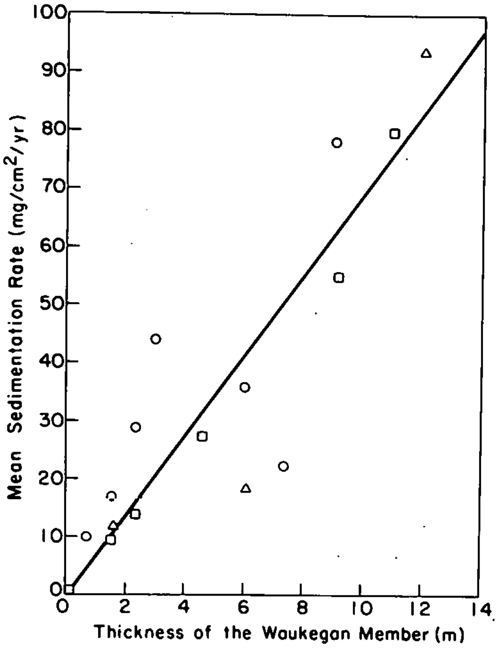


FIG. 4.--The correspondence between the thickness of post-glacial deposits and modern sedimentation rates inferred from either radioactivity measurements or stable lead distributions. (□ , ^{137}Cs data, averages of over 50 cores; O, IGS lead; △, UMAN ^{210}Pb. This relation allows a mean sedimentation rate for the southern basin to be computed as 7 mg/cm^2/yr.

grained sediments. The slope of the regression line shown in Fig. 4 is 6.9 mg/cm^2/yr/m. From this value we compute the average sedimentation rate in the southern part of the lake (below 43°) as 7 mg/cm^2/yr. This amounts to an annual fine-grained sediment input to the southern basin of about 1.3 million metric tons. This is comparable to the total annual fine-grained sediment accumulation in Lake Ontario of about 2.3 million tons.(11)

The information gained from analysis of the IGS cores generally confirms our previous estimates of cultural lead deposition rates in southern Lake Michigan.(1) Taking the natural background to be 23 µg/g, the mean natural lead flux is approximately 0.16 µg/cm^2/yr, which corresponds to a total input of about 30 metric tons/yr. The magnitude of the inputs of lead from unpolluted streams has been calculated by Winchester and Nifong(5) from the data summarized by Turekian.(12) They have estimated this input to be 100 metric tons/yr. If this loading is uniformly mixed in the water column and deposited over the whole lake, then, since the area of the lake south of latitude 43° N is 0.31 of the total area, the natural loading of lead in the southern basin is 30 tons/yr, which is in agreement with our estimate.

It can be seen that the flux of lead shows greater spatial variability than the lead concentration extrapolated to t = 1972 using the model. In other words, the factor f(x,y) in Eq. (2) is, in fact, relatively constant over the area of the fine-grained deposits, and differences in flux are primarily attributable to spatial variations in the mass sedimentation rate. Therefore, the computation of average lead flux to the sediments may be based on an extrapolated value of 190 μg/g in 1972, which is taken to be representative of the concentration of lead in fine-grained material depositing anywhere throughout the lake in 1972. The computed lead deposition rate is then about 1.3 $\mu g/cm^2/yr$, which corresponds to about 240 metric tons/yr in 1972. This is comparable to our previous estimate of 290 tons/yr based on far fewer cores.

It is intriguing to note that in most of our sediment cores the ^{210}Pb and Pb profiles have about the same exponential shape. This appears to be a fortuitous consequence of the fact that the doubling time for lead use and emissions is nearly equal to the half life of ^{210}Pb. However, in many of the same cores, other elements, including copper, have exponential profiles of very similar shape. Cline and Upchurch have generated roughly exponential copper concentration profiles in sediment cores treated with copper, initially homogenized and then stored under in situ conditions.(13) They attribute the development of surficial enrichments after several weeks or months to bacterial mediated diagenesis.

In the case of both Pb and ^{210}Pb, the extent of chemical and diffusional mobility remains undetermined. As greater reliance may be placed on ^{210}Pb and heavy metals for dating sediments of the Great Lakes in the near future, it is of prime importance of understand adequately the geochemistry of lead and uranium series radionuclides in freshwater sediments.

References

1. Edgington, D. N., J. A. Robbins, and J. O. Karttunen. The distribution of ^{210}Pb and stable lead in Lake Michigan sediments. Radiological and Environmental Research Division Annual Report, Part III, January–December 1973. ANL-8060, Part III, pp. 63–76.
2. Edgington, D. N. and J. A. Robbins. Records of lead deposition in Lake Michigan sediments since 1800. In press.
3. Walters, L. S. and T. J. Wolery. Transfer of Heavy Metal Pollutants from Lake Erie Bottom Sediments to the Overlying Water. Project completion Report No. 421X, Water Resources Center, Ohio State University, Columbus, Ohio (1974).
4. Koide, M. R. and E. D. Goldberg. Lead-210 in natural waters. Science 134, 98–99 (1962).

5. Winchester, J. W. and G. D. Nifong. Water pollution in Lake Michigan by trace elements from pollution aerosol fallout. Water, Air, Soil Poll. 1, 50–64 (1971).
6. Robbins, J. A. and D. N. Edgington. Determination of recent sedimentation rates in Lake Michigan using lead-210 and cesium-137. Geochim. Cosmochim. Acta 39, 285–304 (1975).
7. Agnew, R. P. Differential Equations. McGraw-Hill, New York, 1942.
8. Shimp, N. G., J. A. Schleicher, R. R. Ruch, D. W. Heck, and H. V. Leland. Trace Element and Organic Carbon Accumulation in the Most Recent Sediments of Southern Lake Michigan. Illinois Geol. Survey Environ. Geol. Notes 41 (1971).
9. Lineback, J. A. and D. L. Gross. Depositional patterns facies and trace element accumulation in the Waukegan member of the late Pleistocene-Lake Michigan formation in southern Lake Michigan. Ill. State Geol. Surv. Environ. Geol. Notes 58, 1–25 (1972).
10. Edgington, D. N. and J. A. Robbins. Unpublished data.
11. Thomas, R. L., A. L. W. Kemp, and C. F. M. Lewis. Distribution, composition, and characteristics of the surficial sediments of Lake Ontario. J. Sed. Pet. 42, 66–84 (1972).
12. Turekian, K. K. Elements, hydrosphere distribution. 1969 Yearbook of Science and Technology. McGraw-Hill, New York, 1969.
13. Cline, J. T. and S. B. Upchurch. Mode of heavy metal migration in the upper strata of lake sediment. Proc. 16th Conf. Great Lakes Res., Int. Assoc. Great Lakes Res., Ann Arbor, Michigan, 1973, pp. 349–356.

GEOCHRONOLOGY OF LAKE MICHIGAN SEDIMENTS: ANOMALIES IN LEAD-210 DISTRIBUTIONS

J. A. Robbins,* D. N. Edgington, J. Gustinis,* and J. O. Karttunen

The interpretation of ^{210}Pb activity profiles and their use as a geochronological tool is critically dependent on a number of assumptions. When the flux of unsupported ^{210}Pb to the sediment-water interface, the sedimentation rate and unsupported ^{210}Pb activity are constant in time, and there is no physical or chemical postdepositional mobility of lead or bulk sediment, the ^{210}Pb distribution should be exponential in shape. Initial measurements of ^{210}Pb in a series of sediment cores from southern Lake Michigan by Robbins and Edgington revealed nearly exponential decreases in activity with time.(1) However, in some cases the unsupported ^{210}Pb activity was constant over the upper several centimeters of sediment, but exponential at greater depth. By comparing ^{137}Cs and ^{210}Pb profiles, Robbins and Edgington developed a successive quantitative model which attributed zones of constant activity at the surface to steady-state mixing of ^{210}Pb associated with sediment solids.(1) Subsequently, Bruland et al. observed depressed but nonconstant ^{210}Pb activities within the upper centimeter in two sediment cores from Lake Superior.(2) They were unable to decide if the effect was due to partial mixing of sediment solids or if it represented a real increase in sedimentation rates. More recently Robbins and Edgington have reported on subsurface deviations of the ^{210}Pb from exponential shape.(3) In one core from Green Bay, which is a shallow, high-energy depositional environment, the ^{210}Pb distribution is characterized by intervals over which the logarithm of the activity decreases linearly with depth, suggesting periods of constant sedimentation alternating with intervals over which the ^{210}Pb activity is nearly constant. The reason for such large subsurface anomalies as are seen in the Green Bay core are not clear, although they probably result from changes in local sedimentation rates associated with

---

*The University of Michigan.

increased sediment loading of the bay in combination with processes of resuspension and redeposition.

Here we report on the measurements of ^{210}Pb, ^{137}Cs, and stable lead in a series of ten cores from southern Lake Michigan. In nearly every core, significant subsurface anomalies occur, showing that nonexponential and presently uninterpretable features are the rule rather than the exception in the fine-grained sediments from southern Lake Michigan.

The cores were taken aboard the R/V Inland Seas in June, 1973, from a high-sedimentation rate area of southern Lake Michigan (stations UMAN-LM-73-2 and -3) and a transect of the lake (stations UMAN-LM-73-4 through -10) indicated in Fig. 1. Minimally disturbed cores were extruded, sectioned, and frozen aboard ship for later analysis. Analytical methods for the determination of ^{137}Cs and ^{210}Pb have been reported elsewhere.(1) Stable lead was determined by atomic absorption spectrophotometry using aliquots of the lechate used for the determination of ^{210}Pb. The data shown in Fig. 2a-j are presented in terms of the unsupported activity of ^{210}Pb in pCi/g dry weight. Values of

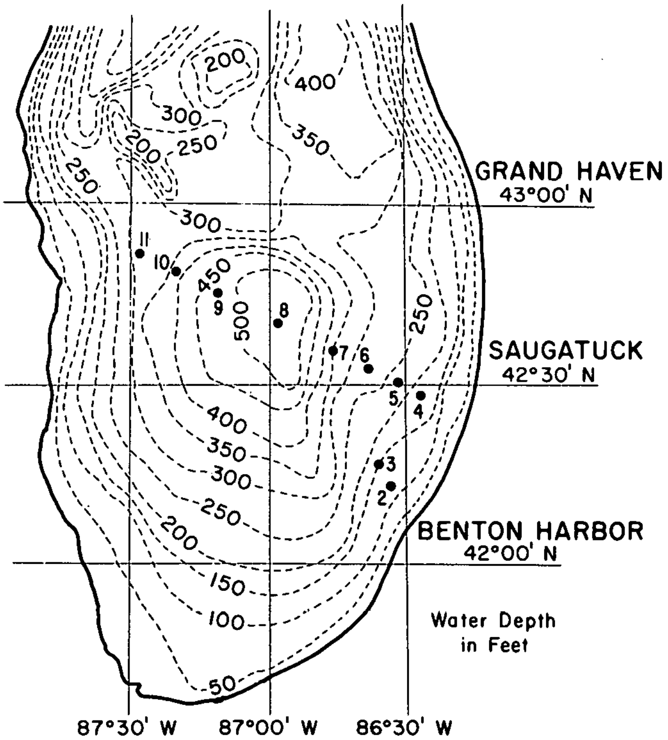


FIG. 1.--Stations occupied during the Argonne National Laboratory-University of Michigan cruise on the R/V Inland Seas, June 1973.
ANL Neg. 149-75-125

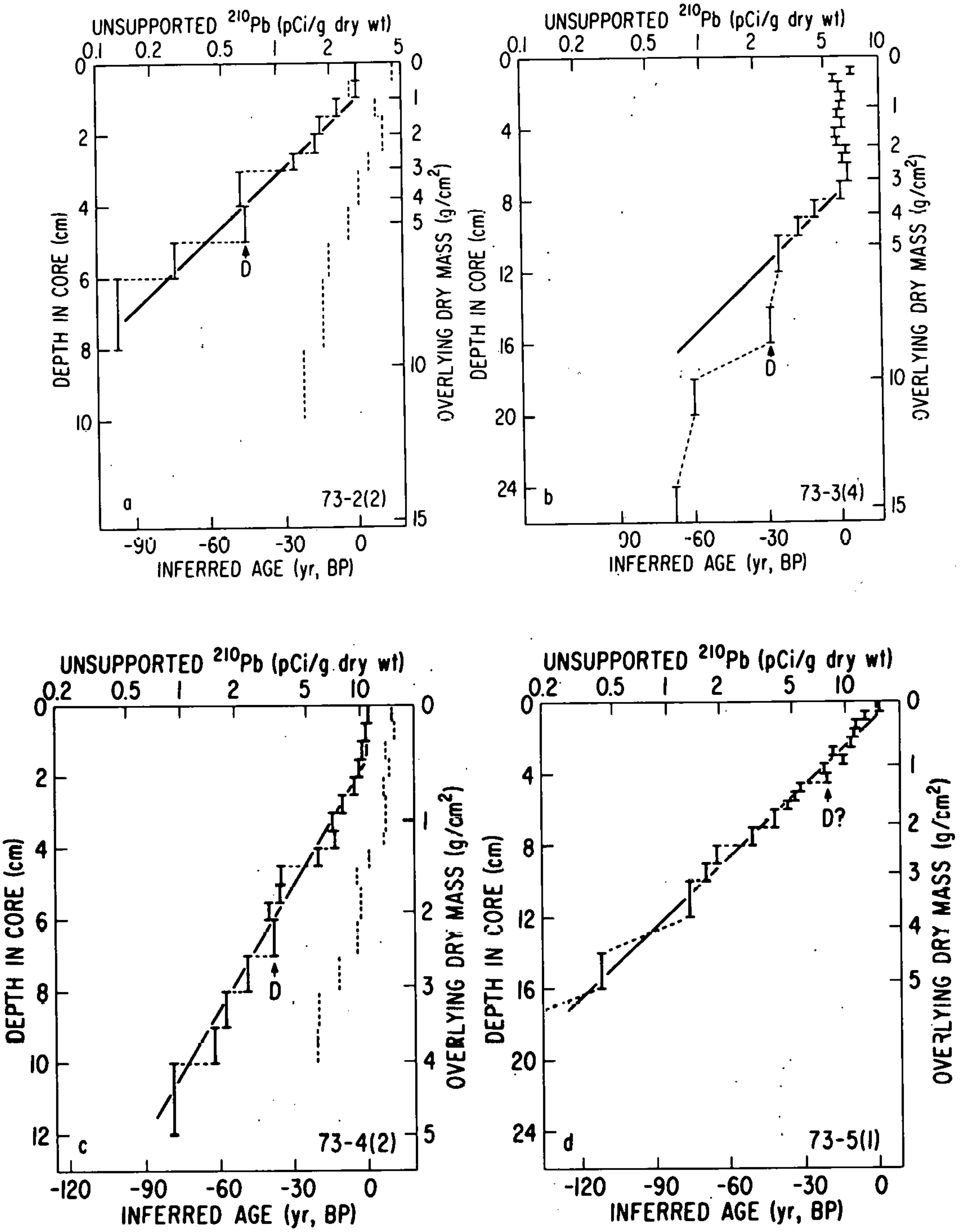


FIG. 2.--^{210}Pb and stable lead profiles in sediment cores. The vertical solid lines represent ^{210}Pb data, and the dashed vertical lines stable lead data on a relative scale. ^{210}Pb data points are joined by dashed lines for ease of visualizing regions of deposition (D) or erosion (E), and the solid line is the best fit calculated from the steady-state mixing model (Ref. 1).
ANL Neg. 149-75-120 and 122

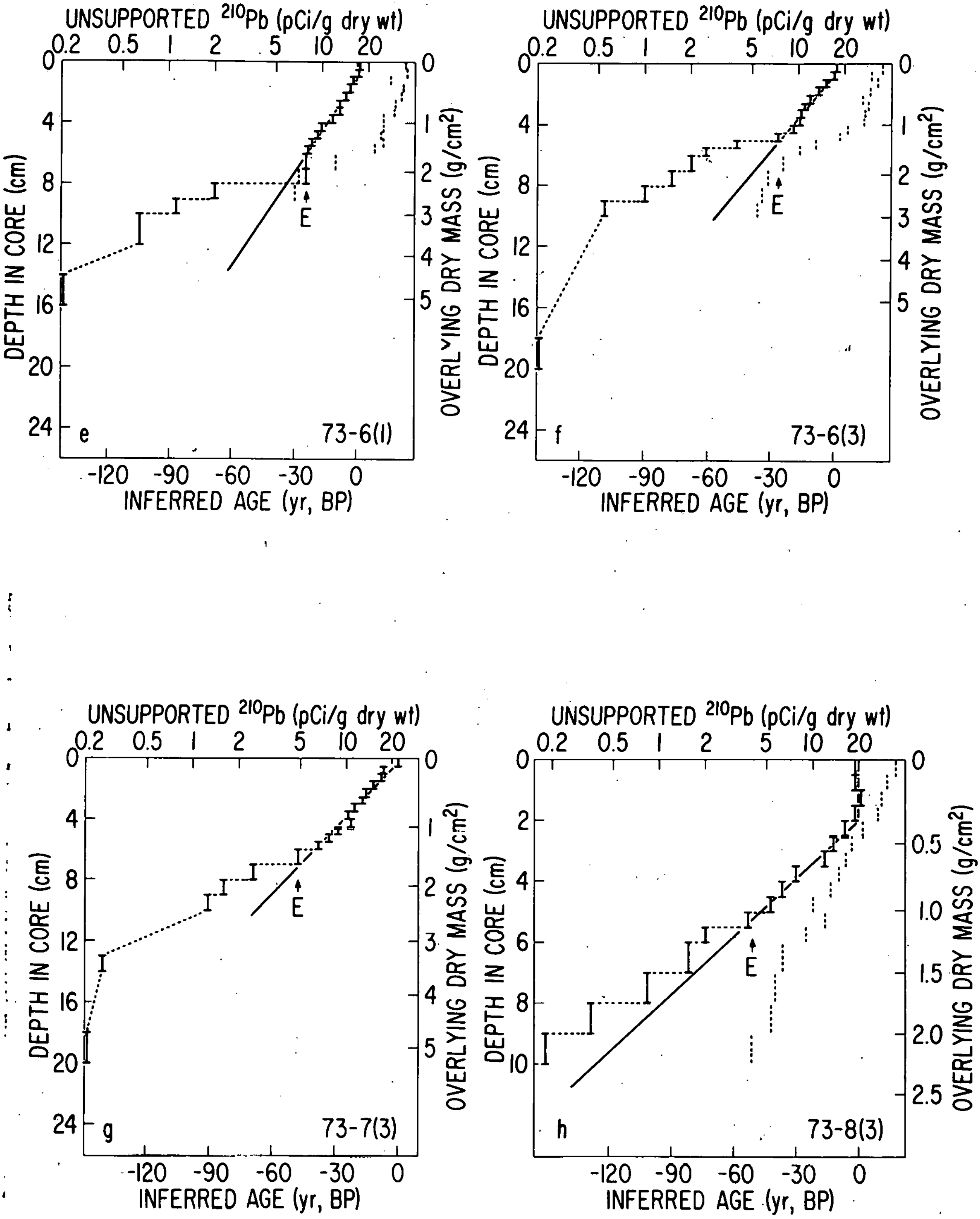


Fig. 2. continued. ANL Neg. 149-75-124 and 119

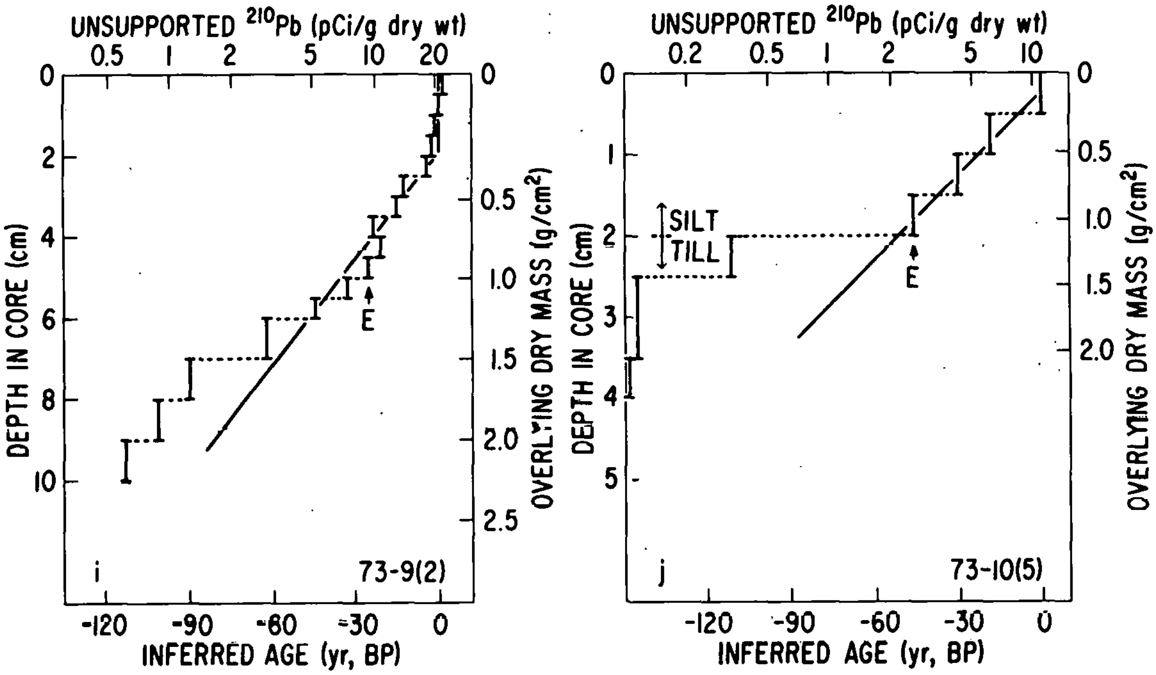


Fig. 2. continued. ANL Neg 149-75-121

^{210}Pb supported by the decay of ^{226}Ra in the sediments are estimated from the values measured at depth in the core. The depth in the core also is expressed in terms of the overlying dry mass in g/cm^3, calculated from fractional weight loss in each slice of sediment upon drying, taking 2.45 g/cm^{-3} as dry sediment density, the mean value obtained for a wide variety of Lake Michigan sediments.(4)

Exponential ^{210}Pb profiles may be expected if the following conditions are met: 1) constant unsupported ^{210}Pb flux to the sediment-water interface, p (pCi/g); 2) constant mass sedimentation rate, ω ($g/cm^2/yr$); 3) no postdepositional mobility of ^{210}Pb or of sediment solids; and 4) constant supported ^{210}Pb activity with depth. Postdepositional mobility includes chemical reactions or diffusion and physical redistribution due to mechanical mixing or bioturbation. Physical processes include erosion and slumping, irregular processes of deposition, or redistribution. Such mobility could readily destroy the information stored in the profile of radioactivity in the cores.

The activity of unsupported ^{210}Pb decreases exponentially with depth according to the relation

$$A = (A_s - A_0)\epsilon^{-\lambda m/\omega} + R_0 , \qquad (1)$$

where m is the mass of sediment (g/cm^2) overlying a given sediment depth, λ is the radioactive constant, ω is the sedimentation rate ($g/cm^2/yr^1$), A_s is the total activity at the sediment-water interface ($A_s = p/\omega$), and A_0 is the unsupported ^{210}Pb activity. The age (in years) of the sediment corresponding to an activity, A, is

$$t = -\lambda \ln (A_t - A_0/A_s - A_0) \ . \qquad (2)$$

The time scale associated with each of the individual profiles in Fig. 2a–j has been calculated from Eq. (2). Intervals of constant ^{210}Pb activity such as for station 3 (Fig. 2b), are assigned no elapsed time. Fits to the data using the steady-state mixing model for the ^{210}Pb data are shown as solid curves in Fig. 2a–j. For ease of visualization, the profiles of the measured ^{210}Pb are shown by dashed lines. The fits for ^{210}Pb, determined using only intervals for which there is measurable ^{137}Cs activity (during which time anomalies are not observed, as can be inferred from the agreement between sedimentation parameters calculated from ^{210}Pb and ^{137}Cs, Table 1) are in reasonable agreement with the experimental data. However, many of the profiles exhibit considerable deviation from the expected behavior. Even for those cores for which the theoretical fits appear to be satisfactory, such as for stations 4 and 5, there is evidence of possible significant deviations. Generally, two types of anomaly are seen in the ^{210}Pb distributions: mass intervals of relatively constant specific activity, suggesting very high sedimentation rates for short times or slumping and steep activity gradients, suggesting very low sedimentation rates for prolonged periods, or erosion. These anomalies are indicated by arrows in Fig. 2a–j.

The distributions of stable lead also show corresponding deposition or erosion-type anomalies (Fig. 2a–j). Edgington and Robbins have shown that the stable lead distribution in the fine-grained sediments reflects the history of cultural lead inputs.(5) As growth of lead emissions has been roughly exponential over the last 70 years, with about a 20 year doubling time, the lead concentration profiles in sediments minus natural background levels should be exponential, as is the case for ^{210}Pb. The appearance of corresponding anomalies in the stable lead distribution adds confidence that these are not an

TABLE 1. Summary of calculated parameters from mixing model for ^{210}Pb in Lake Michigan sediments

Station	Isotope	Supported ^{210}Pb (pCi/g)	Mixing Depth (g/cm^2)	Sedimentation Rate (g/cm^2/yr)	Age(a) of First Subsurface Anomaly (yr B.P.)
2	Pb	0.40	0.76	0.080	---
	Cs		0.70	0.080	
3	Pb	0.45	2.8	0.085	---
	Cs		2.8	0.080	
4	Pb	0.55	0.40	0.046	32
	Cs		0.45	0.042	
5	Pb	0.55	0.27	0.040	28
	Cs		0.25	0.034	
6-1	Pb	0.55	0.37	0.048	30
	Cs		0.34	0.035	
6-3	Pb	0.55	0.11	0.037	31
	Cs		0.17	0.030	
7	Pb	0.75	0.22	0.032	28
	Cs		0.20	0.029	
8	Pb	1.4	0.18	0.020	34
	Cs		0.19	0.021	
9	Pb	1.0	0.15	0.026	25
	Cs		0.16	0.022	
10	Pb	0.65	0.06	0.019	
				Mean	30 ± 3

(a) Age inferred from steady mixing model with constant sedimentation rate. Mean year of first subsurface anomaly is 1942 ± 3 yr.

analytical artifact. Anomalies would be expected in both the ^{210}Pb and lead distributions if there were variable additions or subtractions of the bulk sediment (ω not constant).

The correspondence between time and sediment depth or mass is critically dependent upon the interpretation of such features. As anomalies of constant activity occur below the sediment-water interface, it must be questioned whether those which occur at the sediment surface are due to vertical mixing or are a result of a recent episode of high deposition. No elapsed time is associated with an interval due to a sudden addition of sediment, but if the layer of constant activity were due to physical or biological mixing, then its age would be equal to the number of years of deposition in this layer. For an erosional anomaly the difference in the age of the sediment layer at the top and that at the bottom gives a measure of the number of years of sediment lost at a time corresponding to the smaller value of t (calculated from Eq. 2).

The times of occurrence of indicated anomalies calculated from Eq. (2) with A_2 taken as the highest observed unsupported specific activity in each core, are shown in Fig. 3. The times are scattered. On the other hand, the steady-state mixing model was used to assign a date to the most recent subsurface anomaly. For all of the cores taken on this transect, the first anomaly occurred 30 ± 3 years B.P., or 1942 A.D. Dates associated with anomalies for individual cores are also given in Table 1. It is noteworthy that, using the steady-state mixing model, the uppermost subsurface anomaly falls into registration in this series of widely separated cores at around 1942. Kemp et al. found a similar effect in a series of fine-grained sediment cores from Lake Erie.(6) They observed a narrow band of shells interposed between sections of homogeneous sediment at variable depths from core to core. Pollen dating showed that the shell band developed in all cores about the same time — around 1940. It is suggested that the anomalies are the result of some event common to at least several of the Great Lakes. If such a time correlation is not an artifact of interpretation or of chance, one might expect to find regional causes acting singly or in combination to produce anomalies. Floods and droughts, high or low lake levels, and changing land use may influence inputs of terrigenous material to the lake. Changes in the depth of a surficial mixing zone due to bioturbation or the structure of bottom currents would produce anomalies with little expenditure of energy.

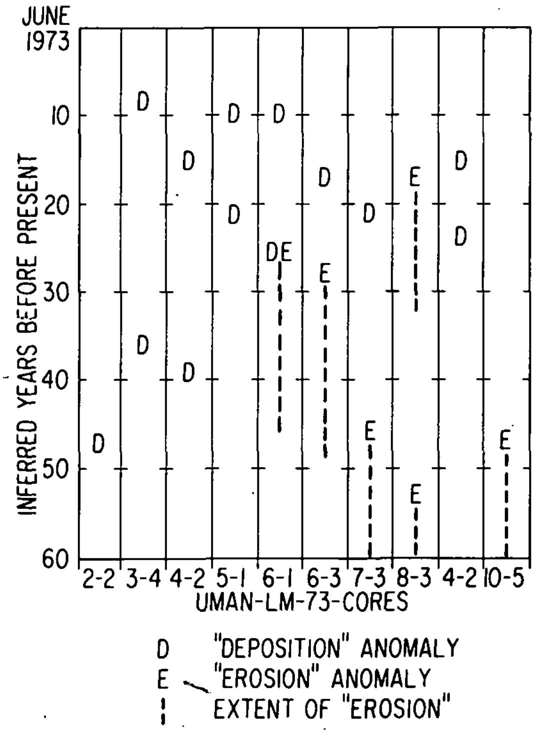


FIG. 3.--Comparison of the time occurrence of depositional and erosional anomalies.
ANL Neg. 149-75-123

If these depositional anomalies are due to increase in deposition of terrigenous material associated with floods, the specific activity of anomalous deposits should not be very similar to that of surficial deposits laid down during periods of constant low sedimentation. The observed specific activities of these anomalies are comparable to those of the immediately overlying or underlying sediments. This suggests that the mass of sediment associated with an anomaly was added or deleted by erosion, transport, and mixing of sediments already deposited in the lake. In small lakes such resuspension of sediments is common.(7)

One possible cause of anomalies may be major storms. The weather reports of the Michigan Section of the U.S. Weather Bureau,(8) indicate two severe storms from 1920 on, both in November. "The most disastrous and widespread storm in the history of Michigan or Lake Michigan occurred on November 11—12, 1940." The storm of November 18, 1958, was less severe. Such an explanation of anomalies is tempting: The erosion anomalies and the deposition anomalies would both be explained, and the surficial activities of resuspended recent sediments would be approximately what would be expected for the next layer of normally depositing sediments. If major storms are an important factor in the redistribution and "final deposition" of fine-grained sediments, several corollaries may follow. Patterns of deposition (post-glacial sediment depth contours, for example) may reflect current circulation patterns established during major storm events. This, rather than the proximity of major tributary rivers, might explain the occurrence of highest sedimentation rates in a zone along the eastern shoreline of Lake Michigan rather than in the deepest part of the southern basin. It is possible that instantaneous mass sedimentation rates are not very different anywhere in the deeper parts of the southern lake basin and that higher average values along the eastern shore originate in part from periodic episodes of redeposition in which there is a net transfer of accumulated sediment from the western to the eastern side of the lake. This would account for the ^{210}Pb profile at station 10 (Fig. 2j). According to Eq. (2), the sediment in the interval from 4 to 5 cm (~ 1.25 g/cm^2) should be roughly 120 years old, whereas the material in the adjacent underlying layer is, in fact, a fine glaciolacustrine clay which is undoubtedly much older. The discrepancy in times would be removed if the material above the clay were periodically swept away and redeposited elsewhere in the lake. It is evident from Fig. 3 that there is a trend toward erosional anomalies westward along the transect into deeper water. In view of our discussion concerning the mechanism for generating average sedimentation rates, this is not surprising because erosional anomalies are associated with sediments offshore possessing lower average sedimentation rates.

Most studies of the behavior of natural or anthropogenic chemical species in sediments assume steady-state, constant sedimentation rates and no resuspension, erosion, or mixing of sediments. In Lake Michigan sediments, such assumptions are undoubtedly oversimplifications. Surficial mixing is usually present, and erosion and redeposition seem to be important factors in determining the average sedimentation rates in a given location. ^{210}Pb profiles contain much information about such processes. Given the complexities of the sedimentation process, ^{210}Pb profiles must be obtained on every core before meaningful interpretations of observed concentration profiles can be made for any but the most mobile chemical species.

Therefore, the behavior of ^{210}Pb in lacustrine environments is very important and should be studied in considerable detail. These studies should include:

1. Delineation of the sources of ^{210}Pb and of sediments, and their spatial and temporal variations. This would include the sampling of rivers and of wet and dry fallout for several years, as well as the periodic maintenance of sediment traps in a number of selected locations and at several depths at each location. Data on ^{137}Cs, stable lead, and other species relatively immobile in the sediments could supplement ^{210}Pb data, especially if the source is localized and known.

2. A study of the spatial variation of anomalies over the lake bottom. ^{210}Pb profiles may vary significantly on a spatial scale of 0.1 m or 1 m, indicating ripple structure, or 10 or 100 m, or perhaps kilometers. Such a study would indicate the number of replicate cores and the spacing of a survey grid that would be required to derive meaningful estimates of various chemical species in the sediments. It would also indicate the spatial extent of anomalies,

better showing the mode of their production.

3. A study of the chemical mobility of lead in the sediments, to better define whether diffusional processes are significant. Up to now, it has been assumed that there is very little postdepositional mobility due to diffusional processes.

References

1. Robbins, J. A. and D. N. Edgington. Determination of recent sedimentation rates in Lake Michigan using ^{210}Pb and ^{137}Cs. Geochim. Cosmochim. Acta 39, 285–304 (1975).
2. Bruland, K. W., M. Koide, C. Bowser, L. J. Maher, and E. D. Goldberg. Lead-210 and pollen geochronologies on Lake Superior sediments. Quat. Res. 5, 89–95 (1975).
3. Robbins, J. A. and D. N. Edgington. Depositional processes and the determination of recent sedimentation rates in Lake Michigan. Proc. 2nd Great Lakes Conf., March 1975, Interagency Committee on Marine Science and Engineering, in press.
4. Robbins, J. A. and D. N. Edgington. The use of natural and fallout radionuclides to measure recent sedimentation rates in southern Lake Michigan. Radiological and Environmental Research Division Annual Report, Part III, January–December 1972. ANL-7960, Part III, pp. 31–53.
5. Edgington, D. N. and J. A. Robbins. Records of lead deposition in Lake Michigan sediments since 1800. To be published.
6. Kemp, A. L. W., C. B. J. Gray, and A. Mudrochova. Changes in C, N, P, and S in the last 140 years in three cores from Lakes Ontario, Erie, and Huron. Nutrients in Natural Waters, Ed. H. Allen and J. R. Kramer, J. Wiley and Sons, Inc., New York, 1972, pp. 251–270.
7. Davis, M. B. Pollen grains in lake sediments: Redeposition caused by seasonal water circulation. Science 162, 796–799 (1968).
8. Climatological Data, Michigan Annual Summary 1914–present. National Weather Service, National Oceanographic and Atomspheric Administration, Department of Commerce, Washington, D.C.

9 ~~THE~~ EFFECT OF SULFUR DIOXIDE ON YIELD AND GROWTH OF KIDNEY BEANS (PHASEOLUS VULGARIS L.)

M. S. Berigari, C. F. Jordan, and C. A. Feickert

Introduction

The increase in human population and the world-wide demand for higher standards of living will tend to result in a continuing air pollution problem involving agriculture and human health everywhere. Evidence exists today of sulfur dioxide and fluoride injuries to vegetation in many areas of the world.

The total national cost of air pollution damage in the United States for 1968 was estimated at $16.1 billion.(1) Although accurate figures are not available, it is known that significant economic loss in crop yields is attributed to sulfur dioxide every year.(2)

Sulfur dioxide is emitted to the atmosphere during the combustion of sulfur-containing fuels, especially coal and petroleum, and in the roasting of sulfide ores during smelting operations. It is also emitted to the atmosphere from volcanic activity.(2)

Since the beginning of this century, sulfur dioxide has been recognized as an air pollutant causing damage to vegetation. In fact, more work has been reported on the response of vegetation to sulfur dioxide than to any other air pollutant.(2) Reviews on this subject are numerous; however, most of the research done in the past is descriptive in nature.

There is growing public concern over the impact of fossil fuel pollutants on human health and on our total environment. This concern is justifiable on the basis of information already available on deleterious effects of a number of air pollutants to living organisms. Thus it was natural for Argonne to submit research proposals on the effects of sulfur dioxide or other pollutants on growth, yield, and food quality of agricultural crops and/or on the total environment.

Visible SO_2 injury to vegetation is well documented. However, little is known about sulfur dioxide effects on physiological processes which affect plant growth and development. The purpose of this work was to see whether sulfur dioxide has any effect on total protein content of kidney beans, the biomass, and the chlorophyll and protein content of trifoliate leaves. We also studied the relative absorption of SO_2 by plants at different stages of growth. Kidney beans were chosen for this study instead of soybeans for several reasons.

1. Kidney bean seeds constitute an important source of protein, and thus, are economically important.
2. Both kidney beans and soybeans belong to the same family, leguminosae, and therefore research on Phaseolus vulgaris L. may be significant to soybeans (Glycine max., Merr.).
3. Kidney bean plants, when grown to full maturity, require less space per plant than soybeans.
4. Kidney bean plants are as sensitive to sulfur dioxide as soybeans.(2)

Materials and Methods

Red kidney field beans (Lot No. 63-386) were obtained from Joseph Harris Co., Rochester, New York. Uniform seeds were selected and rinsed in 5% $KMNO_4$ solution for one minute to inhibit fungus growth on the seed coat during germination. This was followed by thorough rinsing of the seeds with distilled water.

Experiment 1

Three seeds were placed in moist potting soil (available commercially) in 6" clay pots. These were allowed to germinate at room temperatures until seedlings reached 5 to 7 cm in height above soil level. Then only one plant from each pot was allowed to grow in the chamber. Plants were chosen for uniformity in size and appearance (Fig. 1). Nine such pots were placed in a $0.6 \times 0.6 \times 0.6\ m^3$ chamber. Each pot protruded down through a circular hole in a Plexiglass baffle that made good contact with its rim. The bottom of each pot extended below the chamber into a stainless steel tray from which plants received water and nutrients while the chambers were closed (Fig. 1). This was a major modification in size and design of the chambers over that described by Jordan.(3) Plants were provided weekly with 200 ml of All-Purpose Liquid Fertilizer, Stern's Miracle-Gro (15-30-15 concentrated), prepared as recommended by the supplier. Both chambers were kept under 8 hours of dark and 16 hours of light (6:00—22:00) with light intensity ranging from 11 to 19 Klux, depending on the location of the plant in the chamber. However, plants in analogous locations in the two chambers received the same light flux, and thus it was more meaningful to compare results from such plant pairs. Light was provided by 40 CW cool white and orange fluorescent Sylvania lamps. The temperature (minimum and maximum) inside the chambers varied from 14 to 32 ± 1° C during dark and photoperiods, respectively.

Sulfur dioxide mixed with air at $\simeq 0.20$ ppm was introduced on a continuous basis to the plants in the experimental chamber. Both chambers were kept closed except for occasional inspection of plants for any visible damage due to SO_2 toxicity. Air without SO_2 was pumped into the control chamber from the same source and at the same rate (16.0 l/min) as that for the experimental chamber (Fig. 1).(3)

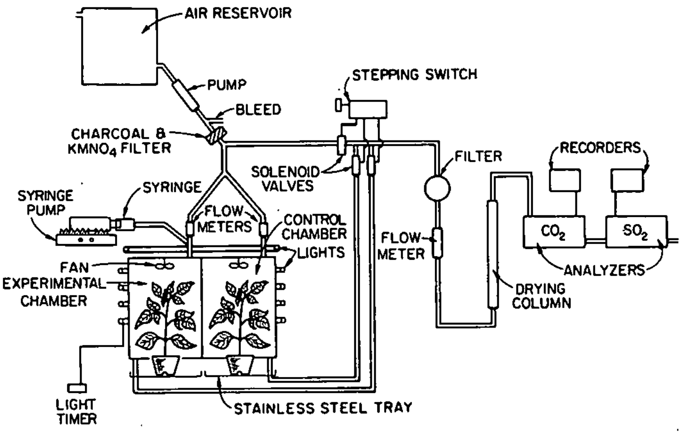


FIG. 1.--System for studying air pollutant effects on plant growth. (ANL Neg. 149-5465)

Exposure of plants to sulfur dioxide was discontinued when legumes began to develop (when plants were about 75 days old). Longer exposure may result in premature falling of legumes.

Legumes were collected when they were mature, and the seeds were weighed before and after drying overnight in an oven kept at 70° C. The dry beans were analyzed for total protein according to the method described by Berigari.$^{(4)}$

Experiment 2

From the above experiment we made several observations:

1. Growing nine plants in a $0.6 \times 0.6 \times 0.6$ m^3 chamber led to overcrowding of plants during later stages of plant growth.

2. Continuous exposure of plants to sulfur dioxide with chambers closed led to water condensation on the walls of the chamber.

