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RADIOLOGICAL AND ENVIRONMENTAL RESEARCH DIVISION ANNUAL REPORT

Ecology

January--December 1981

R. E. Rowland, Division Director

W. R. Penrose, Section Head

July 1982

Preceding Report

ANL-80-115 Part III January--December 1980

FOREWORD

The year 1981 was one of severe reductions in funding and staff in the Ecological Sciences Section as a result of the curtailment of federal support for environmental research. The Environmental Protection Agency, which had funded about 85 percent of the Section's research during the previous year, was forced to make many difficult decisions. Both the Great Lakes Research Program and the Freshwater Microcosm Project were cancelled, and the terrestrial air pollution effects programs were reduced in size and scope. The careers of a number of scientists who had made significant contributions to these research programs were unavoidably disrupted.

On the positive side, new funding from the Electric Power Research Institute enabled the Terrestrial Effects Group to initiate a new project to examine the effects of acid deposition on crop-soil systems. The Transuranics Group was not seriously affected by budget reductions owing to continuing appreciation of the importance of this work.

Although the drastic changes of 1981 were distracting, it was, nevertheless, a year of significant scientific accomplishment. Lessons learned from lakes studies on the behavior of transuranic elements were applied to groundwaters. These invisible and economically important aquatic systems are areas of increasing concern to radioactive waste management, where the unique experience of this analytical group is required. Investigations of the effects of energy-related pollutants on crops have been extended to other species, including field corn, which was found to be quite resistant to both O_3 and SO_2. The synergistic effects of SO_2 and NO_x on soybean productivity were confirmed in a second year of experiments. Studies of the impact of acid rain on crop plants have been broadened to determine the dependence of these effects on the chemical composition of rain; and the investigation of the effects of acid rain on soil systems has been initiated.

During the winding-down of the Great Lakes Research Program, emphasis was placed on consolidating years of experimental findings in published form. Many of the staff members involved have since departed and are, therefore, not represented in this Annual Report. A final report on the Great Lakes Research Program now being completed will consist of expanded abstracts of the research accomplished since the Great Lakes Research Program was transferred to the Environmental Protection Agency in FY 1979.

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RAINFALL ACIDITY INTERLABORATORY NATIONAL STUDY - RAINS

P. M. Irving, J. A. Maley* and C. M. Gradert†

Background and Scope

Investigations of the response of plants to simulated acidic rain have indicated positive, negative or no effects from the acid rain treatments; some reports appear contradictory. The experimental designs used by investigators may differ considerably, and certain components of the design (such as raindrop size or simulant chemistry) may be responsible for the inconsistent results. Interaction among investigators at the experimental level is a way to resolve the inconsistencies and would be more effective than mere discussion and speculation. Accordingly, an interlaboratory cooperative study was initiated with the following objectives: (1) standardize techniques and procedures for acid rain studies so that reasonable agreement is obtained among cooperating laboratories; and (2) devise cooperative and complementary experiments to test hypotheses among the associated laboratories.

A group of six laboratories agreed to participate in such studies: Argonne National Laboratory (ANL), Corvallis Environmental Research Laboratory (CERL), Boyce Thompson Institute (BTI), Brookhaven National Laboratory (BNL), Oak Ridge National Laboratory (ORNL), and Ontario Ministry of the Environment (ONT). The following is a report on the first such experiment performed by this cooperative group.

Progress in 1981

The cooperating laboratories agreed that the experimental procedures must be as similar as possible among laboratories and that the first cooperative experiment should be a relatively simple dose-response greenhouse study using simulated rain.

Radish (Raphanus sativus L. cv. Cherry Belle) was chosen as the experimental plant; seeds and 4" x 4" plastic pots were provided by CERL. The

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potting medium, Pro Mix BX, was mounded above the pot and covered with plastic so that the foliage only would be exposed to the simulated rain treatments. Plants were irrigated from below with deionized water to saturation before planting and as needed during the experiment.

Chemical composition for the eight rain simulants, determined by ANL, was based on the weighted average ion concentrations for NADP (National Atmospheric Deposition Program) sites in New York (sites 330860, 332020), Pennsylvania (392940, 394200), and Ohio (361760, 364900, 367160) for the period 1 June through 30 September 1979 (Table 1). The SO_4^{-2} to NO_3^- ratio (by weight) for those sites was 2.37, and this ratio was maintained for each simulated rain. Simulated rain was applied to ten plants per treatment one hour per day three days each week for a total of 7.6 cm of rain in ten applications.

Table 1. Ion concentrations (mg/L^{-1}) for ambient and simulated rain.

pH	H^+	SO_4^{-2}	NO_3^-	PO_4^{-3}	Cl^-	Ca^{+2}	Mg^{+2}	K^+	Na^+	NH_4^+
4.19[a]	0.065	3.836	1.618	0.007	0.107	0.165	0.035	0.031	0.169	0.258
5.4	0.0025	1.114	0.457	Same as ambient (pH 4.19) for all simulants						
5.0	0.010	1.476	0.610							
4.6	0.025	2.015	0.839							
4.2	0.063	3.422	1.406							
3.8	0.158	6.737	2.841							
3.4	0.398	15.239	6.444							
3.0	1.000	36.591	15.495							
2.6	2.512	90.232	38.233							

[a]Ambient rain: weighted average ion concentrations for New York, Pennsylvania, and Ohio NADP sites, 1 June-30 September 1979.

The radishes were harvested 28 days after planting and wet and dry weights were determined. A comparison of the productivity data among the laboratories indicates variations in growth rates but similar trends in response. Shoot weight was not significantly affected by the treatments at Argonne although treatment at the highest acidity (pH 2.6) resulted in a 21% lower shoot weight than the non-acidic treatment (pH 5.4)(Fig. 1). Pooled data from four laboratories (ANL, BTI, CERL, ONT) suggest a stimulation in shoot growth at pH 5.0 and 4.6 significantly greater than at pH 2.6 (Fig. 1). Wet root weight (marketable yield) in the Argonne experiment was unaffected by all but the three highest acidities; at these pH's yields were significantly lower than with the non-acidic treatment (pH 5.4)(Fig. 2). The decrease in root weight was significant only at the two highest acidity treatments when the data were pooled for analysis.

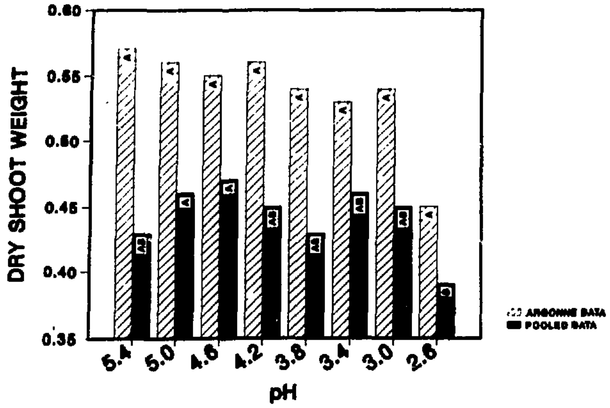

Fig. 1. Dry weight of radish shoots following exposure to simulated rain. Data are means for Argonne and for four cooperating laboratories (ANL, BTI, CERL, ONT). Bars within each group (Pooled and Argonne) with a common letter are not significantly different at the 0.05 level.

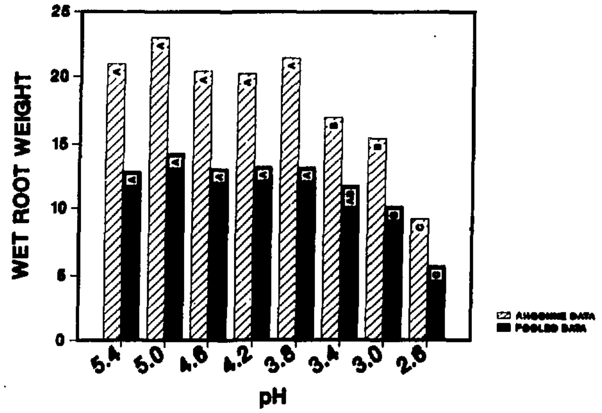

Fig. 2. Root weight (marketable yield) of radishes exposed to simulated rain. Data are means for Argonne and for four cooperating laboratories (ANL, BTI, CERL, ONT). Bars within each group (Pooled and Argonne) with a common letter are not significantly different at the 0.05 level.

The lowest acidity at which visible injury was observed was at pH 3.4 for four laboratories (ANL, BNL, BTI, ORNL) and pH 3.8 for two laboratories (CERL, ONT). The threshold or lowest acidity at which significant negative effects on marketable yield was observed varied among the participants but was established at pH 3.0 after analysis of the pooled data (Table 2).

Table 2. Highest pH of rain treatment resulting in significant negative effects on the yield of radishes.

Laboratory	Threshold pH
ANL	3.4
BNL	4.6
BTI	2.6
CERL	3.0
ORNL	2.6
ONT	3.0
Pooled	3.0

Prospects

Additional data analyses from this experiment are being performed in order to quantify the variability among laboratories. A repeat greenhouse experiment is planned to establish within lab variability, but the participants are most interested in a cooperative field experiment in order to determine the interactions between rainfall chemistry and regional environmental variables (such as soil type and temperature) and the resulting plant response.

EFFECT OF VARIATIONS IN RAINFALL CHEMISTRY ON THE PRODUCTIVITY OF BUSHBEANS AND RADISHES

P. M. Irving, C. M. Gradert* and J. A. Maley†

Background and Scope

Research efforts to assess potential effects of acid precipitation should include investigations to determine the chemical components of precipitation that are important in affecting plant response. These preliminary investigations are necessary to determine which chemical characteristics of rain must be simulated in order to assess effects adequately. Accordingly, a series of greenhouse studies was initiated at Argonne to investigate the influence of the concentration and deposition rate of the important inorganic ions in rain (H^+, NH_4^+, SO_4^{-2}, NO_3^-).

The ionic composition of acidic precipitation may differ considerably among regions and between individual events within a particular region.[1,2] Most researchers investigating acid rain effects have used rain simulants with extremely high sulfate (SO_4^{-2}) to nitrate (NO_3^-) ratios, with the ratio increasing as the pH of their treatment decreased. An examination of precipitation chemistry as reported by the National Atmospheric Deposition Program (NADP) indicates that the SO_4^{-2} to NO_3^- ratios in rain are generally low (Fig. 1). Research at Argonne has demonstrated that soybean yield is significantly affected by the SO_4^{-2} to NO_3^- ratio in precipitation simulants and that the response is dependant on pH.[3]

The acidity of precipitation can vary considerably within a region during a particular season (Fig. 1). Precipitation collected on an event basis at Argonne during the 1977 and 1978 growing seasons had pH values ranging from 3.25 to 7.20.[4] It has been suggested that peak acidity events during a critical plant growth stage may be responsible for damaging effects;[5] however, most investigators have used the same pH value for each treatment event. The following research was designed to determine whether plants respond

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differently to variations in acidity (from rain treatment event to event) compared to a constant acidity for all events.

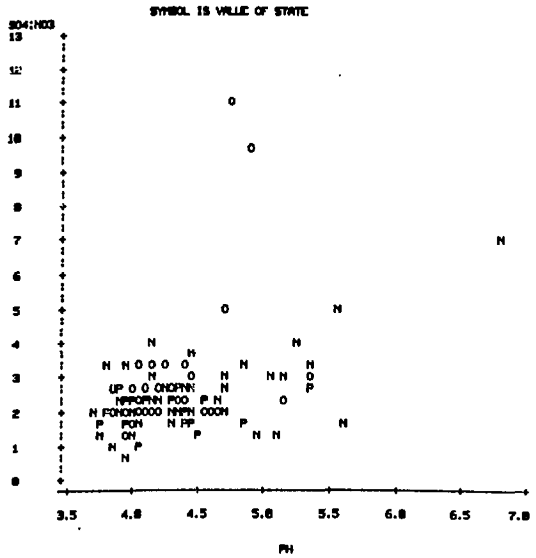

Fig. 1. Sulfate (SO_4^{-2}) to nitrate (NO_3^-) ratio versus pH of rain in New York, Pennsylvania and Ohio during the growing season. NADP data, 1 June-30 September 1979.

Progress in 1981

Two greenhouse experiments were performed to examine the influence of changes in rain chemistry on plant response to acidic precipitation:

1. In an experiment on radishes (Raphanus sativus L. Cherry Belle), two groups of plants, one with the soil covered and one with the soil uncovered, were exposed during their four-week life cycle to ten simulated rain events in three treatment groups: (1) a constant rain chemistry from event to event with no strong acids (pH = 5.6); (2) a constant rain chemistry from event to event with a pH of 3.8; and (3) a variable rain chemistry (pH = 3.0-5.6) with a weighted mean pH of 3.8. Wet and dry shoot and root weights were measured to determine effects.

2. Bushbeans (Phaesolus vulgaris L. Bountiful Stringless) were exposed to treatments of simulated rain based on the chemistry of rain at Argonne (Table 1) using the following treatments: (1) a constant pH of 5.6 (no strong

acids); (2) a constant pH of 4.2 (mean rain pH at Argonne in June and July 1980); (3) a variable pH rain replicating the pH of each rainfall event at Argonne during June and July 1980 (mean pH = 4.2); (4) a constant pH of 3.2 (ten times the June and July acidity); and (5) a variable pH rain replicating ten times the event deposition of H^+ at Argonne (mean pH = 3.2). The plants were treated three times a week for five weeks and were harvested for determinations of wet pod and shoot weights and dry pod, shoot and root weights.

Table 1. Rainfall pH measured at Argonne and simulated in rain treatments.

Date 1980	pH	pH[a] (H^+ x 10)
6-1	4.6	3.6
6-5	4.4	3.4
6-6	4.4	3.4
6-7	6.4	5.4
6-10	4.2	3.2
6-17	4.2	3.2
6-19	4.4	3.4
6-24	4.0	3.0
7-1	4.4	3.4
7-8	4.3	3.3
7-15	4.5	3.5
7-16	3.9	2.9
7-21	4.3	3.3
7-22	4.5	3.5
7-3	3.8	2.8
Mean	4.2	3.2

[a] Simulant pH reflecting 10X the measured pH at Argonne.

The response of radishes to acid rain simulant (pH 3.8) was significantly affected by the chemistry of individual events. Plants that received foliar treatments of rain varying in acidity from event to event with a mean pH of 3.8 had significantly lower marketable yields than plants that received rain of pH 3.8 at each event (Fig. 2a). With both foliar and soil applications of the rain treatments, the variable and constant acid simulants both resulted in significantly greater root dry weights than the non-acid control (pH 5.6)(Fig. 2b), although the wet weights were not statistically different. Visual examination of the foliage indicated that the plants with uncovered soil developed a leaf morphology suggesting water stress while the covered soil plants did not. This difference in moisture availability is evidently the reason for the difference in plant weight between covered and uncovered plant groups.

In bushbeans, the dry root weight was significantly greater in plants that received a variable rain chemistry with a mean pH of 3.2 than in plants treated with constant chemistries at pH 3.2, 4.2, and 5.6 (Fig. 3a). Bushbean wet pod weight was significantly higher at pH 3.2 constant treatment and pH 4.2 variable treatment compared to pH 5.6 (Fig. 3b).

The experiments with radishes indicate that variations in rain chemistry affect root weight differently from a constant rain chemistry when the foliage only is treated. The effect may be related to the absence of water stress in these plants. The bushbean results indicate that peak acidity events affect plant productivity differently from constant acidity with the same total deposition, and that root response may be different from fruit response. These results suggest that experiments utilizing a constant rain chemistry from event to event may not adequately assess effects of acidic deposition having 'peak' loadings of hydrogen ion. The results of these experiments also indicate that acidic rain may stimulate plant response under certain conditions. Sulfur and nitrogen nutrition of plants is interrelated and their increased availability in acidic deposition, especially through foliar application during a critical productivity stage, may increase the yield.

Prospects

There are probably different response functions for the various doses and peaks of acidity, sulfur, nitrogen and other components in precipitation. It is the interaction of precipitation components producing stress with those producing stimulation that will influence plant physiology and the ultimate growth response. The investigation and identification of these stress/stimulant factors and their interaction, is a goal of our future effects research. The next step in our program will be to continue these

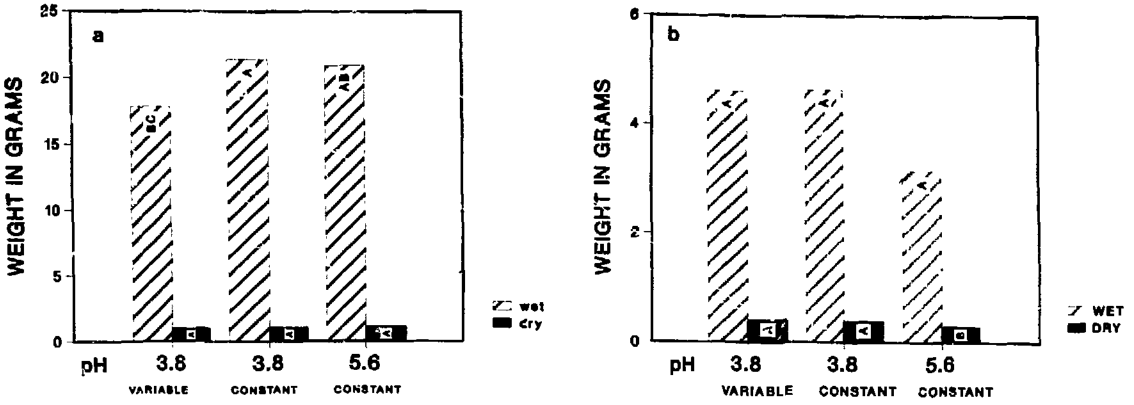

Fig. 2. Marketable yield of radishes exposed to variable and constant chemistries of simulated rain: a, soil covered; b, soil uncovered. Bars with a common letter are not significantly different, $p < 0.05$.

