Dr-513-

ANL-75-60

Part III

6/
11-76

ANL-75-60

Part III

RADIOLOGICAL AND ENVIRONMENTAL RESEARCH DIVISION ANNUAL REPORT

Ecology

January–December 1975

ARGONNE NATIONAL LABORATORY, ARGONNE, ILLINOIS

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

MASTER

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

MEMBERS OF ARGONNE UNIVERSITIES ASSOCIATION

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

NOTICE

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

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

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

ANL-75-60
Part III

ARGONNE NATIONAL LABORATORY
9700 South Cass Avenue
Argonne, Illinois 60439

RADIOLOGICAL AND ENVIRONMENTAL RESEARCH DIVISION ANNUAL REPORT

Ecology

January through December 1975

R. E. Rowland, Division Director
D. N. Edgington, Section Head

Preceding Report: ANL-75-3, Part III, January-December 1974

FOREWORD

In contrast to the previous year, 1975 has been a period of consolidation and reorientation of programs designed to meet the changing priorities associated with the transition from missions defined by the Atomic Energy Commission to the broadened responsibilities of the Energy Research and Development Administration. The effects of this reorientation will be evident from the contents of this report, particularly in relation to the aquatic studies in the Great Lakes.

We have continued to investigate the impacts of sulfur dioxide on crop plants. Studies have been initiated to characterize the chemical properties of acid rains and the effects of such rain on the leaching properties of soils.

Studies of plutonium and other transuranic elements have been continued in the Great Lakes (particularly Lake Michigan) and in the drainage basin of the Greater Miami River in Ohio. Results obtained from the latter sampling area are summarized in this volume. There are no reports updating last year's data for transuranic elements in the Great Lakes because an extensive summary has been given in four papers presented at two major IAEA symposia in 1975, "Impacts of Nuclear Releases into the Aquatic Environment" at Otaniemi, Finland, and "Transuranium Nuclides in the Environment" at San Francisco. The proceedings of the first of these conferences is now in print (see publication list at end of this report) and the other will appear early in 1976. These papers have summarized our present knowledge of the distribution of plutonium and americium in fresh water, biota, and sediments, giving the chemical form in which these elements occur and describing their characteristic modes of association with sediment.

While considerable emphasis has continued to be placed upon attempts to understand the biogeochemical behavior of plutonium and other transuranic elements in the environment, a major new program has been initiated to examine the potential effects on aquatic ecosystems of pollutants related to non-nuclear energy conversion. In particular, studies of the effects of pollutants expected to increase in the Great Lakes environment as the result of the expanding use of coal (such as cadmium and arsenic) have begun. Initially, we have examined the lowest member of the food web, phytoplankton, in a series of controlled laboratory studies. These experiments are being expanded to include representative species of the entire food web in the Great Lakes, and operations are being enlarged to include in situ experimentation as well.

Other laboratory experiments designed to determine the hydrodynamic properties of waterborne particulates may have great bearing on the eventual understanding of the mechanisms which control the removal of pollutants from the water column and effect the resuspension of bottom sediments. In addition, increased emphasis has been placed on the development of new analytical procedures for detecting trace contaminants in water, biota, and sediments. These are expected to be less time consuming and more reliable than previous methods. In support of this effort a new state-of-the-art x-ray fluorescence spectrometer has been designed and constructed.

Studies of the effects on fishes of warm water discharges into Lake Michigan have continued. These confirm that the time-integrated effects of warm water exposure on free-swimming fish are related to active temperature selection behavior on the part of the fish, frequently in combination with fish responses to other stimuli which often override the temperature responses. In addition, we have initiated studies of the relation between fish residence time in warm plumes and the accumulation of toxic materials, such as polychlorinated biphenyls (PCB's), in their tissues. We have also studied the natural hydrological and limnological factors which influence the spatial and temporal distribution of Lake Michigan biota and exposure to cooling systems.

More detailed summaries of the progress achieved during 1975 in these programs are given in the body of this report. A listing of publications by the staff of the section is given at the end.

TABLE OF CONTENTS

EFFECTS OF PHOSPHORUS ON CADMIUM UPTAKE AND DISTRIBUTION IN SOYBEANS

J. E. Miller and P. B. Xerikos

The effects of trace elements from sources such as fossil fuel conversion, sludge application, and industrial emissions on agricultural ecosystems are being studied in a number of contexts by various investigators. The most productive of the approaches being used are those which deal with the interactive effects of various environmental parameters (e.g., acid precipitation, nutrient levels, and edaphic factors) on trace element mobility and toxicity. Previous experimentation concerning the effects of soil parameters on trace element accumulation in soil grown plants established the importance of soil cation exchange capacity, pH, and phosphorus fertility on accumulation of Cd in soybean shoots.[1] The observed increase in Cd uptake by plants with decreasing soil cation exchange capacity and pH was in agreement with results of prior plant fertility investigations. The stimulatory effect of soil phosphorus on Cd accumulation in the soybean shoots was, however, unexpected.

In the present work the effect of phosphorus on Cd accumulation was further studied by exposing 3-week-old soybeans (Glycine max cv. Amsoy) to 0.5 ppm Cd in the presence of 0, 0.05, 0.5, 1.0, and 2.5 mM of added phosphate in a standard Hoagland nutrient solution for 2 days, after which the plant roots were washed and the plants returned to the Hoagland solution containing 0.5 mM phosphate.

The two-day exposure to 0.5 ppm Cd and the differential phosphate concentrations did not result in any observable injury or deficiency symptoms, nor were the fresh or dry weights of the plants affected. Previous experimentation has shown that longer term exposure of soybeans to 0.5 ppm Cd does cause injury and decreased growth. The total Cd content of the soybean plants was reduced by the 2.5 mM phosphate treatment, although this reduction was not significant at the 5% confidence level (Table 1). The Cd in the shoot portion of the soybean plants was not greatly affected by the phosphate, although the Cd concentration was the highest at 2.5 mM of phosphate (Table 1).

Table 1. Cadmium uptake by 3-week-old soybean plants exposed to a range of phosphate concentrations. The results are the mean of 7 replicate samples. Values in each column followed by the same letter are not significantly different at the 5% confidence level.

Phosphate (mM)	Total Cd (µg)	Shoot Cd (µg/g)	Root Cd (µg/g)	Shoot Cd (% of total)
0	40.87 a	12.45 ab	156.0 ab	21.2 a
0.05	40.49 a	11.99 a	163.0 abc	21.4 a
0.5	40.50 a	13.59 ab	175.5 bc	20.0 a
1	41.88 a	13.19 ab	153.1 ab	22.8 a
2.5	32.66 a	14.03 b	128.7	28.1

The greatest phosphate effect was on root Cd content, in which case a slight elevation was seen at 0.5 mM phosphate and a large reduction at 2.5 mM phosphate; both effects were statistically significant at the 5% level (Table 1). If the shoot Cd is expressed as a percentage of the total Cd in the plant, it is seen that the proportion of Cd in the shoots is significantly higher at the highest phosphate level (Table 1). The root-to-shoot ratios were similar for all phosphate levels, and thus disproportionate growth did not account for the observed difference. It appears that high phosphate levels result in a greater translocation of Cd from root to shoot. The reasons for this are not readily apparent since increased cation levels in plant leaves are usually associated with low external phosphorus. However, it has been suggested that high anion concentrations in some cases may stimulate cation uptake through a counterion effect.

From these experiments it may be inferred that the increased Cd accumulation in soybean shoots in high phosphate soils was due to a phosphate effect on the distribution of Cd in the plant. It should be kept in mind that the Cd treatment in the present experiments was of short duration, whereas with the soil grown plants the exposure to Cd lasted from germination until harvest of the plants. These experiments do illustrate the importance of studying the interactive effects of nutrients on toxic trace element uptake and distribution in plants if one is to understand the fate of trace elements in agricultural ecosystems.

Reference

1. J. E. Miller, J. J. Hassett, and D. E. Koeppe, Uptake of cadmium by soybeans as influenced by soil cation exchange capacity, pH, and available phosphorus, J. Environ. Qual. 5, 157–160 (1976).

THE CAPACITY OF SOYBEAN CULTIVARS OF VARYING SO_2 RESISTANCE TO DETOXIFY SULFITE

J. E. Miller and P. B. Xerikos

The injury response of a given variety or species of plant to SO_2 is determined by an interplay of genetic susceptibility with stage of growth and environmental influences. Thus, it has been shown that agricultural species such as alfalfa, barley, and soybeans are very sensitive to SO_2, whereas corn and potatoes are relatively resistant. Considerable differences in SO_2 sensitivity among varieties have been noted for soybeans, the experimental plant used in our studies; however, the reasons for these differences have not been adequately defined.

It is generally accepted that acute SO_2 injury to plant tissues results from the formation of sulfite ions and their effect on enzyme and membrane systems. Sulfite is approximately thirty times more toxic than its oxidation product sulfate, which has been shown to accumulate in plant tissues exposed to SO_2. Although it is inferred that sulfite is the primary toxic chemical form of SO_2, little is known of its residence time in plant cells, and more importantly how this might relate to species or varietal resistance. The following experiments were done with a series of soybean cultivars of known SO_2 sensitivity to further our knowledge concerning mechanisms of SO_2 resistance.

The sulfite ion is unstable in solution, and to determine its concentration in plant tissues it is necessary to change it to a stable complex as the tissue is homogenized. A modification of the pararosaniline procedure,[1] in which the stable disulfitomercurate ion is formed, was found to be suitable in this respect. The recovery of sulfite by this procedure was approximately 90%. For the purpose of these experiments it was necessary to treat the soybean leaf tissue with a controlled quantity of sulfite in a short period of time. In order to overcome difficulties with variable leaf resistance and the resulting uncertainty concerning the magnitude of gaseous SO_2 uptake, the sulfite was introduced to the young, expanding trifoliate leaves as a solution via the excised petiole. In this manner the initial tissue sulfite concentrations were controlled within a factor of two. The average tissue load was approximately 2 mg SO_2/g fresh weight of soybean leaf tissue taken up over a one-half-hour period. This is somewhat less than the concentration considered to be lethal to plant tissue.

A typical plot of leaf SO_2 concentration versus time for 70 min after the 30-min treatment period is shown in Figure 1. The nearly complete disappearance of SO_2 in the leaf tissue within an hour of termination of the treatment period is typical of all cultivars tested, with only minor variations. However, obvious differences between cultivars were apparent if the SO_2 present in the tissue at the completion of the 30-min treatment period was expressed as a percentage of the total SO_2 taken up (Table 1). Although the SO_2 tolerance rank of the eight cultivars tested did not strictly correlate with the percent SO_2

Table 1. Sulfite conversion by soybean cultivars. Values are the mean of four replicate samples.

Cultivar	Relative SO_2 Tolerance Ranking	SO_2 (%)	Averate Rate of SO2 Removal µg SO_2/g fresh wt/min	
			Treatment Period (30 min)	Posttreatment (60 min)
York	1(a)	6.9(b)	75.8	3.17
Arksoy	2	2.9	123.7	1.92
Cutler	3	5.1	62.9	1.45
Kent	4	6.9	69.4	2.23
Dunfield	5	9.3	57.8	4.43
Dare	6	11.5	49.8	2.45
Lee	7	12.6	52.3	2.67
Peking	8	10.2	46.5	3.25
		$LSD_{5\%}$ = 2.9%		

(a) Tolerance as determined by Miller, Howell, and Caldwell.[2]

(b) Values represent SO_2 content of leaf tissue at completion of the 30-min treatment period expressed as a percentage of the total SO_2 taken up.

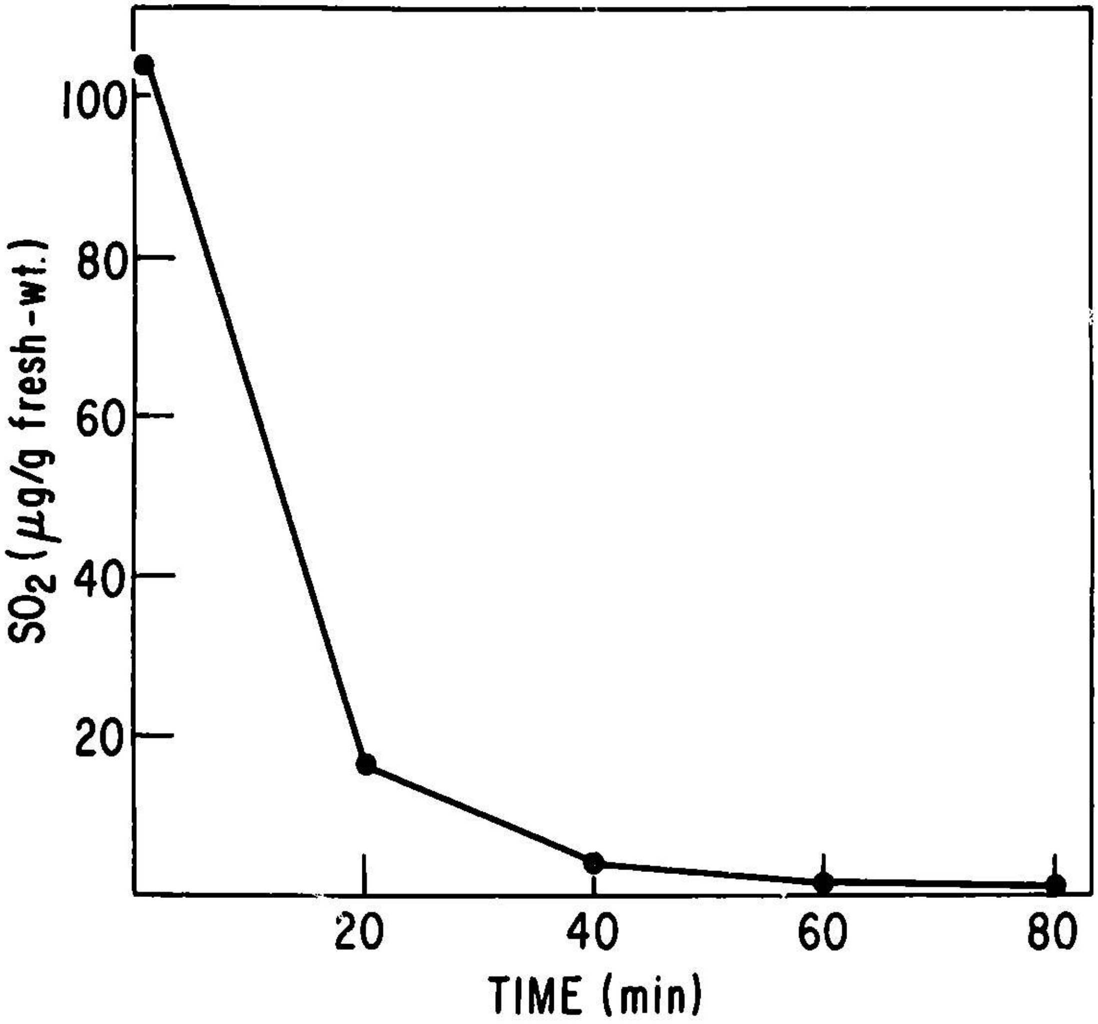

FIG. 1.—Conversion of sulfite over time by soybean leaf tissue (ANL neg.149-76-256)

remaining in the tissue, all of the SO_2-resistant cultivars had a lower percentage of tissue SO_2 remaining than the susceptible cultivars, i.e., an average of 5.4% for York, Arksoy, Cutler, and Kent, as compared to 10.9% for Dunfield, Dare, Lee, and Peking. If the data are expressed as rates of SO_2 conversion per gram of tissue, it is apparent that the resistant cultivars generally convert the SO_2 more rapidly than the susceptible cultivars during the initial 30-min treatment period when tissue SO_2 loads are high. Both resistant and susceptible cultivars convert the SO_2 much slower during the 60-min posttreatment period.

It appears that resistant soybean genotypes may be able to withstand acute exposures to SO_2 by virtue of their capacity to convert the toxic sulfite ion more rapidly. That such relationship exists does not negate the importance of other possible modes of resistance, such as leaf anatomical features which may affect SO_2 uptake rates. It does, however, illustrate that pollutant sensitivity of plants may relate directly to the basic biochemical capabilities of the individual genotypes and, especially in the case of SO_2 stress, to the ability to detoxify sulfite.

References

1. P. W. West and G. C. Gaeke, Fixation of sulfur dioxide as sulfitomercurate III and subsequent calorimetric determination, Anal. Chem. 28, 1816–1823 (1956).
2. V. L. Miller, R. K. Howell, and B. E. Caldwell, Relative sensitivity of soybean genotypes to ozone and sulfur dioxide, J. Environ. Qual. 3, 35–37 (1974).

LEACHING RATES OF SEVERAL CATIONS FROM SOILS BY SIMULATED RAINWATER

M. S. Berigari and P. B. Xerikos

The effects of acid precipitation on the release of major cations from soil was studied by leaching or shaking soils with real and simulated acid rainwater. The amount of water used was equivalent to two years of rainfall in the Midwestern states, assuming a mean annual rainfall of 100 cm. The leachates or filtrates were collected and analyzed for the presence of Ca, Mg, K, and Na by atomic absorption spectroscopy.

The two soils used in these experiments were collected from agricultural regions in the Midwest. Soil A, from Illinois, had a pH of 6.6, a cation exchange capacity (CEC) of 33.6 and a percent base saturation of 71.7. The values of soil B, from Ohio, were 4.5, 12.3, and 53.3, respectively. Ca and Mg accounted for about 98% of the exchangeable cations in both soils. Simulated acid rain was prepared by addition of H_2SO_4, HNO_3, and NH_4Cl in the proper proportions to give 60% $SO_4^{=}$, 20% NO_3^-, and 20% Cl^- as the dominant anions. This solution was diluted with deionized water to give pH's from 2.1 to 6.8. Deionized water was used for the control.

Treatment of the soils with the solutions at pH's less than 4 significantly lowered soil pH. Soil A had pH values of 6.25 and 4.85 after treatment with the simulated rainwater at pH values of 3.1 and 2.1, respectively, while soil B had pH values of 4.00 and 3.25 with the same treatment. Thus, one would not expect any short-term alterations in soil pH due to precipitation with pH values 4 and higher, and effects with more acid precipitation would probably be evident only if rain of low pH were sustained throughout the year. Also, under actual field conditions other factors, such as surface runoff and evaporation, must be considered.

The displacement of cations due to the acid water is summarized in Table 1 for the leaching experiments. As would be expected from the preponderance of Ca and Mg in exchangeable form, these cations were present in the greatest amounts in the leachates. In general, the water with the lower pH removed the larger amounts of cations, and reversals in this trend occurred

Table 1. Displacement of soil cations from soil by simulated acid rainwater.

pH	Cation Displaced[(a)] (meq/10 g)				Percent Exchangeable Bases Removed
	Ca	Mg	K	Na	
			Soil A (leaching)		
2.10	0.4060	0.255	0.0085	0.0101	30.7
3.10	0.0710	0.0563	0.0029	0.0065	5.7
4.05	0.0138	0.0136	0.0015	0.0035	1.5
5.80	0.0047	0.0052	0.0004	0.0024	0.5
6.00(b)	0.0037	0.0041	0.0004	0.0028	0.5
5.50(c)	0.0039	0.0058	0.0014	0.0038	0.6
			Soil B (leaching)		
2.10	0.2560	0.1070	0.0073	0.0042	57.2
3.01	0.0796	0.0339	0.0032	0.0025	18.1
4.00	0.0172	0.0150	0.0013	0.0040	5.9
5.28	0.0052	0.0095	0.0002	0.0051	2.4
5.89	0.0039	0.0056	----	0.0034	2.2
6.82	0.0039	0.0064	0.0007	0.0004	1.9
			Soil B (shaking)		
2.10	0.2620	0.1430	0.0126	0.0043	64.2
3.01	0.1280	0.0575	0.0070	0.0039	28.9
4.00	0.0138	0.0120	0.0032	0.0022	5.5
5.28	0.0052	0.0060	0.0019	0.0016	2.2
5.89	0.0052	0.0057	0.0013	0.0007	2.1
6.82	0.0052	0.0143	0.0020	0.0013	2.6

(a) All values are the mean of 3 replicate samples.
(b) Deionized H_2O.
(c) Rain.

only above pH 5. More cations were removed from soil A than from B; however, if the total amounts removed are expressed as a percentage of the total exchangeable cations, it is evident that the relative depletion was greater in soil B (Table 1). This was probably owing to the relatively low initial pH of the soil and its lower buffering capacity. It is interesting that the results of the shaking experiment with soil B were generally similar to the results of the

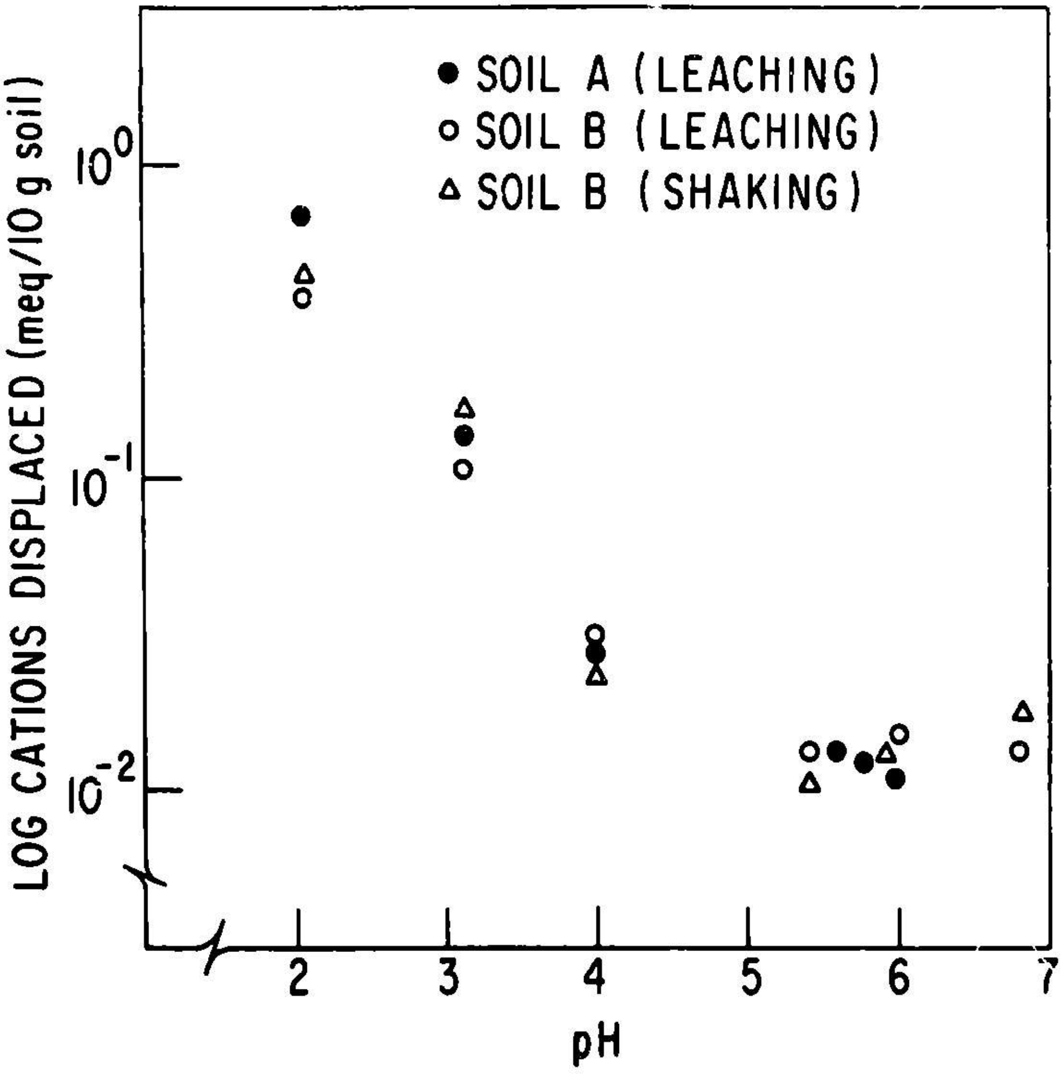

FIG. 1.--Effect of pH on displacement of cations from soil by simulated acid rainwater (ANL neg. 149-76-255)

leaching experiment (Table 1). Shaking did, however, have a tendency to remove more cations than leaching.