3. Using commercially available potting soils for plant growth in 6" clay pots with subirrigation did not allow adequate aeration of the roots, as indicated by their preferential growth on the surface of the soil.

Therefore, Experiment 2 was set up to remedy the conditions described above. Except for the following changes, it was the same as Experiment 1.

1. Plants were grown in Terra-Lite vermiculite supplied by Grace Co., Cambridge, Massachusetts, in 7" clay pots.

2. Only five plants were allowed to grow in each chamber, and each clay pot was covered with a piece of opaque Lucite except for a slit through which the stem of the plant could protrude into the space above the pot. This was done to miniize SO_2 adsorption on the vermiculite and to reduce direct evaporation of water from the vermiculite into the chambers in order to prevent unnecessary water condensation on the chamber during exposure of plants to SO_2.

3. One-week-old kidney bean plants in the experimental chamber were exposed to 1.5 ppm SO_2 in the air for a period of 4 hours, three times per week (Monday, Wednesday, Friday). This was done during the photoperiod and while the chamber doors were kept closed. At other times they were left open to facilitate air exchange and prevent condensation.

Sulfur dioxide was monitored inside the experimental chamber during periods of exposure, using a Theta Sensor, Model LS400 AS, connected to a strip chart Honeywell recorder. Carbon dioxide in the air before and after it passed through the two chambers was analyzed, using a Lira, Model 300, infrared analyzer connected to another strip chart recorder. The CO_2 was recorded prior to and during SO_2 exposure to measure any change in the relative rates of apparent photosynthesis in the two chambers.

Extreme temperature fluctuations from dark to photoperiod inside the chambers were 15 to 37 ± 1° C during cool nights and hot summer days, respectively, especially when the air conditioner was not operative for a few days during the growing period. The humidity ranged from 45% when the chambers were open to $\simeq$ 100% when the chambers were closed. When plants reached maximum heights (no further increase in length) the middle leaflet of the terminal trifoliate leaf was removed from each plant for chlorophyll analysis. The leaflet was cut in half along the midrib vein, and the fresh weight of each half was determined. One half was used for chlorophyll analysis, while the other half was air dried and weighed again. Another leaflet of the same trifoliate leaf of each plant was treated similarly, and one half was used for total protein analysis by the method described in another paper of this Annual Report.(4)

The chlorophylls were extracted with 80% acetone in water (v/v) and analyzed according to the method described by Holden.(5) Optical densities were measured at 645 and 663 nm, and chlorophylls a and b and total chlorophyll were calculated from an empirical formula.

Finally, all plants were harvested at the age of 110 days, and the fresh and oven dry weights (at 70° C) of the legume, seeds, foliage, and roots were determined.

Results and Discussion

Experiment 1

Chronic injury to older trifoliate leaves of the SO_2 exposed plants was visible after two weeks of exposure. This was marked by bleached white areas on the blade of the leaves which turned to brownish-red dead spots within a few days. The dosage of 0.2 ppm SO_2 was lower than the reported threshold level of 0.3 ppm SO_2 for 8 hours. However, other conditions were favorable for maximum SO_2 entry into plants through opened stomata. These conditions include high relative humidity, adequate moisture in the soil, long (16-hour) photoperiod, moderate temperatures, and continuous exposure of plants to sulfur dioxide.(6)

The data presented in Table 1 show that both fresh and oven-dry weights of plants exposed to SO_2 were considerably lower than the corresponding values for control plants. Among nine plants in each chamber, only two plants in the control chamber showed lower values than their counterparts in the experimental chamber. Genetic variability even within a single species may account for individual plant variation in response to air pollution.(7) Total yield of SO_2 exposed plants was reduced by about 15%, relative to control plants. This reduction in yield is quite significant economically when translated to terms of total acreage allocated for production of field kidney beans in the United States or the world.

The data presented in Table 2 show that the protein content of ground beans ranged from 24 to 29% for control plants, compared to 25 to 32% for SO_2 exposed plants. Differences in protein content among beans from each treatment (29 – 24 = 5% and 32 – 25 = 7%) were greater than the difference between mean values of each treatment (28.3 – 26.7 = 1.6%). This indicates that there was no significant difference between the protein contents of the beans obtained under the two sets of conditions, i.e., SO_2 exposed and control plants. In other words, small but continuous levels of SO_2 around plants caused a reduction in yield but did not bring about any measurable change in protein content of the beans when soil was supplemented with major nutrients.

TABLE 1. Yield of kidney beans in grams from Experiment 1

Plant No.	Control Plants		SO_2 Exposed		% of Control	
	FW	ODW	FW	ODW	FW	ODW
1	34.4	25.5	13.8	13.4	40.1	52.5
2	30.4	26.8	30.2	25.0	99.3	93.3
3	30.7	27.0	23.7	20.0	77.2	74.0
4	22.0	15.0	8.7	7.4	39.5	49.3
5	42.1	37.0	40.3	36.2	95.7	97.8
6	29.2	25.1	35.9	32.1	123.0	128.0
7	28.1	24.3	11.1	10.6	39.5	43.6
8	30.2	25.7	26.5	24.5	87.7	95.3
9	27.4	24.2	34.0	26.1	124.1	108.0
Total	274.5	230.6	224.2	195.3	---	---
Mean	30.5	25.6	24.9	21.3	80.7	84.7

FW = fresh weight of beans
ODW = oven dried weight of beans

Experiment 2

Sulfur dioxide was introduced into the experimental chamber at a constant

TABLE 2. Percent protein of kidney bean seeds from Experiment 1 calculated from data for nitrogen analysis

CONTROL PLANTS					SO_2 EXPOSED PLANTS				
Replicates			Average	S.E.	Replicates			Average	S.E.
24.3	23.5	23.9	23.9	0.40	29.7	29.2	29.4	29.4	0.25
24.4	25.4	24.9	24.9	0.50	29.2	28.0	28.6	28.6	0.60
27.2	27.7	26.9	27.3	0.41	29.2	28.5	29.6	29.1	0.56
28.0	27.5	27.1	27.5	0.45	28.1	28.9	29.0	28.7	0.49
26.3	24.3	26.2	25.6	1.07	27.2	27.7	26.9	26.7	0.23
26.6	26.0	27.9	26.8	0.97	28.7	30.0	29.9	29.5	0.72
29.5	29.3	28.4	29.1	0.59	32.7	32.4	32.4	32.4	0.25
29.5	29.2	29.0	29.2	0.25	25.1	26.0	24.9	25.3	0.58
26.4	26.2	25.7	26.1	0.36	25.8	24.5	25.5	25.3	0.68
MEAN			26.7					28.3	

S.E. = standard error.
Each replicate value is an average of three measurements.

concentration of 1.5 ppm. However, its actual concentration inside the chamber (monitored during the 4-hour exposure) varied with the age of the plants. The data presented in Fig. 2 summarize this relationship. Plant growth results from both cell division and cell enlargement. For the foliar portion this means an increase in size and number of leaves and branches. Such increase seems to enhance the capacity of plants to absorb SO_2 and, therefore, reduce its concentration in the ambient air; i.e., bean plants seem to act as sinks for the air pollutant with an efficiency which increases with age. Mathematically, the curve in Fig. 2 may be expressed as $X = K/Y$, where X = the age of plants, $Y = SO_2$ concentration measured in the ambient air, and K = a constant, which is ~ 8 in this case. On the other hand, when we plot the amount of SO_2 absorbed by plants, there is a near linear relation with age up to a point at which there is no further increase in leaf growth (Fig. 3). This information should be useful in calculating the rate of pollutant removal by vegetation near industrial areas where subinjurious levels of pollutant are emitted during various seasons of the year. There is evidence in the literature that low levels of SO_2 (0.15 ppm in ambient air may be beneficial to some plants, as evidenced by an increase in the yield of ryegrass, for example.(8)

The data presented in Table 3 (columns 2 and 4) show that the difference between mean values of the oven dried weights of plant foliage was very small

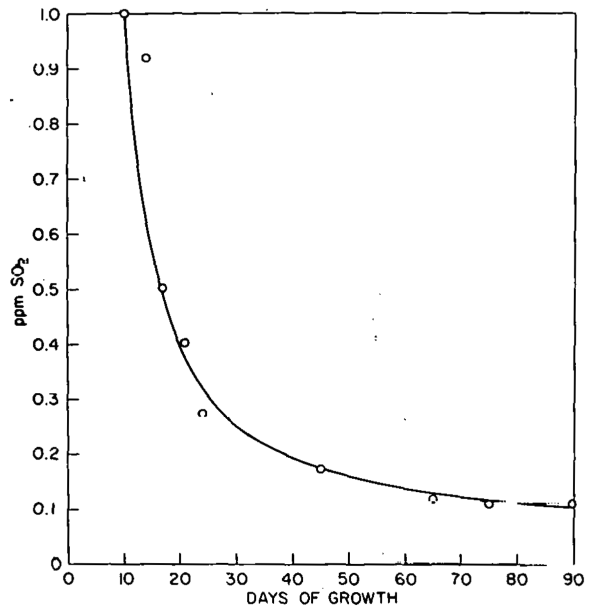


FIG. 2.--SO_2 monitored as a function of plant growth in the chamber. (ANL Neg. 149-6608)

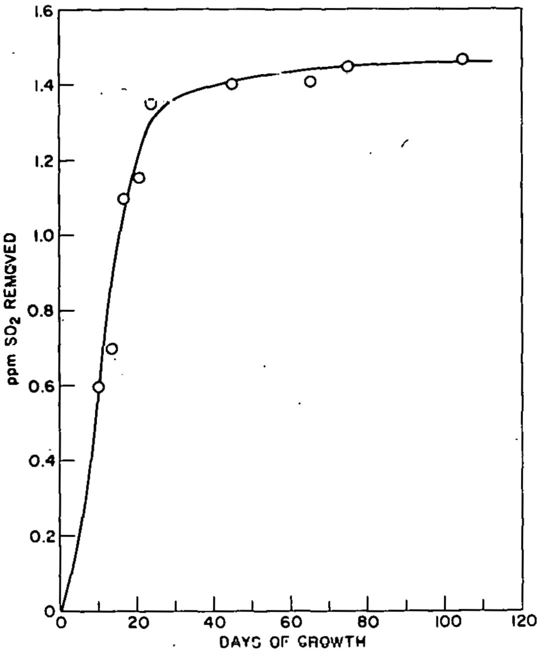


FIG. 3.--SO_2 removed from chamber by plants at various stages of growth. (ANL Neg. 149-6607)

(2%). However, there were considerable differences between mean values of the oven dried roots, legumes, and seeds; i.e., there was 20%, 14%, and 17% reduction in the dry weights of these parts, respectively, for SO_2 exposed plants compared to control plants.

The data for legumes and dried beans are of special interest since these are the edible parts. Only one (#3) out of five plants in the experimental chamber showed actual increase in dry weights of both legumes and beans, which may be attributed to genetic variability within a single species as Hepting(9) suggests. He found that within a tree species, white pine, variation in resistance to sulfur dioxide was often much greater among individual clones of the same species than the differences between various species of pine. Similarly the total biomass (oven dried) of the SO_2 exposed plants was lower than that for the control plants. Among the plants which appeared more sensitive to SO_2, the reduction in weight of dried legumes and beans ranged from 7.6 to 10.1 g and 4.5 to 10.1 g per plant, respectively, which constitute

TABLE 3. Fresh and oven dry weights of various plant parts and total biomass in grams from Experiment 2

Plant No.	Control		SO_2 Exposed			Control		SO_2 Exposed		
	Foliage				% of control	Root				% of control
	FW	ODW	FW	ODW	ODW	FW	ODW	FW	ODW	ODW
1	116.1	29.0	97.3	27.2	93.8	58.7	10.4	50.7	3.8	36.5
2	48.8	16.8	76.9	24.3	145	39.5	7.8	35.1	5.7	73.1
3	72.4	20.3	48.2	17.5	86.2	53.7	8.1	45.2	9.3	115
4	113.0	28.5	99.8	25.1	88.1	40.2	7.2	50.1	6.8	94.4
5	100.0	25.9	110.1	28.0	108	58.1	8.7	66.3	8.1	93.1
Total	450.3	120.4	432.3	122.6	102	250.2	42.2	247.4	33.7	79.9
Mean	90.1	24.1	86.5	24.6	102	50.0	8.4	49.4	6.7	79.8

	Legumes					Seeds		
	FW	ODW	FW	ODW	ODW	ODW	ODW	ODW
1	77.7	33.4	95.6	23.3	69.8	22.1	14.6	66.1
2	56.7	39.9	64.1	31.3	78.4	31.1	23.3	74.9
3	63.0	31.7	61.8	43.1	136	25.6	34.8	136
4	72.1	28.9	53.6	19.9	68.8	18.4	13.9	75.5
5	53.1	34.0	91.4	26.4	77.6	26.7	16.2	60.1
Total	322.6	167.9	366.5	144.1	85.8	123.9	102.8	83.0
Mean	64.4	33.6	73.3	28.8	85.7	24.8	20.6	83.1

	Biomass				
	FW	ODW	FW	ODW	ODW
1	252.5	68.9	243.6	54.2	78.7
2	145.0	64.4	176.1	61.3	95.2
3	189.1	60.0	155.2	70.0	117
4	225.3	64.7	203.5	51.8	80.1
5	211.2	68.5	268.0	63.6	92.8
Total		326.5		300.8	92.1
Mean		65.3		60.1	92.1

FW = fresh weight.

ODW = oven dried weight at 70 °C.

an average of 25% and 31% reduction in the yields of SO_2 exposed plants, respectively (Table 3). Although a constant level of SO_2 was introduced into the chamber, there was a significant reduction of its concentration inside the chamber due to its absorption by plants (Fig. 2). Hence, it seems more relevant to monitor concentrations of airborne pollutants in the immediate vicinity of subjected plant populations and interpret their effects on that basis rather than at distances from plants.

There was about 10 to 30% reduction in the apparent rate of photosynthesis of SO_2 exposed plants relative to the control, depending on the age of plants, which ultimately was reflected in a reduction of the yield in exposed plants due to a decrease in photosynthate.

The data presented in Table 4 clearly show that concentrations of

TABLE 4. Chlorophyll content of trifoliate leaves of the same age in kidney bean plants, mg/g leaf

Plant No.	Chl. a	Difference	% of control	Chl. b	Difference	% of control	Total Chl. (a+b+—)	Difference	% of control
S1	1.07			2.00			3.97		
C1	0.76	0.31	40.8	1.36	0.64	47.0	2.74	1.23	44.9
S2	1.14			2.24			4.39		
C2	0.47	0.37	78.7	0.86	1.38	160.0	1.76	2.63	149.0
S3	0.94			1.69			3.44		
C3	0.63	0.31	49.2	1.08	0.61	56.5	2.21	1.23	55.6
S4	1.06			1.92			3.81		
C4	0.65	0.41	63.1	1.13	0.79	69.9	2.29	1.52	66.4
S5	1.12			2.14			4.27		
C5	0.80	0.32	40	1.35	0.79	58.5	2.71	1.56	57.6

S refers to plants exposed to SO_2 (1.5 ppm initial concentration).
C refers to plants grown in control chamber without SO_2.

chlorophylls a and b and total chlorophyll in similar leaves were much higher for the SO_2 exposed plants than for control plants. This means that either the rate of chlorophyll degradation in control plants is higher or its rate of synthesis is lower than in the SO_2 exposed plants or that a combination of both factors exists.

Table 5 shows the data for protein content of similar leaves which clearly demonstrate higher values for the SO_2 exposed plants compared to control plants. Again, these data indicate higher rates of protein synthesis or higher metabolic rates in the SO_2 treated leaves than in the control plants.

When the data of Tables 4 and 5 are taken together, it becomes obvious that there was a delay in senescence of terminal trifoliate leaves from SO_2 exposed plants compared to those from control plants. This is not surprising since the actual SO_2 concentrations monitored during development and growth of these leaves averaged about 0.1 ppm of SO_2 in the vicinity of the plants (Fig. 2). In other words, at low levels of SO_2 (~ 0.1 ppm) there was an actual stimulation of metabolic processes by SO_2, with the absence of any visible injuries in these leaves. Recent work by Cowling et al.(8) on ryegrass supports the hypothesis that low levels of sulfur dioxide (0.10 to 0.15 ppm) in the absence of other air pollutants could actually correct sulfur deficiency in plants grown in sulfur deficient soil or nutrient solutions, which might be the case with our nutrient solution during the second experiment in which we used vermiculite instead of potting soil.

TABLE 5. Protein content of trifoliate leaves of the same age in kidney bean plants

	% Protein	Difference	% Control
S1	33.5		
C1	29.4	4.1	13.9
S2	23.5		
C2	22.4	1.1	4.9
S3	27.0		
C3	21.0	6.0	28.6
S4	31.5		
C4	18.9	2.6	13.8
S5	33.2		
C5	25.6	7.6	29.6

S refers to plants exposed to SO_2 (1.5 ppm initial concentration).

C refers to plants grown in control chamber without SO_2.

References

1. Barrett, L. B. and T. E. Wadell. Cost of Air Pollution Damage: A Status Report. Environmental Protection Agency, National Environmental Research Center, Research Triangle Park, North Carolina, 1973.
2. Barret, T. W. and H. M. Benedict. Sulfur dioxide. Recognition of Air Pollution Injury to Vegetation: A Pictorial Atlas, Ed. J. S. Jacobson and A. C. Hill. Air Pollut. Cont. Assoc., Pittsburgh, Pa., 1970, pp. C1–C17.
3. Jordan, C. F. Sulfur dioxide resistance in plants. Radiological and Environmental Research Division Annual Report, Part III, January-December 1972. ANL-7960, Part III, 146–148.
4. Berigari, M. S. Determination of total proteins in plant tissues from nitrogen analysis by a modified Kjeldahl digestion and Nesslerization method. This report.
5. Holden, M. Chlorophylls. Chemistry and Biochemistry of Plant Pigments. Ed. T. W. Goodwin. Academic Press, New York, 1965, pp. 461–488.
6. Hindawi, I. J. Air Pollution Injury to Vegetation. U. S. Dept. Health, Education, and Welfare, National Air Pollution Control Administration, Raleigh, North Carolina, 1970.
7. Heggestad, H. E. and W. W. Heck. Nature, extent, and variation of plant response to air pollutants. Advances in Agronomy, 23, Ed., N. C. Brady. Academic Press, New York, 1971, pp. 111–145.
8. Cowling, D. W., L. H. P. Jones, and D. R. Lockyer. Increased yield through correction of sulfur deficiency in ryegrass exposed to sulfur dioxide. Nature 243, 479–480 (1973).
9. Hepting, G. H. Air pollution and trees. Man's Impact on Terrestrial and Oceanic Ecosystems, Ed. W. H. Matthews, F. E. Smith, and E. D. Goldberg. MIT Press, Cambridge, Mass., 1971, pp. 116–129.

DETERMINATION OF TOTAL PROTEIN IN PLANT TISSUES FROM NIGROGEN ANALYSIS BY A MODIFIED KJELDAHL DIGESTION AND NESSLERIZATION METHOD

M. S. Berigari

Introduction

Proteins are immensely versatile macromolecules, each molecule consisting of amino acids bonded in a polypeptide chain to form its primary structure. While some portions of the peptide chain are neatly coiled (ordered), other portions are neatly folded but remain uncoiled (disordered). Their intimate association with other micro- and macro-molecules in biological systems is also well known.(1) Consequently, proteins vary widely in their physicochemical properties. Hence, there is no simple and accurate analytical method available for determination of total proteins in a biological sample. Several methods, however, are available by which an estimate of total proteins in aqueous solutions is made from relatively specific colored products resulting from the reaction between the peptide bonds or some amino acids and certain reagents to yield products which can be determined colorimetrically. Similarly total protein estimate can be made from ultraviolet light absorption by the tryptophan, tyrosine, and to a minor extent, phenylalanine of the parent proteins.(2) Material which is all protein, on the other hand, generally contains 15 to 16% nitrogen.(2) Thus one can calculate the total protein content of a sample from its analysis for nitrogen, provided other nitrogen-containing compounds occur in minute quantities or they can be excluded analytically from protein nitrogen, as nitrate nitrogen, for example, which can be kept in the oxidized form while protein nitrogen is converted to NH_4^+ ions.

The discovery that boiling many nitrogen-containing substances in concentrated sulfuric acid liberates the nitrogen as ammonium bisulfate is probably one of the most significant analytical discoveries ever made.(3) The method was first developed for and applied to the analysis of protein nitrogen by Kjeldahl in 1883, yet in the analysis of protein some of the greatest difficulties inherent in the method are still only partially solved.(3) However, in research, it is practical to contribute to analysis only the amount of work necessary to confine the error within appropriate limits. This principle applies to the analysis of nitrogen in biological material. For example, in the determination of crude tissue extracts, errors up to ± 5% might be acceptable; in the determination of a purified substance, on the other hand, an accuracy of better than ± 1% is usually required.(4)

Keeping these objectives in mind, we attempted to develop a simplified procedure for digestion of plant material in sulfuric acid. This was followed by direct treatment with Nessler reagent of the liberated ammonium and its determination colorimetrically. The main purpose of adopting such a method was to routinely assay changes, if any, in total protein content of plant tissues that have been exposed to specified levels of sulfur dioxide.

Materials and Methods

We used ammonia-free distilled or deionized water and chemicals, except for standard ammonium chloride salt. The reagents needed were: sulfuric acid (95 to 98% H_2SO_4); mercuric oxide (HgO); mercuric iodide (HgI_2); potassium iodide (KI); potassium sulfate (K_2SO_4); sodium hydroxide (NaOH) pellets; EDTA (disodium dihydrogen ethylenediamine tetraacetate dihydrate); and ammonium chloride (NH_4Cl). Stock ammonium chloride solution: dissolve 3.82 g anhydrous NH_4Cl, dried at 100° C, in distilled water and dilute to one liter. Add 2 drops of chloroform to prevent biochemical transformation of NH_4^+ ions. From this stock solution prepare a series of standard solutions containing 0.4 to 2.4 µg nitrogen/ml solution as needed.

Nessler reagent and EDTA solutions were prepared as described in Standard Methods for the Examination of Water and Wastewater.(5)

Procedure

Dry plant material (beans in this example) in an oven at 70° C overnight. Grind this material to pass 0.4-mm screen (40 mesh per inch); redry the ground material at the same temperature. Weigh accurately about 0.5 g of each ground sample in triplicate, and wrap each subsample in a qualitative filter paper; then place it in a 100-ml Kjeldahl digestion flask. Add 10 g of powdered K_2SO_4 along with 0.1 g HgO and a few glass beads or boiling chips for gentle boiling. Add about 15 ml concentrated sulfuric acid, swirl the contents gently. Place flasks on a Kjeldahl rack, and heat gently until frothing ceases (if necessary add small amounts of paraffin to reduce frothing); boil briskly and continue digestion one hour after the mixture has turned to a clear solution.(6) Cool the flasks, transfer the content of each flask quantitatively to a 250-ml volumetric flask, and dilute the content to the 250-ml mark with distilled water. Take a 1-ml aliquot from each sample into a beaker, dilute it to about 10 ml with deionized water, then titrate with 1 N NaOH solution to about pH 6.0 ± 0.5, using any suitable color indicator, record the volume of the base, and then discard the sample. Take another 1-ml aliquot from each sample to a 50-ml volumetric flask, add about 30 ml of distilled water and the predetermined volume of 1 N NaOH solution necessary to bring the pH of the solution to about 6. Add a drop of EDTA solution to prevent precipitation of Ca and Mg following the addition of the alkaline Nessler reagent. Treat 1 ml of standard ammonium solution similarly, and add 2 ml of Nessler reagent to each flask; swirl, then bring the volume to the 50-ml mark with water. Wait about 15 to 20 min for full color development; then read optical density at 410 nm for these solutions in tubes with 1.25-cm path length, using a Bausch and Lomb Spectronic 20 colorimeter. The optical density measurements (beyond a 15-min period) for any given sample were reproducible, even when the samples were left standing for periods over 12 hr at room temperature.

Results and Discussion

Although the original Kjeldahl procedure has been modified many times, the basic principle remains the same: the sample is oxidized by digestion in sulfuric acid. Carbon and hydrogen are expelled as carbon dioxide and water, whereas the nitrogen present in aminoid linkages is converted and retained in the digest as ammonium ion. Once the conversion of aminoid nitrogen to ammonium is complete, the digest is made alkaline, and the ammonia liberated is distilled into standard acid for determination.(7) During this work, however, we simplified the procedure through Nesslerization of liberated ammonia without recourse to distillation (a laborious step). However, it was necessary to dilute the digest containing ammonium by a factor of 10^3 when 0.1 g of HgO per 0.5 g of plant material is used as catalyst. This was done to minimize the effect of the Hg^{2+} from the digest on the Nessler reaction (see below):

$$HgI_2 + 2\ KI \xrightarrow[\text{or KOH}]{\text{NaOH}} K_2\ HgI_4 \qquad \text{(Nessler reagent)}$$

$$2K_2\ HgI_4 + 3KOH + NH3 \rightarrow Hg_2O\,(NH_2I) + 7KOH + 2H_2O\ .$$

This dilution also reduces concentrations of Ca, Fe, and Mg which are present in plant tissues in considerable amounts. Despite this dilution, when Nessler reagent was added with EDTA to aliquots of the digest, Ca and Mg seemed to precipitate and thus interferred with the colorimetric determination of the ammonia complex with Nessler reagent. This problem was solved, however, when one drop of EDTA solution was added to each sample just before the addition of alkaline Nessler reagent; i.e., the EDTA formed complexes with Ca, Mg, or Fe and prevented their precipitation as hydroxides.

Since amino acids constitute the building blocks of protein molecules, we found it logical to test the accuracy of this approach with samples of several amino acids of known purity. The few amino acids chosen represented simple to complex refractory compounds and two sulfur-containing compounds. Table 1 shows the results of nitrogen analysis by this method compared to nitrogen content of pure samples.

TABLE 1. Nitrogen content of several pure amino acids compared to that obtained by the method described in this work.

Amino Acid	% Nitrogen from chemical formula	% Nitrogen obtained experimentally	% Error
L-alanine	15.7	15.4	- 1.90
L-glutamic acid	9.5	9.4	- 1.05
L-glutamine	19.2	19.1	- 0.52
DL-methionine	9.4	9.3	- 1.06
L-tryptophan	13.7	14.0	+ 2.19

The agreement is remarkable between the two sets of data, with a maximum error of about 2.2% in the case of tryptophan. Furthermore, different amounts of L-threonine and L-alanine, corresponding to different amounts of nitrogen, were also digested and treated according to our procedure. The concentration-response curve (Fig. 1) is in excellent agreement with a standard curve (Fig. 2) obtained for NH_4Cl. The latter curve was obtained for NH_4Cl solution directly, i.e., without digestion in sulfuric acid, yet the slopes of the two curves vary less than 1%.

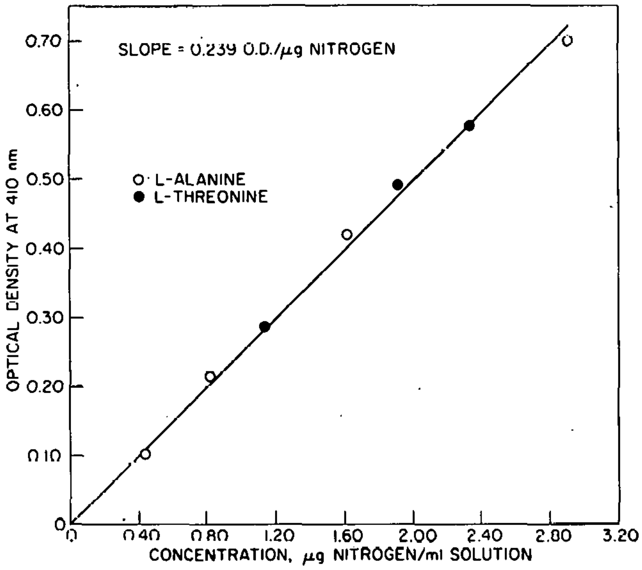


FIG. 1.--Concentration-response curve for two amino acids. Each point is an average of three measurements. (ANL Neg. 149-6610)

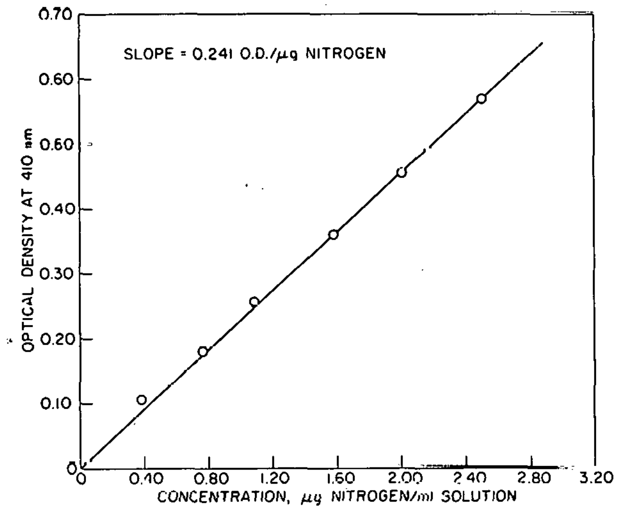


FIG. 2.--Calibration curve for standard ammonium chloride solutions. Each point is an average of three measurements. (ANL Neg. 149-6609)

The data presented in Table 2 were obtained from nitrogen analysis assuming that the proteins from kidney bean seeds contain 16% nitrogen.(8) Each replicate value in Table 2 represents an average of three analyses made for the same subsample. This was done to minimize uncertainty in the values of optical density for each sample. It is clear from the data presented in Table 2 that the experimental error, indicated by a standard error (S.E.) is small, and only in one case did it ever exceed 1, indicating that the method is quite reproducible. However, the accuracy of this method as a measure of total protein content of kidney beans would depend on the reliability of the

TABLE 2. Percent protein of kidney bean seeds calculated from nitrogen determination of the digest by the procedure outlined.

Control plants replicates			Average	S.E.	SO_2 exposed plants replicates			Average	S.E.
29.5	29.2	29.0	29.2	0.25	29.7	29.2	29.4	29.4	0.25
29.5	29.3	28.4	29.1	0.59	29.2	28.0	28.6	28.6	0.60
26.6	26.0	27.9	26.8	0.97	29.2	28.5	29.6	29.1	0.56
24.4	25.4	24.9	24.9	0.50	28.1	28.9	29.0	28.7	0.49
28.0	27.5	27.1	27.5	0.45	27.0	26.6	26.6	26.7	0.23
27.2	27.7	26.9	27.3	0.41	28.7	30.0	29.9	29.5	0.72
24.3	23.5	23.9	23.9	0.40	32.2	32.7	32.4	32.4	0.25
26.3	24.4	26.2	25.6	1.07	25.1	26.0	24.9	25.3	0.59
27.8	27.5	27.7	27.7	0.16	27.4	27.4	28.3	27.7	0.52

S.E. = Standard error. Each replicate value is an average of three measurements.

ratio of total protein to its nitrogen content, i.e., the 6.25 conversion factor. Moreover, it is essential that all the protein nitrogen be converted to ammonia during Kjeldahl digestion. In order to achieve that and to speed up digestion, the ratio of the salt to the acid in the digest must not exceed 1.2 g K_2SO_4 per 1.0 ml H_2SO_4. The mixture is boiled at a temperature range of 340 to 410° C until the solution is clear, and the boiling is continued for one more hour. Boiling the mixture at temperatures greater than 410° C will cause losses of ammonia through volatilization. However, boiling at temperatures below 340° C will result in incomplete recovery of protein nitrogen as ammonium.(7,9) The purpose of adding HgO to the digest is to speed up the process. Baker(10) found that mercuric ion ranked best among 15 catalysts for Kjeldahl digestion.

It is clear that once all the protein nitrogen is converted to ammonium during this modified Kjeldahl digestion, it can be determined rapidly and accurately through the Nesslerization of the ammonia liberated from plant protein and analyzed colorimetrically.

References

1. Haurowitz, F. The Chemistry and Functions of Proteins, 2nd Ed., Academic Press, New York, 1963.

2. Bailey, J. L. Techniques in Protein Chemistry, 2nd Ed. Elsevier Pub. Co., New York, 1967.
3. Kirk, P. L. Kjeldahl method for total nitrogen. Anal. Chem. 22, 354–358 (1950).
4. Miller, G. L. and E. E. Miller. Determination of nitrogen in biological materials. Anal. Chem. 20, 481–488 (1948).
5. Standard Methods for the Examination of Water and Wastewater, 12th Ed. Am. Public Health Assoc., Pub. Inc., New York, 1965.
6. Official Methods of Analysis, 9th Ed. Assoc. Official Agricultural Chemists, Washington, D.C., 1960.
7. Streuli, C. A. and P. R. Averell, Ed. The Analytical Chemistry of Nitrogen and its Compounds, Part I. Wiley-Interscience Pub., New York, 1970.
8. Amino Acid Content of Foods and Biological Data on Proteins. United Nations Pub. No. 24, Rome, 1970.
9. Jackson, M. L. Soil Chemical Analysis. Prentice-Hall, Inc., Englewood Cliffs, New Jersey, 1958.
10. Baker, P. R. W. The micro-Kjeldahl determination of nitrogen: An investigation of the effects of added salt and catalysts. Talanta 8, (1), 57–71 (1961).

NUCLEAR STUDIES

MIAMI RIVER WATERSHED PROJECT: INTRODUCTION

R. N. Muller, D. G. Sprugel, and D. N. Edgington

The Miami River Watershed Project is designed to study cycling characteristics of plutonium in the humid eastern portions of the United States. Although studies of this nature have been conducted in the arid southwestern part of the country, the markedly different climatic and biological charcteristics of the East and Midwest suggest that different cycling mechanisms and pathways might predominate in these areas. Increasing emphasis on nuclear power production near population centers of the East necessitates further study of biogeochemical cycling characteristics of plutonium in this climatic region.

The Miami River Watershed, located in southwestern Ohio, encompasses about 5400 square miles (Fig. 1). Daily mean temperatures in January average around 2° C and in July are near 25° C. Annual precipitation averages 90 cm. Land use throughout the watershed is predominantly agricultural; however, an extensive industrial base along the Miami River between Dayton and Cincinnati employs a large proportion of the population.

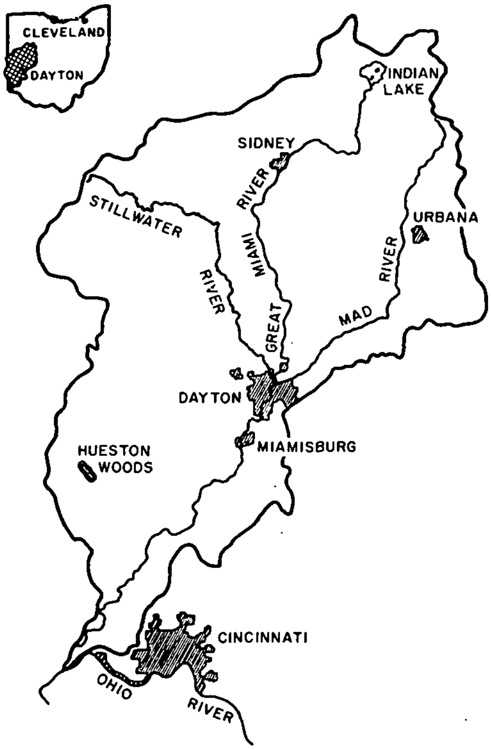


FIG. 1.--Watershed of the Great Miami River, Ohio. (ANL Neg. 149-6726)

The gently rolling topography is formed from a thick mantle of glacial till underlain by limestone, dolomite, and calcareous shale. Soils produced from this regolith are generally silt loams, of which the Miami silt loam is the most extensive. This is a light, well-drained soil which grades off into Celina, Crosby, and finally Brookston silt loams under increasingly poor drainage conditions. Most of the soils of the watershed are, however, moderately well drained and neutral to slightly acid in reaction. Moderate natural fertility makes them suitable for extensive agricultural use, although urban and industrial pressures are currently reducing the proportion of the watershed which is farmed.

Two natural areas in the Miami River watershed are important representatives of presettlement vegetation of the region. Hueston Woods State Park, located at the western edge of the watershed near Oxford, Ohio, contains a virgin beech-maple stand and several other extensive stands of old-age forest. From historical accounts this was the predominant natural vegetation of this region in the pre-Columbian period. Cedar Bog State Memorial, near Urbana in the northeastern part of the watershed, is the only alkaline bog remaining in Ohio. The very wet and highly organic nature of the soils in the bog and adjacent cedar forest is typical of bog areas in the eastern United States.

The Great Miami River itself extends for about 160 miles from its origin in Indian Lake to the Ohio River. Winter flows vary between 2000 and 500 cfs, although peak storm flows may exceed 20,000 cfs. Summer flows average about 1500 cfs with lowest values about 500 cfs. Extensive industrial development along the lower 85 miles of the river has created a considerable pollution problem, particularly during low summer flows. Hydrological and biological aspects of the river and its tributaries are continuously monitored by the Miami Conservancy District and the U.S. Geological Survey.

Three primary isotopes of plutonium are present in the Miami River watershed. ^{239}Pu and ^{240}Pu (which are analytically indistinguishable) are the major isotopes in fallout, and thus are more or less uniformly distributed throughout the watershed. However, levels of these isotopes in the environment are so low that study of their cycling characteristics is rather difficult. ^{238}Pu is also present in fallout at even lower levels than ^{239,240}Pu, but somewhat elevated amounts of this isotope are present near the Mound Laboratory in Miamisburg, a plutonium processing facility. Although levels even in the immediate vicinity of the laboratory are still very low, they are high enough to make possible some studies of plutonium cycling which would be impossible at fallout levels.

^{238}Pu is released from the Mount Laboratory in several forms. Small amounts of particulate plutonium are released into the air from two stacks on the site and disseminated by the wind; it is believed that nearly all of these particles settle out within three to five miles of the plant, predominantly downwind (northwest). Current aerial discharge is about 100 µCi per year, and total discharge since the laboratory opened in 1949 is estimated at about 1 Ci. Plutonium is also discharged directly into the Miami River. A 30,000-gallon waste tank containing about 1 pCi/ml of ^{238}Pu is emptied into the river two or three times a week. In addition to these occasional pulses of plutonium-enriched water, there is a small but continual discharge to the river of plutonium-enriched sediment from ditches on the laboratory site. Most of the plutonium in these ditches is the result of a spill in 1967 on the laboratory grounds, from which a small amount of soil washed into a drainage ditch before the spill could be completely cleaned up. This ditch discharges into the Miami River through a series of canals, pools, and sewers, all of which retain some of the plutonium-containing sediment. Although most of the enriched sediment has presumably been washed into the river by now, that which remains constitutes a minor source of plutonium to the river, particularly during rainstorms when removal of sediment is accelerated.

PLUTONIUM CONCENTRATIONS IN WATER AND SUSPENDED SEDIMENT FROM THE MIAMI RIVER WATERSHED, OHIO

G. E. Bartelt, C. W. Wayman, and D. N. Edgington

Introduction

Preliminary investigation of plutonium concentrations in the water and suspended sediment of streams in the Miami River Watershed was initiated in June 1974. The primary goals of this study were 1) to identify sources and sinks of plutonium in the watershed, and 2) to determine spatial and temporal variability in concentrations of the different plutonium isotopes and thus the range of ^{238}Pu:^{239,240}Pu ratios.

Considerable sampling has been accomplished since the project began; however, analyses have been severely restricted because of a lack of analytical equipment. Therefore, the number of samples analyzed from each station is limited. Results are reported from twelve sites on the Miami River above and below Mound Laboratory, the local ^{238}Pu source, as well as at four sites on tributaries of the river.

Sampling and Analysis

From June to December 1974, a total of 74 one-gallon and five-gallon water samples were collected and analyses completed on 57. The majority were analyzed as whole water, but some samples were fractionated into two parts: 1) suspended sediment not passing through 0.45-μ Millipore filter paper, and 2) the filtered water. The dry weight of the syspended sediment fraction was determined, and both fractions were then analyzed separately according to procedures established at Argonne.(1) The locations of sampling stations are shown in Fig. 1.

Results and Discussion

Plutonium concentrations exhibited extreme variability (Tables 1 and 2). Concentrations of ^{238}Pu and ^{239,240}Pu in whole water increased greatly during rainy periods shown by samples collected 25–27 June, when flooding was

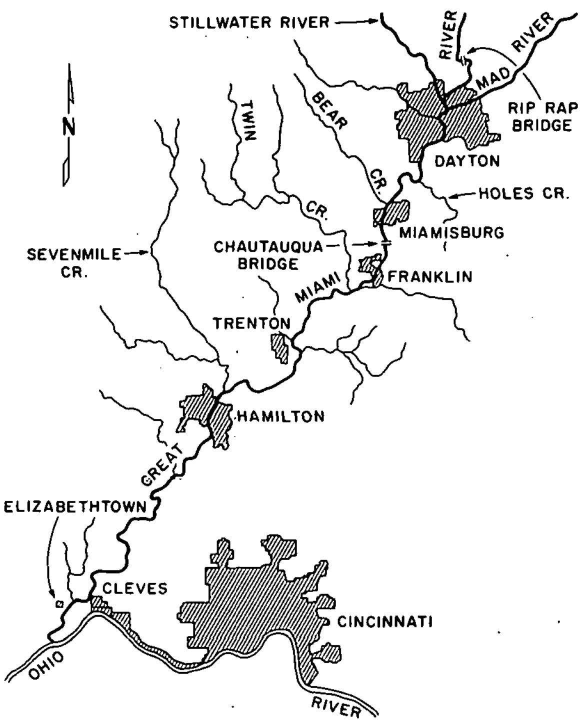


FIG. 1.--Miami River Watershed sampling stations
ANL Neg. 149-6725

TABLE 1. Plutonium concentrations in water collected at locations not exposed to Mound Laboratory's liquid effluent.