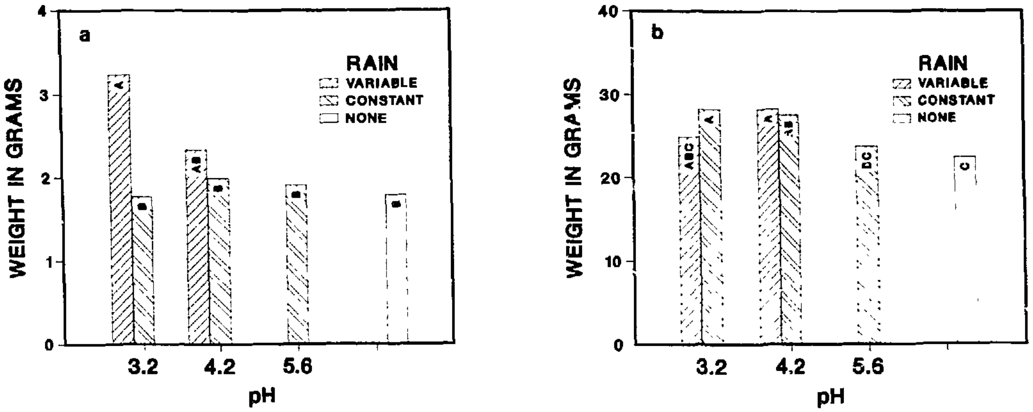

Fig. 3. Root and pod weights of bushbeans exposed to variable and constant chemistries of simulates rain: a, dry root weight; b, wet pod weight. Bars with a common letter are not significantly different, $p < 0.05$.

investigations in the field under agricultural conditions where the response may be quite different, and to include studies of the response of natural vegetation species.

References

1. Gorham, E., Acidic precipitation and its influence upon aquatic ecosystems - an overview, Water, Air, Soil Pollut. 6, 457-479 (1976).
2. Dawson, G. A., Ionic composition of rain during sixteen convective showers, Atmos. Environ. 12, 1991-1999 (1978).
3. Irving, P. M. and D. A. Sowinski, Effect of H^+, $SO_4^=$, NO_3^- and NH_4^+ concentrations and ratios in precipitation applied to greenhouse-grown soybeans, Radiological and Environmental Research Division Annual Report, January-December 1980, ANL-80-115, Part III, pp. 6-10.
4. Irving, P. M., Rainfall acidity at Argonne, Radiological and Environmental Research Division Annual Report, January-December 1978, ANL-78-65, Part III, pp. 21-23.
5. NAPAP, National Acid Precipitation Assessment Plan, January 1981, Council on Environmental Quality, Washington, D. C.

HISTOLOGICAL STUDY OF LEAVES OF SOYBEANS AND CORN EXPOSED TO GASEOUS POLLUTANTS

P. M. Irving, P. Zankowski* and L. Kress

Background and Scope

Exposure of plants to gaseous air pollutants is known to cause visible injury in various forms (i.e., leaf stipple, necrosis, chlorosis), as well as accelerated senescence, which can be quantified through measurements of leaf drop and chlorophyll degradation.[1] These forms of visible injury may or may not be accompanied by decreases in plant productivity, and likewise, plant productivity may be affected without accompanying visible injury.[2] Consequently, predictions of pollutant effects on crop yields based on visible symptoms are unreliable. A histological technique was developed, therefore, to determine whether a microscopic examination of leaf tissue could provide information to relate cellular differences to pollutant exposure and productivity changes. Our technique utilizes fast green and safranin dyes in a procedure by which differential absorption and de-staining provided a clear distinction between living and dead cells.

Our initial study[3] on sulfur dioxide (SO_2) exposure of soybeans indicated that cell death was related to SO_2 exposure and that yield decreases may occur when more than 5% of the mesophyll cells are killed by an acute exposure. Cell death was also observed following chronic SO_2 exposures which caused yield decreases even though visible injury was not observed.

Progress in 1981

In order to determine the limits in the application of this histological technique, we conducted further microscopic examinations of SO_2-fumigated soybeans. We were also interested in determining whether other gaseous pollutants produced a similar histological response in soybeans and whether other plants could also be examined using this technique. To accomplish this, we examined soybeans exposed to SO_2, NO_2, and O_3 and corn exposed to O_3.

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Ozone fumigation was accomplished using open-top chambers for 7 hr each day during most of the life cycle, as described by Kress and Miller.[4] The SO_2 and NO_2 field exposures were made using the Zonal Air Pollution System (ZAPS) on 10 occasions during the pod-filling stage for 3 hr per fumigation.[5] Leaf samples for histologic study were taken from the fifth node at the end of the pod-filling period for soybeans and from the corn ear-leaf at various growth stages.

Chronic exposure of soybeans (cv. Northrup King 1492) to SO_2 ranging from <0.25 ppm·hr to 10.59 ppm·hr resulted in no significant effects on yield and no visible injury. However, cell death increased with SO_2 dose and was statistically significant at the highest dose (Table 1). This indicates that doses of SO_2 that do not affect yield may cause an increase in cell death.

Table 1. Seed yield and leaf cell death in soybeans exposed to SO_2.[d]

		Number of dead cells mm^{-2}			
SO_2 dose, ppm·hr	Yield, % of control	Epidermal	Palisade mesophyll	Spongy mesophyll	Total
<0.25 (control)	100.0a	1.98a	1.97a	0.97a	4.91a
5.01	104.9a	2.63a	2.31a	1.25a	6.20a
7.95	105.0a	2.22a	5.00a	0.93a	8.16a
8.07	104.6a	6.05a	8.72ab	2.36a	17.13a
10.59	98.8a	4.47a	15.35 b	14.01 b	33.82 b

[d] Data are means of 10 plants; those with a common letter are not significantly different according to Duncan's Multiple Range Test, $p < 0.05$.

The exposure of soybeans (cv. Northrup King 1492) to NO_2 resulted in no negative effects on yield and produced neither visible injury nor increases in cell death. Results of the microscopic investigation, interestingly, suggest that NO_2 exposure may protect the leaves from cellular injury since there were significantly ($p < 0.05$) fewer dead adaxial epidermal cells in the NO_2-exposed soybean leaves than in leaves from the unexposed plants (Table 2). The abaxial epidermal and mesophyll leaf cells were unaffected by NO_2 fumigation. Perhaps the NO_2 exposure reduced pathogen attack of the upper leaf surface. The NO_2 could also have interacted with ambient O_3 to reduce oxidant injury to these cells.

Table 2. Seed yield and leaf cell death in soybeans exposed to NO_2.[d]

NO_2 dose, ppm·hr	Yield, % of control	Adaxial epidermis, no. dead cells m^{-2}
<0.29 (control)	100.0 b	4.82 b
3.55	107.5a	1.02a
4.20	103.7ab	2.22ab
7.65	94.2 b	1.14a
10.18	98.9 b	1.37a

[d] Data are means of 10 plants; those with a common letter are not significantly different according to Duncan's Multiple Range Test, $p < .05$.

As ozone (O_3) concentration increased, the number of dead leaf cells of soybean (cv. Corsoy) also increased (Table 3). The differences were significant for palisade mesophyll cells at the two highest O_3 doses (35.39 ppm·hr and 43.69 ppm·hr) and for all cell types (epidermal, palisade mesophyll and spongy mesophyll) at the highest O_3 dose. Seed weight per plant at the two highest O_3 doses was significantly lower than at the filtered-air dose (Table 3).

Cell death from O_3 exposure can be used to predict soybean yield with equation 1:

$$y = \beta_1 + \beta_2(\log x), \tag{1}$$

where

y = seed weight per plant in g

x = total number of dead cells > 0

$\beta_1 = 13.2$

$\beta_2 = -2.02$

model $R^2 = 0.71$

Table 3. Seed yield and leaf cell death of soybeans exposed to O_3.[x]

Ozone		Number dead cells mm^{-2}				Seed yield	
Dose ppm·hr	Concentration, ppm (average 7 hr)	Epidermis	Palisade mesophyll	Spongy mesophyll	Total	wt plant^{-1}	wt seed^{-1}
20.46[y]	0.037	1.58 b	0.23 c	0.28 b	2.08 c	13.0ab	0.149a
27.65[z]	0.050	1.97 b	0.27 c	0.46 b	2.70 c	13.1a	0.142 b
35.39	0.064	2.08 b	6.58 b	0.78 b	9.44 b	10.9 b	0.135 b
43.69	0.079	3.81a	34.90a	11.33a	50.04a	9.7 c	0.124 c

[x] Data are means of 50 sections; those with a common letter are not significantly different according to Duncan's Multiple Range Test, $p < 0.05$.

[y] Filtered air.

[z] Ambient air.

F value = 434.94.

Histological samples of the ear-leaves of two field-corn hybrids (Pioneer 3780 and PAG 397) taken during the vegetative, flowering and mid-grain filling stages revealed no significant differences in cell death as a result of daily ozone fumigations having 7-hr averages of 0.015, 0.044, 0.073, 0.10, 0.129 and 0.156 ppm. A reduction in the number of chloroplasts in the mesophyll cells and reduced size and number of chloroplast grana in bundle-sheath cells was observed in leaves exposed to the highest O_3 dose, and these reductions became more pronounced over time. Leaf chlorosis was visibly evident in these plants also. These results support the theory that O_3 injures plants by damaging membranes and suggest that chloroplast lamellae may be more susceptible than cell membranes. Swanson and Thomson[6] suggested that stromal changes and decreases in chromosome volume are probably an indication of dehydration resulting from permeability changes induced by ozone. Since chlorophyll metabolism was affected by the ozone exposure, leaf sampling at a later date may have revealed that cells were eventually killed. Grain yield was reduced at the three highest O_3 concentrations in the 3780 hybrid and the two highest concentrations in the 397 hybrid.

Prospects

The results of these investigations reveal that this histological technique can be valuable in indicating plant stress resulting from exposure to gaseous pollutants. With SO_2 exposure, a significantly greater number of dead soybean leaf cells was observed at a dose of 10.59 ppm·hr than at doses <8.07 ppm·hr, even though yield was not affected. In soybeans exposed to ozone, leaf cell death was only significant at doses of ozone high enough to reduce yield (>35.39 ppm·hr). With additional experiments, perhaps a mathematical function can be developed to predict yield losses in soybeans resulting from SO_2 or O_3 exposure through the measurement of leaf cell death. Further studies of corn may reveal that in addition to chlorophyll degradation, leaf cells are eventually killed at high O_3 doses. Other crop species and natural vegetation will be studied in order to determine whether histological examinations may be used to predict effects of pollutant exposure on yield in the absence of pollutant monitoring.

References

1. Irving, P. M., J. E. Miller, and P. B. Xerikos, Accelerated senescence in soybeans exposed to sulfur dioxide, Radiological and Environmental Research Division Annual Report, January-December 1979, ANL-79-65, Part III, pp. 45-46.
2. Sprugel, D. G., J. E. Miller, R. N. Muller, H. J. Smith, and P. B. Xerikos, Sulfur dioxide effects, yield and seed quality in field-grown soybeans, Phytopathology 70, 1129-1133 (1980).
3. Irving, P. M., D. G. Martinson and J. E. Miller, A histological study of soybeans injured by exposure to sulfur dioxide, Radiological and Environmental Research Division Annual Report, January-December 1978, ANL-78-65, Part III, pp. 11-13.
4. Kress, L. W. and J. E. Miller, Impact of ozone on yield of field corn, this report.
5. Irving, P. M., P. B. Xerikos and J. E. Miller, Effect on the productivity of field-grown soybeans by combinations of sulfur dioxide and nitrogen dioxide, Radiological and Environmental Research Division Annual Report, January-December 1980, ANL-80-115, Part III, pp. 1-5.
6. Swanson, E. S., W. W. Thomson and J. B. Mudd, The effect of ozone on leaf cell membranes, Can. J. Bot. 51, 1213-1219 (1973).

THE COMBINED EFFECT OF SULFUR DIOXIDE AND NITROGEN DIOXIDE GASES ON THE GROWTH AND PRODUCTIVITY OF SOYBEANS

P. M. Irving, P. B. Xerikos and J. E. Miller

Background and Scope

Studies of effects on vegetation from single pollutants are numerous and provide useful determinations of phytotoxicity. However, pollutants rarely occur alone. Combustion processes which generate SO_2 frequently produce a mixture of nitrogen oxides as demonstrated by ambient air-monitoring data.

Observations of 1979 EPA air quality data from a site in Illinois located near a power plant and affected by urban emissions (Joliet), reveals that ratios of sulfur dioxide (SO_2) to nitrogen dioxide (NO_2) vary widely but frequently range from 3:1 to 2:1 (in ppm) during SO_2 peaks (hourly mean $[SO_2] > 0.08$ ppm) and from 1:3 to 1:5 during peaks in NO_2 (hourly mean $[NO_2] > 0.08$ ppm). The high SO_2:NO_2 ratios probably result from point source emissions while the low ratios may be due to mobile sources of NO_2 with high background SO_2. Air quality data from a rural location (Edwardsville) approximately 24 km northeast of the industrial St. Louis area indicate that NO_2 concentrations are rarely greater than SO_2 concentrations and that during SO_2 peaks (>0.08 ppm) NO_2 concentrations are one-half to one-third as much although sometimes they are approximately equal.

In order to determine the effects of pollutant combinations on crop plants, we conducted investigations on field-grown soybeans exposed to SO_2 and NO_2 alone and in combination, in the presence of ambient ozone. Our studies in 1980 indicated that combinations of SO_2 and NO_2 decreased seed yield by 9 to 18% at concentrations causing no decreases when they occurred alone. The following is a report of the second year of our field studies.

Progress in 1981

Open-air field plots of soybeans (cv. Northrup King 1492) were fumigated with SO_2, NO_2, and combinations of the two through a system of aluminum pipes suspended above the field (Fig. 1). After being released from the pipes, the pollutant gases decreased with distance downwind from the pipe as a result of normal turbulent dispersion.

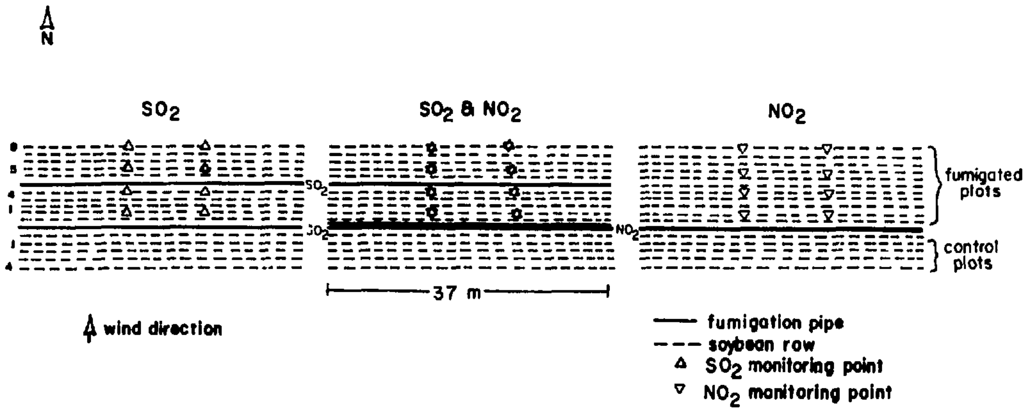

Fig. 1. Experimental field design for SO_2 and NO_2 fumigation.

The soybean plots were fumigated on 10 occasions between 24 July and 30 August 1981 during the pod-filling stage. The average exposure time per fumigation was 2.8 hr, with mean concentrations during fumigation periods ranging from 0.13 to 0.30 ppm of SO_2 and 0.06 to 0.40 ppm of NO_2. In the fumigated plots, total SO_2 doses (concentration x hours of exposure) ranged from 4.35 to 8.39 ppm·hr; NO_2 doses were from 1.97 to 11.48 ppm·hr. The 7-hr ambient ozone concentration varied from 0.006 to 0.095 ppm and averaged 0.045 ppm from June through mid-September 1981. Average ambient concentrations of SO_2 and NO_2 were <0.01 ppm.

Fumigations with NO_2 alone had no effect on seed yield, while SO_2 exposures decreased yield by 0 to 6% (Table 1). Combinations of SO_2 and NO_2 resulted in decreases in yield ranging from 9 to 25% (Table 1). Analysis of variance indicates the yield effect is dependent on the SO_2 dose and an interactive term describing the combined doses of SO_2 and NO_2 (Table 2). The relationship represented by Equation 1 was used to describe the dose-response function:

$$y = \beta_1 + \beta_2(SO_2\ \text{dose}) + \beta_3(NO_2\ \text{dose}) + \beta_4(SO_2\ \text{dose} \times NO_2\ \text{dose}) \qquad (1)$$

where

y = seed dry weight in kg hectare^{-1}

$\beta_1 = 3277 \pm 26$

Table 1. Soybean yield following 10 fumigations of SO_2, NO_2, and combinations of the two in the presence of ambient O_3 (1981).[x]

Row	SO_2		NO_2		Yield, % of control	SO_2:NO_2
	ppm·hr[y]	ppm[z]	ppm·hr[y]	ppm[z]		
Control	0	0	0	0	100.0	
1	0.24	6.71			98.3	
2	0.22	6.02			96.3	
3	0.19	5.34			99.9	
4	0.17	4.65			95.1	
5	0.30	8.39			93.7	
6	0.25	7.04			95.2	
7	0.20	5.69			94.5	
8	0.15	4.35			96.1	
1			0.40	11.48	97.6	
2			0.33	9.24	94.5	
3			0.25	7.00	98.7	
4			0.17	4.82	96.2	
5			0.12	3.29	101.6	
6			0.10	2.85	102.1	
7			0.09	2.42	98.3	
8			0.07	1.97	104.9	
1	0.25	7.14	0.37	10.19	75.0	0.7
2	0.21	6.04	0.29	8.18	87.2	0.8
3	0.17	4.94	0.23	6.22	91.5	0.7
4	0.13	3.83	0.15	4.31	86.2	0.9
5	0.29	8.31	0.11	2.94	79.1	2.6
6	0.25	6.92	0.10	2.74	84.1	2.5
7	0.20	5.53	0.09	2.52	84.1	2.2
8	0.15	4.14	0.09	2.40	80.2	1.7

[x] Mean 7-hr O_3 concentration = 0.045 ppm.
[y] Mean concentration/fumigation.
[z] Total dose for 10 fumigations averaging 2.8 hr/fumigation.