If the total measured cations are summed for each pH treatment and expressed graphically in a semilog plot, it is evident that pH 4 is a critical value below which the rate of displacement of cations is accelerated (Figure 1). That this is the case is also evidenced by the alteration of soil pH by water having a pH of less than 4, as previously mentioned. Since rainwater has become more acid in parts of the industrialized world, it is very important to keep this point in mind when assessing the impact of acid rain on soil environment.

Rainwater with a pH less than 4 could increase the rate of mineral weathering, especially in areas with moderate temperatures and high annual rainfall — typical of areas of great agricultural productivity. The effect of acid rain on forest vegetation is of special concern because it does not seem practical or economical to lime the land under natural forest, although it is well known that Al and Mn may be toxic to plants growing in acid soils. In addition to affecting the chemical status of the inorganic elements [for example, removal of 0.740 meQ of cations/10 g soil, equivalent to a loss of 6.0 metric tons of $CaCO_3$ per hectare from the plow layer (15 cm)], acid rainwater could lower soil pH and thus alter the populations and activities of the micro-organisms responsible for transformations involving N, S, and P in soil, indirectly affecting the availability of these elements to higher plants. Symbiotic and parasitic relationships between higher plants and microbes also may be altered either directly or indirectly with a change in soil acidity. It is very important to recognize that all such effects may occur concurrently, and the change in the balance of these relaionships is characteristic of the soil involved. The impact of acid precipitation on soil and plant environment appears to be very complex, and long-range studies will be required in order to understand these effects.

THE DISTRIBUTION OF PLUTONIUM IN RELATION TO SOIL PARTICLE SIZE CLASSES IN A MIDWESTERN WATERSHED

R. N. Muller and D. G. Sprugel

The remobilization of fallout-derived plutonium in a terrestrial ecosystem is of considerable interest in evaluating the effect this material may have on man. Material entering the environment by this route becomes associated with soil particles[1,2] and, therefore, any subsequent movement of this material, either through resuspension into air or erosion into the aquatic components of the watershed, is partially controlled by the size of the soil particle with which the plutonium is associated. This is a report of a preliminary investigation of the distribution of such plutonium with soil particles of various sizes.

Two soil samples were collected from the Great Miami River watershed in Ohio. One was taken one mile east of the Mound Laboratory (ME-1), a plutonium fabrication facility in Miamisburg, Ohio, and the other from Hueston Woods State Park (HW), approximately 40 miles west of Miamisburg. Both soils are agricultural silt loams (A_p horizons). Physical characteristics of the two soils are given in Table 1.

Table 1. Physical characteristics of the soil and sediment samples used for particle size fractionation.

	pH	% Loss on Ignition	% of Sample by weight Particle size > 50 µm	 50–2 µm	 < 2µm
Hueston Woods	5.7	3.5	11.5	72.0	16.5
Miamisburg	7.6	4.5	23.5	58.0	18.5
Lake Michigan	---	---	10.4	72.2	17.4

The soils were fractionated into five size classes (greater than 45 µm, 45–20 µm, 20–4 µm, 4–2 µm, and less than 2 µm) using a modification of the elutriation technique of Follmer and Beavers.[3] The size range of each fraction was verified with an electronic particle analyzer (Coulter Counter TA-II), and the fractions were then analyzed for plutonium.[4] The description of the actual methods of fractionation and verification have been discussed elsewhere and will not be elaborated upon in this report.[5]

Both soil samples contain concentrations of ^{239,240}Pu as a result of atmospheric fallout (5.3–5.4 fCi/g dry wt), and the ME-1 sample also contains ^{238}Pu (13.8 fCi/g dry wt) resulting from atmospheric discharges of the Mound Laboratory. The distributions of plutonium activity vs. soil-particle size are very similar in both soils for ^{239,240}Pu, and also for ^{238}Pu and ^{239,240}Pu in soil ME-1 (Table 2). This similarity implies that, even if there were differences in the chemical species introduced to the soil or if the adsorption properties of these isotopes to soil particles differed, the observed effects would be small.

Table 2. Distribution of plutonium in particle size fractions of soils from the Great Miami River watershed (fCi/g dry weight).

Particle Size Range (μm)	HW	ME-1	
	^{239,240}Pu	^{239,240}Pu	^{238}Pu
> 45	4.8	2.1	4.6
45–20	0.5	0.75	6.5
20–4	3.5	3.1	8.4
4–2	11.3	9.8	19.9
< 2	15.8	10.9	30.0

Table 3 shows the distribution of the plutonium isotopes with particle size as the percentage of the total activity per gram of soil in each size fraction. More than 40% of the activity in the soil sample is associated with the smallest size fraction and more than 60% is associated with the two smallest size

Table 3. Distribution of plutonium in various soil particle size ranges expressed as percent of the total.

Sample	Particle Size Range				
	>45 µm	45—20 µm	20—4 µm	4—2 µm	<2 µm
HW ^{239,240}Pu	13.4	1.4	9.7	31.5	44.0
ME-1 ^{239,240}Pu	7.9	2.8	11.6	36.8	40.9
ME-1 ^{238}Pu	6.6	9.4	12.1	28.7	43.2

fractions, which are most susceptible to transport via erosional forces of wind and water. While the force of sheet erosion and individual rain drops is sufficient to contribute to the movement of a wide range of particle sizes on land surfaces, once these materials enter either the aquatic or atmospheric environments, the duration of continued suspension is inversely related to particle size. Hence, the association of greater than 60% of the soil plutonium activity with particles in the smallest size classes indicates that there is a greater probability of the activity being redistributed than if it were evenly distributed throughout all particle size ranges. The apparent similarity of particle distribution of material is significant in that atmospheric fallout from two different sources, nuclear testing and industrial stack emission, behave alike, even though their initial chemical and physical forms may be dissimilar.

References

1. D. W. Rhodes, Adsorption of plutonium by soil, Soil Sci. 84, 465–471 (1957).
2. D. W. Rhodes, The effect of pH on the uptake of radioactive isotopes from solution by a soil, Soil Sci. Soc. Amer. Proc. 21, 389–392 (1957).
3. L. R. Follmer and A. H. Beavers, An elutriation method for particle size analysis with quantitative silt fractionation, J. Sed. Petr. 43, 544–549 (1973).
4. D. M. Nelson, E. M. Yaguchi, B. J. Waller, and M. A. Wahlgren, Radiochemical methods, Radiological & Environmental Research Division

Annual Report, January–December 1973, ANL-8060, Part III, pp. 6–17.
5. R. N. Muller and G. T. Tisue, to be published.

AERIAL DISTRIBUTION OF PLUTONIUM IN SOILS AROUND THE MOUND LABORATORY, MIAMISBURG, OHIO

R. N. Muller, D. G. Sprugel, and C. M. Bobula

Local atmospheric inputs of ^{238}Pu and ^{239,240}Pu to the soils in the vicinity of Mound Laboratory were studied and compared to the distribution of background fallout concentrations of these isotopes in the area. Soil samples were collected with a soil corer 1, 3, and 5 miles from the laboratory along transects running in the cardinal and subcardinal directions of the compass. Whenever possible, the samples were collected from cultivated fields to the plow depth (A_p Horizon). In a few instances, it was necessary to take samples from pasture. In the latter cases, samples were collected to a depth of 25 cm. Three cores were taken at each location, combined, returned to the laboratory, air-dried and ground in a ball mill. Replicate 50-g subsamples of the soils (< 1 mm fraction) were extracted with HCl and HNO_3 overnight, and the extracts were then analyzed for total plutonium.[3]

The ^{239,240}Pu activities are relatively constant, ranging between 1.2 and 2.4 nCi/m^2 (Table 1). These are normal background levels for the isotopes associated with regional atmospheric fallout, the observed values being randomly distributed over the study area, indicating little input from the Mound Laboratory. The ^{238}Pu activities range from 11.2 to 0.06 nCi/m^2, the latter being the background value expected from fallout. The concentration of ^{238}Pu is relatively high up to a mile from the laboratory in all directions of the compass (Figure 1). However, the activity falls off rapidly within 3 miles of the laboratory and is at background levels at 5 miles from the laboratory in all but the east to southeast directions. The activity ratio of ^{238}Pu/^{239,240}Pu at the sampling locations, which represents the actual influence of the laboratory on the natural isotopic ratio (~ 0.04) of fallout plutonium in soil, is shown in Figure 2. Again the influence of the laboratory is seen to the east and south, with the ^{238}Pu activity diminishing to atmospheric background levels within 5 miles in all directions.

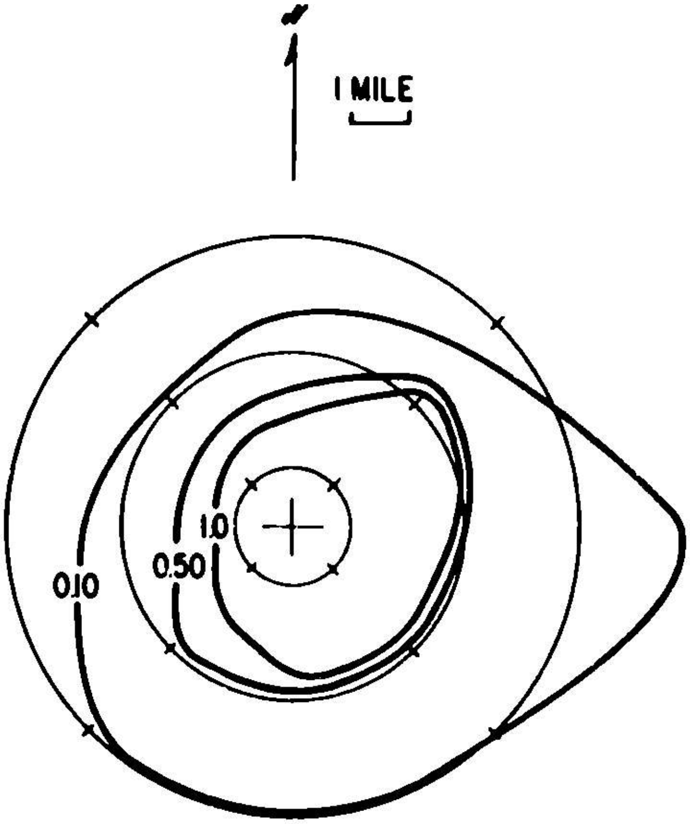

FIG. 1.--Distribution of ^{238}Pu concentrations in surface soils around Mound Laboratory, Miamisburg, Ohio, expressed in nCi/m^2.

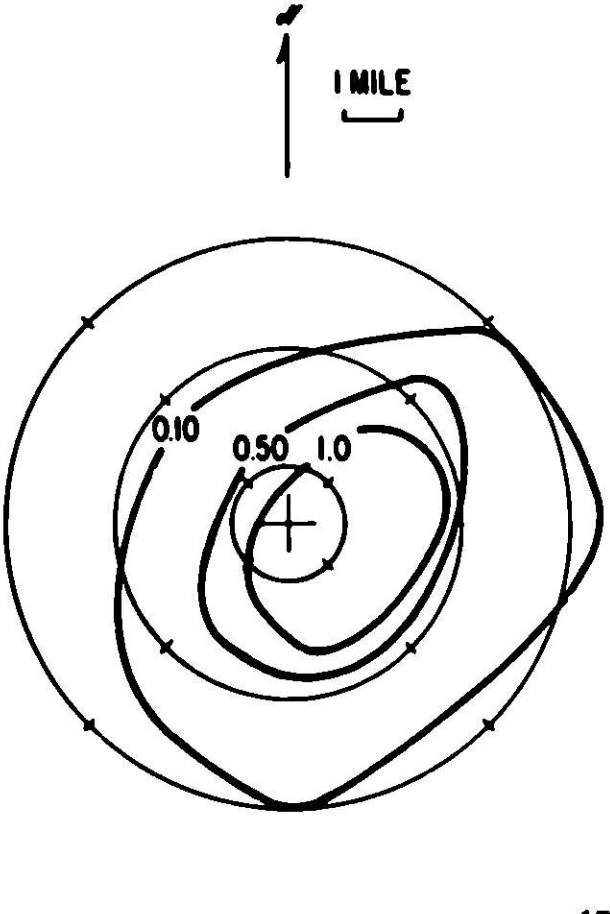

FIG. 2.--Distribution of ^{238}Pu/^{239,240}Pu activity ratios in surface soils around Mound Laboratory, Miamisburg, Ohio.

Table 1. Activity values of ^{238}Pu and ^{239,240}Pu from surface soils in the vicinity of Mound Laboratory, Miamisburg, Ohio (nCi/m^{2}).

Sample	^{238}Pu	^{239,240}Pu	^{238}Pu/^{239,240}Pu
NE - 1 mi	6.64 ± 0.30	1.75 ± 0.15	3.79
3 mi	1.43 ± 0.06	2.09 ± 0.07	0.68
5 mi	0.06 ± 0.01	1.66 ± 0.06	0.036
E - 1 mi	11.2 ± 0.22	1.33 ± 0.08	8.42
3 mi	0.38 ± 0.04	2.01 ± 0.09	0.19
5 mi	0.22 ± 0.03	1.78 ± 0.07	0.12
SE - 1 mi	4.80 ± 0.21	1.87 ± 0.13	2.57
3 mi	0.20 ± 0.02	1.04 ± 0.04	0.19
5 mi	0.10 ± 0.02	1.74 ± 0.08	0.057
S - 1 mi	4.40 ± 0.12	1.23 ± 0.06	3.58
3 mi	0.23 ± 0.02	1.80 ± 0.06	0.13
5 mi	0.15 ± 0.06	1.42 ± 0.09	0.11
SW - 1 mi	1.47 ± 0.07	1.43 ± 0.06	1.03
3 mi	0.38 ± 0.05	2.02 ± 0.10	0.19
5 mi	0.08 ± 0.02	1.74 ± 0.07	0.046
W - 1 mi	0.62 ± 0.05	2.06 ± 0.09	0.30
3 mi	0.18 ± 0.03	2.29 ± 0.08	0.079
5 mi	0.06 ± 0.02	1.65 ± 0.06	0.036
NW - 1 mi	1.47 ± 0.09	2.23 ± 0.11	0.66
3 mi	0.08 ± 0.03	2.40 ± 0.09	0.033
5 mi	0.07 ± 0.02	1.76 ± 0.07	0.040
N - 1 mi	no sample	no sample	--
3 mi	0.15 ± 0.04	1.94 ± 0.09	0.077
5 mi	0.07 ± 0.03	2.22 ± 0.10	0.032

This study agrees with continuing monitoring studies conducted by the Mound Laboratory regarding the direction of plant-derived deposition and extent of elevated concentrations of ^{238}Pu above background. Our results disagree in that our activity values are approximately one to two orders of magnitude lower than those reported by the Mound Laboratory.[2] The reason for this discrepancy is not known at this time, but it may represent an analytical difference rather than an actual loss by remobilization of the ^{238}Pu away from the deposition site. Unfortunately, ^{239,240}Pu activity values are not available for the previously reported ^{238}Pu activities so that comparisons of the activity ratios cannot be made. It does appear, however, that while some material is being introduced into the atmosphere by the laboratory, the amounts are small; the distances the material is transported from the site are short and are controlled by normal wind flow of the region. Hence, unless postdepositional mobilization is occurring at a rate far in excess of the expected 0.03% per annum, the effect of the laboratory-derived atmospheric emissions on the surrounding area is slight.

References

1. D. M. Nelson, E. M. Yaguchi, B. J. Waller, and M. A. Wahlgren, Radiochemical methods, Radiological & Environmental Research Division Annual Report, January–December 1973, ANL-8060, Part III, pp. 6–17.
2. D. G. Carfagno and W. H. Westendorf, Annual Environmental Monitoring Report Calendar Year 1972: Mound Laboratory, MLM-2028, p. 31 (1973).

PRELIMINARY MASS BALANCE OF PLUTONIUM IN A WATERSHED NEAR SIDNEY, OHIO

D. G. Sprugel and G. E. Bartelt

The Great Miami River at Sidney, Ohio, has a drainage area of 541 mi^2 (1401 km^2). Its watershed is predominantly agricultural, with flat to slightly rolling topography and generally calcareous soils; thus, it is typical of the farm country of central Ohio and much of the agricultural Midwest. Flow rates of the Great Miami River at Sidney range from 50 cfs to over 6000 cfs, and average about 500 cfs. From October 1967 through September 1975, the U.S. Geological Survey maintained a sediment sampling station at Sidney, collecting daily samples of river water for determination of suspended sediment content. Sediment concentrations in the river vary from near zero to over 1500 mg dry wt/liter, averaging about 150 mg dry wt/liter. These data can be combined with stream flow measurements from the same location to estimate the total sediment discharge of the river at that point over any given period of time. Daily sediment discharges ranged from 0 to over 10,000 metric tons, while annual sediment discharges over the past five years have ranged from about 40,000 mT (1971) to over 150,000 mT (1973).

The suspended sediment and flow data collected by the U.S.G.S. was used to estimate the amount of ^{239,240}Pu lost from the Sidney watershed in a year. The concentration of plutonium in the water and suspended sediment was determined in 50-liter samples of river water collected each month at Sidney between December 1974 and October 1975. Each sample was filtered through a glass fiber filter and 0.45-μm membrane filter to remove suspended sediment, and the water and filters were analyzed separately for plutonium.[1]

Upon completion of this study (est. July 1976) an attempt will be made to correlate ^{239,240}Pu content of the water and suspended sediment with river parameters such as flow and sediment loading. If correlations are found, a set of regression equations will be developed to predict the plutonium concentrations and distributions from river parameters. However, the preliminary data (Table 1) suggest that the ^{239,240}Pu activities are fairly constant at

Table 1. Miami River parameters and ^{239,240}Pu activities at Sidney, Ohio

Date	Flow Rate (1/sec)	Sediment Concentration (mg/1)	^{239,240}Pu in Suspended Sediment (fCi/1)	^{239,240}Pu in Suspended Sediment (fCi/g)	^{239,240}Pu in Water (fCi/1)
16 Dec 1974	53,500	64.9	0.95 ± 0.12	14.7 ± 1.9	0.11 ± 0.03
7 Jan 1975	16,900	34.1	0.28 ± 0.08	8.2 ± 2.3	lost
15 Jan 1975	19,050	47.8	0.93 ± 0.09	19.4 ± 2.0	0.11 ± 0.05
2 Feb 1975	30,800	50.0	0.83 ± 0.11	16.7 ± 2.2	lost
12 Feb 1975	12,700	15.7	0.18 ± 0.04	11.4 ± 2.3	n.a.
3 Mar 1975	27,800	80.2	1.77 ± 0.26	22.1 ± 1.5	0.06 ± 0.06
20 Mar 1975	47,800	83.0	1.70 ± 0.12	20.5 ± 1.5	0.23 ± 0.06
15 Apr 1975	7,130	13.2	0.26 ± 0.05	19.7 ± 3.8	n.a.
2 May 1975	15,700	50.8	n.a.	n.a.	0.11 ± 0.02
28 May 1975	1,920	74.5	0.48 ± 0.05	6.5 ± 0.7	
10 Sept 1975	3,080	?	n.a.	n.a.	0.09 ± 0.02
14 Oct 1975	2,010	?	n.a.	n.a.	0.22 ± 0.04

n.a. = not analyzed.

about 0.1 fCi/liter and 15 fCi/g dry wt for water and suspended sediment, respectively. Using these preliminary values, it can be calculated that in 1974, a year of average sediment transport, the river exported approximately 0.1 mCi of ^{239,240}Pu from the watershed, of which 5% was in solution. The total loss in 1974 represents 1.0 pCi ^{239,240}Pu per m^2 and is approximately 0.05% of the total ^{239,240}Pu deposited from fallout in the watershed over time (2 nCi/m^2).[2]

References

1. D. M. Nelson, E. M. Yaguchi, B. J. Waller, and M. A. Wahlgren, Radiochemical methods, Radiological and Environmental Research Division

Annual Report, January–December 1973, ANL-8060, Part III, pp. 6–17.
2. E. P. Hardy, P. W. Krey, and H. L. Volchok, Global inventory and distribution of fallout plutonium, Nature 241, 444–445 (1973).

FURTHER INVESTIGATIONS OF PLUTONIUM IN AQUATIC BIOTA OF THE GREAT MIAMI RIVER WATERSHED INCLUDING THE CANAL AND PONDS IN MIAMISBURG, OHIO

C. W. Wayman, G. E. Bartelt, and S. E. Groves

A preliminary investigation of plutonium in aquatic organisms of the Great Miami River Watershed, Ohio, has been conducted.[1] This report is a continuation of that study to include new species and additional samples of old species. For the first time data are available on the plutonium content of aquatic biota from the canal and ponds located adjacent to the Mound Laboratory. These areas have elevated levels of ^{238}Pu in the water and sediments as the result of a past incident. It is the purpose of this report not only to record plutonium activities in aquatic biota but to study trophic level relationships and investigate the mode of plutonium uptake by organisms. Radiochemical analysis of biota follows the methods described by Nelson et al.[2]

Aquatic plants from the watershed (Table 1) were sampled both upstream and downstream from the effluent pipe of Mound Laboratory. Plants collected downstream of the laboratory concentrate more ^{238}Pu than the plants located upstream by two to three orders of magnitude. Activities of ^{238}Pu in background samples are unexpectedly high and may be attributed to contamination. Activities of ^{239,240}Pu in the plants from upstream and downstream are approximately the same.

Aquatic macrophytes, Potamogeton and Myriophyllum, sampled from Franklin contain approximately the same concentrations of plutonium. The green alga, Cladophora, sampled downstream from Mound Laboratory, appears to concentrate ^{238}Pu more than the macrophytes by an order of magnitude.

Cladophora sampled at the Franklin site was transplanted with its substrata intact from Bear Creek, a tributary of the Great Miami River situated upstream from Mound Laboratory. The Cladophora shows an immediate uptake of ^{238}Pu of at least one order of magnitude within 10 hours after transplanting. Another slight increase occurs after an additional 5 hours. It is probable that the Cladophora had reached an equilibrium level and that the second increase represents sample variability. The rapid accumulation of plutonium by

Table 1. ^{238}Pu and ^{239,240}Pu activities (pCi/kg wet wt)$^{(a)}$ in aquatic plants from the Great Miami River watershed, Ohio.

Sample Type and Location	Date	^{238}Pu	^{239,240}Pu	^{238}Pu/^{239,240}Pu
Cladophora				
Rip Rap Bridge	5 Nov 74	0.15 ± 0.04	0.22 ± 0.05	0.7 ± 0.2
Rip Rap Bridge	9 June 75	1.2 ± 0.4	2.0 ± 0.4	0.6 ± 0.2
Mad River	10 Sept 74	0.15 ± 0.08	0.09 ± 0.07	2.0 ± 2.0
Stillwater River	11 Sept 74	0.2 ± 0.2	0.7 ± 0.2	0.3 ± 0.3
Bear Creek	24 June 75	<1	N.D.	
Bear Creek	5 Nov 75	<0.5	N.D.	
Franklin	24 June 75	15 ± 1	0.6 ± 0.3	25 ± 10
Bonham	16 Sept 75	4.4 ± 0.4	0.2 ± 0.1	22 ± 10
Canal	12 Sept 75	910 ± 20	2 ± 1	450 ± 200
Potamogeton				
Mad River	10 Sept 74	0.05 ± 0.01	0.13 ± 0.02	0.4 ± 0.1
Chautauqua	23 July 74	± 0.4	0.22 ± 0.04	150 ± 20
Franklin	24 July 74	1.9 ± 0.1	<0.03	>60
Franklin	14 Aug 74	8.6 ± 0.4	0.24 ± 0.07	36 ± 10
Franklin	24 June 75	5.1 ± 0.4	0.07 ± 0.06	72 ± 60
Franklin	16 Sept 75	1.4 ± 0.1	0.18 ± 0.05	8 ± 2
Myriophyllum				
Franklin	10 June 75	4.1 ± 0.2	0.09 ± 0.04	44 ± 20
Franklin	24 June 75	4.8 ± 0.3	0.05 ± 0.04	95 ± 70
Franklin	16 Sept 75	4.2 ± 0.4	0.5 ± 0.2	9 ± 3
Duckweed				
Canal	7 Nov 74	800 ± 20	5 ± 1	160 ± 40
Canal	13 May 75	2,900 ± 30	8 ± 2	340 ± 70
South Pond	10 June 75	380 ± 20	0.7 ± 0.7	500 ± 500
Canal	12 Sept 75	1,000 ± 20	2.1 ± 0.7	500 ± 200
Canal	15 Oct 75	840 ± 20	8 ± 2	100 ± 30
Canal	17 Dec 75	640 ± 9	2.7 ± 0.6	240 ± 50
Cattails$^{(b)}$				
North Pond	13 May 75	1.9 ± 0.1	<0.05	>40
Canal	13 May 75	7.5 ± 0.4	<0.09	>80
Canal	10 June 75	2.8 ± 0.2	0.42 ± 0.07	7 ± 1

(a) The ± value is 1 σ counting error. When the counting error is >100%, the concentration is recorded as <2 σ.