Stream	Location	Date	Sample Type	Concentrations (fCi/l)[(a)]		^{238}Pu:^{239,240}Pu
				^{238}Pu	^{239,240}Pu	
Bear Creek	Tributary of the Great Miami River	25 June	Whole water	0.70 ± 0.12	17.93 ± 0.53	0.39 ± 0.007
		25 July	Whole water	2.41 ± 0.51	N.D.[(b)]	-
Twin Creek	Tributary of the Great Miami River	27 June	Whole water	0.12 ± 0.08	1.23 ± 0.16	0.10 ± 0.07
Holes Creek	Tributary of the Great Miami River	14 Aug	Filtered water	1.58 ± 0.22	N.D.	-
			Suspended sediment	-------- Not Analyzed --------		
Mad River	Tributary of the Great Miami River	25 June	Whole water	N.D.	0.92 ± 0.16	-
Great Miami River (upstream of effluent discharge)	Rip-Rap Bridge	5 June	Whole water	N.D.	N.D.	-
		25 June	Whole water	0.20 ± 0.08	1.42 ± 0.16	0.14 ± 0.06
		25 July	Whole water	0.26 ± 0.06	0.36 ± 0.08	0.72 ± 0.23
		5 Nov	Whole water	0.27 ± 0.13	< 0.40	> 0.68
		5 Nov	Filtered Water	0.56 ± 0.14	N.D.	-
			Suspended sediment	0.26 ± 0.10	0.33 ± 0.14	0.79 ± 0.60
Great Miami River (upstream of effluent discharge)	Linden Street Bridge (Miamisburg)	5 June	Whole water	N.D.	0.98 ± 0.61	-

(a) The ± value is 1 σ counting error. When the counting error is > 100%, the concentrations recorded as < 3σ.

(b) N.D., not detectable.

TABLE 2. Plutonium concentrations in water from the Great Miami River downstream from Mound Laboratory's effluent discharge point.

Location	Distance downstream from effluent discharge point (miles)	Date	Time	Sample Type	Concentrations (fCi/l)[(a)] ^{238}Pu	^{239,240}Pu	^{238}Pu:^{239,240}Pu
Saxony Road (Miamisburg)	0.5	27 June	1100	Whole water	37.36 ± 2.47	1.98 ± 0.75	18.87 ± 7.25
300 yd. upstream Chautauqua Bridge	1.0	27 June	1000	Whole water	49.73 ± 3.35	6.00 ± 1.33	8.29 ± 1.93
Chautauqua, Site 1	1.4	12 Sept	0715	Filtered water	54.93 ± 4.12	N.D.[(b)]	---
				Suspended sediment	- - - not analyzed - - -		
Chautauqua, Site 2	1.5	27 June	1200	Whole water	84.19 ± 3.02	1.35 ± 0.58	62.36 ± 26.91
		23 July	1030	Whole water	16.38 ± 1.00	< 1.01	> 16.23
		24 July	1930	Whole water	894.44 ± 16.42	3.75 ± 1.32	238.52 ± 89.96
		25 July	0915	Whole water	32.35 ± 2.75	< 2.20	> 14.70
		15 Aug	0915	Filtered water	1.34 ± 0.62	N.D.	---
				Suspended sediment	58.91 ± 4.79	N.D.	---
		15 Aug	0915	Whole water	81.73 ± 6.22	< 4.05	> 20.18
		15 Aug	0915	Filtered water	5.79 ± 1.10	< 2.15	> 2.69
				Suspended sediment	66.75 ± 6.73	< 1.66	> 40.21
		15 Aug	0915	Whole water	58.80 ± 3.82	0.87 ± 0.61	67.59 ± 47.59
		15 Aug	0915	Filtered water	9.64 ± 1.97	N.D.	---
				Suspended sediment	47.04 ± 3.95	< 1.64	> 28.68
		15 Aug	0915	Whole water	126.50 ± 7.36	< 2.23	> 56.73
		9 Sept	1630	Filtered water	42.88 ± 3.60	N.D.	---
				Suspended sediment	41.69 ± 3.55	0.62 ± 0.59	67.24 ± 63.47
		10 Sept	0700	Filtered water	0.89 ± 0.67	N.D.	---
				Suspended sediment	- - - not analyzed - - -		
		11 Sept	0715	Filtered water	10.81 ± 1.31	N.D.	---
				Suspended sediment	- - - not analyzed - - -		
		12 Sept	0715	Filtered water	31.83 ± 3.79	N.D.	---
				Suspended sediment	1452.33 ± 20.33	12.59 ± 1.98	115.36 ± 18.23
		13 Sept	0705	Filtered water	5.46 ± 1.64	N.D.	---
				Suspended sediment	198.30 ± 7.87	0.96 ± 0.69	206.57 ± 147.70
		4 Nov	1730	Filtered water	5.78 ± 0.62	< 0.58	> 9.97
				Suspended sediment	23.47 ± 2.38	N.D.	---
		4 Nov	1730	Whole water	33.36 ± 1.66	2.03 ± 0.46	16.43 ± 3.79
1.8 miles below Chautauqua Bridge	3	27 June	0945	Whole water	15.35 ± 1.09	1.26 ± 0.45	12.18 ± 4.48
		27 June	0945	Whole water	16.68 ± 1.21	0.49 ± 0.45	34.04 ± 31.36
Franklin	6	5 June	1000	Whole water	18.34 ± 1.85	< 1.87	> 9.81
		27 June	0730	Whole water	24.00 ± 1.71	1.43 ± 0.61	17.46 ± 7.61
		27 June	0730	Whole water	19.94 ± 2.51	2.79 ± 1.08	7.15 ± 2.91
		24 July	1900	Whole water	24.03 ± 0.86	0.36 ± 0.19	66.75 ± 35.26
		6 Nov	0830	Filtered water	1.30 ± 0.29	N.D.	---
				Suspended Sediment	19.43 ± 1.03	0.56 ± 0.20	34.70 ± 12.53
Trenton	16	4 June	1820	Whole water	5.53 ± 0.69	0.45 ± 0.40	12.29 ± 10.96
		26 June	1430	Whole water	33.24 ± 4.42	2.79 ± 1.85	11.91 ± 8.05
		24 July	1330	Whole water	43.62 ± 1.01	0.48 ± 0.13	90.88 ± 24.81
		24 July	1330	Whole water	43.40 ± 2.28	0.58 ± 0.26	74.83 ± 33.77
Hamilton	30	4 June	1800	Whole water	8.54 ± 0.89	0.60 ± 0.46	14.23 ± 11.01
		26 June	1315	Whole water	33.25 ± 1.73	9.56 ± 0.94	3.48 ± 0.39
		24 July	1200	Whole water	9.19 ± 1.14	N.D.	---
		24 July	1200	Whole water	9.88 ± 1.02	0.82 ± 0.35	12.05 ± 5.29
Cleves	57	4 June	1700	Whole water	4.09 ± 0.73	N.D.	---
		26 June	0900	Whole water	29.82 ± 1.36	3.51 ± 0.57	8.50 ± 1.45
		26 June	0900	Whole water	28.56 ± 2.82	2.34 ± 0.92	12.21 ± 4.95
		24 July	0945	Whole water	7.32 ± 0.40	< 0.30	> 24.40
		24 July	0945	Whole water	10.81 ± 1.01	2.76 ± 0.65	3.92 ± 0.99
Elizabethtown	60	4 June	1330	Whole water	11.35 ± 1.18	0.78 ± 0.55	14.55 ± 10.41
		26 June	1115	Whole water	30.18 ± 1.72	2.27 ± 0.61	13.30 ± 3.66
		26 June	1115	Whole water	25.54 ± 3.02	< 1.13	> 22.60
		24 July	0900	Whole water	6.17 ± 0.74	0.69 ± 0.47	8.94 ± 6.13
		5 Nov	1630	Filtered water	0.36 ± 0.12	N.D.	---
				Suspended sediment	29.57 ± 2.92	0.52 ± 0.13	56.87 ± 15.29
		5 Nov	1630	Whole water	30.54 ± 0.86	0.88 ± 0.18	34.70 ± 6.97

(a) The ± value is 1 σ counting error. When the counting error is > 100%, the concentrations recorded as < 3 σ.

(b) N.D., not detectable.

occurring, and 9–12 September, when there were heavy rains.(2) The increase was probably due to surface erosion of soil which contains more plutonium activity than water per unit weight,(3,4) and subsequent loading of the streams with sediment.

The major source of ^{238}Pu is the direct discharge to the Miami River from the sanitary water treatment plant at Mound, but it appears that significant concentrations may also result from the erosion of ^{238}Pu enriched sediment from the contaminated ponds and canal area near Mound (Table 1).(5) Concentrations of ^{238}Pu downstream from Mound Laboratory tended to vary more than those of ^{239}Pu because of the intermittant nature of the sanitary treatment plant effluent, differing concentrations of ^{238}Pu in the effluent, differing dilution factors at various river levels, and varying volumes of effluent being released. Imperfect mixing of the effluent and river water at the Chautauqua sampling stations may also have led to some of the variability

TABLE 3. Plutonium concentrations in suspended sediment from the Great Miami River compared to soil and sediment concentrations.

Location	Date	Dry weight of suspended sediment (mg/l)	^{238}Pu Activity (fCi/l)(a)	^{238}Pu Activity (fCi/g)	^{239}Pu Activity (fCi/l)	^{239}Pu Activity (fCi/g)
Rip-Rap Bridge	5 Nov	10.52	0.26 ± 0.10	24.71 ± 9.51	0.33 ± 0.14	31.37 ± 13.31
Chautauqua, Site 2	15 Aug	16.12	58.91 ± 4.79	3654.47 ± 297.15	N.D.(b)	---
	15 Aug	19.92	66.75 ± 6.73	3350.90 ± 337.85	< 1.66	< 83.33
	15 Aug	14.87	47.04 ± 3.95	3163.42 ± 265.64	< 1.64	<110.29
	9 Sept	23.43	41.69 ± 3.55	1779.34 ± 151.51	0.62 ± 0.59	26.46 ± 25.18
	12 Sept	337.82	1452.33 ± 20.33	4299.12 ± 60.18	12,59 ± 1.98	37.27 ± 5.86
	13 Sept	66.48	198.30 ± 7.87	2982.85 ± 118.38	0.96 ± 0.69	14.44 ± 10.38
	4 Nov	52.33	23.47 ± 2.38	449.36 ± 45.57	N.D.	---
Franklin	6 Nov	13.64	19.43 ± 1.03	1424.49 ± 75.51	0.56 ± 0.20	41.06 ± 14.66
Elizabethtown	5 Nov	64.11	29.57 ± 2.92	461.24 ± 45.55	0.52 ± 0.13	8.11 ± 2.03
Average ^{239}Pu concentration in soil for U.S. (c) (3,4)						20
Range of ^{238}Pu concentrations in sediment near Mound Laboratory (d) (5)				678,000 to 3.6		

(a) The ± value is 1 σ counting error. When the counting error is > 100%, the concentrations recorded as < 3 σ .

(b) N.D., not detectable.

(c) Figure based on 30 cm cores. Since most of the ^{239}Pu is associated with the upper few centimeters of a core, the concentrations would be higher in the soil most exposed to erosion.

(d) Sediment collected from ponds and a canal near Mound Laboratory which drain into the Great Miami River, or directly from the river.

in ^{238}Pu concentrations at these sites. Maximum concentrations of ^{238}Pu are attained when an effluent pulse occurs in conjunction with heavy sediment loading following a storm. This can be seen from the data for Chautauqua Site 2 on 12 September (Table 2).

The average concentration of ^{238}Pu in whole water samples decreases as the distance downstream from Mound Laboratory increases (Table 2). This may be due to dilution with additional water and sediment from tributaries, or to the formation of temporary plutonium sinks as suspended sediment settles out in pools behind low dams. These possibilities will be studied during the next field season.

The results from the few fractionated water samples (Tables 1 and 2) that have been analyzed indicate that 80% of the plutonium is associated with the suspended sediment fraction and only 20% is filterable through 0.45-μ Millipore filter paper. Samples collected during periods of high water containing a greater sediment load have, not unexpectedly, a large percentage of the total activity associated with the suspended fraction.

Input of ^{238}Pu to the Miami River may also be due to fallout from the laboratory's stacks and subsequent erosion and runoff into the river. Concentrations of ^{238}Pu in Hole's Creek (Table 1 and Fig. 1) which drains a watershed downwind of (prevailing winds are southwesterly), and relatively close to Mound Laboratory, appear to be about 10 times greater than would be expected from worldwide fallout. The data indicate that ^{238}Pu levels in Bear Creek (Fig. 1) are also above background, but to a lesser degree than in Hole's Creek, probably since the Bear Creek watershed is not as directly downwind from Mound Laboratory. Mad River, which is farther north, and Twin Creek, which is south, show concentrations of ^{238}Pu which are not significantly greater than that expected from worldwide fallout. These streams, plus others, will be sampled during the next field season to help determine the distance that particulate ^{238}Pu from the laboratory's stacks travels and the amount these tributary streams contribute to the Miami River.

References

1. Nelson, D. M., E. M. Yaguchi, B. J. Waller, and M. A. Wahlgren. Radiochemical methods. Radiological and Environmental Research Division Annual Report, Part III, January–December 1973. ANL-8060, Part III, pp. 6–17.
2. U.S. Department of the Interior, Geological Survey. Provisional 1974 Daily Discharge Data for Gaging Stations in the Great Miami River Basin. U.S.G.S. Water Resources Division, Columbus, Ohio.
3. Harky, J. H. Transuranium elements on land. Health and Safety Laboratory Environmental Quarterly, December 1–March 1, 1975. U.S. Energy Research and Development Administration Report, HASL-291, pp. I-104–I-190.
4. Sedlet, J., N. W. Galchert, and T. L. Duffy. Environmental Monitoring at Argonne National Laboratory Annual Report for 1973. ANL-8078 (March 1974), pp. 1–61.
5. Volchok, H. L. Analysis of Environmental Samples from the Mound Laboratory Area. Health and Safety Laboratory Environmental Quarterly, December 1–March 1, 1975. U.S. Energy Research and Development Administration Report, HASL-291, pp. I-127–I-144.

PLUTONIUM IN AQUATIC BIOTA OF THE GREAT MIAMI RIVER WATERSHED, OHIO

C. W. Wayman, G. E. Bartelt, and D. N. Edgington

Introduction

Reports of plutonium cycling in freshwater ecosystems are limited. Noshkin emphasized the lack of environmental plutonium reports in general and stated that the marine studies out numbered the freshwater research programs.(1)

The reports of freshwater plutonium distribution and concentration by organisms have dealt with aquariums, waste ponds, and the Great Lakes. The behavior of plutonium was studied in a 14-acre pond receiving low level radioactive wastes from the Hanford plutonium processing and reclamation facilities.(2) Algae, invertebrates, and goldfish were analyzed for plutonium concentrations. Plutonium distribution in waste ponds was also investigated at Rocky Flats.(3,4) Uptake of ^{238}Pu by goldfish (Carassius auratus) was studied in aquariums at Los Alamos.(5) Plutonium levels in biota and corresponding food chain relationships have been described for Lake Ontario(6) and Lake Michigan.(7,8)

The purpose of this study is to describe the plutonium concentrations in the biota of the Great Miami River. An integral part of plutonium behavior in the Great Miami River Watershed is the distribution in aquatic biota. This is the first report of plutonium concentrations in organisms of a river ecosystem. Preliminary analyses have just been made on organisms such as Cladophora sp., Potamogeton sp., goldfish, carp, and miscellaneous cyprinids.

Methods

Biological samples were collected in the Great Miami River between June and August 1974. Some sampling was done twenty miles upstream from the Mound Laboratory discharge pipe to determine background levels of plutonium in biota.

Cladophora sp., attached to a hard substrata, and Potamogeton sp., rooted in stream beds, were collected by hand. All plant material was rinsed in the main river currents to eliminate sediment and detritus. In addition, roots were detached from the Potamogeton sp. samples.

Fish were collected by several methods, depending on the habitat. Gill netting with $2\frac{1}{2}$" and $1\frac{1}{2}$" stretch mesh nets each 100' long, seining with a 50' beach seine of $\frac{1}{4}$" mesh, and electrofishing with a Smith-Root Type VII backpack direct current fish shocker were the most successful techniques. Several large carp were obtained as a result of a boom shocking survey carried out by the Dayton Power and Light Company.

All biological samples were stored in freezers at Argonne. To prepare samples for analysis, they were thawed and wet weights determined (excess water having been removed in the field). Next, samples were dried to a constant weight at 105° C and ashed to constant weight at 500° C.

Analysis of plutonium distribution within fish was limited to the removal of gastrointestinal tracts from carp bodies, and the gastrointestinal tracts and remaining bodies were analyzed separately. No attempt was made to separate contents from gastrointestinal walls. Stomach contents were preserved in the field from carp specimens for identification in the laboratory.

Radiochemical analysis for ^{238}Pu and ^{239,240}Pu was performed on aliquots of ashed samples: 20-g whole fish and carp bodies minus GI tracts, 1- to 5-g gastrointestinal tracts, 1- to 3-g Cladophora sp. and Potamogeton sp. Electrodeposition onto 19-mm stainless steel planchets was followed by alpha spectroscopy.(9)

Results and Discussion

Tables 1, 3, and 4 summarize all data on plutonium concentrations in aquatic biota of the Great Miami River Watershed. Table 3 is now being expanded to include additional aquatic macrophyte samples, crayfish, and a greater diversity of fish species representing different trophic levels.

The green algae, Cladophora sp., has been known to scavenge ^{239,240}Pu from the water column in Lake Michigan(8) and a waste pond on the Hanford Reservation, Battelle Pacific Northwest Laboratories.(2) Tables 1 and 2 and Figure 1 show responses of Cladophora sp. in the Great Miami River

TABLE 1. ^{238}Pu and ^{239,240}Pu concentrations (pCi/kg wet weight)$^{(a)}$ in Cladaphora sp. of the Great Miami River Drainage Basin, 1974.

Location	Date	^{238}Pu	^{239,240}Pu	^{238}Pu:^{239,240}Pu
Mad River	25 June	0.037 ± 0.035	1.41 ± 0.14	0.026 ± 0.025
Mad River	25 June	not detected	1.88 ± 0.30	
Bear Creek	13 Aug	0.21 ± 0.05	0.13 ± 0.06	1.62 ± 0.82
Rip Rap Bridge	5 June	< 0.15	0.43 ± 0.11	< 0.35
Rip Rap Bridge	25 June	0.08 ± 0.05	1.46 ± 0.16	0.05 ± 0.04
Rip Rap Bridge	25 July	0.18 ± 0.06	0.41 ± 0.09	0.44 ± 0.17
Rip Rap Bridge	12 Aug	0.14 ± 0.07	0.59 ± 0.14	0.24 ± 0.13
Cleves	4 June	7.82 ± 0.76	0.32 ± 0.23	24.44 ± 17.38
Cleves	26 June	13.63 ± 0.96	0.49 ± 0.39	27.82 ± 22.17
Hamilton	24 July	24.56 ± 1.11	0.63 ± 0.26	38.98 ± 16.22
Trenton	26 June	17.88 ± 0.53	0.83 ± 0.14	21.28 ± 3.55
Trenton	24 July	55.87 ± 1.79	0.89 ± 0.26	62.78 ± 18.65
Franklin	27 June	35.42 ± 1.06	2.72 ± 0.33	13.02 ± 1.65
Franklin	24 July	64.33 ± 2.41	0.63 ± 0.30	102.11 ± 48.55
Franklin	14 Aug	148.18 ± 3.11	0.87 ± 0.27	170.32 ± 53.82
Chautauqua Site 1	27 June	78.88 ± 1.97	2.26 ± 0.41	34.90 ± 6.46
Chautauqua Site 2	23 July	256.41 ± 12.54	5.75 ± 2.33	44.59 ± 18.23
Chautauqua Site 2	14 Aug	518.32 ± 6.22	1.44 ± 0.37	359.94 ± 93.58
Saxony Road (Miamisburg)	27 June	51.62 ± 1.39	1.63 ± 0.30	31.67 ± 5.95

(a) The ± value is 1 σ counting error. When the counting error is > 100%, the concentration is recorded as < 3 σ.

TABLE 2. Relationship between ^{238}Pu concentration in Cladophora sp. and Great Miami River unfiltered water collected at the same time in 1974.

Location	Date	pCi ^{238}Pu/kg Wet Weight$^{(a)}$		Cladophora sp.: Water
		Cladophora sp.	Water	Numerical Ratio of Activities$^{(b)}$
Cleves	4 June	7.82 ± 0.76	0.0041 ± 0.0007	1907.32 ± 375.74
Cleves	26 June	13.63 ± 0.96	0.0298 ± 0.0014	457.38 ± 38.42
Trenton	26 June	17.66 ± 0.53	0.0332 ± 0.0044	531.93 ± 71.28
Trenton	24 July	55.87 ± 1.79	0.0436 ± 0.0010	1281.42 ± 49.98
Franklin	27 June	35.42 ± 1.06	0.0248 ± 0.0017	1428.23 ± 107.12
Franklin	24 July	64.33 ± 2.41	0.0240 ± 0.0009	2680.42 ± 142.06
Franklin	14 Aug	148.18 ± 3.11	0.0481 ± 0.0009	3080.67 ± 86.26
Rip Rap Bridge	25 June	0.08 ± 0.05	0.0002 ± 0.0001	400.00 ± 320.00
Rip Rap Bridge	25 July	0.18 ± 0.06	0.0003 ± 0.0001	600.00 ± 282.60

(a) The ± value is 1 σ counting error. When the counting error is > 100%, the concentration is recorded as < 3 σ.

(b) This is not to be interpreted as a concentration factor because there is great variability in the ^{238}Pu activity of water samples.

TABLE 3. ^{238}Pu and ^{239,240}Pu concentrations (pCi/kg wet weight)[a] in miscellaneous aquatic biological samples from the Great Miami River Watershed, 1974.

Sample Type	Location	Date	No. of Fish Analyzed	Average Total Length (cm)	^{238}Pu	^{239,240}Pu	^{238}Pu:^{239,240}Pu
Potamogeton sp.	Mad River	25 June			not detected	0.16 ± 0.03	
Potamogeton sp.	Franklin	27 June			48.19 ± 1.59	0.17 ± 0.03	3.23 ± 0.11
Cyprinus carpio	Trenton	26 June	3	21.0	0.31 ± 0.02	0.016 ± 0.005	19.38 ± 6.12
Carassius auratus	Franklin	27 June	12	14.5	0.60 ± 0.02	0.012 ± 0.004	50.00 ± 15.05
Carassius auratus	Trenton	26 June	14	16.5	0.55 ± 0.01	0.042 ± 0.004	13.10 ± 1.23
Carassius auratus	Franklin	24 July	41	14.6	3.05 ± 0.06	0.037 ± 0.005	82.43 ± 14.18
Cyprinids	Chautauqua Site 1	25 July	1 kg wet weight	6.0	0.73 ± 0.04	< 0.013	> 56.04

[a] The ± value is 1 σ counting error. When the counting error is > 100%, the concentration is recorded as < 3 σ.

TABLE 4. ^{238}Pu and ^{239,240}Pu concentrations (pCi/kg wet weight)[a] in *Cyprinus carpio* bodies and removed gastrointestinal tracts from the Great Miami River, 1974.

Location	Date	No. of Fish Analyzed	Average Total Length (cm)	Bodies			Gastrointestinal Tracts			% Activity	
				^{238}Pu	^{239,240}Pu	^{238}Pu:^{239,240}Pu	^{238}Pu	^{239,240}Pu	^{238}Pu:^{239,240}Pu	Bodies	GI
Chautauqua Site 1	22 July	9	22.2	0.36 ± 0.02	0.005 ± 0.004	72.00 ± 52.27	15.53 ± 0.35	0.19 ± 0.04	81.74 ± 18.39	29.1	70.9
Chautauqua Site 1	23 July	18	21.4	0.17 ± 0.02	0.008 ± 0.005	21.25 ± 12.00	16.77 ± 0.40	0.59 ± 0.08	28.42 ± 3.75	15.0	85.0
Chautauqua Site 1	23 July	17	23.0	0.23 ± 0.02	0.005 ± 0.004	46.00 ± 36.25	18.71 ± 0.38	0.15 ± 0.04	124.70 ± 30.16	19.0	81.0
Chautauqua Site 1	25 July	7	19.4	0.18 ± 0.02	0.009 ± 0.005	20.00 ± 11.30	12.94 ± 0.50	0.19 ± 0.07	68.10 ± 23.71	15.8	84.2
Chautauqua Site 1	13-15 Aug	5		0.35 ± 0.02	< 0.009	> 38.89	38.18 ± 0.95	0.10 ± 0.06	381.80 ± 226.23	14.7	85.3
Franklin	24 July	28	20.0	0.17 ± 0.02	not detected		14.17 ± 0.23	0.18 ± 0.03	78.72 ± 11.81	16.7	83.3
Franklin	24 July	13	19.8	0.14 ± 0.01	0.013 ± 0.004	10.77 ± 3.40	11.81 ± 0.30	0.18 ± 0.04	62.11 ± 13.98	12.2	87.8
Franklin	24 July	24	21.4	1.60 ± 0.04 (b) 0.15 ± 0.02	0.006 ± 0.003 0.017 ± 0.007	266.67 ± 145.07 8.82 ± 3.70	11.32 ± 0.26	0.13 ± 0.03	87.08 ± 21.25	28.3	71.7
Franklin	14 Aug	11	19.6	0.56 ± 0.03	0.010 ± 0.005	56.00 ± 27.81	18.87 ± 0.57	0.50 ± 0.09	37.74 ± 7.18	30.5	69.5

(a) The ± value is 1 σ counting error. When the counting error is > 100%, the concentration is recorded as < 3 σ.

(b) Carp bodies from two different packages of the same collection were analyzed separately. The gastrointestinal tracts were combined for analysis.

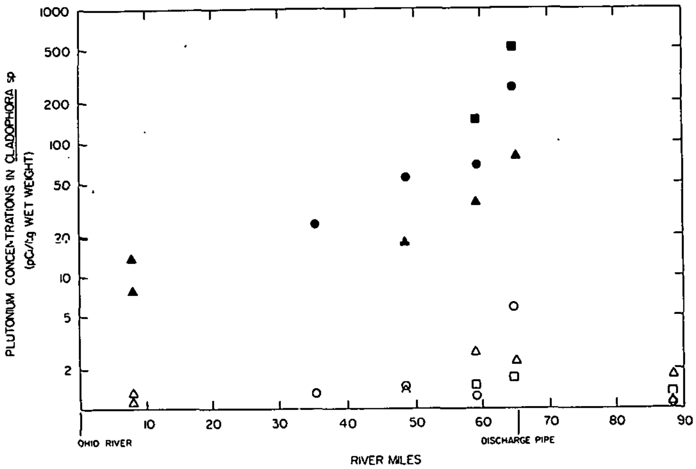


FIG. 1.--Relationship between distance from the Mount Laboratory discharge pipe and concentrations of ^{238}Pu and ^{239,240}Pu in Cladophora sp. Solid symbols represent ^{238}Pu, open ^{239,240}Pu, triangles, June samples; circles, July; squares, August. ANL Neg. 149-6735

to the presence of both ^{238}Pu and ^{239,240}Pu in the water. The recorded concentrations of ^{239,240}Pu in water do not fluctuate as widely as the concentrations of ^{238}Pu.(10) ^{239,240}Pu is deposited generally throughout the Great Miami River Watershed as a result of fallout from weapons tests. ^{239}Pu, in contrast, is periodically released from a localized source, Mound Laboratory, in low level radioactive waste effluent. Figure 1 reflects the difference between the variability of plutonium isotopes found in Cladophora sp. The levels of ^{239,240}Pu in Cladophora sp. remain relatively constant except in the vicinity of the Mount Laboratory discharge pipe where the ^{239,240}Pu levels are slightly elevated indicating that in addition to fallout, there may be another source of ^{239,240}Pu in this area. ^{238}Pu concentrations found in Cladophora sp. are influenced by the timing of effluent releases in relation to sample collection and distance from discharge pipe. The amount of ^{238}Pu available for scavenging by Cladophora sp. diminishes with distance from the source (Fig. 1), illustrating the effect of increased dilution and dispersion of the effluent pulse downstream. These irregular pulses of ^{238}Pu to the Great Miami River make it almost impossible to calculate concentration factors for aquatic biota without an understanding of the kinetics of uptake and elimination.

The concentration of ^{238}Pu in Cladophora sp. is related to the level of ^{238}Pu in the water at the time of collection. It appears from Table 2 that when ^{238}Pu in the water is elevated, so is the concentration of ^{238}Pu in the algae. Although the mechanism of plutonium uptake by Cladophora sp. is unknown, it is thought to be a combination of adsorption and absorption. Studies on marine algae indicate plutonium is primarily adsorbed on surfaces.(11–14)

The aquatic macrophyte, Potamogeton sp., appears to concentrate ^{238}Pu to the same extent as Cladophora sp. A Cladophora sp. sample collected June 27 from the Great Miami River at Franklin was found to contain 35.42 ± 1.06 pCi ^{238}Pu/kg wet weight (Table 1). The Potamogeton sp. sample obtained at the same place and time had a concentration of 48.19 ± 1.59 pCi ^{238}Pu/kg wet weight (Table 3). Additional samples will have to be analyzed to verify a trend.

It is important to study the accumulation of plutonium by algae because this represents a starting point of aquatic food chains. Previous reports have indicated that there is a discrimination against plutonium in the higher trophic levels.(2,7,8) This also appears to be true for biota from the Great Miami River as shown by the limited food chain relationships presented in this report. Concentrations of plutonium found in Cladophora sp. are 10^2 to 10^3 times greater than plutonium activity associated with carp.

Carp (Cyprinus carpio) are bottom feeders, known to have a mixed diet of algae, macrophytes, periphyton, and detritus.(15) Stomach analyses of carp from the Great Miami River indicated plant material was a major food item. Table 4 summarizes the plutonium data for carp, including the analysis of segregated gastrointestinal tracts and contents. An average of 80% of the activity was associated with the gastrointestinal tract and contents. Consequently, in bottom feeders, the majority of the activity will be eventually eliminated, and the amount which could conceivably become available to man in fish muscle is minimal. Tissue distribution of plutonium in bottom dwelling fish described in other reports, confirms the findings of this study. The guts of carpsuckers (Carpiodes sp.) from Lake Ontario contained more $^{239,240}Pu$ than the other tissues combined.(6) Bowen emphasized that plutonium analysis of guts from bottom dwellers would be a reflection of contents rather than intestinal tissue.(6) As a result of aquarium uptake experiments with goldfish (Carassius auratus), it has been confirmed that most of the ^{238}Pu associated with fish is in the gills and the gut.(5) Two orders of magnitude more activity was found in the gut, including contents, than in flesh and bones. Adams et al. concluded that almost all of the plutonium taken into the gut is eliminated and does not relocate in the fleshy edible portions of the fish.(5)

Two-year-old goldfish (Carassius auratus) without gut contents, inhabitants of the Hanford rad-waste pond which spent their lives feeding on contaminated detritus and plant material, had low levels of plutonium in their body tissues.(2) The low concentrations in body tissues suggest that even after years of feeding on contaminated substrata there is little transfer of plutonium across intestinal walls into other body tissues. It appears that the concentration of plutonium within fish body tissues must reach a steady state. In situ experiments in the Hanford pond indicated that goldfish reach an equilibrium level of plutonium concentration after a few days and they may remain active in the pond for months without further accumulation.(2)

Fish uptake rate response to a short-lived pulse of radionuclides was investigated near Big Rock Point Nuclear Plant.(16) Analyses of suckers (Catastomus sp.), smallmouth bass (Micropterus dolomieui), minnows (Notropis sp.), and juvenile rainbow trout (Salmo gairdneri) collected prior to and after a scheduled radioactive release showed no apparent rapid uptake of radionuclides. It was concluded that fish exposed to intermittent pulses of radioactivity must integrate radionuclides over a longer period of time.

Mound Laboratory's low level radioactive waste releases to the Great Miami River provide a source of ^{238}Pu for uptake by carp. As can be seen from Table 4, there is a minimal variability in the body concentrations of ^{238}Pu, but there is a greater variability in the concentration of ^{238}Pu in the gastrointestinal tracts, which reflects the activity of the contents. It is probable that the ^{238}Pu concentration in carp body tissue was accumulated over a period of several effluent releases and that no single release would noticeably affect the ^{238}Pu levels found in carp.

In summary, there appears to be discrimination against plutonium moving up the food chain in the Great Miami River, based on analyses of Cladophora sp., Potamogeton sp., carp, and goldfish. Concentration of plutonium by algae and macrophytes is 10^2 to 10^3 that of fish (excluding GI tract and contents). An average of 80% of ^{238}Pu found in carp is associated with the gastrointestinal tract and contents. Consequently, the plutonium located in the fish muscle, which becomes available to man, is minimal. Since plutonium uptake by Cladophora sp. is thought to be rapid and dependent on the immediate concentration in the water, a single release of plutonium could be monitored by Cladophora sp. The levels of ^{238}Pu in Cladophora sp. were a function of the distance from the release site. The plutonium concentrations found in Cladophora sp. sampled near the discharge point were the highest and decreased as distance from Mound Laboratory increased. Uptake of ^{238}Pu by fish occurs over a longer period of time and would not be signficantly influenced by a single effluent release.

References

1. Noshkin, V. E. Ecological aspects of plutonium dissemination in aquatic environments. Health Phys. 22, 537–549 (1972).
2. Emery, R. M., D. C. Klopler, and W. C. Weimer. The ecological behavior of plutonium and americium in a freshwater ecosystem: Phase I. Limnological characterization and isotopic distribution. Battelle Pacific Northwest Laboratory Report, BNWL-1867 (1974).
3. Johnson, J. E. and R. L. Watters. The study of plutonium in aquatic systems of Rocky Flats environs. 1st Tech. Prog. Rept., Dept. of Radiology and Radiation Biology and the Dept. of Animal Sciences. Colorado State University, Ft. Collins (1971).
4. Johnson, J. E., S. Svalberg, and D. Paine. The study of plutonium in aquatic systems of the Rocky Flats environs. 2nd Tech. Prog. Rept., Dept. of Radiology and Radiation Biology and the Dept. of Animal Sciences. Colorado State University, Ft. Collins (1972).
5. Adams, W. H. and E. B. Fowler. Studies of the apparent solubility of $^{238}PuO_2$ microspheres in an aquatic environment and the uptake of plutonium from a soil matrix containing $^{238}PuO_2$. Proc. 2nd AEC Environmental Protection Conf., Albuquerque, N.M., April 1974. USAEC Report CONF-740406, pp. 615–645.
6. Bowen, V. T. Plutonium and americium concentration along freshwater food chains of the Great Lakes, U.S.A. Woods Hole Oceanographic Institute, General Summary of Progress, 1973–1974. Report COO-3568-4 (1974).
7. Waller, B. J., D. M. Nelson, and J. S. Marshall. Plutonium in Lake Michigan fish. Radiological and Environmental Research Division Annual Report, Part III, January–December 1973. ANL-8060, Part III, pp. 27–31.

8. Yaguchi, E. M., D. M. Nelson, and J. S. Marshall. Plutonium in Lake Michigan plankton and benthos. Radiological and Environmental Research Division Annual Report, Part III, January—December 1973. ANL-8060, Part III, pp. 18—26.
9. Nelson, D. M., E. M. Yaguchi, B. J. Waller, and M. A. Wahlgren. Radiochemical methods. Radiological and Environmental Research Division Annual Report, Part III, January—December 1973. ANL-8060, Part III, pp. 6—17.
10. Bartelt, G. E., C. W. Wayman, and D. N. Edgington. Plutonium in water of the Miami River Watershed, Ohio. This report.
11. Hodge, V. F., F. L. Hoffman, and T. R. Folsum. Rapid accumulation of plutonium and polonium on giant brown algae. Health Phys. 27, 29—35 (1973).
12. Wong, K. M., V. F. Hodge, and T. R. Folsom. Plutonium and polonium inside giant brown algae. Nature 237 (5356), 460—462 (1972).
13. Zlobin, V. S. and M. F. Perlyuk. Photosynthesis and the mechanism of the action of cyanide on cell respiration and plutonium-239 accumulation by marine algae. Murmansk, Trudy Polyarnogo Nauchno-Issledovatel' skogo i Proyektnogo Instituta Morskogo Rybnogo Khozyaystava i Okeanografii, No. 29, 159—168 (1971).
14. Zlobin, V. S. Active phase of assimilation of plutonium-239 by the marine algae ascophyllum nodosum. Murmansk, Trudy Polyarnogo Nauchno-Issledovatel' skogo i Proyektnogo Instituta Morskogo Rybnogo Khozyaystva i Okeanografii, No. 29, 169—175 (1971).
15. Hubbs, C. L. and K. F. Lagler. Fishes of the Great Lakes Region. University of Michigan Press, Ann Arbor, Michigan, 1970.
16. Nelson, D. M., G. P. Romberg, W. Prepejchal, and S. A. Spigarelli. Effects of a routine radioactive release on aquatic radionuclide concentrations. Proc. 15th Conf. Great Lakes Res. Internat. Assoc. Great Lakes Res., Ann Arbor, Michigan, 1972, pp. 260—269.

MIAMI RIVER WATERSHED PROJECT: TERRESTRIAL STUDIES

D. G. Sprugel, R. N. Muller, and D. N. Edgington

Once plutonium enters a natural or man-modified ecosystem, it is cycled through a series of transport mechanisms, sinks, and biological pathways. The importance and magnitude of any of these characterizes the behavior of plutonium in the environment. The Miami River Watershed area allows the study of plutonium in both terrestrial and aquatic systems.

Movement of plutonium particles and aerosols in the air is greatly influenced by wind; and the distribution around a point source, such as the Mound Laboratory, should be quite similar to wind rose patterns of that region. Plutonium may enter terrestrial ecosystems either through dry fallout and rain or through interception of particulates by plant surfaces. In either case, most of it eventually reaches the soil. Soil samples have been collected at 1, 3, and 5 miles from the laboratory in each of 9 cardinal and subcardinal directions to determine the distribution of ^{238}Pu around the Mound Laboratory and to provide baseline data for future studies in the Miamisburg area. Samples for background levels were taken in similar soils near Hueston Woods State Park and around Urbana.

Earlier studies have indicated that plutonium is immobile in the soil system and is not taken up by plants. The validity of these assumptions under the humid conditions of southwestern Ohio will be investigated by examining depth distributions in undisturbed forest and pasture soils and discrimination ratios (ratio of concentration of plutonium in plants to concentration in the soil) for plants grown under field conditions. It is likely, however, that the major transport mechanism for terrestrial plutonium is through erosion of soil particles.

Fractionation studies of soils immediately downwind of Mound Laboratory have been initiated to determine the distribution of plutonium in the soil relative to particle size. Gross redistribution of plutonium by erosion may be determined from studies within small watersheds. Increased movement through erosion and the influence of land use upon transport will be reflected in the distribution of plutonium in the watershed. Gross movement of ^{239}Pu in the Miami River watershed above Sidney, Ohio, is being monitored through analysis of suspended sediments and filtered water samples from the river. If transport is solely a function of soil particle movement, a strong correlation should be observed between plutonium movement and sediment loading of the river.

Plutonium released directly into a river may behave differently from that which is washed in attached to sediment particles. A combination laboratory and field study is under way to determine the rate and extent of adsorption of ^{238}Pu in the Mound Laboratory effluent onto sediment particles in the river water. In the laboratory phase, effluent and river water are mixed in proportions similar to river conditions and then filtered after 1/2, 1, 2, 4, 8, 16, and 24 hours to determine rate of adsorption under semicontrolled conditions. Simultaneously, the effluent pulse is followed downstream using fluorescent dye techniques and sampled at 8-hour intervals to determine association rates under actual river conditions. These experiments will be repeated several times under varying temperature, pH, and sediment load conditions to determine the effect of these factors on association rates.

THE CHEMICAL SPECIATION OF ^{239,240}Pu AND ^{137}Cs IN LAKE MICHIGAN WATERS

J. J. Alberts, M. A. Wahlgren, P. J. Jehn, D. M. Nelson,
and K. A. Orlandini

Introduction

The possible introduction of radionuclides into the environment through atmospheric fallout from weapons testing and from the use of nuclear power as an energy source is of considerable importance. A necessary condition of the increased use of nuclear power is the knowledge of the nature of the isotopes likely to be introduced and their ultimate fate in the environment. Data are available regarding the identity and quantity of isotopes produced in both weapons testing(1) and nuclear power production.(2) However, the fate of these isotopes is not well known.