$\beta_2 = -36 \pm 7$

$\beta_3 = -11 \pm 7$

$\beta_4 = -7 \pm 2$

model $R^2 = 0.52$

F value = 48.44

PR > F = 0.0001

The highly significant negative value ascribed to the multiplicative term in the function indicates that combinations of SO_2 and NO_2 have an adverse effect on soybean yield and that the effect is more than additive, or synergistic. Leaf bronzing was observed in the SO_2 plot and SO_2-NO_2 combined plot six days after the SO_2 concentration reached a 3-min peak of 1.0 ppm during a fumigation in late July. Premature senescence as indicated by chlorophyll degradation, was observed in the combined plot in late August. No forms of visible injury were observed in the NO_2-fumigated plot.

Table 2. Analysis of variance of the effect of SO_2 and NO_2 on soybean seed weight.[a]

Source	DF	SS	F value	PR > F
SO_2 dose	1	1060994	26.94	0.0001
NO_2 dose	1	107257	2.72	0.1012
SO_2 dose x NO_2 dose	1	662016	16.18	0.0001
Model	3	5722635		
Error	134	10999465		

[a] DF = degrees of freedom; SS = sum of squares; F = F distribution; PR = probability.

Extraction of chlorophyll from leaves of the fifth node sampled on 1 September 1982 indicated 13 to 44% decreases in the combined plot (Table 3). This demonstrates the correlation between pollutant exposure and leaf senescence which, in turn, appear to be related to the yield.

Table 3. Leaf chlorophyll concentration of soybean plants exposed to SO_2 and NO_2.[x]

Exposure, ppm·hr[y]		Total chlorophyll,[z]
SO_2	NO_2	mg/g
	0	12.86ab
	4.82	13.24a
	7.00	11.61ab
	9.24	11.99ab
	11.48	11.48ab
0		13.43a
4.65		11.89ab
5.34		12.20ab
6.02		12.05ab
6.71		10.87 b
0	0	13.38a
3.835	4.315	11.36ab
4.94	6.22	10.87 b
6.04	8.18	11.04 b
7.14	10.185	7.47 c

[x] Leaves at fifth node from apex, sampled 1 September 1981.
[y] Total dose for 10 fumigations averaging 2.8 hr per fumigation.
[z] Means with a common letter are not significantly different according to Duncan's Multiple Range Test, $p < 0.05$, $n = 20$.

The results from this field season are consistent with those of the 1980 field season[1] and indicate the synergistic effect of SO_2 and NO_2 gases on soybean yield. Since these pollutants frequently occur in combination, as evidenced by ambient monitoring data, research utilizing only single pollutant exposures will not adequately assess potential damage from fossil fuel combustion. Air pollution standards should, therefore, be based on the interactive effects of pollutant combinations rather than single pollutant impacts.

Prospects

Two years of field studies with consistent results indicate that the data may be combined for the purpose of generating a dose-response model that may be applicable under various environmental conditions. The necessity of examining the response of other crops to combined pollutant exposures in the field is also indicated by these results.

Reference

1. Irving, P. M., P. B. Xerikos and J. E. Miller, Effect on the productivity of field-grown soybeans by combinations of sulfur dioxide and nitrogen dioxide, Radiological and Environmental Research Division Annual Report, January-December 1980, ANL-80-115, Part III, pp. 1-5.

IMPACT OF OZONE ON YIELD OF FIELD CORN

L. W. Kress and J. E. Miller

Background and Scope

Corn is the third most important cereal crop in the world. In the U.S., field corn is number one in terms of both acres planted and dollar value (about 25% of total cash value of U.S. crops). About 70% of the field corn is produced in six states: Iowa (20%), Illinois (17%), Nebraska (10%), Indiana (9%), Minnesota (8%), and Ohio (5%).

The major air pollutant of national concern is ozone (O_3). It is the most ubiquitous air pollutant and often is found far removed from the sources of the precursors from which it is formed. Hydrocarbons and oxides of nitrogen (primarily from transportation-related and power generation sources) participate in photochemical reactions to produce O_3. Climatic conditions producing air stagnation during long bright sunny days are conducive to O_3 buildup, and these conditions often coincide with the growing season for much of the corn producing region. A recent estimate indicates seasonal 7-hr average O_3 concentrations of 0.04 to 0.06 ppm for much of the Midwest.[1]

Limited research concerning effects of O_3 on field corn indicates its relative insensitivity compared to other crops in terms of both foliar injury and growth.[2,3] Heagle et al.[4] have reported the only field-generated dose-response information for field corn. They exposed the hybrid, Coker 16, to four concentrations (0.02, 0.07, 0.11, 0.15 ppm seasonal 7-hr average) of O_3 in open-top chambers and found a significant seed yield reduction (total seed weight, 16%; and weight/100 seeds, 9%) only for plants treated with 0.15 ppm O_3. Regression analysis of the data produced an estimate of a 0.2% increase in seed yield at a seasonal 7-hr average O_3 concentration of 0.06 ppm (compared to 0.02 ppm) and less than a 4% yield reduction at 0.10 ppm O_3.[2]

Since field corn has such great economic importance, even a small yield reduction may have a significant dollar impact. The ambient air and other environmental conditions at Argonne are more representative of the major corn growing regions than those at Raleigh, North Carolina (where the Heagle et al. study was performed), so a dose-response study of O_3 and field corn was undertaken. The experimental equipment and procedures were similar to those used in 1980 for soybean.[5]

This report reflects a portion of the research conducted at Argonne for its part in the National Crop Loss Assessment Network (NCLAN). The objective of the study was to evaluate the impact of current and increased O_3 concentrations on crop yield.

Progress in 1981

Two commonly planted field corn hybrids were utilized for this study. A randomized complete block design incorporating three replicates of seven treatments was used. The treatments were no chamber, charcoal-filtered air chamber, unfiltered air (O_3 concentration equal to that in ambient air), and unfiltered air plus 0.03, 0.06, 0.09, and 0.12 ppm O_3 above ambient. Ozone was added to the chambers from 0900 to 1600 CST daily. Ozone was not added on rainy days; thus the actual seasonal 7-hr average concentrations were somewhat less than 0.03, 0.06, 0.09, and 0.12 ppm above ambient in those treatments (Table 1). The growing period for the corn was approximately June 3 through September 10, 1981. The experimental treatments began on June 20 and ended on September 10. The ears were harvested on October 5 after field drying.

The yield data demonstrated that field corn was much less sensitive to O_3 than soybean (Ref. 5, Table 1). The data also suggested the presence of a threshold concentration of O_3 for significant effects, which was appreciably different for the two hybrids. The hybrid, Pioneer 3780, exhibited a significant 25% reduction of yield in response to the 0.10 ppm O_3 treatment (compared to 0.015 ppm O_3). The hybrid, PAG 397, exhibited an insignificant 7% reduction in yield at 0.10 ppm O_3, but a 30% reduction at 0.129 ppm O_3. Once the threshold O_3 concentration was exceeded, both hybrids appeared similar in sensitivity to increasing O_3 concentration. The effects were similar, but not as great, when weight per 100 seeds was determined, indicating that seed size as well as seed number was being reduced. The amount of the cob that was filled with kernels (% kernelled) was not appreciably reduced except for the highest O_3 treatment (0.156 ppm), indicating the overall yield effects were due primarily to reduced cob length and seed size.

Regression analysis of the data indicated that the ambient O_3 (0.044 ppm) had no effect on field corn yields. A plateau-linear function appeared to be

Table 1. Yield response of two field corn hybrids exposed to charcoal-filtered air (CF), ambient air open plot (AA), and ambient air plus O_3 from June 20 to September 10.*

Treatment	Average 7-hr O_3 ppm	Hybrid Pioneer 3780			Hybrid PAG 397		
		bushels/acre	wt/100 seeds, g	% kernelled	bushels/acre	wt/100 seeds, g	% kernelled
AA	0.044	167a	24.2a	89.5a	181a	23.7 b	91.0ab
CF	0.015	175a	25.7a	88.3a	188a	25.8ab	89.8ab
1	0.044	171a	24.3a	87.4ab	205a	26.6a	93.0a
2	0.073	173a	24.7a	88.2a	182a	25.3ab	89.4ab
3	0.100	131 b	20.0 b	87.5ab	175a	24.0 b	91.0ab
4	0.129	97 c	17.6 c	88.5a	132 b	18.6 c	89.0ab
5	0.156	67 d	15.4 d	82.1 b	80 c	15.9 d	84.2 b

*Values with a common letter are not significantly different at $P = 0.05$.

a good description of the curves for both hybrids, with an O_3 threshold value of 0.0707 ppm for 3780 and 0.0899 ppm for 397. At a concentration of 0.10 ppm yields were reduced by 21.4% for 3780 and 8.7% for 397. At 0.14 ppm O_3, yield reductions were 50.5% for 3780 and 43.3% for 397.

This study indicates that field corn is more sensitive than predicted by Heagle et al.[4] However, at the O_3 concentrations currently occurring in corn producing regions (which are below the threshold for O_3 effects) no significant adverse effects would be expected.

References

1. Reagan, J., U.S. Environmental Protection Agency, personal communication (1981).
2. Heagle, A. S. and W. W. Heck, Field methods to assess crop losses due to oxidant air pollutants, Crop Loss Assessment, Proc. E. C. Stakman Commemorative Symposium, Agric. Exp. Sta., Univ. of Minn., St. Paul, MN 55108, Misc. Pub. 7-1980, pp. 296-303 (1980).
3. Milier, J. E., H. J. Smith, and W. Prepejchal, The relative sensitivity of 14 hybrids of field corn to ozone, this report.
4. Heagle, A. S., R. B. Philbeck, and W. M. Knott, Thresholds for injury, growth, and yield loss caused by ozone on field corn hybrids. Phytopathology 69, 21-26 (1979).
5. Kress, L. W. and J. E. Miller, Impact of ozone on soybean yield, Radiological and Environmental Research Division Annual Report, January-December 1980, ANL-80-115, Part III, pp. 11-14.

EVIDENCE FOR EXTREME RESISTANCE OF FIELD CORN TO INTERMITTENT SULFUR DIOXIDE STRESS

J. E. Miller, H. J. Smith and W. Prepejchal

Background and Scope

Effects of sulfur dioxide (SO_2) emissions from fossil fuel combustion and industrial processes are of concern because of their potential impact on agricultural productivity. Previous studies have established that soybeans are sensitive to SO_2 stress and that yield reductions may occur with intermittent exposure to relatively low concentrations.[1,2] Reduction of soybean yields was observed at concentrations below the current National Secondary Air Quality Standards for SO_2 and in the absence of injury symptoms.[1] Field corn (*Zea mays*) is the most economically important crop in the U.S. and is extensively grown in areas having a high density of SO_2 emission sources. Previous research has suggested that field corn may not be very sensitive to SO_2, but experiments have not previously been performed under actual growing conditions in the field. Also, even a slight effect on the total corn yield for the U.S. would be significant since it is such an important commodity.

Progress in 1981

As in previous studies with soybeans, a modified Zonal Air Pollution System (ZAPS) was used to deliver the SO_2 gas.[2] Two field corn hybrids (Pioneer 3780 and PAG 397) were planted on June 1 and exposed to SO_2 on 12 occasions (total of 36 hr) between July 15 and August 31. There were eleven SO_2 treatments with mean concentrations ranging from 0.07 to 0.67 ppm. Background SO_2 concentrations averaged <0.01 ppm.

Regular inspections of the treated plots did not reveal any symptoms of SO_2 injury, nor did the treated plots senesce more rapidly at the end of the growing season. The yield response data also indicate that the two hybrids of field corn tested are indeed resistant to SO_2 pollution (Table 1). Analysis of variance indicated no significant treatment effects, nor was a linear regression of yield as a function of SO_2 concentration significant. Visual observations of the experimental plots made prior to the initiation of SO_2

treatments indicated that the corn plants in the control plots were less vigorous than in the plots to be treated with SO_2. Because of these systematic differences the controls were not included in the data analysis. The reason for the early differences in plant vigor are not known but probably relate to differences in the fertility or drainage of the field.

Table 1. Yield of two hybrids of field corn exposed to SO_2 in the field.

SO_2 ppm	Grain yield,[a] g dry weight/plant PAG 397	Pioneer 3780
0.07	117	129
0.09	110	132
0.11	112	116
0.13	116	105
0.17	97	100
0.21	125	126
0.26	104	132
0.32	113	132
0.41	123	119
0.52	122	126
0.67	112	131
LSD[b] (5%)	30.7	40.8

[a] The values are the mean of two replicates each consisting of ~28 plants.
[b] Least significant difference.

The highest SO_2 dose given in these experiments was 24 ppm·hr. Previous experiments indicate that this dose would cause at least a 20% reduction in soybean yields.[1,2] These experiments further suggest that the dose-threshold for reductions in soybean yield is ~10 ppm·hr. Since yield reductions in corn did not occur at 24 ppm·hr (0.67 ppm for 36 hours), the threshold for yield reductions in field corn is at least two and one-half times greater than for soybeans. It is clear that field corn is exceptionally resistant to SO_2 damage.

Prospects

Based on this experiment it would seem that yield loss in field corn due to SO_2 pollution is extremely rare. Sulfur dioxide emissions have been reduced in recent years by the use of low sulfur coal, the installation of scrubbers and construction of taller stacks to aid plume dispersion. It is unusual for ground-level SO_2 concentrations in excess of 0.67 ppm to occur with any frequency. For these reasons, further research on the effects of SO_2 on field corn will not be pursued, and the work will be directed to other important crops.

References

1. Miller, J. E., H. J. Smith, and P. B. Xerikos, Variability of the yield response of field-grown soybean cultivars to SO_2, Radiological and Environmental Research Division Annual Report, January-December 1980, ANL-80-115, Part III, pp. 15-18.
2. Sprugel, D. G., J. E. Miller, R. N. Muller, H. J. Smith, and P. B. Xerikos, Sulfur dioxide effects on yield and seed quality in field-grown soybeans, Phytopathology 70, 1124-1128 (1980).

RELATIVE SENSITIVITY OF FIELD CORN HYBRIDS TO OZONE: A FIELD STUDY

J. E. Miller, W. Prepejchal and H. J. Smith

Background and Scope

Of the various air pollutants known to damage vegetation, it is believed that ozone (O_3) has the greatest impact on crop production. Unlike other gaseous air pollutants such as sulfur dioxide or fluoride which are primarily of concern near point sources, O_3 is often present in potentially damaging concentrations over extensive areas of the U.S. The midwestern and southeastern regions are of particular concern since a substantial portion of the nation's crops are produced there and O_3 concentrations are suspected to be high enough to cause damage. For example, previous studies have suggested that current levels of O_3 may be limiting the production of important commodities such as soybeans.[1] Field corn, the nation's most economically important crop, is also principally grown in the Midwest and is subjected to elevated O_3 concentrations. Limited research has suggested that field corn is very resistant to O_3. Heagle et al.[2] found that statistically significant yield reductions for Coker 16 field corn did not occur until the O_3 concentration reached 0.15 ppm (mid-day 7-hr average concentration during growing season). This concentration is more than double that normally found in the Corn Belt. However, since field corn is such an important commodity and since previous field research has been conducted on only one hybrid, it was decided that a field experiment to screen for relative O_3 sensitivity was required. The following work was conducted as a part of the Central States Regional Crop Loss Assessment Project of the National Crop Loss Assessment Network.

Progress in 1981

The technique previously used to treat field plots of crops with O_3 (i.e., open-top chambers) was thought unsuitable for a large screening experiment since it would require too many chambers to treat several hybrids with a range of O_3 concentrations. For this reason the modified Zonal Air Pollution System (ZAPS) used in studies of sulfur dioxide effects on crops was adapted for use with O_3. (See Miller et al.[3] for a discussion of the ZAPS fumigation technique.)

The fumigation system consisted of a single gas release pipe (2.5 cm diameter aluminum) installed in the field perpendicular to the prevailing southerly winds (Fig. 1). The release pipe was approximately 95 m long with 0.08 cm holes at 61 cm intervals. Ozone was generated with an OREC Model O3DV-AR O_3 generator using liquid oxygen. Air and O_3 flow through the pipe was provided by a Dietz Model SV-80 ring compressor. The feed pipe delivering the O_3-air mixture intersected the release pipe midway to minimize the pressure differential along the release pipe. The O_3 concentrations in the treated plots were sampled at the points indicated in Figure 1 by use of a time sharing system. Ozone concentrations between sampling points were estimated from curves fit to the values at the sampling points. Ozone concentrations were measured with a Dasibi Model 1003AH which was calibrated weekly with a Columbia Scientific Instrument Model 3000 Photocal O_3 calibrator.

Fourteen hybrids of field corn were planted in rows perpendicular to the O_3 release pipe on May 27-28. The row spacing was 76 cm and seeds were planted at 15 cm intervals. The experimental design consisted of four blocks with single rows of the individual hybrids randomized within each block. Since the various hybrids would tassel and silk at different times, a mixture of all 14 hybrids was planted in the areas indicated by the cross-hatched lines in Figure 1. It was hoped this would insure a good density of pollen for all the hybrids despite the difference in maturity dates. To reduce the average distance a given hybrid would be from the source of mixed pollen the blocks were divided into two 7-row sub-blocks.