(b) Whole plants minus the roots.

N.D. = not detectable.

Cladophora suggests that uptake is probably more a function of adsorption than absorption. A study of the distribution of plutonium in giant brown algae showed that most of the activity was associated with the outer surfaces.[3]

The accumulation of plutonium in crayfish and fish species from the river was also studied (Table 2). Activities of $^{239,240}Pu$ are approximately the same in all samples from both above and below the Mound Laboratory effluent pipe. The activities of ^{238}Pu in all upstream samples are one to three orders of magnitude less than the levels in specimens from downstream. Downstream crayfish contain twice as much ^{238}Pu as goldfish and minnows. Also, the crayfish contain two to three orders of magnitude more ^{238}Pu than carp minus gastrointestinal tracts; however, their activity is almost equal to that of shad collected downstream.

In a separate study of crayfish from the Great Miami River, it was found that most of the plutonium was concentrated in soft tissues rather than in the sclerotized shell. Similar results have been found for the Tridacna clam and lobster from Eniwetok Atoll.[4] In other studies, however, shell or skeletal portions of animals contain higher levels of plutonium than the soft tissue.[5-7]

A comparison among four species of river fish shows that shad (only one sample) had the greatest ^{238}Pu activities. Minnows and goldfish contain the same level of ^{238}Pu, which is about half the value exhibited in shad. The ^{238}Pu activity in carp minus gastrointestinal tracts and in their GI tracts combined is lower than the activities in the other fish species, with the exception of one GI sample. The higher level of ^{238}Pu in this sample is attributed to sediment present in the gastrointestinal tract.

Biological samples have also been analyzed from the canal and ponds which are known to contain elevated levels of ^{238}Pu. Aquatic plants collected from these sites are duckweed, cattail, and Cladophora (Table 1). Duckweed contains the highest levels of plutonium of all the biota sampled from the watershed. Duckweed from the canal is two to eight times higher in ^{238}Pu activity than duckweed from the ponds, reflecting the slight difference that exists in ^{238}Pu activity levels of the two bodies of water. ^{238}Pu activities in the canal average about 1.0 pCi/l as compared to 0.7 pCi/l in the ponds.

Table 2. ^{238}Pu and ^{239,240}Pu activities (pCi/kg wet wt)[a] in crayfish and fish from the Great Miami River, 1974.

Sample Type and Location	Date	Number of Individuals	Average Total Length (cm)	^{238}Pu	^{239,240}Pu	^{238}Pu/^{239,240}Pu
Crayfish (whole)						
Rip Rap Bridge	11 Sept	1		<0.1	0.14 ± 0.08	<0.7
Chautauqua	23 July	0.6[b]		6.2 ± 0.4	0.11 ± 0.06	56 ± 30
Chautauqua	13 Aug	0.8[b]		3.6 ± 0.4	0.09 ± 0.05	96 ± 50
Franklin	14 Aug	0.5[b]		8.7 ± 0.4	0.03 ± 0.03	300 ± 300
Carp (minus GI)						
Dayton	17 Nov	3		0.009 ± 0.001	.0022 ± .0005	4 ± 1
Chautauqua	15 Nov	4	44.8	0.25 ± 0.09	0.04 ± 0.02	6 ± 4
Chautauqua[c]	13 Aug	1	54.0	0.17 ± 0.02	0.024 ± 0.008	7 ± 2
Chautauqua[c]	15 Nov	1	48.0	0.031 ± 0.004	<0.003	>10
Chautauqua[c]	15 Nov	1	54.0	0.054 ± 0.006	0.029 ± 0.004	1.9 ± 0.4
Carp GI (for above)						
Dayton	17 Nov			0.05 ± 0.01	0.010 ± 0.005	5 ± 3
Chautauqua	15 Nov			0.05 ± 0.02	N.D.	
Chautauqua	13 Aug			6.5 ± 0.3	N.D.	
Chautauqua	15 Nov			0.15 ± 0.04	N.D.	
Chautauqua	15 Nov			0.09 ± 0.02	0.16 ± 0.03	0.6 ± 0.2
Goldfish (whole)						
Chautauqua	23 July	17	15.1	3.12 ± 0.09	0.03 ± 0.01	100 ± 30
Chautauqua	13 Aug	15	15.2	5.5 ± 0.2	0.47 ± 0.06	12 ± 2
Chautauqua	14-15 Aug	5	18.1	3.2 ± 0.1	0.07 ± 0.02	46 ± 10
Franklin	14 Aug	13	13.0	1.35 ± 0.07	0.011 ± 0.006	120 ± 70
Minnows (whole)						
Rip Rap Bridge	10-11 Sept	1[b]		0.11 ± 0.02	0.04 ± 0.01	2.4 ± 0.6
Chautauqua	25 July	1[b]		0.73 ± 0.04	<0.01	>70
Chautauqua	13 Aug	1[b]		5.7 ± 0.2	0.19 ± 0.03	30 ± 5
Shad (whole)						
Rip Rap Bridge	10-11 Sept			0.011 ± 0.004	0.15 ± 0.01	0.08 ± 0.03
Chautauqua	25 July 13 Aug 6 Nov			10.7 ± 1.2	0.13 ± 0.02	82 ± 10

(a) The ± value is 1 σ counting error. When the counting error is >100 , the concentration is recorded as <2 σ.

(b) kg wet weight.

(c) Samples collected by DePauw University, Greencastle, Indiana.

N.D. = not detectable.

The study of plutonium activities in aquatic organisms presented in this report does not mean to imply that complete food chains have been examined. The plants and animals investigated represent different trophic levels, which may or may not be interrelated. Generally, aquatic plants accumulate more plutonium than either crayfish or fish. Crayfish appear to concentrate ^{238}Pu to a greater extent than fish with the possible exception of shad. This report reiterates the finding of previous studies that plutonium is discriminated against at higher trophic levels.

References

1. C. W. Wayman, G. E. Bartelt, and D. N. Edgington, Plutonium in aquatic biota of the Great Miami River Watershed, Ohio, Radiological and Environmental Research Division Annual Report, January-December 1974, ANL-75-3, Part III, pp. 78–86.
2. D. M. Nelson, E. M. Yaguchi, B. J. Waller, and M. A. Wahlgren, Radiochemical methods, Radiological and Environmental Research Division Annual Report, January-December 1973, ANL-8060, Part III, pp. 6–17.
3. K. M. Wong, V. F. Hodge, and T. R. Folson, Plutonium and polonium inside giant brown algae, Nature 237, 460–462 (1972).
4. V. Nelson and V. E. Noshkin, Eniwetok Radiological Survey, U.S. Atomic Energy Commission, Nevada Operations Office, NOV-140 (1973).
5. A. Aardrog, Radioecological investigations of plutonium in an arctic marine environment, Health Phys. 20, 31–47 (1971).
6. V. E. Noshkin, Ecological aspects of plutonium dissemination in aquatic movements, Health Phys. 22, 537–549 (1972).
7. E. E. Ward, Uptake of plutonium by the lobster, *Homarus vulgaris*, Nature 209 625–626 (1966).

DISPERSAL OF PLUTONIUM FROM AN EFFLUENT PULSE IN THE GREAT MIAMI RIVER

D. G. Sprugel, R. N. Muller, G. E. Bartelt, C. W. Wayman, and C. M. Bobula

---

Very little is known about the reactions and dispersal of chemicals entering a river as the result of a pulsed discharge from an industrial facility. Therefore, as part of the study of the Great Miami River watershed, an experiment was undertaken to tag an effluent release from the Mound Laboratory with a harmless dye and follow its dispersal downstream in the river. Coincident with the investigation of the dispersal of the pulse, water samples and biota were collected to investigate the reactions that plutonium, released into the river in this manner, undergoes during a period of approximately two days.

Two releases were studied, one during June and another in September 1975. The low level waste storage tanks at the Mound Laboratory were spiked with Rhodamine WT dye. A fluorometer was used to observe the dispersion of the dye, which served as a marker for the progress of the pulse of plutonium downstream. Downriver sampling stations were established at Chautauqua (1.5 miles), Floodgate (2 miles), Franklin (6 miles), and Bonham (25 miles). The water was monitored with a continuous recording fluorometer, and samples of water and biota were taken before, during, and after the passage of the pulse at each sampling site. Water samples were collected and filtered through 0.45-μm membrane filters to determine the plutonium activity of dissolved and particulate components.[1] The water flow in the river was approximately 1000 cfs during both experiments and represents normal summer and fall flow rates for the river.

The fluorescence curve produced by the passage of the spiked pulse at the Franklin sampling location is shown in Figure 1 for the September 1975 run. This curve is representative of those observed at all stations during both studies and clearly shows the passage of the dye as indicated by the fluorometer. In addition, values of both the dissolved and particulate ^{238}Pu activities (totals ranging from 200 fCi/l to 10 fCi/l downstream) followed the same time pattern as exhibited by the dye at all stations. It was not possible to determine the

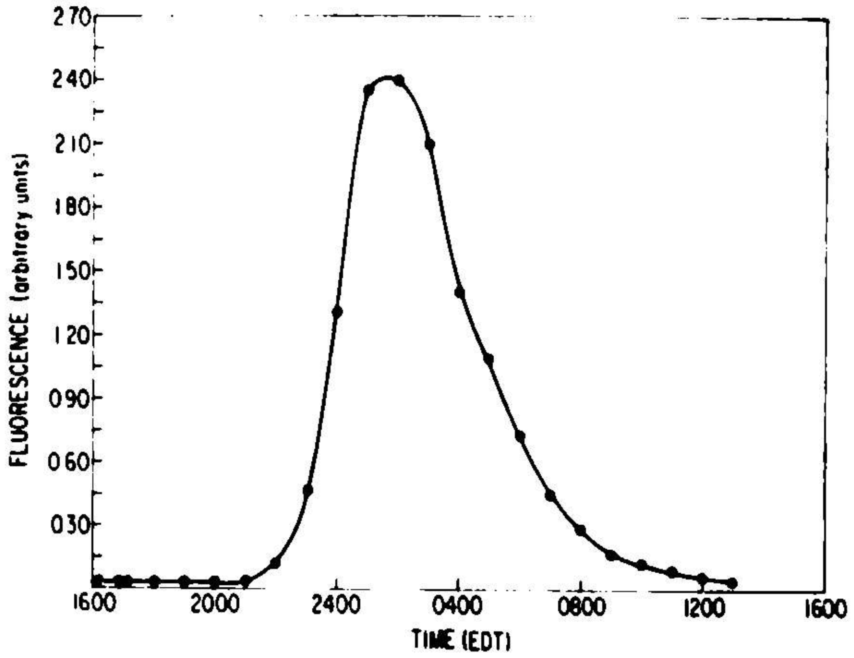

FIG. 1.--Fluorescence curve of rhodamine WT dye at Franklin station during September 1975 dye study on Great Miami River.

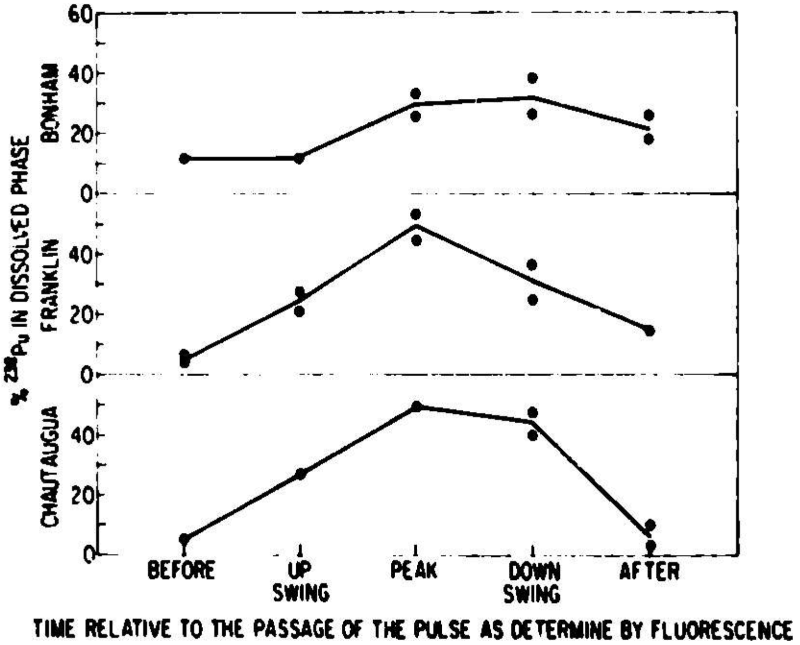

FIG. 2.--Percentage of ^{238}Pu in the dissolved phase at three downriver stations during the September 1975 pulse effluent release study on the Great Miami River.

activities of ^{239,240}Pu from the water samples at any of the stations because of the extremely low levels involved (approximately 0.5 fCi/l).

The concentration of soluble plutonium was found to be proportional to the concentration of the Rhodamine WT dye. This correlation permitted the integration of the area under the curves obtained from the dye monitoring to be equated to the total soluble ^{238}Pu present in the pulse. Integration of the areas under the fluorescence curves for the Franklin and Bonham stations in the September studies give values for Rhodamine dye of 12.7 ppb-hr and 10.1 ppb-hr, respectively. The agreement of the concentrations in the September study implies that the amoung of dissolved material passing the two points is the same since the slight decrease in dye values at Bonham can be explained by dilution from tributaries between the two points. Hence, it would appear that since the soluble ^{238}Pu gives a positive correlation with the dye concentration, it is not being removed from the river once the water passes Franklin.

It was not possible to carry out such a comparison on the data from the sampling station farthest upstream at Chautaugua because it was visually clear from the dye pattern that the effluent plume was not being mixed with the entire river volume, but remained as a separate water mass along the shore until it was turbulently mixed by passage over the dam at Floodgate (2 miles) and the subsequent narrows downstream of that dam.

The distribution of ^{238}Pu between the particulate and dissolved phases indicates that the plutonium in the river prior to a pulse is mainly in the particulate phase. However, during the passage of a pulse, the distribution shifts until approximately 50% of the plutonium is in the particulate phase and the other 50% is dissolved, as can be seen from Figure 2. The apparent broadening of the curve at the Bonham station is most likely due to the effects of dilution and diffusion of the pulse with distance below the discharge point.

The uptake of plutonium by sediments results in a quasi-equilibrium distribution between particulate matter and water. This is apparently a rapid process since the data taken at Chautauqua also exhibit this distribution, even though the pulse had not had sufficient time to mix thoroughly with river water and the suspended matter.

To investigate this phenomenon further a sample from the low level waste tank was taken and diluted with raw river water so that the concentration of ^{238}Pu was approximately the same as that expected in the river when the effluent is discharged. Samples of water were taken at intervals for one-half to 24 hours; they were filtered, and ^{238}Pu was determined in the filtrate. The results confirm that uptake of plutonium by the sediments is rapid with equilibrium being set up in less than one hour after dilution with raw river water.

It appears that ^{238}Pu discharged in the effluent is rapidly partitioned between the suspended sediment in the water and a dissolved phase in approximately equal proportions. This distribution is maintained downriver as the effluent pulse travels as an identifiable water mass for a distance of at least 20 miles. It appears that under the flow conditions studied, the soluble plutonium associated with the effluent pulse is not removed from the water mass in the lower reaches of the river.

Investigations of the uptake of pulse-associated plutonium by organisms in the river, while undertaken during both studies, proved inconclusive. It does appear, however, that organisms including the alga, Cladophora, which is known to concentrate plutonium,[2] do not exhibit rapid changes in uptake coincident with the passage of the pulse.

References

1. D. M. Nelson, E. M. Yaguchi, B. J. Waller, and M. A. Wahlgren, Radiochemical methods, Radiological and Environmental Research Division Annual Report, January-December 1973, ANL-8060, Part III, pp. 6–17.
2. E. M. Yaguchi, D. M. Nelson, and J. S. Marshall, Plutonium in Lake Michigan plankton and benthos, Radiological and Environmental Research Division Annual Report, January-December 1973, ANL-8060, Part III, pp. 18–26.

PRELIMINARY INVESTIGATIONS OF THE CHEMICAL SPECIATION OF PLUTONIUM IN NATURAL WATERS OF THE NORTHEASTERN AND SOUTHEASTERN UNITED STATES

J. J. Alberts, M. A. Wahlgren, and D. M. Nelson

Investigations are in progress to determine the chemical speciation of plutonium in natural waters by means of ultrafiltration and ion exchange techniques. These studies have been directed during the past year to defining the gross submicron size and charge characteristics of plutonium which has been dispersed in the atmosphere as a result of nuclear testing, been deposited in surface waters of the northeast and southeast, and been scavenged by precipitation.

Samples were taken at a station in the southern basin of Lake Michigan (approximately 7 miles WSW of Grand Haven, Michigan) from depths of 3 m, 22 m, and 60 m during August 1975. These samples are representative of water from the epilimnion, thermocline, and hypolimnion at that time of year and location. Water samples of the southeast were collected (by Dr. James Schindler of the University of Georgia) from Banks Lake in the southern portion of Georgia. This lake, which has a high level of organic carbon and a low pH (3.9), is a shallow lake with little sediment load and receives its water from a moderate size watershed.[1] Samples were taken of only the surface water since the lake is very shallow (~ 6 feet) and completely wind-mixed at most times. Finally, a snow sample was collected in November 1974 on the Argonne site by placing polyethylene sheets on the ground and transferring the snow to polypropylene containers. The snow was allowed to melt, and the water was then processed as usual. All samples were filtered through 3.0- and 0.45-μm membrane filters. The filtrate was passed through an ultrafilter (Bio-Rad 30,000 Molecular Weight, MW, dialyzer), and the effluent was then passed through anion and cation exchange columns. Fifty-liter aliquots of water which passed through each step of the process were analyzed for plutonium. The exact techniques of fractionation and analysis of the aliquots have been described previously.[2]

It may be seen (Table 1) that the concentration of ^{239,240}Pu in Lake Michigan waters is in agreement with published values for the lake[3] and is

Table 1. Activities of $^{239,240}Pu$ (fCi/l) in various particle size and charge classes from natural waters.

	Lake Michigan Station 5			Banks Lake	Argonne Site Snow
	Aug 1975 3 m	Aug 1975 22 m	Aug 1975 60 m	May 1975 3 m	Nov 1974
Filtered H_2O	0.35	0.58	0.65	4.3	1.35
30,000 MW Ultrafiltered H_2O	0.29	0.50	0.62	3.6	0.92
Ultrafilter Backflush	0.06	0.09	0.03	0.73	0.02
Anion Exchangeable	0.26	0.42	0.35	ND*	0.40
Cation Exchangeable	0.04	0.16	<0.03	ND*	0.47
Ultrafilterable Noncharged	<0.03	<0.01	<0.27	---	<0.03
pH	~8	~8	~8	3.9	5.3

*ND = not determined

lower than that in either snow or surface waters from Banks Lake. In addition, the concentration in snowmelt is in the range to be expected from present concentrations of plutonium in surface air samples. The higher concentration of plutonium water from Banks Lake cannot be explained at present, but may be related to the low pH of the water and the low sediment loading in comparison to that in Lake Michigan.

Further study of the data (Table 1) shows that the plutonium in Lake Michigan waters is not retained by the 30,000-MW ultrafilter, indicating that the plutonium in this water is either of a particle size less than approximately 28-Å diameter or is in true solution. Samples from Banks Lake and snowmelt contain a significant fraction of non-ultrafilterable plutonium (16.3 and 31.9%, respectively). The reason for this difference in size distribution between precipitation or Banks Lake water and Lake Michigan water is not known. It is possible that the lower pH values of the Banks Lake water and the snowmelt can stabilize a colloidal form of plutonium with an effective diameter greater than 28 Å, while the higher pH of Lake Michigan water is more conducive to the formation of a species of smaller diameter. Alternately, the differences in ionic strength and composition of counter ions in the various waters may cause the different size distribution. In Lake Michigan waters the major anions are carbonate and bicarbonate, and there are extremely low organic acid concentrations. Conversely, Banks Lake contains a high concentration of organic acids, but because of the low pH, both it and the snowmelt would be low in carbonate and bicarbonate. Hence, in low carbonate-bicarbonate waters there may be a stabilization of relatively larger sized colloidal species of plutonium, which may not occur in the waters of Lake Michigan because of their higher pH and higher alkalinity. In waters of high alkalinity, the small size of the plutonium species may be due to the formation of a carbonate or bicarbonate complex.

The formation of such a complex is supported by the behavior of plutonium in the ion exchange experiments, which provides information on the charge of the species absorbed in the resin. The data in Table 1 indicate that for Lake Michigan water, the species absorbed is predominantly anionic. However, the snowmelt water exhibits an approximately even division of plutonium into anionic and cationic species. Unfortunately, the data for the charge distribution of the material in Banks Lake water are not yet available.

Of additional interest is the apparent depth difference in charge distribution of the plutonium in the August 1975 Lake Michigan water samples. It appears that there is a decrease in the percentage of plutonium in the anionic state from approximately 90% anionic in the surface waters to only 56.5% anionic in the deep waters. Also, the apparent increase in plutonium in the cationic fraction at the thermocline may indicate either an electrostatic change taking place at the pycnocline or the release of differently charged plutonium from remains of organisms as they settle to this level. The lack of plutonium in the cationic fraction in the deep water may be significant, but may also be an artifact of the poor recovery observed in the analysis of this sample (~ 20%). In either case, further work is required to determine if a real change is occurring in the charge distribution of plutonium with depth in this lake.

In summary, this preliminary investigation indicates that the concentration of ^{239,240}Pu in lake water from the northeast differs from that in the southeast or from snowmelt and that the submicron size distribution and charge distributions appear different for the various water samples.

References

1. J. E. Schindler and J. J. Alberts, Analysis of organic-inorganic associations of four Georgia reservoirs, Arch. Hydrobiol. 74, 429–440 (1974).
2. J. J. Alberts, M. A. Wahlgren, P. J. Jehn, D. M. Nelson, and K. A. Orlandini, The chemical speciation of ^{239,240}Pu and ^{137}Cs in Lake Michigan waters, Radiological and Environmental Research Division Annual Report, January-December 1974, ANL-75-3, Part III, pp. 86–96.
3. M. A. Wahlgren and D. M. Nelson, Plutonium in the Laurentian Great Lakes: Comparison of surface waters, Verh. Internat. Verein. Limnol. 19, 317–322 (1975).

THE ASSOCIATION OF TRANSURANIC ELEMENTS WITH LACUSTRINE SEDIMENTS

J. J. Alberts, M. A. Wahlgren, R. N. Muller, and K. A. Orlandini

Approximately 97% of the fallout ^{239,240}Pu and an even greater fraction of the ^{241}Am in Lake Michigan is in the sediments.[1] In addition, studies of gross sediment samples taken with a grab sampler have shown that the ^{239,240}Pu in the sediments is almost entirely associated with the hydrous oxides of iron and manganese.[2] Since these observations indicate that the vast majority of plutonium and americium introduced into the lake is associated with sedimentary phases, studies were continued to determine (1) if the americium is also associated with the hydrous oxides; (2) if the association of plutonium with the oxides remained unchanged with depth in the sediment; and (3) if the particle size of the sediment is important in the distribution of the plutonium.