To date, most of the research into environmental radiochemistry has been of a descriptive nature or has been concerned with areas of very high isotope concentration. No work has been undertaken to investigate the chemistry and physical state of radionuclides in natural waters at extremely low levels. Knowledge of the chemistry of these nuclides is required if a truly predictive model is to be constructed for the fate of these isotopes in the environment and the direct relationship of this fate to man.

Studies of the submicron size distribution and charge characteristics of naturally occurring levels of ^{239,240}Pu and ^{137}Cs were undertaken to help define the physico-chemical state of these fallout derived nuclides in Lake Michigan waters and in precipitation samples taken in the Argonne Laboratory area. The question of the valence state of the species, while interesting in the case of ^{239,240}Pu, was not addressed in these preliminary studies. Rather, the initial time was spent attempting to determine the particle size distribution in the submicron region and the total charge of the dissolved species (whether ionic or complexed).

Methods

Sample Collection

Lake water samples were taken during September, October, and November, 1974, in Lake Michigan from the University of Michigan vessel R/V Mysis. All samples were taken at Argonne permanent Station 5. Sampling depths were determined each month with consideration of the existing thermocline. An attempt was made to sample above, in, and below the thermocline whenever possible.

Water samples taken from above 40 m (Table 1) were obtained by pumping with a deck pump through a deck filtration cell containing two nylon screens and a flow meter into several large carboy (55 l). This procedure was the same as that used in the collection of the half- and one-cubic meter water samples previously described.(3) The water was then filtered through membrane filters (Millipore Corp., 3.0 and 0.45 μ) and was collected in additional carboys. An aliquot of the filtered water was stored without preservation until it could be processed for submicron particle size distribution at the laboratory. Another aliquot of filtered water was pumped first through an anion exchange resin bed (Dowex-1x8, 200-400 mesh, Cl^- form), then through a cation exchange resin bed (Dowex-50, 100-200 mesh, H^+ form) and, in the case of the September sample, finally through an activated carbon filter. During the September sampling, the water which passed through the carbon filter was discarded. However, on subsequent samples the water which passed through the resin beds was retained and spiked with 2.65 dpm ^{242}Pu and with 5 mg Cs in 100 ml concentrated HCl. This water was then returned to the Laboratory for further analysis.

The resin beds were drained, placed in polyethylene bags and returned for analysis.

Water samples taken from below 40 m were collected by multiple lowerings of a 30 l Nisken sampling bottle. The water thus collected was placed directly in plastic carboys after passing through a deck cell and nylon screens. The samples were then treated exactly as those taken in shallower depths.

TABLE 1. Concentration of ^{239,240}Pu (fCi/l) in various fractions of lake water and snow melt water.

	September		October			November		
Fraction	3 m	33 m	3 m	40 m	60 m	3 m	Grand River	Snow
Total	0.55	0.70	0.28	0.28	0.75	0.35	0.21	1.5
3.0-μ filter	0.13	0.12	0.08	0.10	ND(a)	0.08	0.18	
0.45-μ filter	0.02	0.01	ND	ND	ND	ND	ND	
30-Å dialyzer effluent	0.25	0.50	ND	ND	ND	0.26	ND	0.9
12-Å dialyzer effluent	BKG(b)	0.46	ND	ND	ND	ND	ND	ND
Anion Resin	0.42	0.48	0.14	0.46	0.43	ND	Lost	0.40
Cation Resin	0.01	0.01	0.07	0.03	0.04	Lost(c)	Lost	0.47

(a) ND = not determined.

(b) BKG = < 0.01 f Ci/l .

(c) Lost = sample lost when muffle furnace overheated.

Two carboys of raw water (unfiltered) were taken at all depths and immediately spiked with ^{242}Pu, Cs, and HCl as previously described. These samples were transported and analyzed.

Snow samples were collected on the Argonne Laboratory Site by placing large sheets of polyethylene on the ground at the beginning of a snow storm. The sheets were allowed to collect snow until dusk (about 4 hr). The sheets were then removed and emptied into a large polypropylene container. The sheets were then replaced and allowed to collect snow overnight and in the morning were again emptied into a separate polypropylene container.

After the samples melted (approximately 2 days) each sample was pumped through a 35-μ screen before the usual filtration procedure with the membrane filters used for the Lake Michigan water samples. Aliquots of the individual samples were taken for ^{239,240}Pu and ^{137}Cs analysis, and then the filtered water was combined. This combined water was ultrafiltered through 30,000 molecular weight ultrafilters, and separate aliquots of the combined samples were passed through anion and cation resins as the Lake Michigan water had been. Water which had passed through either the ultrafilter or the resin beds was retained, spiked, and analyzed as before.

Size Distribution Determination

Upon delivery to the Laboratory, the unspiked samples were pumped through ultrafiltration membranes (Bio-Rad Corporation). The membranes were designed to retain material of greater than 30,000 molecular weight (Bio-Fiber 50 Miniplant, nominal pore size ~ 30 Å diameter). The samples taken during September were then passed through a membrane designed to withold material greater than 5,000 molecular weight (Bio-Fiber 80 Miniplant, nominal pore size ~ 12 Å diameter). The samples taken at other times during the year and the snow samples were not passed through the smaller ultrafilter.

The water which passed through the ultrafilters was collected and spiked as before. In addition, the ultrafilters in every case were backwashed with three separate washes of 1000 ml deionized water. These backwashes were also collected and spiked.

Analysis of the Ion Exchange Resins

Upon returning to the Laboratory, the Dowex anion and cation resins were placed in 4 l glass beakers and ashed (500° C) in the muffle furnace for one week. This procedure completely destroyed the anion resin; however, the cation resin often contained what appeared to be unoxidized carbon (charcoal) particles. The ash residues of both types were treated with boiling concentrated nitric acid for 3 to 6 hours or until the organic residue and charcoal-like substances were solubilized. Concentrated hydrochloric acid equal to one-half the volume of the remaining nitric acid solution was then added to the sample to assist in the solubilization of metallic oxides. The solution was heated and the volume reduced until approximately 200 ml of solution remained or precipitation occurred. This final precipitation was usually gypsum resulting from the calcium loading of the sulfonic acid resins by the lake water. The minimum volume was diluted 1:1 (v/v) with deionized water to give an 8 <u>M</u> nitric acid feedstock solution for the plutonium separation. This solution was then treated as before.(3)

Plutonium Determination by Evaporation

Instead of using the standard CaF_2 precipitation technique for the isolation of plutonium from large volumes of water (30 to 50 liters), a technique involving evaporation of the water as the concentration step was employed. In this procedure, the spiked water sample was placed in 17 l glass carboys and treated with 200 ml concentrated nitric acid. The sample volume was reduced by heating on a hot plate to a new volume of approximately one liter. A white precipitate usually formed at this point, and the remaining solution and precipitate were transferred quantitatively to glass beakers and the volume reduced to ~ 300 ml. The precipitate (mainly hydrated silica) was separated from the acid solution and treated with concentrated hydrofluoric-nitric acids to volatize the silicon. The residue from the HF-HNO_3 treatment was dissolved in nitric acid and recombined with the bulk sample solution. The volume was reduced by heating to approximately 200 ml and then diluted 1:1 (v/v) with deionized water to make a final concentration of 8 M nitric acid. This solution was used as the feedstock in the plutonium separation.(3)

^{137}Cs Analyses

^{137}Cs was determined in all samples by the standard method.(3)

Results and Discussion

The results of the $^{239,240}Pu$ analyses for the various water column fractions (Table 1) indicate that most of the $^{239,240}Pu$ in the waters of Lake Michigan is in an anionic form with a particle diameter of less than 30 Å. A possible exception to this observation is found in the data from the surface waters of the September water sample. In this sample, the dialyzer, designed to retain 30 Å or greater diameter particles, apparently retained a significant fraction (27.3%) of the smaller than 0.45 μ $^{239,240}Pu$ particles, while the same dialyzer retained only 10% of the $^{239,240}Pu$ from that month's 33 m sample. The relatively large retention in the surface sample may be an indication of colloidal or small polymeric $^{239,240}Pu$ in the surface waters or may be an artifact of the small total activity involved in the analysis. The fact that the November water samples showed no retention by this dialyzer indicates that the latter may be the case. No ^{239,240}Pu was retained by either the 12 Å dialyzer or the charcoal filter.

Examination of the data from the Grand River water sample taken in November showed that essentially all the ^{239,240}Pu in the river was in the fraction retained by the 3.0 μ filter and most likely was associated with clay particles.

An additional experiment, which was carried out in October, involved reversing the order of the cation and anion resin beds for surface water samples. In these experiments the sodium form of the cation exchange resin was used because the reaction between the bicarbonate in the water and the hydrogen ion of the cation resin caused the formation of gas bubbles which disrupted the resin bed. The results of this experiment exhibited good agreement. The majority of the plutonium was retained by the anion resin bed regardless of its position with respect to the cation resin bed. This indicates that plutonium is predominantly anionic and is not simply being retained by a filtering effect of the resin beds.

Unfortunately, the resin experiments for the other depths of the October sampling did not give good mass balances. Considerable difficulty was experienced at this time with contamination resulting from heterogeneous particles in the dry reagents. This problem was alleviated by adding the reagents in a liquid form which had previously been filtered and tested for background contamination. An attempt to analyze the November lake water and river water ion exchange resins failed because the muffle furnace in which the samples were being prepared overheated and the resins were lost. Further work on the ion exchange properties of both lake and river water ^{239,240}Pu will be carried on during the 1975 field season.

The apparent lack of retention of ^{239,240}Pu by the 30 Å dialyzer in water samples from Lake Michigan is in sharp contrast to the data obtained for a snow melt water sample collected in November (Table 1). In the latter case, a significant amount of the ^{239,240}Pu in the melt water (39.0%) was retained by the 30 Å dialyzer. In addition, approximately equal amounts of ^{239,240}Pu were retained on the anion and cation resins. It would appear from the limited data that ^{239,240}Pu in snow melt water and that found in the water column of Lake Michigan is significantly different in physico-chemical nature. This difference may help to explain the apparent changing residence time observed for ^{239,240}Pu in the water column.$^{(4)}$ Considerably more data are required and will be collected during the 1975 field season.

Examination of the ^{137}Cs analyses for the water column (Table 2) show good agreement for the fractions analyzed from the September and November samples. The data indicate that approximately 12% of the ^{137}Cs in the water column is in the fraction larger than 3.0 μ. In addition, unlike the case of ^{239,240}Pu, approximately 25% of the ^{137}Cs is retained by the 30 Å dialyzer. Values have not yet been obtained for the ^{137}Cs retained by the resins.

TABLE 2. Concentration of ^{137}Cs (fCi/l) in various fractions of lake water and snow melt water.

	September		November	
Fraction	3 m	33 m	3 m	Snow
Total	ND(a)	43.0	47.0	205.0
3.0-μ filter	ND	4.9	5.9	1.9
0.45-μ filter	ND	0.2	ND	4.1
30-Å dialyzer effluent	ND	33.0	33.8	172.0
12-Å dialyzer effluent	ND	ND	ND	ND
Anion Resin	ND	ND	ND	36.0
Cation Resin	ND	ND	Lost(b)	53.0

(a) ND = not determined.

(b) Lost = sample lost when muffle furnace overheated.

The data from the November snow sample show a very different distribution of ^{137}Cs. Less than 3% of the material is retained by any of the membrane filters and only 13.2% is retained by the dialyzer. However, 17.6% appears to be anionic and 27.3% appears to be cationic. Again, the mass balance of material in this analysis is poor, with only approximately 60% of the material accounted for in the reported fractions. Although an investigation of the amount of ^{137}Cs which passed through the entire fractionation scheme is underway, no values for this fraction are yet available.

Conclusions

The preliminary work in this study of the physico-chemical states of ^{239,240}Pu and ^{137}Cs in natural waters indicates that the radioisotopes exist in several different fractions within the water column and that the total charge of these fractions is different from what would be predicted by simple solution chemistry. In addition, the distribution of these isotopes in snow appears to be quite different from that in the water column, indicating that considerable chemical and/or physical transformations must take place after the atmospheric input has reached the lake surface. Unfortunately, there are insufficient data available to determine rate constants for the processes or even give truly quantitative values for the individual fractions present in the waters. This work is continuing through the 1975 field season, and it is hoped that more specific answers to these problems can be obtained.

References

1. Diamond, H., P. R. Fields, C. S. Stevens, H. M. Studier, S. M. Fried, M. G. Inghram, D. C. Hess, G. L. Pyle, J. F. Mech, W. M. Manning, A Ghiorso, S. G. Thompson, G. H. Higgins, G. T. Seaborg, C. I. Browne, H. L. Smith, and R. W. Spence. Heavy isotope abundances in Mike thermonuclear device. Phys. Rev. 119, 2000–2004 (1960).
2. Blomeke, J. O., C. W. Kee, and J. P. Nichols. Projections of Radioactive Wastes to be Generated by the U.S. Nuclear Power Industry. U.S. Atomic Energy Commission Report, ORNL-TM-3965 (1974).
3. Nelson, D. M., E. M. Yaguchi, B. J. Waller, and M. A. Wahlgren. Radiochemical methods. Radiological and Environmental Research Division Annual Report, Part III, January–December 1973. ANL-8060, Part III, pp. 6–17.
4. Wahlgren, M. A. and D. M. Nelson. Residence time of ^{239}Pu and ^{137}Cs in Lake Michigan water. Radiological and Environmental Research Division Annual Report, Part III, January–December 1973. ANL-8060, Part III, pp. 85–89.

EFFECT OF MUNICIPAL TREATMENT PROCESSES ON ^{239,240}Pu AND ^{137}Cs

J. J. Alberts, P. J. Jehn, D. M. Nelson, J. S. Marshall, and
M. A. Wahlgren

Introduction

With the increasing concern over introduction of man-made radionuclides into the human food chain, studies were undertaken to investigate the role of municipal water and waste treatment upon fallout ^{239,240}Pu and ^{137}Cs present in Lake Michigan. Although the existing concentrations of both ^{239,240}Pu and ^{137}Cs are seven orders of magnitude below the allowable level for human consumption, knowledge of either the concentration or removal of these nuclides is necessary in the event of future contamination of water supplies through accidental injection. For this reason, water was obtained at the Chicago Municipal Water Filtration Plant and returned to Argonne for analysis. In addition, a sample of the "organic" fertilizer, distributed to the public without charge at the Sanitary District, was obtained and similarly analyzed.

Methods

Water samples were obtained of both the Lake Michigan intake water of the filtration plant and the outflow water which is distributed to the residents of the Chicago area. These samples were obtained in the chemical laboratory of the filtration plant from a series of taps, which allow water samples to be taken after any step in the filtration process. Samples taken in October 1974 were placed in 55-liter carboys which had been acid washed and rinsed several times before sample collection. The water samples were spiked by addition of 100 ml of concentrated hydrochloric acid containing 2.65 dpm ^{242}Pu and 5 mg of stable Cs. The samples were transported back to Argonne National Laboratory where one set of intake and outflow waters was analyzed for ^{239,240}Pu and ^{137}Cs.(1)

The sampling procedure was repeated in December 1974; however, in addition to the samples taken for total ^{239,240}Pu and ^{137}Cs, an additional 100 liters of both the inflow water and the outflow water were passed through a series of anion (Dowex-1X, 200–400 mesh, Cl^- form) and cation (Dowex 50, 100–200 mesh, H^+ form resins). These samples were collected in 55-liter carboys at the same time as the total samples, but were not spiked. The latter samples were transported to the Laboratory and passed through the ion exchange resins the same day they were collected. The samples were passed through the anion exchange resin first then through the cation resin. The water which had passed these resins was collected and spiked the same way as the total samples. The resins were drained, transferred to 4-liter beakers, and ashed in a muffle furnace at 500° C for 7 days. The resulting material was taken up in 8 M HNO_3 and analyzed as before.

The sample of "organic" fertilizer was collected from the large open pile at the Sanitary District Plant in Stickney, Illinois. The solid material was dried overnight at 105° C and then ashed at 500° C in a muffle furnace overnight. The resulting ash was then treated as a sediment sample(2) and analyzed for $^{239,240}Pu$ and ^{137}Cs.

The results of the analyses are shown in Table 1. The data from the November sampling shows that the total levels of material in the lake water are low and that the filtration plant removes approximately 25% of the plutonium and 18% of the radioactive cesium present in the water. The data shown for the December sampling are not as straightforward. The high value for plutonium in the total intake water is probably representative of suspended material since the total samples were not passed through any form of filtration before analysis. Two additional facts support this conclusion. The first is the low value of plutonium in the anion exchange resin. The resins are covered with a fine mesh frit which will serve as a prefilter for particulate material and, therefore, the value in the anion resin is more representative of the dissolved plutonium. Secondly, filtered water samples from the lake, taken during the regular sampling schedule, yielded a total value of 0.35 fCi $^{239,240}Pu/l$. The day that the December samples were taken was quite windy and the water was very rough. Since the intake cribs lie in about 20 feet of water, it is quite probable that wind and wave action had stirred the bottom sediments and increased the particulate content of the water near the intake crib. The fact

TABLE 1. Concentrations of ^{239,240}Pu and ^{137}Cs in water filtered in metropolitan Chicago and in Chicago sanitary sludge.

Sample	Chicago Municipal Water Filtration Plant: Intake Crib Raw Water	Chicago Municipal Water Filtration Plant: North Outflow Treated Water	Organic Fertilizer: NaOH Extract	Organic Fertilizer: Total Ashed Sample
November 1974				
Total ^{239,240}Pu	0.39 fCi/l (2)	0.29 fCi/l (2)	Background	28.5 fCi/g
Total ^{137}Cs	33.5 fCi/l (2)	27.5 fCi/l (2)	Background	1.43 pCi/g
^{137}Cs/^{239,240}Pu	85.9	94.8		50.0
December 1974				
Total ^{239,240}Pu	1.38 fCi/l (3)	0.12 fCi/l (3)		
^{239,240}Pu Retained by Anion Resin	0.26 fCi/l	1.8 fCi/l		
^{239,240}Pu Retained by Cation Resin	Background	Background		

Numbers in () represent number of replicate samples.

that the water which was being distributed to the populace that day was an order of magnitude lower in plutonium concentration attests to the efficiency of the filtration plant process. The high value in the anion resin of the outflow water is anomalous and can only result from contamination in the Laboratory during analysis.

The values for plutonium and radioactive cesium in the organic fertilizer are approximately 25% of the values found in natural lake sediments. To determine the availability of these nuclides to plants grown in this material, the fertilizer was extracted with 0.1 N NaOH. This extractant removes natural organic chelators which have been shown in many studies to complex trace elements and increase their availability to plants. The sodium hydroxide extracts were analyzed and shown to contain no radionuclides. Therefore, it appears that the radioisotopes found in the fertilizer are in a form that is not readily available to plants.

An attempt was made to determine a mass balance for ^{239,240}Pu and

^{137}Cs in the Chicago metropolitan area, using the data collected in this study. The water filtration plant processes approximately 1 billion gallons of water per day (1×10^9 gal/day). If we use the average value for the outflow shaft of the plant (0.20 fCi ^{239,240}Pu/l), the total annual amount of ^{239,240}Pu leaving the water filtration plant for the city is

$$(0.20 \text{ fCi } ^{239,240}\text{Pu/l})\ (3.65 \times 10^{11} \text{ gal/yr})\ (3.79 \text{ l/gal})$$
$$= 2.77 \times 10^{11} \text{ fCi } ^{239,240}\text{Pu} = 0.28 \text{ mCi } ^{239,240}\text{Pu/yr}.$$

This number may be somewhat low since the concentration of plutonium in the lake water appears to be seasonal, with lows occurring in the fall of the year. However, even during the spring, the concentration of ^{239,240}Pu in lake water rarely exceeds 0.75 fCi ^{239,240}Pu/l. Assuming 25% efficiency in the filtration plant, the concentration going to the city would be 0.56 fCi/l, and the total for the year would be 0.77 mCi ^{239,240}Pu. In the case of ^{137}Cs, using the value of 28 fCi ^{137}Cs/l in the above calculations gives a total annual value of ^{137}Cs leaving the plant of 0.039 Ci ^{137}Cs/yr. Since the value of ^{137}Cs in lake water changes much less with season than that of ^{239,240}Pu, no further correction will be made on this value.

Using values reported here, calculations of the total removal of ^{239,240}Pu and ^{137}Cs by organic sludge follows:

21.5 fCi ^{239,240}Pu/g dry weight
1.08 pCi ^{137}Cs/g dry weight
3.53×10^5 tons/yr sludge removed by Sanitary District Plants (personal communication)
5% dry solids in sludge$^{(3)}$,

$$(21.5 \text{ fCi } ^{239,240}\text{Pu/g dry wt})\ (3.53 \times 10^5 \text{ tons/yr})\ (9.1 \times 10^5 \text{ g/ton})\ (0.05)$$
$$= 3.45 \times 10^{11} \text{ fCi } ^{239,240}\text{Pu/yr}$$
$$= 0.35 \text{ mCi } ^{239,240}\text{Pu/yr}$$

and

$$(1.08 \text{ pCi } ^{137}\text{Cs/g dry wt})\ (3.53 \times 10^5 \text{ tons/yr})\ (9.1 \times 10^5 \text{ g/ton})\ (0.05)$$
$$= 1.73 \times 10^{10} \text{ pCi } ^{137}\text{Cs/yr}$$
$$= 0.017 \text{ Ci } ^{137}\text{Cs/yr} .$$

From the above values, we see an extremely good balance, indicating that the sanitary removal process is approximately 50% efficient in removing ^{239,249}Pu and ^{137}Cs from waste water. However, the 3.53×10^5 tons of sludge represents a total of 465×10^9 gallons of waste water treated. This value is 100×10^9 gallons more than was processed by the filtration plant and must represent storm runoff in the city.

No values exist for the concentration of plutonium or cesium in storm runoff. However, a reasonable number may be reached by assuming that the runoff in an urban area is approximately that of the precipitation falling in that area, as little water is lost through penetration into the surface. Hence, using a mean value for precipitation of 9.1 fCi ^{239,240}Pu/l and 5.6×10^2 fCi ^{137}Cs/l [based on HASL reports for precipitation in New York City for the year 1973)] (4) we find the annual input of radioisotopes from precipitation to the waste treatment plant is

$$(9.1 \text{ fCi } ^{239,240}\text{Pu/l})\ (1 \times 10^{11} \text{ gal/yr})\ (3.79 \text{ l/gal})$$
$$= 3.45 \times 10^{12} \text{ fCi } ^{239,240}\text{Pu/yr} = 3.45 \text{ mCi } ^{239,240}\text{Pu/yr}$$

and

$$(5.60 \times 10^2 \text{ fCi } ^{137}\text{Cs/l})\ (1 \times 10^{11} \text{ gal/yr})\ (3.79 \text{ l/gal})$$
$$= 2.12 \times 10^4 \text{ fCi } ^{137}\text{Cs/yr} = 0.212 \text{ Ci } ^{137}\text{Cs/yr} .$$

These values represent approximately 5 times the activity supplied by the water passing through the water filtration plant, and indicate that the sewage treatment process is approximately 7 to 8% efficient in removing ^{137}Cs and ^{239,240}Pu from waste water.

These calculations, while only first approximations, show that a far greater quantity of plutonium and radioactive cesium are impinged on the metropolitan area of Chicago than is supplied through the drinking water system. This conclusion is given some substantiation by examination of the ratios of ^{137}Cs/^{239,240}Pu in the materials investigated. The ratio in Lake Michigan water is approximately 86, while that of the material coming out of the filtration plant is 95. The increase in ratio is indicative of the greater efficiency of removal of plutonium over that of cesium. Atmospheric ratios of cesium to plutonium are approximately 60, while the ratio in the organic fertilizer is 50. Therefore, there can be little contribution to the overall $^{137}Cs/^{239,240}Pu$ ratio from the filtration plant water, since any significant contribution would tend to increase rather than decrease the ratio in the fertilizer.

It appears that very little $^{239,240}Pu$ is reaching the public through the drinking water source, which is in agreement with the fact that the lake water concentration of these elements is very low. The only possible source of high levels of radioactive materials could be particulate matter, which is efficiently removed through the filtration process. Although significant amounts of radioisotopes may be concentrated in the organic sludge at the sewage treatment plant, the material appears to be in a form that is not readily available for removal and is unlikely to remobilize.

Acknowledgements

We wish to thank Mr. Phillip Reed and the Chicago Water Filtration Plant personnel for their help in collecting samples.

References

1. Nelson, D. M., E. M. Yaguchi, B. J. Waller, and M. A. Wahlgren. Radiochemical Methods. Radiological and Environmental Research Division Annual Report, Part III, January—December 1973. ANL-8060, Part III, pp. 6—17.
2. Alberts, J. J., M. A. Wahlgren, C. A. Reeve, and P. J. Jehn. Sedimentary $^{239,240}Pu$ phase distribution in Lake Michigan sediments. This report.
3. Clark, J. W., W. Veissman, Jr., and M. J. Hammer. Water supply and pollution control. International Textbook Co., Scranton, Pa., 2nd Ed., 1971.
4. Health and Safety Laboratory, Oct. 1, 1974. Fallout Program Quarterly Summary Report, HASL-286, Appendix, USAEC, N.Y. B1—B131.

SEDIMENTARY ^{239,240}Pu PHASE DISTRIBUTIONS IN LAKE MICHIGAN SEDIMENTS

J. J. Alberts, M. A. Wahlgren, C. A. Reeve, and P. J. Jehn

Introduction

The possible environmental fates of the man-made element, plutonium, have become of great public concern as proposals are brought forward to heighten the role of nuclear power in the field of energy production in the United States. This concern can also be extended to the increased use of plutonium-238 as a heat source in satellites, which may accidentally re-enter the atmosphere and become dispersed through burnup.(1) For these reasons, considerable effort is being put forth to understand the cycling and fate of plutonium isotopes in the natural environment, with the goal of forming a predictive model for a hypothetical accident involving nuclear materials.

Previous work(2) has shown that 95% of the ^{239,240}Pu added to Lake Michigan is rapidly removed from the water column to the sediments. In addition, the general deposition patterns of total ^{239,240}Pu in the sediment of this lake are known (D. N. Edgington, ANL, personal communication). However, little is known regarding the environmental chemistry of low concentrations of plutonium and how this chemistry bears on the ultimate fate of the material. It is of great importance to know if the plutonium deposited in the sediment is in a fixed phase which will either be transported by actual movement of the sediment through resuspension or burial, as opposed to existing in a more mobile state, such as occupying ion exchangeable sites on clay minerals or as a soluble organic or inorganic complex. The present investigation was designed to develop opperational classifications of the forms of plutonium found in particulate matter and to determine the relative distribution of natural levels of plutonium in different sedimentary phases.

This study was conducted using sediment grab samples obtained along a transect starting in the Grand River (Michigan) and extending into deep water of Lake Michigan. The sediment collected in this manner was then subjected to a series of extractions designed to differentiate material which exists in the ion exchangeable, reductant-soluble, organic, and crystalline phases within the sediment. The procedure was, in fact, a modification of techniques already used to study distribution of trace elements in riverine suspended material(3) and soils.(4) It is recognized that the use of extraction techniques such as those outlined below do not define materials absolutely in the categories previously mentioned; however, these extraction techniques are useful in determining the relative mobility of various elements in the natural environment.

Methods

All chemicals used in these extractions were reagent grade. All solutions were prepared with deionized water. Absolute ethyl alcohol was obtained from Commercial Solvents Corporation. Anion exchange resin was Bio-Rad AGl-X8, chloride form. Solutions used in the preparation of extracted fractions for counting have been described previously.(5)

Samples used in this study were obtained along a transect beginning at a point downstream of the bridge in the Grand River, Michigan, to a point approximately 25 miles offshore of the mouth of the Grand River. Sample stations are shown in Fig. 1. All samples were taken using a Ponar grab from the University of Michigan vessel, R/V Mysis, between 18 September and 24 September 1974. The samples, which ranged in wet weight from 2 to 5 kg, were transported to the laboratory, homogenized, and subsampled for total ^{239,240}Pu, fractionation, and dry and ash weight determinations.

Aliquots of the samples were oven dried for 2 days at 110 to 105° C and averaged for dry weight values. The dry samples were then ashed at 500° C for 24 hr in a muffle furnace.

^{239,240}Pu Determinations on Sediments

Total ^{239,240}Pu Determinations by Acid Extraction. 20.00 g of wet sample were weighed into a 600-ml beaker. About 300 ml of concentrated HNO_3 were added, along with 0.5 ml of ^{242}Pu spike, and the mixture was stirred and heated at moderate temperatures on a hotplate for about 7 hr. The solution was then cooled, and 50 ml of concentrated HCl were added. The mixture was coole and filtered through paper to remove solid materials, and the solid was discardea.

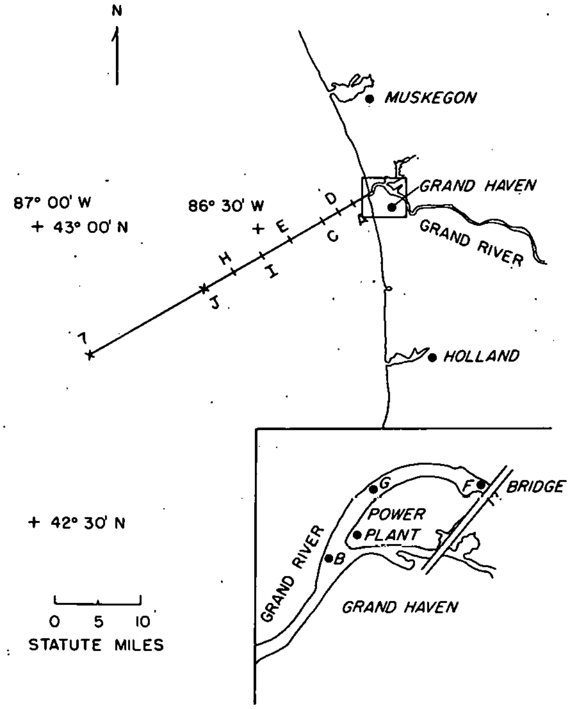


FIG. 1.--Grand Haven transect stations
ANL Neg. 149-6612

The filtrate was evaporated to dryness on a hotplate. The residue was dissolved in 8 $\underline{M}$ HNO$_3$, and the solution was evaporated to dryness again. The resulting residue was dissolved in 8 $\underline{M}$ HNO$_3$ and treated as usual.(5)

Fractionation of Samples. 10.00 g wet sediment were placed in a one-liter Erlenmeyer flask fitted with a plastic cap. 500 ml of 0.1 $\underline{N}$ magnesium chloride were added, and the mixture was stirred at room temperature for about 24 hr. The reaction mixture was then centrifuged (23,000 × g). The solids were washed twice by shaking with distilled water and centrifuging. The washings were added to the liquid, which was filtered through paper to remove any trace of residual solid and stored in a 2-liter polyethylene bottle. The average pH of the magnesium chloride solutions was found to be 7.5.

The remaining sediment was placed in a solution composed of 10 g sodium dithionite dissolved in 400 ml of 0.3 $\underline{N}$ sodium citrate. This mixture was heated to 80 to 90° C in a water bath, with constant stirring, for 15 min. The solid was centrifuged out and washed as before, and the supernatant and washings were filtered through paper and stored in a 1-liter polyethylene bottle. The average pH of the citrate-dithionite solution was found to be 5.9.

The remaining sediment was placed in 500 ml of 0.1 $\underline{N}$ sodium hydroxide in a 1-liter Erlenmeyer flask with a plastic cap and stirred for about 12 hr. The solid was centrifuged out and washed as above, and again the liquid was filtered through paper. The remaining sediment was dried in an oven at about 100° C to be used for fusion.

^{239,240}Pu Determinations for Magnesium Chloride Fractions. The magnesium chloride solution to be treated was poured into a 3-liter beaker,

acidified with 100 ml of 8 M HNO_3, and 0.5 ml of ^{242}Pu spike was added. The solution was evaporated to dryness, and the residue was dissolved in 8 M HNO_3. The solution was then treated as before for plutonium analysis.

^{239,240}Pu Determinations for Citrate-Dithionite Fractions. Upon acidification with 8 M nitric acid, the sulfur in the dithionite tended to be oxidized to its elemental form and precipitate. In an attempt to avoid this situation, the solution, after addition of 0.5 ml of ^{242}Pu spike, was heated in order to evaporate it without previous acidification; 30% hydrogen peroxide was added to promote the oxidation of the sulfur to sulfate ion. This, combined with strong heating of the residue, seemed to eliminate most of the free sulfur, and the residue could be dissolved in 8 M HNO_3 to run through anion exchange. However, in every case except those of samples A, B, and C, a flocculent precipitate appeared in the 8 M HNO_3 solution. This was centrifuged out and treated with about 300 ml of concentrated HNO_3 and 15 ml of 48.2% hydrofluoric acid to destroy any siliceous material by the formation of silicon tetrafluoride gas. In the case of samples D and E, the residues, upon evaporation to dryness, appeared soluble in 8 M HNO_3, so they were dissolved in 8 M HNO_3 and added to the original solutions. With samples, F, G, H, I, and J, there were still traces of insoluble precipitates with hydrofluoric acid treatment, so the residues were taken to dryness with aqua regia. This treatment caused residues I and J to be soluble in 8 M HNO_3, so they could be dissolved and added to the original solutions. Residues F, G, and H remained insoluble and were centrifuged out and saved.

In every case, about 200 ml of 8 M HNO_3 were required to dissolve all of the residue. This solution was run through anion exchange and the plutonium electroplated as described above.

^{239,240}Pu Determinations for Sodium Hydroxide Fractions. Each sodium hydroxide solution was acidified in its container with 8 M HNO_3 to about pH 1 (using pH paper) and left to sit at least overnight before further treatment. Acidification produced a brownish, flocculent precipitate in every case. This precipitate probably consisted of humic acids, which precipitate from acid solutions. 0.5 ml of ^{242}Pu spike was added, the solution was taken to dryness, and the residue was dissolved in 8 M HNO_3; the precipitate was still present and was centrifuged out. Each precipitate was taken to dryness with 48.2% hydrofluoric acid and concentrated HNO_3 in a small Teflon beaker, then treated with aqua regia and taken to dryness again, dissolved in 8 M HNO_3, and taken to dryness, and dissolved once more in 8 M HNO_3. Only in the case of samples A and F did the precipitate survive this treatment; the other precipitates dissolved, and the 8 M HNO_3 solutions were added to the original solutions. Precipitates A and F were centrifuged out and saved, and the supernates added to the original solutions.

The 8 M HNO_3 solutions were run through anion exchange, and the plutonium was electroplated as described previously.

^{239,240}Pu Determinations for Fusion Fractions. In a 100-ml platinum crucible, 4 g boric acid and 6 g lithium fluoride were mixed. Into a small hollow in this mixture was placed 1 g of the material to be fused, which had previously been finely ground using a mortar and pestle. (The total weight of the dried material left after fractionation of each sample was measured and recorded, but only one gram of this material was actually used in fusion.) 0.5 ml of ^{242}Pu spike was added to the mixture, and the crucible was tapped on the side to cover the sediment. The crucible was then covered and heated gently for 2 to 3 min over a low flame. The flame was increased gradually until the contents of the crucible reached their melting point, and the mixture was heated strongly until it was entirely melted. The crucible was cooled quickly by half immersing it in a stream of cold tap water. Then, 20 ml of concentrated H_2SO_4 were added to the contents, and the covered crucible was gently heated on a wire gauze over a Bunsen burner until gas bubbles evolved. The heating was regulated so that the reaction would not be too vigorous. When the evolution of gas ceased (after about 90 min), the temperature was increased until copious fumes of sulfur trioxide appeared, and this temperature was held for 2 to 3 min. The crucible was cooled in about 400 ml of deionized water in a one-liter beaker; 10 ml of concentrated HNO_3 were added to its contents; and the crucible and cover were boiled until all the contents were dissolved. The resulting solution was clear, often yellowish.

This solution was evaporated to dryness on a hotplate, and the residue was dissolved in 8 M HNO_3. In every case except for samples A, B, and G, a cloudy white precipitate appeared in this solution. It was centrifuged out and found to be soluble in deionized water with a little heating, so that it could be dissolved in water and returned to the rest of the solution. This solution was diluted to 200 ml with 8 M HNO_3 in a volumetric flask. The solution was run through anion exchange, prepared for plating, and electroplated in the usual way.

A fusion blank was run, using the above procedure and no sample. 82% recovery of the spike was achieved, and 2 background counts appeared in the $^{239,240}Pu$ region in 1343 min of counting.

Fulvic Acid vs. Humic Acid Distribution of Sedimnetary $^{239,240}Pu$. Between 125 and 180 g of wet sample were shaken with 500 ml 0.1 N NaOH overnight. The liquid phase was removed from the sediment by centrifugation at 14,000 × g and decanting. The liquid was acidified with 10 ml 6 N HCl and allowed to stand overnight. Again the liquid was removed by centrifugation and decantation. The liquid was spiked and analyzed for $^{239,240}Pu$ in the normal manner. The solid was redissolved in 200 ml 0.1 N NaOH and analyzed for $^{239,240}Pu$.

Results and Discussion

The results of the analyses are shown in Table 1. It can be seen that the concentrations of $^{239,240}Pu$ are low in all samples; and consequently, the analysis of the fractions containing low concentrations have relatively large associated counting errors. In addition, the total activity of $^{239,240}Pu$, which is usually confined to the first few centimeters of sediment, may have been diluted in some samples by mixing with sediment from a lower depth which did not contain plutonium. The results, however, are indicative of the areal distribution and phase distribution of the cumulative $^{239,240}Pu$ deposition at the sample stations. The extremely low value at the 4-mile station is consistent with the sediment type in that area, which is mostly sand and coarse material.(6) The value at the 10-mile station appears to be anomalously

TABLE 1. Distribution of ^{239,240}Pu in Lake Michigan sediments

Sample	Total		MgCl$_2$		Citrate-Dithionite		NaOH		Fusion		% Total Recovery
	N[a]	pCi/g	N	%[b]	N	%	N	%	N	%	
(F) Grand River near bridge	5.2	0.006	0	0	2.49	47.9	0	0	0	0	47.9
(G) Grand River upstream of the power plant	3.6	0.005	0.22	6.1	2.30	63.9	0	0	0	0	70.0
(B) Grand River downstream of the power plant	13.1	0.017	0.50	3.8	12.56	95.9	0	0	0	0	99.7
(A) 2 miles offshore Lake Michigan	12.1	0.016	0.07	0.6	9.68	80.0	0.02	0.17	0	0	80.0
(D) 4 miles offshore Lake Michigan	0.6	0.001	0.24	40.0	0.37	61.7	0.02	3.30	0	0	105.0
(C) 6 miles offshore Lake Michigan	10.3	0.013	0	0	8.25	80.0	0	0	0	0	80.1
(E) 10 miles offshore Lake Michigan	1.7	0.002	0.05	2.9	2.55	150.0	0	0	0	0	152.9
(I) Station 5A (85 m depth)	13.4	0.017	0	0	6.12	45.7	0	0	0	0	45.7
(H) Station 5B (84 m depth)	34.9	0.045	0	0	31.30	89.7	0	0	0.51	1.46	91.2
(H) Station 5B NaOH before Citrate-Dithionite			1.94	5.6	33.60	96.3	1.75	5.00	ND		106.9
(H) Station 5B Citrate without Dithionite			0	0	12.20	35.0					
(H) Station 5B Citrate with Dithionite			0	0	31.90	91.4					
(H) Station 5B MgCl$_2$ with Dithionite			3.40	9.7							
(J) Station 6 (88 m depth)	18.7	0.024	0	0	24.20	129.4	0.12	0.60	0	0	130.0

[a] N = number of counts/1000 minutes/g dry weight sediment.

[b] % = ± a maximum of 20%.

low and cannot be explained by sediment characteristics. This value is further suspect when the rest of the data are considered and it is shown that the sum of the fractions add up to ~ 150% of this total value.

Examination of the data does show one extremely interesting characteristic, which is evident in spite of the data scatter. This is the marked predominance of the distribution of $^{239,240}Pu$ in the citrate-dithionite fraction. This fraction was described by Chang and Jackson(4) as representing the occluded or reductant-soluble fraction. They recognized the fraction as representing that material occurring in a solid phase which required a reducing environment before dissolution could occur. This fraction contains at least 60% of the recovered $^{239,240}Pu$ in all but two cases. In both of these two exceptions, Bridge Station and Station 5A, the citrate-dithionite fraction represented only 47.9 and 45.7%, respectively; however, these values represent the entire recovery of plutonium in the fractionation scheme.

The question may be raised that, since the citrate-dithionite extraction preceded the base extraction, the distribution coefficient for the citrate-plutonium complex may be much higher than that of the natural organic-plutonium complex, which may have existed, and a redistribution may have occurred in the extraction solution. Although the period of time that the sediment was exposed to the citrate-dithionite solution (15 min) was very short for such an exchange to occur, an experiment was conducted in which another subsample of sediment from Station 5B (chosen because of its high total $^{239,240}Pu$ concentration) was extracted as before, except that the base extraction was conducted prior to the citrate-dithionite extraction. The results of this experiment (Table 1) indicate that while there is some activity in both the $MgCl_2$ and NaOH fractions, the major part of the activity is still in the citrate-dithionite extractable phase.