Ozone fumigations were conducted between the hours of 900 to 1600 CST from June 29 to August 31 on any day that the wind direction was within the boundaries that would result in fumigation of the treated plots (the 90 degree sector from SE to SW). Fifteen treatments giving 65 total hours of fumigation were administered. An unusually frequent passage of storm systems precluded more frequent fumigations. The average O_3 concentrations across the treated plots during fumigation periods ranged from 0.370 to 0.012 ppm above the average ambient concentrations during this period, 0.053 ppm.

The plots were harvested October 26-27. Starting 1 m away from the release pipe, eight 1-m row segments were sampled. Three control row segments

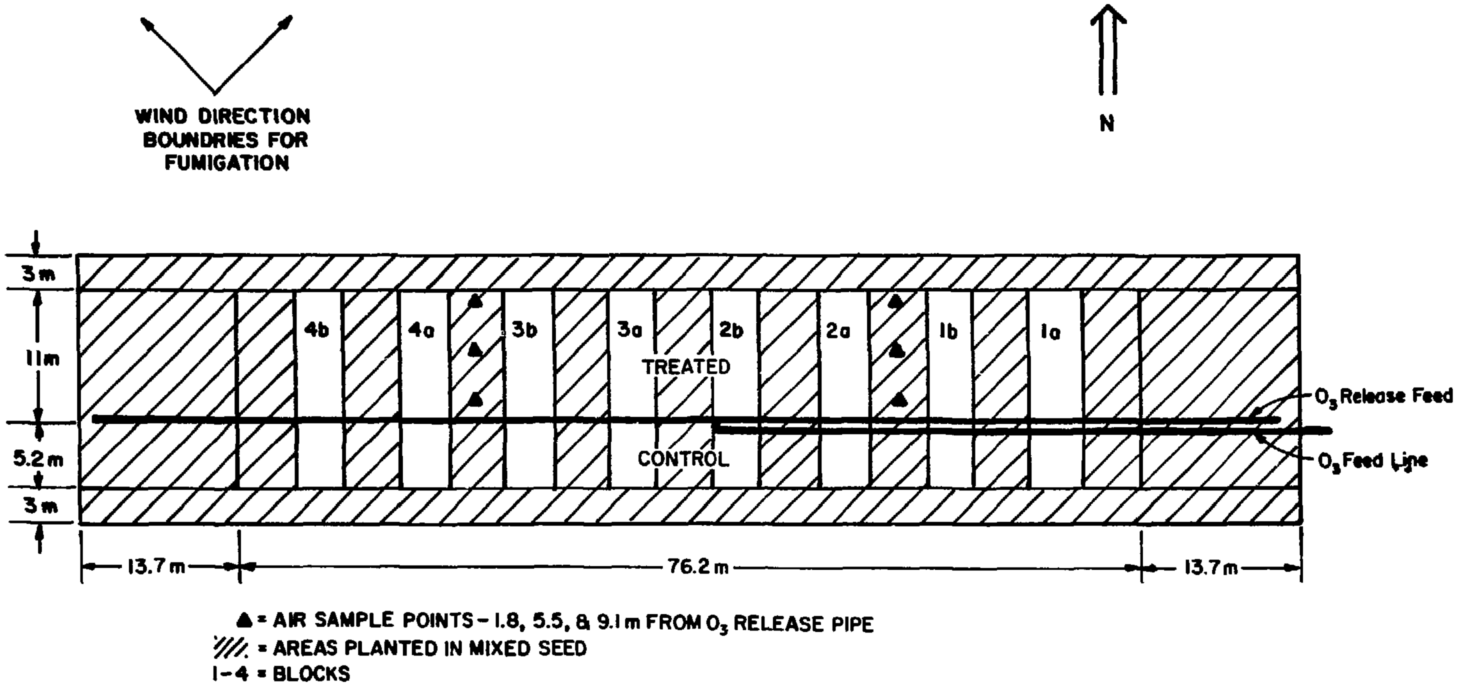

Fig. 1. Diagram of plot design for screening field corn for sensitivity to O_3.

in each row were similarly sampled upwind of the O_3 release pipe.

Analysis of variance indicated significant treatment and hybrid effects and a significant treatment-hybrid interaction. Analysis of each hybrid individually by Duncan's Multiple Mean Test illustrates that the yield of most of the hybrids was reduced only at the two highest O_3 treatments (Table 1). Since the hybrids appear to have responded differently, the data for each individual hybrid was normalized by expressing the yield from each treated plot as a percentage of its respective control. Linear regressions of yield (% of control) versus O_3 treatment concentration were generated forcing the line through 100% at the ambient (control) treatment concentration. This was done since by definition the actual relationship must pass through this point. The slope estimates of the individual regression lines for each hybrid are then an indicator of the relative sensitivity of each hybrid to the O_3 treatment (Table 2). The slopes for the individual hybrids ranged from -175 (indicating the most sensitivity) to -79 (indicating the most resistance), but the data were quite variable as indicated by the 95% confidence limits for the slopes (Table 2). Regardless, it seems clear that field corn hybrids have a range of sensitivity to O_3 stress.

The commercial corn hybrids used in this screening experiment were selected to be representative of those grown in the major corn growing regions. The other hybrids are experimental crosses between inbred lines. The inbred lines are used by seed production companies for production of commercial hybrids and the inbred lines are therefore present in commercial corn hybrids. While the experiment was not designed to study the genetic control of O_3 sensitivity, it is interesting to note that at least four of the five most sensitive hybrids have one FRMO17 parent. Three of the four most resistant hybrids have one FRB73 parent, although this line also shows up in both an intermediate and relatively sensitive hybrid. The PAG and Pioneer pedigrees are unknown since they are proprietary information, but all fell into an intermediate sensitivity range.

Prospects

This experiment illustrates that field corn hybrids vary in O_3 sensitivity but that they are relatively resistant to O_3 when compared to other crop species. Corn yields are probably not threatened by current O_3

Table 1. Yield (g/plant) of thirteen field corn hybrids treated with ozone in the field.

Sample No.[a]	Ozone concentration, ppm[b]	Hybrid identification No.												
		1	2	3	4	5	6	7	8	9	10	11	12	13
1a	0.423	62	63*	47*	74*	64*	81*	94*	75*	55*	71*	47*	50*	86*
1b	0.281	74	62*	61*	95	66*	98*	72*	91	71*	107	58*	90*	76*
2	0.203	74	95	93	112	110	116	110	132	83	116	77*	108	97*
3	0.147	72	90	105	114	120	142	122	144	76*	118	90	134	135
4	0.108	87	118	124	123	126	148	134	130	98	144	90	123	126
5	0.087	70	104	111	115	112	149	137	139	96	115	94	133	116
6	0.076	76	101	116	121	105	144	129	138	87	125	93	126	121
7	0.069	91	111	116	122	114	128	110	109	100	117	101	108	133
8	0.065	70	113	115	105	120	104*	120	117	84	130	95	109	126
c	0.053	89	121	127	122	121	150	122	127	103	137	93	139	144

[a] Each sample (except 1a, 1b, and c) is the mean of four 1-m row segments expressed as g of grain/plant. The 1a and 1b samples are one-half m row segments and c (control) is the mean of three 1-m row segments.

[b] Mean concentrations during 15 treatments totalling 65 hr. The ozone concentration for sample c (control) is the ambient concentration during treatment periods.

*Significantly different from the control at the 5% level by Duncan's Multiple Mean Test.

Table 2. Ranking of apparent field corn hybrid sensitivity to ozone.[a]

Sensitivity ranking	Hybrid I.D.	Pedigree[b] female x male	Slope estimate	PR > T	95% Confidence limits for slope	
					Upper	Lower
1	3	FRMO17 x FR634	-175	0.0001	-130	-220
2	2	FRMO17 x FR19	-157	0.0001	-122	-192
3	12	FRB73 x FRMO17	-157	0.0001	-110	-204
4	13	(PAG 397)	-147	0.0001	-110	-184
5	6	FRMO17 x H100	-133	0.0001	-92	-174
6	9	(Pioneer 3780)	-132	0.0001	-97	-167
7	5	FRB73 x FR19	-130	0.0001	-97	-163
8	11	(Pioneer 3901)	-130	0.0001	-100	-160
9	10	(Pioneer 3541)	-119	0.0001	-86	-152
10	4	FRB73 x MS71	-94	0.0001	-52	-136
11	1	FR19 x W117	-86	0.0001	-46	-126
12	7	FRB73 x FR16	-81	0.0004	-40	-122
13	8	FRB73 x PA91	-79	0.0128	-18	-140

[a] Sensitivity ranking is based on linear regressions of yield (expressed as a percent of the control) as a function of ozone concentration during treatment. The more negative the slopes the greater the ozone sensitivity.

[b] Pedigrees for the commercial hybrids in parentheses are not available.

concentrations in the Corn Belt, nor will they be unless O_3 levels dramatically increase. This is confirmed by another experiment in this report.[4] For these reasons future experiments will address other important crop species.

References

1. Kress, L. W. and J. E. Miller, Impact of ozone on soybean yield, Radiological and Environmental Research Division Annual Report, January-December 1980, ANL-80-115, Part III, pp. 11-14.
2. Heagle, A. S., R. B. Philbeck and W. M. Knott, Thresholds for injury, growth, and yield loss caused by ozone on field corn hybrids, Phytopathology 69, 21-26 (1979).
3. Miller, J. E., D. G. Sprugel, R. N. Muller, H. , Smith and P. B. Xerikos, Open-air fumigation system for investigating sulfur dioxide effects on crops, Phytopathology 70, 1124-1128 (1980).
4. Kress, L. W. and J. E. Miller, Impact of ozone on yield of field corn, this report.

$^{239,240}Pu$, ^{241}Am, and $^{243,244}Cm$ IN A CORE FROM THE SAGUENAY FJORD, QUEBEC

D. M. Nelson, J. O. Karttunen, D. N. Metta and K. A. Orlandini

Background and Scope

It is well known that plutonium transfers rapidly from water into sediments in many natural systems. However, there is disagreement as to its fate once it has moved into the sediments. Indeed, it has been suggested[1] that a substantial loss of both plutonium and americium has occurred from shallow water sediments along the east coast of North America. It has been our view that plutonium and americium on sediments are very strongly bound and that any loss back to the water would involve a very small fraction of the sediment inventory.

To assess the stability of plutonium within sediments, we have analyzed a set of sediment core samples from the Saguenay Fjord, Quebec. This is a unique experimental area in that the sedimentation rate is high, the post-depositional mixing is low, and there is a clear stratographic record in the sediments. Dr. John Smith of Bedford Institute of Oceanography (Canada), who furnished the samples, has characterized the depositional regime in the area[2] and has proposed a model[3] to describe the distribution of ^{137}Cs and ^{210}Pb within the sediments. A comparison of the ^{239}Pu distribution with those of ^{137}Cs and ^{210}Pb as well as with the known ^{239}Pu input function should provide information about any changes in plutonium distribution which may have occurred with time.

In addition, the data obtained can be used to improve the estimate of the atmospheric input function for plutonium prior to the early 1960's. This can be accomplished by establishing the relationship between plutonium input from the atmosphere and yearly deposition on the sediments within the upper part of the core. Plutonium concentrations in the lower part of the core can then be used to estimate the atmospheric input in the years before direct measurements were made.

Progress in 1981

Plutonium analyses have been completed on a core from station D-1, which is located at the head of the Fjord in 87 m of water. The core was sliced into 1 cm thick segments, and 100 of these were analyzed individually. This covered the period 1947 to 1980. The results of these analyses are presented in Figure 1 along with the ^{238}Pu to $^{239,240}Pu$ ratios where the ^{238}Pu could be measured.

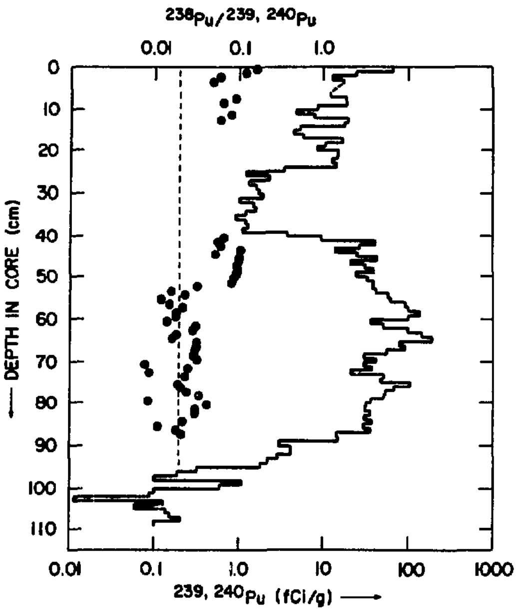

Fig. 1. $^{239,240}Pu$ concentrations and $^{238}Pu/^{239,240}Pu$ concentration ratios (●) in a sediment core from the Saguenay Fjord.

The total plutonium inventory in this core approaches 2 pCi/cm^2, approximately 10 times higher than the atmospheric deposition in the area. Thus most of the plutonium in this core was transported from elsewhere in the system to the head of the Fjord where it has accumulated. The sediment accumulation rate at this location is 2 to 3 cm/yr as measured by the ^{210}Pb decrease with depth. The primary sediment source for the Fjord is the Saguenay River.

Several prominent features of the plutonium profile can be used to fix dates independently within the core. The broad minimum between 25 and 40 cm corresponds to a landslide in 1971 on a tributary of the Saguenay River. Some of this material, which was very low in ^{239,240}Pu content, was then transported into the Fjord where it subsequently deposited. The concentrations of ^{137}Cs and ^{210}Pb in the 25 to 40 cm band are correspondingly low. The pronounced increase in concentration between 85 and 95 cm corresponds to the first period of extensive weapons testing between 1952 and 1955. The peak at 65 cm corresponds to the years of maximum inputs, 1963-1964. The arrival at ground level of debris from the burnup of the SNAP-9A device (1967) can be easily seen in the abrupt change in ^{238}Pu:^{239,240}Pu ratio at 52 cm.

In addition to those concentration changes resulting from changes in atmospheric deposition, other variations can be related to the flow characteristics of the Saguenay River. For example, the low concentrations at 11, 15, 44 and 60 cm correspond to high river flows recorded during 1974, 1972, 1970 and 1964. The assumed mechanism involves a greater removal of low activity particles from the watershed during high flow periods and hence a dilution of the deposited activity.

Several distributional features within this core can be used to demonstrate the absence of plutonium mobility within the sediments. The most unequivocal is the abrupt change in ^{238}Pu to ^{239,240}Pu ratio at 52 cm. Any movement of plutonium in either direction would have obliterated this sharp change and smeared the distribution. Similarly the precipitous decrease in plutonium concentration above 40 cm could not have been maintained if plutonium were mobile in the sediments.

The values of the ^{239,240}Pu to ^{137}Cs ratio within this core show a distinct pattern with depth. Ratios as high as 0.03 are observed for material deposited during the mid-1950's (~85 cm), decreasing to about 0.01 by 1970. This pattern is in general agreement with observations of ^{239,240}Pu to ^{137}Cs ratios at different depths in an Antarctic glacier.[4] Since the inputs of ^{239,240}Pu to the northern hemisphere are frequently estimated using the known inputs of ^{137}Cs (or ^{90}Sr), a systematic change in this ratio could affect the estimates of ^{239,240}Pu deposition during the 1950's and early 1960's.

Measurements of other transuranic elements within this core can be used to clarify the estimates of their inputs. ^{241}Am, which is produced by the decay of ^{241}Pu, was measured at several locations within the core. The ratio of ^{241}Am to ^{239,240}Pu was 0.19 to 0.29 in segments corresponding to deposition during the late 1970's, the early 1960's and the late 1950's. However, ratios as high as 0.58 were observed in material corresponding to deposition in the mid 1950's. This is consistent with the high ratios of ^{241}Pu to ^{239,240}Pu observed in glacial ice formed at this time[5] and with the known high production of heavy actinides in the "Mike" device tested in November of 1952.[6]

Recently, it has been suggested[7] that ^{243,244}Cm was present in weapons debris prior to 1961 (based on measurements of ^{243,244}Cm in sediments of the Columbia River). Ratios of ^{243,244}Cm to ^{241}Am as high as 0.1 were reported. We have looked for ^{243,244}Cm in the sediments of the Saguenay core and have found the ^{243,244}Cm to ^{241}Am ratio to be <0.01 at all depths. We therefore conclude that the ^{243,244}Cm found in the Columbia River systems comes from a source other than fallout, most likely the operation of the reactors at Hanford.

Prospects

We feel that the well-resolved, undisturbed record of sediment accumulation in the Saguenay Fjord makes it a valuable area in which to test models of the transport and accumulation of reactive pollutants attached to particles. Smith's model, used to describe ^{137}Cs dynamics in the watershed, will be applied to plutonium and, if necessary, modified.

References

1. Livingston, H. D. and V. T. Bowen, Plutonium and ^{137}Cs in coastal sediments, Earth Planet. Sci. Lett. 43, 29-45 (1979).
2. Smith, J. N. and A. Walton, Sediment accumulation rates and geochronologies measured in the Saguenay Fjord using the Pb-210 dating method, Geochim. Cosmochim. Acta 44, 225-240 (1979).
3. Smith, J. N. and K. Ellis, Transport mechanism for Cs-137 to estuarine sediments, Impacts of Radioactive Releases into the Marine Environments, IAEA, Vienna, pp. 119-130 (1981).
4. Koide, M., R. Michel, E. D. Goldberg, M. M. Herron and C. A. Langway, Jr., Depositional history of artificial radionuclides in the Ross ice shelf, Antarctica, Earth Planet. Sci. Lett. 44, 205-223 (1979).
5. Koide, M. and E. D. Goldberg, ^{241}Am/^{239,240}Pu ratios in Polar glaciers,

Earth Planet. Sci. Lett. 54, 239-247 (1981).