Sediment samples were taken using a 3" "Benthos" gravity corer at a station (approximately 7 miles WSW of Grand Haven, Michigan). In addition, material was collected at the same location from a sediment trap placed approximately 5 m off the bottom at a water depth of 60 m. The core was sectioned into one centimeter subsections which were freeze-dried as were the sediment trap samples. The dried sediment trap material and material from the top four subsections of the core (depth to which significant ^{239,240}Pu concentrations were found) were sequentially extracted into the ion exchangeable, hydrous oxide and organic phases present in the sediment. This separation was carried out using solutions of $MgCl_2$, citrate-dithionite and NaOH. The exact procedure for the separations and subsequent analysis of the extracts has been discussed previously.[2]

The results of this investigation confirm earlier studies[2,3] in that the ^{239,240}Pu is primarily associated with the reducible hydrous oxides phase of the sediment and also show that there is no apparent change in the phase distribution with depth in the sediment core. The maximum in the ^{239,240}Pu activity at the 1- to 2-cm interval is normal for this station, being a function of the sedimentation rate.[3] The activity in the 0- to 1-cm interval is identical to that of material collected in a sediment trap set at 5 m above the bottom. The

Table 1. ^{239,240}Pu and ^{241}Am activities in several chemically defined phases of Lake Michigan sediment and sediment trap material (activities in fCi/g dry wt).

	$MgCl_2$		Citrate-Dithionite		NaOH	
Station	^{239,240}Pu	^{241}Am	^{239,240}Pu	^{241}Am	^{239,240}Pu	^{241}Am
0—1	<0.5	--	80.0 ± 4.5	--	<0.5	--
1—2	3.1 ± 0.5	ND	155.0 ± 5.2	35.7 ± 1.3	0.6	0.6
2—3	<0.5	--	27.3 ± 1.5	--	<0.5	--
3—4	<0.5	--	0.6	--	<0.5	--

	Total		$MgCl_2$		Citrate-Dithionite		NaOH	
	^{239,240}Pu	^{241}Am	^{239,240}Pu	^{241}Am	^{239,240}Pu	^{241}Am	^{239,240}Pu	^{241}Am
May—June 60 m Sediment Trap	80.2 ± 13.8	15 ± 2.9	1.3	<0.5	103 ± 10.0	15 ± 1.4	~6.0	<0.5

distribution of ^{239,240}Pu between the phases is also identical within the statistical accuracy of these experiments.

The results shown in Table 1 indicate that the ^{241}Am is also strongly associated with the hydrous oxides in sediment trap materials and the sediments. This similarity in behavior is not unreasonable if it is recognized that a majority of the ^{241}Am is formed in situ by the decay of ^{241}Pu, which is already absorbed on the hydrous oxides, and is probably fixed without migration to another phase.

The similarity in the concentration of ^{239,240}Pu in the upper sediment layer and in the sediment trap material strongly suggests that resuspension of the surface sediments occurs and that this mechanism may be responsible for the remobilization and translocation of plutonium with the sediments.[3,4] To further investigate the possible role of resuspension and mobilization of sediments in the translocation of plutonium, a study was undertaken to determine the distribution of plutonium with respect to the size of the sediment particles. A sample from a separate 0- to 2-cm sediment increment from the same location was subdivided by elutriation into particle sizes, greater than 45 μm, 45 to 20 μm, 20 to 4 μm, 4 to 2 μm, and less than 2 μm.[6] These fractions were dried and analyzed for plutonium. The results are shown in Table 2. Almost 50% of the ^{239,240}Pu occurs in the 20 to 4 μm, or silt, fraction of the sediment which comprises approximately 45% of the sediment by weight. In addition, 80% of the total activity is present in the sedimentary fractions with a size less than

Table 2. Distribution of ^{239,240}Pu activity in various particle size ranges of Lake Michigan sediments.

	Station 5 Core 0—2 cm				
	>45 μm	45—20 μm	20—4 μm	4—2 μm	<2 μm
% of Total Activity	7.9	10.2	50.5	10.9	20.5

20 μm, with almost 20% of the total activity in the clay fraction. This distribution indicates that a major portion of the plutonium in the sediments is associated with particle sizes that are easily resuspended by physical mixing. Analyses have not been completed for the ^{241}Am, so it is not possible to determine at this time if the particle size distribution for this isotope follows that of ^{239,240}Pu as does the chemical phase.

It appears that in Lake Michigan sediments the transuranic elements ^{239,240}Pu and ^{241}Am are associated with reducible hydrous oxides of iron and manganese and hence are inert to chemical mobilization as long as the sediments remain aerobic. However, a significant quantity of ^{239,240}Pu is associated with a highly transportable fraction of the sediment column. The consequences of this association are not fully understood, but it is possible to imagine circumstances in which clay-size particles could be transported with their attendant ^{239,240}Pu to areas where the necessary chemical changes required to remobilize the attached isotopes chemically can occur.

References

1. M. A. Wahlgren and J. S. Marshall, The behaviour of plutonium and long-lived radionuclides in Lake Michigan. I. Biological transport, seasonal cycling, and residence times in the water column, Impacts of Nuclear Releases into the Aquatic Environment, Proc. Symp., Int. Atomic Energy Agency, Vienna, pp. 227–243 (1975).
2. J. J. Alberts, M. A. Wahlgren, C. A. Reeve, and P. J. Jehn, Sedimentary ^{239,240}Pu phase distribution in Lake Michigan sediments, Radiological and Environmental Research Division Annual Report, January-December 1974, ANL-75-3, Part III, pp. 103–112.
3. D. N. Edgington, J. J. Alberts, M. A. Wahlgren, J. O. Karttunen, and C. A. Reeve, Plutonium and americium in Lake Michigan sediments, Proc. Int. Symp. on Transuranic Nuclides in the Environment, San Francisco, November 17–21, 1975, Int. Atomic Energy Agency, Vienna, pp. 493–516 (1976).
4. D. N. Edgington and J. A. Robbins, The behaviour of plutonium and other long-lived radionuclides in Lake Michigan. II. Patterns of deposition in the sediments, Impacts of Nuclear Releases into the Aquatic Environment, Proc. Symp., Int. Atomic Energy Agency, Vienna, pp. 245–260 (1975).
5. M. A. Wahlgren, J. J. Alberts, D. M. Nelson, and K. A. Orlandini, Study of the behaviour of transuranics and possible chemical homologues in Lake Michigan water and biota, Proc. Int. Symp. on Transuranic

Nuclides in the Environment , San Francisco, November 17–21, 1975, Int. Atomic Energy Agency, Vienna, pp. 9–24 (1976).

6. R. N. Muller and G. T. Tisue, Preparative scale size fractionation of soils and sediments and an application to studies of plutonium geochemistry, submitted to Soil Science.

EXPERIMENTAL APPARATUS AND ANALYSIS TECHNIQUE FOR STUDYING THE LOW REYNOLDS NUMBER HYDRODYNAMIC BEHAVIOR OF WATER-BORNE PARTICULATES

R. R. P. Chase and G. T. Tisue

A unique laboratory apparatus has been designed, constructed, and tested for analyzing the low Reynolds number hydrodynamic behavior of water-borne particulates. The system consists of an isothermal sedimentation chamber, collimated light sources, photographic optics, and monitoring devices. This apparatus is capable of providing dynamic information on water-borne particulates in the size range 2 μm to 700 μm, while simulating a realistic environment. Because of its flexibility, the equipment is being used to determine the kinematic behavior of gravitationally unstable organic mineral aggregates.

The importance of organic mineral aggregates has been well established during the past decade. This material is believed to be a potential food source for marine biota at the lowest levels of the food chain. Organic mineral aggregates are also known to concentrate trace elements and other toxic substances and may be part of the control mechanism by which elemental concentrations are maintained in the water column. The benthic "fluid mud layer" and deep pelagic nepholoid layer consist, in part, of these sediments. Subsea petroleum reserves are thought to be the result of biogeochemical cycling of the organic-mineral complex. Undoubtedly, a fundamental study of these aggregates would be of value to many research interests.

Organic mineral aggregates are a cohesive sediment type composed of an organic matrix sorbed to the surface of mineral flocculates. These complexes form the interface between the water column and the substrate of both the saline and freshwater benthos and, in general, are characteristic of a relatively low energy environment. The size range of this particulate material extends from a few microns to a nominal maximum of 200 μm. The aggregates appear tan in reflected light and have a loosely bound globular structure, which often contains void spaces. Bulk densities of these sediments are only slightly in excess of the density of their natural waters. Additionally, their sedimentation velocities are inordinately low for their sizes and densities and appear to follow a more complex formulation than previously believed.

The kinematic behavior of organic mineral aggregates is determined by use of the apparatus shown in Figure 1. In the present experiment, aggregates are gathered and released into the isothermal sedimentation chamber with a modified plankton pipette sampler, which does not alter the size distribution of the sample. Particulates entering the chamber pass through a specially designed diffuser in which a positive static pressure head is maintained in order to eliminate initial momentum input. An optical quartz glass window mounted midway between the top and base of the chamber provides undistorted observation of the settling aggregates. They are illuminated in the central test area with collimated light sources. The collimators are placed at right angles to the optical window providing reflected light observations, or behind the chamber for transmitted light studies.

These observations are made both in real-time and photographically. The present investigation uses telemicroscopes which provide magnifications from 0.3× to 10×. One telemicroscope is equipped with 35-mm motion picture camera equipment for precision recording of the kinematic data. The optical equipment makes it possible to observe these minute particulates, located well away from the wall, thus avoiding both boundary effects and possible secondary flow perturbations.

Analysis of the photographs is performed by an on-line scanning microdensitometer controlled by a PDP-10 computer.* The entire film sequence is scanned, and the motion of each aggregate is followed from first to last appearance. The computer is programmed to return particle/aggregate identification, aggregate dimensions, vector velocities, and spectral rotation/precession data. Aggregate dimensions are currently measured to within ± 2 microns, yielding dynamic data accurate to within 1% of the true value. The apparatus and analysis schemes that have been developed thus allow for precise kinematic characterization of the environmentally important organic mineral aggregates.

---

*The ALICE system, Applied Mathematic Division, Argonne National Laboratory.

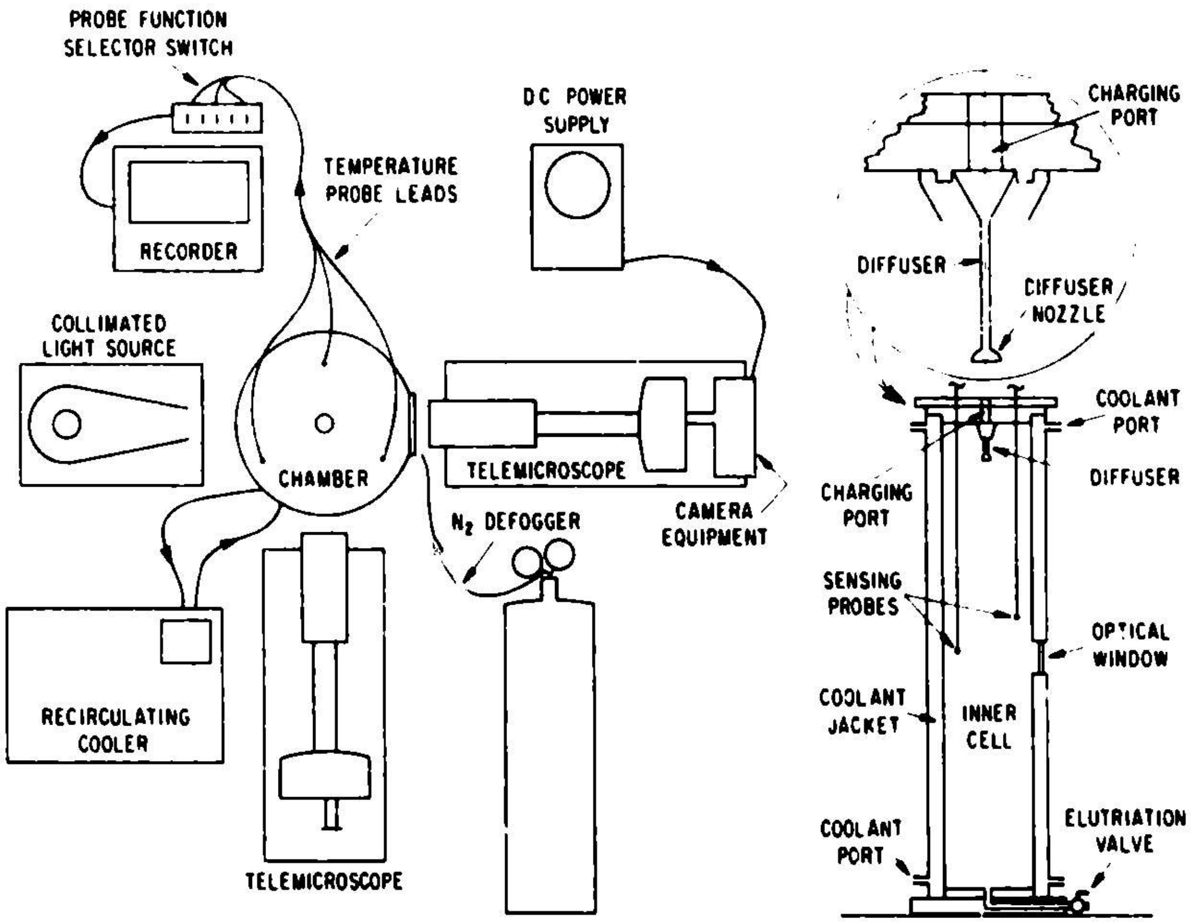

FIGURE 1A

FIGURE 1B

FIG. 1.--(A) Schematic arrangement of apparatus used for transmitted light observations. (B) Isothermal sedimentation chamber cross section with detail of diffuse charging port.

The data obtained from these experiments have many potential applications. Of immediate interest is the incorporation into large scale transport models using Lagrangian dynamics, as well as the study of resuspension phenomena and their modeling, the determination of vertical eddy diffusivities, and resolution of residence-time problems. The data are also of fundamental importance in extending our understanding of natural particle dynamics.

ACIDITY IN RAINFALL

G. T. Tisue and J. Kacoyannakis

The reported increasing acidity of rainfall raises many interesting ecological and chemical questions.[1] In spite of extensive studies in Europe and North America there are, for example, great uncertainties in the relative contributions of strong and weak acids to the acid-base properties of rainwater.[2] Unravelling this and similar problems may require even more rigorous sample collection and analytical procedures than previously employed. Careful analysis of titration curves permits inferences to be made regarding chemical composition, the possible response of rainwater to further inputs of acidic components to the atmosphere, and the behavior to be expected when rainwater interacts with the buffers present in biological materials and natural waters.

Rainwater samples collected during several precipitation events at Argonne National Laboratory during October and November 1975 have been analyzed for pH, acid and base neutralizing properties, and the ions — ammonium, nitrate, chloride, sulfate, and calcium. The results are shown in Table 1.

The acidity of rainwater is due to the presence of dissolved CO_2, strong acids such as H_2SO_4 and other inorganic or organic acids of varying acidity. Since the solubility of CO_2 in water can be calculated from the Henry's Law constant, its contribution to the base neutralizing capacity of rainwater may be predicted. In the absence of other acid-base species the pH of rainwater would be approximately 5.5 for $pCO_2 \cong 10^{-3.5}$ atm. Below pH 5.2, dissolved CO_2 exists primarily as the undissociated acid $H_2CO_3^*$ ($= CO_2(aq) + H_2CO_3$), with a total carbonate concentration $\cong 10^{-5}$ $\underline{M}$. Therefore, when rainwater is titrated with a strong base to pH 8.5, the first neutralization point of carbonic acid, the base neutralizing capacity (BNC) should be approximated by

$$[H^+] + [H_2CO_3^*] = C_A + 10^{-5} \text{ equiv/liter} , \qquad (1)$$

Table 1. Analysis of Rainwater at Argonne National Laboratory, October and November 1975.

Event	Date/Time	Site	pH	Acidity(a,b)	$[NO_3^-]$(b)	$[Cl^-]$(b)	$[NH_4^+]$(b)	$[SO_4^=]$(b)	Ca^{++}(c)	$[H_3O^+]$(b)
1A	9/19/75	1	4.82						1.75	1.51
1B		2	4.86						1.30	1.38
2A	10/14/75	1	4.30	7.26	3.0	9.5	4.1		0.71	5.01
2B	17:00–21:00	2	4.21	7.65	4.0	9.5	5.0		1.30	6.17
3A	10/14–15/75	1	4.37	7.21	6.5	5.5	3.6			4.27
3B	21:45–01:00	2	4.31	7.31	4.5	5.2	4.5			4.90
4A	10/18–19/75	1	4.34	9.50	3.8	25	2.8	5.4	0.80	4.57
4B	20:00–02:00	2	4.47	8.46	5.0	33	2.4	7.5	1.30	3.39
5A	10/24/75	1	4.32	7.14	3.5	12	6.0	4.5		4.79
5B	15:45–16:30	2	4.53	6.17	3.7	12	6.0	4.5		2.95
6A	10/24/75	1	4.52	5.41	3.5	12	5.1	3.9		3.02
6B	16:30–23:45	2	4.46	5.98	4.0	10	4.2	3.0		3.47
7A	11/3/75	1	3.79	18.9		11	9.2	8.9		16.2
7B	20:00–24:00	2	4.17	13.8		6.3	9.2	9.5		6.76
8A	11/6/75	1	4.54	8.22		23	10	10.3		2.88
8B	20:00–22:00	2	4.35	10.9		28	8.4	13.5		4.47
9A	11/10/75	1	4.99	5.01		11	9.4	4.2		1.02
9B	00:00–03:00	2	4.98	5.14		12	9.4	4.4		1.05
10A	11/20/75	1	4.47	6.83		15	5.2	40		1.82
10B	05:00–09:00	2	4.60	5.42		10	5.6	45		2.51

(a) Acidity = BNC from initial pH' to pH = 8.50.
(b) Equivalents liter $^{-1}$ × 10^5.
(c) Parts per million.

Table 2. Measured and Calculated Base Neutralization Capacity of Rainwater Samples.

Event	[BNC] (a)	Theoretical BNC $(10^{-5} + 10^{-pH})$ (a)	BNC, (a) Excess of measured over calculated	$[BNC]/[H_3O^+)$
2A	7.62	6.01	1.25	1.52
2B	7.65	7.17	0.48	1.24
3A	7.21	5.27	1.94	1.69
3B	7.31	5.90	1.41	1.49
4A	9.50	5.57	3.93	2.08
4B	8.46	4.39	4.07	2.50
5A	7.14 (5.77) (b)	5.79	1.35 (-0.02) (b)	1.49
5B	6.17	3.95	2.22 (0.91) (b)	2.09
6A	5.41	4.02	1.39	1.79
6B	5.98 (5.00) (b)	4.47	1.51 (0.53) (b)	1.72
7A	18.9	17.2	1.70	1.17
7B	13.8	7.76	6.40	2.04
8A	8.22	3.88	4.34	2.85
8B	10.9	5.47	5.43	2.44
9A	5.01	2.02	2.99	4.91
9B	5.14	2.05	3.09	4.90
10A	6.83	2.82	4.01	3.75
10B	5.42	3.51	1.91	2.16

(a) Equivalents/liter × 10^5 .

(b) The values in parentheses refer to samples from which volatile acids had been removed by thorough purging with N_2.

where C_A is the concentration of the strong acid or

$$BNC = (10^{-pH} + 10^{-5}) \text{ equiv/liter} , \qquad (2)$$

and the pH is that of the freshly collected rainwater.

Ten rainwater samples have been examined: the initial pH's varied between 3.79 and 4.99 and the base neutralizing capacities between 5.01 and 18.9×10^{-5} equiv/liter. In almost every case the measured base neutralizing capacity is greater than that calculated from Eq. 2 above, the excess varying between 0.48 and 6×10^{-5} equiv/liter (Table 2). Since the dissolution of

CO_2 in rainwater is strongly dependent upon temperature, some variation in $[H_2CO_3^*]$, i.e., between < 1 and $\sim 2 \times 10^{-5}$ equiv/liter, is to be expected. Even after allowing for this effect, it is clear that there is still an overall excess of base neutralizing capacity in many of the samples.

The titration curve for a representative sample of rainwater (event 4A) is shown in Figure 1. The best fit to the data points was calculated by iterative solution of the quartic equation for $[H_3O^+]$ obtained by substitution of the required equilibrium relationships and mass balances for each component into the ion balance equation:

$$[M^+] + [H_3O^+] + [NH_4^+] = [X^-] + [OH^-] + [HCO_3^-] \ , \qquad (3)$$

where $[M^+]$ is the concentration of strong base added and X^- represents strong acids, such as H_2SO_4, HCl, and HNO_3. In this calculation two weak acids are assumed to be present, $H_2CO_3^*$ and NH_4^+. The value of $[X^-]$ is obtained from the initial pH and $[NH_4^+]$ from an independent analysis (Table 1). The best fit in this case (line) requires that $C_{H_2CO_3^*} = 4.33 \times 10^{-5}$ equiv/liter. While the fit is not quite perfect, it is clear that the excess base neutralizing capacity in this sample is due to a weak acid whose pK_a is not significantly different from that of H_2CO_3, i.e., 6.5. The results of titrating these rainwater samples with dilute strong acids further support this conclusion. If the samples contained significant concentrations of weak acids with pK_a's ≤ 5, there should be an effective buffering against pH lowering when strong acid is added.

The data plotted in Figure 2 show the linear relationship between the negative logarithmic of the added mineral acidity (pC_{HX}) and the measured pH's, indicating that there is no buffer capacity in the pH range 3 to 5 due to the presence of weak acids.

In addition to carbonic acids there are many other acids with pK_a's in the range 6 to 7 which could be present in rainwater and contribute to the excess base neutralizing capacity. These include arsenic acid, $pK_2 = 6.98$; phosphoric acid = 7.21; sulfurous acid, $pK_2 = 7.21$ (all pK_1's are $\cong 2$, and therefore titrate as a strong acid). Organic acids would include carboxylic and

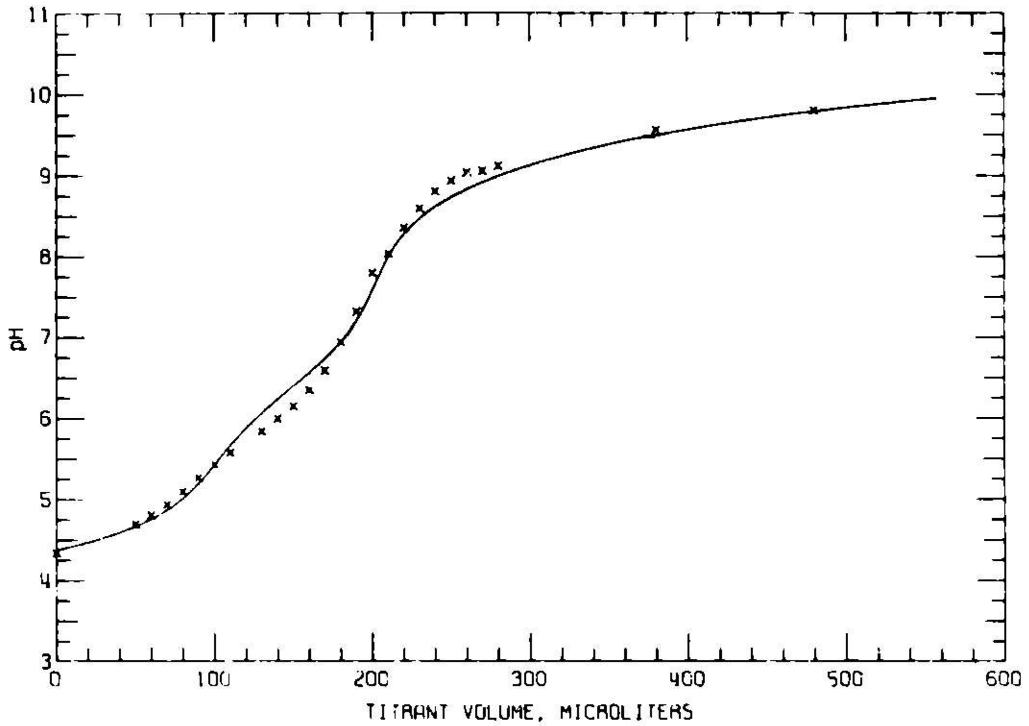

FIG. 1.--Titration curve for rainfall from event 4A. The titrant was 0.02 M NaOH.