One further question that arises from the observation that most of the sedimentary $^{239,240}Pu$ is in the citrate-dithionite extractable fraction is whether dithionite is required or if citrate is capable of extracting the plutonium as is the case in some soils.(7) To investigate this possibility, additional subsamples of sediment from Station 5B were extracted as before, except that in one sample citrate was used in the procedure without dithionite. Also, a third experiment was undertaken in which dithionite was added to the $MgCl_2$ extraction. The results of these experiments are also shown in Table 1.

It is apparent that the addition of a reducing agent to the $MgCl_2$ solution increases the extractable ^{239,240}Pu concentration. However, the twofold increase in plutonium extracted in this fraction indicates that simple reduction is not sufficient to release large amounts of plutonium through ion exchange processes. Similarly, the significant reduction in the amount of ^{239,240}Pu extractable by citrate solution without a reducing agent would suggest that a complexing agent must be present in conjunction with reducing conditions to remove plutonium effectively from sedimentary phases.

Additional confirmation of the fact that plutonium in natural sediments does not exist in the base soluble or humic acid phase is shown in Table 2. These results are from sediments taken from the same grab samples as those used in Table 1. Larger samples were taken in this case in an attempt to quantify the amount of ^{239,240}Pu in the fulvic acid (FA) vs. the humic acid (HA) fraction of the sediments. As can be seen from the data, less than 7% of the total sedimentary ^{239,240}Pu is found in the base soluble fraction. One interesting note regarding the data in Table 2 is the apparent consistency of the fraction of plutonium in the FA fraction vs. the apparent decrease in plutonium content of the HA fraction in lake sediments compared to river sediments.

TABLE 2. Fulvic acid vs. humic acid distribution of ^{239,240}Pu in Lake Michigan and Grand River sediments.

Sample	^{239,240}Pu Fulvic Acid Fraction		^{239,240}Pu Humic Adid Fraction		^{239,240}Pu Total Sediment
	fCi/g dry wt	% total	fCi/g dry wt	% total	fCi/g dry wt
Grand River upstream of power plant	0.04	0.80	0.3	6.0	5.0
Grand River downstream of power plant	0.14	0.58	0.8	3.3	24.0
Lake Michigan 4 miles off Grand Haven	0.008		0.01		1.0
Lake Michigan Station 5A	0.16	0.80	0.1	0.5	20.0
Lake Michigan Station 6	0.10	0.36	0.2	0.7	28.0

However, although this is an interesting observation, more data are required before it can be shown whether this trend is real.

The results of this study indicate that ^{239,240}Pu in Lake Michigan sediments is relatively immobile and that essentially none is in the form of refractory particles. However, the study does raise the question of the fate of plutonium in environments which undergo reducing conditions. These naturally occurring systems, caused by natural stratification or pollution, are characterized by highly reducing sediments and high concentrations of organic matter which has been shown to contain natural complexing agents.(8) In these systems, the fate of plutonium is much less certain that in aerobic systems, and re-entry into the hydrosphere, and eventually the biosphere, must be considered as a possibility.

References

1. Hardy, E. P., P. W. Krey, and H. L. Volchok. Global inventory and distribution of fallout plutonium. Nature 241, 444–445 (1973).
2. Wahlgren, M. A. and D. M. Nelson. Residence times for ^{239}Pu and ^{137}Cs in Lake Michigan waters. Radiological and Environmental Research Division Annual Report, January–December 1973, Part III. ANL-8060, Part III, p. 85.
3. Gibbs, R. J. Mechanisms of trace metal transport in rivers. Science 180, 71–73 (1973).
4. Chang, S. C. and M. L. Jackson. Fractionation of soil phosphorus. Soil Sci. 84, 133–144 (1973).
5. Nelson, D. M., E. M. Yaguchi, B. J. Waller, and M. A. Wahlgren. Radiochemical methods. Radiological and Environmental Research Division Annual Report, January–December 1973, Part III, ANL-8060, Part III, pp. 6–17.
6. Ayers, J. C. The surficial bottom sediments of Lake Michigan. Studies on the Environment and Eutrophication of Lake Michigan. University of Michigan, Great Lakes Research Division, Ann Arbor, Special Report No. 30 (1967), pp. 247–254.
7. Bondiette, E., Environ. Sciences, Oak Ridge National Laboratory. Personal communication.
8. Schnitzer, M. and S. U. Khan. Humic Substances in the Environment. Marcel Dekker, New York, 1972.

THE DISTRIBUTION OF PLUTONIUM IN LAKE MICHIGAN SEDIMENTS

J. O. Karttunen and D. N. Edgington

Introduction

Plutonium, along with other radionuclides, was introduced into the earth's environment through weapons testing, as well as from other sources.(1,2) Significant concentrations of plutonium isotopes are found in sediments from Lake Michigan with values ranging between 0.14 and 0.40 pCi/g dry sediment in sediment just below the water-sediment interface.

There are many processes which control the distribution of radionuclides and chemical compounds in the water, sediments, and biota. From the present information on the chemical reactivity and transport of plutonium in freshwater environments, it is known that approximately 97% of the plutonium entering the lake water column is found in the sediment which indicates a short residence time in the water column.(3)

The purpose of this study is to provide 1) baseline information as to the present content of plutonium in sediments from Lake Michigan, 2) to determine the utility of plutonium isotopes for estimating sedimentation rates, 3) to assess the extent of additional radionuclide inputs to Lake Michigan from nuclear power plants and other sources, and 4) to determine the vertical distribution in recent sediments.

Methods

Core samples were collected in 1972, 1973, and 1974 from Lake Michigan on the University of Michigan's research vessels, Inland Seas and Laurentian. A Benthod gravity corer was used to obtain the sediment core samples which were extruded, trimmed, sectioned on board ship, and frozen in individual polyethylene bottles or bags. Fourteen of these cores were analyzed for plutonium, ^{210}Pb, ^{137}Cs, porosity, wet density, and fraction dry weight. The ^{90}Sr content and distribution were also determined on two of the cores.

After the wet density, fraction dry weight, and ^{137}Cs are determined on a section of the core, an aliquot is accurately weighed out for the plutonium analysis. 2.65 dpm of ^{242}Pu is added to the sample prior to dissolution as an isotopic dilutent. The method used to leach the sediment is essentially that reported by Harley.(4)

The sample is digested for approximately 1½ days, initially with HNO_3 and later with aqua regia. Undissolved sediment residue is filtered off and the filtrate taken to semidryness. To insure isotopic exchange between the ^{242}Pu tracer and the Pu in the sample, the salts are redissolved in 7.8 $\underline{M}$ HNO_3, 10 drops of 30% H_2O_2 are added, and the solution is boiled for several minutes. Upon cooling, the solution is passed through a Dowex 1-X8 (200 mesh) anion exchange resin column which has been preconditioned with 7.8 $\underline{M}$ HNO_3.

Plutonium is adsorbed under these conditions, while uranium is washed off the resin column with additional 7.8 $\underline{M}$ HNO_3. Thorium, which is also adsorbed, is eluted with concentrated HCl. It is essential that the elution of U and Th be complete, otherwise interference will arise in the pulse-height analysis. Plutonium is subsequently eluted with 0.1 $\underline{M}$ HCl + 0.01 $\underline{M}$ HF and electroplated onto a stainless steel disk.(5) The activity of the plutonium is determined by alpha spectroscopy and pulse-height analysis. A typical plutonium spectrum is shown in Fig. 1. The small amounts of ^{234}U and ^{210}Po seen in the spectrum were not completely removed in the separation procedure but do not interfere with the plutonium determination.

Results and Discussion

Fallout plutonium is a mixture of isotopes of ^{238}Pu to ^{242}Pu, but only the more abundant isotopes ^{238}Pu, ^{239}Pu, and ^{240}Pu are measured. The concentrations of $^{239,240}Pu$ and ^{137}Cs for selected Lake Michigan stations are summarized in Table 1. Fallout plutonium is approximately 84% ^{239}Pu and 16% ^{240}Pu; however, these isotopes cannot be resolved by alpha spectrometry. Sampling locations in Lake Michigan where cores were examined for $^{239,240}Pu$ and ^{137}Cs are shown in Fig. 2.

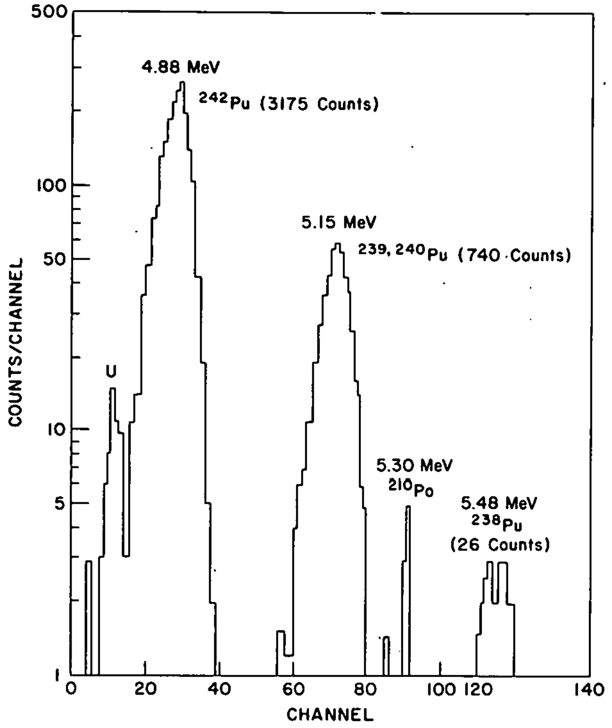


FIG. 1.--Alpha spectrum of plutonium isotopes extracted from a Lake Michigan sediment. The sample was counted for 65 hr. The ^{242}Pu isotope is added as a tracer. ANL Neg. 149-75-55R1

The $^{239,240}Pu$ introduced into the earth's atmosphere by the testing of nuclear weapons and other devices is circulated globally and eventually transferred to the earth's surface by wet and dry deposition as radioactive fallout. Probably the principal route of entry of plutonium into the aquatic system is by direct deposition onto the water surface, as only a minor contribution to the total activity in the lake has been estimated to come from runoff from tributary rivery and streams.(6) In view of the fact that the transfer of ^{239}Pu as atmospheric fallout to the lake bottom has a comparatively uncomplex history, it is possible to develop a simple model for the relationship between the atmospheric input and the vertical distribution observed in the sediments. The total concentration of $^{239,240}Pu$ or ^{137}Cs at any location in the lake will depend upon three factors: the flux (in pCi/cm^2/yr) at the air-water interface, the sedimentation rate (mg/cm^2/yr), and a factor by which the flux measured at the sediment-water interface is normalized to the flux at the air-water interface.

From the data in Table 1 it appears that the specific activity of the surficial sediment is almost constant at all the stations occupied; the concentration of $^{239,240}Pu$ in the top sections of cores ranges between 0.14 and 0.40 pCi/g, values significantly higher than those previously reported in oceanic sediments.(7,8) This is because in the open ocean, in contrast to Lake Michigan, a larger proportion of the plutonium is still in the water column. The sedimentation rates in various areas of Lake Michigan are 40 to 400 times greater than for deep sea sediments.(7,9) From the data shown in Table 2, the

TABLE 1. Summary of measured ^{239,240}Pu and ^{137}Cs activities (p/Ci/g dry weight) in selected sediment cores taken from Lake Michigan in 1972, 1973, and 1974. The serial distribution in the cores is shown.

Sampling Depth (cm)	Pu	Cs	Pu	Cs	Pu	Cs	Pu	Cs	Pu	Cs	Pu	Cs
Station	72-11		72-17(2)		72-29		72-54		72-101'		72-103'	
Floc	---	---	---	12.5	---	---	0.24	18.8	---	---	0.23	---
0 - 1	0.18	9.8	0.16	7.5	---	---	0.20	15.6	0.401	20.1	0.09	21.7
1 - 2	0.06	3.0	0.04	2.3	0.12	8.0	0.03	2.1	0.202	8.2	---	0.53
2 - 3	---	0.45	0.01	0.57	---	---	0.00	0.10	0.053	1.8	---	0.34
3 - 4	---	0.07	0.01	0.13	0.16	8.4	---	---	0.10	---	0.01	---
4 - 5	---	---	0.01	---	---	---	---	---	0.006	---	---	---
5 - 6	---	---	---	---	0.14	7.2	---	---	0.001	---	---	---
Station	73-5 (c.1)		73-6 (c.1)		73-6 (c.3)		73-7 (c.3)		73-8 (c.3)			
0.0 - 0.5	0.205	16.5	0.233	15.7	0.211	19.2	0.291	14.9	{0.206}	12.1		
0.5 - 1.0	0.247	16.6	0.235	17.3	---	17.8	0.274	17.3		18.8		
1.0 - 1.5	0.275	17.4	0.220	21.0	0.263	19.2	0.216	17.8	0.245	14.1		
1.5 - 2.0	0.305	18.1	0.265	17.2	0.259	19.3	0.239	16.6	0.222	14.7		
2.0 - 2.5	0.202	12.7	0.228	18.7	---	13.0	0.250	17.6	{0.165}	13.5		
2.5 - 3.0	0.173	6.9	0.241	15.4	0.135	8.2	0.211	14.2		6.2		
3.0 - 3.5	0.103	3.7	0.156	10.4	0.064	4.6	0.105	6.5	0.059	2.0		
3.5 - 4.0	0.043	3.6	0.083	6.1	0.029	2.2	0.041	1.1	0.010	1.0		
4.0 - 5.0	0.011	0.4	0.038	2.2	0.010	1.2	0.010	0.2	0.003	0.1		
5.0 - 6.0	0.003	0.2	0.008	0.4	0.003	0.9	0.003	0.4	---	---		
6.0 - 8.0	---	---	---	---	---	---	---	---	---	---		
Station	74-5 (c.1)		74-1 (c.1)		74-2 (c.1)		74-3 (c.4)					
0.0 - 0.5	{0.143}		0.116	10.2	0.144	10.4	0.286	16.2				
0.5 - 1.0			0.158	8.5	0.110	10.3	0.213	17.5				
1.0 - 1.5	{0.114}		0.126	10.3	0.148	10.8	0.293	17.9				
1.5 - 2.0			0.106	9.1	0.150	9.2	0.258	17.6				
2.0 - 2.5	---		0.167	10.6	0.095	6.2	0.260	15.5				
2.5 - 3.0			0.110	9.7	0.028	1.9	0.155	7.4				
3.0 - 3.5	{0.056}		0.139	9.7	0.007	1.2	0.101	6.0				
3.5 - 4.0			0.153	11.4	0.004	1.0	0.070	3.1				
4.0 - 5.0	0.004		0.087	11.6	---	0.8	---	0.66				
5.0 - 6.0	0.002		0.231	12.9	---	---	---	---				
6.0 - 8.0	0.004		0.160	7.3	---	---	---	---				

total deposition of plutonium in these Lake Michigan cores is seen to vary by approximately a factor of three.

The profiles for ^{137}Cs and ^{239,240}Pu in the cores examined are compared in Figs. 3–5. The similarity in the ^{137}Cs and ^{239,240}Pu profiles, especially for the 1972 and 1974 cores, may be seen in Figs. 3 and 5. This similarity indicates that these elements, though chemically very dissimilar, are removed from the water column to the sediments at the same rate in Lake Michigan. However, the mechanisms responsible for removal of each of these nuclides are probably very different. The shapes of the profiles will depend upon the time variability of the input of ^{239,240}Pu or ^{137}Cs to the lake, the residence times in the water column, the sedimentation rate, the effects of vertical mixing due to biological or physical processes in the uppermost

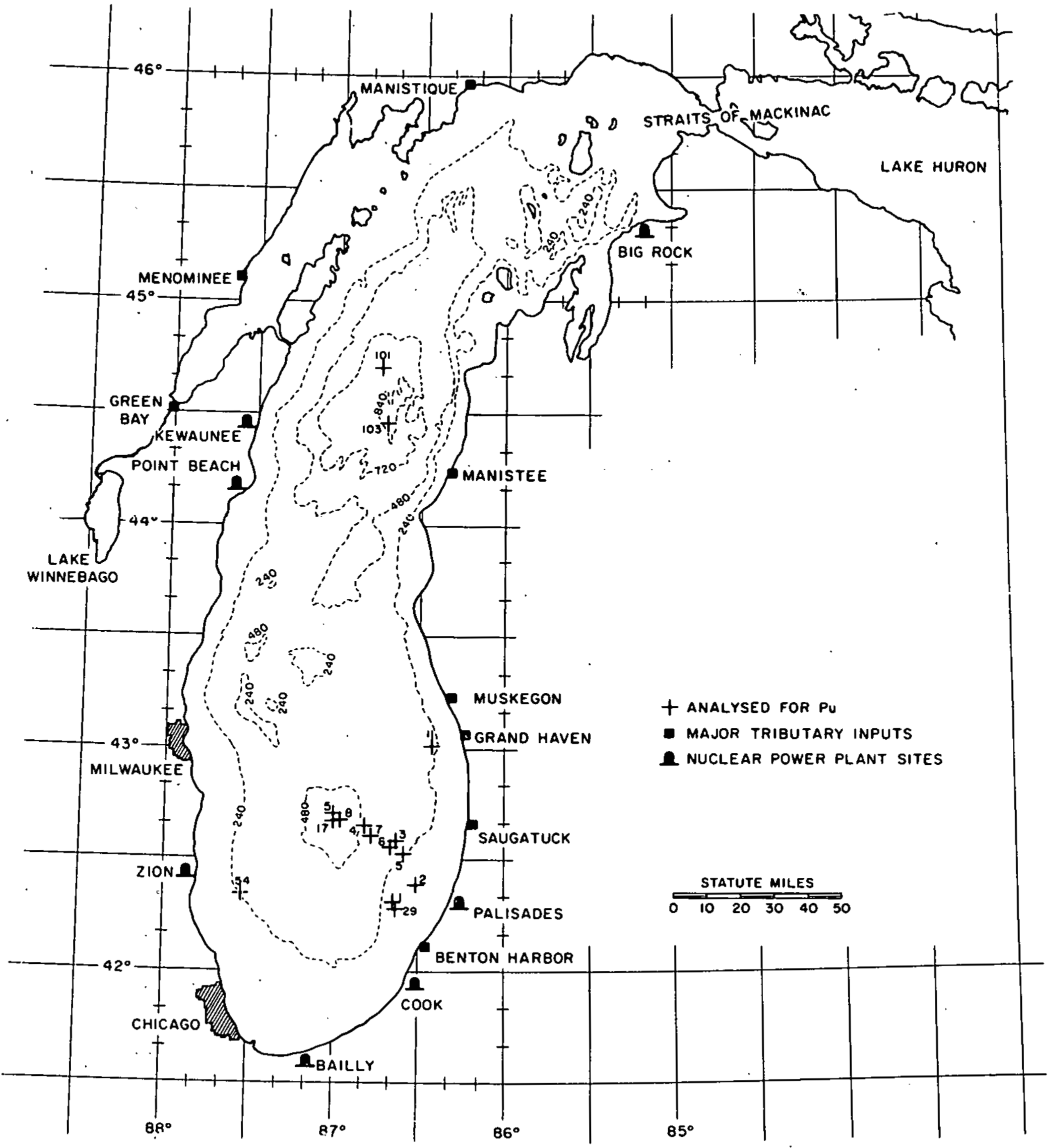


FIG. 2.--Sampling locations in Lake Michigan where ^{239,240}Pu has been measured. ANL Neg. 149-75-16R1

sediment layers, and the finite thickness of the sampling interval.(9,10) The effects of vertical mixing are especially evident in 74-1 (c.1), where ^{239,240}Pu and ^{137}Cs activities are nearly constant down to 8 cm (Table 1), and in core 72-29 (Fig. 3).

In all the cores studied, with the exception of 74-1 (c.1), the ^{239,240}Pu and ^{137}Cs activity was confined to the uppermost 6 cm of the sediment (Table 1). In most of the 1972 samples, no activity was found below 3 cm (Fig. 3). These findings indicate that surveys of radionuclides performed using less exact sampling techniques, such as taking Ponar grab samples, are probably quite

TABLE 2. Measured sedimentation rates and calculated mixing depths, flux normalization factors, and total activity of ^{239,240}Pu, ^{137}Cs, and ^{210}Pb in sediment cores taken from Lake Michigan in 1972, 1973, and 1974.

Station	Sedimentation Rate$^{(a,b)}$						Total Activity		Mixing Depth						Flux Normalization Factor		
	^{239,240}Pu		^{210}Pb		^{137}Cs		(pCi/cm^2)		^{239,240}Pu		^{137}Cs		^{210}Pb				
	(a)	(b)	(a)	(b)	(a)	(b)	^{239,240}Pu	^{137}Cs	cm	yr	cm	yr	cm	yr	f_{Pu}	f_{Cs}	f_{Pb}
72-11	0.07	21.8	0.08	23.0	0.08	23.0	0.068	3.81	0.5	7	0.5	7	0.0	0	0.46	0.50	1.04
72-17 (2)	0.07	15.1	0.08	16.9	0.05	11.1	0.05	2.32	0.5	7	1.0	18	1.0	14	0.30	0.37	2.46
72-29	0.32	113.6	0.24	85.2	0.26	92.3	0.347	19.37	2.5	8	3.2	12	3.8	16	2.18	2.39	4.51
72-54	0.02	5.6	0.02	5.9	0.013	3.8	0.08	7.45	1.0	68	1.0	104	1.0	68	0.58	0.59	0.91
72-101'	0.05	11.0	0.06	14.0	0.05	13.0	0.168	7.55	1.0	24	1.0	20	2.0	36	0.91	0.86	2.69
72-103'	0.05	10.5	0.08	15.2	0.07	12.8	0.020	0.715	1.0	20	0.5	8	0.0	0	0.31	0.080	1.58
73-5	0.17	34.3	0.20	40.4	0.17	34.3	0.195	11.92	0.0	0	0.0	0	0.0	0	0.08	1.03	2.94
73-6 (c.3)	0.17	32.0	0.23	43.4	0.17	32.0	0.117	13.10	0.0	0	0.0	0	0.0	0	0.65	1.04	3.80
73-7	0.15	28.5	0.18	32.1	0.15	28.5	0.170	11.00	1.0	10	1.5	10	0.0	0	0.95	1.15	3.82
73-8	0.06	8.7	0.10	14.5	0.07	10.0	0.081	7.61	2.0	35	2.0	35	2.0	25	0.48	0.88	2.43
74-1	0.50	96.3	0.48	92.8	0.50	96.3	0.427	27.12	4.0	12	4.0	12	5.2	16	2.50	3.14	5.26
74-2	0.10	23.8	--	--	0.08	19.0	0.115	8.73	2.0	18	2.0	29	--	--	0.61	0.89	--
74-3	0.12	18.8	0.28	44.2	0.10	15.8	0.140	10.94	2.0	25	2.0	25	0.0	0	0.93	1.15	3.30
A74-5	0.14	31.0	0.19	42.0	--	--	0.083	--	2.0	18	--	--	2.5	16	0.77	--	2.09

(a) cm/yr
(b) mg/cm^2/yr

unreliable because of the likelihood of losing the uppermost flocculent layer during sampling. The ^{239,240}Pu and ^{137}Cs profiles illustrate the different observed types of distribution of these two radionuclides with depth in sediment cores taken from Lake Michigan. The observed values for the total activity of ^{239,240}Pu (pCi/cm^2) in the sediment cores are given in Table 2.

Since the ratio of ^{137}Cs to ^{90}Sr is fixed in the fission process, the cumulative fallout input of ^{137}Cs to Lake Michigan can be determined quite accurately. A ^{137}Cs-to-^{90}Sr ratio of 1.5 and a ^{137}Cs-to-^{239}Pu ratio of 60 has been calculated.$^{(2,11)}$ The ^{137}Cs-to-^{239}Pu ratio in the most surficial section of the fourteen sediment cores examined varies from 50 to 90.

The global inventory and distribution of fallout plutonium and its relation to latitude and precipitation have been reported for the years 1954 to 1973.$^{(1,2,11)}$ The delivery to Lake Michigan is estimated to be 2 mCi/km^2 or a total deposition of 1.9 kg ^{239}Pu. The data in Table 2 show that the estimated fallout via precipitation and the observed cumulative deposition of ^{239,240}Pu are in fair agreement for the lake cores examined. This agreement further suggests that in freshwater environments, such as Lake Michigan, plutonium is removed to the sediments from the water column shortly after its entry.

Measurements of $^{239,240}Pu$ and ^{137}Cs in samples of water from the lake during the period 1966 to 1973 have shown that the residence time of these radionuclides in the water column is of the order of 1 yr (in contrast to ≥ 100 yr for conservative elements).(12) The result is that approximately 97% of the total activity that entered the lake over 20 yr has been removed from the water column, and also, since the annual flux to the lake has been extremely variable, two horizons should be preserved in the sediments — one corresponding to the onset of nuclear testing around 1950 and the other to the maximum activity resulting from the 1963 input. Present day inputs are more than an order of magnitude lower than the 1963 value.(13)

However, in several cores it has been observed that the two horizons appear to be deeper in the core than would be expected on the basis of sedimentation rates from the ^{210}Pb measurements, and that there was a corresponding interval of constant activity of ^{210}Pb at the top of the sediment cores. These observations have been interpreted in terms of a homogenous layer at the surface of the sediment column due to either physical or biological disturbances, as has been postulated elsewhere.(14) A depositional model can be altered to take account of this process. It is assumed that this homogenous layer is of constant thickness, all new inputs are instantaneously mixed within it, and a constant fraction of the total mass of sediment contained within it (equivalent to the annual deposition) is premanently buried each year.

The dashed lines in Figs. 6–9 represent the best fits to the data calculated from a depositional model. Values of the sedimentation rate, mixing depth, normalization factor, and the total activity per unit area of the lake bottom are given in Table 2. In those cores for which the sedimentation rate has been determined radiometrically from the ^{210}Pb profiling (Table 2), the depth to which $^{239,240}Pu$ and ^{137}Cs activities are found are consistent with the known history of deposition from the atmosphere as a result of nuclear testing.(9) The agreement between the values of the sedimentation rates calculated from the measured profiles of these radionuclides indicates that this

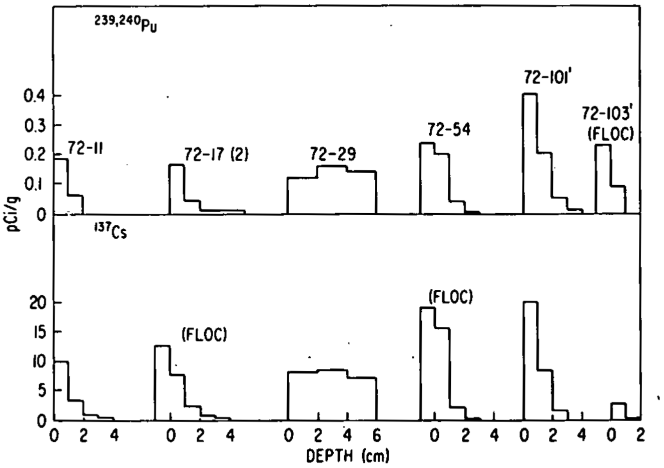


FIG. 3.--Measured ^{137}Cs and ^{239,240}Pu profiles in sediment cores taken from Lake Michigan in 1972.
ANL Neg. 149-75-56

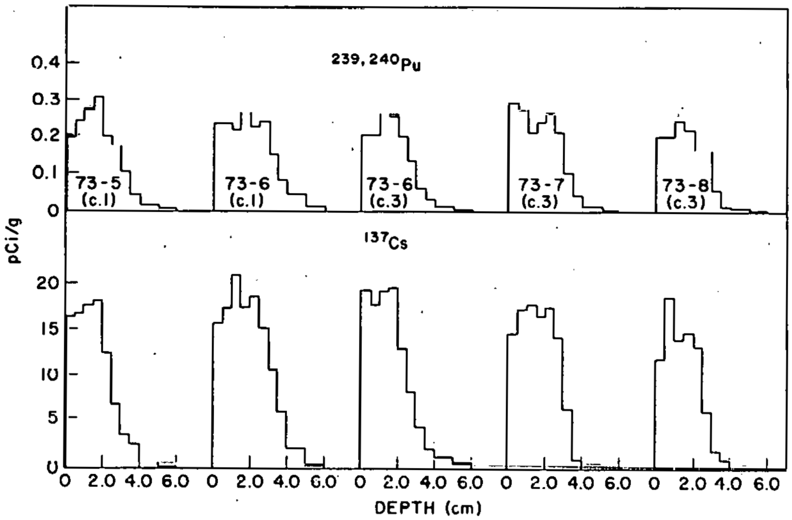


FIG. 4.--Measured ^{137}Cs and ^{239,240}Pu profiles in sediment cores taken from Lake Michigan in 1973.
ANL Neg. 149-75-57R1

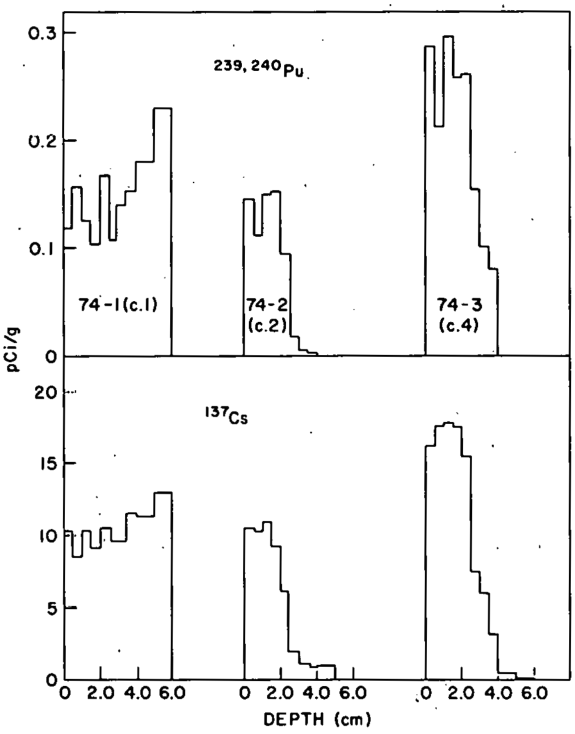


FIG. 5.--Measured ^{137}Cs and ^{239,240}Pu profiles in sediment cores taken from Lake Michigan in 1974.
ANL Neg. 149-75-58R1

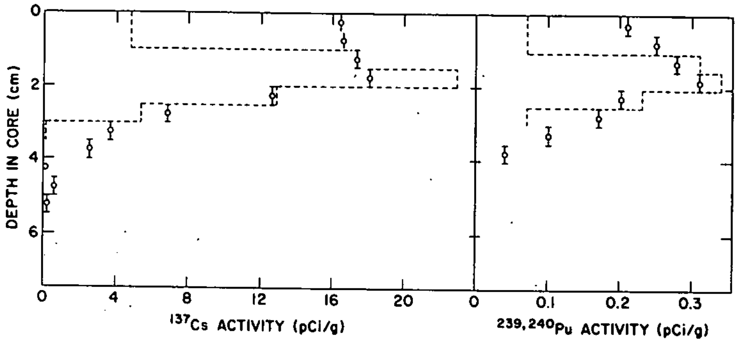


FIG. 6.--Measured and calculated ^{137}Cs and $^{239,240}Pu$ profiles in the sedimentary column at station 73-5. The sedimentation rate is 34 mg/cm^2/yr or 0.17 cm/yr at the surface, and there is no mixing.
ANL Neg. 149-75-17

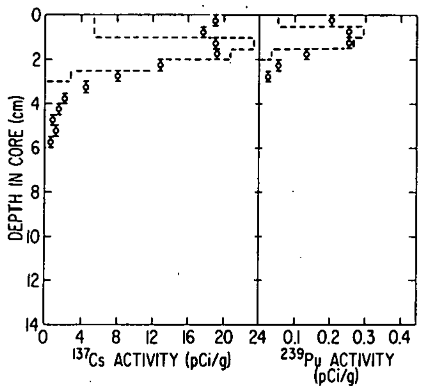


FIG. 7.--Measured and calculated ^{137}Cs and $^{239,240}Pu$ profiles in the sedimentary column at station 73.6. The sedimentation rate is 32 mg/cm^2/yr or 0.17 cm/yr at the surface, and there is no surficial mixing. ANL Neg. 149-6649B

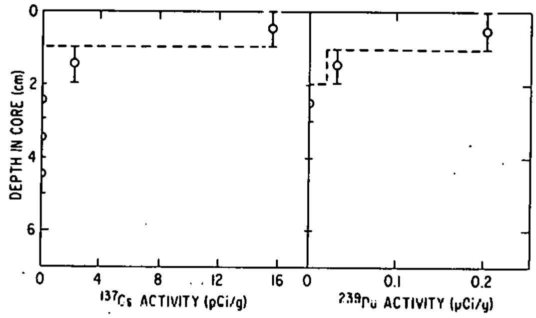


FIG. 8.--Measured and calculated ^{137}Cs and $^{239,240}Pu$ profiles in the sedimentary column at station 72-54. The sedimentation rate is 4.8 mg/cm^2/yr or 0.015 cm/yr at the surface, and there is mixing down to a depth equivalent to 82 years deposition.
ANL Neg. 149-6650B

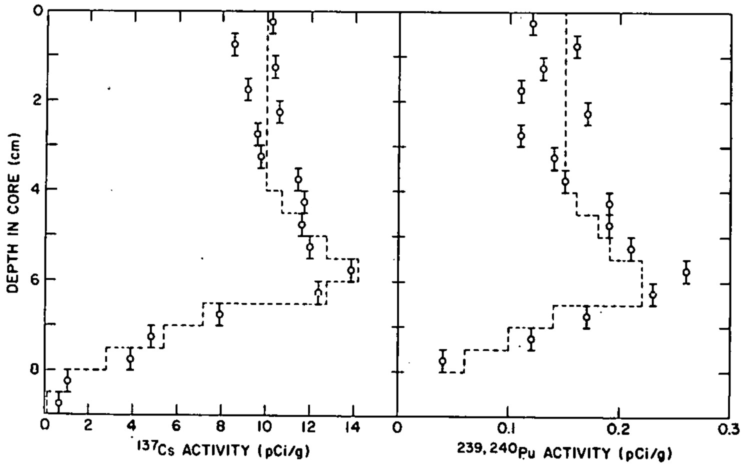


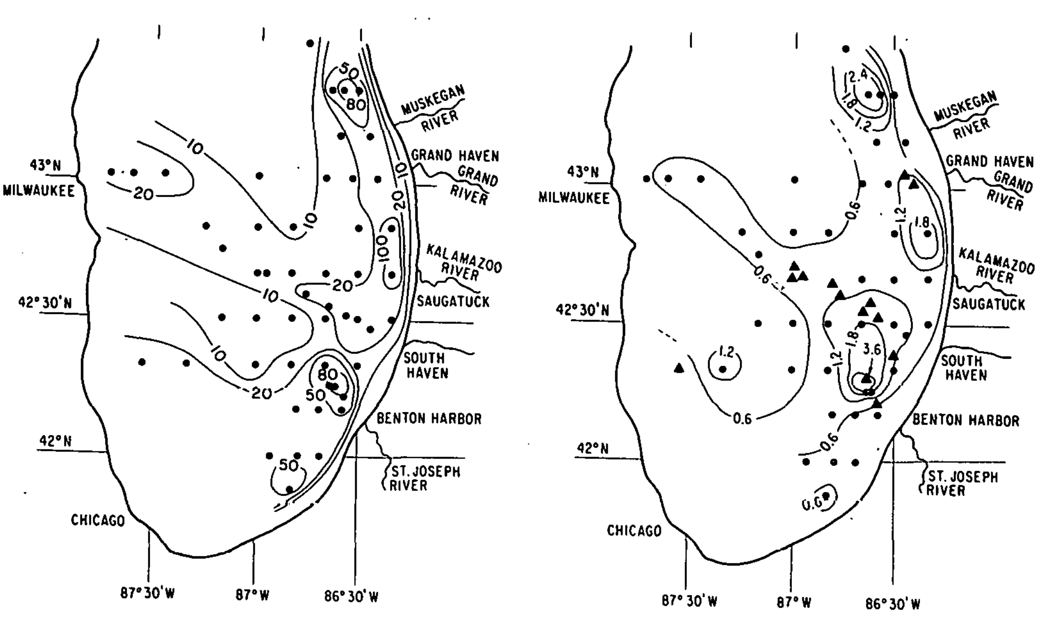
FIG. 9.--Measured and calculated ^{137}Cs and $^{239,240}Pu$ profiles in the sedimentary column at station 74-1. The sedimentation rate is 96.3 mg/cm^2/yr or 0.50 cm/yr at the surface, and there is mixing to a depth equivalent to 12 years deposition.
ANL Neg. 149-75-14

method of sampling resulted in no significant losses of material from the sediment-water interface. If significant losses of material had occurred during sampling, the sedimentation rates calculated from the ^{239,240}Pu and ^{137}Cs profiles would be lower than those calculated from the ^{210}Pb profiles. This arises because the flux of ^{210}Pb to the lake is constant (0.2 pCi/cm^2/yr), and the sedimentation rate is calculated solely from its rate of decay, while the flux is variable for the other two nuclides, and the estimate of the sedimentation rate is almost entirely based upon the position of two horizons, as mentioned earlier.

It has been shown that for recent sedimentation processes, the distribution of the longer-lived fission product radionuclides, such as ^{137}Cs from nuclear bomb fallout, can provide information on the sedimentation rate.(9) Although the chemistry of ^{239}Pu has not been well defined in natural environments, the similarity between ^{137}Cs and plutonium profiles shown in Figs. 3–5 indicates that this nuclide may also be used to calculate sedimentation rates. Calculated sedimentation rates using ^{239,240}Pu for 14 cores taken from Lake Michigan are shown in Table 2.

As a result of the seismic profiling experiments conducted in southern Lake Michigan, it is known that the distribution of sediments is extremely variable.(15) Large areas of the western side of the lake exhibit virtually zero sedimentation, but in other areas close to the eastern shore, where there are several large rivers (Fig. 10), the postglacial sediment layer is up to 10 m thick. The ^{239,240}Pu and ^{137}Cs profiles shown in Figs. 4, 6, and 7 (stations 73-5 and 73-6) are for areas where there is an intermediate rate of sedimentation. The profiles shown in Figs. 3 and 8 (72-54) are for areas of low and in Figs. 5 and 9 (74-1) for areas of high sedimentation rates.

The profile for 72-54 shown in Figs. 3 and 8 is representative of many areas on the western side of the lake, where there is a thin layer of brown floc (1 or 2 cm thick) overlying glacial till or clean sand. Since detectable concentrations of ^{239,240}Pu and ^{137}Cs have been found within the sampling interval that includes the interface between the floc and the till, it is reasonable to suppose that this floc layer is of a transitory nature and that the



(a)

(b)

FIG. 10.--Comparison of the mass sedimentation rate and total deposition of ^{137}Cs or ^{239,240}Pu in southern Lake Michigan. (a) The variation in mass sedimentation rate (mg/cm^2/yr). (b) The variation in the flux normalization factor for ^{137}Cs. Sampling locations where ^{239,240}Pu have been measured are identified by a triangle. ANL Neg. 149-6386A

sediments represented by this core are undergoing episodic periods of deposition and erosion. As a result, there is a large probability that this flocculent material, which contains relatively high concentrations of ^{239,240}Pu or ^{137}Cs, is undergoing resuspension and transport to other locations in the lake.

Assumption of such a remobilization of sedimentary material is required in interpreting the two profiles representative of regions of intermediate sedimentation (73-5 and 73-6) (Figs. 4, 6, and 7). Profiles calculated on the basis of the least-squares fits indicate a much greater drop in the expected concentration in the upper few centimeters (as a result of the large decrease in atmospheric flux since 1963) than is reflected in either the ^{239,240}Pu or ^{137}Cs data.(16) This excess plutonium or cesium can originate from two possible sources: runoff from the watershed or remobilization of surficial sedimentary material. The present estimate of the contribution of cesium (or plutonium) from the watershed due to erosional losses from the soil is still less than the atmospheric inputs.(6) Therefore, it would appear that the excess radioactivity in these two cores is due to remobilization of surface sediments, probably from those areas where little permanent sedimentation occurs. The profile 74-1 (Figs. 5 and 9) is representative of an area in which there is a high sedimentation rate and considerable mixing. At this station, the sedimentation rate is 0.5 cm/yr, and the mixing depth is 4 cm. The effect of mixing is to produce a region of nearly constant activity at the top of the core and to broaden the maximum in concentration corresponding to the 1963 maximum in input. The effect of mixing is also evident in the profile 72-29 (Fig. 3).

