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

ANL-82-65
Part III

ANL--82-65-Pt.3

DE84 001670

ARGONNE NATIONAL LABORATORY
9700 South Cass Avenue
Argonne, Illinois 60439

RADIOLOGICAL AND ENVIRONMENTAL
RESEARCH DIVISION ANNUAL REPORT

Ecology

January—December 1982

A. F. Stehney, Acting Division Director

J. E. Miller, Section Head

NOTICE
PORTIONS OF THIS REPORT ARE ILLEGIBLE.
It has been reproduced from the best
available copy to permit the broadest
possible availability.

September 1983

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

Preceding Report

ANL-81-85 Part III January—December 1981

TABLE OF CONTENTS

The RAINS Experiment - Part II P. M. IRVING and J. KRISTOFZSKI	1
Effect of the Sulfate-to-Nitrate Ratio on the Response of Radish to Simulated Rain Acidity P. M. IRVING and A. KESTNER	5
Experimental Field Facility for Long-Term Studies of Acidic Deposition Effects on Plant/Soil Systems P. M. IRVING, J. E. MILLER, W. PREPEJCHAL, J. HOFF and J. SEGERS	9
A Comparison of Soil-Water and Groundwater Quality of Two Reconstructed Soil Systems Exposed to Ambient Precipitation P. M. IRVING, W. PREPEJCHAL, S. MABURY and L. WILLMAN	15
Impact of Ozone on Yield of Three Cultivars of Winter Wheat L. W. KRESS, H. J. SMITH and J. E. MILLER	20
Impact of Ozone on Yield of Grain Sorghum L. W. KRESS, H. J. SMITH and J. E. MILLER	27
The Flux of Plutonium from Sediments to Water in Lake Michigan D. M. NELSON and D. N. METTA	31
Plutonium Solubility in Natural Waters D. M. NELSON, R. P. LARSEN and J. O. KARTTUNEN	37
Plutonium Concentrations in the Great Lakes - An Update D. M. NELSON and D. N. METTA	45
Behavior of Plutonium and Americium in Two Groundwater Systems D. M. NELSON, K. A. ORLANDINI and R. P. LARSEN	49
Comparison of Dynamic and Mass-Loading Models used for Long-Term Prediction of Lake Michigan Water Quality B. M. LESHT	54
Box-Jenkins Modeling of Chicago Water Intake Phosphate Data 1966-1982 B. M. LESHT	58
Ten-Year Forecasts of Water Quality in Lake Michigan Using a Deterministic Model and Monte Carlo Inputs B. M. LESHT	63
Publications	67

FOREWORD

The year 1982 can be characterized as one of regrouping following the upheaval of program reductions suffered in the previous year, and one of planning and building for the future. The two larger remaining programs, Transuranics and Terrestrial Ecology, retained their relative stability, while new initiatives were made by the remnants of the Aquatic Ecology and Physical Transport components of the section.

In the continuing National Crop Loss Assessment Project studies of the effects of ozone on crop growth and yield, the Terrestrial Ecology Group has found that winter wheat is intermediate in relative sensitivity to ozone, while sorghum is quite resistant in comparison to other crops studied. The data obtained in these studies are being incorporated by the U.S. Environmental Protection Agency (EPA) into a national assessment of ozone-induced crop losses. The Microcosms for Acid Rain Studies (MARS) facility, sponsored by the Electric Power Research Institute (EPRI), was completed in the early summer. Controlled investigations of plant and soil responses in acid rain were initiated with crop plants grown in two different midwestern soil types.

The Transuranics Group has found that the solubility and adsorptive behavior of plutonium previously observed at fallout concentrations in natural waters ($\sim 10^{-16}$ to 10^{-18} M) is applicable at plutonium concentrations as high as 10^{-8} M. This information is of considerable importance in the accurate prediction of the consequences of larger-scale releases of plutonium to the environment. Results of studies on actinide mobility in groundwater have generally conformed to expectations based on previous work with surface waters, with the notable (and as yet unexplained) exception that americium is unexpectedly soluble, and hence unusually mobile, at the Los Alamos National Laboratory site.

The Lake Michigan eutrophication model has been adapted to operation in a Monte Carlo mode. Simulations based on yearly phosphorus loadings and winter conditions were selected at random from prescribed probability distributions and used to estimate some of the uncertainties associated with model forecasts of Lake Michigan water quality.

A good deal of staff time was expended in 1982 to fortify existing research programs and to initiate new work in an attempt to strengthen and rebuild the section. Funding was obtained from the National Oceanic and Atmospheric Administration to update the inventories of long-lived fallout radionuclides in the Great Lakes and to measure their present input to Lake Michigan via rivers. Commitments were obtained from EPA and EPRI to fund new studies of the importance of temporal variations in rain acidity to crop response, and to support further studies of the interactive effects of sulfur dioxide and ozone on crop physiology and productivity. Program Development Funds obtained from the Laboratory were used to prepare for investigations of acid rain-gaseous pollutant interactions and to continue a modest program of research-directed water quality sampling in Lake Michigan through FY 83.

While dramatic changes in the Ecological Sciences Section did not occur in 1982, major programs remained stable, and in a few instances, received some expanded support.

THE RAINS EXPERIMENT - PART II

P. M. Irving and J. Kristofzski*

Background and Scope

A group of six laboratories performed a cooperative greenhouse experiment in 1981 to examine interlab variability in the dose-response relationship between radish (Raphanus sativus L. cv. Cherry Belle) yield and acidity of simulated rain. The study was initiated in order to standardize techniques and procedures for acid rain studies so that reasonable comparisons may be made through complementary experiments. The results of the first experiment revealed variations in the growth rates of radish among the laboratories; however, trends in the response to the treatments were similar.¹ Most of the investigators found a threshold acidity level. No negative effects on yield occurred above that level, and a negative linear relationship between yield and acidity was found below that level. The highest pH level (lowest acidity) at which there were significant negative effects on yield varied between 2.6 (2.5 mg/L H^+) and 4.6 (0.025 mg/L H^+) among the six laboratories. To determine the statistical significance of the variability among the laboratories it first is necessary to determine the variability within each laboratory. After these determinations it may be possible to resolve the inconsistencies in experimental results reported by different investigators.

Progress in 1982

In 1982 the dose-response experiment was performed again exactly as it had been in 1981 with the exception that the radish plants were placed on a rotating turntable beneath the spray nozzle to ensure equal distribution of simulated rain among the ten replicates per treatment. In addition to measuring the yield response, the investigators determined photosynthetic rates just prior to harvest.

*Undergraduate research participant, Argonne National Laboratory, Division of Educational Programs; University of Washington, Seattle, Washington.

As in the first experiment, radish yield decreased with increasing acidity below a threshold pH value (Fig. 1). Wet weights of the radishes were 11% to 38% lower in 1982 than in 1981, although the overall response to the treatments was approximately the same for both years. Shoot weight was found to be less affected by the treatments than root weight (Fig. 1). A plateau-linear model best describes the relationship between acidity and radish yield when data from both years are used:

$$y = 17.45 - t (4.098 [H^+ - 0.0797])$$

where:

y = radish yield (hypocotyl and root wet weight) in grams,

$t = 1$ when $H^+ > 0.079$, $t = 0$ when $H^+ \leq 0.079$;

H^+ = hydrogen ion concentration of simulant in mg/L.

Figure 1. Wet weight of radishes as a function of the pH of simulated rain. Bars with a common letter are not significantly different according to Duncan's Multiple Range Test, $P \leq 0.05$.

This model indicates that pH 4.1 (0.0797 mg/L H^+) is the threshold for acid rain effects on radish yield (Fig. 2). This acidity level is approximately equal to that currently measured in rain in the Midwest during the growing season.

Photosynthetic activity, as measured by the rate of CO_2 uptake (mg/s) per plant, decreased with increasing acidity, although the results were statistically significant only at the lowest pH level (Fig. 3). Similar to the results in 1981, visible injury was observed in plants at pH treatments of 3.4, 3.0, and 2.6.

Figure 2. Dose-response curve describing radish yield as a function of rain simulant acidity - means and model comparison. Data are means from 1981 and 1982 experiments.

Figure 3. Photosynthetic rate per plant as a function of acidity of simulated rain.

Prospects

Data from all laboratories which repeat this experiment will be analyzed for intralab variability, and then compared to interlab variability. The results of this comparison will then be used to assess the feasibility of performing cooperative field experiments. It is hoped that eventually results from a specific location can be utilized to estimate acid rain impacts for a larger region.

Reference

1. Irving, P. M., J. A. Maley and C. M. Gradert, Rainfall acidity interlaboratory national study - RAINS, Radiological and Environmental Research Division Annual Report, January-December 1981, ANL-81-85, Part III, pp. 1-4.

EFFECT OF THE SULFATE-TO-NITRATE RATIO ON THE RESPONSE OF RADISH TO SIMULATED RAIN ACIDITY

P. M. Irving and A. Kestner*

Background and Scope

The term "acid rain", which is used to describe wet deposition that has been affected by combustion emission products, is misleading in that it suggests a single pollutant, or variable. Analysis of the ionic composition of precipitation reveals many variables which may have important effects on vegetation. In addition to hydrogen ion (H^+), those constituents with the greatest potential of eliciting a response are the sulfate (SO_4^{-2}) and nitrate (NO_3^-) ions, which also are the two ions having the highest concentrations in rain. Since sulfur and nitrogen nutrition in plants is interrelated, the concentrations and ratios of SO_4^{-2} and NO_3^- in combination with acidity may together determine plant response to rain.

In areas of the United States currently receiving acid rain, the SO_4^{-2} to NO_3^- ratio is approximately 2:1, and is slightly higher in the Northeast than in the Midwest. This ratio can be expected to change under different scenarios of energy production and emission restrictions.

In a previous study of greenhouse-grown soybeans, the ratio of SO_4^{-2} to NO_3^- in rain affected various parameters of plant growth, although acidity had little effect.¹ The weight of root nodules and number of pods produced were affected by the SO_4^{-2} to NO_3^- ratio in the acid treatment, while the non-acid control plants exhibited differences in shoot and nodule weight, depending on the ratio.

Progress in 1982

Radish (Raphanus sativus cv. Cherry Belle) was chosen as the experimental plant for a study to determine whether the ratio of SO_4^{-2} to NO_3^- in acid rain affects the response of a root crop since a seed crop had previously been

*Undergraduate research participant, Argonne National Laboratory, Division of Educational Programs; Miami University, Ohio.

found to be affected. An acid rain treatment with a pH of 3.0 was used in this study because the results of a prior study indicated that the yield of radish would be reduced by simulated rain with a hydrogen ion concentration at this level.² Plants were sprayed with simulated rain from one of four treatment groups (Table 1) beginning on the sixth day after planting and continuing three times a week for a total of ten rain events. Simulated rains were intermittent, one-hour events in which ten plants per treatment group were placed on a revolving turntable to ensure even distribution of 0.3 inches of simulant per event.

Table 1. The pH and concentration and ratios of ions in rain simulants.

pH	Concentration (mg/L)			
	H ⁺	SO ₄ ⁻²	NO ₃ ⁻	SO ₄ ⁻² :NO ₃ ⁻
3.0	1.00	27.07	27.07	1:1
3.0	1.00	34.62	17.31	2:1
3.0	1.00	38.17	12.72	3:1
5.6	0.0025	1.11	0.56	non-acid control

Plants were harvested on the 28th day after planting, and the weights of above- and below-ground portions were determined. Dry-weight measurements were made after plants had reached constant weight in a 65°C oven. Immediately prior to harvesting, net CO₂ uptake of one leaf per plant was measured to estimate treatment effects on net photosynthesis.

Analysis of variance of the results revealed no significant treatment effects on photosynthetic rate or shoot weight. Rain acidity had a negative effect on radish yield, although the effect on dry weight was statistically significant only from treatments with the 2:1 and 1:1 SO₄⁻² to NO₃⁻ ratios (Fig. 1). The data suggest that radish shoots may develop at the expense of roots since the 2:1 acid treatment had statistically greater leaf area than the other treatments (Fig. 2) but the lowest yield (Fig. 1).

The results emphasize the need for a complete description of rain simulant chemistry when defining acid rain and reporting its effects. This

Figure 1. Radish yield versus simulated rain treatment - comparison of sulfate-to-nitrate ratio.

Figure 2. Leaf area per plant versus simulated rain treatment - comparison of sulfate-to-nitrate ratio.

study of radishes suggests that impacts of acid rain on dry weight may increase with decreasing SO_4^{-2} to NO_3^{-} ratios. A similar conclusion was made on the basis of the previous study on soybeans.¹

Prospects

More complex field experiments are warranted by the results of these preliminary greenhouse studies. Emission-control strategies under consideration by the federal government will result in changes in the ratio of sulfur and nitrogen in rain. The possible consequences of these changes on vegetative growth require further investigation.

References

1. Irving, P. M. and D. A. Sowinski, Effect of H^+ , $\text{SO}_4^{=}$, 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.
2. Irving, P. M., J. A. Maley and C. M. Gradert, Rainfall acidity interlaboratory national study - RAINS, Radiological and Environmental Research Division Annual Report, January-December 1981, ANL-81-85, Part III, pp. 1-4.

EXPERIMENTAL FIELD FACILITY FOR LONG-TERM STUDIES OF ACIDIC DEPOSITION EFFECTS ON PLANT/SOIL SYSTEMS

P. M. Irving, J. E. Miller, W. Prepejchal, J. Hoff* and J. Segers*

Background and Scope

Considerable speculation exists that acid rain occurring in the Midwest may be causing or may have the potential to cause reductions in agricultural productivity. The results of a number of investigations conducted to determine the direct effects of acid rain on crops have ranged from findings of no effect to both stimulation and reduction in yield. The differences in results may be due to plant species studied, the chemistry of the rain simulants, or soil type and conditions.¹ One hypothesis is that nutrient inputs from acid rain may be counteracting the stress from rain acidity, but research has been insufficient to substantiate this view.

Equally uncertain is the potential for acid rain to affect the long-term productivity of soils. Although acid rain may add nutrients to the soils, it may also be responsible for cation leaching, toxic metal mobilization, and reduced microbial activity. The subtle nature of these possible effects makes detection difficult and requires controlled studies.