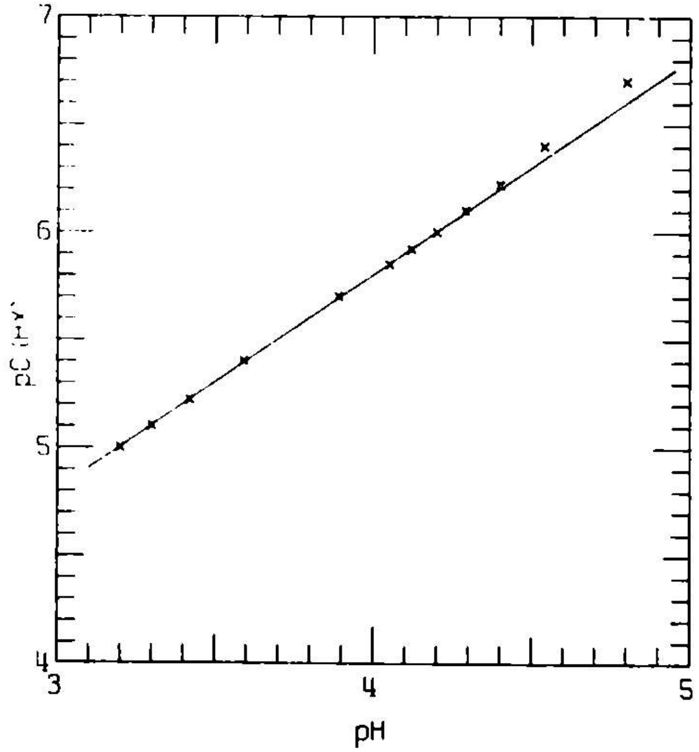

FIG. 2.--pH-log concentration diagram for titration of rainfall from event 4A with strong acid. The titrant was 0.02 M H_2SO_4 $pC_{HX} = -\log C_{HX}$ (in equiv/liter).

dicarboxylic acids as well as phenols.[3] From this list phosphoric and sulfurous acids are most likely to be present because of the relatively high concentrations of SO_2 in local air and of H_3PO_4 in other samples of precipitation collected in the same vicinity as the samples described in this paper.

Even though the base neutralizing capacity of these rainwater samples is greater than would be predicted from simple theory for a mixture of strong acids and carbonic acid, the ratio of the total acidity, (BNC), to the free acidity, $[H_3O^+]$, i.e., $BNC/[H_3O^+]$ (Table 1) is well below the values reported for that quantity by Frohliger and Kane.[2]

References

1. First International Symposium on Acid Precipitation and the Forest Ecosystem, May 1975, Columbus, Ohio, U.S. Dept. of Agriculture and Ohio State University Atmospheric Sciences Program.
2. J. O. Frohliger and R. L. Kane, Science 189, 455–457 (1975).
3. D. Schuetzle, D. Cronn, A. L. Crittenden, and R. J. Charlson, Environ. Sci. Technol. 9, 838–845 (1975).

SECONDARY-SOURCE ENERGY-DISPERSIVE X-RAY SPECTROMETER

R. P. Larsen and G. T. Tisue

A secondary-source energy-dispersive x-ray spectrometer has been built and tested. In this instrument the primary source of x rays is a tungsten-target tube powered by a high-voltage (75 kV), a high-power (3.7 kW) generator from a wavelength spectrometer (G.E. XRD-6). The primary polychromatic x rays irradiate an elemental foil, the secondary source. Its characteristic essentially monochromatic x rays are used to irradiate the sample. Fluorescent x rays from the sample are detected and resolved by a lithium-drifted silicon detector, multichannel-analyzer system. The design of the instrument provides a convenient means for changing the secondary, and hence, the energy of the excitation radiation.

In most commercially available x-ray spectrometers excitation is accomplished by irradiating the sample directly with a low-power tube. As a result, the whole spectrum is cluttered with white radiation from the tube scattered by the sample into the detector. With monochromatic excitation the scattered radiation is outside the energy region of interest, the signal-to-noise ratio is hence quite superior, and the detection limit for most elements is markedly lower.

Our instrument is also superior to the commercial secondary-source instruments in that the determination of a larger number of elements can be based on the measurement of the K x rays. With an x-ray tube operating at 75 kV, a secondary source having an atomic number as high as 67 (holmium) can be used, permitting determination with K x rays of such elements as iodine, cesium, barium, and the light rare earths. For instruments operating at ≤ 50 kV, determination of these elements must be based on the L x rays. Because these L x rays are readily absorbed by the sample matrix, the composition of the matrix must be stringently controlled. Also, since these L x rays are in the same energy range as the K x rays of such common elements as potassium, calcium, and titanium, determinations based on the L x rays are more subject to interference.

A cross section of the spectrometer along the optical path is shown in Figure 1. The housing, which is fabricated from steel pipe, consists of two chambers, one for the tube which has a 5/8" wall, and one for the sample changer, which has a 3/8" wall. The design reflects an attempt to minimize both the amount of scattered radiation within the instrument and the length of the optical path. The instrument can be operated in air or under vacuum.

The secondary sources are periscope shaped and have 2- × 2-in openings at both the upper and lower ends (A and B in Figure 1). The copper, molybdenum, and silver sources are fabricated from 10-mil metal sheet stock. The tellurium, samarium, and holmium sources are made by covering over the sloped face (C) of a copper source with a 2- × 3-in piece of these metals. As these sources are used only for the determination of elements having atomic numbers greater than 40, the copper x rays that impinge on the sample and are scattered into the detector can be absorbed by interposing a thin sheet of aluminum between the sample and the detector. A port in the upper chamber permits manual changing of the secondary sources.

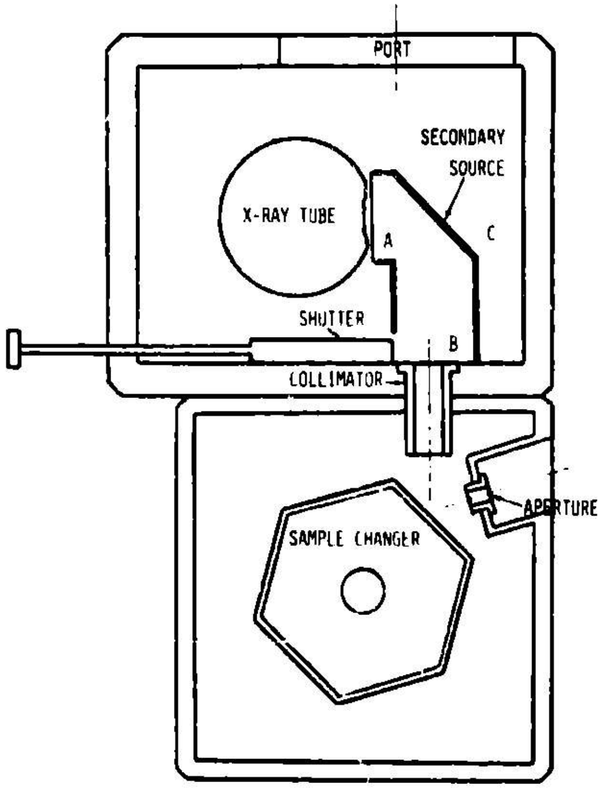

FIG. 1.--Cross sectional view (along the optical path) of the x-ray spectrometer.

The cylindrical collimators and apertures are made from high purity copper or cadmium. The copper set is used in determinations of elements with atomic numbers in the range 40 to 65; the cadmium set is used for elements with atomic numbers less than 40 or greater than 65.

The hexagonal sample holder is made from 1/8-in thick Lucite sheet and is mounted on the end of a steel rod which penetrates the back face of the sample chamber. This holder permits the analysis of up to six samples without opening the spectrometer. Samples are mounted through a port in the front face of the sample chamber. This port is interlocked electrically with the shutter; it cannot be opened when the shutter is in the open position without interrupting power to the x-ray tube.

A novel method has been developed to package and mount both powder and liquid samples for presentation to the spectrometer. The packages are prepared by bonding 1.5-mil Mylar laminated film (0.5-mil Mylar bonded to 1.0-mil polyethylene) to the outer face of a 2- × 2-in cardboard slide mount. The sample is then placed on the film in the center of one frame, the mount folded, and a film-to-film seal made around the sample. Liquid samples of up to 250 µl are contained in a dimple impressed in the center of one frame and sealed as above.

The detection limit for elements having atomic numbers from about 20 (calcium) to 48 is in the range of 10 to 40 ng. These values are the amounts of the individual elements which, when mounted between two sheets of 1.5-mil Mylar and assayed for 1000 sec, would produce a signal that is twice the standard deviation of the background. For the elements which have atomic numbers in the range 48 to 65, the detection limit is about 200 ng if the analysis is based on the measurement of their K x rays. This decrease in sensitivity is due to the fact that the intensity of x rays that can be obtained from a secondary source with a relatively high atomic number, e.g., holmium (67), is much lower than that from secondary sources such as molybdenum (42) and silver (47). However, a detection sensitivity for these elements of about 40 ng can be obtained if the analysis is based on measurement of the L x rays. The disadvantages of this are: (1) there is high mass absorption due to the relatively low energies of these x rays and (2) resolution of the several peaks from each element is incomplete. The latter disadvantage is particulary pronounced for those elements at the low end of this range, e.g., cadmium.

At present the reproducibility of measurements made with this instrument is about 5%. This variation is due primarily to a problem of positioning the mount in the slots on the sample changer. The errors due to such other factors as the reproducibility with which a particular position of the sample changer can be made and the geometric equivalency of the six positions on the sample changer were shown to be negligible. Thus it appears that the reproducibility can be improved by designing a system for holding the sample mounts which eliminates their movement on the sample changer.

The reported reproducibility was achieved by normalizing integrated photopeak intensities to the integrated intensity of the backscattered exciting radiation. Even greater precision will, of course, result from incorporating an internal standard in the sample.

BIOLOGICAL UTILIZATION AND REGENERATION OF SILICON IN LAKE MICHIGAN

H. L. Conway and E. M. Yaguchi

The present study is concerned with the dynamics of silicon and the importance of biological utilization and recycling of this element in Lake Michigan.

Water samples were collected in January 1975 during a cruise on the USCGC Westwind. Four stations were selected along a transect from Milwaukee, Wisconsin, to the Straits of Mackinac. Monthly cruises were conducted aboard the R/V Mysis from April through November 1975 among four stations along a SW transect from Grand Haven, Michigan, to the approximate center of the southern basin of Lake Michigan. Water depths at these four stations were 26 m, 67 m, 87 m, and 155 m, respectively. Primary emphasis is devoted to data from station 5, 13 km offshore.

Values of reactive and amorphous silicon concentrations, integrated over three depth intervals at station 5, are presented in Figure 1. The reactive silicon concentration in the water column declined during the period from April to June as the result of biological utilization, as shown by the peak in amorphous silicon during May. The dissolved silicon concentration in the surface water remained at a low value during the summer (< 1.8 μmol Si until September, when mixing with the deeper water elevated the reactive silicon concentration. From June through October the reactive silicon concentration at depth increased significantly. The May peak in particulate silicon was followed by a decrease that was attributed to zooplankton grazing. The zooplankton biomass in the surface water remained high during the summer and fall resulting in low values of amorphous silicon during these seasons. Amorphous silicon levels in the surface water increased slightly after August as a result of the fall bloom of diatoms.

Values of reactive plus amorphous silicon [Si (r + a)] for station 5, integrated over the entire water column, showed a loss of approximately half the biologically active silicon during the spring and early summer and its subsequent return, in a soluble form, to the deep water during the fall (Figure 2).

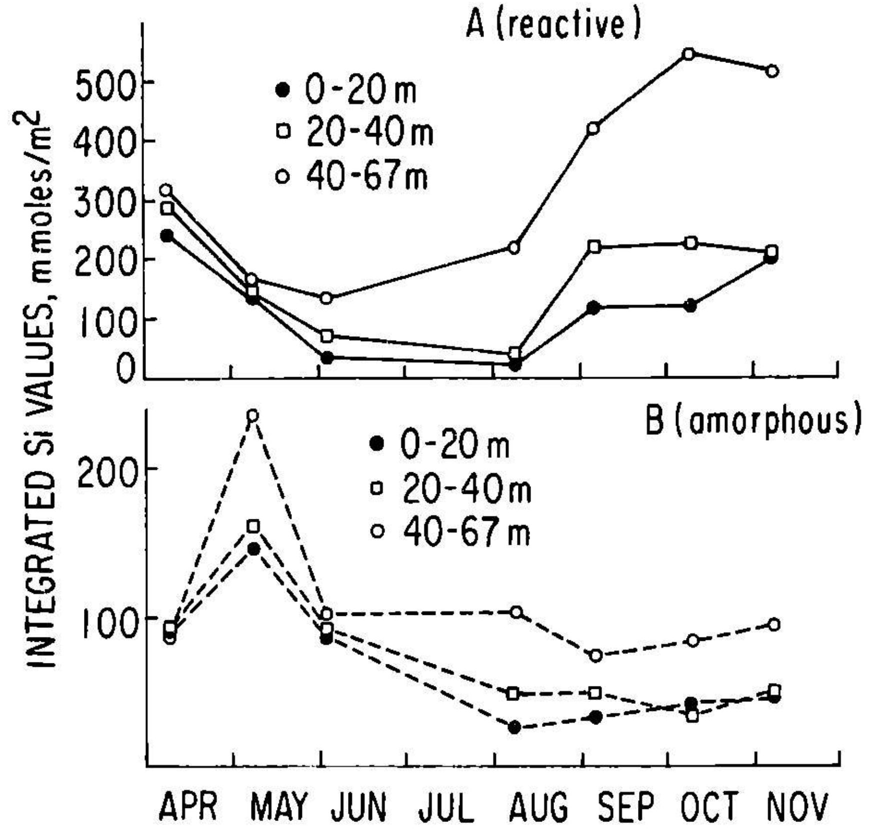

FIG. 1.--Integrated silicon values at station 5. (A) reactive; (B) amorphous (ANL neg. 149-76-137)

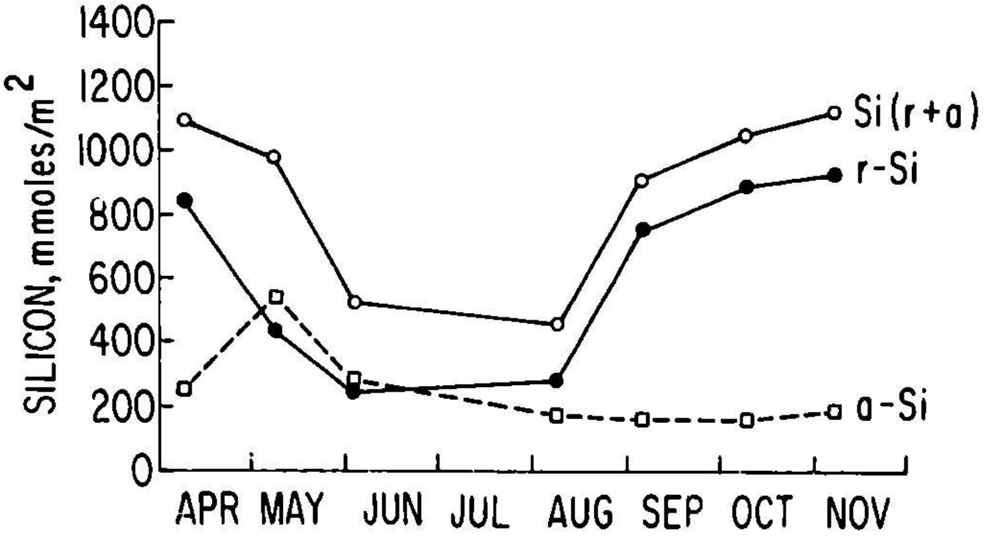

FIG. 2.--Integrated values (0 to 67 m) for reactive (r-Si) and amorphous silicon (a-Si), and their total [Si(r+a)], station 5 (ANL neg. 149-76-135 Rev. 1)

Integrated values of Si (r + a) divided by the depth of the water column, lead to a mean concentration of biologically active silicon per unit volume for the entire water column. Table 1 shows these values for April and November at station 5, April at station 6, and the Westwind stations taken in January. A mean value of approximately 19 μmol for Si (r + a) was observed for the four Westwind stations. This value appears to be a good approximation for the entire lake in offshore waters (> 50 m) during the winter months. The value of Si (r + a) was slightly lower for stations 5 and 6 than observed for the Westwind stations.

Table 1. Mean concentrations of reactive silicon (r-Si), amorphous silicon (a-Si), and the sum of reactive plus amorphous silicon [Si (r + a)] for the entire water column.

Station	Date 1975	Mean silicon concentration for the entire water column (μmolar)		
		r-Si	a-Si	Si (r + a)
5	April	13.4	4.0	17.4
5	November	14.3	2.9	17.2
6	April	10.1	5.9	16.0
W-1	January	16.2	2.3	18.5
W-2	January	17.4	1.8	19.3
W-3	January	17.4	1.8	19.2
W-4	January	14.9	3.9	18.7

During the period June to August, 80% of the total biologically active silicon had been utilized by the diatom community, with only 20% remaining as reactive silicon. If one assumes the data collected along this SW transect from Grand Haven to be representative of the entire lake, then at least 80% of the total biologically active silicon is recycled each year in Lake Michigan, and most likely this value approaches 100%.

DISSOLUTION OF AMORPHOUS SILICON ON LAKE MICHIGAN

J. I. Parker, H. L. Conway, and E. M. Yaguchi

The characteristics of diatom frustule dissolution and the recycling of silicon in lake ecosystems are not well known. We collected samples monthly from sediment traps suspended in Lake Michigan, counted diatom frustules, and measured amorphous silicon concentrations. These data were compared with those for the water column above the traps and for sediment core samples collected at the same station. The concentrations of frustules and amorphous silicon were normalized to dry weight of sediment to facilitate equitable comparisons among the water column, sediment traps, and core samples (Figure 1).

Frustules per gram dry sediment in the water column ranged from 2.51×10^8 to 3.85×10^8, averaging 3.08×10^8. However, the average concentration in the 37-m sediment traps was 1.16×10^8 frustules/g dry wt, three times lower than the water column average. A further reduction in frustule concentration was observed as the settling frustules reached the 60-m traps, where the average was 5.03×10^7 frustules/g dry wt, six times lower than the water column average. Frustule concentration per unit of bottom sediment was measured in the 0- to 0.5-cm layer of the sediment core. The value was 6.31×10^6 frustules/g dry wt, which was 50 times lower than the water column average.

The vertical distribution of particulate amorphous silicon was similar to that of frustules, and each showed a progressive reduction with water depth (Figure 1). The loss of amorphous silicon during settling from the water column to the surficial sediment was $\simeq$ 80%. Further losses in amorphous silicon and frustules were noted in the bottom sediment (Figure 1).

These observations suggested that most of the siliceous diatom frustules produced in the euphotic zone were decomposed before they could be incorporated in the bottom sediment.

To determine the significance of this silicon recycling process in Lake Michigan, the annual input of soluble reactive silicon from the watershed was compared to the quantity of silicon required for the annual production of diatom

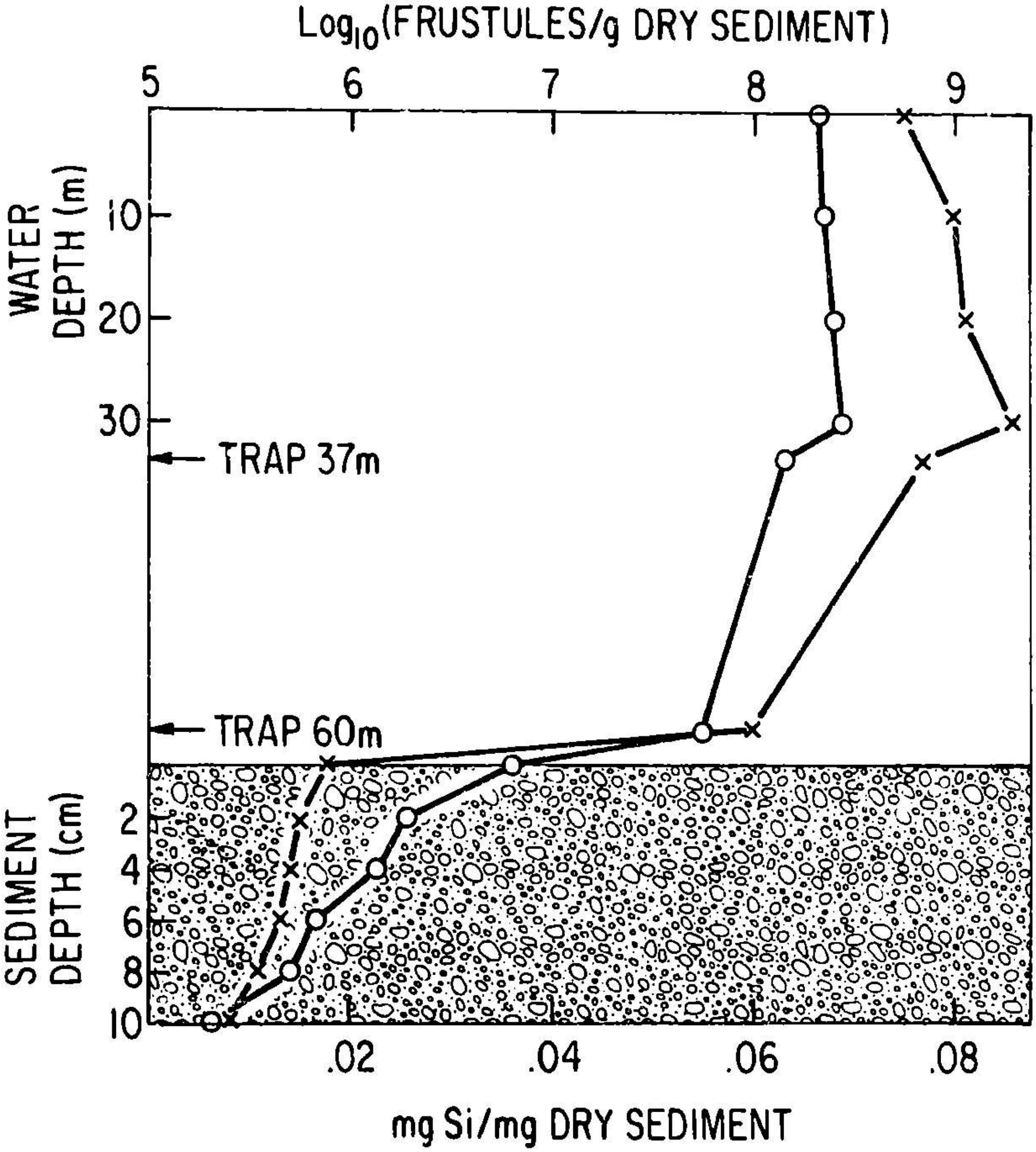

FIG. 1.--The seasonal-average concentration of diatom frustules (o—o) and amorphous silicon (x—x) per gram of dry sediment in the water column, sediment traps, and sediment core samples at station 5. (ANL neg. 149-76-150)

frustules. The estimated annual silicon requirement by diatoms in the offshore water was 53 g $Si/m^2 \cdot yr$. By comparison, the annual input of dissolved reactive silicon was 1.66 g $Si/m^2 \cdot yr$. This represented only about 3.0% of the annual silicon requirement by diatoms and suggested that ≃97% of the silicon is recycled per annum.

SEASONAL DEVELOPMENT OF PHYTOPLANKTON POPULATIONS IN OFFSHORE LAKE MICHIGAN IN 1975

J. I. Parker, H. L. Conway, and E. M. Yaguchi

Relationships between phytoplankton bloom sequences and environmental factors that may account for seasonal variations have not been thoroughly evaluated in Lake Michigan. We investigated the seasonal periodicity of phytoplankton in the offshore water from April to December, 1975.