The resuspension and transport of sediments will have far-reaching effects on the long-term distribution of long-lived radionuclides, such as plutonium, in Lake Michigan and other lakes. These effects will be particularly important in terms of the fate of radionuclides discharged by nuclear power plants and in determining the validity of present and proposed monitoring schemes. From the data shown in Tables 1 and 2, it is clear that there are significant variations in the distribution of ^{239,240}Pu and ^{137}Cs in the sediments of the lake. The total deposition of plutonium varies between 0.02 and 0.427 pCi/cm^2 and that for cesium between 0.38 and 31.6 pCi/cm^2. The average deposition per unit area has been 0.2 pCi/cm^2 and 8.0 pCi/cm^2 for Pu and Cs, respectively, and therefore, the flux normalization factors vary between 0.05 and 3.1. These results suggest that there are large differences in the fluxes of plutonium and cesium arriving at the sediment-water interface. These differences in concentration at the surface, which the data presented in Tables 1 and 2 show to be very local, could arise from either a large variability in the flux from the atmosphere to the lake surface or differences associated with the hydrodynamic and scavenging processes removing plutonium and cesium from the water column. Since it is well known from the monitoring of world-wide fallout for ^{90}Sr that there are only small variation in flux within any latitude band,(13) the observed differences in deposition probably arise for the latter reason.

Therefore, with techniques developed earlier, the sedimentation rates of ^{239,240}Pu and ^{137}Cs have been calculated from their depth distribution in the cores.(9,10,16) These are computed and given in Table 2 along with the values obtained from ^{210}Pb. The data indicate that the rates based on ^{137}Cs and ^{239}Pu are in surprisingly close agreement. Interestingly, the results are consistent with the ^{210}Pb values, which, however, are slightly higher. The good agreement between ^{137}Cs, ^{239}Pu, and ^{210}Pb specific activities from location to location suggests that the modes of transport of these radionuclides are analogous, i.e., attachment to settling particles.

The radionuclide ^{137}Cs is very strongly adsorbed by the clay component of soils,(17) and consequently, a comparatively greater scavenging in the inshore regions of Lake Michigan, where there may be a large proportion of fine-grained clays in the water column, is not unexpected. The strong association between plutonium and ^{137}Cs is rather unexpected because of their widely differing chemical properties. However, it has been shown that the plutonium is associated primarily with the hydrous oxide fractions of the sediment from Lake Michigan.(18) Therefore, since earlier it has been shown that there is a strong correlation between hydrous oxides (such as Fe_2O_3) and the < 2-μm clay fraction, the observed similarity between the behavior of plutonium and cesium in the lake can readily be understood.(19)

The apparent similarity between the behavior of plutonium and cesium in Lake Michigan is fortunate because it means that measurements of ^{137}Cs, which are far less costly and time consuming to perform than those for ^{239,240}Pu, can provide the necessary information to predict the long-term behavior of plutonium in the sediments. The two maps shown in Fig. 10 compare the deposition of ^{137}Cs and, by inference, ^{239,240}Pu (presented in terms of the flux normalization factor f) and the mass sedimentation rate ω. The triangles denote stations where plutonium has been measured. It will be noted that the distribution of radioactivity parallels that of the sediments. Particularly high depositions occur to the north and west of the major river inputs, and the greater part of the radioactivity is concentrated within the sediments of the eastern half of the lake. The pattern of sedimentation in the southern half of the lake is very interesting in that whereas the bottom topography indicates an almost continuous slope down to the maximum depth of 540 ft, the maximum depth of sediment occurs at a water depth of only 240 ft (80 m).

In addition, no sedimentation occurs at water depths less than 150 ft (50 m), even on the east side of the lake near the rivers, and therefore, very little radioactivity is being deposited in the nearshore zone. From this one concludes that the deposition of radioactivity in the lake is being controlled mainly by lake-wide processes, such as current structure and sources of the sediment. Therefore, because of the very short residence times in the water column, radioactivity which is released to the lake along the western shore will be rapidly transported to areas where there is a significant deposition of sediment; and for Lake Michigan, these areas are the band of sedimentation parallel to the eastern shore. Discharges of radioactivity would also be found predominantly in this band of high sedimentation along the eastern shore.

These results are important since they suggest that any monitoring schemes to determine the long-term fate of effluents from nuclear power reactors must take account of the limnological properties of the receiving body of water. For Lake Michigan, a fixed sampling grid for sediments in the immediate environs of the plant would provide no significant information because of the physical and current structure of the lake.

References

1. Hardy, E. P., P. W. Krey, and H. L. Volcok. Global inventory and distribution of fallout plutonium. Nature 241, 444—445 (1973).
2. Krey, P. W., M. Schongerg, and I. Toonkel. Updating stratospheric inventories of January 1973. USAEC Report HASL-281 (1973), pp. 130—141.
3. Wahlgren, M. A. and D. M. Nelson. Plutonium in Lake Michigan water. Radiological and Environmental Research Division Annual Report, Part III, January—December 1972. ANL-7960, Part III, pp. 7—14.
4. Harley, J. H. Health and Safety Laboratory Procedure Manual. USAEC Report HASL-300 (1972).
5. Talvitie, N. A. Radiochemical determination of plutonium in environmental and biological samples by ion exchange. Anal. Chem. 43, 1827—1830 (1971).
6. Edgington, D. N., J. C. Ritchie, and J. A. Robbins. Comments on the paper "Use of rivers to predict accumulation in sediments of radionuclides discharged from nuclear power plants" by P. Plato. Health Phys., in press.
7. Noskin, V. E. and V. T. Bowen. Concentration and distribution of long-lived fallout radionuclides in open ocean sediments. Proc. IAEA Symp.

on Interaction of Radioactive Contaminants with Constituents of the Marine Environment, Seattle, Wash., 1972. Int. Atomic Energy Agency, 1973, pp. 671–686.

8. Wong, K. M. Radiochemical procedure for the determination of plutonium in seawater sediment and organisms, Anal. Chim. Acta 56, 355 (1971).
9. Robbins, J. A. and D. N. Edgington. Determination of recent sedimentation rates in Lake Michigan using ^{210}Pb and ^{137}Cs. Geochim. Cosmochim. Acta 39, 285–304 (1975).
10. Edgington, D. N. and J. A. Robbins. Determination of recent sedimentation rates in Lake Michigan using ^{210}Pb and ^{137}Cs. Radiological and Environmental Research Division Annual Report, Part III, January–December 1973. ANL-8060, Part III, pp. 39–63.
11. Michels, D. E. and L. D. Miller. Plutonium fallout in the Great Plaines: Relation to latitude and precipitation. Program and Abstracts: Eighteenth Annual Conference on Bioassay, Environmental, and Analytical Chemistry, Argonne National Laboratory, October 10–11, 1972. ANL-8014, pp. 10–11.
12. Wahlgren, M. A. and D. M. Nelson. Residence times for ^{239}Pu and ^{137}Cs in Lake Michigan water. Radiological and Environmental Research Division Annual Report, Part III, January–December 1973. ANL-8060, Part III, pp. 85–89.
13. Health and Safety Laboratory. Environmental Quarterly Appendix, April 1, 1975. USERDA Report HASL-291, pp. A43–45 — A101–102, (1975).
14. Davis R. E. Pollen studies of near surface sediments in Marine Lakes. Quarterly Paleoecology, Ed. E. J. Cushing and W. E. Wright. Yale University Press, New Haven, 1967, pp. 153–177.
15. Lineback, J. A. and D. L. Gross. Depositional patterns, facies, and trace element accumulation in the Waukegan member of the Lake Pleistocene–Lake Michigan formation in southern Lake Michigan. Ill. State Geol. Survey Environ. Geol. Notes ENG-58 (1972).
16. Edgington, D. N. and J. A. Robbins. The behavior of plutonium and other long-lived radionuclides in Lake Michigan: II. Patterns of deposition and sediments. Paper IAEA-SM/198/40. Presented at IAEA Symp. on Radiological Impacts of Releases from Nuclear Facilities into Aquatic Environments, Otaniemi, Finland, 1975, in press.
17. Jenne, E. A. and J. S. Wahlberg. Role of certain stream-sediment components of radio-ion sorption. U.S. Geol. Survey. Prof. Paper 443-F (1968).
18. Alberts, J. J. and M. A. Wahlgren. Unpublished data.
19. Shimp, N. F., J. A. Schleicher, R. R. Ruch, D. B. Heck, and H. V. Leland. Trace element and organic carbon accumulation in the most recent sediments of southern Lake Michigan. Ill. State Geol. Survey Environ. Geol. Notes 41 (1971).

DEVELOPMENTS IN UNDERWATER RADIOTELEMETRY AND PRELIMINARY FISH TRACKING IN THERMAL PLUMES

W. Prepejchal, J. Haumann,* and S. A. Spigarelli

Introduction

Through the use of various techniques we have been able to describe the density-distribution, migratory patterns, and long-term residence behavior of salmonids at thermal discharge sites. However, these studies have provided almost no information on temperature selection or thermoregulatory behavior. During 1973, we initiated investigations of telemetry systems applicable to fish tracking in the vicinity of thermal discharges to Lake Michigan.(1) These studies served to establish the following system requirements: 1) miniature transmitters capable of being attached to or implanted within fish; 2) operating range of 2 to 3 km, at depths of 8 to 10 m for location mode; 3) a useful transmitter life of about 10 days; and 4) multichannel capability for inclusion of environmental and fish physiological sensors.

Design Philosophy

Two general types of information are to be monitored by this system: 1) fish location, and 2) physical and physiological parameters. Location information is derived by triangulation with directional antenna arrays. In this mode, a combination of continuous signal and sensitive detection methods allows the transmitted power level to be quite low. Because of the high rate of physical and physiological data to be transmitted, a greater bandwidth, and thus less sensitive signal processing techniques, are required. To resolve these conflicting requirements between location and data transmission, the transmitter was designed to operate continuously at 3.5 milliwatts for location, and at 14 milliwatts for data transmission: data are transmitted in a time multiplex mode with a low-duty cycle, resulting in low power consumption. Since the overall sensitivity of the receiving system directly

---

*ANL Electronics Division.

affects the power requirements, size, and useful life of transmitters, we attempted to optimize receiving capabilities by using large high-gain antennas and state-of-the-art signal processing techniques.

Receiving Station

The main receiving antenna was located ~ 12 m above lake level and consisted of 2 Yagi antennas (6 elements each) spaced ~ 6 m apart and oriented for vertical polarization. Vertical polarization is a system requirement for completely submerged transmitters.(2,3) The system has a computed gain of 14 db and includes low noise (2.0 db) preamplifiers to facilitate impedance matching and to minimize interference from high-voltage transmission lines. The entire receiving antenna was rotated by remote control.

A stable receiver with controlled bandwidth and BFO (Beat Frequency Oscillator) detection was used for location information, while synchronous detection was used for physical and physiological data. These data were decoded with a period counter.

Transmitters

Prototype transmitters were constructed with readily available commercial components. The radiofrequency stage consists of a modified Pierce oscillator. The data coding circuits are designed to operate with specific sensors (transducers) with resistances that vary in proportion to the parameters of interest. A clock-driven switch sequentially connects each transducer to an astable multivibrator; the output pulse rate is proportional to the resistance of the sensor being sampled. A 3-msec monostable multivibrator couples this pulse rate to the oscillator output stage so that the oscillator voltage increases from a continuous level of 3.5 V to 7.0 V for each data pulse. This increase in voltage provides the higher power level required for data transmission. Data coding circuitry is mainly CMOS (complimentary metal oxide semiconductor) and requires negligible operating power; therefore, virtually all of the battery capacity is utilized in the signal transmission process.

Since the coding circuitry is affected by ambient temperature, it is necessary to substitute a precision resistor in one of the data channels. This output is used to adjust all other data channels for temperature-induced drift. A second reference channel (blank) is included in the time sequential format as a timing mark. A total of ten time segments for data transmission is available from the multiplex switch. The clock frequency is 1 Hz and the total scanning time is 2 sec plus 1 sec per sensor.

Test Results

In the location mode, detectable signals were received at distances of 3 km from a depth of 11 m, and in excess of 6 km from a depth of 2 m. In the data transmission mode, usable data signals were received at distances of 1.5 km from a depth of 10 m, and approximately 6 km from a depth of 1 m. Under these conditions, the receiving antenna allowed directional location of transmitters to within ± 5°. The prototype transmitter package weighed 45 g, displaced 15 ml of water, and had a useful life of about 7 days.

Improvements in transmitter design are now being directed at further miniaturization and extension of operating life. Receiving system modifications are underway to automate totally data collection, processing, and storage.

Preliminary Fish Tracking

Between 23 and 25 October 1974, we field tested the prototype telemetry system by tracking brown and rainbow trout in the Point Beach thermal discharge area. Trout were collected from the discharge flumes, fitted with transmitters, and immediately released back into the flume. Transmitters were attached to a plastic saddle which was positioned anterior to the dorsal fin and held in place by a Petersen disc tag. Two brown trout and one rainbow trout were successfully tracked for continuous periods of up to 10 hr.

One brown trout was fitted with a data transmitter (water temperature, body temperature, and location), the other with a single channel (location) transmitter. Unfortunately, the data transmission failed, and we only were able to monitor the movements of both fish. Both brown trout left the discharge flume shortly after release, meandered around the plume area for a few hours, and eventually swam beyond the range of our receiving equipment (distance or depth). During the time that we tracked these fish, they often moved through large temperature gradients (≤ 10 C) in passing from ambient to plume water.

A rainbow trout was fitted with a data transmitter and tracked for about 10 hr in the vicinity of the plume. In this case usable temperature data were transmitted and recorded showing the water temperature orientation and body temperature change over the entire tracking period (Fig. 1). Upon leaving the discharge flume (18 C), the rainbow trout moved to near ambient temperature (~ 15 C) at 140 min, and continued to make excursions between warm and cool water for the entire period. It is notable that this fish's body temperature never exceeded 15 C after leaving the discharge flume, despite brief periods spent at temperatures exceeding 15 C. Although this limited track shows little or no evidence of behavioral thermoregulation, it does demonstrate the ability of adult salmonids to traverse large temperature gradients with no great effect on internal body temperature. Apparently this ability allows fish to enter warmed areas briefly (e.g., to feed) without experiencing significant heat exposure.

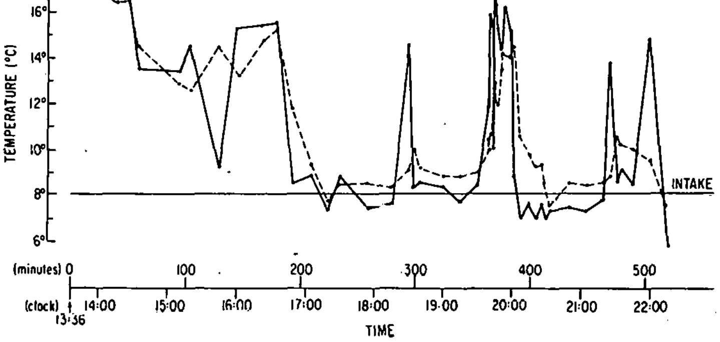


FIG. 1.--Record of selected water temperature and body temperature response of a rainbow trout (#3829, October 24, 1974) (ANL Neg. 149-6763).

References

1. Prepejchal, W. and L. S. Van Loon. Development in radiotelemetry of fish at thermal discharges. Argonne National Laboratory Radiological and Environmental Research Division Annual Report, January—December 1973. ANL-8060, Part III, pp. 152—155.
2. Moore, R. K. Radio communications in the sea. IEEE Spectrum 4, 42—51 (1967).
3. Gabillard, R., P. Degauque, and J. R. Wart. Subsurface electromagnetic telecommunication — a review. IEEE Trans. Commun. Technol. COM-19(6), 1217—1228 (1971).

COMPARISON OF THE MOVEMENT AND RECAPTURE OF SALMONID FISHES TAGGED AT TWO POWER PLANTS

G. P. Romberg and M. M. Thommes

Introduction

During 1974, fish tagging studies were expanded to include both the Point Beach Nuclear Plant and the Waukegan Power Plant (located in northern Illinois). Fish tagging at Waukegan was directed at determining whether there were any seasonal or site specific differences in the residence behavior of salmonids at thermal discharges. Fish tagging was conducted again at Point Beach to obtain additional data on discharge residence times through the use of temperature-sensitive tags. Additional returns of 1973 tags throughout 1974 also provided further indications of the long-term migration behavior of certain species.

Methods

Fish were tagged at Waukegan once a week for all but two of the weeks between May 24 and July 25. The Waukegan Power Plant is a coal-fired steam electric plant (≅ 950 MWe), which utilizes Lake Michigan water for once-through cooling. Physical characteristics of the discharge and thermal plume have been reported previously.(1) Fishermen have access to the beach immediately north of the discharge and to a breakwater which extends into the lake and separates the discharge channel (north side) from the intake channel (south side).

Fish were collected north of the discharge with a shore seine (305 m × 3.7 m × 10 cm stretch mesh) and placed in holding pens until they were tagged and released in the inshore water. An identification string tag was anchored at the base of the dorsal fin, and species, weight, length (TL), and fin clips were recorded.

At Point Beach, fish were tagged primarily during the first two weeks of October. Physical characteristics of this plant's two production units (523 MWe each) and two shoreline discharges have been reported.(2) Fish were collected primarily from the discharge flumes using lift nets. Tagging procedure was the same as at Waukegan except that the majority of fish were tagged with temperature sensitive tags (TLD) and released back into the discharge flumes. Argonne personnel selectively recaptured tagged fish from the discharge flumes at weekly intervals between October 5 and November 11, 1974.

Statistical comparisons between species, locations, and years involved the use of contingency tables and the chi-square statistic. Correlation between distances traveled and elapsed times were tested by the significance of the linear regression slope.

Results and Discussion

A total of 1230 salmonids was tagged during 1974, 408 fish at Waukegan and 822 fish at Point Beach (Table 1). At Waukegan, salmonids are most abundant in the spring and early summer, while at Point Beach they occur in greatest numbers during the fall spawning migrations. The numbers tagged indicate a greater concentration of salmonids at Point Beach (during fall) than at Waukegan (during spring and early summer); however, collection of fish was somewhat easier at Point Beach owing to the concentration of fish in the discharge flumes. Coho salmon (44%) and brown trout (38%) were the predominant species at Waukegan, while brown trout (48%) and rainbow trout (40%) were the most abundant species collected and tagged at Point Beach.

As of February 12, 1975, 14% (170) of the fish tagged in 1974 had been recaptured by fishermen, and an additional 33 fish were collected at Point Beach by Argonne personnel (total = 203 or 16%). A significantly greater ($P < .001$) proportion of Point Beach fish have been recaptured by fishermen than Waukegan fish (7%), primarily because of a low return of the many coho salmon tagged at Waukegan.

Because of the small numbers of fish tagged at Waukegan, there was no significant difference ($P > .10$) between the proportions of rainbow trout (18%), brown trout (12%), and chinook salmon (5%) recaptured; however, coho salmon recaptures (< 1%) were significantly fewer ($P < .001$) than those of other species. At Point Beach, there was a significantly greater ($P < .025$)

TABLE 1. Number and species of fish tagged during 1974 and recaptured as of February 12, 1974.

	Location				
	Waukegan		Point Beach		
Species	Number Tagged	Recaptured by Fishermen	Number Tagged	Recaptured by Fishermen	Recaptured by Argonne
Coho salmon	182 (44%)$^{(a)}$	1 (<1%)$^{(b)}$	15 (2%)	1 (7%)	0
Brown trout	155 (38%)	18 (12%)	398 (48%)	58 (15%)	10 (3%)
Rainbow trout	39 (9%)	7 (18%)	327 (40%)	72 (22%)	23 (7%)
Chinook salmon	19 (5%)	1 (5%)	62 (7%)	11 (18%)	0
Atlantic salmon	7 (2%)	0	1 (<.05%)	0	0
Lake trout	4 (1%)	0	15 (2%)	0	0
Brook trout	2 (<1%)	0	4 (<.05%)	1 (25%)	0
Total	408 (100%)	27 (7%)	822 (100%)	143 (17%)	33 (4%)

(a) Percentage of total fish tagged.
(b) Percentage of each species recaptured.

TABLE 2. Recapture-locations of fishermen tag returns as of February 12, 1974.

			Location		Direction		
Location	Species	Total Known	At Plant	Away	North	South	At Power Plants
WAUKEGAN	Brown trout	17	0	17	15	2	2
	Rainbow trout	7	1	6	5	1	3
	Chinook salmon	1	0	1	1	0	0
	Coho salmon	1	0	1	0	1	0
	Total	26	1 (4%)	25 (96%)	21 (84%)	4 (16%)	5 (19%)
POINT BEACH	Brown trout	56	14	42	23	19	38
	Rainbow trout	71	16	55	34	21	28
	Chinook salmon	10	1	9	6	3	2
	Coho salmon	1	0	1	1	0	0
	Brook trout	1	0	1	0	1	1
	Total	139	31 (22%)	108 (78%)	64 (60%)	44 (40%)	69 (50%)

proportion of rainbow trout (22%) recaptures than of brown trout (15%), but neither was significantly different ($P > .10$) from the proportion of chinook salmon (18%) recaptured. Rainbow trout and brown trout were the only species recaptured by Argonne personnel, and the proportion of rainbow trout was significantly greater ($P < .005$).

The majority of recaptures by fishermen were made away from the location of tagging (Table 2), indicating that most fish did not remain at either tagging location for extended periods. The predominant direction of movement was to the north of each site; however, many Point Beach fish (40%) also went south, probably as a result of the numerous stocking locations, both north and south of that location. Of those fish which had migrated away from the tagging site, 31% (42/134) were caught at other power plants, indicating the likelihood of increased plume residence times due to accumulated exposure at multiple thermal discharges. A significantly greater (P < .01) proportion of Point Beach fish (50%) than of Waukegan fish (19%) was recaptured at power plants. Forty-three percent of all recaptures by fishermen were made at power plants.

After only 135 days, the proportion of recaptures for Point Beach fish tagged in 1974 (21%) was equal to the total return of fish tagged at Point Beach in 1973 (21) (Table 3). Recovery for both years is significantly greater (P < .001) than the total recovery of 1972 tags (12%). The proportion recaptured by Argonne remained fairly constant (3 to 4%) between years, while fishermen recaptures increased each year.

Table 3. Comparison of Recaptures Fish Tagged at Point Beach in 1972, 1973, and 1974.

Year	Total tagged	Recaptures		
		Fishermen	Argonne	Total
1972	722	62 (9%)	22 (3%)	84 (12%)
1973	886	152 (17%)	39 (4%)	191 (21%)
1974	821	143 (17%)	33 (4%)	176 (21%)
Total	2429	357 (15%)	94 (4%)	451 (19%)

Coho Salmon

Coho salmon responded differently to the Point Beach discharge than they did to the Waukegan discharge, as evidenced by the large difference in numbers tagged at each site. At Point Beach only a limited number of coho salmon are caught by fishermen (primarily during the fall),(3) and only a few were collected during tagging operations in 1972 through 1974(4) despite the fact that large numbers are planted both to the north and south and many are caught in offshore sport fisheries.(5) Mature coho salmon appear to avoid the thermal discharge during their fall spawning migrations, while only a few months earlier the slightly younger fish are abundant at the Waukegan discharge. This difference is probably due to fish selecting the warmer discharge water when lake temperatures are low in the spring and early summer, but avoiding the higher temperatures that occur in the fall after the lake has warmed.

Low recovery (< 1%) of the many coho salmon tagged at Waukegan is surprising since large numbers are taken by sport fishermen in both Illinois and Wisconsin. The majority were year class III fish due to spawn in the fall of 1974, and although small in size (mean wt = 1.34 kg), they were feeding heavily on the high concentrations of alewives. The low recovery is unexplained but may be due partially to poor survival after tagging. Many became gilled in the net (10-cm square mesh) because of their small size, and there were often notable scale losses caused by the collection and tagging procedure. Approximately 10% of the coho salmon collected were not tagged owing to their poor condition.

Brown Trout

Brown trout, which are stocked heavily by the state of Wisconsin and to a lesser extent by Illinois, was the second most abundant fish tagged at Waukegan (38%) and the most abundant at Point Beach (48%). Waukegan fish were generally smaller than Point Beach fish. A correlation ($r = .58$; $P < .02$, T-test) between distance traveled and elapsed time for recaptured Waukegan fish indicated a northerly migration rate of 0.4 mile/day (Fig. 1). Recaptured Point Beach (Fig. 2) fish had dispersed in both directions up to 95 miles, and as in previous years, there was no correlation ($r = .15$; $P > .30$, T-test) between distance traveled and elapsed time. Since 25% of the brown trout recaptured by fishermen were taken at Point Beach Power Plant and another 43% at other power plants, it appears that during the fall, thermal discharges influence distribution and harvest of this fall spawning species. A significant increase ($P < .01$) in the proportion recaptured by fishermen in 1974 (15%) compared to 1973 (7%)(4) is correlated with the approval (by the state of Wisconsin) of snagging as a method of catching all species of salmonids both in Lake Michigan and tributaries. A creel census in 1973(3) indicated a lower sport catch of brown trout than rainbow trout in the fall, probably as a result of reduced feeding. High snagging pressure at power plants in 1974 undoubtedly increased the harvest of brown trout, which are abundant at thermal discharges during the fall.

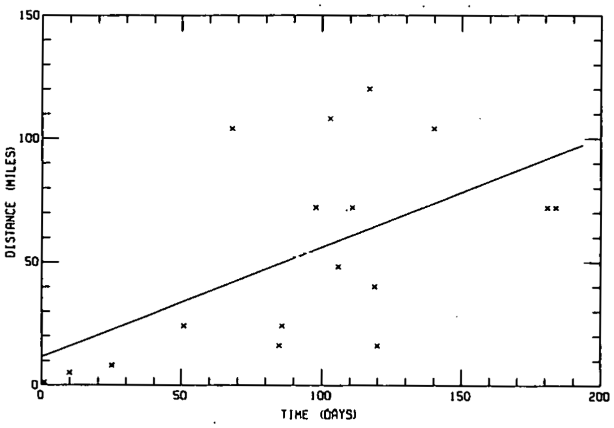


FIG. 1.--Brown trout tagged at Waukegan in 1974 and recaptured by fishermen.

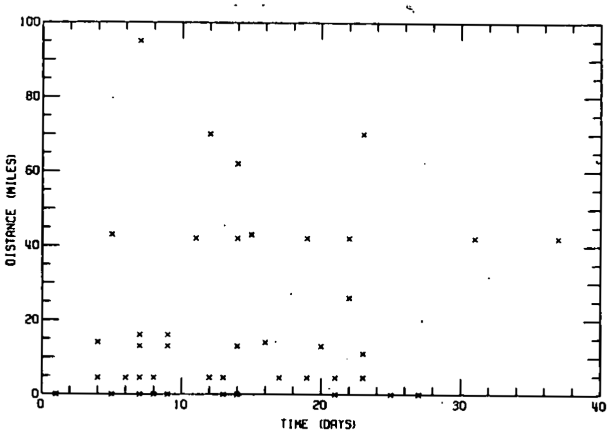


FIG. 2.--Brown trout tagged at Point Beach in 1974 and recaptured by fishermen.

Rainbow Trout

Rainbow trout, which are stocked heavily by the state of Wisconsin, were both more abundant and larger at Point Beach than at Waukegan. For both locations, this species had the highest proportion of recoveries (of those species with more than one recapture). Five of the six recaptured Waukegan fish had migrated north; however, there was no significant correlation ($r = .53$; $P > .21$; T-test) between distance traveled and elapsed time (Fig. 3). Recaptured Point Beach fish had dispersed in both directions up to 384 shoreline miles away; however, there was a correlation ($r = .42$; $P < .001$; T-test) between distance and time, indicating a migration rate of 2.0 mile/day (Fig. 4). Similar dispersion rates were also indicated for fall recaptures during 1972 and 1973

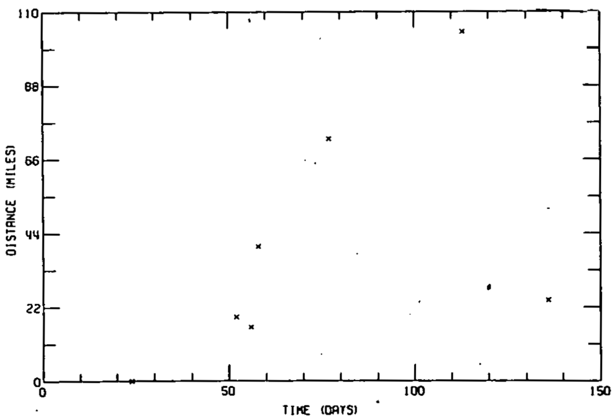


FIG. 3.--Rainbow trout tagged at Waukegan in 1974 and recaptured by fishermen.

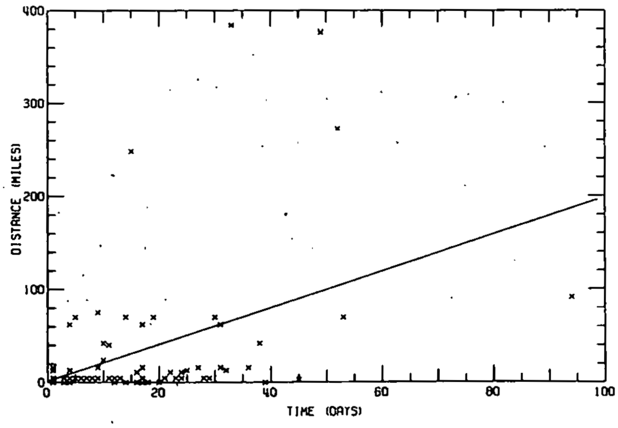


FIG. 4.--Rainbow trout tagged at Point Beach in 1974 and recaptured by fishermen

(1.6 mile/day each year), and it has been theorized that the apparent difference between the dispersion of rainbow trout and brown trout is due to the fact that the rainbow trout population consists of both spring and fall spawners.(4) Although the state of Wisconsin has been stocking about 50% spring and 50% fall spawners the past few years, we do not know what proportion makes up the population at Point Beach during fall. An apparent increase each year in the numbers of rainbow trout observed in the discharge flumes and also recaptured by Argonne may reflect an increase in the proportion of fall spawners. The increased recovery by fishermen of Point Beach fish in 1973 was attributed to a greater survival after tagging and the addition of return information to the tags.(4) A further increase in 1974 may reflect an increased harvest due to snagging, but the effect would be less pronounced than for brown trout, since rainbow trout has previously been the most abundant salmonid caught during the fall by sport fishermen at Point Beach.(3) The influence of thermal discharges on the recapture of rainbow trout is also evidenced by the fact that nearly 40% of those taken by fishermen were at power plants.

Chinook Salmon

Chinook salmon tagged at Waukegan were small (1 – 2 kg), immature fish, while those tagged at Point Beach were large (5 – 14 kg), sexually mature fish. Only one of the Waukegan fish was recaptured, and it had migrated north. Point Beach fish dispersed in both directions up to 70 miles, but as in the previous years, there was no correlation (r = .51; P > .15; T-test) between distance traveled and elapsed time (Fig. 5). Lack of recaptures by Argonne and a reduced number of chinook salmon in the discharges during the weeks after tagging suggests that fish were remaining at Point Beach for shorter periods than they had the previous year. This may only reflect the difference in timing since the

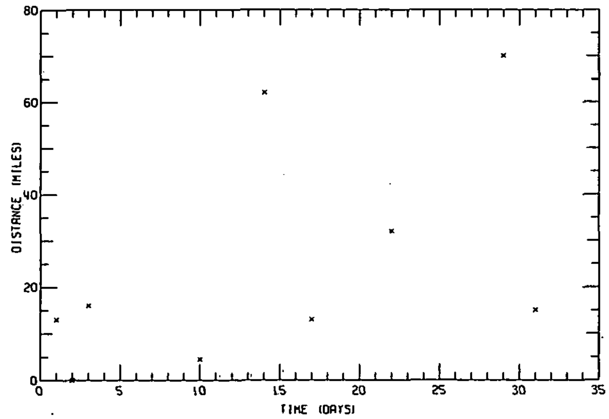


FIG. 5.--Chinook salmon tagged at Point Beach in 1974 and recaptured by fishermen.

majority of fish were tagged a couple of weeks later in 1974 than in 1973. The proportion recaptured by fishermen was about the same as in 1973, and there would be no expected change due to snagging since snagging has been an accepted method of catching chinook salmon in previous years.

Atlantic Salmon, Lake Trout, and Brook Trout

Only a few Atlantic salmon, lake trout, and brook trout were tagged at each location. Similarities in appearance of Atlantic salmon to that of brown trout initially complicated identification and may have resulted in some wrong identifications. These fish had come from Michigan waters since that is the only state stocking Atlantic salmon in Lake Michigan. There are few lake trout in Illinois waters, and at Point Beach only a few have been observed to enter the discharge flume where most of the fish were collected for tagging. Brook trout, which tend to remain inshore, are stocked in fewer numbers than major salmonid species, and the majority are small fish that are not effectively captured by our collection nets.

Annual Migratory Behavior

A difference in annual migratory behavior between brown trout and rainbow trout can be expected due to differences in spawning seasons. An indication of how their migratory behavior differs and how this affects the proximity of fish to Point Beach is apparent in a plot of distance traveled vs. elapsed time for recaptured 1973 tags (Figs. 6 and 7). During the fall of 1973

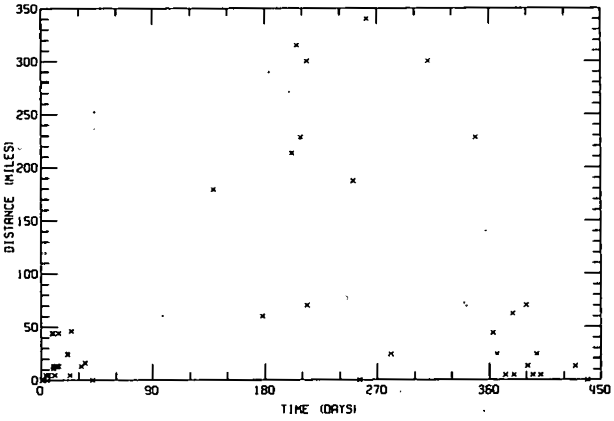


FIG. 6.--Brown trout tagged at Point Beach in 1973 and recaptured by fishermen.

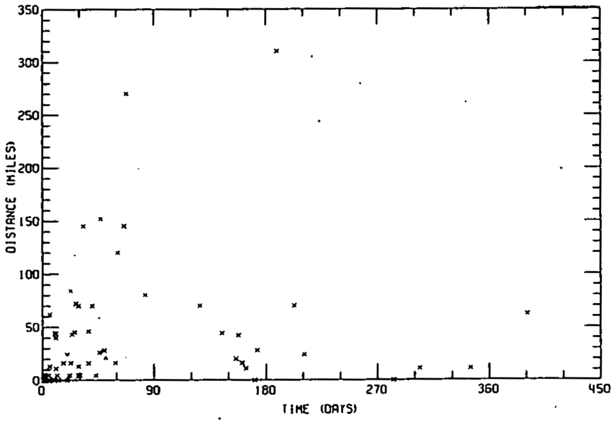


FIG. 7.--Rainbow trout tagged at Point Beach in 1973 and recaptured by fishermen.

(< 90 days) brown trout had dispersed to only short distances (< 46 miles), while numerous rainbow trout had traveled greater than 50 miles and some greater than 145 miles. By spring and summer (127 – 211 days) brown trout had migrated to considerable distances (9 recaptured at > 179 miles); however, rainbow trout appeared to have returned to the general tagging area, with all but one of the numerous recaptures at < 70 miles. Brown trout returned to the general tagging area again in the fall as numerous fish were recaptured one year after tagging (360 – 440 days) at distances from Point Beach similar to those observed the previous fall (< 90 days). The few rainbow trout (4 fish) recaptured during summer and fall were at or near Point Beach; however, there was no large return to the area as observed for brown trout.

Conclusions

1. There were differences in the abundance and time of peak abundance at the two power plant discharges.
2. Because of this difference in timing, certain species (i.e., coho salmon) reacted differently to the two discharges probably as a result of maturity and water temperature.
3. Salmonids did not appear to remain at either discharge for long periods.
4. Although fish migrated away, many were caught at other power plant discharges.
5. The concentration of certain species at thermal discharges undoubtedly enhances their harvest, especially when snagging is employed.
6. Direction of migration is affected by stocking location and water temperature.
7. Differences in the annual migratory behavior of brown trout and rainbow trout affect the proximity of these fish to Point Beach.

References

1. Romberg, G. P., W. Prepejchal, and D. M. Nelson. Thermal plume measurements, Proc. 14th Conf. Great Lakes Res., 1971, 625–639.
2. Frigo, A. A. and D. E. Frye. Physical measurements of thermal discharges

into Lake Michigan: 1971. ANL/ES-16 (1972).

3. Spigarelli, S. A. and M. M. Thommes. Sport fishing survey at the Point Beach Nuclear Plant during 1973. Argonne National Laboratory Radiological and Environmental Research Division Annual Report, Jan.—Dec. 1973, ANL-8060, Part III, pp. 143—149.
4. Romberg, G. P., S. A. Spigarelli, W. Prepejchal, and M. M. Thommes. Migratory behavior of fish tagged at a nuclear power plant discharge into Lake Michigan. Proc. 17th Conf. Great Lakes Research, in press.
5. Daly, R. A., J. Moore, and P. Schultz. Progress Report of Fish Management on Lake Michigan, Annual Reports for 1973 and 1974, Wisconsin Department of Natural Resources, Madison, Wisconsin, 1974 and 1975.

ORIGIN OF FIN-CLIPPED SALMONIDS COLLECTED AT TWO THERMAL DISCHARGES ON LAKE MICHIGAN

G. P. Romberg, M. M. Thommes, and S. A. Spigarelli

Introduction

Studies of fish at several thermal discharges into Lake Michigan show considerable seasonal variation in abundance and species composition, primarily due to migrations of anadromous species (e.g., alewife, smelt, and salmonids).(1–3) The impact of thermal discharges on migratory fish is dependent on spatial distribution (migratory behavior) and temperature exposure (temperature selection behavior). Since salmonid species contribute greatly to this seasonal variation and the majority are artificially propagated and stocked in Lake Michigan, the location and date of stocks and subsequent migration behavior are important to an analysis of distribution patterns relative to discharge sites. To identify certain fish stocks, federal and state agencies employ the fin-clip marking procedure and coordinate the use of various combinations of clips through the Great Lakes Fishery Commission. Unfortunately, only a small percentage of the fish stocked are marked, and fin-clip records are not always complete. However, marked fish collected at discharge sites do provide insight into the migration patterns.

Methods

Fin clips observed on fish collected during tagging studies at the Point Beach (1973–1974) and Waukegan (1974) thermal discharges were recorded and the data were tabulated by species. Additional fin-clip data obtained from a creel census at Point Beach during 1973 are also included and account for the large difference between numbers of fish sampled during 1973 and 1974.(4) Using fin clip and fish size, we attempted to identify probable stocking locations and dates from agency records. For those cases where the fish was subsequently recaptured, the direction of movement provides an additional clue to migration patterns.

Results

Lake Trout

All but a few lake trout bore identifiable fin clips, since stocking agencies mark all lake trout planted in Lake Michigan (Table 1). Although eight different clips were observed at Point Beach (representing stocks from 1965 through 1971) the most frequently observed clips (LV, AdLV, LP, and RP) were stocked at Kewaunee, Algoma, and Manitowoc, Wisconsin, less than 30 miles (48 km) away. In many cases, Michigan also stocked fish with the same marks, but in different years, and although size is an indication of age, a scale analysis would be necessary to distinguish among age groups. Only three clips were not stocked by Wisconsin and two of these were stocked by Michigan. The other clip is not reported as stocked in Lake Michigan, and probably represents an incorrect fin clip since approximately one percent of the lake trout sampled by the Michigan Department of Natural Resources have an incorrect fin clip and are labeled origin unknown.(5) At Waukegan all four lake trout collected had fin clips different from each other and from any of those observed at Point Beach. Three of the four marks had been stocked in southern Lake Michigan by either Illinois, Indiana, or Michigan.

Five of the fin-clipped lake trout tagged at Point Beach have been recaptured (as of May 1, 1975). All but one of these fish were recaptured at or near a stocking location. The data suggest that most lake trout captured at these two power plant discharges were stocked in that general area of the lake and often returned to the stocking location prior to spawning.