Since the influence of acid rain is not limited to just one component of an ecosystem, an assessment of its effects must include consideration of how all sensitive components of the system are affected and of how these responses interact to control the net ecosystem change. To determine the mechanisms of action of a stress on the most sensitive or most obvious receptor, it is necessary to study interactions within the entire system. For example, the cause-effect relationship between acid rain and the acidification of surface waters can only be established through the study of watershed biogeochemical processes. These processes can be studied only in well-defined systems where inputs can be controlled but where conditions are similar to the natural environment.

*Undergraduate research participants, Argonne National Laboratory, Division of Educational Programs; Williams College, Massachusetts, and Shorter College, Georgia, respectively.

To conduct such process-oriented studies of acid-rain interactions in sensitive agro-ecosystems, a research facility was designed and constructed to achieve a controlled environment with characteristics similar to the natural environment.

Progress in 1982

A field microcosm facility with two reconstructed soil systems was designed for the purpose of conducting long-term, controlled field investigations of acid-rain impacts. The Microcosms for Acid Rain Studies (MARS) facility consists of a 186 x 30 ft (57 x 9 m) structure with a polyethylene roof, to eliminate deposition of ambient rain, and 6 ft (1.8 m) open sidewalls. Within this structure a series of 8 x 4 x 4.5 ft (2.4 x 1.2 x 1.4 m) rectangular fiberglass containers (microcosms) are positioned in the ground in pairs. Each holds one of two reconstructed soils (Fig. 1). Spray nozzles are positioned above each microcosm pair for rain simulation (Fig. 2).

Ceramic samplers are placed at various depths in the microcosms for extraction of soil water and groundwater (Fig. 3). Sensors to measure soil temperature and moisture levels are positioned near the water samplers in order to follow the flux of incoming water through the soil column. Runoff collectors are installed in each microcosm to collect water that would normally have been lost from the soil surface (i.e., during snowmelt).

Soils were selected for the facility on the basis of their agronomic importance in the Midwest and their potential sensitivity to acidic deposition. A loam - "LaHogue," a mixed mesic Aquic Argiudoll - and a sandy loam - "Alvin," a mixed mesic Typic Hapludalf - were reproduced, by horizon, in the microcosms. Determinations of pH, cation-exchange capacity, and neutralization potential suggest that the Alvin soil may be more sensitive to acid-rain effects than the LaHogue. However, measurements of sulfur levels in the soil and soil water indicate that the Alvin soil has a much higher sulfate absorption capacity and thus may be less susceptible to cation leaching and acidification from sulfate mobility. Comparisons of the two soils should contribute to the determination of the characteristics most important in estimating soil sensitivity to acidic deposition.

The microcosms were planted with a grass-legume mixture typical of a low-level management pasture or hay crop. Management techniques associated with

Figure 1. Microcosm facility consisting of covered and uncovered plots of two reconstructed soil systems.

Figure 2. **Top:** Cross-sectional diagram of research facility at Argonne National Laboratory for acid-rain studies of plant-soil systems. **Bottom:** Photo of facility with two soil types arranged in microcosm pairs beneath rain shelter.

Figure 3. Microcosm soil-water and groundwater extraction system.

Figure 4. Schematic of rain simulant metering and pumping system with feedback control.

row-crop agriculture (e.g., cultivation, fertilization, liming) are so disruptive that subtle effects from acid rain would be overwhelmed. Therefore, a perennial crop was selected as the vegetative component of the system, thus permitting no-till culture and little management.

A metering and pumping system with feedback capabilities was designed to create and distribute the rain simulant treatments (Fig. 4). Six different treatments of simulated rain are sprayed on the plots in a replicated block design. Treatment chemistries are based on data from the National Atmospheric Deposition Program (NADP) Northcentral Region and include acidity levels ranging from "no strong acids" to "10 times the mean-weighted average NADP acidity." Plots receiving ambient rain (unsheltered) are also examined.

Prospects

Research objectives are to determine the short- and long-term effects of acid rain on the productivity of the two systems. Plant growth and yield quantity and quality, as well as photosynthetic rates, will be measured to determine dose-response functions for the vegetative component of the system. Mass balance calculations based on input (simulated precipitation) and output (harvested crop, soil absorption, and groundwater) are being used to determine nutrient budgets and carbon, sulfur, and nitrogen cycling since it is hypothesized that acid rain may deplete soil minerals and plant nutrients through leaching. Mobility of heavy metals is also being examined.

Soil microbial activity is being measured to investigate acid-rain impacts on soil microbial processes that are important to plant growth and nutrient cycling.

Reference

1. Irving, P. M., Acidic precipitation effects on crops: A review and analysis of research, J. Environ. Qual. 12(4), in press.

A COMPARISON OF SOIL-WATER AND GROUNDWATER QUALITY OF TWO RECONSTRUCTED SOIL SYSTEMS EXPOSED TO AMBIENT PRECIPITATION

P. M. Irving, W. Prepejchal, S. Mabury* and L. Willman*

Background and Scope

It has been theorized that acid deposition may influence the solubility and thus mobility of metals in soil. Enhanced availability of certain metals may be toxic to vegetation in the affected ecosystem and may harm aquatic life if leached from the drainage basin. It has also been suggested that the leaching of soil nutrients is accelerated by the acidity of wet deposition. This too may affect the terrestrial and aquatic components of the system. Few controlled studies have been performed to substantiate these hypotheses. Accordingly, a field microcosm facility was constructed to examine the impact of rainfall acidity on two plant/soil systems.¹ The two reconstructed soils are a loam, "LaHogue", and a sandy loam, "Alvin."

Progress in 1982

After the microcosms were installed, a ten-month period was allowed for equilibration of the system. All microcosms were exposed to ambient rainfall, and baseline measurements were made before treatments were initiated. There were no differences in soil chemical properties among microcosms of the same soil type from samples taken during reconstruction of the soils, but there were significant differences between the two soil types (Table 1).

Baseline sampling also indicated that there were no differences in the chemistry of soil water or groundwater among microcosms of the same soil type prior to initiation of treatments. There were differences between the two soils, however, in a number of groundwater ions (Table 2). These differences are similar to the differences in soil chemistry.

*Undergraduate research participants, Argonne National Laboratory, Division of Educational Programs; Northland College, Ashland, Wisconsin; and University of Nebraska, Lincoln, respectively.

Table 1. Chemical properties of two soils reconstructed in microcosms.*

Soil Parameters	LaHogue		Alvin		
	Topsoil 0-24"	Subsoil 24-54"	Topsoil 0-10"	Subsurface 10-20"	Subsoil 20-54"
pH (1:1 H ₂ O extract)	5.8 c	7.4a	5.8 c	5.7 c	5.9 b
Electrical conductivity [†]	0.3	0.3	0.2	0.2	0.1
Neutralization potential [‡]	2.7	12.6	2.5	2.0	2.0
CEC meq/100 g	14.4	11.4 b	5.3 c	4.7 c	5.4 c
Organic C, %	2.1	1.0	1.5	0.9	0.6
Ca	2126 b	4119 a	897 c	741 c	954 c
Mg	364 b	671 a	253 c	188 c	214 c
P-Bray	2.0 c	1.2 d	4.3a	1.9 b	1.8 c
K	84.7 c	70.4 d	143.8a	103.8 b	89.5 c
NH ₄ -N	1.6ab	1.0 b	2.0a	1.4ab	1.2 b
Na	221 a	191 a	259 a	225 a	198 a
Fe	156.3a	48.8 b	56.1 b	50.3 b	40.2 c
Al	2.2 cd	1.3 d	3.0 bc	3.8ab	4.7a
Mn	11.6 b	8.0 c	13.2a	6.8 c	4.1 d
Cl	636 a	447 a	662 a	177 b	138 b
SO ₄	38.3 c	50.9a	47.6ab	39.3 bc	36.1 bc
NO ₃	17.6a	14.9a	15.5a	11.0 b	9.0 b
Total Phosphorus	453	245	247	221	170
Total Kjeldahl Nitrogen	1792	1135	1209	986	687

* Row means with a common letter are not significantly different; P < 0.05.

[†] mmhos/cm of supernatant.[‡] tons CaCO₃/1000 tons soil.

Table 2. Values for pH and mean concentration of ions in groundwater sampled in October 1982.^a

Variable	Soil	
	Alvin	LaHogue
pH	7.34	7.58*
Mn	9.42**	2.82
Fe	0.70	0.72
Na	2.43	2.41
Ca	52.36	116.86**
K	1.88*	0.92
Mg	23.53	59.94**
SO ₄	17.56	30.06**
NO ₃	1.32	1.87**

^aSymbols following the higher value of the two soils indicate differences which are statistically significant: * = P ≤ 0.01; ** = P ≤ 0.0001.

Measurements of pH in the soil water compared to that of the incoming precipitation indicate that precipitation acidity is rapidly neutralized as it percolates through the soil column (Fig. 1) and is closely related to the soil pH (Fig. 2). Sulfate concentrations present in the soil water suggest that the Alvin soil has a greater sulfate absorption capacity than the LaHogue, especially at lower depths (Fig. 3).

Heavy rains that occurred in early February 1983 when the surfaces of the soils were frozen resulted in collection of water in the microcosm runoff samplers. Analysis of those samples indicates a much greater loss of ions from the surface of the Alvin soil as compared to the LaHogue soil (Table 3). Analyses of samples for baseline determinations of metals is being completed.

Prospects

Simulated rain treatments were initiated in the fall of 1982, and soil-water measurements are being continued to determine the influence of acidic rain. Mass balance calculations will be performed to determine input-output budgets for important ions. Of particular interest will be the determination of leaching rates of nutrient cations and the mobilization of toxic metals.

Table 3. Acidity and mean concentrations of sulfate (SO_4), nitrate-N ($\text{NO}_3\text{-N}$) and phosphorus (P) in runoff water sampled in February 1983.^a

Variable		Soil	
		Alvin	LaHogue
pH		6.40	6.22
SO_4	mg/L	42.79	22.22
$\text{NO}_3\text{-N}$		6.14	3.91
P		0.38	0.20

^aThe two soils are significantly different for all variables; $P < 0.05$.

Figure 1. Values for pH of water at the surface and various depths for Alvin and LaHogue soils.

Figure 2. Soil pH values by horizon for Alvin (left) and LaHogue (right).

Figure 3. Soil water sulfate concentrations at various depths for Alvin and LaHogue soils sampled in August 1982.

Reference

1. Irving, P. M., J. E. Miller, W. Prepejchal, J. Hoff and J. Segers, Experimental field facility for long-term studies of acid deposition effects on plant/soil systems (this report).

IMPACT OF OZONE ON YIELD OF THREE CULTIVARS OF WINTER WHEAT

L. W. Kress, H. J. Smith and J. E. Miller

Background and Scope

Since 1980, Argonne National Laboratory has been a participant in the National Crop Loss Assessment Network (NCLAN). A major objective of this program is to determine the dose-response relationships between ozone (O_3) and the yield of important agricultural crops. In 1980¹ and 1981,² soybean and field corn were the crops investigated; winter wheat was chosen for study in 1982.

Wheat is the fourth most important crop in the United States in terms both of planted acreage (19%) and dollar value (13%). Previous work with four cultivars of winter wheat exposed to O_3 in open-top chambers indicated that wheat was relatively sensitive to O_3 . Yield reductions predicted from linear regressions ranged from 8.7% to 14.2% at 0.06 ppm O_3 and 18.6% to 30.4% at a 7-h seasonal average of 0.10 ppm O_3 .³

This study was initiated to provide biological response data suitable for use in setting ambient air quality standards and in the economic assessment of the consequences of O_3 exposure. Specifically, the objective was to examine the regression relationship between yield of three important cultivars of soft red winter wheat and chronic exposure to ambient or simulated ambient O_3 concentrations.

Progress in 1982

Field plantings (seed was fall sown) of three cultivars of winter wheat (Abe, Arthur-71, Roland) were exposed to various concentrations of O_3 in open-top chambers. A randomized complete block design utilizing four replicates of six treatments was used. The treatments were: AA, no chamber (ambient air); CF, charcoal-filtered air chamber; NF, non-filtered air chamber with a small amount of O_3 added to provide a concentration equal to that in the AA plot; NF+.03, NF with O_3 added to 0.03 ppm above ambient; NF+.06, NF with O_3 added to 0.06 ppm above ambient; and NF+.09, NF with O_3 added to 0.09 ppm above ambient. The chambers were placed over the plots on 7 May, and O_3 exposures began on 8 May. Ozone was added to the chambers 7 h/day (1000-1700 CDT). All

chamber fans were turned off nightly from 2230-0630 CDT. Ozone was not added on two full days and five half-days due to rain. Ozone additions were terminated 2 July, and the chambers were removed 13 July, following plant harvest. The wheat plants had just begun their spring growth and were about 15 cm tall when the exposures began. When the exposures were terminated, the plants in all treatments had brown leaves, stems, and heads. Ozone concentrations were monitored in each chamber and in the ambient air, and SO₂ was monitored in the ambient air throughout the experiment.

An ANOVA test of the data indicated significant treatment effects for the yield variables kilogram/hectare (kg/ha), seed weight/head (SW/head), and weight/100 seeds (wt/100) (oven-dry weights) for all cultivars (Table 1). There were considerable differences in the number of heads per treatment (significant for cultivar Abe) that did not appear related to treatment, so an analysis of covariance was performed for kg/ha using number of heads as the covariate. These results also indicated significant treatment effects for each cultivar. There were no significant plot differences in any of the soil variables measured (pH, OM, P, K).

The data have been plotted (Fig. 1) according to a Weibull regression model, which is being used in the NCLAN program because of its versatility. The model can take many different forms (shapes) and thus is useful in presenting dissimilar data sets in a similar format. The Weibull regression equation is given as:

$$\text{yield} = \alpha e^{-\left(\frac{O_3}{\text{sig}}\right)^c},$$

where alpha is the yield at 0.00 ppm O₃ concentration; O₃ is the O₃ dose (seasonal 7-h/day mean O₃ concentration in ppm); sig is the O₃ concentration at which yield is 0.37 alpha; and c is a dimensionless shape parameter. Omitting alpha from the equation will give the percentage yield reduction. Yield reductions predicted from the Weibull equation are 10%, 10%, and 24% at 0.06 ppm, and 33%, 32%, and 53% at 0.10 ppm O₃ (based on the 0.023 ppm control) for Abe, Arthur-71, and Roland, respectively.