6. Diamond, H. et al., Heavy isotope abundances in Mike thermonuclear device, Phys. Rev. 119, 2000-2004 (1960).

7. Beasley, T. M. and L. A. Ball, ^{243,244}Cm in Columbia River sediments, Nature 287, 524-625 (1980).

RATE OF REMOVAL OF NATURAL THORIUM ISOTOPES FROM LAKE MICHIGAN WATER

D. M. Nelson and D. N. Metta

Background and Scope

The rate at which thorium is removed from ocean water has been determined[1-3] using the extent of disequilibrium that exists between the radioactive nuclides ^{238}U, ^{228}Ra and ^{234}U and their thorium daughters ^{234}Th, ^{228}Th and ^{230}Th. The method depends upon the fact that the precursor isotopes of thorium are relatively soluble and are, therefore, present at appreciable concentrations. The thorium isotopes formed by decay are removed by both radioactive decay and sedimentation. The amount of thorium remaining in the water is controlled by the balance between these competing processes. Since the rate of radioactive decay is known, this balance is a direct measure of the rate of removal by sedimentation.

The thorium removal rates can then be used to estimate the rates at which the particles, to which the thorium is attached, are removed. Particle removal rates can in turn be used to estimate rates of removal of plutonium and other pollutants that react with particles. For example, this technique can be used to estimate plutonium removal rates in the Great Lakes, if the thorium isotopes and their precursers are measurable and if the degree to which plutonium behavior mimics thorium behavior is known.

Progress in 1981

In order to assess the utility of this method in the Great Lakes, a set of samples was collected from Lake Michigan on 1 September 1981. The sampling location was 30 km northeast of Chicago. The water depth was 60 m, and a sharp thermocline existed just above 20 m.

The concentrations of ^{234}Th, ^{228}Th, ^{230}Th and ^{232}Th were determined in triplicate 50-L samples collected at depths of 15, 35, 45 and 55 m. Each sample was filtered through a 0.45 μm membrane filter, and both the water and filters were analyzed. Thorium was isolated by coprecipitation with $Fe(OH)_3$, purified by nitric acid-anion exchange and electrodeposited onto stainless steel discs. Chemical recoveries were monitored using ^{229}Th as the isotopic diluent. The alpha emitting thorium isotopes (228, 229, 230 and 232) were assayed using silicon surface barrier detectors. The beta emitting isotope (234) was assayed in a low background (<0.5 cpm) flow proportional counter at various times after deposition over a two-month period.

Results of these analyses (Table 1) show that all four of the natural thorium isotopes were present at measurable concentrations on the particulate material. None of the isotopes was detectable in the filtered water. Concentration on the suspended particulate matter exceed 10^7 mL/g for thorium — even for the short-lived ^{234}Th. (This shows that the half-time for thorium transfer from water to particles is less than a few days.)

The precision in determining the alpha emitting nuclides is limited primarily by counting statistics, since counter backgrounds are very low (~0.001 cpm). The uncertainty is simply a function of sample size, chemical recovery and counting time. Counting errors for these nuclides were typically 5 to 20%. The precision in determining the ^{234}Th concentration includes these factors as well as uncertainties associated with slight fluctuations in the background of the counter and differences in the degree of decontamination from other beta emitting nuclides in the sample. These uncertainties in measuring ^{234}Th are more difficult to deduce than for the other isotopes but can be estimated by considering the dissolved fractions at all depths (including the blanks) to be replicates from a single population. Here the mean is 2 ± 9 fCi/L (one standard deviation). This uncertainty seems consistent with the scatter among the triplicate samples of particulates and is probably a reasonable estimate of the analytical error.

The concentrations of the three isotopes produced by decay in the water column are all less than the concentrations of their parents. In Lake Michigan the concentrations of ^{238}U, ^{228}Ra and ^{234}U are 92, ~10 and 105 fCi/L, respectively. In theory each of these isotopes could be used to estimate thorium removal rates. In practice only ^{234}Th and ^{228}Th are usable in Lake Michigan, since the in situ production of ^{230}Th is so low in comparison with the removal rate that the concentration on the particles is dominated by the concentration existing at the time of their introduction into the water.

The relationship between chemical removal half-life τ_C, parent isotope activity, A_P, thorium isotope activity, A_T, and radioactive half-life of the thorium isotope, τ_T, has been shown[2] to be

Table 1. Concentrations (fCi/L) of ^{228}Th, ^{230}Th ^{232}Th and ^{234}Th in Lake Michigan water, in suspended sediments, SS (>0.45 μm), and filtered water, FW (<0.45 μm), at various water depths.

Water depth and replicate No.	^{228}Th		^{230}Th		^{232}Th		^{234}Th	
	FW	SS	FW	SS	FW	SS	FW	SS
15 m #1	0.13	0.44	0.03	0.13	0.03	0.06	-3	16
#2	0.13	0.39	0.01	0.11	0.02	0.05	-2	14
#3	0.24	0.38	0.10	0.13	0.02	0.05	-4	9
Average	0.17	0.40	0.05	0.12	0.02	0.05	-3	13
Net[a]	0.02	0.31	0.01	0.11	0.01	0.04	-3	12
35 m #1	0.30	0.70	0.15	0.14	0.07	0.10	10	51
#2	0.11	0.75	0.01	0.18	0.02	0.13	-4	52
#3	0.19	0.84	0.03	0.19	0.02	0.12	16	61
Average	0.20	0.76	0.06	0.17	0.04	0.12	7	55
Net[a]	0.05	0.67	0.02	0.16	0.03	0.11	7	54
45 m #1	0.13	1.18	0.07	0.27	0.02	0.17	0	90
#2	0.13	1.11	0.02	0.22	0.01	0.18	14	83
#3	0.24	0.94	0.04	0.25	0.02	0.20	9	46
Average	0.17	1.08	0.04	0.25	0.02	0.18	8	73
Net[a]	0.02	0.99	0.00	0.24	0.01	0.17	8	72
55 m #1	0.21	1.34	0.02	0.53	0.01	0.41	2	65
#2	0.08	1.36	0.01	0.50	0.00	0.39	-5	53
#3	0.35	1.28	1.35[b]	0.46	0.08	0.35	-11	50
Average	0.21	1.33	0.02	0.50	0.03	0.38	-5	56
Net[a]	0.06	1.24	0.02	0.49	0.02	0.37	-5	55
Blank #1	0.21	0.07	0.05	0.01	0.01	0.01	9	-4
#2	--	0.09	--	0.01	--	0.01	--	1
#3	0.08	0.12	0.02	0.01	0.01	0.01	-9	6
Average	0.15	0.09	0.04	0.01	0.01	0.01	0	1

[a] Average value less average blank.
[b] Not used in average.

$$\tau_C = \tau_T \frac{A_T}{A_P} \left(1 - \frac{A_T}{A_P}\right)^{-1} .$$

A graph of this function for ^{234}Th (τ_T = 24 days) and ^{228}Th (τ_T = 697 days) is presented in Figure 1.

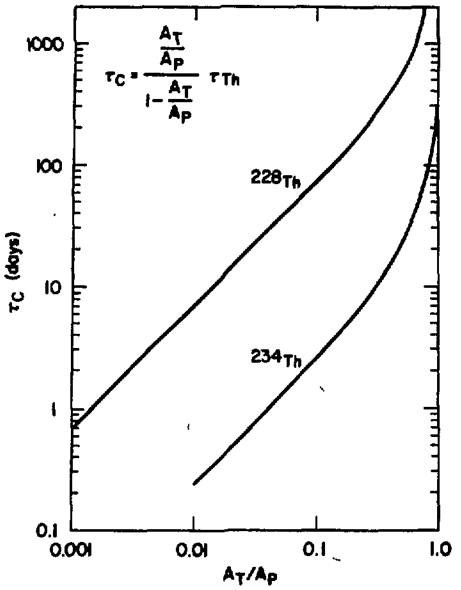

Fig. 1. Relationship between thorium removal rate from natural water (by sediment adsorption) and radiogenic thorium to parent-nuclide activity ratio.

Thorium removal rates below the thermocline can be calculated using this relationship and the data in Table 1 if the data from the bottom 3 depths are averaged. For ^{234}Th, where A_T is 60 fCi/L and A_T/A_P is 0.66, τ_C is 45 days. For ^{228}Th, where A_T is 0.97 fCi/L and A_T/A_P is 0.097, τ_C is 75 days. This rather large difference between the removal rates of the two thorium isotopes can be reduced if the concentration of ^{228}Th supported by ^{232}Th within the particles is taken into consideration. In the underlying sediments the ^{228}Th to ^{232}Th ratio is ~1.0 and hence a concentration of ^{228}Th equal to the ^{232}Th concentration must be subtracted from the measured value of ^{228}Th in each sample. After this correction, A_T is 0.75 fCi/L, A_T/A_P is 0.075, and τ_C is 55 days.

Removal rates above the thermocline can be calculated in a similar manner and show removal half-times of 3.5 and 20 days for ^{234}Th and ^{228}Th, respectively. We believe the difference in these rates is due to the presence of small, slowly settling particles which remain in the epilimnion throughout the period of stratification. This view is supported by the fact that appreciable concentrations of ^{230}Th and ^{232}Th remain above the thermocline. Since the inputs of ^{230}Th and ^{232}Th from fallout and radioactive decay are negligible, the most plausible explanation for their presence is a population of slowly removed particles. A corrected removal rate of freshly introduced ^{228}Th can therefore be calculated if the ^{228}Th concentration on these slowly settling particles is subtracted from the total ^{228}Th concentration. This ^{228}Th background can be estimated by assuming the ^{228}Th to ^{232}Th ratio on particles in surface waters before stratification was equal to the ratio observed just below the thermocline. Using a corrected value of 0.06 for A_T ($0.31 - 0.67/0.11 \times 0.04$), the corrected value for τ_C is 4 days, not significantly different from the ^{234}Th result.

The thorium removal half-times can be used to calculate removal half-times of other substances reacting with particles and having similar distribution patterns on particles. Plutonium appears to meet this criterion since the adsorbed form, Pu(IV), is a close chemical analog of Th(IV). However, because of the presence of unadsorbed Pu(V), only 20% of the plutonium in the water column of Lake Michigan is typically associated with particles. Since 100% of the thorium is on particles, the plutonium removal times would therefore be expected to be 5 times as long as those of thorium. Thus, removal half-times for plutonium above and below the thermocline are estimated to be 20 and 250 days, respectively, during this late summer period. While a complete understanding of plutonium removal kinetics would require measurements at various locations throughout the year, these plutonium removal rates are not inconsistent with any of the observations in Lake Michigan over the past decade.

Prospects

We have shown this method to be a practical way of establishing the rate at which plutonium is removed from Lake Michigan and probably many other large lakes. In many of these lakes the concentration of plutonium in the water appears to be related to (controlled by) the concentration in the surficial sediments, implying that a return of plutonium from the sediments to the water must be considered. The concentration of plutonium in the water is, therefore, determined by the balance between loss to the sediments and remobilization. Hence, this independent method of estimating removal rates will allow estimates to be made of the rate of remobilization.

References

1. Matsumoto, E., ^{234}Th-^{238}U radioactive disequilibrium in the surface layer of the ocean, Geochim. Cosmochim. Acta 39, 205-212 (1975).
2. Broecker, W. S., A. Kaufman and R. M. Trier, The residence time of thorium in surface sea water and its implications regarding the rate of reactive pollutants, Earth Planet. Sci. Lett. 20, 35-44 (1973).
3. Nozaki, Y., Y. Horibe and H. Tsubota, The water column distributions of thorium isotopes in the western North Pacific, Earth Planet. Sci. Lett. 54, 203-206 (1981).

INFLUENCE OF COLLOIDAL DISSOLVED ORGANIC CARBON (DOC) ON THE SORPTION OF PLUTONIUM ON NATURAL SEDIMENTS

D. M. Nelson, J. O. Karttunen and P. Mehlhoff*

Background and Scope

Last year we demonstrated that dissolved organic carbon (DOC) plays an important role in determining the concentration of dissolved plutonium in many natural waters.[1] A strong, inverse correlation was observed between the concentration of DOC and the concentration ratio (K_D) of Pu(IV) in a number of natural waters (K_D = concentration of Pu(IV) in suspended solids divided by the concentration of Pu(IV) in the water). In addition, laboratory experiments in which concentrations of natural colloidal-sized DOC were varied in a controlled manner showed a clear response of K_D to changing DOC. The relationship between K_D and DOC concentration was assumed to result from the operation of two competitive equilibria, one between uncomplexed Pu(IV) and the solid adsorber, and the other between uncomplexed Pu(IV) and the colloidal organic compounds.

It now appears possible to formulate a practical model to describe the absorption of Pu(IV) by suspended solids. In such a model the constants describing the association of plutonium with both soluble organics and solid adsorbers must be known, as well as any variation in these constants due to solution properties such as pH and ionic strength. If the complexing ability of DOC is sufficiently constant, such a model could describe plutonium behavior in a wide variety of surface and ground waters. Our observations to date indicate that the variation in K_D among water bodies is due primarily to differences in water chemistry and that differences in the character of the adsorbing solid are less important.

Progress in 1981

The response of K_D to varying concentrations of natural DOC has now been determined for nine water bodies using the laboratory equilibration technique

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described in last year's report.[1] For these equilibrations we have used a fine-grained sediment collected from an abandoned canal near the Mound Laboratory, Ohio. These data were fitted to the equation

$$\frac{1}{K_D} = \frac{1}{K_D^{\circ}} + \frac{K}{K_3} (\mathrm{DOC})^n \ , \tag{1}$$

which is a simple algebraic rearrangement of the equation proposed last year. In this equation K_D has units of $L \cdot kg^{-1}$, DOC has units of $kg \cdot L^{-1}$, (ppm x 10^{-6}), n is the number of organic ligands per plutonium atom in the soluble complex, K_D° is the concentration ratio at zero DOC concentration, and K and K_3 are conditional formation constants describing the association of plutonium with the complexing ligand and the solid adsorber, respectively. This relationship adequately described the adsorption of Pu(IV) to Mound sediment in each water studied over a range of DOC concentrations from zero to several hundred ppm. For some waters, however, the estimated value of n was a non-integer with a value between 1 and 2, an unlikely result since it implies a fractional number of ligands per plutonium atom in the complex. A more reasonable explanation is that two complexes are formed, one with one ligand per plutonium atom, and the other with two ligands. Consequently, the form of Eq. 1 has been changed to

$$\frac{1}{K_D} = \frac{1}{K_D^{\circ}} + \frac{K_1}{K_3} (\mathrm{DOC}) + \frac{K_2}{K_3} (\mathrm{DOC})^2 \ , \tag{2}$$

where K_1 and K_2 are conditional formation constants for the 1:1 and 2:1 complexes, respectively.

The reciprocal of K_D is used since it is a normalized concentration, i.e., concentration in the water per unit concentration on the solids. When written in this form the equation emphasizes the fact that the dissolved plutonium concentration is composed of three components. The first term represents solubility attributed to the uncomplexed ions and all low molecular weight inorganic and organic complexes. The second and third terms represent solubility contributions of the 1:1 and 2:1 complexes.

The absolute values of K_1, K_2, and K_3 cannot be deduced from these experiments. However, since aliquots of the same sediment were used in all experiments, the value of K_3 should be the same in each experiment. The relative complexing power of the colloidal DOC from two bodies of water can therefore be compared by comparing the values of K_1/K_3 and K_2/K_3 for the two waters.

The data from the nine equilibration experiments (8 data points per experiment) were fitted to Eq. 2 using a least squares curve fitting technique to estimate values for the parameters $1/K_D^\circ$, K_1/K_3, and K_2/K_3. These estimates are presented in Table 1 along with estimates of the standard error for each (expressed as percent).

Table 1. Concentration and formation constant ratios.

	$1/K_D^\circ \times 10^6$[a]	K_1/K_3[b]	K_2/K_3[c]
Okeefenokee Swamp	0.35 (40)	3.85 (9)	-0.002 (90)
Volo Bog	2.3 (14)	2.94 (13)	0.003 (50)
Banks Lake	0.98 (16)	0.56 (15)	0.001 (40)
Argonne Pond	0.80 (12)	0.43 (30)	0.027 (5)
Saganashkee Slough	0.72 (12)	0.42 (30)	0.023 (24)
Bay of Fundy	0.85 (15)	0.35 (30)	0.012 (60)
ELA Lake 239	0.81 (11)	0.20 (60)	0.048 (20)
Gulf of Mexico	0.38 (13)	0.16 (30)	-0.002 (110)
Lake Michigan	0.26 (10)	0.03 (40)	0.001 (24)

[a] Units of kg sediment$\cdot L^{-1}$ solution.
[b] Units of kg sediment$\cdot kg^{-1}$ DOC.
[c] Units of kg sediment$\cdot kg^{-2}$ DOC$\cdot$L solution.

The values of K_D° for all of these water samples were very high ($\approx 10^6$), indicating that in the absence of colloidal-sized organic ligands (those having molecular weight >1000 Dalton), Pu(IV) would be efficiently removed from each system due to adsorption onto solids. We have measured the ambient K_D of Pu(IV) in the Irish Sea, the Bay of Fundy and Lake Michigan (all systems having low concentrations of DOC), and have found the values to be in the range of 1 to 4 x 10^6. The excellent agreement between field K_D and laboratory K_D° convinces us that our laboratory procedures produce results which are directly applicable to the field. No significant effect of pH on K_D° was observed for waters which ranged from a pH of 4 (Okeefenokee Swamp) to a pH of 8 (Lake Michigan). In addition, there was no effect of ionic strength on K_D° for waters which ranged in composition from that of the oceans to that of very "dilute" lakes (conductivity <20 μS/cm).