Rainbow Trout

Less than 3% of all rainbow trout examined at Point Beach were fin-clipped (28/1442 in 1973, 20/327 in 1974). Of the 12 different clips, only 6 have been tentatively identified; the others may represent incorrect clips, misidentifications (possible correct clip listed), or unrecorded stocks (Table 2). The large size range of LP- and RP-clipped fish also prompted us to divide them into subgroups based on size. While the majority of identified clips can be accounted for by Wisconsin stockings, the occurrence of several clips stocked in Indiana and Michigan indicates that some rainbow trout migrate

TABLE 1. Probable Stocking Locations and Dates for Fin-Clipped Lake Trout Collected at Point Beach and Waukegan Power Plants

					1973		1974			
Clip	Stocking locations	Year	Number	Collection and tag locations	No.	Wt. range, kg	No.	Wt. range, kg	Recapture locations	No.
LV	N. Lake Michigan (Michigan)	1965	867,000	Point Beach	47	2.7 - 5.5	1	(4.9)	Kewaunee, Wisconsin	1
	Kewaunee, Algoma (Wisconsin)	1968	439,000						Pilot Is., Wisconsin	1
	Indiana	1971	105,000						Algoma, Wisconsin	1
Ad LV	Kewaunee, Sand Bay, Sturgeon Bay (Wisconsin)	1967	844,500	Point Beach	31	3.4 - 5.5	3	3.0 - 5.2	Milwaukee	1
RV	Grand Traverse Bay (Michigan)	1965	100,500							
	N.E. Lake Michigan (Michigan) (3 sites)	1968	257,700	Point Beach	0		1	4.8		
Ad RV	Illinois-Indiana	1970	185,000	Waukegan	—		1	1.9		
	Michigan (10 sites)	1970	875,000							
	Wisconsin (7 sites)	1970	900,000							
LP LV	Lake Superior (?)	1967	258,900	Point Beach	0		1	3.3		
RP LV	N.E. Lake Michigan (Michigan)	1969	252,900	Point Beach	0		1	3.6		
BV	Milwaukee Reef (Wisconsin)	1966	201,500	Waukegan	—		1	2.7		
LP	Sturgeon Bay, Rawley's Point, Kewaunee (Wisconsin)	1966	369,100	Point Beach	9	2.7 - 6.2	0		Kewaunee	1
	Michigan sites	1969	433,700							
RP	Michigan (9 sites)	1966	790,900	Point Beach	7	2.3 - 4.3	5	3.4 - 3.7		
	Kewaunee, Manitowoc (Wisc.)	1969	393,800							
Ad RP	S.E. Lake Michigan (Michigan)	1967	470,600	Waukegan	—		1	2.4		
D	N.E. Michigan, Reef and Island areas	1965	102,000	Point Beach	2	4.5 - 4.6	0			
	Ferry-Ludington-Manistee; Sheboygan - Pt. Wash	1967	567,600	Waukegan	—					
Ad	S.E., S.W. Lake Michigan	1968	445,000	Waukegan	—		1	2.9		
unknown					7	2.7 - 6.0	3	4.5 - 5.3		
		1965-1970			103	2.3 - 6.2	19	1.9 - 5.3		5

TABLE 2. Probable Stocking Locations and Dates for Fin-Clipped Rainbow Trout Collected at Point Beach and Waukegan Power Plants

					1973[a]		1974[b]			
Clip	Stocking locations	Year	Number	Collection and tag locations	No.	Wt. range, kg	No.	Wt. range, kg	Recapture locations	No.
LP	L. Calumet R., Indiana	1969	80,000	Point Beach	4	3.1 - 4.4	2	2.5 - 4.3		
	Milwaukee, Wisconsin	1972	3,000	Point Beach	4	0.9 - 2.0	1	1.0		
				Waukegan	-		1	1.5		
	Lake Huron (10 sites)	1972	75,000	Point Beach	2	0.3 - 0.4	0	---		
	(Ad LP) Sheboygan, Wisconsin	1972	10,000							
RP	L. Calumet R., Indiana	1970	70,000	Point Beach	4	2.4 - 4.2	5	---	Menominee, Michigan	1
	Milwaukee, Wisconsin	1972	3,000		3	0.4 - 0.8	0	2.7 - 4.0	Manitowoc, Wisconsin	1
				Waukegan	-		2	3.3 - 4.0		
BP	Lake Superior ?	1972		Point Beach			3	2.5 - 4.3	Point Beach	2
RPD	?			Point Beach	1	1.5				
LP Anal	(Ad LP) Sheboygan, Wisconsin	1972	10,000	Point Beach	1	1.9				
RP LV	?			Point Beach	1					
LV D	(LV) Manitowoc, Wisconsin	1973	15,000	Point Beach	1	0.4				
RV	Manitowoc, Wisconsin	1973	15,000	Point Beach	1	0.6				
Ad RV	Sheboygan, Wisconsin	1972	20,000	Point Beach	1	1.5	1	2.4		
D	Wisconsin	1969	?	Point Beach	4	0.3 - 1.2	6	0.7 - 3.9		
	Manitowoc, Wisconsin	1973	9,500	Waukegan	-		1	0.9		
Ad	Manistee R. Michigan	1968	12,000	Point Beach			2	4.1 - 4.3	Manitowoc, Wisconsin	1
	L. Calumet R. Indiana	1971	120,000							
Anal	?			Point Beach	1	2.8				
		1968 1973			28	0.3 - 4.2	24	0.7 - 4.3		5

(a) 1442 fish examined at Point Beach

(b) 327 fish examined at Point Beach and 39 fish examined at Waukegan.

considerable distances from their origin. The four fin-clipped rainbow trout collected at Waukegan in 1974 (10% of those examined) bore marks no different from those observed at Point Beach and could have originated from Wisconsin or, in one case, Indiana.

Five fin-clipped rainbow trout tagged at Point Beach were subsequently recaptured (as of May 1, 1975) by fishermen in northwestern Lake Michigan. Only three are tentatively identified as to stocking location, and two of these had migrated in that direction.

Brown Trout

Approximately 5% (61/1202) of all brown trout examined at Point Beach were fin-clipped. Seven different marks were observed, with LP and RP clips being divided into subgroups based on size (Table 3). The majority of fish (49/62) had some form of pectoral fin clip, and even with subgrouping there is difficulty in identification due to size, limited numbers stocked, and lack of stocking records. While many clips can be accounted for by Wisconsin stocks, the data indicate that several brown trout had migrated long distances from Illinois and Indiana. At Waukegan, 8% (13/155) of the brown trout collected were fin-clipped. The four marks observed were also the most abundant marks on brown trout at Point Beach, and the majority probably originated from Wisconsin.

Nine of the fin-clipped brown trout tagged at Point Beach and three of those tagged at Waukegan were subsequently recaptured (as of May 1, 1975). While the identified stocking locations for Point Beach fish were all to the south, only one fish (caught at stocking site) moved in that direction, which further suggests unrecorded stockings to the north. All Waukegan fish moved north although none were recaptured at any identified stocking location.

Coho Salmon

Relatively few coho salmon were collected at Point Beach, and none bore fin clips. Three of the 182 coho collected at Waukegan in 1974 were fin-clipped (Table 4). The majority of fish stocked in 1973 with these fin clips were released in Michigan. None of the marked coho stocked in Illinois in

TABLE 3. Probable Stocking Locations and Dates for Fin-Clipped Brown Trout Collected at Point Beach and Waukegan Power Plants

					1973[a]		1974[b]			
Clip	Stocking locations	Year	Number	Collection and tag locations	No.	Wt. range, kg	No.	Wt. range, kg	Recapture locations	No.
LP	Diversey Harbor, Illinois	1969	?	Point Beach	6	2.1 - 3.7	2	3.4 - 4.5	Kewaunee, Wisconsin	1
	Milwaukee, Wisconsin	1972	300		3	0.4 - 1.1	8	0.7 - 2.7	Kewaunee NPP	1
									Algoma, Wisconsin	1
	(Ad LP) Two Rivers, Wisconsin	1973	5,000						Point Beach	1
				Waukegan	-		5	1.5 - 3.2	Sheboygan, Wisconsin	1
									Manitowoc, Wisconsin	1
RP	Waukegan Harbor, Illinois	1969	?	Point Beach	3	1.3 - 3.5	7	2.3 - 3.2	Kewaunee	1
	Milwaukee, Wisconsin	1972	300		4	0.3 - 0.6	1	1.8	Point Beach	1
	Indiana (3 sites)	1973	57,000	Waukegan	-		3	1.3 - 2.2		
BP	?			Point Beach	9	0.5 - 0.9	6	1.5 - 3.4	Manistee, Michigan	1
				Waukegan	-		5	0.9 - 2.8	Sheboygan, Wisconsin	1
RV	Diversey Harbor, Illinois	1970	?	Point Beach	2	0.9 - 1.5				
	Great Lakes Harbor, Illinois	1973	?							
RVD	?			Point Beach	1	1.6				
D	Two Rivers, Wisconsin	1973	10,000	Point Beach	1	0.7	1	1.6	Kewaunee NPP	1
Ad	Sheboygan, Kewaunee, Wisc.	1972	40,000	Point Beach	1	3.5	6	2.3 - 4.8	Sheboygan PP	1
				Waukegan	-		1	1.9		
		1969-1973			30	0.3 - 3.7	45	0.7 - 4.8		12

(a) 804 fish examined at Point Beach

(b) 399 fish examined at Point Beach and 155 fish examined at Waukegan

TABLE 4. Fin-Clipped Coho Salmon Collected at Waukegan during 1974

Clip	Stocking location	Year	Number	Collection and tag location	1974[a] No.	1974[a] Wt. range, kg
RP	L. Manistee R., Michigan	1973	56,900	Waukegan	1	1.2
	Kewaunee, Algoma, Wisconsin	1973	4,900			
LP	L. Manistee R., Michigan	1973	52,800	Waukegan	1	1.0
	Kewaunee, Algoma, Wisconsin	1973	4,900			
LV	Thompson Cr., Michigan	1973	67,400	Waukegan	1	2.3
		1973			3	1.0 - 2.3

(a) 182 fish examined at Waukegan.

1973 were collected by us.

Acknowledgements

We wish to thank the numerous personnel from state and federal stocking agencies who provided fin-clip records and also those fisherman who returned tags from fin-clipped fish.

References

1. Industrial Bio-Test Lab., Ind. Operational Environmental Monitoring in Lake Michigan near Zion Station, July 1973—June 1974. Annual Report to Commonwealth Edison Co., Chicago, Ill., Vol. III, October 15, 1974.
2. Jude, D. J., T. J. Tesor, J. A. Dorr, III, T. J. Miller, P. J. Rago, and D. J. Stewart. Inshore Lake Michigan Populations near the Donald C. Cook Nuclear Power Plant, 1973. The University of Michigan, Great Lakes Research Division, Ann Arbor, Michigan, Special Report No. 52, 1975.
3. Romberg, G. P., S. A. Spigarelli, W. Prepejchal, and M. M. Thommes. Fish behavior at a thermal discharge into Lake Michigan. Thermal Ecology, Ed. J. W. Gibbons and R. R. Sharitz. U.S. Atomic Energy Commission Symp. Ser. CONF-730505 (1973), pp. 296—312.
4. Romberg, G. P. and S. A. Spigarelli. Seasonal variation in species composition and abundance of fish at the Point Beach Nuclear Plant between March and November 1973. Argonne National Laboratory Radiological and Environmental Research Division Annual Report, Jan.—Dec. 1973. ANL-8060, Part III, pp. 104—112.
5. Scott, John A. State of Michigan Department of Natural Resources. Personal communication.

EFFECTS OF SEASON, LOCATION, AND DISCHARGE TYPE ON FISH DISTRIBUTION AND DENSITY IN THERMAL PLUMES

W. Prepejchal, G. P. Romberg, and S. A. Spigarelli

Introduction

Fish density and distribution in Lake Michigan thermal plumes are being investigated by a technique developed at ANL which combines standard plume mapping and echo-location (sonar) procedures.(1) During 1972 and 1973, this technique was used to study the effects of reactor shutdown and season on fish distribution behavior at the Point Beach Nuclear Plant.(2)

Results of fish marking and recapture experiments at the Point Beach and Waukegan power plants(3,4) have shown that Lake Michigan salmonids exhibit strong seasonal migrations; the major forage fishes (alewife and smelt) migrate inshore (spring) and offshore (summer-fall). During migrations, these fishes encounter various types of thermal discharges in different areas of Lake Michigan; this allows us to study the effects of time, location, and discharge type on the "attraction" of fishes.

Study Sites

The Point Beach Nuclear Plant (Two Rivers, Wisconsin) consists of two pressurized water reactors of approximately 500 MWe capacity each. Cooling water is drawn directly from Lake Michigan through an offshore intake at a maximum flow rate of 690,000 gpm (44 m^3/sec) and is returned to the lake through two surface discharge flumes extending 150 ft (46 m) offshore. The maximum temperature rise at (Δt) in the cooling water is 10.5° C, except during periods of recirculation in winter. Discharge velocities at the ends of the flumes range between 1.1 fps (0.33 m/sec) and 3.1 fps (0.93 m/sec).(5)

The Waukegan Power Plant (Waukegan, Illinois) is a fossil-fueled steam-generating station consisting of four units with a combined total generating capacity of 994 MWe. Cooling water intake and discharge are both shoreline channels separated by a breakwater. The volume of flow is approximately 720,000 gpm (45 m^3/sec) at full plant operation, with a normal temperature rise of approximately 7° C and a discharge velocity of about 1.0 m/sec.(6)

The Zion station consists of two pressurized water reactors, each capable of a net generating capacity of 1100 MWe. Cooling water is obtained through a submerged intake crib approximately 790 m offshore and is discharged to the lake via two submerged, high-velocity (diffuser) discharges approximately 231 m offshore. At maximum power, a flow rate of 1,530,000 gpm (48 m^3/sec) is required for each unit, resulting in a discharge velocity of 290 cm/sec at the diffuser ports and a temperature rise of 11.1° C.(5) Both units were operating during two of the five surveys, and on no occasion did power levels exceed 77% of capacity.

Methods

Details of the combined mapping technique and data analysis are reported by Spigarelli et al.(1) In order to determine temporal changes in fish behavior and to compare sites over time, five replicate mapping studies were conducted at the three power plants between April and September. In each study mapping runs were made in the plume area and reference areas to compare fish density and distribution in heated vs. unheated regions. Similar depth strata were sampled in both reference and plume areas (2.5 to 11 m) by following depth contours. Differences in the volumes sampled at various depths have been normalized by expressing results as number of fish/10,000 m^3 of water sampled.

Results and Discussion

A summary of the results of the 11 fish distribution surveys conducted during 1974 is presented in Table 1. For each study (date) the densities of fish in the plume area(s) and reference area(s) are compared in terms of 1) total area density, 2) distribution relative to bottom depth (contour), 3) depth in the water column (stratum), and 4) water temperature. Near-field plume attraction is reflected by densities within 400 meters (radius) of the discharges at each site.

TABLE 1. Summary of fish distribution and density at Point Beach, Zion and Waukegan power plants during 1973 (density = fish/10,000 m^3).

	Total Area Density	400-m Radius Density	Zones of Maximum Density					
			Depth Contour		Depth Stratum		Temperature	
			Meters	Density	Meters	Density	°C	Density
17 April								
Waukegan	32	29	5-8	40	5-8	48	--	--
Zion	30	21	5-8	42	5-8	40	9-10	104
Reference 1	25	--	3-5	41	> 8	50	5-7	25
25 April								
Point Beach	24	84	2-5	164	0.5-1	134	8-9	201
Reference 1	28	--	2-5	558	2-3	54	7-8	558
23 May								
Waukegan	156	217	3	539	3-5	251	9-10	188
Zion	279	56	5-8	480	5-8	331	9-10	966
Reference 1	71	--	3	301	1-3	90	8-9	813
21 May								
Point Beach	318	494	2-5	1172	3-5	518	10-11	1106
Reference 1	522	--	2-5	7462	0.5-1	1991	9-10	2335
18 June								
Point Beach	392	4981	3-5	1318	3-5	787	11-12	1966
Reference 1	159	--	2.5	2573	2-3	398	8-9	2573
20 June								
Waukegan	107	595	2.5	737	2-3	385	14-15	414
Zion	308	724	2.5	877	2-3	546	13-14	2782
Reference 1	272	--	2.5	3585	2-3	1003	9-10	510
Reference 2	75	--	3-5	258	2-3	191	11-12	151
30 July								
Point Beach	15	189	2-5	293	0.5-1	145	14-15	497
Reference 1	26	--	2-5	572	1-2	162	11	118
1 August								
Waukegan	37	82	3-5	172	2-3	01	30 31	106
Zion	68	256	2.5	466	2-3	166	20-21	577
Reference 1	41	--	2.5	317	2-3	130	16-18	54
4 September								
Point Beach	17	70	2-5	122	0.5-1	101	16-17	86
Reference 1	25	--	2-5	335	1-2	77	13-14	30
10 September								
Waukegan	24	31	3.0	96	1-2	89	18-19	86
Zion	29	48	2.5	234	0.5-1	138	16-17	113
Reference 1	36	--	3-5	106	> 8	106	11-12	93
10 October								
Point Beach	22	72	2.5	194	0.5-1	147	10-11	62
Reference 1	231	--	2.5	3128	1-2	762	9-10	4528

In general, overall fish density followed a pattern similar to that observed in 1973 at the Point Beach Plant,(2) i.e., low densities in all areas in April, maximum densities in May and June, and reduced densities during July through October. Peak densities in May and June are attributed to massive schools of alewives which migrate inshore to spawn during this period. During the spring (rainbow trout) and fall (other trout and salmon) spawning periods there was no evidence of increased densities of salmonids in plumes. However, during spawning periods salmonid fishes tended to congregate in near-field plume areas, as evidenced by relatively high net catches within 400 m of the discharges.

The comparison of sites in these 5 studies (months) shows that Point Beach (northern site) had higher total plume densities than Zion or Waukegan (southern sites) in May and June, the period when alewives predominated; from July through September, Zion and Waukegan had higher total plume densities than Point Beach. The same trend was observed in reference areas. In April, all three sites had similar densities. On four out of five occasions (May through September) total plune densities at Zion exceeded those at Waukegan.

The phenomenon of fish concentration in thermal plume areas was observed in May at both Waukegan and Zion and in June at Point Beach; similar aggregations (high densities) of fish were observed in June 1973 at Point Beach.(2) Fish sampling during these periods by ANL and other research groups showed that alewife was the most abundant species in the area and accounted for the increased densities in plumes. During April, July, August, September, and October, there was no indication of increased fish density in total plume areas relative to reference areas. However, as indicated above, there was evidence of localized high concentrations within a 400-m radius of the discharges; similar results were obtained in every survey conducted at Point Beach in 1973. These observations indicate that Lake Michigan fishes tend to orient themselves to the near-field plume, effectively decreasing densities in far-field regions.

Although there were no striking trends in fish distribution relative to bottom depth (contour) and depth stratum, there were subtle differences between dates and locations, reflecting differential responses with time, species, and discharge type. On the other hand, temperature orientation by fish was significantly different between plume and reference areas. In every case, the temperature at which maximum density occurred was at least 1° C higher (often 8 or 9° C higher) in the plume area than in the reference area, demonstrating that plume fish were oriented to elevated (higher than ambient) water temperatures during each survey. Reference area fish often were most concentrated in the warmest ambient water, while plume fish generally were most concentrated at intermediate plume temperatures (near-field plume area). Low densities at maximum plume temperatures may be partially due to the limited volumes of water at maximum temperature or may imply an avoidance of maximum discharge temperature or current. The temperature at which maximum fish density occurred at Waukegan (channel discharge) was occasionally higher (never lower) than that at Zion, suggesting an avoidance reaction to turbulence created by diffuser discharges at Zion.

References

1. Spigarelli, S. A., G. P. Romberg, and R. E. Thorne. A technique for simultaneous echo-location of fish and thermal plume mapping. Trans. Am. Fish. Soc. <u>102</u> (2), 462–466 (1973).
2. Spigarelli, S. A. and G. P. Romberg. Studies of fish distribution in thermal plumes and fish responses to reactor shutdown. Radiological and Environmental Research Division Annual Report, Part III, January—December 1973. ANL-8060, Part III, pp. 113–119.
3. Romberg, G. P., S. A. Spigarelli, W. Prepejchal, and M. M. Thommes. Migratory behavior of fish tagged at a nuclear power plant discharge into Lake Michigan. Proc. 17th Conf. Great Lakes Res., Int. Assoc. Great Lakes Res., Ann Arbor, Mich., 1975, pp. 68–77.
4. Romberg, G. P. and M. M. Thommes. Comparison of the movement and recapture of salmonid fishes tagged at two power plants. This report.
5. Frigo, A. R. and D. E. Frye. Physical measurements of thermal discharges into Lake Michigan: 1971. Argonne National Laboratory Report ANL/ES-16 (1972).
6. Industrial Bio-Test. Environmental Monitoring in Lake Michigan near Zion and Waukegan Generating Stations, January 1972—December 1972. Report to Commonwealth Edison Company, Chicago, Ill., 1974.

CHARACTERISTICS OF TEMPERATURE-SENSITIVE FISH TAGS USED IN 1974

G. P. Romberg and W. Prepejchal

Introduction

Predosed thermoluminescent dosimeters (TLD's) used as temperature-sensitive fish tags provide a unique method for determining maximum discharge residence time and an indication of integrated average temperature exposure. TLD fish tags were successfully used in 1973; however, individual variability of the TLD's and a nonlinear relationship between temperature and fade response limited their application.(1) In an effort to eliminate these problems, changes were made in the construction and pretreatment of tags used in the 1974 fish tagging study. The relationship between fade response of these tags and temperature was more clearly defined through the use of additional laboratory controls. Limitations for calculating an integrated average temperature value from the observed fade in a fluctuating temperature environment were determined.

Methods

The TLD's used in 1974 tags were special order Teflon rods (8 mm × 1 mm O.D.) which contained 8% $CaSO_4$:Mn by weight. These rods were shorter than 1973 TLD's to reduce rod curvature and contained double the $CaSO_4$:Mn to increase total light response. The TLD's were annealed for one hour at 525° C and for 24 hours at 80° C prior to loading into a dosimeter packet. A packet consisted of 12 rods sealed in a section of thin-walled stainless steel tubing (30 mm × 3 mm O.D.). Metal tubing was used for ease of packaging, to provide a positive light seal, and to increase thermal conductivity. Ends were coated with black rubber cement and crimped to provide a seal against water and light. Packets were joined to standard fish tags by a section of brightly colored plastic tubing (30 mm × 3 mm I.D.). Colored tubing aided in tag recognition and also provided an air bubble which helped compensate for weight of the TLD packet.

Tags were placed in an aluminum holder and exposed to 250 R in 69 minutes (compared to 100 R in 1973). Following irradiation, fish tags were prefaded at 26° C for 267 hours. Laboratory control tags were prefaded for a shorter time because a temperature bath malfunction resulted in a short period of 30° C temperature. Samples of these tags were read to determine when the amount of prefade was equal to that of fish tags. Prior to use tags were stored at dry ice temperature (-78° C).

Variability in the TLD's was determined by exposing a subgroup of rods to 89 R over 22 hours and determining their light response and weight. Decay characteristics and radiation sensitivity of the TLD's were tested by Dr. Moran at the University of Wisconsin Medical School in Madison, Wisconsin.

Fade response at constant temperature was determined by placing eleven tags in each of five laboratory temperature baths. The baths were regulated at 10, 14, 18, 22, and 26° C and remained relatively stable (± 0.1 – 0.2° C) about the reported values. Tags were removed at 3- and 4-day intervals (Monday and Thursday) over a period of 39 days.

The TLD reader used was a Harshaw Model 2000A and B. A background and standard source reading were taken at the beginning, middle (after six rods), and end of reading each packet. Background was subtracted from all values, and the sample light values were normalized according to the average of all standard source readings. Sample values were also normalized by weight of the rod prior to calculating a mean of all rods in the packet.

Results

The variation between rods was found to be far greater than the specified 4% maximum range for weight and light response. In a sample of 35 rods, exposed to 89 R, weight and light values had a range of 25 to 35% (12.37 to 16.66 mg) and 31 to 44% (31.2 to 45.2 light units), respectively. Normalizing light values by weight reduced the range to 19 to 23% (0.234 to 0.288 L/mg) and resulted in a mean value with a standard error of 0.8%. Given this variability and the limited available space per tag, it was calculated that 12 rods per packet was the best compromise and would yield a mean with a standard error of 3.0% at the .95 confidence level. Changes in the TLD rods, the packets, and the readout procedure, which were intended to reduce the standard deviation, were outweighed by the great variability between individual rods. Since no better TLD rods cold be obtained prior to the required fish tagging date. the 12-rod TLD packets were used despite the excessive 4.6% standard error.

Fade response observed for laboratory control tags at constant temperature did not follow the first order kinetics relationship $S = S_0 e^{-m_t t}$ typical for $CaSO_4:Mn$(2) but closely approximated a second order relationship of the form $1/S = S_0 + m_t t$,(3) where S_0 = light signal at t = 0; S = light signal at time t; m_t = rate constant for change in S at a given temperature T.

Rate constants (m_t) for each of the five bath temperatures were calculated by a linear regression of the data shown in Fig. 1. The natural log of m_t ($\ln m_t$) appeared to have a linear relationship with the reciprocal of absolute temperature ($1/T_a$) such that a linear regression (Fig. 2) yielded the following expression:

$$10^3/T_a = -.089719 \ln(m_t) + 2.3808 . \tag{1}$$

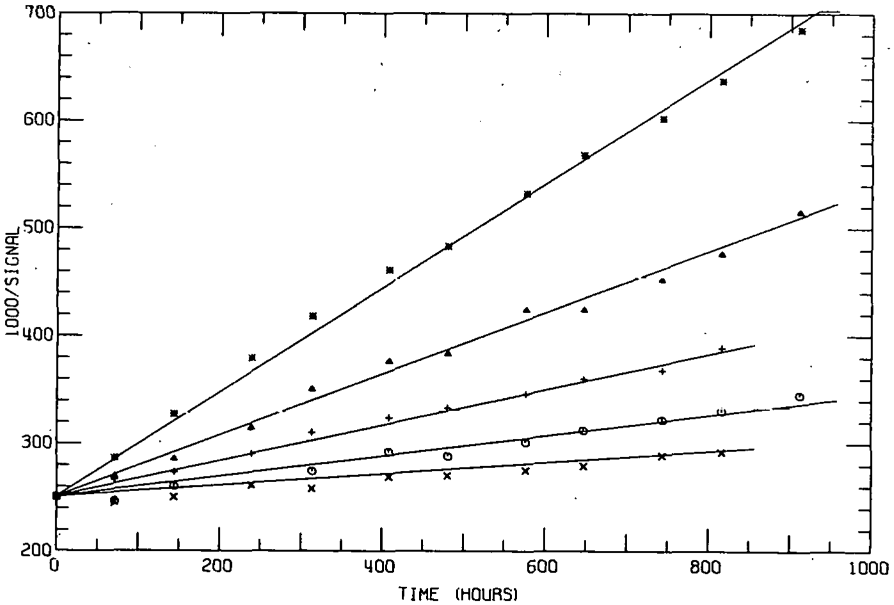


FIG. 1.--Fade response for laboratory control tags at each of the five bath temperatures. 10 C, (×); 14 C, (O); 18 C, (+); 22 C, (Δ); 26 C (*) .

While the observed fade characteristics are similar to bilinear decay, a test of the TLD rods for radiation sensitivity indicates the decay kinetics are not a true second order function.(4) Pretreatment of the tags results in a distribution of activation energies such that isothermal decay of the total light response is approximated by a hyperbolic decay function.

The rate constant m_t at any measured temperature (T_m) can be defined by rearranging Eq. (1) and substituting $T_m + 273$ for T_a so that

$$m_t = e^{-\left(\frac{11145.9}{T_m + 273} - 36.5676 \right)} . \qquad (2)$$

This value does not change uniformly with temperature, but changes more rapidly with increasing temperature (Fig. 1). Higher temperatures, therefore, contribute far more to the fade than do lower tamperatures. This increased sensitivity to higher temperatures is an advantage for the purpose of distinghishing whether a fish tag was in ambient water (intake temperature) or in the discharge (Δt ≅ 9° C) since it increases the difference in fade between the two locations. However, in a fluctuating temperature environment this property complicates the relationship between integrated fade and average temperature.

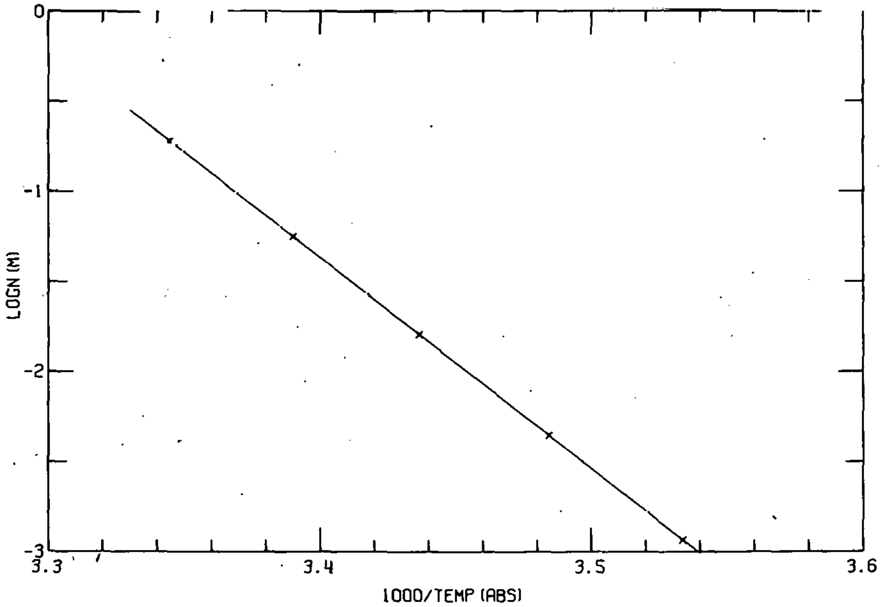


FIG. 2.--Linear regression of fade rate vs. temperature.

The constant temperature required to produce an observed fade in a given amount of time can be derived by substituting Eq. (2) for m_t in the original relationship $1/S = 1/S_0 + m_t t$ and solving for T_m.

$$T_m = \frac{11145.9}{\ln\left(\frac{t}{1/S - 1S_0}\right) - 36.5675} - 273 \qquad (3)$$

If the integrated fade due to a fluctuating temperature environment is attributed to a single temperature (integrated average temperature) as in Eq. (3), then the calculated value will be greater than the true average temperature because fade is dominated by higher temperatures. This property is illustrated in Fig. 3 where an average temperature exposure of 15° C is obtained by equal times at 10 and 20° C. The resultant 1/S value (point A) is greater than it would be from a constant exposure to 15° C (point B). Use of the integrated fade observed at point A to calculate integrated average temperature [Eq. (3)] yields a value of 16.5° C, which is 1.5°C greater than the true average. The size of the error is dependent on temperature range and apportionment of time between temperatures. Within the range of environmental temperatures available to tagged fish the maximum error is in the order of 1.5 to 2° C.

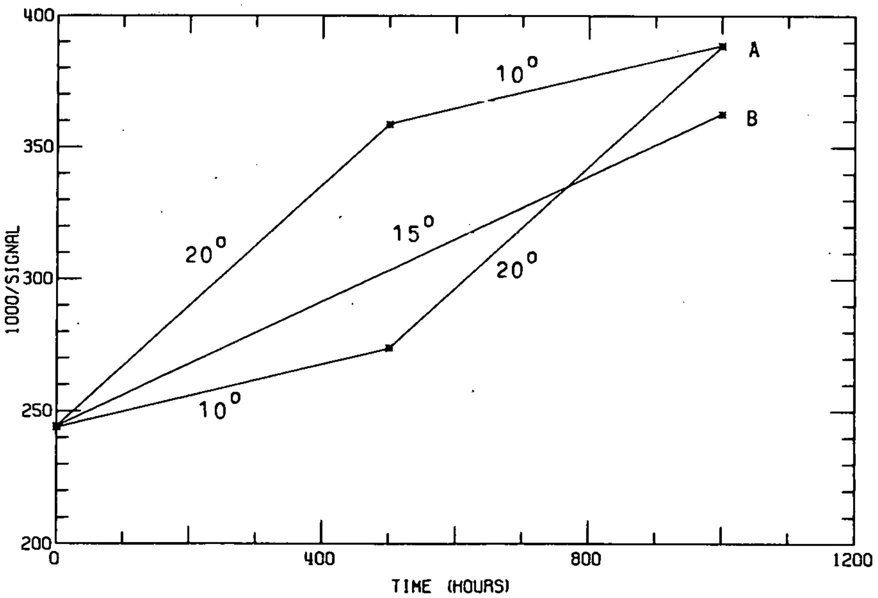


FIG. 3.--Comparison of fade differences due to fluctuating (A) and constant temperatures (B).

Conclusions

High variability of the TLD rods masked any small reductions in variability due to improved methods. Because temperature and exposure time are determined by the total change in signal (fade), the 4.6% standard error of a packet measurement is often a larger percentage of the absolute difference and consequently increases the minimum detectable differences. Since change in fade rate increases with increasing temperature, some advantage is gained when determining maximum discharge residence time; however, integrated fade in a fluctuating temperature environment is not directly related to true average temperature. By knowing these limitations, the integrated average temperature value, although higher than true average temperature, can still provide useful information about thermal exposure to fish.

Acknowledgements

We extend our thanks to Dr. P. R. Moran, University of Wisconsin Medical School, Madison Wisconsin, for his testing of the TLD's and helpful consultation.

References

1. Romberg, G. P. and W. Prepejchal. Temperature sensitive TLD fish tags: Improvements in technique. Radiological and Environmental Research Division Annual Report Part III, January—December 1973. ANL-8060, Part III, pp. 120—127.
2. Bjarngard, Bengt. The properties of $CaSO_4$:Mn thermoluminescence dosimeters. Akliebolaget atomenergi, Stockholm Report AE-109 (1963), p. 24.
3. Podgorsak, E. B. and P. R. Moran. Radiation and Impurity Induced Thermally Activated Charge Transport in Calcium Fluoride. USAEC Technical Report COO-1105-184 (1974).
4. Moran, P. R. Medical physics laboratories, Medical Physics and Engineering Center, Department of Radiology, University of Wisconsin Medical School, Madison, Wisconsin 53706. Personal communication.

DISCHARGE RESIDENCE OF TLD TAGGED FISH

G. P. Romberg and W. Prepejchal

Introduction

Residence time of free-swimming fish at a thermal discharge is an important factor in determining possible effects due to elevated temperature exposure. Temperature-sensitive fish tags were successfully used in 1973 to determine the maximum time that 22 recaptured fish could have resided in the thermal discharge from the Point Beach Nuclear Plant.(1) Although visual observations suggested that fish remained in the discharge for considerable periods, temperature-sensitive tags indicated the majority of fish spend less than 50 hr or 10% of the time at discharge temperatures. During 1974, a second fish tagging study was conducted, using temperature-sensitive tags to yield discharge residence times of Lake Michigan salmonids at Point Beach thermal discharge.

Methods

A total of 522 trout and salmon were collected from the two Point Beach discharge flumes (using lift nets) and tagged with temperature-sensitive tags, primarily during the first week of October, 1974. Tagged fish were periodically recaptured from the discharges by selective spearing, and recovered tags were immediately stored at dry-ice temperature (-78°C) to prevent further fade. Additional tags turned in at Point Beach by fishermen or collected by University of Wisconsin personnel conducting a creel census were also stored by freezing.

Temperatures of the intake and both discharges were measured at one-half hour intervals throughout the study by an automated temperature recording system. Hourly averages were used to calculate integrated average temperature exposure over a given time period. Anticipated fade was then calculated, based on the response of laboratory control tags.(2)

Results and Discussion

Although 122 temperature-sensitive tags were recaptured (as of July, 1975), only 43 were obtained soon enough after recapture to be properly stored for analysis. These included 23 tags (from 8 brown trout and 15 rainbow trout) collected at Point Beach by Argonne personnel and 20 tags (from 8 brown trout, 11 rainbow trout, and 1 chinook salmon) obtained from fishermen. Percentage recovery of usable tags for 1974 (45/522 = 8%) was the same as for 1973 (22/274 = 8%). Cooperation of fishermen and creel census personnel from the University of Wisconsin compensated for lack of a fishing pier attendant collecting tags at Point Beach during 1974.

The reciprocals of the observed signals in recaptured fish tags are plotted as a function of time in Fig. 1. Superimposed on this plot are lines representing the anticipated incremental fade due to existing average temperatures at the intake and both discharges. Greatest residence times could occur in Unit 1 since initial average temperature is lower and Unit 2 was down for about one-half the study period. A line-segment-fitting program is being adapted to determine maximum residence times mathematically rather than by the previously used graphic method. Proximity of the fish tag values to anticipated fade lines

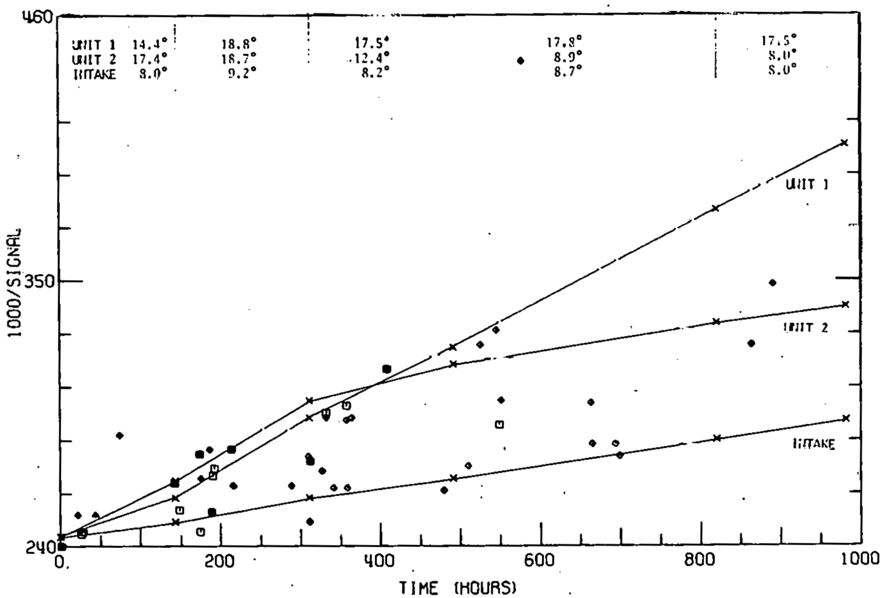


FIG. 1.--Fade of tags from recaptured fish at Point Beach. □ , brown trout (ANL); ■ , brown trout (fishermen); ◇ , rainbow trout (ANL); ◆ , rainbow trout (fishermen); ▲, chinook salmon (fishermen).

for the intake or Unit 1, however, provides a relative indication of the length of time spent at either location. This preliminary analysis reveals that many fish tag values were close to Unit 1 line indicating that calculated maximum discharge residence times for these fish will be nearly 100% of the elapsed time. As in 1973, brown trout again appeared to have had longer residence in warmer water (closer to Unit 1 line) than did rainbow trout. Excessive fade (greater than possible from discharge temperatures) observed for two tags returned by fishermen (74 and 576 hr), indicates that all fishermen tags must be viewed with some degree of uncertainty due to the unknown history between recapture and storage. Lower discharge temperatures during 1974 (12.4 to 18.8° C) compared to 1973 (18.7 to 25.1 ° C) are closer to preferred salmonid temperatures(3) and may account for the apparent longer residence times for fish in 1974.

Acknowledgements

We are grateful to those fishermen who returned tags and also to the University of Wisconsin personnel conducting the creel census.

References

1. Romberg, G. P. and W. Prepejchal. Plume residence of TLD tagged fish. Radiological and Environmental Research Division Annual Report, Part III, January—December 1973. ANL-8060, Part III, pp. 127—134.
2. Romberg, G. P. and W. Prepejchal. Characteristics of temperature-sensitive fish tags used in 1974. This report.
3. Ferguson, P. G. The preferred temperature of fish and their mid-summer distribution in temperate lakes and streams. J. Fish. Res. Board Can. 15 (4), 607—624 (1958).

BODY TEMPERATURE CHANGE CHARACTERISTICS OF LAKE MICHIGAN FISHES

S. A. Spigarelli, M. M. Thommes, and T. L. Beitinger

Introduction

Internal body temperature change rates in poikilothermic fishes exposed to elevated or reduced water temperatures have significance in the investigation of thermal effluent effects on fish. These internal temperature changes influence the effects of rapid water temperature change resulting from reactor shutdown and most likely constitute physiological thresholds which govern fish behavior relative to thermal gradients.

A limited number of studies have measured the rates of change in body temperature of a few freshwater fish species, and the heat exchange process is assumed to follow Newton's Law of Excess Temperature.(1,2) Significant differences in temperature change rate are known to occur between species and sizes of fish. In general, an inverse relationship has been observed between fish weight and the temperature change rate.(2,3) Although a few marine fishes (i.e., tunas, lamnid sharks) are thought to regulate their body temperatures by means of circulatory heat exchangers,(4) the majority of fish are capable of only very limited physiological regulation, as evidenced by slight differences between fish body temperature and water temperature.(2,3)

Preliminary experiments on change rate of fish body temperature were conducted by ANL investigators during 1972 at the Point Beach Nuclear Plant.(2) These studies were expanded in 1973 to provide 1) an improvement in temperature monitoring technique; 2) a wider size range within and between species; and 3) overall larger sample sizes to facilitate statistical comparisons and multivariate analyses.

Methods

The rates of body temperature change and the half-time ($t\frac{1}{2}$) for temperature stabilization(2) were calculated for 5 species of Lake Michigan fish: Alewife (Alosa pseudoharengus), brown trout (Salmo trutta), rainbow trout (Salmo gairdneri), brook trout (Salvelinus fontinalis), and carp (Cyprinus carpio).

Body temperature change rate experiments were conducted on fish collected from the discharge flumes and inshore areas near the Point Beach Nuclear Plant, Two Rivers, Wisconsin. Test fish were exposed to immediate water temperature changes of up to ± 10.6° C by transfer between ambient and discharge water holding tanks. Fish body temperature changes were continuously monitored with a rapid response thermistor (inserted through the anus into the intestine) coupled to a multichannel temperature recording system. The temperature of the bath was also monitored continuously to provide an accurate record of the temperature difference between fish and bath. Test fish were allowed sufficient time to stabilize with the external temperature and in some cases to maintain an excess temperature. In most cases, individual fish were exposed to both ambient and discharge temperature baths to compare cooling and warming rates. Exposures were repeated on some fish to test reproducibility of results.