Regressing the yield as a function of the other characterizations of O₃ exposure produces similar curves skewed to the right as the characterization goes from seasonal 7-h average (O₃7A), peak daily hourly concentration

Table 1. Yield response of three cultivars of winter wheat exposed to charcoal-filtered air (CF), ambient air open plot (AA), and ambient air plus O₃ (NF) during 1982.[†]

Cultivar	Treatment	O ₃ , ppm	kg/ha	Adj., kg/ha	Wt/100, g	SW/head, g	SW/plant, g	# heads/ m	# plants/ m
Abe	AA	0.041	6202a [‡]	5811a	4.25a	1.06a	3.68a	103.9ab	30.1a
	CF	0.023	4926abc	5315ab	4.29a	0.97ab	2.91 b	90.6ab	29.8a
	NF	0.041	5343ab	5050ab	4.36a	0.94ab	2.69 b	100.8ab	35.5a
	NF+.03	0.068	4211 bcd	4633 b	3.80 b	0.84 b	2.53 bc	89.3 b	29.4a
	NF+.06	0.095	3174 d	3606 c	3.10 c	0.64 c	1.93 c	87.4 b	29.9a
	NF+.09	0.122	3344 cd	2736 d	2.60 d	0.52 c	1.85 c	113.5a	32.3a
Arthur-71	AA	0.041	5398a	4746a	4.23ab	0.95a	3.30a	100.8a	29.1a
	CF	0.023	4358ab	4647a	4.32a	1.00a	3.11a	78.4a	25.1a
	NF	0.041	4481ab	4300a	4.26ab	0.92a	3.03a	86.8a	26.9a
	NF+.03	0.068	3768 b	3958a	3.94 b	0.86a	2.52 ab	78.4a	27.1a
	NF+.06	0.095	3295 bc	3151 b	3.24 c	0.67 b	1.97 bc	86.9a	30.0a
	NF+.09	0.122	2443 c	2412 b	2.65 d	0.52 c	1.69 c	84.1a	25.8a
Roland	AA	0.041	6620a	5771a	3.56a	1.15a	4.25a	102.6a	28.0ab
	CF	0.023	5159 b	5007a	3.64a	1.12a	3.34ab	82.3 b	27.6ab
	NF	0.041	4405 bc	4668ab	3.32a	1.03a	2.92 bc	75.4 b	27.9ab
	NF+.03	0.068	3744 cd	3557 b	2.73 b	0.79 b	2.17 cd	84.0 b	30.8a
	NF+.06	0.095	2655 de	2455 c	2.07 c	0.55 c	1.75 d	85.9ab	27.5ab
	NF+.09	0.122	1687 e	1859 c	1.83 c	0.42 c	1.33 d	72.0 b	22.6 b

[†]kg/ha adjusted using # heads as the covariate;

Wt/100 = weight of 100 seeds;

SW/head = seed weight per head;

SW/plant = seed weight per plant.

[‡]Means (within a cultivar) in a column followed by the same letter are not significantly different at P = 0.05 according to Duncan's New Multiple Range Test.

averaged over the season (O_3 1A), highest 7-h average (O_3 7H), and the highest seasonal hourly value (O_3 1H)(Fig. 2). The same regressions were performed with data from the other crops studied since 1980 at Argonne (Fig. 3).

Figure 1. Exposure-response curves for seed yield (Adj., kg/ha) of three cultivars of winter wheat as a function of the seasonal 7-h daily average O_3 concentration. Weibull regression equations are:

$$\text{Abe} \quad Y = 5339.7 e^{-\left(\frac{O_3}{.1432}\right)^{2.455}}$$

$$\text{Arthur-71} \quad Y = 4590.5 e^{-\left(\frac{O_3}{.1472}\right)^{2.339}}$$

$$\text{Roland} \quad Y = 5450.7 e^{-\left(\frac{O_3}{.1126}\right)^{1.69}}$$

These results indicate that winter wheat may be somewhat more sensitive to O_3 than previously estimated³ (using different cultivars), although the most sensitive cultivar (Roland) in this study is considerably less widely planted than the other two. The predicted yield reductions from Corsoy soybean¹ (17% at 0.06 ppm and 42% at 0.10 ppm) rank soybean as more sensitive than Abe and Arthur-71 but less sensitive than Roland. All three wheat cultivars are considerably more sensitive to O_3 than field corn² or sorghum.⁴

Figure 2. Exposure-response curves (Weibull) for seed yield of winter wheat and sorghum as a function of O_3 characterized as: Seasonal 7-h daily average (—); single 7-h daily maximum (---); seasonal 1-h daily peak average (- - -); single 1-h maximum (····).

Figure 3. Exposure-response curves (Weibull) for seed yield of field corn, soybean, sorghum, and wheat as a function of O_3 characterized as: Seasonal 7-h daily average (—); single 7-h daily maximum (---); seasonal 1-h daily peak average (- - -); single 1-h maximum (····).

Prospects

These data will be combined with data from five other field sites for evaluation of the effects of O₃ on important agricultural crops. This information will be important to the current re-evaluation of the National Ambient Air Quality Standard for O₃ in terms of the biological response data and as input into a comprehensive economic analysis of air pollution induced yield losses.

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. Kress, L. W. and J. E. Miller, Impact of ozone on yield of field corn, Radiological and Environmental Research Division Annual Report, January-December 1981, ANL-81-85, Part III, pp. 23-26.
3. Heagle, A. S., S. Spencer and M. B. Letchworth, Yield responses of winter wheat to chronic doses of ozone, Can. J. Bot. 57, 1999-2005 (1979).
4. Kress, L. W., H. J. Smith and J. E. Miller, Impact of ozone on yield of grain sorghum (this report).

IMPACT OF OZONE ON YIELD OF GRAIN SORGHUM

L. W. Kress, H. J. Smith and J. E. Miller

Background and Scope

As part of Argonne National Laboratory's role in the National Crop Loss Assessment Network (NCLAN), the effects of ozone (O_3) on winter wheat were studied in 1982.¹ Because winter wheat was harvested early in the summer, a second, late-season crop, grain sorghum, was also selected for study in 1982.

Grain sorghum is the fifth most important in the United States in terms of acreage planted (4%), and seventh in terms of dollar value (5%). It is an important crop in some areas of the Midwest, primarily where rainfall amounts are inadequate for significant field corn production.

The specific objective of this study was to examine the relationship between yield of sorghum and chronic exposure to ambient or simulated ambient O_3 concentrations.

Progress in 1982

Field-grown sorghum plants (DeKalb A28+) were exposed to various O_3 concentrations in open-top chambers. Seeds were planted 24 June, chambers were placed over the plants 13 July, and O_3 additions began 16 July. A randomized complete block design utilizing three replicates of seven treatments was employed. The treatments were: AA, no chamber (ambient air); CF, charcoal-filtered air chamber; NF, non-filtered air chamber with a small amount of O_3 added to provide a concentration equal to that in the AA plot; NF+.02, NF with O_3 added to 0.02 ppm above ambient; NF+.04, NF with O_3 added to 0.04 ppm above ambient; NF+.07, NF with O_3 added to 0.07 ppm above ambient; and NF+.10, NF with O_3 added to 0.10 ppm above ambient. In addition there was an extra NF+.02 and an extra NF+.04 treatment in one replication. Exposure treatments were terminated on 8 October and the grain heads were harvested on 14 October. There also were 46 companion plots of two 1-m rows each regularly placed throughout the plot. The yield data from these plots were used in an analysis of covariance to normalize the open-top chamber plot data. The average yield of the four companion plots around each NF plot was used as the AA plot in the evaluation for chamber effect.

The ANOVA test indicated significant treatment effects for kg/ha and wt/100 seeds (oven-dry weight; Table 1). The companion plot data (ambient plots) and soil analysis data (pH, OM, P, K) indicated no significant plot differences. There appeared to be a chamber effect on the yield of sorghum (Table 1). Yield was significantly greater but the seeds were significantly smaller in open plots (AA) compared to the ambient air chamber (NF). The reason for this apparent chamber effect is not known.

Table 1. Yield response of grain sorghum (DeKalb A28+) exposed to charcoal-filtered air (CF), ambient air in open plots (AA), and ambient air plus O₃ during 1982.

Treatment	O ₃ , ppm	kg/ha	wt/100, g [†]
AA	0.039	8560a [‡]	2.17 bc
CF	0.016	8282ab	2.43a
NF	0.040	7643 bcd	2.39a
NF+.02	0.059	8107ab	2.42a
NF+.04	0.078	7784 bc	2.35a
NF+.07	0.102	7272 cd	2.23 b
NF+.10	0.129	6994 d	2.14 c

[†]Each value is estimated from the yield of 252 plants (336 plants for NF+.02 and NF+.04).

[‡]Means in a column followed by the same letter are not significantly different at P = 0.05 according to the Duncan's New Multiple Range Test.

The Weibull and plateau-linear model regressions are shown in Figure 1. The AA plots were not used in the regressions. The Weibull model was defined in the preceding paper in this report.¹ The plateau-linear model is given as:

$$\text{yield} = \alpha + \tau (-b[\text{O}_3 - \chi])$$

where alpha is the yield at an O₃ concentration ≤ a threshold (χ); χ is the O₃ concentration at or below which there is no effect on yield (threshold); b is the slope of the regression line; and τ is 0 at or below the O₃ threshold and

1 above the O_3 threshold. Neither model permits an increase in yield. Yield reductions predicted from the Weibull equation are 3% at 0.06 ppm and 8% at 0.10 ppm O_3 (based on the 0.016 ppm control). The plateau-linear regression predicts a threshold for kg/ha yield effects of 0.061 ppm O_3 .

Figure 1. Exposure-response curves for seed yield of grain sorghum as a function of the seasonal 7-hr daily average O_3 concentration. Regression equations are:

$$\text{Weibull} - Y = 8137 e^{-\left(\frac{O_3}{.2963}\right)^{2.217}}$$

$$\text{Plateau-linear} - Y = 8020 + \tau (-16104.2 [O_3 - 0.0615])$$

where:

$$\begin{aligned} O_3 \leq 0.0615, & \text{ then } \tau = 0 \\ O_3 > 0.0615, & \text{ then } \tau = 1. \end{aligned}$$

Regressing the yield against the other characterizations of O_3 exposure indicated similar curves skewed to the right as the characterization goes from the seasonal 7-h average (O_{37A}), peak daily hourly concentration averaged over the season (O_{31A}), highest 7-h average (O_{37A}), and the highest seasonal hourly value (O_{31H}) (see Fig. 3 in the preceeding paper in this report).¹

Prospects

These results indicate that sorghum is considerably less sensitive to O₃ than soybeans² or wheat.¹ While the threshold for O₃ effects is similar for sorghum and field corn,³ sorghum is considerably less sensitive than field corn once the threshold is exceeded.

These data will be useful in the re-evaluation of the National Ambient Air Quality Standard for O₃ and will be part of the input into a comprehensive economic analysis of air pollution induced yield losses.

References

1. Kress, L. W., H. J. Smith and J. E. Miller, Impact of ozone on yield of three cultivars of winter wheat (this report).
2. 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.
3. Kress, L. W. and J. E. Miller, Impact of ozone on yield of field corn, Radiological and Environmental Research Division Annual Report, January-December 1981, ANL-81-85, Part III, pp. 23-26.

THE FLUX OF PLUTONIUM FROM SEDIMENTS TO WATER IN LAKE MICHIGAN

D. M. Nelson and D. N. Metta

Background and Scope

The concentration of $^{239,240}\text{Pu}$ in Lake Michigan water has changed little over the past decade. By 1972, less than ten years after the major weapons-fallout input, only 3% of the added plutonium remained in the water.¹ This demonstrated a rapid (at least 40%/year) initial transfer of plutonium to sediments. In the following ten years the water column inventory has only decreased to 2% of the total input. This slowing in the rate of decrease of plutonium concentration suggests that by 1972 a steady-state situation had developed in which the flux of plutonium from the water to the sediments is approximately balanced by a flux of plutonium from the sediments to the water. If plutonium concentration in lake water had been measured during the years of maximum input, and hence of maximum concentration change, it would have been possible to deduce directly the magnitude of the downward flux. As it is, all of the measurements apparently were made after the establishment of a steady-state condition, and neither the downward nor upward flux can be estimated directly.

Last year we estimated the rate at which thorium was transferred from the water to the sediments of Lake Michigan and outlined a method by which this information could be used to calculate the analogous downward flux of plutonium.² The estimate of thorium-removal rate was based upon measurement of the degree to which ^{228}Th and ^{234}Th were found to be out of radioactive equilibrium with their parent isotopes, ^{228}Ra and ^{238}U . Those measurements were made at only one time and place, and hence the measured thorium-removal rate could not be considered to be representative for the entire lake.

Progress in 1982

Measurements of ^{228}Th and ^{234}Th have now been completed on samples of water collected from offshore locations in Lake Michigan on 18 October 1981, 11 March 1982, and 29 April 1982. The lake was thermally stratified on the first date and was isothermal on the last two. The results of the ^{228}Th analyses on these samples are summarized in Table 1 along with the previously

Table 1. Concentrations of ^{228}Th in water from Lake Michigan as a function of water depth and date of sampling.