The nine water bodies can be divided into three categories based upon the values of the K_1/K_3 ratio. For the first category, Okeefenokee Swamp and Volo Bog, the value of K_1/K_3 was ~3. This means that in a volume of water containing equal weights of the colloidal DOC and Mound sediment (e.g., a liter of water that has 10 ppm DOC and is in equilibrium with 10 mg of sediment), three times as much plutonium would be in solution bound to the DOC as was adsorbed on the sediment. For the second category, consisting of small lakes and two samples of coastal seawater, the DOC forms somewhat weaker complexes with K_1/K_3 ranging from 0.16 to 0.56. For the third category, Lake Michigan, the organic complexes are much weaker with K_1/K_3 equal to 0.03. The effect of these differences in ability to form 1:1 complexes can be illustrated by considering a water of typical K_D° (~10^6) and having 10 ppm of DOC from each of these three categories. Substitution of typical values of K_1/K_3 for each category of water in Eq. 2 shows that the K_D would be reduced by a factor of ~30 for category 1 water, a factor of 3 for category 2 waters, and only a factor of 1.3 for category 3 waters.

The effect of pH on K_1/K_3 was investigated in experiments using natural organic matter from two of these waters. When the pH of Okeefenokee Swamp water was raised to 8 from its ambient value of 4, the value of K_1/K_3 decreased from 3.85 to 0.46. When the pH of ELA Lake 239 water was lowered to 4 from its ambient value of 7, the value of K_1/K_3 increased from 0.20 to 3.63. Acidity clearly influenced the competitive equilibria between Pu(IV), Mound sediment, and the natural organic matter in these two waters, with the 1:1 organic complexes being relatively more important at the lower pH's.

The estimates of K_2/K_3 suggest that the DOC in four of the water bodies, all from category 2, forms 2:1 complexes with Pu(IV) with the values of K_2/K_3 being between 0.01 and 0.05. In these waters the complexation of Pu(IV) due to the 2:1 complex exceeds that due to the 1:1 complex when the DOC concentration exceeds ~10 ppm. At higher DOC concentrations, this complexation increases as the square of the DOC concentration. For the other five waters, the value of K_2/K_3 is a factor of ten lower, suggesting that 2:1 complexes are unimportant in these waters at ambient DOC concentrations.

The value of K_2/K_3, like that of K_1/K_3, appears to be dependent upon pH;

but with increasing pH, the value of K_2/K_3 increases, while K_1/K_3 decreases. When the pH of water from Okeefenokee Swamp was increased from 4 to 8, K_2/K_3 increased from <0.002 to 0.59. When the pH of water from ELA Lake 239 was lowered from 7 to 4, K_2/K_3 decreased from 0.048 to <0.001.

Since an increase in pH apparently causes a decrease in K_1 and an increase in K_2, the effects that these changes have on the concentration ratio offset each other at moderate DOC concentrations. The principal effect of a pH change is to alter the type of complex ion formed, with only minor changes in the concentration ratio.

Prospects

The mathematical relationship and parameter values presented in this report adequately describe the adsorption of Pu(IV) on one specific sediment. Variations in K_D due to sediment type (i.e., varying K_3) must be investigated now that the general dependence on DOC is understood. In addition to the soluble organic complexes of Pu(IV), many of these waters have Pu(V) concentrations comparable to or higher than those of the Pu(IV) complexes. The total plutonium concentration is dependent on both the K_D of Pu(IV) and the ratio of Pu(V) to Pu(IV). The concentration of Pu(V) seems to be inversely related to the DOC concentration. There is a need for a better understanding of this relationship.

Reference

1. Nelson, D. M., J. O. Karttunen, K. A. Orlandini, and R. P. Larsen, Influence of dissolved organic carbon on the sorption of plutonium to natural sediment, Radiological and Environmental Research Division Annual Report, January-December 1980, ANL-80-115, Part III, p. 19.

OBSERVATIONS ON THE BEHAVIOR OF AMERICIUM IN NATURAL WATERS

K. A. Orlandini

Background and Scope

The increasing amounts of americium and curium produced by the nuclear industry have raised the potential for environmental contamination.[1] Consequently there is a need to describe the geochemical behavior of these toxic elements. Useful information can be gained by studying the americium already deposited in the environment as a result of weapon tests. Fallout-derived americium can be measured in a variety of natural materials in spite of its very low levels.

A preceding report[2] in this series presented a brief survey of americium concentrations in selected soils, surface waters, and their underlying sediments. The present report describes the geochemical behavior of americium under different sets of limnological conditions in north, temperate zone surface waters. The data gathered during this study indicate that the factors controlling americium concentration in fresh waters include uptake by suspended particulate matter and solubilization because of dissolved organic carbon (DOC).

Progress in 1981

Sampling techniques and limnological characterizations of the surface waters studied were given in a recent report comparing the geochemical behaviors of plutonium, thorium, and uranium.[3]

Americium was isolated from other actinides with ion exchange and solvent extraction techniques. From the measured americium concentrations in the suspended matter and in the dissolved phase a distribution coefficient (K_{dF})* was calculated and plotted against various limnological parameters including lake flushing time, pH, conductivity, alkalinity, concentration of suspended solids and dissolved organic carbon. The distribution coefficient for americium was found to be a function of the dissolved organic carbon content

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*K_{dF} = the ratio of the americium concentration in the <35 to >0.45 μm suspended particulates (dried) to that in the water.

of the water. Except for a possible correlation with high alkalinity values (e.g., >300 mg/L $CaCO_3$), no significant correlation was found with any of the other limnological parameters measured. The relationship is shown in Figure 1. Distribution coefficients of quadrivalent plutonium are included for comparison.

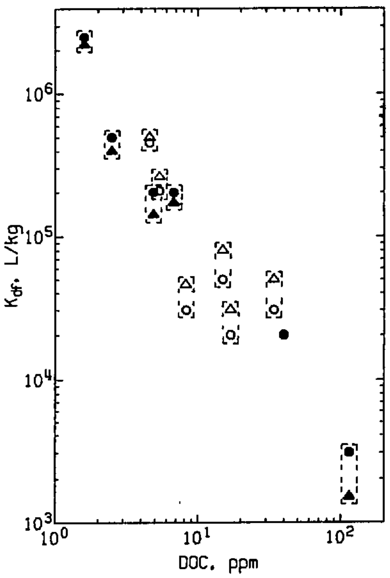

Fig. 1. Relationship of the K_{dF} for $^{241}Am(III)$ or $^{239,240}Pu(IV)$ to the concentration of dissolved organic carbon (DOC). Solid points refer to lake water with >40 mg/L $CaCO_3$ alkalinity. Open points refer to <40 mg/L $CaCO_3$ alkalinity; O and ●, Pu(IV); Δ and ▲, Am(III). Pairs of points within brackets are for the same lake.

Several observations can be made about the behavior of americium in the surface waters studied: (1) The distribution coefficient of americium is inversely proportional to the DOC concentration, and (2) the distribution coefficient for trivalent americium is, in general, not much different from that of quadrivalent plutonium. A consequence of the first observation is an increase in the solubility of americium with increasing DOC concentration. Because the values of the distribution ratios of americium and tetravalent plutonium are comparable over a range of DOC concentrations, it is possible that the americium, like plutonium, is in the tetravalent state. However, some of the waters in which this relationship exists are known to be chemically reducing in nature, particularly when the DOC concentration is greater than 5 ppm. This suggests that the americium is trivalent, rather than tetravalent, since it would be expected that Am(IV) would be reduced to Am(III).

In waters having alkalinity values <40 mg/L $CaCO_3$ and DOC values above 5 ppm, there is an indication that the americium distribution coefficient is greater than that of tetravalent plutonium. (The value of the ^{241}Am to ^{239,240}Pu activity ratio in the suspended particulates from these low alkalinity-high DOC waters ranges from 0.3 to 0.5.) For those waters having alkalinity values above 40 mg/L $CaCO_3$, the americium distribution coefficients tend to be equal to or less than those for tetravalent plutonium (Fig. 1). A similar, but inverted relationship was observed between the distribution coefficients of tetravalent plutonium and thorium occurring in the water bodies investigated.[3]

Prospects

Further studies of the geochemical behavior of americium will include an effort to describe the size and charge species associated with this actinide in its movement through natural waters both surficial and underground.

Some effort will be made to establish the concentration of fallout derived ^{243,244}Cm in natural sediments. Analysis of sediments from Lake Michigan and a sediment core from the Saguenay Fjord covering the period 1950 to 1981 shows that the ^{243,244}Cm concentrations in these materials are less than 0.5% of the ^{241}Am concentrations.

References

1. Thomas, C. W. and R. W. Perkins, U.S. DOE Health and Safety Laboratory Environmental Quarterly, HASL-291, I-87 (1 April 1975).
2. Orlandini, K. A., Americium in freshwater systems, Radiological and Environmental Research Division Annual Report, January-December1979, ANL-79-65, Part III, pp. 64-66.
3. Wahlgren, M. A. and K. A. Orlandini, Comparison of the geochemical behavior of plutonium, thorium and uranium in selected North American

lakes, Migration in the Terrestrial Environment of Long-Lived Radionuclides from the Nuclear Fuel Cycle, Proc. IAEA Symp., Knoxville, Tennessee, IAEA-SM-257-89, pp. 757-774 (1981).

OBSERVATIONS OF NEAR-BOTTOM CURRENTS AND SEDIMENT RESUSPENSION IN SOUTHERN LAKE MICHIGAN

B. M. Lesht, A. K. Barth* and N. Hawley†

Background and Scope

Although lacustrine sediment particles are understood to be carriers of many types of pollutants, very little is known about the processes that control the transportation and distribution of sediments in the Great Lakes. Fundamental problems, such as defining the chemical and physical pathways by which sediments pass from their point of entrance into the lakes to their point of deposition, are just beginning to be studied. Our work is concentrated on defining the physical processes that result in sediment transportation and remobilization in the water column. As a first step we are conducting a series of exploratory field experiments designed to determine the relationship between lake currents, resuspension of bottom sediments and meteorological forcing conditions.

Progress in 1981

In past years we have developed unique instrumentation which enables us to make simultaneous in situ observations of sediment and flow conditions near the lake bottom.[1] We have added to our instrumentation this year, putting a new tripod system into operation. The new system (EMP) consists of an aluminum tripod, in the shape of a triangular prism (1.5 m high with 2 m sides). Various combinations of sensors can be mounted on the tripod, data from which are recorded using our microprocessor-based data acquisition system.[2] Pressure cases capable of withstanding the highest pressures found in the lakes are used to house the data acquisition system and instrument power pack. We have also added acoustic release modules so that the system can be deployed and recovered without divers. In almost all anticipated sampling modes, the experiment duration will be limited by the capacity of the instrument power pack, which is ~30 days.

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Table 1 shows the deployment record of the new tripod in 1981. In each experiment, the instrumentation included a short path-length transmissometer mounted 93 cm above the bottom, a two-axis electromagnetic current meter 67 cm above the bottom, a solid state temperature probe and auxiliary sensors to determine the orientation of the tripod on the bottom (tilt and direction).

Table 1. Experiment locations for the 1981 Lake Michigan sediment resuspension study.

Date	Location	Depth, m	Hours of data recovered
18 Jun-23 Jun	Indiana Shoals (41°46'N, 87°23'W)	10	121.5[a]
29 Jun-23 Jul	Grand Haven (43°02'N, 86°18'W)	26	399.5[a]
13 Aug-31 Aug	Station EC2 (42°06'N, 87°22'W)	59	432.0[b]
30 Sept-27 Oct	Grand Haven (43°02'N, 86°18'W)	28	649.5

[a] No transmissometer data.
[b] No transmissometer data; temperature data incomplete.

Problems in the data-acquisition system that caused the loss of transmissometer data were not recognized and corrected until after the August deployment. Therefore, the first three experiments are missing information about sediment transport. Although the current meter and temperature data from these experiments will be valuable, we have concentrated our efforts on analysis of the data taken during the October experiment off Grand Haven.

Figure 1 shows time series of water temperature, current speed, and concentration of suspended material above the bottom. The transfer function that allows us to estimate concentration from the transmittance measured by our sensor was obtained from in situ measurements. The output of a transmissometer identical to the one on the tripod was regressed against measurements of total suspended solids made from water samples taken at several depths. The calibration is linear over the range of expected concentrations.

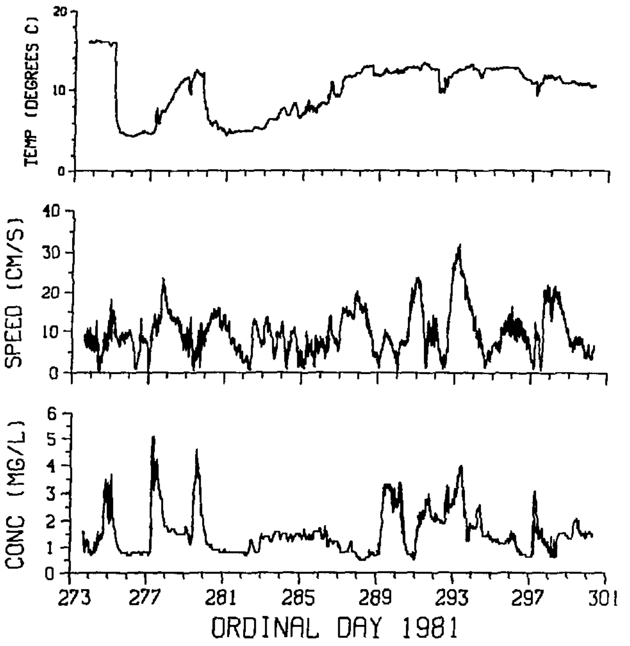

Fig. 1. Time series of water temperature, current speed, and concentration of suspended materials.

Changes in concentration shown in Figure 1 may be attributed to two causes, local resuspension and advection of turbid water past the sensor. Detailed analysis of these data shows that local resuspension occurs when current speeds are in excess of ~18 cm/s. The derived function relating concentration due to local resuspension to average current speed is shown in Figure 2. Although local resuspension occurs infrequently, about half of the sediment flux observed in this experiment occurs during these events. The remainder is due to advection past the sensor. This is not surprising in this area, where previous research[3] has shown the existence of a well-defined nepheloid layer. A polar plot of the flux vectors (Fig. 3) measured in this experiment shows that bottom sediments may be expected to move offshore and to the north.

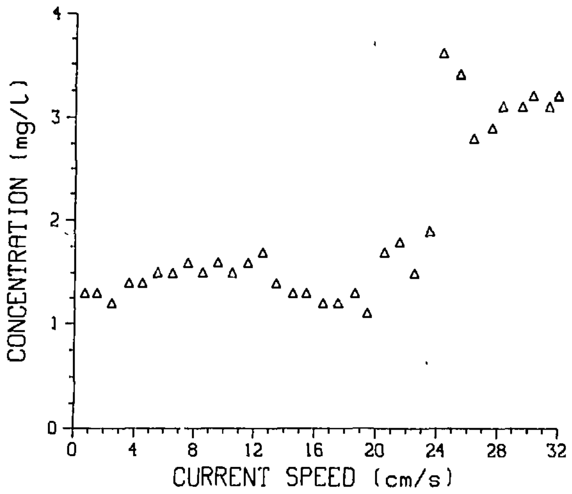

Fig. 2. Concentration of suspended material versus mean current speed. Data points are averages of all observations with nearly equal current speed (±0.5 cm/s).

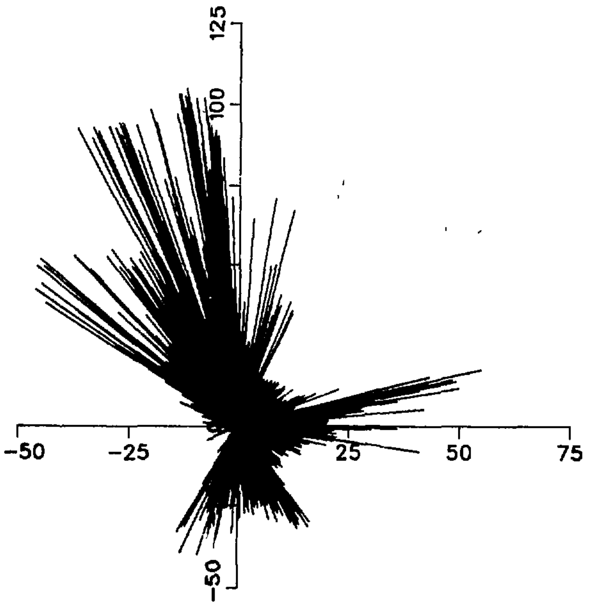

Fig. 3. Horizontal sediment flux vectors. Top of figure is north. Units are μg/cm^2/s.

Prospects

Analysis of these data will continue. Still to be determined are sediment entrainment rates and the relationship between the observed flows and the local meteorological conditions. In addition, we intend to make a detailed analysis of the flow data taken at station EC-2. No other detailed observations of currents so near the bottom in the hypolimnion of Lake Michigan are known to exist. Experiments planned for 1982 will be concentrated on defining the mechanisms that produce and maintain the benthic nepheloid layer in southeastern Lake Michigan.

References

1. Lesht, B. M. and R. V. White, Development of a time-lapse camera for benthic research, Radiological and Environmental Research Division Annual Report, January-December 1979, ANL-79-65, Part III, pp. 68-69.
2. Williams, R. M., J. R. Haumann, and R. V. White, Development of a battery-operated data acquisition system for atmospheric and limnological research, Radiological and Environmental Research Division Annual Report, January-December 1978, ANL-78-65, Part III, pp. 82-87.
3. Chambers, R. L. and B. J. Eadie, Nepheloid and suspended particulate matter in southeastern Lake Michigan, Sedimentology 28, 439-447 (1981).