The seasonal distributions of phytoplankton biomass, chlorophyll a, and primary productivity per unit of lake surface area were measured at station 5. These measurements demonstrated a bimodal seasonal distribution, with maxima occurring in June and October. Previous investigators have shown that the seasonal periodicity was unimodal, with a summer maximum. Our observations demonstrated year to year variations in this abundance pattern.

An evaluation of the contribution to total phytoplankton biomass by algal species clearly showed that diatoms contributed ≃ 95% of the total biomass during the period of investigation (Figure 1). Since diatoms are the dominant floral component of the phytoplankton in the offshore water and they have an absolute requirement for silicon, an analysis was made of the relationship between bloom sequencing and the dissolved silicon concentration.

Seasonal distributions of soluble reactive silicon and diatom biomass showed a strong relationship (Figure 2). Progressive reduction in silicon corresponded to a rapid increase in diatom biomass during the spring bloom. By the middle of May the growth rate of diatoms had apparently decreased and the corresponding silicon concentration was 6.76 μmol Si. Through the summer months diatoms and silicon concentrations were extremely low. However, by early September the supply of silicon was replenished to a concentration of 6.56 μmol Si and diatom biomass began to accumulate shortly thereafter. The concentrations of silicon that corresponded to a decline in diatom biomass in the spring and to an increase in diatom biomass in the fall were very similar. These silicon values may approximate the limiting concentration.

S. Kilham[1] showed that the limiting concentration (K_{lim}) for two fresh-

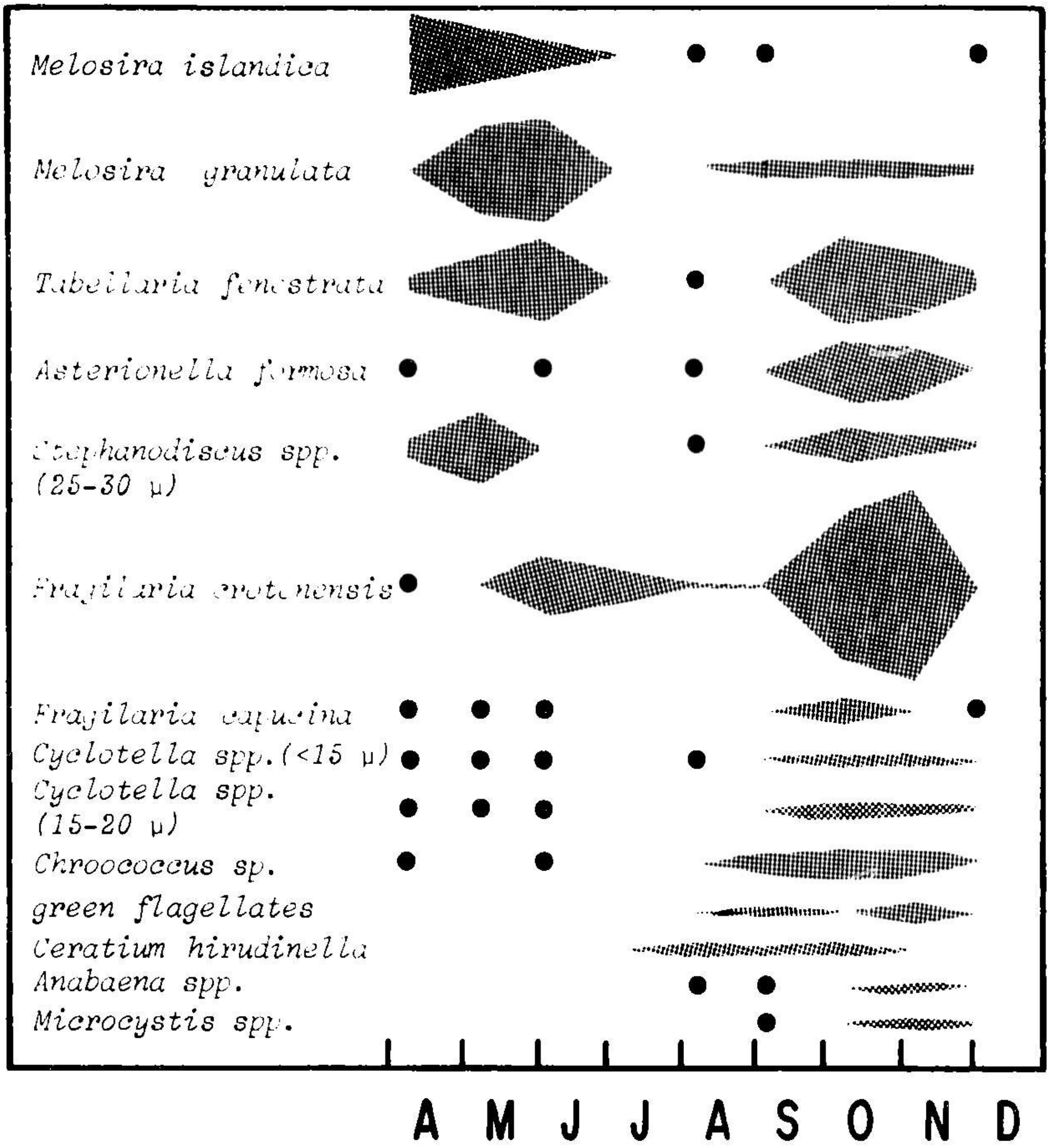

FIG. 1.--Seasonal distribution of the phytoplankton species which collectively contributed > 95% of the total biomass in the euphotic zone on each sampling date at station 5 (●, species observed).

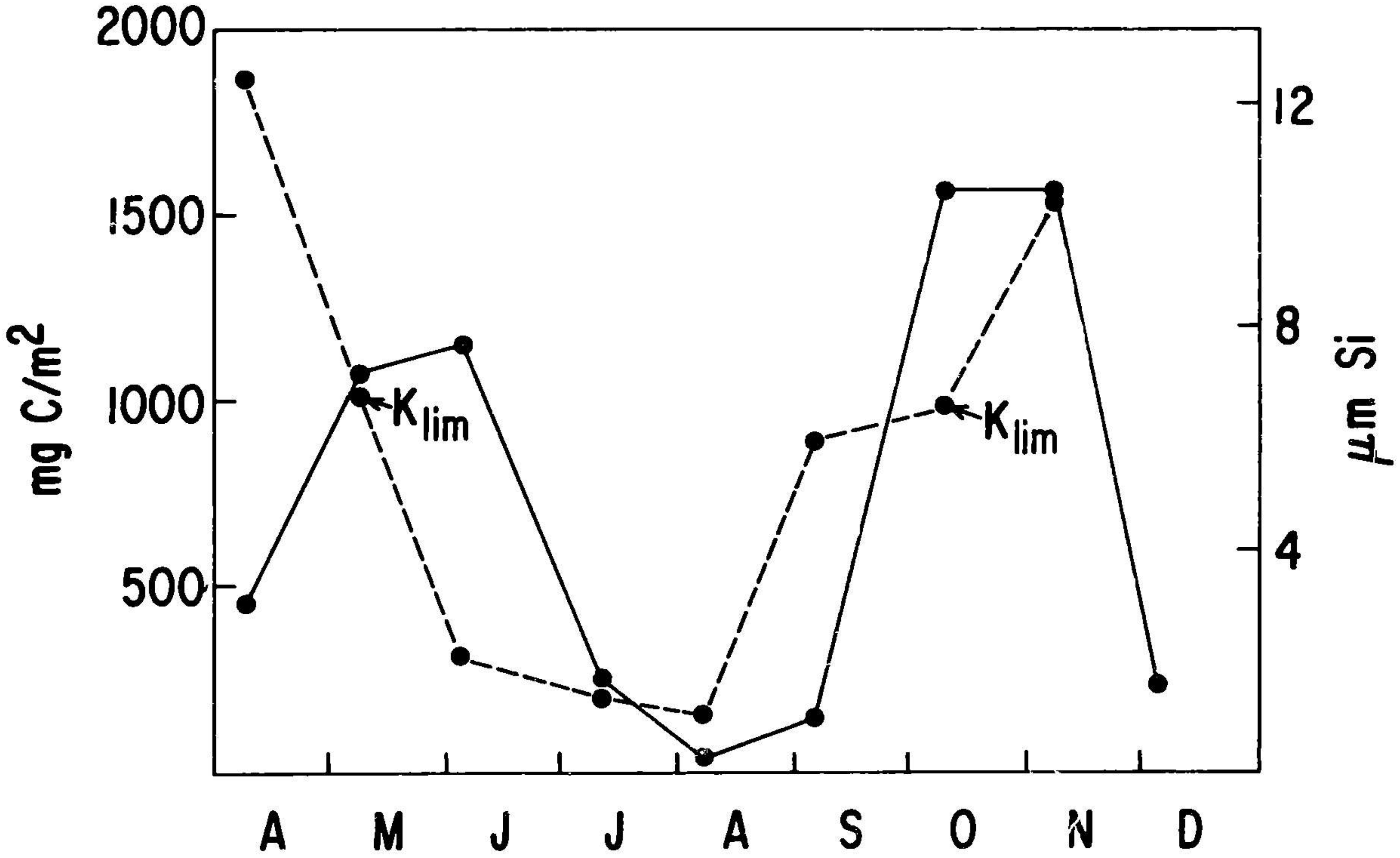

FIG. 2.--Seasonal distribution of diatom biomass (o—o) and the average concentration of dissolved reactive silicon in the euphotic zone at station 5. Limiting silicon concentrations (K_{lim}) were selected where the accumulation rate (slope) of diatom biomass is maximal.

water diatoms was 6.5 and 13.8 μmol Si, and Lund[2] suggested that the limiting concentration in Lake Windermere (U.K.) was 8.3 μmol Si. The similarity between these K_{lim} values and those estimated from our study suggests that silicon limitation in the offshore water of Lake Michigan occurs when the concentration of soluble reactive silicon is reduced below ≃ 6.5 μmol Si.

These observations suggest that the development of a fall diatom bloom is regulated by the restoration of dissolved silicon to the level of the limiting concentration. This process may account for the bimodal periodicity pattern observed in 1975. However, if the spring diatom bloom is delayed until the summer months by unusually cloudy and/or cool spring weather, the critical events of silicon restoration and redistribution into the euphotic zone may occur later in the fall months. Reduced incident radiation may then effectively preclude the development of a recognizable fall bloom, although sufficient silicon is available. This alternative may account for the unimodal diatom abundance patterns not infrequently observed in the offshore water of Lake Michigan.

References

1. S. Kilham, Kinetics of silicon-limited growth in the freshwater diatom *Asterionella formosa*, J. Phycol. 11, 306–399 (1975).
2. J. W. G. Lund, Primary production and periodicity of phytoplankton, Verh. Int. Ver. Limnol. 13, 37–56 (1964).

VERTICAL DISTRIBUTION, COMPOSITION, AND ABUNDANCE OF CRUSTACEAN ZOOPLANKTON IN THE OFFSHORE WATERS OF LAKE MICHIGAN

D. L. Mellinger

During 1975, zooplankton samples were collected on eight cruises (April to November) in the southern basin of Lake Michigan. Four stations in the northern basin were also sampled in January during a cruise aboard the USCGC Westwind. At each station, a series of at least three collections was taken at sequential depth intervals using a 50-cm closing net of 80 μm mesh. As a result of this sampling procedure, the vertical distribution of zooplankton can be described in terms of upper (0 to 20 m), middle (20 to 40 m), and lower (> 40 m) layers. The data presented in this report are from stations with depths of 67 m to 155 m, which represent approximately 60% of the surface area of Lake Michigan.

One of the goals of this study was to quantitatively estimate the standing crop of herbivorous crustacean zooplankton in units that would represent their functional roles as consumers of phytoplankton. Therefore, subsamples were divided into 24 categories, and each category was assigned an average dry weight. An estimate of the standing crop biomass was obtained by multiplying the number of organisms in a category by the average dry weight.

The distribution of herbivorous zooplankton biomass/m^3 is shown in Figure 1. Although the food habits of some species of Lake Michigan zooplankton are not yet clearly defined, the herbivorous crustacean zooplankton category in this study includes all species except cyclopoid copepods, Leptodora kindtii, and Polyphemus pediculus. There is a similar amount of biomass/m^3 in each of the three layers when the water is homothermous (April-May). The winter (January) vertical distribution and abundance in the northern basin were quite similar to those found in April in the southern basin. In contrast to the relative uniformity between winter and spring distributions, the biomass/m^3 of the upper layer increased dramatically with stratification in late June.

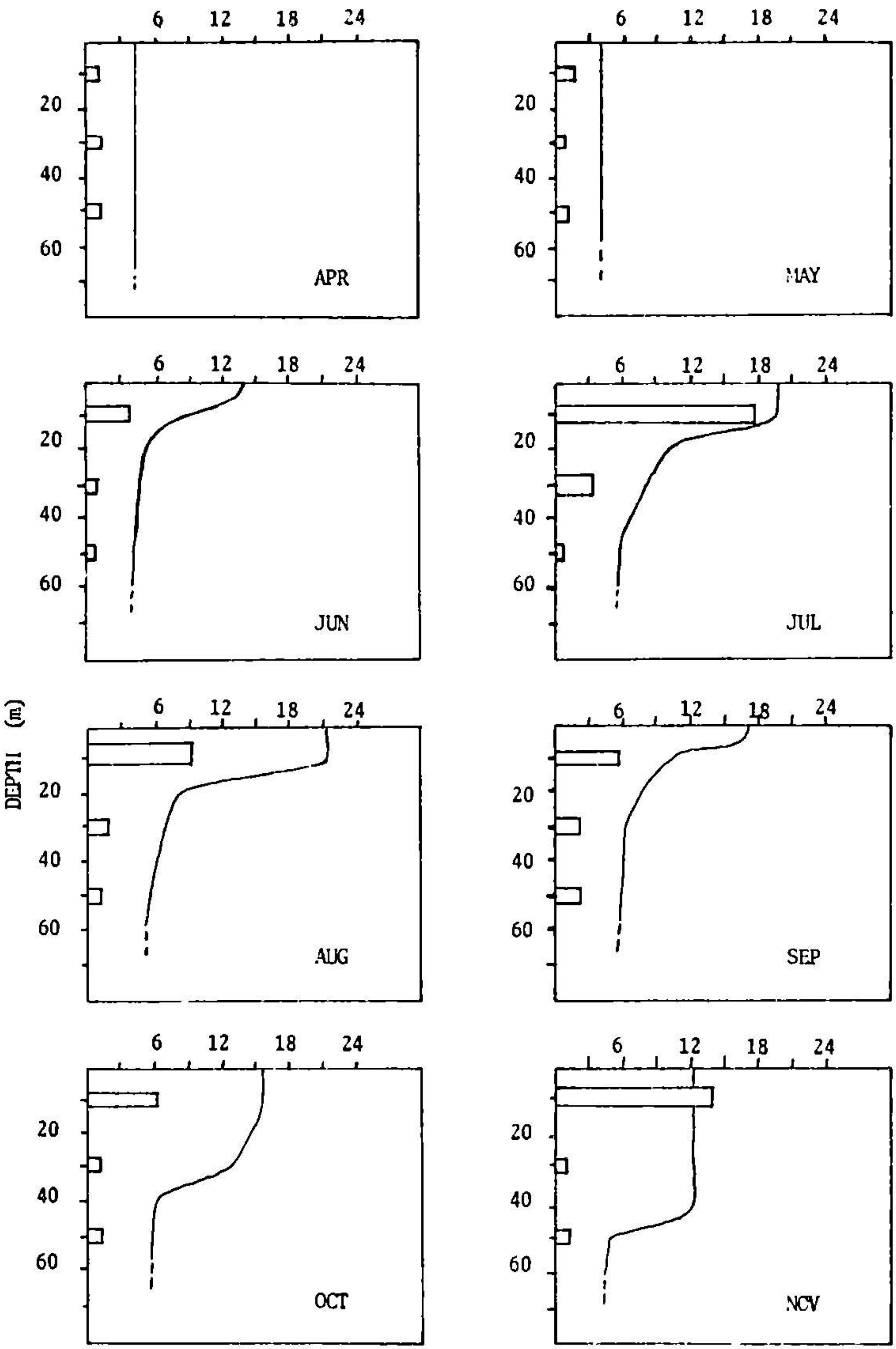

FIG. 1.--Mean values of estimated herbivorous zooplankton biomass (mg dry wt/m^3 × 10) and temperature (°C) profiles in the offshore region of the southern basin of Lake Michigan in 1975.

During the winter and spring, the herbivorous zooplankton component is composed almost entirely of calanoid copepods. By July, cladocerans (mainly Bosmina longirostris) represented 23% of the total herbivorous biomass in the upper layer. The mean percentage of cladoceran biomass (June-November) in the upper layer was 18%. It is clear, therefore, that calanoid copepods dominate this offshore region of Lake Michigan in terms of estimated standing crop biomass. The major portion of the annual production of the herbivorous crustacean biomass appears to occur in the upper 20 m of the water column.

THE UTILIZATION OF DIATOMS AS A FOOD SOURCE BY CALANOID COPEPODS AND THE ABUNDANCE AND DISTRIBUTION OF ZOODETRITUS IN SOUTHEASTERN LAKE MICHIGAN

J. G. Ferrante

The transfer of material from phytoplankton to zooplankton is important in understanding the movement and cycling of substances in aquatic systems. Since Lake Michigan phytoplankton are predominantly diatoms, their utilization for nutrition by calanoid copepods is an important aspect that is currently being investigated.

The contents of fecal pellets were examined with the scanning electron microscope and the diatoms enumerated. Twenty-one species and subspecies of diatoms in eight genera were observed in calanoid pellets. Both centric and pennate forms are utilized by the copepods. The majority of the frustules were fractured to some degree, and many were reduced to small pieces.

Large species, up to approximately 80 μm in length, were utilized by calanoid copepods, often being ingested lengthwise with little apparent fracturing. It seems as though the copepods are able to break off individual cells from the long chains before ingesting them, since Fragilaria crotonensis and Tabellaria fenestrata were commonly observed as single cells in pellets.

Cyclotella ocellata (≈ 5μm in diameter) was also observed in pellets, usually unfractured. These small diatoms were often present in pellets which also contained pieces of Synedra ulna, which is > 80 μm in length. This extremely wide range of particle sizes suggests that calanoid copepods are not size limited in their use of diatoms throughout the year.

Samples of zoodetritus (calanoid copepod fecal pellets, exuviae and carcasses) were collected at selected stations along a transect extending from Grand Haven, Michigan to the center of the southern basin of Lake Michigan.

In general, calanoid copepod fecal pellets were most abundant near the surface (0 – 20 m) throughout the sampling period from April to November, 1975 (Figure 1). The range of concentration of calanoid pellets during this period was from ~ 0.1 to 6.6/liter. During September and October pellets

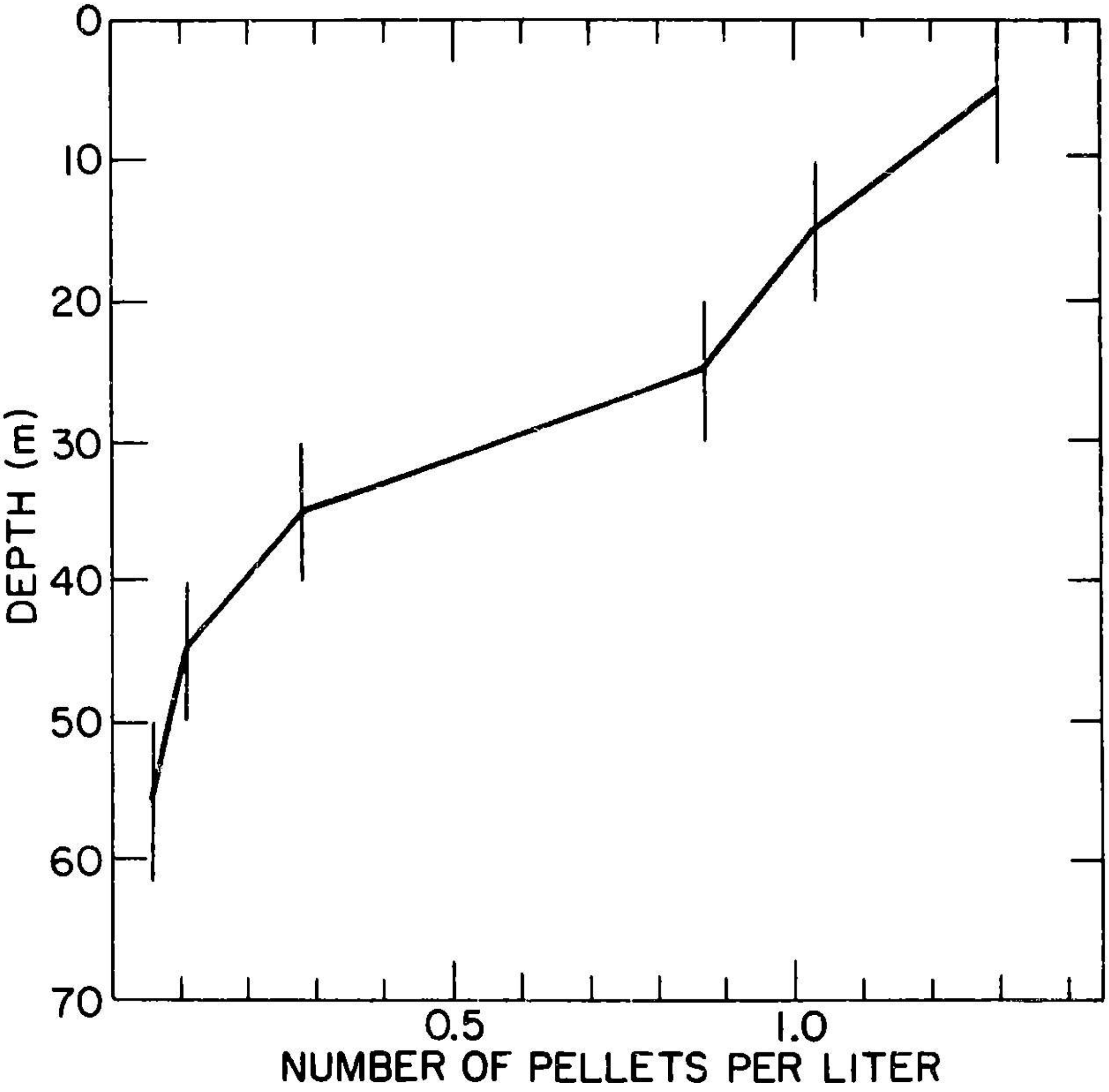

FIG. 1.--Vertical distribution of calanoid copepod fecal pellets in the study area. Vertical bars show the range in depth of the net tow.

were also abundant at a depth of ~ 40 to 50 m. In August the highest number of pellets/liter (0.4) was found between 30 and 40 m. The usual pattern of vertical distribution is exemplified by a peak of abundance followed by a rapid decrease in numbers with depth reaching a minimum at approximately 40 to 50 m. The drop in pellet density with depth is attributed to bacterial decomposition of the peritrophic membrane and breakup of the pellets.

In general the vertical distribution of copepod and cladoceran exuviae and carcasses followed that of the fecal pellets; the range of abundance was between 0.3 and 15.5/liter. The decrease in their abundance with depth, like that of the fecal pellets, was probably due to bacterial and/or fungal decomposition as they settled through the water column.

Mysis relecta fecal pellets and exuviae were normally found in deeper water (> 30 m) although on occasion specimens were found near the surface.

The horizontal distribution of detrital particles was uniform from nearshore to offshore stations. However, with increasing distance from the shore they became more abundant at greater depths. This slight shift downward is probably due to the concentration of zooplankton at greater depths.

The distribution and abundance of zoodetritus in time and space is affected by the pulses of zooplankton, their vertical migration, depth of active feeding, time of day, and other factors; therefore, limitations are recognized in this investigation which employed monthly sampling at specific station locations. However, the distributions and densities indicated are supported by synoptic data on phytoplankton and zooplankton components and represent realistic patterns.

CONTINUOUS CULTURE APPARATUS AND METHODOLOGY

H. L. Conway

At present, we are investigating the sorption of potentially toxic trace elements by phytoplankton under controlled laboratory conditions. Continuous culture techniques were used to study the mechanism of the sorption of the trace elements by unialgal diatom populations and the factors influencing this sorption. Continuous culture methodology has been used extensively to study bacterial kinetics. It is an excellent technique for obtaining a known physiological state of phytoplankton populations.