Date	Depth, m	^{228}Th Concentration, fCi/L			Average ^a
		Dissolved	Particulate	Total	
1 September 1981	15	<0.05	0.25	0.25	0.74
	35	<0.05	0.56	0.56	
	45	<0.05	0.81	0.81	
	55	<0.05	0.86	0.86	
18 October 1981	20	--	0.11	0.11	0.77
	50	--	0.23	0.23	
	75	--	0.61	0.61	
	100	--	0.74	0.74	
	127	--	0.95	0.95	
11 March 1982	2	0.22	0.54	0.76	0.80
	45	0.33	0.50	0.83	
29 April 1982	3	0.25	0.48	0.74	0.72
	100	0.24	0.45	0.69	

^aValues represent average total ^{228}Th concentration for each sampling date, exclusive of samples collected above the thermocline during stratification.

reported data from 1 September 1981. These data show a remarkable uniformity in the concentration of ^{228}Th . With the exception of the samples collected above the thermocline during stratification, the ^{228}Th concentration is within the range of 0.5-1.0 fCi/L. Between 60% and 100% of the ^{228}Th was associated with suspended particulate matter, with the lowest values occurring in the water samples having the lowest concentrations of suspended particles. These ^{228}Th concentrations can be used to calculate the thorium removal rate, λ_c , using the following relationship:

$$\lambda_c = \lambda_T \left(\frac{A_T}{A_P} - 1 \right)$$

where λ_T is the radioactive decay constant of ^{228}Th and A_T and A_P are the activities of the ^{228}Th and its parent ^{228}Ra , respectively. We have measured the concentration of ^{228}Ra in Lake Michigan and found it to be constant throughout the lake at ~17 fCi/L. Thorium-removal rates calculated using this

relationship are presented in Table 2. The average removal rate is ~2% per day, with little spatial and temporal variation.

Table 2. Removal rate (λ_c) and half removal time ($t_{1/2}$) of thorium from Lake Michigan, based on concentrations of ^{228}Ra - ^{228}Th in water.^a

Date	^{228}Th , fCi/L	λ_c day ⁻¹	$t_{1/2}$, day
1 September 1981	0.74	0.022	32
18 October 1981	0.77	0.021	33
11 March 1982	0.80	0.020	34
29 April 1982	0.72	0.023	31
Average		0.0215	

^aAt a constant ^{228}Ra concentration of ~17 fCi/L.

A similar analysis was done using the concentrations of ^{234}Th in the same samples. The removal rates as presented in Table 3 were calculated using a mean ^{238}U parent concentration of 92 fCi/L. These removal rates are less consistent than those derived from ^{228}Th data, but the average value is nearly the same for both methods. The greater variability of the results from the ^{234}Th data is probably related to the shorter half-life of ^{234}Th (24 days) relative to ^{228}Th (1.91 years). Estimates of thorium-removal rate based on ^{234}Th may, therefore, be more sensitive to short-term fluctuations in the rate. General agreement of the two estimates of average removal rate demonstrates that the return of ^{228}Th from the sediments to the water is a minor component which can safely be neglected.

Thorium is lost from the water column as a result of its attachment to settling particulate matter. Plutonium is presumably lost in a similar manner but at a slower rate, since only about 20% of the plutonium in Lake Michigan water is present as Pu(IV), the form analogous to thorium. The remainder is present as Pu(V), a poorly sorbed form. As a result, only 10% to 30% of the plutonium in Lake Michigan water is associated with suspended particles, in contrast to the nearly complete association of thorium with such particles.

The rate at which plutonium is removed from the water via the settling of these particles must therefore be proportionally lower, i.e., about 20% of the rate of thorium removal, or 0.4% per day. This yields an annual flux of plutonium to the sediments which is 150% of the water column inventory. The average annual change in plutonium concentration over the past ten years has been about 3% to 5%.

Table 3. Removal rate (λ_c) and half removal time ($t_{1/2}$) of thorium from Lake Michigan, based on concentrations of ^{238}U - ^{234}Th in water.^a

Date	^{234}Th , fCi/L	λ_c day ⁻¹	$t_{1/2}$, day
1 September 1981	65	0.012	58
28 October 1981	35	0.047	15
11 March 1982	41	0.036	19
29 April 1982	60	0.015	45
Average		0.027	

^aAt a constant ^{238}U concentration of 92 fCi/L.

Since the observed change in water column inventory of plutonium is far less than the change expected from the removal flux, an input flux of approximately equal magnitude must exist. The current inputs from atmospheric fallout, watershed erosion, and nuclear reactor discharges are known to be very small, and hence the only plausible remaining plutonium source is the sediments. A flux of plutonium out of the sediments equal to that entering from the water would require 3% of the current sediment inventory (~200 fCi/cm²) to be recycled through the water each year.

Although the fluxes of plutonium into and out of the sediments can be calculated in this manner, no information is gained regarding the mechanism of transfer. The simplest mechanism, and one which is consistent with our other knowledge, is one in which the fluxes result from adsorption and desorption reactions of plutonium atoms with sediment particles either at the sediment-water interface or via resuspended particles.

Care should be taken in the choice of words used to describe this phenomenon. The term "remobilization" is sometimes used to describe the transfer of material from sediments to water, but its use to describe the transfer of plutonium from sediment to water in Lake Michigan may not be justified in this instance. Remobilization suggests that material was at some time immobile and through some process, e.g., a change in chemical form, has become mobile. The situation in Lake Michigan is consistent with a model in which the plutonium atoms have a steady-state distribution between dissolved and adsorbed forms, and in which any given atom exchanges forms frequently. The processes responsible for returning plutonium to the water are probably the mirror image of those responsible for removing it in the first place. The flux of plutonium from the sediments will not result in increased concentrations in the water in the future, i.e., "remobilization" will not occur, but instead the flux will merely maintain the concentration near its present level. Ultimately the surficial sediments, those which are the source of the plutonium returning to the water, will be diluted by and buried under new sediments entering from the watershed. This process is probably responsible for the slow decrease in plutonium concentrations observed over the past decade.

Prospects

The cycling of plutonium between sediments and water is undoubtedly not restricted to Lake Michigan. It probably occurs in all bodies of water, and we feel that the rate at which it proceeds is measurable anywhere using the above technique. Because the magnitude of the flux from sediments to water in Lake Michigan is far larger than the current inputs from other sources, it is certainly a factor which needs to be considered in any model designed to predict the long-term behavior of plutonium in this or any similar system. Similarities in the chemical speciation and adsorptive behavior of plutonium in Lake Michigan and those in coastal areas of the ocean suggest that plutonium may be lost from marine sediments at a rate comparable to that in Lake Michigan.

Areas which have been contaminated with plutonium in the past would be particularly valuable places in which to test the utility of this method for estimating plutonium fluxes. In such areas, e.g., the Enewetok and Bikini

lagoons, the net loss of plutonium from sediments is directly measurable as an increase in plutonium concentration following influx of noncontaminated water from outside of the system. These fluxes could be compared with those derived by analogy from the thorium-removal rate, and if the values are consistent, the latter method could be used in other areas with greater confidence.

References

1. Wahlgren, M. A. and J. S. Marshall, The behaviour of plutonium and other long-lived radionuclides in Lake Michigan, in Impacts of Nuclear Releases into the Aquatic Environment, Proc. IAEA Symp. Otaniemi, Finland, IAEA-SM-198/39, pp. 227-243 (1975).
2. Nelson, D. M. and D. N. Metta, Rate of removal of natural thorium isotopes from Lake Michigan water, Radiological and Environmental Research Division Annual Report, January-December 1981, ANL-81-65, Part III, pp. 42-47.

PLUTONIUM SOLUBILITY IN NATURAL WATERS

D. M. Nelson, R. P. Larsen, and J. O. Karttunen

Background and Scope

Most of our knowledge of the behavior of plutonium in natural waters has been derived from systems with very low plutonium concentrations (10^{-17} to 10^{-15} M). At these low concentrations, interactions between plutonium atoms are rare, and the observed behavior can be explained as that of single plutonium atoms interacting with various environmental constituents. At higher concentrations, interactions between plutonium atoms will increase, and at some concentration, aggregates of plutonium atoms will become important. The plutonium concentration at which this transition from monoatomic to polyatomic species occurs in a given water marks the upper limit of "true" solubility for the monoatomic species in that water. It is important to establish at what concentration this transition occurs relative to the maximum permissible concentration (MPC) of plutonium in drinking water, since if a plutonium compound precipitates at a lower concentration, plutonium can never become a radiological hazard.

The current MPC of ^{239}Pu is $\sim 10^{-10}$ M, well above the concentrations currently found in natural systems. Therefore, information concerning plutonium behavior at concentrations near the MPC must be derived from laboratory experiments using added plutonium. Because the chemistry of plutonium is complex, caution must be exercised in the planning, execution, and interpretation of such experiments to ensure that they are actually relevant to natural systems. Our method of ensuring relevance has been first to characterize the plutonium currently existing in natural systems. Second, an experimental protocol is devised in which the characteristics of the added plutonium closely match those of the ambient plutonium. Finally, the parameter of interest (in this case the concentration of added plutonium) is varied and the response of the system is noted.

The point at which increasing concentrations of plutonium alter an aquatic system can be detected in two ways. One is to look for the appearance of a filterable solid phase in a series of filtered test waters containing varying concentrations of plutonium. The second (and we feel more sensitive)

method is to monitor the adsorptive behavior of plutonium toward a well-characterized solid phase as a function of plutonium concentration. A change in adsorptive behavior signals a change in the chemical form of the dissolved plutonium and could mark the point at which a polyatomic species begins to form. Both of these approaches have been applied to samples of natural water.

Progress in 1982

An important aspect of this problem has been to devise a technique to introduce elevated concentrations of plutonium into natural waters in such a way that the resulting chemical forms of the added plutonium are the same as those of the ambient plutonium. The simplest spiking procedure, the addition of tetravalent plutonium in strong acid solution, is unacceptable because of the conflicting requirements of maintaining the ambient pH in a natural water while adding a sufficient quantity of acid to forestall polymerization of the added plutonium during the dilution process. This problem is particularly acute at higher plutonium concentrations where polymerization during dilution, followed by very slow depolymerization, might be mistaken for the appearance of a stable solid phase.

A solution to this problem which we have found to be satisfactory is to introduce the plutonium as Pu(IV) in 1 M NaHCO₃. A thousand-fold dilution of such a plutonium solution increases the total carbonate concentration of a natural water by only 1 mM. This technique completely eliminates the transient passage of the tracer through the low acidity, low pH range where polymerization is a particular problem. In the two waters we have tested so far, dilution is accomplished at an essentially constant pH (~8.3).

The plutonium solutions which we add to the natural waters consist of mixtures of ²³⁷Pu and ²⁴²Pu. ²³⁷Pu is used because of its convenient γ-ray emission, while varying amounts of ²⁴²Pu are added to establish the total molar concentration of plutonium. Stock solutions of these two isotopes are maintained as the tetravalent form in 8 M HNO₃. Just before use, appropriate portions of these two solutions are pipetted into a small glass beaker and the resultant mixture is evaporated to dryness under low heat. When the mixture is dry, the appropriate amount of 1 M NaHCO₃ is added and the beaker is again heated gently. The resulting solution, containing nearly all of the plutonium, is transferred to the equilibration vessel, and the water is added

accomplishing a very rapid dilution and mixing. Most of our experiments are conducted using 200 mL of sample water and 200 μ L of NaHCO_3 tracer solution.

Using this method of introducing plutonium, we have conducted a series of experiments over a range of plutonium concentrations from 10^{-14} to 10^{-7} M. In this set of experiments, plutonium was added to samples of water collected from Lake Michigan and from a pond at Argonne National Laboratory (ANL). These waters were then equilibrated for seven days with a small amount of a natural Lake Michigan sediment (11 mg/200 mL). The samples were then filtered and the plutonium in the filtrate was separated into reduced (oxidation states III and IV) and oxidized (oxidation states V and VI) fractions by LaF_3 precipitations. The amount of plutonium in each fraction was then measured. Results of these measurements were used to calculate the total concentration of plutonium remaining in solution at the end of the experiment, the oxidation-state distribution of that plutonium, and the distribution ratio:

$$K_D = \frac{\text{concentration of Pu(III,IV) on the particles}}{\text{concentration of Pu(III,IV) in the water}}$$

for the reduced plutonium. The plutonium on the particles has been shown to be overwhelmingly in the reduced form.

Examination of these data (Table 1) reveals systematic differences in oxidation-state distribution and in K_D values between the two waters, but no difference related to the variation in dissolved plutonium concentration. The differences between the two waters are consistent with previous observations of the ambient plutonium in lakes.¹ Lake Michigan is representative of oligotrophic waters having low concentrations of dissolved organic carbon (DOC $\sim$ 1 ppm). The plutonium in such lakes is primarily oxidized, and the K_D of the reduced form is high. The ANL pond is representative of more productive waters, having higher concentrations of dissolved organic carbon (DOC $\sim$ 11 ppm). In such lakes the plutonium is primarily reduced, and the K_D of the reduced form is lower than the K_D found in lakes with low levels of dissolved organic carbon. These features have been reproduced in the laboratory equilibrations, confirming that the added plutonium was present in the same forms and proportions found for ambient plutonium.

Table 1. Plutonium oxidation-state distribution in water, and sediment-to-water distribution ratio (K_D) of Pu(III,IV) as a function of plutonium concentration in two natural waters.

	Dissolved Plutonium		K_D Pu(III,IV)
	Concentration, <u>M</u>	Pu(V,VI), % Total Pu	
Lake Michigan	1.6×10^{-15}	86	6.7×10^5
	2.0×10^{-14}	86	5.5×10^5
	1.5×10^{-13}	78	5.0×10^5
	1.5×10^{-12}	80	5.0×10^5
	1.5×10^{-11}	73	4.0×10^5
	1.6×10^{-10}	84	6.2×10^5
	1.7×10^{-9}	85	6.1×10^5
	1.6×10^{-8}	<u>82</u>	<u>5.3×10^5</u>
	AVERAGE	82	5.5×10^5
ANL Pond	0.7×10^{-15}	17	3.3×10^5
	1.8×10^{-14}	25	1.2×10^5
	2.1×10^{-13}	26	1.0×10^5
	1.9×10^{-12}	21	1.1×10^5
	2.6×10^{-11}	19	0.7×10^5
	2.1×10^{-10}	17	0.9×10^5
	2.1×10^{-9}	19	0.9×10^5
	2.2×10^{-8}	<u>30</u>	<u>1.0×10^5</u>
	AVERAGE	22	1.3×10^5

The lack of variation in either oxidation-state distribution or in K_D as a function of plutonium concentration is persuasive evidence that the chemical speciation of the plutonium has remained constant throughout this entire concentration range. Unchanged speciation over a range of concentrations in turn implies that the environmental constituents with which the plutonium species interact have not become saturated. The basic environmental behavior of plutonium would therefore not be expected to change until dissolved plutonium concentrations exceeded the highest values found in this study ($\sim 2 \times 10^{-8}$ M). This is more than 100 times higher than the current MPC for ^{239}Pu .