MULTI-YEAR SIMULATIONS OF WATER QUALITY IN LAKE MICHIGAN MADE WITH A DYNAMIC LAKE EUTROPHICATION MODEL

B. M. Lesht

Background and Scope

Dynamic lake eutrophication models are designed, in part, as tools for resource management. In this context they are intended to be used to predict the long-term response of the modeled lakes to external changes, such as the enforced limitation of nutrient loading. Although the exact degree to which these models serve this forecasting purpose in large bodies of water has yet to be determined, at least one model of this type has been shown to reproduce the past behavior of the Great Lakes (Lake Ontario) over a ten-year period when driven with measured nutrient loads and water temperature distributions.[1]

The apparent success of the Lake Ontario eutrophication model does not necessarily imply similar results for our Lake Michigan model even though they are much alike in kinetic and computational structure. Significant differences between the two do exist. The Lake Ontario model, for instance, uses distinct state variables dividing phytoplankton into "diatoms" and "others". This distinction is made possible by the extent of the Lake Ontario data set, which is far more comprehensive than that for Lake Michigan. On the other hand, the Lake Michigan model incorporates an explicit winter removal process for particulates, which allows the model to account for material removed from the water column during periods of prolonged ice cover, an effect which has been found to be significant in several of the Great Lakes.[2] Since the addition of the winter removal process is the major distinction between the Lake Michigan model and the models formulated for the other Great Lakes, we have examined the response of the model to this change. Our experiments show that the winter removal processes found necessary for model verification have a major effect on long-term forecasts made using the model.

Progress in 1981

The Lake Michigan model was calibrated by Paul Rodgers[3] using the 1976 U.S. Environmental Protection Agency's intensive survey data and installed on our computer system in 1981. A subsequent water quality survey of Lake

Michigan made by the U.S. EPA Great Lakes National Program Office in 1977 showed a significant decline in total phosphorus, which is the limiting nutrient in the Lake Michigan model. The Lake Michigan model does not predict the decrease in total phosphorus observed between 1976 and 1977 without adding a mechanism for the winter removal of suspended particles. In terms of the model output, which is most often illustrated using the predicted time-series of epilimnion phytoplankton chlorophyll concentration, the model overestimates the chlorophyll concentration in 1977 (Fig. 1) without winter removal.

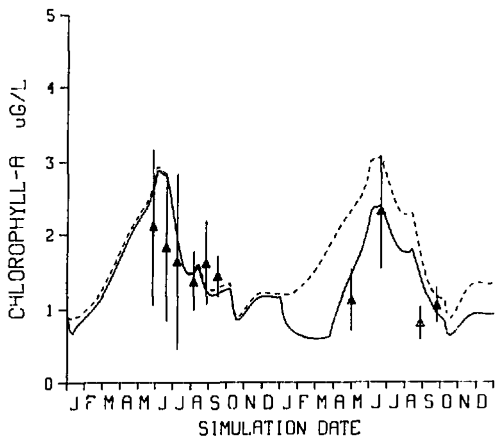

Fig. 1. Two-year simulation of chlorophyll concentration in southern basin epilimnion. The solid line is the model prediction with increased settling under ice. The dashed line is the unmodified model. Data are 1976-1977 intensive survey data.

Assuming that the winter removal mechanism added to the Lake Michigan model improves its performance in forecasting, we may ask how significant a difference it makes when the model is used for longer term prediction. We have examined this question by using estimates of the actual phosphorus loadings to Lake Michigan in the five-year period 1976-1981 along with observations of the lake ice cover to drive the model in hindcast mode. Phosphorus loading information was obtained from the International Joint Commission and the ice cover data was supplied by David Rockwell of the Great Lakes National Program Office. The model was set up with the same data used in the calibration experiment, and run for five simulation years using the estimated loads for each year. In one run the settling velocity of suspended particles was increased from 0.2 m/day to 1.6 m/day during the period that the lake was ice covered. In the other run the settling velocity was held constant at its usual value.

As may be expected from the result of the two-year simulation, the predictions for epilimnion chlorophyll tend to diverge over the five simulation years (Fig. 2). The difference between the two predictions in the last year (simulated 1980) ranges from over 300% (winter values) to 100% (peak of summer bloom) and down to ~50% (late summer). Also shown in Figure 2 are values of epilimnion chlorophyll measured by Jon Parker using continuous fluorometry[4] during 1979-1980 and one measurement of epilimnion chlorophyll made by the U.S. EPA in September 1980.

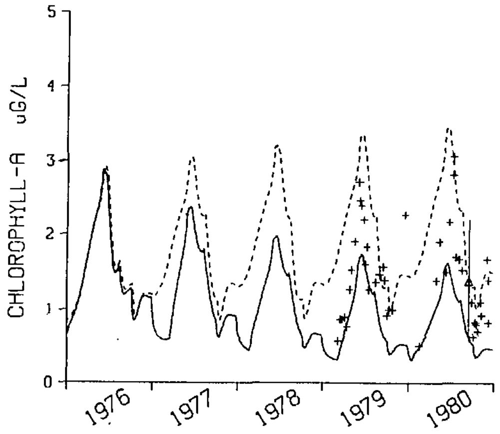

Fig. 2. Five-year simulation of chlorophyll concentration. The solid line is the model prediction with increased settling under ice. The dashed line is the unmodified model. Crosses are Argonne data, triangle is EPA datum.

An important feature of the eutrophication model is that it provides a deterministic prediction of an essentially stochastic process. Similarly, measurements of parameters such as epilimnion chlorophyll must be considered as discrete samples of a random variable. Thus we could not expect agreement between observation and model prediction at any one time, but must rather compare patterns of observations with the model predictions to evaluate the utility of the model.

The results shown in Figure 2 indicate that the two models may represent limits of the lake response, and as expected, the data fall within these limits. Detailed analysis shows that the model with explicit winter removal processes is closer to the observations early in the year, but underestimates the peak chlorophyll levels. On the other extreme, the original model (unmodified) is much better for predicting the peak values of phytoplankton concentrations.

The situation for total phosphorus is a bit more complex. In Figure 3 are plotted the model predictions and data available for 1976, 1977 and 1980. This figure shows that the model including winter removal processes is more dynamic, in terms of total phosphorus, than the unmodified model. Total phosphorus levels are predicted to depend on both loading and the amount removed during the winter, one factor controllable, the other not. Obviously, more data will be required before the degree to which this model represents the processes underway in Lake Michigan can be established.

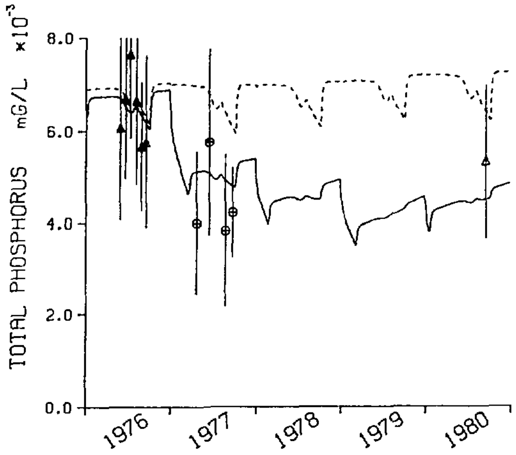

Fig. 3. Five-year simulation of total phosphorus concentration. The solid line is the model prediction with increased settling under ice. The dashed line is the unmodified model. All data are EPA.

Prospects

The purpose of the models is long-term prediction. Our next experiments will define the ten-year limits of predicted lake response, and examine, using

Monte Carlo techniques, the statistical distribution of predicted responses when the model is driven with random combinations of loading and ice cover.

References

1. Thomann, R. V. and J. S. Segna, Dynamic phytoplankton-phosphorus model of Lake Ontario: Ten-year verification and simulations, Phosphorus Management Strategies for Lakes, R. C. Loehr, C. S. Martin and W. Rost, Eds., Ann Arbor Science Publrs., Ann Arbor, Michigan, pp. 135-152 (1981).
2. Rockwell, D. C., Maximum percent ice cover as an indicator mechanism for changes in large lakes total phosphorus concentrations. XXIV Conference on Great Lakes Research, International Association for Great Lakes Research, 28-30 April 1981, p. 38 (1981).
3. Rodgers, P. and D. K. Salisbury, Modeling of water quality in Lake Michigan and the effect of the anamolous ice cover of 1976-1977. Great Lakes Basin Commission, Ann Arbor, Michigan (1981)
4. Parker, J. I., C. W. Kennedy and K. A. Stanlaw, Measurement of the spatial and temporal distributions of chlorophyll and total suspended solids in southern Lake Michigan by fluorometry and nephelometry, respectively. Radiological and Environmental Research Division Annual Report, January-December 1980, ANL-80-115, Part III, pp. 74-79.

UPPER TROPHIC LEVEL INTERACTIONS IN A DYNAMIC LAKE EUTROPHICATION MODEL

R. Sweet* and B. M. Lesht

Background and Scope

The dynamic lake eutrophication model on which we have based our Lake Michigan modelling program is the LAKE1 formulation developed by Thomann et al.[1] This model uses up to ten compartments or state variables to represent the biological and chemical components important in the eutrophication process. Five of these compartments involve nutrients: three forms of nitrogen and two forms of phosphorus; and the other five compartments constitute the trophic structure of the model including phytoplankton, herbivorous zooplankton, carnivorous zooplankton and two undefined upper trophic levels.

The most important feature of the eutrophication model is the representation chosen for the interactions among the ten compartments. These are the so-called kinetic interactions. In LAKE1, for example, the two unidentified trophic levels are not used, and the interaction among the remaining three trophic levels is modelled as a linear food chain in which each trophic level feeds only on the compartment directly below it. Obviously, this choice of structure is somewhat arbitrary and is only one of the possible representations of the interaction between the biota in the lake. Among our initial concerns, therefore, was the question of how sensitive is the LAKE1 model to changes in the upper trophic level structure. We conducted a series of simple numerical experiments designed to answer this question.

Progress in 1981

The first experiments we conducted involved adding another trophic level (referred to as UT1) to the model. We investigated three separate formulations for the interaction between the added level and the other trophic compartments. These formulations were (1) linear food chain: UT1 feeds only

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on carnivorous zooplankton; (2) food web: UT1 feeds on both carnivorous and herbivorous zooplankton; and (3) food web: UT1 feeds on all trophic levels.

Once a model structure has been defined, the problem becomes one of assigning values to the parameters in the kinetic interaction equations. Since the original model involves 8 state variables in each of two physical segments (hypolimnion and epilimnion) there are a total of 16 coupled, nonlinear differential equations to be solved. These equations involve over 30 parameters, the precise number depending on the details of the interactions. The parameters are essentially free, being constrained only by "reasonable" values determined by laboratory and field experimentation. We used values based on experiments reported in the literature for the new parameters added by our modifications. All other parameters were kept constant.

The particular model on which we tested our modifications was devised for Lake Ontario. An earlier comparison with field data has shown that the model is successful in reproducing Lake Ontario's annual phytoplankton cycle.[2] In our work we chose to judge performance of the new models by comparing their output to that of the unmodified Lake Ontario model.

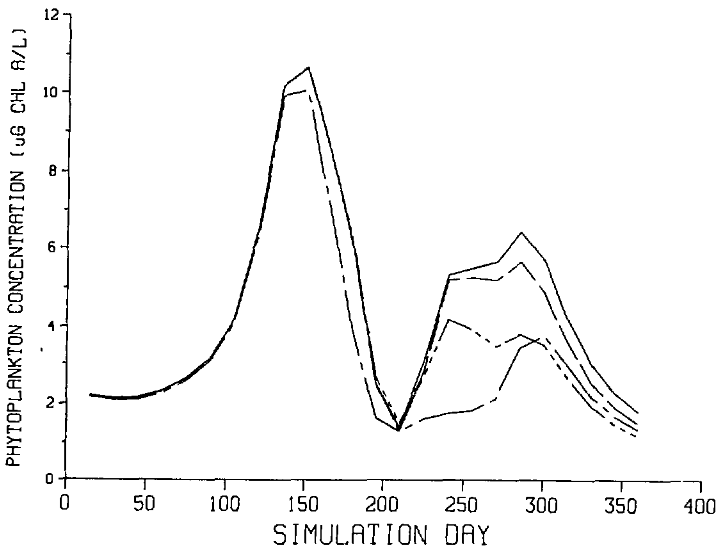

Fig. 1. Eutrophication model (LAKE1, ——) output (concentration of chlorophyll-a) for four different model formulations. Linear food chain, — —; web zooplankton, — — — —; web all plankton ——).

Figure 1 shows the basic result of these first experiments. In this figure, which shows phytoplankton biomass as a function of time, we compare the unmodified Lake Ontario model to cases 1, 2 and 3 above. The most obvious result of the test modifications is the change in the magnitude of fall phytoplankton bloom. Given the uncertainty in the data, however, the only significant difference among models occurs when the added trophic level (UT1) is modelled as an omnivore. In any other case, small parameter adjustments, within the range of experimental data, can be used to remove the effects of modified kinetics. The basic model is thus shown to be relatively insensitive to changes in the upper trophic structure. Further experiments showed that the model is also relatively insensitive to changes in the form of nutrient limitation used (multiplicative versus limitation by smallest available) and to changes in the form of the phytoplankton respiration function as proposed by Rodgers.[3]

We conclude that the LAKE1 formulation is fairly robust. In our experiments, refining the kinetic interactions did not result in significant changes. Furthermore, each refinement in structure actually added uncertainty in terms of the unknown equation parameters. Clearly more is to be gained by using laboratory and field experiments to define the kinetic processes currently in the model than by adding additional unconstrained processes.

References

1. Thomann, R. V., D. M. DiToro, R. P. Winfield and D. J. O'Connor, Mathematical modeling of phytoplankton in Lake Ontario. Part I. Model development and verification, U.S. Environmental Protection Agency Report EPA-660/3-75-005, Corvallis, OR (1975).
2. Thomann, R. V., R. P. Winfield, D. M. DiToro and D. J. O'Connor, Mathematical modeling of phytoplankton in Lake Ontario. Part II. Simulations using LAKE1 model. U.S. Environmental Protection Agency Report EPA-600/3-76-065, Duluth, MN (1976).
3. Rodgers, P. W. and D. K. Salisbury, Modeling of water quality in Lake Michigan and the effect of the Anomalous Ice Cover of 1976-77, Great Lakes Basin Commission, Ann Arbor, MI (1981).

RESPONSE OF A BENTHIC MICROCOSM TO 2,4-DICHLOROPHENOL

P. A. Szczepanik-Van Leeuwen and W. R. Penrose

Background and Scope

The sediment-water interface of lakes has several functions that ultimately affect man's activities. These functions are (a) oxidation and recycling of carbon and nutrients, (b) secondary production and introduction of energy into the food chain leading to man, and (c) biodegradation or sequestering of toxic chemicals, each sufficiently distinct to require individual assessment. Traditional approaches that attempt to express ecosystem "health" as a single index, such as a diversity index or a species list, do not address any of these vital functions. Other approaches that have proved convenient in the laboratory, such as lethal toxicity tests, cannot be related either empirically or theoretically to the ecosystem functions listed above.

Our approach was to begin by designing experiments to measure each of the functions as directly as possible. The ultimate purpose was to design test methods for newly-manufactured chemicals to predict their potential environmental effects.

Work in 1980 established the utility of laboratory microcosms, in the form of undisturbed benthic cores, for measuring rates of carbon and nutrient movement among ecosystem compartments. Continued research was directed at comparing energy sources in the microcosms, quantitatively estimating the role of benthic fauna, and establishing a dose-response curve for an exemplary chemical, 2,4-dichlorophenol (DCP).

Progress in 1981

Microcosm Configuration

Equipment was designed and constructed for the recovery and handling of 3-inch diameter microcosms to replace the 5-inch ones used previously. This equipment included a hydraulic extruder, racks to hold 12 cores apiece, and caps for 3-inch diameter microcosm housings. A rack of 12 filled cores could be handled by one person and occupied less space than 6 of the larger microcosms.

Effect of Carbon Source

Fresh plankton from Lake Michigan was gathered with a hand net and suspended in 20 L lake water to a concentration that was translucent but not transparent. Upon return to the laboratory, the suspension was placed in an incubator at 7°C for 24 hr with 100 μCi $NaH^{14}CO_3$. The labelled seston was then washed repeatedly by decantation and filtration. Samples (75 mg dry wt; 3.10^5 cpm) were added to four replicate microcosms. Four controls received 5 μCi L-(U-^{14}C)-alanine. It has been established that this operation labels bacterioplankton exclusively.

The controls behaved in the normal first-order fashion; the rate constant for the disappearance of non-acid volatile (NAV) carbon was 0.178 ± 0.014 day^{-1}. Where the labelled seston was added, it settled immediately to the bottom; neither NAV nor particulate (PART) radioactivity in the water phase was high enough to be distinguished from background. Introduction of radiocarbon by the seston route (which is the route by which most energy enters the benthic ecosystem) did not, therefore, prove to be a practical means of measuring kinetic parameters in the microcosms.

At the end of the experiment, the cores were sifted; the animals were recovered, weighed, and counted for radioactivity. The results were expressed as the percentage of the total dose found in each of the three major groups of animals (Table 1). The ratios of absorption from seston (detritus) and from alanine (bacterioplankton) reflected the feeding habits of each group. Pontoporeia are detritus feeders and absorbed carbon mainly from seston; sphaerid clams are filter feeders and absorbed carbon from bacterioplankton. Oligochaetes are sediment feeders; labelled carbon would reach them second-hand, as the label is transferred to sediment-bound bacteria and organic carbon. Oligochaetes therefore show intermediate ratios.

Dose-Response Behavior

The chemical, 2,4-Dichlorophenol (DCP), was selected for these experiments because (1) it was toxic at concentrations that could be easily measured with a simple colorimetric procedure; (2) it was water-soluble at the concentrations needed for the experiments; and (3) it was not noticeably degraded in aerobic aquatic systems.

Table 1. Carbon source and mode of feeding.