In the chemostat, cells are grown at a constant rate and in a constant chemical environment. The inflow medium is pumped into the chemostat at a steady flow rate (f) and is dispersed throughout the vessel. A portion of the culture growing in the vessel is continuously washed out at a constant rate. The number of complete volume changes/hr, called the dilution rate (D), is defined as $D = f/v_0$, where f is the flow rate (ml/hr) and v_0 is the volume of the chemostat (ml).

The net growth in the vessel resulting from the difference between the culture growth and the amount of culture forced out by the inflowing media is

$$\frac{dx}{dt} = (\mu - D)\,x ,$$

where x is the concentration of cells (cell/liter) at time t, and μ is the specific growth rate (hr^{-1}), also defined as $\frac{1}{x}\frac{dx}{dt}$. When $dx/dt = 0$, then from the equation above, $\mu = D$; this is the steady-state condition.

Continuous culture techniques allow a long-term evaluation of the effect of trace elements on the growth and nutrient utilization rates of phytoplankton species and sorption of these elements through many generations of the phytoplankton population.

An automated method for the synthesis of continuous culture medium has been developed for use in these experiments. Synthetic medium similar to natural Lake Michigan water was used because it (1) reduced the possibilities of contamination by spores that could not be eliminated by filtration

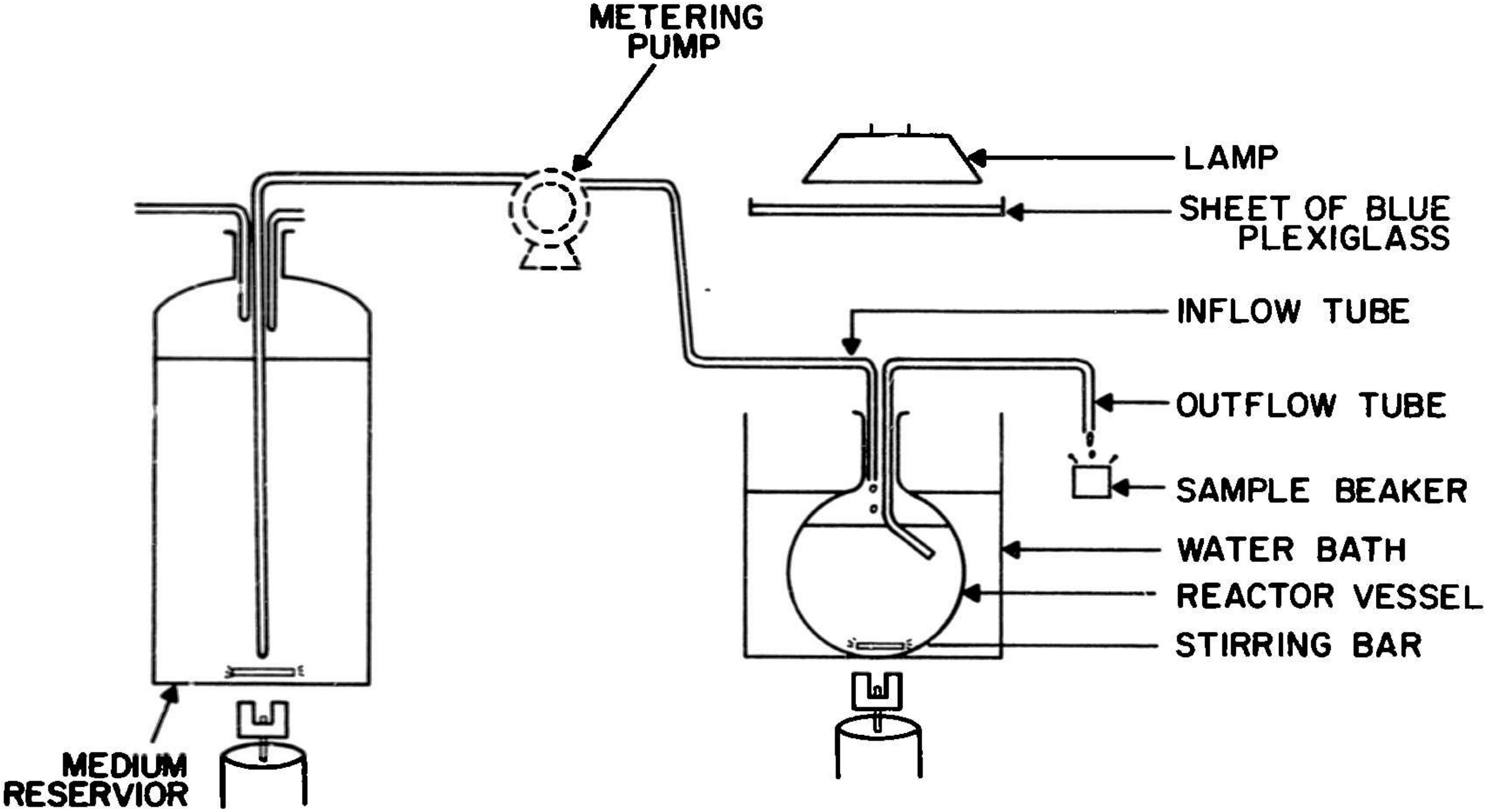

FIG. 1.--Schematic diagram of the chemostat system.

or autoclaving natural Lake Michigan water, (2) eliminated the normal fluctuation of micronutrients found in natural water, (3) reduced the level of potentially toxic compounds in the medium, and (4) reduced the storage problems of Lake Michigan water in large reservoirs since substantial quantities of medium were used (~ 20 liters/day).

Synthetic lake water is made by mixing the correct proportions of (i) deionized water, (ii) concentrated solution of trace metals and micronutrients, (iii) solution of a mixture of $MgSO_4 \cdot 7H_2O$, $MgCl_2 \cdot 6H_2O$, $NaHCO_3$, KCl, and H_3BO_3, (iv) solution of $CaCl_2 \cdot 2H_2O$, and (v) air with a peristaltic pump when the level in a storage carboy drops below a given level.

The chemostat system is shown in a schematic diagram in Figure 1. The synthetic Lake Michigan water was pumped at a dilution rate of 0.02 hr^{-1} by separate metering pumps into each chemostat or reactor vessel.

The reactor vessels were 6-liter boiling flasks (Pyrex) sealed with rubber stoppers so that a constant volume could be maintained inside the flasks. Switching valves in the inflow and outflow lines on top of each chemostat allowed the flow to be diverted for sampling. The cultures were stirred with Teflon-coated magnetic stirring bars with pieces of polyethylene on the ends, to increase stirring efficiency. The reactor vessels were placed in a water bath regulated to 15.0 ± 0.1 C.

The lighting system consisted of high intensity fluorescent lights (~0.08 g/cal/cm^2/min). A sheet 0.4-cm thick of blue Plexiglas was placed directly below the lights. This yielded an energy spectrum very close to that occurring a few meters below the lake's surface.

EFFECT OF ARSENIC AND CADMIUM ON THE GROWTH RATE AND NUTRIENT UTILIZATION RATES OF ASTERIONELLA FORMOSA

H. L. Conway and E. M. Yaguchi

Many volatile trace elements are released during combustion of fossil fuels. They may eventually be transported to aquatic ecosystems by wet or dry deposition, and some of them may be toxic to aquatic organisms. We are investigating the effects of arsenic and cadmium on an algal species found in Lake Michigan. Little information is available on chronic effects of these elements. Cadmium is widely used in the plating, pigment, and plastics industries. Arsenic and cadmium also enter the lake as a result of their use in agricultural pesticides and insecticides. Increased fossil fuel utilization in this region may result in increased arsenic and cadmium levels in the lake water if the present levels are not under geochemical control.

We are using continuous culture techniques to assess biological effects of arsenic and cadmium concentrations between 2 and 20 times ambient levels. Uptake of arsenic and cadmium and their effects on nutrient utilization and growth rate are being measured for *Asterionella formosa*, an important diatom, in spring and fall in Lake Michigan. Continuous culture techniques permit evaluation of subtle pollutant effects, such as physiological impairment and decreased reproductive rates, over many generations.

At a level of 2 μg Cd/liter, the amount of sorbed cadmium was $\sim 3 \times 10^{-11}$ μg Cd/μm^{3}* after 6 days, nearly an order of magnitude less than the level at 6 days in a previous experiment using 10 μg Cd/liter. A third experiment with even greater cadmium levels showed a corresponding increase in cadmium sorption, suggesting sorption of cadmium is a function of ambient concentration.

Very different results were obtained for arsenic. Over a range of 10 to 150 μg As/liter, the diatoms consistently sorbed similar levels of arsenic. The level of As sorption also differed from those of Cd. Also, the relationship

---

*Normalized to cell volume as μm^{3}.

between cellular arsenic content and time was quite different. Approximately 4 days were required to reach a steady state level of arsenic in the cells, even though the arsenic level in the medium did not become constant until the sixth day. This implies that the cells reached a saturation level at a relatively low arsenic concentration. At an ambient arsenic concentration of ~ 10 μg/liter, the level of sorbed arsenic initially increased to 7×10^{-11} μg As/μm^3, then decreased to 4.5×10^{-11} μg/μm^3, suggesting desorption of the arsenic.

Arsenic did not affect nutrient utilization or growth rates at concentrations of 10 to 150 μg As/liter (Figure 1). Cadmium concentrations of ~ 10 μg Cd/liter resulted in cessation of growth and nutrient utilization in less than 24 hr, while at 2 μg Cd/liter (Figure 1), the growth rate began to decrease after 2 days as indicated by decrease in population cell volume. Silicon utilization was not affected within the 6-day experiment, but NO$_3$ utilization decreased after 5 days.

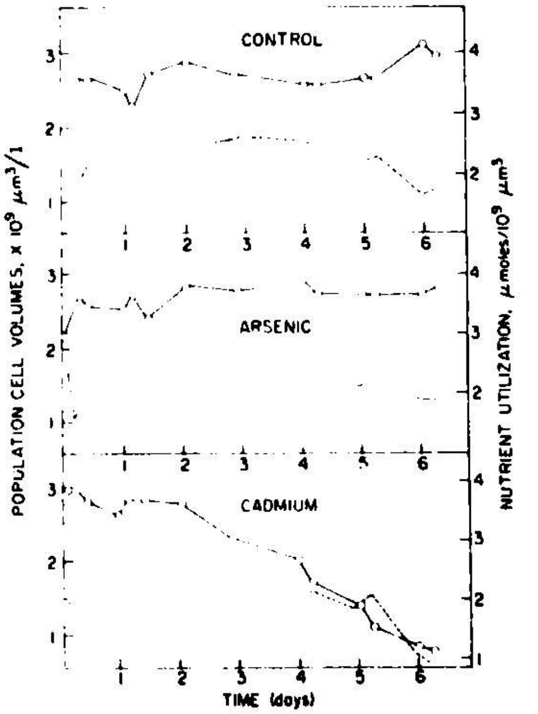

FIG. 1.— Total population biovolume and nutrient utilization at ~10 μg As/liter or ~2 μg Cd/liter. —o—, population cell volume; ---, NO$_3$; ..., Si.

The ability of A. formosa to maintain a constant arsenic level in or on the cells was examined by studying the sorption kinetic of arsenic at 10 μg As/liter on live cells, dead cells (killed with mercuric chloride), and "cleaned" frustules (irradiated with a high-intensity, ultraviolet lamp to remove all organic material). Samples were taken for 48 hr to measure sorption of ^{74}As. In live cells, arsenic sorption occurred very rapidly within the first hour, but fluctuated around a steady-state level for the rest of the experiment (Figure 2). Both killed cells and cleaned frustules had nearly the same initial sorption rate as live cells, but continued to take up arsenic at a somewhat slower rate during the course of the experiment. Apparently there is both an active process regulating arsenic uptake in living cells and a process of surface adsorption.

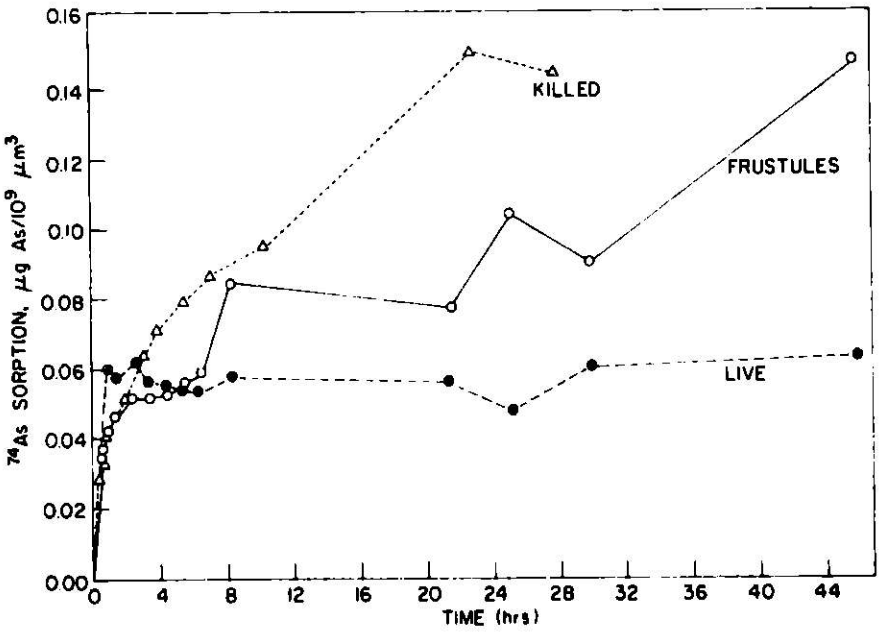

FIG. 2.--Short-term uptake of arsenic-74

Table 1. Location of radioactive labels in *Asterionella formosa*.

Fraction	Percent of Label	
	^{74}As	^{115m}Cd
Cell contents (<0.45 μ)	36	58
Organic coating around frustule	48	25
Siliceous frustule	16	17

Preliminary experiments have been made to isolate various cell fractions and determine their relative arsenic and cadmium contents. A large fraction of the arsenic occurs in the organic layer surrounding the diatom frustule (Table 1). Most of the cadmium, however, was taken into the cytoplasm.

THERMAL DISCHARGE RESIDENCE BY LAKE MICHIGAN SALMONIDS

G. P. Romberg and W. Prepejchal

Lake Michigan salmon and trout were tagged with a thermoluminescent dosimeter (TLD) temperature tag to estimate their thermal exposure and residence time at a warm water discharge. Fish were collected, tagged, and released at the Point Beach Nuclear Plant, Two Rivers, Wisconsin, in the fall of 1973 and 1974. Tags were recovered during the same season, primarily from fish recaptured at Point Beach.

Average uniform temperature exposure and maximum possible discharge residence time were determined, as previously described.[1,2] Appropriate hourly intake and discharge temperatures were averaged to calculate mean temperature exposure for the case of maximum discharge residence. Lowest discharge temperature not included within the period of maximum residence was identified to serve as a possible indicator of avoidance temperature. Mean values for the above parameters were calculated for fish species for each tagging year and are reported in Table 1 with the accompanying range of intake and discharge temperatures.

Water temperatures during the 1974 study were typically less than during 1973. Total tag recoveries each year were in excess of 15% for the three species; however, only a limited number were collected at locations where TLD tags could be properly preserved. Recaptures typically occurred over a long time span and mean number of hours vary greatly between species and years. Residence times were converted to percent of total tag time (% residence time) to allow direct comparison between species and years.

In 1973, mean percent residence time for rainbow trout, brown trout, and chinook salmon approximated 20%. Temperature exposure values were lowest for rainbow trout and highest for brown trout. The 0.3 to 0.4 C differences between mean residence temperature exposures and average uniform temperature exposures is due to the nonsymmetric change in TLD fade with varying temperatures. Lowest discharge temperatures during the assumed

Table 1. Maximum discharge residence time and temperature exposure for salmonids tagged at Point Beach.

	1973			1974		
Intake Temperature Range (°C)	8.6 — 17.2			6.9 — 10.4		
Discharge Temperature Range (°C)	14.5 — 27.0			14.2 — 20.3		
Species	Rainbow Trout	Chinook Salmon	Brown Trout	Rainbow Trout	Chinook Salmon	Brown Trout
Number tagged with TLD tags	92	37	124	211	38	252
Usable recaptures	5	4	10	20	1	11
Tag time (hrs)	255 ± 99(a)	474 ± 76	483 ± 49	482 ± 47	44	274 ± 39
Maximum residence (hrs)	35 ± 11	102 ± 35	107 ± 32	149 ± 37	14	166 ± 31
Percent residence time (°C)	18 ± 9	20 ± 5	22 ± 6	31 ± 6	32	61 ± 9
Mean residence temperature (°C)	13.5 ± 1.0	15.2 ± 0.4	15.8 ± 0.4	11.5 ± 0.6	10.8	14.3 ± 0.9
Average uniform temperature	13.9 ± 1.2	15.5 ± 0.4	16.1 ± 0.4	11.8 ± 0.8	12.2	14.7 ± 0.9
Lowest non-residence discharge temperature	19.3 ± 0.1	19.2 ± 0.8	20.3 ± 0.6	17.0 ± 0.3	17.1	18.0 ± 0.4

(a) mean ± S.E.

period of nonresidence (at temperatures > 19 to 20 C) approximate reported avoidance temperatures for these species and correspond with temperatures at which visual observations indicate most salmonids leave the discharge flumes.

With lower discharge temperatures during 1974, mean percent residence times increased to approximately 30% for rainbow trout and chinook salmon and to 60% for brown trout. Corresponding temperature exposures decreased for all species; however, the value for brown trout remained highest. Lowest assumed nonresident discharge temperatures decreased to 17 to 18 C, well below predicted avoidance temperatures.

TLD tag data suggest that during 1973 discharge residence times were limited by the occurrence of upper avoidance temperatures. While the percent residence times increased with lower discharge temperatures in 1974, even greater residence times would have been required to raise temperature exposures to levels observed in 1973. The implication is that factors other than temperature, such as spawning migrations, feeding habits, or energy requirements limited residence times in 1974.

References

1. G. P. Romberg and W. Prepejchal, Characteristics of temperature-sensitive fish tags used in 1974, Radiological and Environmental Research Division Annual Report, January-December 1974, ANL-75-3, Part III, pp. 155–160.
2. G. P. Romberg and W. Prepejchal, Improvements in TLD temperature tag calculations, this report.

PLUME RESIDENCE AND TOXIC MATERIAL ACCUMULATION

S. A. Spigarelli and R. Holpuch

Increased growth rates[1] and ^{137}Cs concentrations[2] in plume resident trout are thought to be the result of increased metabolism, food consumption, and activity caused by exposure to increased water temperature and flow in thermal discharges. These exposure conditions could contribute to increased accumulation of biologically active, toxic substances by primary forage and predator fish species in the Great Lakes. Uptake and retention of various toxic substances by predators depend on concentrations in forage species (trophic transfer), ambient water, and point source effluents (direct uptake). Contaminants of immediate concern in Great Lakes systems (e.g., chlorinated hydrocarbons) accumulate in adipose tissue, and body concentrations have been correlated with total lipid content in fish. In addition to direct toxic effects on fish, many lipophilic contaminants are known to cause severe human health problems when ingested at concentrations commonly found in Lake Michigan salmonids. Although power plants may or may not be the direct source of a toxic substance, the thermal discharge environment may contribute to the accumulation of toxic substances in fish and the transfer of these materials to man.

Epaxial muscle (loin) samples taken from TLD tagged and reference bown and rainbow trout[1] were analyzed for lipid content (% by weight) to detect possible changes in lipid deposition resulting from recent plume residence. For both species, plume resident fish had statistically higher percent fat contents than fish from unheated (reference) areas (Table 1). In addition, there was a significant interspecific difference, i.e., mean reference and plume rainbow trout had 78% and 69% more fat, respectively, than had related brown trout samples. Percent fat values were adjusted for significant size effects (size proportional to fat content) and correlated to RNA/DNA ratios (indicator of recent growth) and maximum residence times (hrs) of each fish. Although neither of these correlations was statistically significant, a

Table 1. Mean percent fat (extractable oil) contents of plume resident and reference rainbow and brown trout.

Sample	N	Percent Fat Content (± S. D.)
Brown trout		
Reference	22	3.94 ± 2.04
Plume	15	7.16 ± 3.39
Rainbow trout		
Reference	13	7.00 ± 3.67
Plume	6	11.79 ± 4.83

relatively high coefficient of determination ($r^2 = 0.45$) was obtained between fat and maximum residence time of plume brown trout; however, the small sample size and high variance within samples precluded statistical significance.

Fat content of trout in this study ranged from 1 to 19%; Reinert et al.[3] report extractable lipids to be 2.9 to 6.6% by weight in loin muscle of coho salmon and 7.8 to 11.2% in lake trout. Veith and Lee[4] report maximum fat values of 10 to 11% in whole large rainbow trout collected from the Kewaunee area of Lake Michigan (loin values would be lower). Our limited number of samples suggests that plume resident brown and rainbow trout have considerably higher lipid contents than previously reported for these species and that levels in plume resident fish equal or exceed levels reported for lake trout.

Future controlled experiments will investigate the effects of thermal plume residence on lipid deposition and toxic material accumulation in Great Lakes salmonids.

References

1. S. A. Spigarelli and D. W. Smith, Growth of salmonid fishes from heated and unheated areas of Lake Michigan — as measured by RNA/DNA ratios, Thermal Ecology II, G. W. Esch, R. W. McFarlane, eds., ERDA Symp. Series CONF-750425 (1976), in press.

2. S. A. Spigarelli, Cesium-137 activities in fish residing in thermal discharges to Lake Michigan, Health Phys. 30, 411–413 (1975).
3. R. E. Reinert, D. Stewart, and H. L. Seagran, Effects of dressing and cooking on DDT concentrations in certain fish from Lake Michigan, J. Fish. Res. Board Can. 29, 525–529 (1972).
4. G. D. Veith and G. F. Lee, PCB's in fish from the Milwaukee region, Proc. 14th Conf. Great Lakes Res. (1971) pp. 157–169.

SUMMARY OF RECAPTURES OF FISH TAGGED AT TWO POWER PLANTS BETWEEN 1972 AND 1974

M. M. Thommes and G. P. Romberg

Fish tagging studies were conducted at the Point Beach Nuclear Plant, Two Rivers, Wisconsin, in the fall of 1972–1974, and at the Waukegan fossil-fueled plant, Waukegan, Illinois, during the spring of 1974.

A summary of tags returned by fishermen is given in Table 1. As of June 1, 1976, tag returns by fishermen equal 14%, while combined tag recoveries (by fishermen and ANL) total 18%.

Potential for recovery is highest for 1972 tags (maximum accumulated time) and decreases with each succeeding tagging year. However, recovery success for Point Beach fish shows an opposite trend, i.e., 1974 > 1973 > 1972. Lower returns of fish tagged in 1972 have been attributed to inadequate tag return instructions, while high recoveries in 1974 are, in part, due to the legalization of snagging by the State of Wisconsin. Total percentage of tags recovered from Waukegan fish is substantially lower than that for Point Beach fish. This difference has been attributed to poor survival of the large number of coho salmon tagged at Waukegan.

Dominant species collected and tagged at Point Beach were brown and rainbow trout, while at Waukegan, coho salmon and brown trout were prevalent. With the exception of fish tagged in 1972, percent tag recovery was higher for rainbow trout than for brown trout. This difference may be due to differences between the seasonal feeding and spawning habits of the two species. The greatest percentage of recaptures of all species occurred within 3 months (September–December) after tagging at Point Beach; this is the period when sport fishermen typically catch more rainbow trout than brown trout.[1] However, more brown trout than rainbow trout were recaptured after 90 days, and this trend is tending to equalize recapture percentages for these species.

Although recapture percentages for fish tagged in 1973 and 1974 were similar for brown and rainbow trout, the 1974 fish had significantly fewer long-term recaptures than the 1973 fish.[2] The reason for this difference is

Table 1. Percentage of Tagged Fish Recaptured by Fishermen as of June 1, 1975.