Although these experiments have not yet been carried out at sufficiently high plutonium concentrations to detect the transition from monoatomic to polyatomic behavior, it is unlikely that any moderate-sized natural system

could ever be contaminated beyond the levels in our most concentrated samples. The sediment phases in these two experiments contained ~ 0.4 mg Pu/g of sediment. If it is assumed that any realistic natural system contains at least 1 g sediment/cm² of area, then it would take a prodigious amount of plutonium, 4×10^6 g, to contaminate even a 1-km² system to a level equivalent to our highest samples. Therefore, it appears that throughout the entire range of plausible plutonium contamination events, the behavior of plutonium will be ultimately dominated by reactions of individual plutonium atoms with other environmental constituents, that these constituents will not become saturated, and that reactions between plutonium atoms are comparatively unimportant.

The preceeding discussion is based on the assumption that the plutonium was introduced in a monoatomic form. For plutonium initially present in a polyatomic form, e.g., Pu(OH)₄ or PuO₂, the monoatomic solubility behavior would be approached with time as an upper limit, provided the total plutonium concentrations did not exceed those used in this study. The rate of conversion to the monoatomic form would depend on the rate of dissolution of the initial source, which in turn would vary with particle size and crystallinity.

We also conducted experiments in which no added solid phase was present. Samples of filtered water from Lake Michigan and from the ANL pond were tested over a range of plutonium concentrations from 10^{-14} M to 10^{-6} M. Subsamples were removed from each sample at various times after spiking, and the distribution of plutonium among several separable forms was measured. The separation scheme consisted of sequential filtrations through 0.2- μ m Nucleopore (polycarbonate) and 0.45- μ m Millipore (cellulose acetate/nitrate) filter membranes, followed by separation of the filtrate plutonium into reduced and oxidized fractions. (The two filtrations were done because in previous spiking experiments we have occasionally found evidence for an as yet unidentified form of plutonium which adsorbs strongly to Millipore filters.) The Nucleopore filter removed the plutonium bound to filterable particles, while the Millipore filter removed the plutonium in the "surface-active" form.

The distribution of plutonium among these four forms in Lake Michigan water is presented in Figure 1 for three concentrations of plutonium. At the highest concentration of added plutonium, 10^{-6} M, the plutonium was rapidly

Figure 1. Distribution of plutonium among four physical/chemical forms in Lake Michigan water as a function of time after spiking. Total plutonium concentrations equal 10^{-6} M in (a), 10^{-10} M in (b), and 10^{-14} M in (c). NF is retained by an 0.2- μ m Nucleopore filter. MF is retained by an 0.45- μ m Millipore filter after Nucleopore filtration. Pu_{ox} and Pu_{red} are dissolved fractions in the oxidized and reduced forms.

converted from dissolved Pu(III,IV) into a particulate form that was retained by the Nucleopore filter. This is assumed to be the hydroxide or other hydrous oxide. A significant amount of the plutonium was present in the "surface-active" (Millipore) fraction, which may consist of colloidal plutonium polymer. The fraction in this form decreased gradually with time. The proportion of Pu(V,VI) increased gradually during the experiment, although it was always a minor fraction.

At an intermediate concentration, 10^{-10} M (corresponding to the present MPC of ^{239}Pu), the distributions were quite different from those at 10^{-6} M. The fraction present as dissolved Pu(III,IV) decreased much more slowly with time, although it did decrease. Particle-associated plutonium was never a major component and probably did not represent a precipitate of a plutonium compound since at 10^{-6} M only 90% of the plutonium had precipitated. It probably consisted of plutonium adsorbed to other particles which formed in the water. The surface-active form was most abundant a few days after spiking, when it was more abundant than the particulate form, and appeared to decrease with time. The oxidized form, in contrast to its minor role at 10^{-6} M, increased dramatically with time and by the end of the experiment accounted for over half of the total plutonium.

At the lowest concentration (10^{-14} M), the distribution of plutonium among the four fractions was quite similar to that observed at 10^{-10} M. The particle-associated fraction was somewhat less abundant and almost certainly consisted of plutonium atoms associated with other solid material. The oxidized plutonium fraction had become even more dominant and at the end contained about 75% of the plutonium.

In general, the results of this series of experiments (conducted in the absence of a pre-existing solid phase) confirmed the results of those experiments done in the presence of sediments. The results were, however, much harder to interpret. We have previously found that when sediment particles are present, both redox and adsorption/desorption equilibria are established within a few days. In the absence of added particles, these systems were still changing after a month. Because of the very slow kinetics, the probability for formation of extraneous solid phases (mineral and/or organic) increases, and hence it is very difficult to detect the point at which a true plutonium precipitate forms. Both experimental methods support the conclusion that plutonium concentrations higher than the MPC value can be supported in Lake Michigan water without the formation of a solid plutonium mineral phase.

Experiments conducted in sediment-free ANL pond water show that ~90% of the added plutonium remained in solution as Pu(III,IV) for at least a month when the plutonium concentration was 10^{-7} M or less. At 10^{-6} M, a precipitate did develop, but at a much slower rate than in Lake Michigan water. This

observation supports the conclusion that in pond water, as in Lake Michigan water, the intrinsic solubility of plutonium is higher than its MPC, and the behavior of plutonium in this system is dominated by adsorption/desorption reactions rather than by precipitation processes.

Prospects

We have shown that the solubility of plutonium exceeds 1×10^{-8} M in both Lake Michigan and ANL pond water when natural particulate matter is present. Additional experiments will be conducted at higher molar concentrations to establish the actual upper limit to solubility. Also, additional experiments will be carried out using neptunium and americium to determine the concentration range over which their solubilities are limited by adsorption, rather than precipitation, processes.

Reference

1. Wahlgren, M. A. and K. A. Orlandini, Comparison of the geochemical behavior of plutonium, thorium and uranium in selected North American lakes, in Environmental Migration of Long-Lived Radionuclides, Proc. IAEA Symp., Knoxville, Tennessee, IAEA-SM-257/89, pp. 757-774 (1982).

PLUTONIUM CONCENTRATIONS IN THE GREAT LAKES - AN UPDATE

D. M. Nelson and D. N. Metta

Background and Scope

The Great Lakes, and in particular Lake Michigan, were among the first lakes in which plutonium concentrations were systematically investigated.^{1,2} This early work, along with other periodic measurements, comprise the most complete historical record of plutonium behavior available for any freshwater system. A record of plutonium concentrations over a long time period is essential to the development and testing of realistic models of plutonium behavior. In particular, the question of the return of plutonium from sediments to water can best be addressed if a complete record is available. Although Lake Michigan is no longer our primary focus, we do attempt to maintain this record of plutonium concentrations whenever possible.

Progress in 1982

Data on plutonium concentration in Lake Michigan were last published in 1978.³ Table 1 summarizes the data collected since then and includes the earlier data from offshore locations for comparison. These most recent data are restricted to stations in excess of 20 km offshore, and except for October 1981 were collected while the lake was isothermal. The slow decrease in total plutonium concentration noted in 1978 has continued through 1982 at a rate of ~5% per year. The removal rate, following the major nuclear weapons fallout inputs in the early 1960s, needed to decrease plutonium concentrations to the levels found in 1972 must have been much greater, at least 40% per year. This difference in removal rate implies that the mechanism of plutonium removal from Lake Michigan must be considered at least a two-step process -- a rapid initial step in which most (>97%) of the plutonium is removed from the water, followed by a much slower removal of the remainder.

One possible explanation for this behavior is suggested by the presence of two distinct chemical forms of plutonium in Lake Michigan, a strongly sorbed reduced form and a weakly sorbed oxidized form. The rapid initial decrease might correspond to removal of the reduced form, and the slow decrease might correspond to removal of the oxidized form. This hypothesis

requires that the two forms of plutonium be considered nonexchangeable, i.e., reduced atoms remain reduced and oxidized atoms remain oxidized. Two lines of evidence argue that this is not true and that exchange does occur. First, extensive laboratory tracer experiments show the two forms of plutonium to be readily exchangeable in mixtures of Lake Michigan water and sediment. Secondly, measurement of the oxidation-state distribution of plutonium in the deep ocean shows roughly half of the total plutonium in each form, far different from the distribution in Lake Michigan. Interconversion of oxidized and reduced plutonium atoms must have occurred in at least one, and most probably both, of these systems. Therefore the suggestion that the two-step removal process results from a segregation of two nonexchangeable forms is invalid.

Table 1. Concentrations of $^{239,240}\text{Pu}$ in Lake Michigan water.

Time Period	$^{239,240}\text{Pu}$, fCi/L		Number of Samples
	Total	Dissolved	
1972	0.80 ± 0.16^a	$(0.62)^b$	14
1973	0.77 ± 0.11^a	$(0.59)^b$	5
1974	0.73 ± 0.10^a	$(0.56)^b$	4
1975	0.62 ± 0.10^a	$(0.48)^b$	4
1976	0.63 ± 0.12^a	$(0.49)^b$	9
1977	0.58 ± 0.06^a	$(0.45)^b$	6
Dec 1979	0.57 ± 0.09	0.41 ± 0.06	12
Mar 1980	0.55 ± 0.11	0.42 ± 0.09	14
Dec 1980-Feb 1981	0.51 ± 0.12	0.40 ± 0.10	17
Oct 1981	0.44 ± 0.15	0.40 ± 0.13	5
Mar 1982-Apr 1982	0.45 ± 0.10	0.39 ± 0.07	5

^aData from reference 1.

^bAssumed to be 77% of the total plutonium concentration.

A much more plausible explanation supposes that the two chemical forms are always near equilibrium. The initial rapid removal corresponds to the establishment of an adsorption/desorption equilibrium between plutonium atoms in solution and those in the surficial sediments. This decrease, the rate of which can be estimated using a method described elsewhere in this report,⁴

ends when the flux of plutonium atoms leaving the sediment equals the flux entering. After this initial equilibration phase, the concentrations decrease much more slowly, at a rate determined by the rate at which the surficial sediments are (1) diluted by mixing with deeper non-contaminated sediments and (2) diluted by less contaminated sediments from the watershed or from shoreline erosion. The data in Table 1 indicate this rate is about 5% per year.

A similar but less extensive set of data that is available for Lakes Ontario, Erie, and Huron is presented in Table 2. Because of the good reproducibility of the data from Lake Michigan, we feel that the concentrations reported here are fairly representative of the lakes as a whole in spite of the limited number of samples. In each lake the trend of concentrations is similar to that already seen in Lake Michigan. The concentrations in 1973 imply a rapid initial clearance of plutonium from the water, while the much slower decreases since then imply that a steady-state condition has developed. The conceptual model outlined above is thus compatible with the data from each of these lakes. Differences in equilibrium plutonium concentration between the lakes are related to differences in sediment accumulation rate and mixing, and we feel that these differences will be shown to correlate with differences in plutonium concentration in the surficial sediments.

Table 2. Concentrations of $^{239,240}\text{Pu}$ in unfiltered water from four of the Great Lakes.

	$^{239,240}\text{Pu}$, fCi/L		
	1973	1976	1981
Ontario	0.24 (2) ^a	0.20 (2)	0.17 (8)
Erie	0.20 (2)	0.14 (4)	0.18 (4)
Huron	0.62 (2)	0.52 (4)	0.48 (8)
Michigan ^b	0.77 (5)	0.63 (9)	0.44 (5)

^aNumber in parenthesis is the number of samples analyzed.

^bSouth basin.

Prospects

Occasional measurements of plutonium in the Great Lakes should be continued, particularly if fallout inputs remain low. This will allow a more accurate estimate of the long-term removal rate constant. If, as we suspect, this rate constant is determined by the rate at which surface sediments are diluted and buried, then its value is of fundamental importance to a number of lake-wide processes. The value derived using data on plutonium could be used to explain the behavior of a variety of other particle-reactive pollutants.

References

1. Wahlgren, M. A. and J. S. Marshall, The behavior of plutonium and other long-lived radionuclides in Lake Michigan, in Impacts of Nuclear Releases into the Aquatic Environment, Proc. IAEA Symp., Otaniemi, Finland, IAEA-SM-198/39, pp. 227-243 (1975)
2. Wahlgren, M. A. and D. M. Nelson, Plutonium in the Laurentian Great Lakes: comparison of surface waters, Verh. Internat. Verein. Limnol. 19, 317-322 (1975)
3. Wahlgren, M. A., D. M. Nelson, K. A. Orlandini and E. T. Kucera, $^{239,240}\text{Pu}$ in Lake Michigan: 1971-1978, Radiological and Environmental Research Division Annual Report, January-December 1978, ANL-78-65, Part III, pp. 70-73.
4. Nelson, D. M., R. P. Larsen and J. O. Karttunen, Plutonium solubility in natural waters (this report).

BEHAVIOR OF PLUTONIUM AND AMERICIUM IN TWO GROUNDWATER SYSTEMS

D. M. Nelson, K. A. Orlandini and R. P. Larsen

Background and Scope

Our studies of plutonium and americium in surface waters have shown a basic similarity in adsorptive behavior between americium and the reduced form of plutonium.¹ It is reasonable to expect that this similarity might extend to groundwater systems and lead to similar mobilities in these systems. In contrast to surface waters, which have all been contaminated by fallout with measurable concentrations of these two elements, in most groundwaters neither plutonium nor americium is detectable. Comparative studies of their mobilities are therefore restricted to the few areas where additional local sources have caused elevated groundwater concentrations of these two elements.

Two areas having measurable concentrations of americium and plutonium in groundwater are the Four Mile Creek floodplain on the Savannah River Plant site and the Mortendad Canyon at Los Alamos National Laboratory. At Four Mile Creek, the contamination is in surface soil in an area of slow groundwater movement. In Mortendad Canyon, contaminated water is released at the head of the canyon and moves rapidly downslope through coarse aluvial soil. We have initiated studies of the concentrations and chemical speciation of plutonium and americium in these areas in cooperation with J. Alberts of the Savannah River Ecology Laboratory and T. Hakonson of the Los Alamos National Laboratory.