Results and Discussion

The relationships between half-time ($t\frac{1}{2}$), weight, and species are shown in Figs. 1 and 2 for all fish exposed to elevated (N = 74) and reduced (N = 81) temperatures. As expected, increases in size resulted in increased half-times, demonstrating that the rate of body temperature change is inversely related to fish size. This is confirmed by comparisons by means of $t\frac{1}{2}$ by species (Table 1). In both heating and cooling experiments, ordering species by mean weight also ordered them in terms of their mean half-times. Mean time to stabilization ($t\frac{1}{2} \times 10$) varied from less than 10 minutes in alewives, the smallest species, to more than 5 hours for carp, the largest species tested. This relationship between heat-exchange and size means that larger fish have more time to explore and escape potentially lethal temperatures.

In addition to interspecies differences in thermal exchange rates, mean heating half-times of each species were smaller than their corresponding mean cooling $t\frac{1}{2}$. Statistical analyses were limited to the 62 individual fish which experienced both heating and cooling to eliminate possible size-related interference. A highly significant number of these fish, 51 (82.3%), had cooling

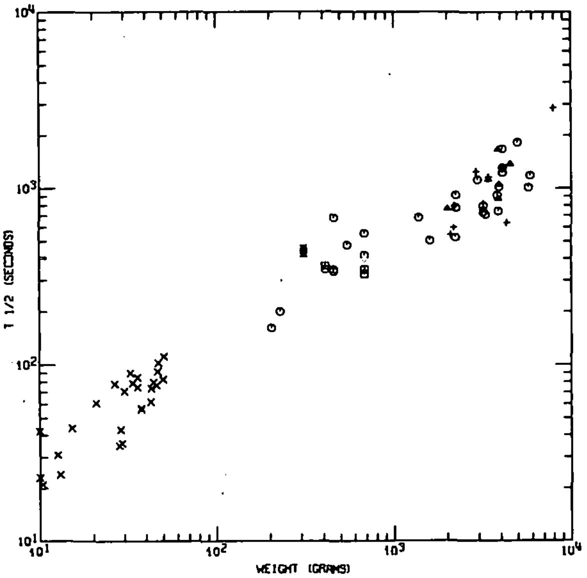


FIG. 1.--Heating half-times as function of body weight for all fish tested (n= 4). X, alewife; O, brown trout; +, carp; Δ, lake trout; *, rainbow trout; ▢, brook trout.

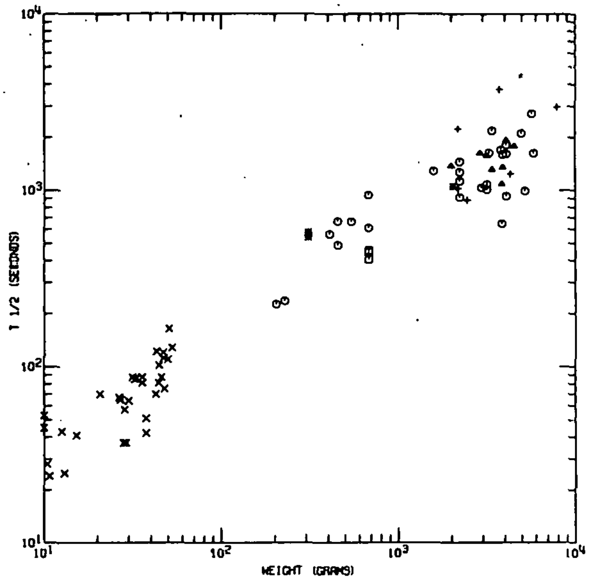


FIG. 2.--Cooling half-times as function of body weight for all fish tested (n= 81). Symbols as in Fig. 1.

TABLE 1. Data summary by species.

	Heating			Cooling		
Species	N	Weights (g) $\bar{x}$, (Range)	$t_{\frac{1}{2}}$ (sec) $\bar{x}$, (Range)	N	Weights (g) $\bar{x}$, (Range)	$t_{\frac{1}{2}}$ (sec) $\bar{x}$, (Range)
Alewife	26	31.4 (9.1 - 50.5)	62.8 (21 - 112)	32	32.2 (9.1 - 52.5)	73.3 (24 - 164)
Brown trout	28	2395.1 (203 - 5851)	774.1 (163 - 1830)	29	2711.3 (203 - 5851)	1175.9 (225 - 2720)
Carp	8	3521.0 (2087 - 7938)	1086.9 (550 - 2860)	6	3795.0 (2177 - 7938)	2014.2 (875 - 3750)
Lake trout	8	3600.5 (1996 - 4536)	1120.0 (765 - 1670)	8	3481.4 (1996 - 4536)	1500.0 (1085 - 1920)
Rainbow trout	2	309 *	445 (430 - 460)*	3	886.3 (309 - 2041)†	721.6 (540 - 1050)†
Brook trout	2	680 *	340 (330 - 350)*	3	680 **	435 (405 - 455)**

* Same fish, 2 trials.
† Two fish, 1 ran twice.
**Same fish, 3 trials.

$t_{\frac{1}{2}}$ greater than their associated heating $t_{\frac{1}{2}}$ (Wilcoxon, matched pairs, signed ranks, $Z > 3.9$, $P < 0.0001$). An example of the relationship between cooling and heating rates is shown in Fig. 3 for alewives. These results support previously reported data for alewife and carp.(2) Although a mechanism to account for the difference in rates of body heating and cooling in fish is not known, a

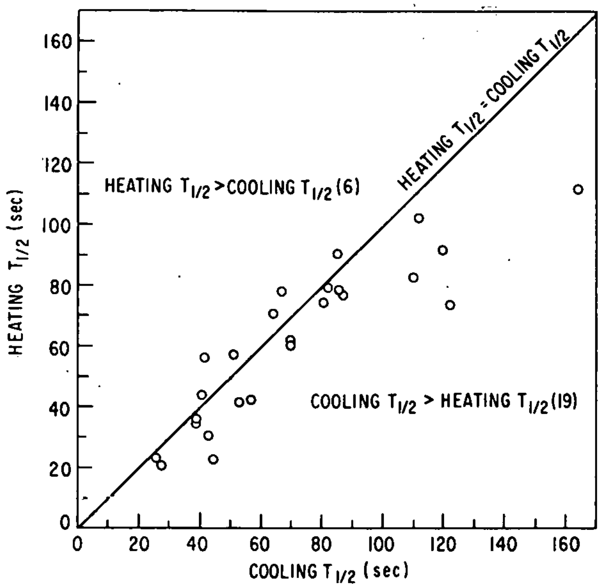


FIG. 3.--Comparison of heating and cooling rates for alewives exposed to both tests (n = 25). ANL Neg. 149-7522

temperature moderated cardiovascular process is intimated.

Previous studies have related variable fish body temperature change rates to fish weight without regard to other morphological parameters. Since we intend to develop predictive equations for heating and cooling times (rates) in Lake Michigan fishes, we measured total length, standard length, and girth for each test fish. Multivariate analyses are now being performed to determine which morphological character or combination of characters yields the highest correlation coefficient (i.e., best predictive model).

Although excess temperature determinations were made in 38 exposure trials (15 alewives, $\overline{x} = 0.35°$ C and 23 brown trout, $\overline{x} = 0.42$ ° C), we were unable to demonstrate a significant correlation either with species or size. Other workers have demonstrated a correlation with size, but high variability in their data suggests the need for larger samples to show this effect.

This study provides new information on the body-temperature change characteristics of these species of fish. This is pertinent to fish residing in or near thermal discharges and equilibrating to elevated temperatures, particularly in the event of a rapid shutdown. From our results, it is apparent that the temperature change rate is related to fish size, species, and direction of change, suggesting that rapid temperature changes would have a more pronounced effect on smaller fish.

References

1. Fry, F. E. J. Responses of vertebrate poikilotherms to temperature. Thermobiology, Ed. A. H. Rose, Academic Press, Inc., New York, 1967, pp. 375–409.

2. Spigarelli, S. A., G. P. Romberg, W. Prepejchal, and M. M. Thommes. Body temperature characteristics of fish at a thermal discharge on Lake Michigan. Thermal Ecology, Ed. J. W. Gibbons and R. R. Shartiz. AEC Symposium Series CONF-730505 (1974), pp. 119–132.
3. Stevens, E. D. and F. E. J. Fry. The rate of thermal exchange in a teleost, *Tilapia mossambica*. Can. J. Zool. 48, 221–226 (1970).
4. Carey, F. G. Fishes with warm bodies. Sci. Am. 228 (2), 36–44 (1973).

BODY TEMPERATURES OF FISH FEEDING IN THE POINT BEACH THERMAL DISCHARGE

S. A. Spigarelli and M. M. Thommes

Introduction

The body temperature of a poikilothermic fish can be regulated only through behavioral responses. Experimental and field studies suggest that all fish have finite temperature ranges and rather specific seasonal temperature preference. The theory of preferred temperature predicts that fish will eventually seek out and acclimate to their final preferred temperature (if available), assuming that other conditions (e.g., food availability and social interactions) are favorable. This concept is extremely important in terms of heated discharges since, theoretically, fish would be attracted and become acclimated to discharge temperatures when ambient water temperatures are below preferred. The implication of this reasoning is that fish will reside in thermal plumes resulting in extended periods of above normal temperature exposure.

Limited measurements of fish body temperatures at the Point Beach Nuclear Plant during 1972(1) showed that, under most conditions, fish were not equilibrated to maximum discharge temperatures and often appeared to be exercising behavioral thermoregulation. These studies were expanded in 1973 to include 9 species and approximately 1300 individual body temperature measurements made on fish caught by fishermen from the Unit 1 pier. These data will provide an excellent description of seasonal temperature selection and feeding temperatures of many important fishes found at Point Beach.

Methods

Between April and November 1973, measurements of internal body temperature were made on 1310 fish caught by sport fishermen at the Point Beach Nuclear Plant. Creel survey personnel measured fish body temperature immediately after capture by inserting a fast response thermistor through the anus into the intestine. In addition, a record was made of 1) fish weight, length, and sex; and 2) intake and discharge temperatures at that time. The numbers and species of fish measured for internal body temperature depended on the seasonal variability of sport catch at Point Beach, resulting in heterogeneous distribution of data among months and species.

Results

A summary of the mean monthly body temperatures and numbers of each species are presented in Table 1. Approximately 76% of the measurements were made on rainbow and brown trout, since these species accounted for 74% of the total sport fishing catch.(2) Comparisons over the entire seven-month period (April through October) will be possible for rainbow and brown trout but not for other species.

Although mean monthly body temperatures must be interpreted cautiously, the data in Table 1 do indicate both temporal and taxonomic differences in feeding temperatures. Because of the relatively large Δt at Point Beach (~ 10° C), fish could have maintained a stable body temperature over most of the study period by exercising behavioral thermoregulation. However, as ambient and discharge water temperatures increased through August, fish body temperatures also increased to a maximum in August for all species. Decreasing water temperatures in the fall months resulted in decreased body temperatures. With few exceptions, body temperatures of individual and species (means) were intermediate between intake and discharge temperatures, even though discharge temperature seldom exceeded upper avoidance temperatures. These results suggest that each species has rather specific seasonal temperature requirements and that the maximum discharge temperature was normally avoided by feeding fish. The fact that in most cases body temperatures were higher than the intake temperature indicate that feeding fish were 1) warming after recent movement from ambient waters into the plume, or 2) thermoregulating at selected intermediate temperatures.

Body temperatures of fish feeding in thermal discharges are not necessarily equal to optimum metabolic or preferred temperatures, but certainly indicate temporal and species related temperature orientation behavior. The

TABLE 1. Mean (± S.D.) body temperatures of fishes caught by sport fishermen at the Point Beach Pier in 1973 (number in parentheses)

Species	April	May	June	July	Aug	Sept	Oct	Nov	Average (Total)
Rainbow trout (*Salmo gairdneri*)	9.8 ± 1.2 (3)	13.9 ± 1.9 (8)	14.9 ± 1.4 (24)	18.3 ± 2.3 (129)	18.7 ± 2.5 (143)	15.5 ± 2.1 (226)	15.9 ± 2.7 (143)	12.4 (1)	16.7 (677)
Brown trout (*Salmo trutta*)	10.4 ± 1.8 (97)	12.9 ± 1.7 (61)	15.5 ± 1.8 (44)	17.6 ± 1.4 (27)	18.1 ± 2.2 (27)	15.9 ± 1.9 (47)	14.7 ± 2.4 (8)	15.4 (1)	13.8 (312)
Brook trout (*Salvelinus fontinalis*)	11.5 ± 1.4 (10)	12.3 ± 1.0 (8)	15.0 ± 1.5 (6)	18.0 (1)	18.7 ± 1.9 (8)	16.6 ± 1.9 (15)	13.9 ± 1.4 (4)	-- (0)	14.9 (52)
Lake trout (*Salvelinus namaycush*)	11.8 (1)	--- (0)	--- (0)	--- (0)	13.3 ± 0.9 (3)	11.9 ± 1.1 (8)	10.5 ± 0.5 (2)	-- (0)	12.0 (14)
Coho salmon (*Oncorhynchus kisutch*)	--- (0)	--- (0)	--- (0)	14.6 ± 0.7 (3)	17.8 ± 2.4 (13)	16.5 ± 1.5 (26)	13.5 ± 0.5 (2)	-- (0)	16.6 (44)
Chinook salmon (*Oncorhynchus tshawytscha*)	--- (0)	--- (0)	--- (0)	13.0 ± 0 (2)	18.9 ± 1.9 (9)	18.0 ± 2.7 (17)	17.0 ± 1.7 (7)	-- (0)	17.7 (35)
Carp (*Cyprinus carpio*)	--- (0)	16.8 ± 2.1 (28)	16.2 ± 1.6 (70)	18.4 ± 2.3 (15)	20.6 ± 0.5 (3)	20.4 (1)	--- (0)	-- (0)	16.8 (117)
Yellow perch (*Perca flavescens*)	--- (0)	--- (0)	13.8 ± 0.8 (3)	16.8 ± 2.4 (3)	21.4 ± 2.4 (7)	--- (0)	--- (0)	-- (0)	18.6 (13)
Sucker (*Catostomus* spp.)	--- (0)	15.0 ± 1.2 (4)	16.0 ± 1.2 (7)	20.2 ± 1.8 (23)	21.2 ± 0.0 (2)	--- (0)	--- (0)	-- (0)	18.9 (36)
Hybrid trout (?)	--- (0)	--- (0)	--- (0)	--- (0)	--- (0)	16.9 ± 1.4 (3)	--- (0)	-- (0)	16.9 (3)
Whitefish (*Coregonus clupeaformis*)	--- (0)	--- (0)	13.1 (1)	--- (0)	--- (0)	--- (0)	--- (0)	-- (0)	13.1 (1)
White bass (*Roccus chrysops*)	--- (0)	--- (0)	16.2 (1)	--- (0)	--- (0)	--- (0)	--- (0)	-- (0)	16.2 (1)
Smallmouth bass (*Micropterus dolomieui*)	--- (0)	--- (0)	--- (0)	--- (0)	28.1 ± 1.3 (2)	--- (0)	--- (0)	-- (0)	28.1 (2)
Bullhead (*Ictalurus* spp.)	--- (0)	--- (0)	19.0 (1)	18.9 ± 0.1 (2)	--- (0)	--- (0)	--- (0)	-- (0)	18.9 (3)
								ΣN =	1310

fact that few fish were equilibrated to the maximum discharge temperature suggests an avoidance of high temperatures; similar results were obtained from mark and recapture experiments with temperature-sensitive fish tags.(3)

These data are now being analyzed to determine the effects of 1) season, 2) species, 3) fish size, and 4) intake and discharge temperatures, on body temperatures of feeding fish.

References

1. Spigarelli, S. A. Behavioral responses of Lake Michigan fishes to a nuclear power plant discharge. Environmental Effects of Cooling Systems at Nuclear Power Plants, Proc. IAEA Symp., Oslo, Norway, August 1974. Int. Atomic Energy Agency, Vienna, 1975, pp. 479–498.
2. Spigarelli, S. A. and M. M. Thommes. Sport fishing survey at the Point Beach Nuclear Plant during 1973. Radiological and Environmental Research Division Annual Report, Part III, January–December 1973. ANL-8060, Part III, pp. 142–149.
3. Romberg, G. P. and W. Prepejchal. Plume residence of TLD tagged fish. Radiological and Environmental Research Division Annual Report, Part III, January–December 1973. ANL-8060, Part III, pp. 127–134.

GROWTH OF PLUME "RESIDENT" FISHES IN LAKE MICHIGAN

S. A. Spigarelli and D. W. Smith*

Introduction

A few studies have attempted to document _in situ_ growth of fishes which "reside" in thermal discharge areas. In most cases, results were inconclusive because of very small sample sizes or an obvious lack of thermal history on sampled fish. Also, the techniques used to indicate growth (length-weight relationships and condition factor) are insensitive to short-term changes in metabolic rates of feeding responses. Such considerations are extremely important in the case of migratory fishes, since one cannot assume that such fishes remain within the heated waters for extended periods of time.

Research in protein synthesis and growth of animals has shown that ribonucleic acid (RNA) increases in rapidly growing cells because it is a protein precursor.(1–3) The potential value of RNA as an indicator of growth is enhanced by the fact that cellular RNA concentrations change almost immediately in response to changes in feeding regime.(4) On the other hand, concentrations of deoxyribonucleic acid (DNA) are known to remain relatively constant despite changes in growth rate, feeding regime, or cell number.(3) These considerations led Bulow(4) and Haines(5) to test the RNA-DNA ratio as an indicator of recent and long-term growth. Both of these studies demonstrated that the RNA-DNA ratio is a sensitive measure of growth and can be used to evaluate relative growth rates of fishes under various feeding regimes or under varying environmental conditions. The applicability of this technique to studies of growth effects on thermal discharge "resident" fish is apparent.

Our experiments with temperature-sensitive fish tags have provided preliminary estimates of discharge residence times and temperature exposures of Lake Michigan salmonids and have given us the opportunity to apply the RNA-DNA technique to a comparison of the relative growth in fish with known

---

*ACM Student, Colorado College, Colorado Springs, 1974.

recent plume exposures and fish collected from unheated areas of the lake.

Methods

In 1973, we collected brown trout (Salmo trutta), rainbow trout (Salmo gairdneri) and chinook salmon (Oncorhynchus tshawytscha) from the Point Beach thermal discharge area, tagged them with commercial dart tags and temperature-sensitive tags, and released them back into the discharge area. Subsequently, some of these fish were recaptured at Point Beach by fishermen or by Argonne field crews. We anticipated that the fish recaptured in the Point Beach discharge area would have been exposed to heated waters for varying periods of time and the time-at-temperature histories would be very useful in a study of the effects of elevated temperatures on the growth of these fishes. Control brown and rainbow trout were collected by the Wisconsin Department of Natural Resources from two areas north of Point Beach, Marinette (C_1), and Bailey's Harbor (C_2); control chinook salmon were collected from Strawberry Creek on two separate occasions, November 1, 1973 (a) and November 5, 1973 (b).

Because our temperature-sensitive tags only relate to the period between tagging and recapture (no previous temperature history), we used the RNA-DNA technique to indicate recent growth. RNA and DNA analyses were performed on epaxial muscle samples taken from each tagged fish recaptured in the plume area and from control fish. The procedure used to determine RNA and DNA concentrations$^{(4,6)}$ involves an extraction of the nucleic acids from dry fat-free muscle samples and colorimetric determinations of phosphorus by means of orcinol (RNA) and diphenylamine (DNA) reactions.

We calculated condition factors ($K = \frac{\text{total weight} \times 10^5}{\text{length}^3}$) for each fish in order to compare the results of two independent indicators of growth. We expected that condition factors would be less sensitive indicators of recent growth (during the time fish were tagged) than RNA-DNA ratios; on the other hand, condition factors could reflect long-term growth abnormalities resulting from extended plume residence prior to tagging.

Statistical analyses of the data involved the Mann-Whitney U test for comparisons of group means ($\alpha = .05$) and the Spearman-Rank Correlation test for linear relationships between parameters.

Results and Discussion

The mean RNA-DNA ratios of plume "resident" rainbow trout and chinook salmon were not statistically different ($P > .05$) from mean ratios of combined controls (1 and 2). The mean ratio of plume "resident" brown trout was significantly higher ($P < .002$) than the combined controls ratio. For each species, the ratios of the two controls were statistically different ($P < .002$), emphasizing the difficulty in obtaining representative control or reference samples.

Table 1 shows the mean weights, condition factors, and RNA-DNA ratios for each group of fish. We intentionally collected fish from two control areas (2 dates for chinook salmon) in order to gain a more meaningful comparison with plume fish. Although the differences between control groups seem to confound the interpretations, we initially assumed that the two controls would be lumped for each species. These data show that the RNA-DNA ratios of plume "resident" fish were within the range of values observed in populations inhabiting natural waters. The differences between control groups are consistent in that control area 1 (Marinette, Wisconsin) ratios are low for both brown and rainbow trout, while control area 2 (Bailey's Harbor) ratios are relatively high and not statistically different ($P > .05$) from plume ratios. Chinook salmon controls were collected from the same area during spawning runs; these samples obviously represent different populations in that

Table 1. Mean Weights, Condition Factors, and RNA-DNA Ratios of Fish from Heated Waters (Point Beach Nuclear Plant Plume) and Unheated Waters of Lake Michigan

Sample	N	Weight, kg	Condition factor, k	RNA-DNA ratio
Brown trout	40			
Plume	20	2.95 ± 0.25[a]	1.41 ± .06	15.4 ± 0.6
Control	20	2.77 ± 0.33	1.50 ± .04	11.1 ± 0.8
1	9	2.18 ± 0.35	1.38 ± .07	7.5 ± 0.4
2	11	3.31 ± 0.48	1.59 ± .03	14.1 ± 0.5
Rainbow trout	32			
Plume	16	2.36 ± 0.30	1.29 ± .06	17.0 ± 1.1
Control	16	2.72 ± 0.20	1.38 ± .06	14.9 ± 1.5
1	10	2.95 ± 0.27	1.44 ± .06	11.2 ± 0.5
2	6	2.40 ± 0.27	1.28 ± .11	21.2 ± 2.2
Chinook salmon	28			
Plume	13	7.98 ± 0.63	1.11 ± .04	11.8 ± 1.1
Control	15	8.98 ± 0.63	1.00 ± .04	14.3 ± 0.9
a	8	10.20 ± 0.70	1.07 ± .04	16.8 ± 1.0
b	7	7.30 ± 0.76	0.92 ± .05	11.3 ± 0.7

[a] ± Standard error.

weights, condition factors and RNA-DNA ratios were significantly different between the control groups. Thus, the RNA-DNA ratios of plume brown and rainbow trout were relatively high but not statistically different from control group 2. Plume chinook salmon had relatively low ratios, but these fish were apparently of a small size class and resembled control group b.

In order to compare the RNA-DNA results with another indicator of growth, we calculated condition factors for each group of fish (Table 1). The statistical comparisons show that, in general, plume fish condition factors were not statistically different ($P > .05$) from those of the combined control group for each species. The obvious conclusions from both indicators of growth are that: (1) plume "residence" does not cause obvious growth abnormalities during September and October; or (2) plume fish did not remain at elevated temperatures for long periods of time.

Table 2 shows the results from temperature-sensitive tags which were placed on plume fish to determine the percentage of time spent at maximum discharge temperature. Although the majority of fish were recaptured within about 20 days, it is apparent that none of these fish resided at maximum temperatures for more than 50% of the time; in fact, the majority spent less than 10% of the time at maximum temperature. Based on these data, it appears that brown trout spent the most time at elevated temperature followed by rainbow trout and chinook salmon in decreasing order. The fact that these fishes did not reside permanently at maximum discharge temperatures is not too surprising when one looks at the intake and discharge temperature records over this period (Fig. 1).

Table 2. Mean Days between Mark and Recapture and Estimated Times at Maximum Discharge Temperature for Plume "Resident" Fish Bearing Temperature-Sensitive Tags (Point Beach, September 5–October 24, 1973

Species	Days tagged	Hours at max. temp.	% time at max. temp.
Brown trout	20 (1–83)[a]	66.8 (0–300)	17.0 (0–50.0)
Rainbow trout	8.5 (1–21)	16.6 (0– 52)	14.9 (0–50.0)
Chinook salmon	14.3 (2–28)	45.0 (0– 75)	9.2 (0–19.5)

[a] Numbers in parentheses are ranges for individual fish.

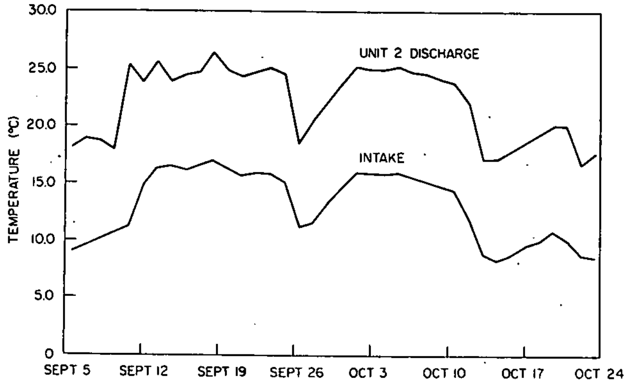


FIG. 1.--Intake and discharge temperatures at the Point Beach Nuclear Plant during the temperature-sensitive fish tag study. (ANL Neg. 149-6630)

Discharge temperature varied between 16.5 and 26.5° C and exceeded 22° C approximately 70% of the time. The upper avoidance temperature of brown trout has been reported to be 20°;(7) that of rainbow trout, 22° C;(8) no upper avoidance temperature data are available for chinook salmon. Thus it would seem that these fishes avoided the high discharge temperatures and either (1) resided at intermediate temperatures which more nearly approximated their optimum temperatures; or (2) moved between warm and cool areas in response to physiological demands.

Our use of time at maximum temperature is a "worst case" approach and is based on our observations of many of these fishes in the discharge flumes during periods when discharge temperatures were below 22° C. We made measurements of body temperature immediately after capturing brown and rainbow trout from the discharge flumes; the maximum body temperatures were approximately 20° C.(9) Body temperature measurements also were made of hundreds of brown and rainbow trout and chinook salmon caught by sport fishermen from the near-field plume; the maximum body temperatures measured were: brown trout, 21.3° C; rainbow trout, 23.5° C, chinook salmon, 23.3° C.(10) All evidence to date suggests that these species are avoiding discharge temperatures exceeding 22° C.

Since these fishes obviously were not residing at maximum temperature, and there was some variability in tag time and percent times at maximum temperature between individuals of a species, we tested for linear correlations between growth indicators and residence times. There were no significant relationships between growth indicators (RNA-DNA and condition factor) and exposure times (tag days and % time). The lack of correlation between RNA-DNA ratios and residence times indicates that fish growth rates were not linearly related to the times spent at elevated temperatures. Since RNA-DNA ratios were not related to K factors, we concluded that these two measures of growth are independent and reflect different growth histories (K-factor = long term; RNA-DNA = short term).

Although the sample sizes in this study are limited, we feel that our data on recent temperature exposures amply support the conclusion that these fishes did not experience any severe growth abnormalities during September and October as a result of their residence in the Point Beach thermal plume area. The RNA-DNA data suggest that plume brown trout were growing at a faster rate than average control brown trout; plume rainbow trout were growing at a similar rate to control rainbows; and plume chinook resembled the slowest growing control group. K-factors generally indicated that plume fish were in similar condition to control fish. The fact that these fishes were exposed to elevated temperatures for varying periods of time indicates that this discharge does attract salmonids under certain conditions during the fall, but that accelerated metabolic demands are compensated by food availability and the ability of motile fish to regulate their temperature exposures behaviorally.

References

1. Sutcliffe, W. H. Growth estimates from ribonucleic acid content in some small organisms. Limnol. Oceanogr. 10, R253–R258 (1965).
2. Leslie, I. The nucleic acid content of tissues and cells. The Nucleic Acids, Chemistry and Biology, Vol. 2. Academic Press, Inc., N.Y. Ed. E. Chargaff and J. N. Davidson, 1955, pp. 1–50.
3. Davidson, J. N. and I. Leslie. A new approach in the biochemistry of growth and development. Nature 165 (4185), 49–53 (1950).
4. Bulow, F. J. RNA-DNA ratios as indicators of recent growth rates of a fish. J. Fish. Res. Bd. Can. 27, 2343–2349 (1972).
5. Haines, T. A. An evaluation of RNA-DNA ratio as a measure of long-term growth in fish populations. J. Fish. Res. Bd. Can. 30, 195–199 (1973).
6. Spigarelli, S. A. and P. R. Harbach. Preliminary use of RNA-DNA ratios to estimate recent growth of Lake Michigan fishes. Argonne National Laboratory Radiological & Environmental Research Division Annual Report, Jan.–Dec. 1973. ANL-8060, Part III, pp. 156–159.
7. Alabaster, J. S. and A. L. Downing. A field and laboratory investigation of the effect of heated effluents on fish. U.K. Min. Agric. Fish. Food Fish. Invest. Sec. I: 6(4):1, 1966.

8. McCauley, R. W. and N. L. Pond. Temperature selection of rainbow trout (*Salmo gairdneri*) fingerlings in vertical and horizontal gradients. J. Fish. Res. Bd. Can. 28, 1801–1804 (1971).
9. Spigarelli, S. A., G. P. Romberg, W. Prepejchal, and M. M. Thommes. Body-temperature characteristics of fish at a thermal discharge on Lake Michigan. *Thermal Ecology*, Ed. J. W. Gibbons and R. R. Sharitz. AEC Symposium Series, CONF-730505 (1974), pp. 119–132
10. Spigarelli, S. A. Behavioral responses of Lake Michigan fishes to a nuclear power plant discharge. Environmental Effects of Cooling Systems at Nuclear Power Plants, Proc. IAEA Symp., Oslo, August 1974. Int. Atomic Energy Agency, Vienna, 1975, pp. 479–498.

EFFECT OF PLUME RESIDENCE ON THE ACCUMULATION OF ^{137}Cs BY LAKE MICHIGAN SALMONIDS

S. A. Spigarelli and J. Edwards*

Introduction

Since 1970, Argonne has investigated the levels of fallout and reactor-produced radioisotopes in Lake Michigan water, biota, and sediments.(1–4) Cesium-137 has been the most common gamma-ray emitter in all samples, and in general, the concentrations in water and biota have decreased since 1966 as a result of decreased fallout. However, the potential exists for increased accumulation of ^{137}Cs by biota in the vicinity of nuclear power plant discharges,(1,3) especially by those organisms that experience increased metabolic rates due to elevated discharge temperatures. In 1971, we sampled and analyzed fish from various areas of Lake Michigan, including the Point Beach Nuclear Plant site and found no evidence of increased accumulation of ^{137}Cs in fish from the power plant discharge area. Since that time, we have demonstrated that although most fish are not permanent plume residents, some salmonids do reside at warm discharge temperatures for significant periods of time.(5,6) Therefore, we recognized that our 1971 sample was probably biased in that we had no "residence" or time-at-temperature histories for fish that were assumed to be plume residents. Our experiments with temperature-sensitive fish tags have provided preliminary estimates of discharge times and given us the opportunity to compare ^{137}Cs levels between fish with known exposures and fish collected from reference (unaffected) areas of the lake.

Methods

In the fall of 1973, we collected brown trout (Salmo trutta), rainbow trout (Salmo gairdneri), and chinook salmon (Oncorhynchus tshawytscha) from the Point Beach thermal discharge area, tagged them with temperature-sensitive tags and released them back into the discharge area. Subsequently,

---

*Undergraduate Research Participant, Summer 1974.

3

(September—October) some of these fish were recaptured at Point Beach by ANL field crews. We anticipated that these recaptured fish would have been exposed to elevated temperatures and low level radioactive waste for varying periods of time and that the residence histories would be very useful in a study of the effects of elevated temperatures on uptake of ^{137}Cs. The Wisconsin Department of Natural Resources collected brown and rainbow trout from northwestern Lake Michigan (Bailey's Harbor area) and chinook salmon from Strawberry Creek (Sturgeon Bay); these fish were used as reference samples.

^{137}Cs measurements were made on a low background gamma counting system consisting of a 4" × 4" NaI(Tl) crystal detector and a 400-channel pulse-height analyzer. Gamma spectral analysis was performed by a least squares technique to fit the observed spectra to appropriate standards. Samples were counted for at least 100 minutes.

Comparison between plume resident fish and reference fish were made using covariance techniques (fish weight as covariate). The relationship between exposure time and ^{137}Cs activity was tested by linear regression analysis.

Results and Discussion

Gamma spectral analysis detected only ^{137}Cs and ^{40}K in these fish samples. Although the mean ^{137}Cs concentrations of plume fish were higher than those of control fish for each species (Table 1), there were no significant differences ($P > .05$) between groups for rainbow trout and chinook salmon. However, plume brown trout had significantly higher ($P < .05$) ^{137}Cs activities than reference brown trout.

Results of our temperature-sensitive fish tag study show that plume fish did occupy warmed discharge waters for significant periods of time.(5) Brown trout had the highest mean percentage of time at maximum temperature (17%), followed by rainbow trout (14.9%), and chinook salmon (9.2%). However, correlations (by species) between: 1) discharge residence times (%) and ^{137}Cs concentration; and 2) estimated plume residence times (total tag days) and ^{137}Cs were not significant ($P > .05$).

TABLE 1. Mean total lengths, weights, ^{137}Cs concentrations and ^{137}Cs/K ratios for plume resident and reference salmonids (1973).

	n	Length (cm)	Weight (g)	^{137}Cs (pCi/kg)	^{137}Cs/K (pCi/g)
Brown Trout					
Plume	10	53.6	2476.4	335.6 ± 27.6[a]	103.5 ± 7.6
Reference	8	54.6	2773.3	278.0 ± 21.4	112.2 ± 11.0
1973 Total	18	54.1	2608.4	310.3 ± 18.8	107.4 ± 6.3
1971 Total	8	-	2758.5	450.6 ± 23.4	138.6 ± 5.2
Rainbow Trout					
Plume	10	56.5	2420.6	216.9 ± 23.1	72.0 ± 8.5
Reference	9	56.3	2612.1	195.4 ± 15.1	72.2 ± 6.9
1973 Total	19	56.4	2511.3	206.7 ± 13.7	72.1 ± 5.4
1971 Total	8	-	2618.5	292.0 ± 33.9	85.0 ± 10.9
Chinook Salmon					
Plume	7	80.0	6991.5	290.9 ± 12.2	104.9 ± 4.2
Reference	7	79.9	5776.1	277.0 ± 16.3	92.3 ± 2.7
1973 Total	14	79.9	6337.1	284.0 ± 9.8	98.6 ± 2.4
1971 Total	3	-	2944.7	409.2 ± 18.3	119.0 ± 11.0

(a) ± standard error

There were significant positive correlations between fish size (length or weight) and ^{137}Cs in most sample groups, supporting results of previous studies that demonstrated a similar effect of fish size on ^{137}Cs concentration in fish.(7) Consequently, all ^{137}Cs values used in comparisons were adjusted for the weight effect (by species). This size effect is probably a reflection of age-related differential uptake rates and biological half-times for ^{137}Cs rather than size-specific plume exposures.

A comparison of mean ^{137}Cs concentrations in all groups for 1971 and 1973 for each species showed that 1971 levels were significantly higher ($P < .02$) than 1973 levels. The reduction in ^{137}Cs concentrations in these fishes between 1971 and 1973 is a direct result of decreased availability of ^{137}Cs in Lake Michigan waters; reduced fallout levels and rapid biogeochemical removal processes (sorption, sedimentation) are principal factors in decreased availability.

Between-species comparisons for both years were identical: ^{137}Cs concentrations of brown trout and chinook salmon were significantly higher ($P < .02$) than those of rainbow trout. The differences in ^{137}Cs concentration between species (brown trout $\approx$ chinook salmon > rainbow trout) may be the result of differential feeding habits or trophic position, rather than a reflection of plume exposure differences; this is also evidenced by the fact that reference samples showed the same trends as plume samples. Since all three of these species are considered to be pelagic fishes (as opposed to benthic) that utilize alewife as a major food source, they reflect the highest levels of ^{137}Cs in the water-plankton-alewife-salmonid food chain. A recent study (4) with Lake Michigan alewife and sculpin (forage species) has shown that ^{137}Cs levels are declining at a much faster rate in pelagic fishes than in benthic fishes.

References

1. Nelson, D. M., G. P. Romberg, and W. Prepejchal. Radionuclide concentrations near the Big Rock Point Nuclear Power Station. Proc. 14th Conf. Great Lakes Research. Int. Assoc. Great Lakes Res., Ann Arbor, Mich., 1971, pp. 268–276.
2. Nelson, D. M., G. P. Romberg, and W. Prepejchal. Radionuclides in Lake Michigan fish. Radiological and Environmental Research Division Annual Report, Part III, January–December 1971. ANL-7860, Part III, pp. 141–150.
3. Nelson, D. M., G. P. Romberg, W. Prepejchal, and S. A. Spigarelli. Effects of a routine radioactive release on aquatic radionuclide concentrations. Proc. 15th Conf. Great Lakes Research. Int. Assoc. Great Lakes Res., Ann Arbor, Mich., 1972, pp. 260–269.
4. Spigarelli, S. A. and D. M. Nelson. Cesium-137 concentrations of Lake Michigan alewives and sculpins between 1960 and 1972. Radiological and Environmental Research Division Annual Report, Part III, January–December 1972. ANL-7960, Part III, pp. 25–30.
5. Romberg, G. P. and W. Prepejchal. Plume residence of TLD tagged fish. Radiological and Environmental Research Division Annual Report, Part III, January–December 1973. ANL-8060, Part III, pp. 127–134.
6. Romberg, G. P. and W. Prepejchal. Characteristics of temperature sensitive fish tags used in 1974. This report.
7. Spigarelli, S. A. Ecological factors affecting the accumulation of cesium-137 fallout by a natural population of largemouth bass (*Micropterus salmoides*). Proc. 3rd Symp. Radioecology, Oak Ridge, May 10–12, 1971. U.S. Atomic Energy Commission Report CONF-710501, P. 1, pp. 328–333.

PUBLICATIONS BY THE STAFF OF THE ECOLOGY SECTION IN THE PERIOD JANUARY THROUGH DECEMBER, 1974

Journal Articles, Book Chapters, Etc.

Jaffey, A. H., K. F. Flynn, W. C. Bentley, and J. O. Karttunen. New determination of the ^{233}U specific activity and half-life. Phys. Rev. C 6(5), 1991–2000 (1974).

Kline, J. R. and M. A. Stewart. Tritium uptake and loss in grass vegetation which has been exposed to an atmospheric source of tritiated water. Health Phys. 26, 567–573 (1974).

Perlow, G. J., W. Potzel, and D. N. Edgington. Serial study of Lake Michigan sediments by ^{57}Fe Mossbauer spectroscopy. J. Physique Colloque C 6 (Suppl. 12) 35, C6-547–548 (1974).

Contributions to Conference Proceedings

Nelson, D. M. Studies of plutonium cycling and sedimentation in Lake Michigan. Proc. 17th Conf. Great Lakes Res. Int. Assoc. Great Lakes Res., Ann Arbor, Mich., 1974, pp. 212–218.

Romberg, G. P., S. A. Spigarelli, W. Prepejchal, and M. M. Thommes. Migratory behavior of fish tagged at a nuclear power plant discharge into Lake Michigan. Proc. 17th Conf. Great Lakes Res. Int. Assoc. Great Lakes Res., Ann Arbor, Mich., 1974, pp. 68–77.

Romberg, G. P., S. A. Spigarelli, W. Prepejchal, and M. M. Thommes. Fish behavior at a thermal discharge into Lake Michigan. Thermal Ecology, Ed. J. W. Gibbons and R. R. Sharitz. AEC Symp. Ser. CONF-730505 (1974), pp. 296–312.

Spigarelli, S. A. Behavioural responses of Lake Michigan fishes to a nuclear power plant discharge. Environmental Effects of Cooling Systems at Nuclear Power Plants, Proc. Int. Atomic Energy Agency, August 1974, pp. 479–498.

Spigarelli, S. A., G. P. Romberg, W. Prepejchal, and M. M. Thommes. Fish body temperature characteristics at a thermal discharge on Lake Michigan. Thermal Ecology, Ed. J. W. Gibbons and R. R. Sharitz. AEC Symp. Ser. CONF-730505 (1974), pp. 119–132.

Wahlgren, M. A. and D. M. Nelson. Studies of plutonium cycling and sedimentation in Lake Michigan. Proc. 17th Conf. on Great Lakes Res. Int. Assoc. Great Lakes Res., Ann Arbor, Mich., 1974, pp. 212–218.

Yaguchi, E. M., B. J. Waller, and J. S. Marshall. Plutonium distribution in Lake Michigan biota. Proc. 17th Conf. Great Lakes Res. Int. Assoc. Great Lakes Res., Ann Arbor, Mich., 1974, pp. 150–157.