	Labeling, % of dose		Ratio
	Bacterioplankton	Seston	
Pontoporeia (detritus feeder)	0.0756 ± 0.0173	1.58 ± 1.15	0.048
Sphaerid clams (filter feeders)	0.0242 ± 0.0147	0.0083 ± 0.0036	2.92
Oligochaetes (sediment feeders)	0.0409 ± 0.0171	0.034 ± 0.025	1.20

To determine the range of concentrations to use in the microcosms, we explored the use of a simpler system. Heterotrophic potential is a measure of the ability of a water or sediment sample to cope with an increment in nutrient concentrations. We therefore enclosed a sample of water in a bottle with known amounts of L-(U-^{14}C)-alanine and DCP. After 4 hr, the radioactive $^{14}CO_2$ was distilled into a phenylethylamine absorbent and counted; the radioactivity fixed in particles was filtered and counted. The results are shown in Table 2, expressed as a percentage of the added dose. The concentration 50% effective against alanine oxidation was between 25 and 100 mg/L, and against alanine incorporation about 25 mg/L.

Table 2. Effect of DCP on heterotrophic potential of lake water.

Treatment	Percent added radiocarbon	
	Oxidation	Incorporation
Blank	0	0
Control	1.82 ± 0.50	2.75 ± 0.62
4 mg/L DCP	1.38 ± 0.36	2.76 ± 0.57
25 mg/L DCP	1.32 ± 0.23	1.23 ± 0.18
100 mg/L DCP	0.09 ± 0.01	0.16 ± 0.04

As a result of this preliminary experiment, the concentrations of DCP chosen for the dose-response experiment selected were 0, 1, 3, 9, 27, and 81

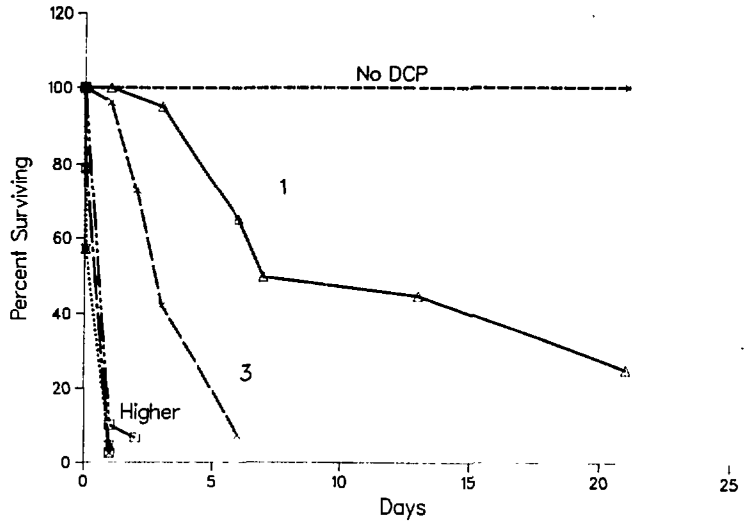

Fig. 1. Survival of pontoporeia exposed to varying concentrations of DCP (mg/L, indicated by numbers 1,3, etc.). The number of organisms surviving to the end of the experiment was added to the number of dead organisms removed to estimate the total initial number of pontoporeia. Because of the agitated behavior induced by DCP, dead pontoporeia were always found on the sediment surface and were removed immediately.

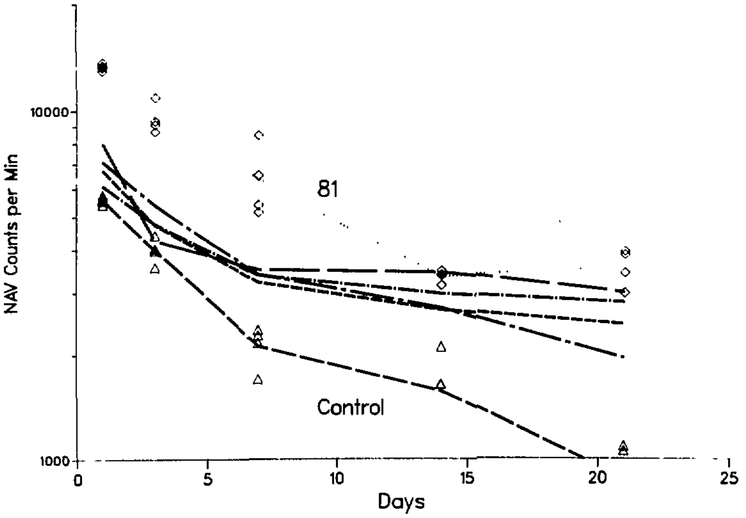

Fig. 2. Effect of different concentrations of DCP on the turnover of nonacid-volatile (NAV) radiocarbon.

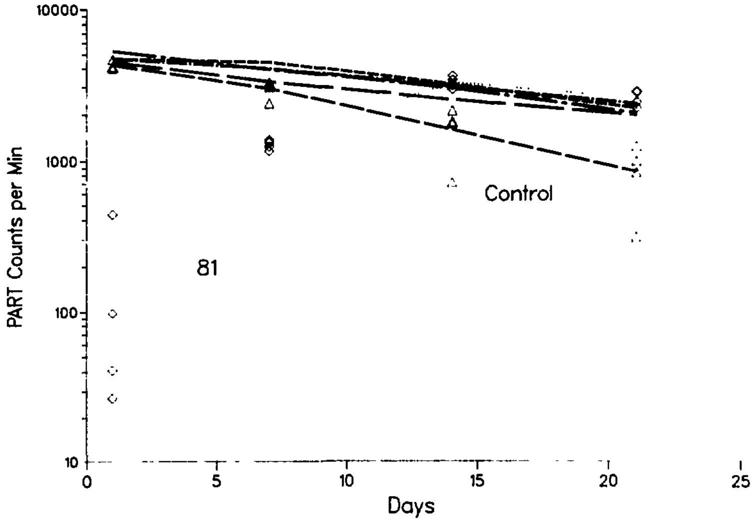

Fig. 3. Effect of DCP concentration on turnover of particulate (PART) radiocarbon.

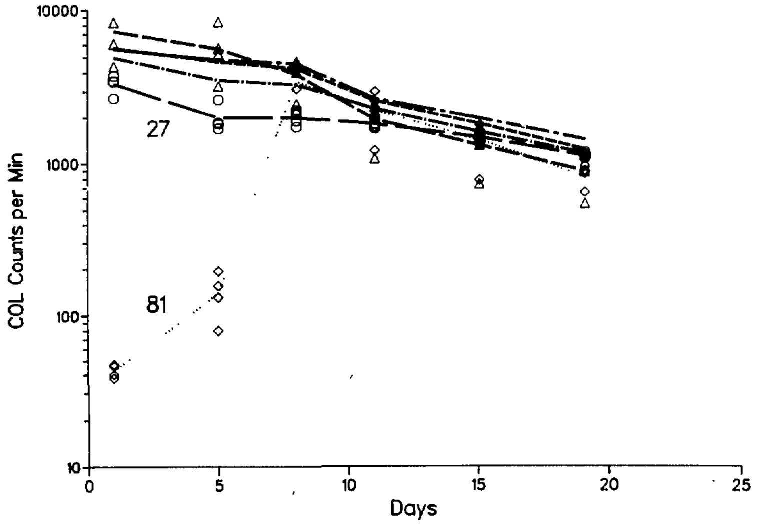

Fig. 4. Effect of DCP concentration on colonization of surfaces (COL) by radiocarbon.

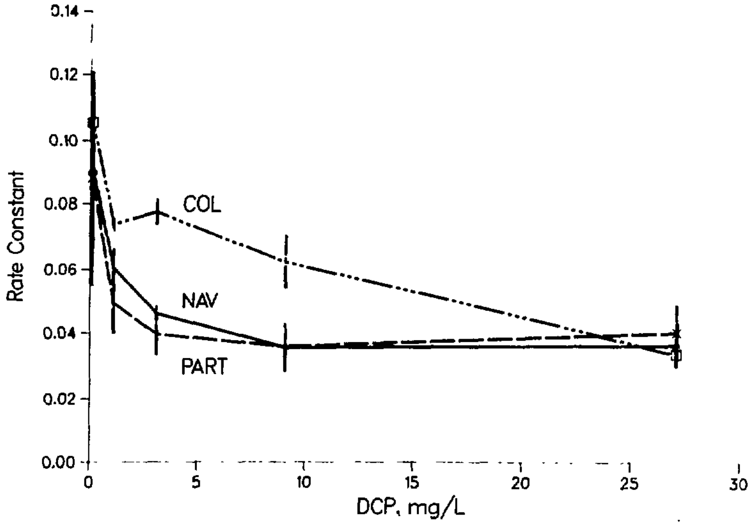

Fig. 5. Rate constants of radiocarbon turnover derived from the data in Figures 2, 3, and 4.

mg/L. Four replicates per treatment were used.

The pontoporeia reacted dramatically to the dichlorophenol (Fig. 1). Inspection of the data shows that the so-called LC_{50} is strongly dependent on the duration of exposure. Even at 1 mg DCP/L, it is possible that mortality would have continued beyond the 21 days of the experiment. The 96-hr toxic levels (2-3 mg/L) agree with those available in the literature.

NAV and particulate (PART) carbon and the ability to deposit radiocarbon on glass slides (COL or colonization; Figs. 2-4) are measures of the microbial population. The highest level of DCP (81 mg/L) causes a dramatic inhibition of radiocarbon uptake by bacteria, expressed as an initial low level of PART and COL. However, these parameters recover their normal levels in six days. Measurements of bacterial numbers showed that DCP caused the proportion of bacteria resistant to 100 mg/L to increase from 5% of the total population to 50%.

The effects of DCP on rate constants of NAV, PART, and COL are shown in Figure 5. This quantitative method reveals a greater sensitivity of the system which is not apparent from the time plots. Substantial decreases in

NAV and PART rates were caused by 1 mg/L DCP and reached a minimum at 3 mg/L. This result implies that there are two populations of microorganisms present, one as sensitive as the macrofauna and the other resistant.

The high adaptability of the microbial population means that the ability of the benthic ecosystem to recycle nutrients and organic carbon is not affected by concentrations of DCP much higher than those that affect secondary production. Standard lethal toxicity tests may predict the effect of DCP on secondary production, but they do not predict the behavior of organisms (such as bacteria) with a much higher capacity for adaptation.

PUBLICATIONS BY THE STAFF OF THE ECOLOGICAL SCIENCES SECTION JANUARY THROUGH DECEMBER 1981

Articles, Book Chapters, Etc.

J. J. Alberts and M. A. Wahlgren, Concentrations of $^{239,240}Pu$, ^{137}Cs, and ^{90}Sr in the waters of the Laurentian Great Lakes: Comparison of 1973 and 1976 values, Environ. Sci. Technol. 15, 94-98 (1981).

J. J. Alberts and K. A. Orlandini, Laboratory and field studies of the relative mobility of $^{239,240}Pu$ and ^{241}Am from lake sediments under oxic and anoxic conditions, Geochim. Cosmochim. Acta 45, 1931-1939 (1981).

P. M. Irving and J. E. Miller, Productivity of field-grown soybeans exposed to acid rain and sulfur dioxide alone and in combination, J. Environ. Qual. 10, 473-478 (1981).

J. S. Marshall, J. I. Parker, D. L. Mellinger and S. G. Lawrence, An in situ study of cadmium and mercury stress in the plankton community of Lake 382, Experimental Lakes Area, northwestern Ontario, Can. J. Fish. Aquat. Sci. 38, 1209-1214 (1981).

J. S. Marshall, D. L. Mellinger and J. I. Parker, Combined effects of cadmium and zinc on a Lake Michigan zooplankton community, J. Great Lakes Res. 7, 215-223 (1981).

J. Muhlbaier and G. T. Tisue, Cadmium in the southern basin of Lake Michigan, Water, Air, Soil Pollut. 15, 45-59 (1981).

J. I. Parker, G. T. Tisue, C. W. Kennedy and C. A. Seils, The effects of atmospheric precipitation on phytoplankton photosynthesis in Lake Michigan, J. Great Lakes Res. 7, 21-28 (1981).

Contributions to Conference Proceedings and Miscellaneous Reports

W. K. Derickson, S. A. Spigarelli and M. M. Thommes, A simulation of Lake Michigan brown trout energetics under cyclic and constant temperature conditions, Energy and Ecological Modelling, Proc. Symp. Louisville, Kentucky, 20-23 April 1981, International Society of Ecological Modelling.

R. M. Goldstein, S. A. Spigarelli and M. M. Thommes, Temperature selection of brown trout monitored by radiotelemetry, Abstract, American Fisheries Society Meeting, Albuquerque, New Mexico, 16-18 September 1981.

P. M. Irving, P. B. Xerikos and J. E. Miller, Effect of sulfur dioxide and nitrogen dioxide alone and in combination on the productivity of field-grown soybeans, 1980 Annual Report, U.S. Environmental Protection Agency.

P. M. Irving and D. A. Sowinski, Effect of acidity, sulfate, nitrate and ammonium concentrations and ratios in precipitation applied to greenhouse-grown soybeans, 1980 Annual Report, U.S. Environmental Protection Agency.

J. O. Karttunen, Cesium-137 in various Chicago foods, U.S. Department of Energy report EML-390, pp. III3-III6 (1981).

J. O. Karttunen, Cesium-137 in various Chicago foods, U.S. Department of Energy Report EML-395, pp. III3-III6 (1981).

L. W. Kress and J. E. Miller, Impact of ozone on soybean yield, National Crop Loss Assessment Network (NCLAN), 1980 Annual Report, U.S. Environmental Protection Agency, Corvallis, Oregon, pp. 12-21 (1981).

L. W. Kress and J. E. Miller, Impact of ozone on soybean yield, Abstract, American Phytopathological Society Meeting, New Orleans, Louisiana, 2-6 August 1981, Paper No. 44, p. 12.

J. R. Krezoski and J. A. Robbins, Dual radiotracer measurement of zoobenthos-mediated particle and solute transport in lake sediments, Abstract, 44th Annual Meeting, American Society of Limnology and Oceanography, Milwaukee, Wisconsin, 15-18 June 1981.

B. M. Lesht and R. M. Williams, Time-series observations of sediment transport on Indiana Shoals, Lake Michigan, Abstract, XXIV Conference on Great Lakes Research, Columbus, Ohio, 28-30 April 1981, International Association for Great Lakes Research.

J. E. Miller, H. J. Smith and P. B. Xerikos, Effects of periodic SO_2 fumigation on the yield of Williams and Corsoy soybeans, 1980 Annual Report, U.S. Environmental Protection Agency.

D. M. Nelson and M. B. Lovett, Measurements of the oxidation state and concentration of plutonium in interstitial waters of the Irish Sea, Impacts of Radionuclide Release into the Marine Environment, Proc. Symp. Internat. Atomic Energy Agency, Vienna, Austria, 6-10 October 1980, IAEA-SM-248/145, pp. 105-118 (1981).

D. M. Nelson and D. N. Edgington, The chemical cycling of fallout radionuclides in the Great Lakes, Abstract, American Chemical Society Meeting, Dayton, Ohio, 20-22 May 1981.

J. I. Parker and J. G. Ferrante, A survey of discharges from a natural gas drilling operation in Lake Erie, Abstract, XXIV Conference on Great Lakes Research, Columbus, Ohio, 28-30 April 1981, International Association for Great Lakes Research.

J. I. Parker and G. T. Tisue, Seston sorption and sedimentation of Zn and Cd in Lake Michigan, Abstract, 44th Annual Meeting, American Society of Limnology and Oceanography, Milwaukee, Wisconsin, 15-18 June 1981.

S. A. Spigarelli, A. L. Jensen and M. M. Thommes, An assessment of the impacts of water intakes on alewife, rainbow smelt, and yellow perch populations in Lake Michigan, U.S. Environmental Protection Agency Report EPA-905/3-81-001; Agonne National Laboratory Report ANL/ES-109 (1981).

S. A. Spigarelli, M. M. Thommes and W. Prepejchal, Feeding, growth and PCB accumulation by brown trout exposed to fluctuating and constant temperatures, Abstract, 1981 American Fisheries Society Meeting, Albuquerque, New Mexico, 16-18 September 1981.

G. T. Tisue and B. M. Lesht, Depth profiles of suspended particulate forms of trace elements in the southern basin of Lake Michigan, Abstract, XXIV Conference on Great Lakes Research, Columbus, Ohio, 28-30 April 1981, International Association for Great Lakes Research.

G. T. Tisue, J. I. Parker and B. M. Lesht, Distribution factors and settling rates for Zn, Fe, and Pb in Lake Michigan's southern basin, Abstract, 44th Annual Meeting, American Society of Limnology and Oceanography, Milwaukee, Wisconsin, 15-18 June 1981.

T. Tisue and C. A. Seils, Preconcentration of nanomolar amounts of trace elements from natural waters for x-ray spectrofluorimetric analysis using pyrollidine carbodithioic acid, Abstract, 4th Midwest Water Chemistry Workshop, Milwaukee, Wisconsin, 23-24 October 1981.

M. A. Wahlgren and K. A. Orlandini, Comparison of the geochemical behaviors of plutonium, thorium and uranium in selected North American lakes, Migration in the Terrestrial Environment of Long-Lived Radionuclides from the Nuclear Fuel Cycle, Proc. Symp. Intern. Atomic Energy Agency Knoxville, Tennessee, 27-31 July 1981, IAEA-SM-257/89.

R. M. Williams, A model for the dry deposition of particles to natural water surfaces, Abstract, Environmetrics 81, U.S. Environmental Protection Agency, Washington, D. C., 6-8 April 1981.

R. M. Williams, A model for the dry deposition of particles to natural water surfaces, Summary, Environmetrics 81, U.S. Environmental Protection Agency, Washington, D. C., 6-8 April 1981.