Progress in 1982

Initial measurements of plutonium, americium, curium, and thorium in soil pore water at Four Mile Creek show that all four elements are present at measurable concentrations. The samples were collected using a porous cup sampler implanted ~30 cm below the soil surface. Concentrations measured during three collection periods in July 1982 are presented in Table 1 along with the distribution ratio: K_D = concentration on particles/concentration in water relative to floodplain soil.

Table 1. Concentrations and K_D values for actinide elements in shallow groundwater from the Four Mile Creek floodplain (SRP).

Date	^{238}Pu	^{241}Am	$^{243}, ^{244}\text{Cm}$	^{228}Th
Concentration, fCi/L				
14-15 July 1982	113	2.7	--	45
15-20 July 1982	69	5.2	8.0	36
20-25 July 1982	72	0.5	13.5	36
K_D				
14-15 July 1982	29,000	9,000	--	34,000
15-20 July 1982	48,000	5,000	27,000	43,000
20-25 July 1982	46,000	48,000	16,000	43,000

Comparison of the data for ^{238}Pu and ^{228}Th show these two elements to have similar K_D values. Furthermore, the values of K_D are consistent with those values found previously in surface waters having similar concentrations (7-11 ppm) of dissolved organic carbon (DOC).² This suggests that the adsorption/desorption processes occurring in these shallow groundwaters are similar to those in surface water.

The K_D values of the two trivalent actinides, americium and curium, are more variable than those of plutonium and thorium and may be lower by about a factor of two. If this is the case, the rate at which americium and curium are carried through this system by water flow would be twice that for plutonium and thorium. Nevertheless, because even the lowest of these K_D values are still quite high, the actual rate of movement would be expected to be extremely slow. A K_D value of 10,000 implies the velocity of radioactivity movement will be 10,000 times slower than the velocity of the water, under equilibrium conditions.

Unlike the low-flow situation in the Four Mile Creek floodplain, in Mortendad Canyon the groundwater flow rate is substantial, and the progress of radionuclide migration can be monitored at several sampling wells downslope from the discharge. Concentrations of $^{239}, ^{240}\text{Pu}$, ^{228}Th , and ^{241}Am were measured in four of these test wells on 19-20 May 1982. These concentrations,

along with the associated K_D values, are listed in Table 2. The four wells are 1460, 1841, 2234, and 2844 meters below the discharge. The K_D values were calculated relative to the filterable particulate matter pumped from the wells along with the water and not relative to the bulk solid phase of the aquifer, which was not sampled. Liquid effluent flows as a surface stream as far as well 4, and normally sinks into the underlying alluvium before reaching well 5. Non-adsorbed nuclides such as tritium and chloride ions travel from the outfall to well 7.5 in less than one year.

Table 2. Concentrations and K_D values for actinide elements in groundwater from Mortendad Canyon (LANL).

Well	$^{239,240}\text{Pu}$			^{228}Th K_D	^{241}Am	
	pCi/L	% Pu(III,IV)	K_D		pCi/L	K_D
MCO 4	6.8	97	45,000	18,000	7.8	8,700
MCO 5	0.53	91	14,000	51,000	10.9	230
MCO 6	0.23	91	23,000	16,000	12.2	96
MCO 7.5	0.028	93	15,000	171,000	15.3	61

Concentrations of $^{239,240}\text{Pu}$ decrease dramatically with distance from the outfall, dropping by more than a factor of 200 between well 4 and well 7.5. Almost all of the dissolved plutonium is present in the reduced form, demonstrating that plutonium transport here is not dependent upon the presence of the poorly sorbed oxidized form. The K_D values for plutonium are similar to those for natural ^{228}Th , confirming, at yet another site, the similarity in adsorptive behavior between these two elements. The moderately high K_D value for plutonium (>10,000), coupled with the fact that measurable plutonium has traveled almost 3 km from its discharge point, implies that the K_D value relative to the bulk solid phase in the aquifer must be far lower than the K_D value relative to the mobile solids which we were able to sample.

Laboratory investigations similar to those summarized in previous annual reports^{3,4} failed to demonstrate that natural organic colloids are responsible for maintaining plutonium in solution. It was concluded that the soluble species were probably inorganic or low molecular weight organic complexes.

In contrast to the decreases in plutonium concentration with distance from the discharge, concentrations of ^{241}Am actually increased somewhat with distance. These increasing concentrations were accompanied by a regular decrease in the K_D values for ^{241}Am . The ratio of ^{241}Am to ^{239}Pu increased from 1.1 at well 4 to 550 at well 7.5. Corresponding ratios in the discharge water averaged 0.4 during 1981 and 0.2 during the first five months of 1982. Americium is obviously being transported through this system at a far faster rate than plutonium. Plutonium is in turn being transported faster than would be expected based upon its moderately high K_D value.

The surprisingly high mobility of ^{241}Am in Mortendad Canyon is unlike any behavior we have seen elsewhere. No explanation is yet apparent, although we suspect it may be related to the chemical form of ^{241}Am in the discharge.

Prospects

To develop and test hypotheses of plutonium and americium migration, it is essential to have field data from a variety of geographic areas. These data should include measurements of both the natural and man-made actinides. Deviations from the general similarities in behavior of certain pairs of elements can then be used to spot situations where site-specific factors, such as the character of the source or the nature of the adsorber, are important. Once detected, these factors must be identified and incorporated into a general theory of actinide mobility. The increased solubility and hence mobility of ^{241}Am in Mortendad Canyon is apparently an example of anomalous behavior. We are currently attempting to identify its cause.

In addition to the two locations discussed in this report, we have begun measurements on the migration of plutonium and americium from a dispersal area on the Hanford site in the State of Washington. Studies at these three areas will continue and will emphasize the relationship between chemical speciation and mobility.

References

1. Orlandini, K. A., Observations on the behavior of americium in natural waters, Radiological and Environmental Research Division Annual Report, January-December 1981, ANL-81-65, Part III, pp. 53-56.
2. Wahlgren, M. A. and K. A. Orlandini, Comparison of the geochemical

behavior of plutonium, thorium and uranium in selected North American lakes, in Environmental Migration of Long-Lived Radionuclides, Proc. IAEA Symp., Knoxville, Tennessee, IAEA-SM-257/89, pp. 757-774 (1982).

3. 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 sediments, Radiological and Environmental Research Division Annual Report, January-December 1980, ANL-80-115, Part III, pp. 19-25.
4. Nelson, D. M., J. O. Karttunen and P. Mehloff, Influence of dissolved organic carbon (DOC) on the sorption of plutonium in natural sediments, Radiological and Environmental Research Division Annual Report, January-December 1981, ANL-81-85, Part III, pp. 48-52.

COMPARISON OF DYNAMIC AND MASS-LOADING MODELS USED FOR LONG-TERM PREDICTION OF LAKE MICHIGAN WATER QUALITY

B. M. Lesht

Background and Scope

The phosphorus load targets established by the International Joint Commission for the Great Lakes are based on simple mass-balance models. These models, such as the one presented by Chapra,¹ can be written:

$$V \frac{dP}{dt} = W' - QP - vA_s P, \quad (1)$$

where V is lake volume, P is total phosphorus concentration, Q is advective water outflow, W' is annual phosphorus loading, v is the apparent settling velocity of total phosphorus, and A_s is the surface area of the lake bottom.

Although more complicated in its structure, the dynamic, deterministic eutrophication model of Lake Michigan we have been using for water-quality analysis is based on the same type of mass-balance equation. Among the significant differences between the two models are that the dynamic model calculates the mass balance for each of eight state variables instead of one, and that the dynamic model has been modified to account for variable rates of particle settling throughout the year, particularly in response to winter ice cover.

As a check on our ten-year forecasts made using the dynamic model, we incorporated time-variable particle settling into the mass-balance model and compared the results for ten-year simulations with the dynamic model. We found that the two models agreed remarkably well. To check the concept of accelerated winter particle removal further, we used the mass-balance model, modified to include variable particle settling, to compute a historical simulation of phosphorus levels in Lake Michigan for the period 1850-1970. The results show that the modified model yields realistic estimates of phosphorus concentration given the assumed loading history and average winter conditions.

Progress in 1982

The key parameter for phosphorus removal, both in the dynamic eutrophication model and in the mass-balance model, is particle settling or removal rate. In both cases these values are arrived at empirically, typically by calibration in the case of the dynamic model and by solution of equation (1) using observed values for dP/dt , W' , Q in the case of the mass-balance model. Work on the other Great Lakes has led to a value of 0.2 m/d (73 m/y) for use in the dynamic model, and Chapra and Sonzogni² suggest that 12.4 m/y is appropriate for mass-balance modeling of Lake Michigan. The values are different because the parameters represent different processes and scales in the two different models.

In our study using the dynamic model, we found that for the model prediction to match observations, the base removal rate must be increased by a factor of eight during the period that the lake is ice covered. Since Chapra and Sonzogni's value is based on observations during three years with almost no ice cover (1974-1976), it seems reasonable to assume that 12.4 m/y is representative of the ice-free removal rate in Lake Michigan. Using the empirical acceleration factor of eight, the annual removal rate, and hence the output of the mass-balance model, can be calculated as a function of winter ice days. This was done for a ten-year forecast under two loading scenarios, which are plotted along with the corresponding dynamic model predictions in Figure 1.

Figure 1. Comparison of mass balance (curves) and multi-compartment (points) phosphorus-loading models; whole-lake average after ten years of constant loading and ice cover, for two loading scenarios.

Phosphorus removal obviously is a dominant process in both models. Although the agreement between the two is encouraging, the time scale of the simulation is too short to judge whether the assumed accelerated removal is realistic over much longer time periods. One way to check this is to do a very long historical simulation that includes accelerated removal. This was done using the mass-balance model; historical loads from 1850 to 1970 were estimated by Chapra's¹ phosphorus loading model, and the settling velocity was based on an average winter of 45 ice days. The estimated loads and results are shown in Figure 2.

Figure 2. Historical phosphorus loading estimate and output of mass balance model for the period 1850-1970.

Few observations exist of total phosphorus in Lake Michigan water before 1970. Thomas et al.³ give a value of 9 µg/L for the late 1960s and early 1970s. The result of the modified model agrees closely with this value. It should be noted that the unmodified model (i.e., $r = 12.4$ m/y) predicts that the 1970 phosphorus concentration would be 16 µg/L, well in excess of the observed value.

Prospects

If accelerated phosphorus removal is significant in Lake Michigan, it may be important in the other Great Lakes too. We will modify models of Lakes

Erie, Ontario, and Huron to include winter ice effects and test the sensitivity of the models to this change.

References

1. Chapra, S. C., Total phosphorus model for the Great Lakes, J. Environ. Eng. Div., ASCE 103(EE2), 147-161 (1977).
2. Chapra, S. C. and W. C. Sonzogni, Great Lakes total phosphorus budget for the mid-1970's, J. Water Pollut. Contr. Fed. 51(10), 2524-2532 (1979).
3. Thomas, N. A., A. Robertson, and W. C. Sonzogni, Review of control objectives: New target loads and input controls, in Phosphorus Management Strategies for Lakes, R. C. Loehr, C. S. Martin and W. Rast (eds.), Ann Arbor Science, Ann Arbor, Michigan, pp. 61-90 (1980).

BOX-JENKINS MODELING OF CHICAGO WATER INTAKE PHOSPHATE DATA 1966-1982

B. M. Lesht

Background and Scope

Considerable effort and expense have been expended to control municipal and industrial phosphorus inputs to the Great Lakes. For example, several states and municipalities have banned the use of phosphate detergents and have diverted waste-treatment effluents from lake outfalls. Since it has been over ten years since the first of these control measures was implemented on Lake Michigan, one might ask whether the lake has shown any response to these efforts. It might be expected, for instance, that lake phosphorus levels would have declined in recent years. The problem is complicated, however, by the observation that significant fluctuations in lake phosphorus levels may be caused by more or less random natural processes. These random processes may mask the effects of enforced phosphorus controls and make conclusions concerning their effectiveness difficult.

As part of our work involving model forecasts of Lake Michigan water quality and the response of the lake to phosphorus controls, we have begun a study using classical methods of time-series analysis to evaluate a detailed set of water quality data -- the monthly phosphorus measurements made at the Chicago water intake. This report presents some of the preliminary results of that study.

Progress in 1982

The data used in this study were collected by the Chicago Department of Water and Sewers and provided to us by David Rockwell of the U.S. Environmental Protection Agency. Although the details of collection and analysis have changed several times since the observations were started in 1966, the data we used are essentially monthly averages of phosphate concentration in raw nearshore Lake Michigan water. While these samples may not be representative of the entire lake, no comparable or more appropriate time series of data is known to exist. The data are plotted in Figure 1.

Our purpose in applying Box-Jenkins modeling techniques¹ to these data is twofold. First, we wish to answer the diagnostic question of how well can the

water intake phosphate data be represented by a simple stochastic model. Second, we are interested in determining, if possible, whether the effects of the various discrete control measures have had a statistically significant effect on the data. This second phase of the study, often called intervention analysis, has not been completed. Thus, this report deals exclusively with the first, diagnostic, question.

Figure 1. Total phosphate concentration measured at the Chicago water intake, 1966-1982.

Classical application of Box-Jenkins techniques consists of three stages of model development: model identification, parameter estimation, and diagnostic checking. The general model we considered is termed autoregressive, integrated, moving-average (ARIMA) and may be written:

$$\phi(B)\nabla^d Z_t = \theta(B)a_t \quad , \quad (1)$$

where Z_t is phosphate concentration at time t , B is the backward shift operator defined by $BZ_t = Z_{t-1}$ and $B^s Z_t = Z_{t-s}$, $\phi(B) = 1 - \phi_1 B - \phi_2 B^2 - \dots - \phi_p B^p$ is the autoregressive polynomial of order p , $\theta(B) = 1 - \theta_1 B - \theta_2 B^2 - \dots - \theta_q B^q$ is the moving average polynomial of order q , ∇^d is a differencing operator of order d , and a_t is the independent, normally distributed white-noise residual of mean 0 and variance σ_a^2 . Details of Box-Jenkins modeling may be found in Reference 1.

The identification stage, in which the orders of p , d , and q in equation (1) are determined, depends on analysis of the autocorrelation function (ACF)

and the partial autocorrelation function (PACF) of the data series. These are shown in Figure 2.

Figure 2. **Top:** Autocorrelation function (ACF) of Chicago water intake phosphate data. **Bottom:** Partial autocorrelation function (PACF) of same data.

The ACF and PACF suggest that an appropriate model would be ARIMA (2,0,0), that is, a second order autoregressive model based on the undifferenced raw data. This model would have the form:

$$Z_t = C_0 + \phi_1 Z_{t-1} + \phi_2 Z_{t-2} + a_t \quad (2)$$

This tentative identification was confirmed by an analysis of the normalized residual sum of squares of several models with different orders of p and q. The values of the parameters ϕ_1 and ϕ_2 , as well as the mean value of the data series and constant term, C_0 , were determined in the estimation stage of the modeling process. These are given in Table 1. The fact that the constant parameter is significant indicates that a transfer function model also would

be appropriate for these data. However, one major problem with a transfer function model is the identification of a suitable input variable.

Table 1. Maximum likelihood estimates for parameters in ARIMA (2,0,0) model.

Parameter	Estimate	Standard Deviation	T-ratio
ϕ_1	0.4856	0.0705	6.89
ϕ_2	0.2460	0.0708	3.48
Constant	0.0151	0.0012	12.82
Mean	0.0564	0.0044	
Residual SS = 0.0504, df = 189			

The third stage of model development consists of diagnostic checking. This checking, which includes analysis of the residuals as well as comparison of the estimated model with the original data, shows that the residuals are uncorrelated and normal and that the estimated model autocorrelation function closely approximates the observed ACF (Fig. 3).

Figure 3. Comparison of model ACF (dashed) and actual ACF (solid) for Chicago water intake phosphate data.

Prospects

The conclusion drawn from this preliminary analysis is that the data series can be described well by a stochastic model of the form (2). Phosphate concentrations in raw, nearshore Lake Michigan water are correlated in successive months, after which this information is lost in the system noise. Whether the noise in the nearshore data will overwhelm any signal due to changes in phosphorus loads is a question that will be addressed in the next phase of this study when intervention and transfer function models will be applied to the data.

Reference

1. Box, G. E. P. and G. M. Jenkins, Time-Series Analysis: Forecasting and Control, Holden-Day, San Francisco, 1976.

TEN-YEAR FORECASTS OF WATER QUALITY IN LAKE MICHIGAN USING A DETERMINISTIC MODEL AND MONTE CARLO INPUTS

B. M. Lesht

Background and Scope

The primary purpose of our Lake Michigan eutrophication model is long-term prediction of the response of the lake to changes in phosphorus loading. Our previous work¹ with the model has shown that the output depends both on the assumed phosphorus loads and on assumptions concerning the severity of yearly winter conditions. The five-year hindcast presented last year² demonstrated the importance of accounting explicitly for winter removal processes that affect the springtime concentrations of phosphorus and of phytoplankton in the lake. In this year's work we extended this application to ten-year forecasts of water quality. In addition to using the deterministic model to estimate limits of the lake response to different combinations of phosphorus load and winter conditions, we used Monte Carlo techniques, in which yearly load and winter conditions were selected randomly from prescribed probability distributions, to estimate the uncertainty in the ten-year forecasts associated with random loads and winter conditions.

Progress in 1982

Two sets of ten-year simulations were conducted in 1982. In the first set, different combinations of phosphorus loading and winter conditions (ice-days parameterized as days of more than 30% ice cover) were assumed to remain constant during the simulation period. In the second set, ice days and phosphorus loads were chosen randomly from prescribed probability distributions. In all, over 350 ten-year runs were made. The simulation conditions are summarized in Table 1.

The importance of winter conditions can be seen in Figure 1, which shows some of the results of six of the constant-condition simulations. Plotted in the figure are predicted peak chlorophyll-a concentrations for the two constant-loading scenarios. These loading scenarios were based on the International Joint Commission (IJC) target load for Lake Michigan (5600 tonnes), and on our analysis of IJC loading data available for the period

1975-1980. The three curves plotted for each load represent mild, average and severe winters, characterized by 16, 45, and 74 ice days, respectively. The assumed winter conditions are based on ice-cover data for the period 1975-1981 from the U.S. Environmental Protection Agency. There is some question as to how representative these years may be, especially since the period includes one winter (1976-1977) that was among the most severe in history. The data for loading and ice cover used in this study are summarized in Table 2.

Table 1. Number of simulations conducted for each loading - winter condition combination.

Phosphorus Loading, tonnes/y	Ice Days				
	0	16	14	75	45 ± 29
5600	1	1	1	1	50
6350	1	1	1	1	50
4000 ± 1000	50	50	50	50	50

Table 2. Total phosphorus load and days of greater than 30% ice cover for Lake Michigan.

Year	Winter	Total Load, tonnes	Days of Ice Cover
1976	1975-1976	6656	7
1977	1976-1977	4666	83
1978	1977-1978	6245	56
1979	1978-1979	7651	70
1980	1979-1980	6574	21
1981	1980-1981	n.a.	35

Figure 1 shows that the model with constant-condition inputs predicts that water quality, as expressed in peak epilimnion chlorophyll-a concentration, will remain at current levels or improve under both loading scenarios as long as the winters remain near the assumed average.

Figure 1. Sensitivity of ten-year constant condition forecast of peak southern basin epilimnion phytoplankton to phosphorus loads and winter conditions for (left) water-quality agreement load (5600 tonnes phosphorus per year) and (right) realistic load (6350 tonnes per year); mild = 16 ice days, average = 45, severe = 74.

To answer the question concerning the importance of year to year variability in both loads and winter conditions, similar ten-year simulations were conducted choosing each year's load and days of ice cover randomly from probability distributions based on the observations given in Table 2. Both the distributions were normal but truncated at the low end. That is, neither phosphorus loads of less than 4000 tonnes nor ice days less than zero were allowed. Since the data sample is small, considerable uncertainty remains as to the exact form of the probability distribution chosen. The truncated normal distribution is only one simple possibility.

The results of the 50 simulations conducted in which both ice days and loads were random are plotted in Figure 2. Shown is the mean value of predicted yearly peak epilimnion chlorophyll-a, as well as the one standard deviation limit around the mean. As would be expected, the Monte Carlo mean follows the same trend as the corresponding constant-condition simulation. Of

particular interest is the fact that the one standard deviation solution band seems to be bounded and stable, implying that the modeled system is stable, at least with respect to loads and ice cover.

Figure 2. Southern basin epilimnion peak annual chlorophyll-a. One standard deviation limits around Monte Carlo mean. Annual phosphorus load = 6350 tonnes; ice days random.

Prospects

The narrow band of solutions shown in Figure 2 does not imply that any single ten-year trajectory will fall within this band. Even with Monte Carlo inputs the model is still an imperfect deterministic representation of a stochastic system. The results do imply, however, that given the limitations of the model, water quality in Lake Michigan, as measured by peak epilimnion chlorophyll-a concentration and by whole-lake total phosphorus concentration, can be expected to improve or, at worst, remain stable over the next ten years. However, our analysis also suggests that if the amount of phosphorus loaded into the lake increases drastically, or if the region experiences a long succession of very mild winters, the trend toward improvement would reverse.

References

1. Lesht, B. M., Comparison of dynamic and mass-loading models used for long-term prediction of Lake Michigan water quality (this report).
2. Lesht, B. M., Multi-year simulations of water quality in Lake Michigan made with a dynamic lake eutrophication model, Radiological and Environmental Research Division Annual Report, January-December 1981, ANL-81-85, Part III, pp. 62-66.

PUBLICATIONS BY THE STAFF OF THE ECOLOGICAL SCIENCES SECTION JANUARY THROUGH
DECEMBER 1982

Articles, Book Chapters, Etc.

- T. L. Clarke, B. M. Lesht, R. A. Young, D. J. P. Swift and G. L. Freeland, Sediment resuspension by surface-wave action: an examination of possible mechanisms, *Mar. Geol.* 49, 43-59 (1982).
- W. W. Heck, O. C. Taylor, R. Adams, G. Bingham, J. Miller, E. Preston and L. Weinstein, Assessment of crop loss from ozone, *APCA Journal* 32(4), 353-361 (1982).
- A. L. Jensen, S. A. Spigarelli and M. M. Thommes, Use of conventional fishery models to assess entrainment and impingement of three Lake Michigan fish species, *Trans. Am. Fish. Soc.* 111, 21-34 (1982).
- A. L. Jensen, S. A. Spigarelli and M. M. Thommes, PCB uptake of five species of fish in Lake Michigan, Green Bay of Lake Michigan, and Cayuga Lake, New York, *Can. J. Fish. Aquat. Sci.* 39, 700-709 (1982).
- J. Muhlbaier, C. Stevens, D. Graczyk and G. T. Tissue, Determination of cadmium in Lake Michigan by mass spectrometric isotope dilution analysis or atomic absorption spectrophotometry following electrodeposition, *Anal. Chem.* 54, 496-499 (1982).
- J. I. Parker and J. G. Ferrante, A survey of discharges from a natural gas drilling operation in Lake Erie, *Environ. Sci. Technol.* 16, 363-367 (1982).
- J. I. Parker, K. A. Stanlaw, J. S. Marshall and C. W. Kennedy, Sorption and sedimentation of Zn and Cd by seston in southern Lake Michigan, *J. Great Lakes Res.* 8(3), 520-531 (1982).
- S. A. Spigarelli, Feeding, growth and fat deposition by brown trout in constant and fluctuating temperatures, *Trans. Am. Fish. Soc.* 111, 199-209 (1982).
- S. A. Spigarelli, R. M. Goldsmith, W. Prepejchal and M. M. Thommes, Fish abundance and distribution near three heated effluents to Lake Michigan, *Can. J. Fish. Aquat. Sci.* 39, 305-315 (1982).
- R. M. Williams, A model for the dry deposition of particles to natural water surfaces, *Atmos. Environ.* 16, 1933 (1982).

Contributions to Conference Proceedings and Miscellaneous Reports

- P. M. Irving, Influence of the chemical properties of precipitation on the response of crops to acidic deposition, U.S. Environmental Protection Agency, Review Meeting, Raleigh, North Carolina, 8-11 February 1982.
- P. M. Irving, J. E. Miller and P. B. Xerikos, The effect of NO₂ and SO₂ alone and in combination on the productivity of field-grown soybeans by nitrogen

- oxides, Air Pollution Proc. U.S./Dutch Internat. Symp. on NO_x, Maastricht, The Netherlands, 24-28 May 1982, pp. 521-531, T. Schneider and L. Grant (eds.), Elsevier Publ. Co., Amsterdam.
- P. M. Irving, Methodology for estimating crop loss from acidic deposition, Atmospheric Deposition, Proc. APCA Specialty Conference, Detroit, Michigan, November 1982, pp. 439-453.
- L. W. Kress, Effects of air pollutants on corn, Effects of Air Pollution on Farm Commodities, Proc. Symp. Izaak Walton League of America, Washington, D.C., 18 February 1982, pp. 91-100 (1982).
- L. W. Kress and J. E. Miller, Impact of ozone on corn yield, Abstract, Northcentral Division Poster Session, The American Phytopathological Society, Madison, Wisconsin, 17-18 June 1982.
- L. W. Kress and J. E. Miller, Impact of ozone on corn yield, Phytopathology 72, 940 (1982).
- J. E. Miller, Effects of air pollutants on soybeans, Effects of Air Pollution on Farm Commodities, Proc. Symp. Izaak Walton League of America, Washington, D.C., 18 February 1982, pp. 57-75 (1982).

Distribution for ANL-82-65 Part III

Internal:

W. E. Massey	P. M. Irving	W. R. Penrose
H. Drucker	J. O. Karttunen	W. Prepejchal
E. G. Pewitt	L. W. Kress	J. P. Schubert
E. J. Croke	R. P. Larsen	H. J. Smith
P. F. Gustafson	B. M. Lesht	A. F. Stehney
E. Huberman	D. N. Metta	J. D. Taylor
R. W. Springer	J. E. Miller	M. L. Wesely
M. W. Findlay	R. M. Miller	A. B. Krisciunas (15)
P. Frenzen	D. M. Nelson	ANL Patent Dept.
R. R. Hinchman	K. A. Orlandini	ANL Contract File
R. H. Huebner	M. Pacholok (100)	ANL Libraries (2)
M. Inokuti		TIS Files (6)

External:

DOE-TIC, for distribution per UC-11 (239)

Manager, Chicago Operations Office, DOE

Radiological and Environmental Research Division Review Committee:

A. K. Blackadar, Pennsylvania State U.
A. W. Castleman, Jr., U. Colorado
R. E. Gordon, U. Notre Dame
R. A. Hites, Indiana U.
D. Kleppner, Massachusetts Inst. Technology
G. M. Matanoski, Johns Hopkins U.
R. A. Reck, General Motors Research Lab.
L. A. Sagan, Electric Power Research Inst.
R. E. Wildung, Battelle Pacific Northwest Labs.
J. W. Ahlen, Illinois Legislative Council, Springfield
H. Allen, Illinois Inst. Technology
D. Anderson, Ohio Dept. of Natural Resources, Columbus
A. W. Andren, U. Wisconsin-Madison
T. Armentano, Butler U.
E. J. Aubert, National Oceanic and Atmospheric Administration, Ann Arbor
S. I. Auerbach, Oak Ridge National Lab.
C. E. Axtel, Big Rock Plant, Consumers Power Co., Charlevoix, Mich.
J. Ayres, U. Michigan
R. Ball, Michigan State U.
A. G. Ballert, Great Lakes Commission, Ann Arbor
T. M. Beasley, Oregon State U.
M. Becker, Hiram College, Hiram, O.
A. M. Beeton, U. Michigan
D. G. Bellinger, U. S. Environmental Protection Agency, Cincinnati
J. O. Blanton, Skidaway Inst. Oceanography, Savannah, Ga.
J. C. Blomgren, Commonwealth Edison Co., Zion
L. Botts, Northwestern U.
G. R. Bouck, U. S. Environmental Protection Agency, Corvallis
V. T. Bowen, Woods Hole Oceanographic Lab.
I. L. Brisbin, Savannah River Ecology Lab.
J. Cairns, Jr., Virginia Polytechnic Inst.
P. Casey, Intern. Assoc. of Great Lakes Research, Fairport, N.Y.
H. Cember, Northwestern U.

D. M. Chittenden, Arkansas State U.
 E. W. Christoffers, National Marine Fisheries Service, Oxford, Md.
 E. E. Clark, National Science Foundation
 J. Cooper, U. S. Environmental Protection Agency, Washington
 J. C. Corey, Savannah River Lab.
 C. C. Coutant, Oak Ridge National Lab.
 C. E. Cowan, U. Washington
 U. M. Cowgill, U. Pittsburgh
 C. E. Cushing, Pacific Northwest Lab.
 D. D. Davis, Pennsylvania State U.
 J. J. Davis, U. S. Nuclear Regulatory Commission, Washington
 P. H. Dernehl, U. Wisconsin-Milwaukee
 J. Dewey, ETA Engineering, Westmont, Ill.
 T. R. Doyle, Michigan Dept. of Natural Resources, Lansing
 W. J. Drescher, U. S. Geological Survey, Madison
 P. B. Dunaway, Nevada Operations Office, USDOE
 M. P. Durso, Environmental Measurements Lab., USDOE, New York
 R. Dyer, U. S. Environmental Protection Agency, Washington
 B. Eadie, National Oceanic and Atmospheric Administration, Ann Arbor
 D. N. Edgington, U. Wisconsin-Milwaukee
 R. J. Engelmann, National Oceanic and Atmospheric Administration, Boulder
 L. Evans, Brookhaven National Lab.
 T. R. Folsom, Scripps Institution of Oceanography
 W. Forster, Office of Health and Environmental Research, USDOE
 S. Frank, Economic Regulatory Admin., Washington
 R. E. Franklin, Office of Health and Environmental Research, USDOE
 J. C. Frye, Illinois State Geological Survey, Urbana
 A. Galli, U. S. Environmental Protection Agency, Washington
 J. W. Gibbons, Savannah River Ecology Lab.
 N. R. Glass, U. S. Environmental Protection Agency, Corvallis
 R. Goldstein, Electric Power Research Inst.
 D. A. Gruber, Metropolitan Sewerage District, Milwaukee
 J. F. Haney, U. New Hampshire
 F. L. Harrison, Lawrence Livermore National Lab.
 W. L. Hartman, U. S. Bu. of Sport Fisheries and Wildlife, Sandusky
 N. M. Hawley, National Oceanic and Atmospheric Administration, Ann Arbor
 A. S. Heagle, North Carolina State U.
 W. W. Heck, North Carolina State U.
 H. E. Heggstad, U. S. Department of Agriculture, Beltsville
 D. Hendricks, U. S. Environmental Protection Agency, Las Vegas
 C. Hesse, Illinois Pollution Control Board, Chicago
 B. E. Hoduski, U. S. Environmental Protection Agency, Kansas City, Mo.
 R. L. Holton, Oregon State U.
 F. F. Hooper, U. Michigan
 J. Huckabee, Electric Power Research Inst., Palo Alto
 R. S. Hunter, American Electric Power Service Corp., New York
 Illinois Environmental Protection Agency, Director, Springfield
 Illinois Environmental Protection Agency, Library, Springfield
 Illinois Inst. for Environmental Quality, Library, Chicago
 Illinois State Geological Survey, Library, Champaign
 G. J. Jacobs, NASA Goddard Space Flight Center
 J. Jacobson, Cornell U.
 N. Jaworski, U. S. Environmental Protection Agency, Duluth
 E. A. Jenne, Battelle Pacific Northwest Lab.

G. Jones, U. New Hampshire
 J. H. Jordan, U. S. Environmental Protection Agency, Chicago
 R. W. Jurgensen, Donald C. Cook Nuclear Plant, Bridgman, Mich.
 B. Kahn, U. S. Environmental Protection Agency, Cincinnati
 N. Kevern, Michigan State U.
 P. Kilham, U. Michigan
 H. Kohn, Ohio Power Siting Commission, Columbus
 J. F. Koonce, Case Western Reserve University
 L. M. Kristoff, Metropolitan Sanitary District, Cicero
 S. Krupa, U. Minnesota
 Lake Michigan Federation, Librarian, Chicago
 J. M. Lattimer, U. S. Environmental Protection Agency, Denver
 M. Lazaro, Mesomet, Inc., Chicago
 G. F. Lee, Texas Tech U.
 J. Lee, U. S. Environmental Protection Agency, Corvallis
 A. Lerman, Northwestern U.
 P. Levin, U. S. Environmental Protection Agency, Philadelphia
 R. Lieberman, U. S. Environmental Protection Agency, Montgomery, Ala.
 G. Likens, Cornell U.
 P. Linsalata, New York U. Medical Center, Tuxedo
 L. L. Lohr, Jr., U. Michigan
 J. J. Magnuson, U. Wisconsin-Madison
 H. McCammon, Office of Health and Environmental Research, USDOE
 J. H. McCormick, U. S. Environmental Protection Agency, Duluth
 D. McGinnis, Dept. of Agriculture, St. Paul, Minn.
 M. McGrath, U. S. Environmental Protection Agency, Chicago
 J. R. McKersie, Wisconsin Dept. of Natural Resources, Madison
 M. A. McWhinnie, De Paul U.
 Michigan State University, Librarian, Hickory Corners
 W. Mills, U. S. Environmental Protection Agency, Washington
 C. H. Mortimer, U. Wisconsin-Milwaukee
 D. I. Mount, U. S. Environmental Protection Agency, Duluth
 S. Mozley, North Carolina State U.
 T. Murphy, De Paul U., Chicago
 R. E. Nakatani, U. Washington
 J. Neuhold, Utah State U.
 B. L. Nichols, Atomic Industrial Forum
 C. R. Norden, U. Wisconsin-Milwaukee
 V. E. Noshkin, Lawrence Livermore National Lab.
 Oak Ridge National Lab., Ecological Sciences Information Center
 W. S. Osburn, Jr., Office of Health and Environmental Research, USDOE
 R. A. Parker, Washington State U.
 C. A. Paulson, Oregon State U.
 H. M. Pawlowski, Water Purification Lab., Chicago
 H. J. Peterson, Jr., Silver Spring, Md.
 C. F. Powers, National Environmental Research Center, Corvallis
 H. Quinn, U. S. Environmental Protection Agency, Washington
 D. Rea, U. Michigan
 E. B. Reed, Ecology Consultants, Fort Collins
 D. E. Reichle, Oak Ridge National Lab.
 H. S. Reinstra, U. S. Fish and Wildlife Service, Bay St. Louis, Miss.
 W. Richardson, U. S. Environmental Protection Agency, Grosse Ile
 C. Risley, U. S. Environmental Protection Agency, Chicago
 J. Robbins, National Oceanic and Atmospheric Administration, Ann Arbor

D. C. Rockwell, United States Environmental Protection Agency, Chicago
 D. Rolt, British Embassy, Washington
 W. D. Rowe, U. S. Environmental Protection Agency, Washington
 E. Salmon, McLean, Va.
 C. Sanders, Oak Ridge National Lab.
 G. W. Saunders, Office of Health and Environmental Research, USDOE
 Savannah River Ecology Laboratory, Director
 W. T. Sayers, U. S. Environmental Protection Agency, Washington
 C. L. Schelske, U. Michigan
 V. Schultz, Washington State U.
 R. K. Seidman, U. S. Environmental Protection Agency, Boston
 A. H. Seymour, U. Washington
 W. Shabica, Northeastern Illinois U., Chicago
 C. Shafer, Illinois Coastal Zone Management Program, Chicago
 M. L. Shaw, W. K. Kellogg Biological Station, Michigan State U.
 N. F. Shimp, Illinois Geological Survey, Urbana
 D. S. Shriner, Oak Ridge National Lab.
 H. S. Sievering, Governors State U., Park Forest South, Ill.
 W. B. Silker, Pacific Northwest Lab.
 N. Simpson, Illinois Environmental Protection Agency, Springfield
 L. Smith, U. S. Environmental Protection Agency, Washington
 S. Smith, Texas Parks and Wildlife Dept., Tyler
 Smithsonian Institution, Director, Oceanography and Limnology Program
 J. H. Snyder, U. California, Davis
 C. Steinke, U. Illinois, Chicago
 R. H. Strange II, National Science Foundation
 J. Swinebroad, Office of Environment, Safety, and Health, USDOE
 W. L. Templeton, Pacific Northwest Lab.
 S. M. Thomas, U. S. Environmental Protection Agency, Washington
 R. C. Thompson, Pacific Northwest Lab.
 T. W. Tibbitts, U. Wisconsin-Madison
 L. Tilley, U. S. Environmental Protection Agency, Chicago
 H. C. Torno, U. S. Environmental Protection Agency, Washington
 U. S. Environmental Protection Agency, Region V, Enforcement, Chicago
 U. S. Environmental Protection Agency, Region V, Federal Activities, Chicago
 U. S. Environmental Protection Agency, Region V, Library, Chicago
 U. S. Environmental Protection Agency, Central Regional Lab., Chicago
 U. S. Environmental Protection Agency, Illinois District Office, Chicago
 U. S. Environmental Protection Agency, Michigan District Office, Grosse Ile
 U. S. Environmental Protection Agency, Library, Region II, New York
 U. S. Environmental Protection Agency, Librarian, National Environmental
 Research Center, Cincinnati
 U. S. Dept. of the Interior, U. S. Fish & Wildlife Service, Ann Arbor
 G. M. Van Dyne, Colorado State U.
 S. D. Vesselinovitch, Billings Hospital, Chicago
 P. Vidal, Illinois Dept. of Conservation, Chicago
 H. L. Volchok, Environmental Measurements Lab., USDOE, New York
 W. H. Wahl, Amersham-Searle Corp., Arlington Heights, Ill.
 D. G. Watson, Pacific Northwest Lab.
 R. L. Watters, Office of Health and Environmental Research, USDOE
 D. Webber, U. S. Environmental Protection Agency, Washington
 A. Weir, U. S. Environmental Protection Agency, Seattle
 L. Wells, Great Lakes Fishery Lab., Ann Arbor
 R. G. Wilhour, U. S. Environmental Protection Agency, Corvallis

B. F. Willey, Water Purification Lab., Chicago
 J. D. Williams, Illinois Environmental Protection Agency, Springfield
 J. W. Winchester, Florida State U.
 D. Wohlschlag, U. Texas, Port Aransas
 J. Wood, U. Minnesota, Navarre
 W. B. Wrenn, Tennessee Valley Authority, Decatur, Ala.
 T. E. Yeates, U. S. Environmental Protection Agency, Chicago
 H. Zar, U. S. Environmental Protection Agency, Chicago
 K. Zar, U. Chicago
 F. Bradley, Div. of Environmental Mechanics, C.S.I.R.O., Canberra City, Australia
 O. T. Denmead, Div. of Environmental Mechanics, C.S.I.R.O., Canberra City, Australia
 J. R. Philip, Div. of Environmental Mechanics, C.S.I.R.O., Canberra City, Australia
 D. Balsillie, Ontario Ministry of the Environment, Sudbury, Canada
 D. P. Bernard, U. British Columbia, Canada
 M. J. Bewers, Atlantic Oceanographic Lab., Halifax, Canada
 J. P. Bruce, Canada Centre for Inland Waters, Burlington
 Canada Centre for Inland Waters, Librarian, Burlington
 P. J. Colby, Ministry of Natural Resources, Thunder Bay, Canada
 R. W. Durham, Canada Centre for Inland Waters, Burlington
 F. E. Fry, U. Toronto, Canada
 A. L. C. Kemp, Kemble, Canada
 J. R. Kramer, McMaster University, Canada
 A. R. Lefevre, Canada Centre for Inland Waters, Burlington
 S. N. Linzon, Ontario Ministry of the Environment, Toronto, Canada
 K. E. Marshall, The Freshwater Institute, Winnipeg, Canada
 J. W. McMahon, Chalk River Nuclear Labs., Canada
 D. P. Meyerhof, Radiation Protection Bu., Ottawa, Canada
 I. L. Ophel, AECL, Chalk River, Canada
 V. C. Runeckles, U. British Columbia, Canada
 D. W. Schindler, Freshwater Research Inst., Winnipeg, Canada
 R. Thomas, Canada Centre for Inland Waters, Burlington
 Toronto, U. of, Resource Centre, Inst. for Environmental Studies, Canada
 R. A. Vollenweider, Canada Centre for Inland Waters, Burlington
 N. E. Busch, Risø National Lab., Roskilde, Denmark
 J. P. Day, U. Manchester, England
 E. Hamilton, Inst. for Marine Environmental Res., Plymouth, England
 N. T. Mitchell, Fisheries Radiobiological Lab., Suffolk, England
 J. Pentreath, Fisheries Radiobiological Lab., Suffolk, England
 M. Roberts, Central Electric Research Labs., Leatherhead, England
 A. Ali-Laurila, Inst. Radiation Protection, Helsinki, Finland
 J. K. Miettinen, U. Helsinki, Finland
 L. Foulquier, CEN, Cadarache, France
 G. G. Leynaud, Centre Technique du Genie, Paris, France
 K. Reimann, Bayerische Biologische Versuchsanstalt, Munich, Germany
 S. Krishnaswami, Tata Institute of Fundamental Research, Bombay, India
 D. Lal, Physical Research Lab., Ahmedabad, India
 G. F. Clemente, Centro di Studi della Casaccia, Rome, Italy
 C. S. Yull, Korean Atomic Energy Research Inst., Seoul, Korea
 S. Fowler, IAEA, Monaco
 R. Fukai, IAEA, Monaco
 A. Walton, IAEA, Monaco
 A. Teixeira, Estacao Agronomica Nacional, Oeiras, Portugal

R. D. Cherry, U. Cape Town, South Africa
E. Holm, Lunds Universitet, Sweden
J. Roden, Swedish State Power Board, Vallingby
D. G. Fleishman, Sechenov Inst. of Evolutionary Physiology and Biochemistry,
Leningrad, USSR
V. V. Gromov, Inst. of Physical Chemistry, Academy of Sciences, Moscow, USSR