Species	Point Beach 1972	Point Beach 1973	Point Beach 1974	Waukegan 1974	Total
Brown trout	10% (49/506)[a]	15% (48/314)	17% (67/398)	13% (20/153)	13% (184/1371)
Rainbow trout	9% (7/74)	22% (71/329)	22% (73/327)	21% (8/39)	21% (159/769)
Lake trout	4% (5/135)	8% (7/92)	6% (1/16)	(0/4)	5% (13/247)
Chinook salmon	50% (1/2)	21% (26/121)	19% (12/62)	5% (1/19)	20% (40/204)
Coho salmon	(0/0)	5% (1/20)	7% (1/14)	0.5% (1/182)	1% (3/216)
Brook trout	20% (1/5)	43% (3/7)	25% (1/4)	(0/2)	28% (5/18)
Atlantic salmon	(0/0)	(0/0)	(0/1)	(0/7)	(0/8)
Total	9% (63/722)	18% (156/883)	19% (155/822)	7% (30/406)	14% (404/2834)

[a] % (# recap/#tagged).

not completely apparent, but may be attributed to a reduction in the number of smaller fish tagged in 1974. Smaller fish (< 50 cm for brown and < 58 cm for rainbow) show a consistently higher recapture percentage than larger fish. Movement patterns for 1974 fish were not significantly different from those reported for 1973 fish.[3]

The influence of thermal discharges on Lake Michigan salmonids is evidenced by the fact that 50.5% of the total tag recoveries were made at power plants. While tag returns indicate that salmonids do not remain at one thermal discharge for long periods, it appears that during the course of normal migrations these species spend a considerable amount of time at various thermal discharges. This behavior would substantially increase their exposure to elevated water temperatures, resulting in increased metabolic rates, food consumption, and vulnerability to sport fishermen.

References

1. S. A. Spigarelli and M. M. Thommes, Sport fishing at a thermal discharge into Lake Michigan, J. Great Lakes Res., in press.
2. G. P. Romberg, S. A. Spigarelli, W. Prepejchal, and M. M. Thommes, Migratory behavior of fish tagged at a nuclear power plant discharge into Lake Michigan, Proc. 17th Conf. Great Lakes Research, Int. Assoc. Great Lakes Res., Ann Arbor, MI. , pp 68–77 (1974).
3. G. P. Romberg and M. M. Thommes, Comparison of the movement and recapture of salmonid fishes tagged at two nuclear plants, Radiological and Environmental Research Division Annual Report, January-December 1974, ANL-75-3, Part III, pp. 133–142.

TEMPERATURE SELECTION AND AVOIDANCE BEHAVIOR OF SALMONIDS

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

---

In 1974 and 1975 we developed and tested a radiotelemetry system[1,2] designed to monitor temperature orientation of fish in thermal discharge areas. Between October and December 1975, we used this system to track 20 brown trout, 8 rainbow trout, and 1 chinook salmon collected from the Point Beach discharge flumes (Table 1). Since we are primarily interested in temperature selection and avoidance (exposure) behavior in plume areas (~ 1 square mile), we did not follow fish that moved beyond the effective range of the shore-based system. Consequently, many of these tracks were (1) not continuous (i.e., fish moved in and out of range) and in a few cases record gaps indicate departure from the area and subsequent returns up to 2 weeks later; and (2) quite variable in total hours duration. These features are indicative of the migratory tendencies of these species and tend to substantiate previous studies showing variable residence behavior among individuals and species.

Table 1. Summary of radiotelemetry studies at Point Beach during 1975.

Species	Month	n	$\bar{x}$ Hours	Total Hours	Range (hrs)	Recaptures
Brown trout	Oct	14	76.4	1070	4—409	3
	Nov	2	64.5	129	11,118	0
	Dec	4	31.5	126	5—73	0
Subtotal		20	66.3	1325	4—409	3
Rainbow trout	Oct	2	29.5	59	5,54	2
	Nov	2	50.0	100	29,71	0
	Dec	4	18.5	74	2—24	1
Subtotal		8	29.1	233	2—71	3
Chinook salmon	Oct	1	2	2	—	1
Total		29	53.8	1560	2—409	7

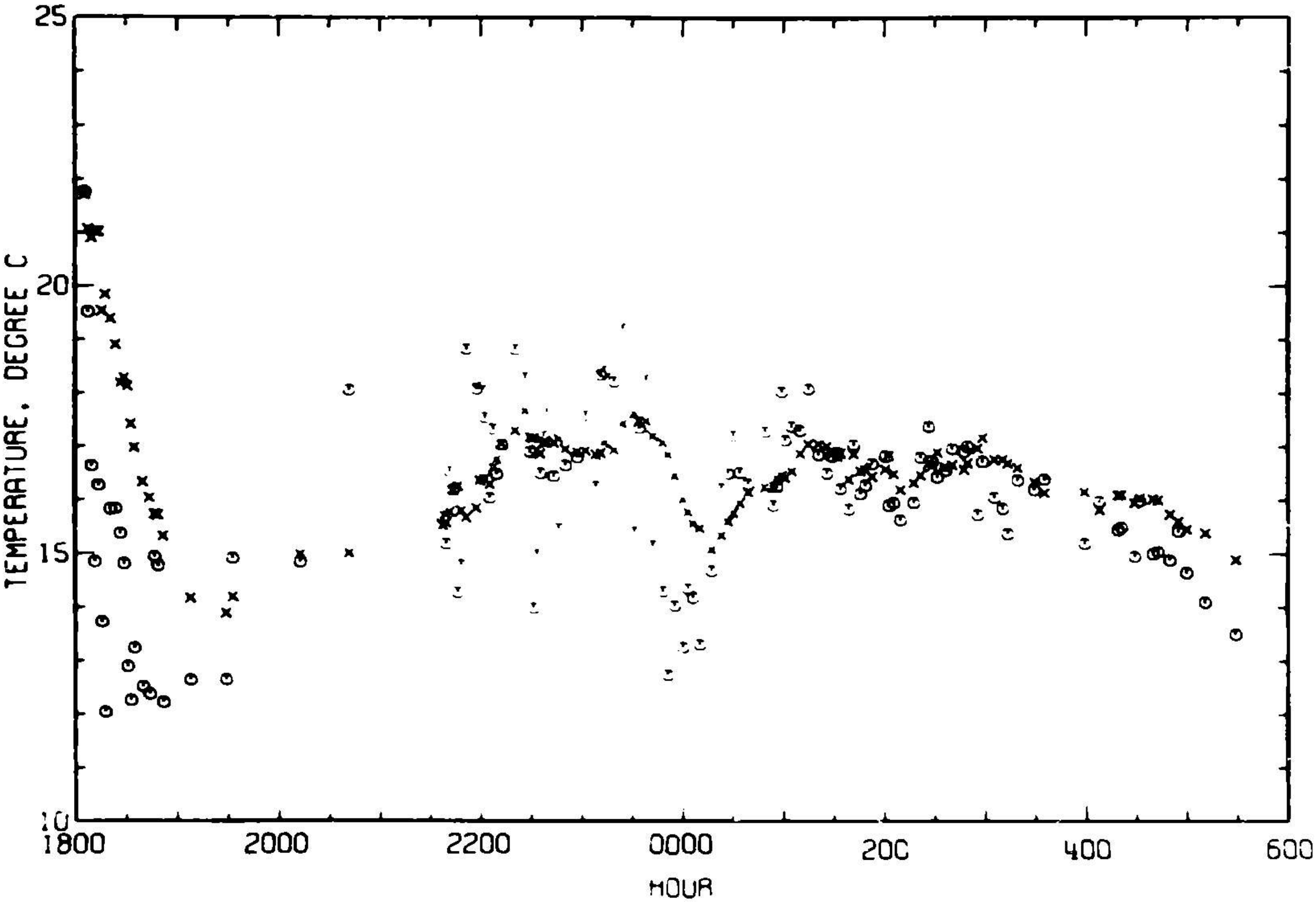

FIG. 1.--Temperature exposure of a 2.5-kg brown trout followed by radiotelemetry. x, fish; o, water (ANL neg. 149-76-236)

Although we did not follow migrant fish, we gained some information on direction and destination of migration from recaptures made by fishermen. A total of 6 fish tracked during this period (21%) were recaptured by fishermen at other locations, up to 60 miles away; the seventh recapture was made by ANL at Point Beach.

Data (time, water and body temperature) from the 29 tracks in 1975 and subsequent tracks in early 1976 are being analyzed by an expanding computer program that will sort, test, calibrate, plot, and print temperature records over time. Subsequent analyses of these data will address (1) the effects of size, species, season, and time of day on temperature responses; (2) temperature preference, avoidance, and behavioral regulation responses; (3) the influence of rate of change in body temperature on water temperature orientation; and (4) the role of the acclimation state in temperature selection behavior.

An example of a 12-hour track is shown in Figure 1. After its release into the discharge flume (1805 hours), this brown trout traversed a 9.8 C ΔT into ambient temperatures in about 15 minutes (from 21.8 to 12.0 C) and, over the next two hours (1820–2020), moved between 16 C plume and 12 C ambient water. During the remaining 9+ hours this fish moved between 19 C and 13 C water, and gradually reduced this range of temperature exposure to 15 to 17 C such that body temperature became fairly constant.

References

1. W. Prepejchal, J. Haumann, and S. A. Spigarelli, Developments in underwater radiotelemetry and preliminary fish tracking in thermal plumes, Radiological and Environmental Research Division Annual Report, January-December 1974, ANL 75-3, Part III, pp. 128–132.
2. W. Prepejchal and J. Hausmann, Underwater radiotelemetry system, this report.

BODY TEMPERATURE CHANGE IN LIVE AND DEAD GIZZARD SHAD, *DOROSOMA CEPEDIANUM*

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

Temperature change kinetics were determined for a sample of 22 gizzard shad, ranging in weight from 13.2 to 467.5 grams. Tests consisted of monitoring the intestinal temperatures of shad transferred between two well aerated water baths held at 9.2 ± 0.13 C (mean and standard error) and 18.7 ± 0.08 C. Details of the method are described by Spigarelli et al.[1]

None of the 22 live shad subjected to the ± ΔT of 9.5 C died during exposure. The similarity of double logarithmic regressions of body weight and half-time (Table 1) indicate that neither the direction of exposure nor the state of the test fish greatly influenced temperature change kinetics. An exponent of 0.64 relating weight and half-time for live shad (cooling) compares favorably with exponents for other fishes[1,2] subjected to cooling. Consistent

Table 1. Equations for double logarithmic regressions of half-time in minutes and fish weight in grams for 22 shad under all 4 experimental exposures.

Exposure	Equation*
Alive	
Heating	$\log t_{\frac{1}{2}} = -1.15 + 0.64 \log wt$
Cooling	$\log t_{\frac{1}{2}} = -1.13 + 0.64 \log wt$
Dead	
Heating	$\log t_{\frac{1}{2}} = -1.08 + 0.66 \log wt$
Cooling	$\log t_{\frac{1}{2}} = -1.08 + 0.66 \log wt$

* All coefficients of determination, R^2, ≥ 0.939, $P < 0.00001$.

with results for other fish species,[1,3-5] a significant number of live shad heated more rapidly than they cooled (Table 2). Computations comparing half-times of live and dead shad indicate that conduction accounts for approximately 80%, and, therefore, convection only 20% of the total heat transport. These percentages are dependent upon morphology of the fish, size range examined, and locomotory activity of the fish during testing.

Table 2. Comparison of heating and cooling half-times in live and dead gizzard shad.

Exposure	N	Heating Half-Time		Probability*
		Smallest	Largest	
Alive	22	18	3**	0.002
Dead	22	13	9	0.88

* 1 tie, i.e., heating and cooling half-times were equal.

** Computed from Wilcoxon matched pairs, signed ranks analyses.

References

1. S. A. Spigarelli, M. M. Thommes, and T. L. Beitinger, The influence of body weight on heating and cooling of selected Lake Michigan fishes, Comp. Biochem. Physiol., in press.
2. E. D. Stevens and F. E. J. Fry, Heat transfer and body temperature in non-thermoregulatory teleosts, Can. J. Zool. <u>52</u>, 1137–1143 (1974).
3. J. R. Stauffer, K. L. Dickson, A. G. Heath, G. W. Lane, and J. Cairns, Jr., Body temperature change of bluegill sunfish subjected to thermal shock, Prog. Fish-Cult. <u>37</u>, 90–92 (1975).
4. G. A. Bartholomew and R. C. Lasiewski, Heating and cooling rates, heart rates, and simulated diving in the Galapagos marine iguana, Comp. Biochem. Physiol. <u>16</u>, 573–582 (1965).
5. L. I. Crawshaw, Effect of rapid temperature change on mean body temperature and gill ventilation in carp, Am. J. Physiol., in press.

THERMOGRAPH RECORDS OF UPWELLING EVENTS IN SOUTHWESTERN LAKE MICHIGAN

K. D. Saunders[*] and L. S. Van Loon[*]

Early in May 1975, four thermograph stations were moored off Illinois Beach State Park between Zion and Waukegan, Illinois. Each mooring consisted of one electronic recording package and four thermistors, placed at various depths. Temperature data were collected from May 2 through October 21. For various reasons not all instruments returned data during each recording period. The data return was about 70% of the total possible. A typical plot of the unfiltered thermograph data is presented in Figure 1.

Preliminary analysis of the data indicates that intrusions of cold water, typically 10C below normal ambient for an unforced system, can occur over periods of several hours and can last for periods of several days. The most intense periods of upwellings can result in temperatures at or near 5 C at all depths in the region of the study. Some parts of the record indicate the presence of Poincari-type internal waves with periods near the inertial period. The correlation of upwelling events between stations appears to be very high. In most cases, the strong upwellings are felt even at the near shore station, about 500 m offshore. At least some upwelling events appear to be correlated with the strengthening of winds from the southwest and/or the shifting of winds from the north or east to the southwest. The thermograph locations do not appear to be significantly contaminated by the thermal effluent from either the Zion generating station or the Waukegan generating station.

---

[*] Energy and Environmental Systems, ANL.

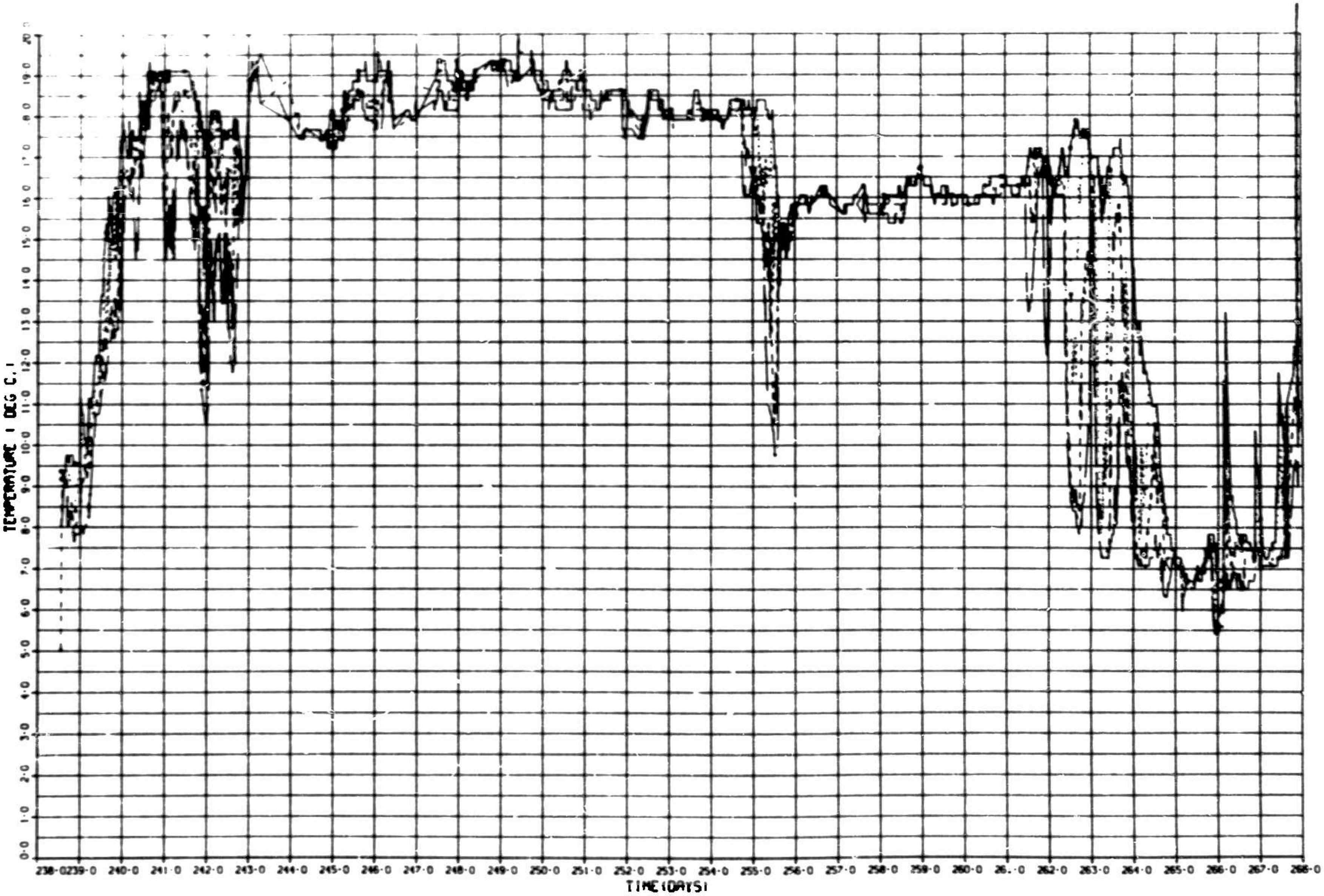

FIG. 1.--Thermograph plot–temperature vs. time.

PHYTOPLANKTON AND NUTRIENTS NEAR THE ZION NUCLEAR PLANT DURING UPWELLING

E. M. Yaguchi

During the summer of 1975, a study was undertaken to examine separate and combined effects of upwelling and a warm-water discharge on nutrients, assimilation ratios, and phytoplankton populations near the Zion Nuclear Plant. Sampling was conducted during three days of upwelling conditions in July, and two days of stable hydrological conditions in August. On each date, samples were collected from two or three depths at each of three stations in the thermal plume and three stations in a control area 2.5 km south of the plant.

Many significant differences in chemical and biological parameters were related to upwelling conditions (Table 1). During upwelling, reactive silicate concentrations were more than twice as great as during non-upwelling; phytoplankton diversity, chlorophyll *a* concentrations, and cell numbers per milliliter

Table 1. Significant differences in chemical and biological parameters related to upwelling (Student's *t*-test, $\alpha = 0.05$).

	Mean Value	
	Upwelling	Non-upwelling
Greater during upwelling		
amorphous silica, mg Si/m^3	170	120
reactive silicate, mg Si/m^3	371	161
ammonia, mg NH_4-N/m^3	30	22
phosphate uptake, mg PO_4-$P/m^3/hr$	1.09	0.85
phytoplankton diversity, $\bar{H}$	1.61	1.16
chlorophyll *a*, mg/m^3	1.86	1.25
carotenoids, mg/m^3	4.38	2.66
phaeopigments, mg/m^3	0.76	0.26
carotenoid/biomass ratio	0.13	0.10
phaeopigment/biomass ratio	0.025	0.008
cell numbers/ml	815	454
Lower during upwelling		
biomass ratio (diatoms/total)	0.88	0.97
primary productivity (mg $C/m^3/hr$)	1.88	3.60
assimilation ratio (mg C/hr/mg chlorophyll *a*)	0.05	0.13
specific growth rate (hr^{-1})	1.45	2.80

Table 2. Significant differences[a] in chemical and biological parameters related to the thermal plume.

	Mean Value	
	Plume	Control
During upwelling		
amorphous silica (mg Si/m^3)	181	158
ammonia (mg NH_4-N/m^3)	1.77	2.49
specific growth rate (hr^{-1})	0.056	0.052
During non-upwelling		
amorphous silica (mg Si/m^3)	143	97
ammonia (mg NH_4-N/m^3)	1.78	1.40
chlorophyll a (mg/m^3)	1.51	0.99

(a) For specific growth rate, difference is significant by the Mann-Whitney U test ($\alpha = 0.05$). For all others, the criterion was the least significant difference ($\alpha = 0.05$) of the analysis of variance.

were greater. Productivity quotients were lower by nearly one-half during upwelling.

Only minor differences were attributable to the thermal discharge of the Zion Nuclear Plant (Table 2), including significantly ($\alpha = 0.05$) increased temperature and amorphous silica concentration in the plume. Phytoplankton specific growth rates in the plume were increased over those in the control area only during upwelling, implicating nutrient limitation as an important factor in the response of phytoplankton to locally increased temperature.

FISH SPECIES COMPOSITION, DENSITY-DISTRIBUTION PATTERNS, AND IMPINGEMENT DURING UPWELLING

S. A. Spigarelli and R. K. Sharma*

The effects of cooling system intakes and discharges on Lake Michigan fishes are highly dependent on inshore species composition and spatial distribution which, in turn, are affected by natural hydrological conditions. Significant (5 to 10 C) short-term decreases in water temperature (due to upwelling) could cause (1) cold shock in fish equilibrated to either ambient or plume temperatures; (2) substantial changes in distribution due to avoidance or attraction responses; and (3) resultant changes in susceptibility to impingement.

The objectives of this study are to characterize the changes in fish species composition, density, and thermal distribution as a result of natural upwellings, and to relate these factors to intake and discharge effects. Day and night sampling was conducted in ambient (reference) and thermal plume waters near the Zion Nuclear Plant on four occasions between 17 July and 11 September 1975.

Density-distribution patterns and species composition of fish were determined by means of gill nets, bottom trawls, seines, and a sonic fish locater. Gill nets were placed at two depths (mid-depth and bottom) near the 22-to-24-foot contour and were checked every 12 hours. Ten-minute bottom trawls were made at the 10-, 20-, and 30-foot contours in plume and reference areas during each sampling period. The 0-to-10-foot contours were sampled with 1000' and 200' beach seines. Sonar surveys were made on the contours at 8, 12, 15, 20, 25, 30, 35, and 40 feet. Coordinated sonar and trawl runs were made on appropriate contours, while seines and gill nets were being used. Traveling screens were sampled at regular intervals during the study.

Numbers and species of fish sampled in inshore waters and impinged on traveling screens during and following upwellings will be compared to impingement data from stable hydrological periods.

---

*Environmental Impact Studies Division.

UNDERWATER RADIOTELEMETRY SYSTEM

W. Prepejchal and J. Haumann*

A previous report[1] outlined our requirements and design philosophy for a telemetry system which allows the monitoring of fish movements, physiological parameters, and environmental conditions in thermal discharge areas. This report describes the system that was developed at ANL between 1974 and 1975 and which has been used to track salmonid fishes since fall 1975.

From one to seven data intervals (channels) are transmitted in a time multiple. [illegible] the periods ($T_1, T_2, ---T_8$) (Figure 1) are a function of each sensor's resistance (e.g., thermistors), and these are proportional to the parameter of interest. A reference signal, transmitted with a higher tone frequency, served to define the start of data sequences and provides an incoding standard to correct for circuit drift. Each period consists of a "no signal" section and a tone-burst section. The overall duty cycle is less than 5% and results in a useful transmitter (battery) life of ~ 3 weeks from a 7-volt, 190-mA-hr mercury battery. This transmitter package is assembled from commercially available components at a cost of ~ $50 per transmitter; assembly time is ~ 2 hr. Various physical configurations have been designed to minimize weight and drag; the present transmitter design is cylindrical in shape, weighs 31 g, displaces 15 cm^3, and has a frontal area of 1.8 cm^2. A variety of other transmitter configurations has been assembled and tested for special purpose studies, such as laboratory data collection and small (1- or 2-sensor) field transmitters.

Receiving

A shore-based receiving system was designed to be housed in a 16-ft house trailer and operated in a continuous, unattended mode. The programmable receiver recognizes valid transmissions and performs limited data processing. A flow diagram of the system appears in Figure 2. A maximum of 16 channels (discreet transmitter frequencies) can be sequentially scanned and the received data stored and processed. Provisions are included to continue

---

*Electronics Division

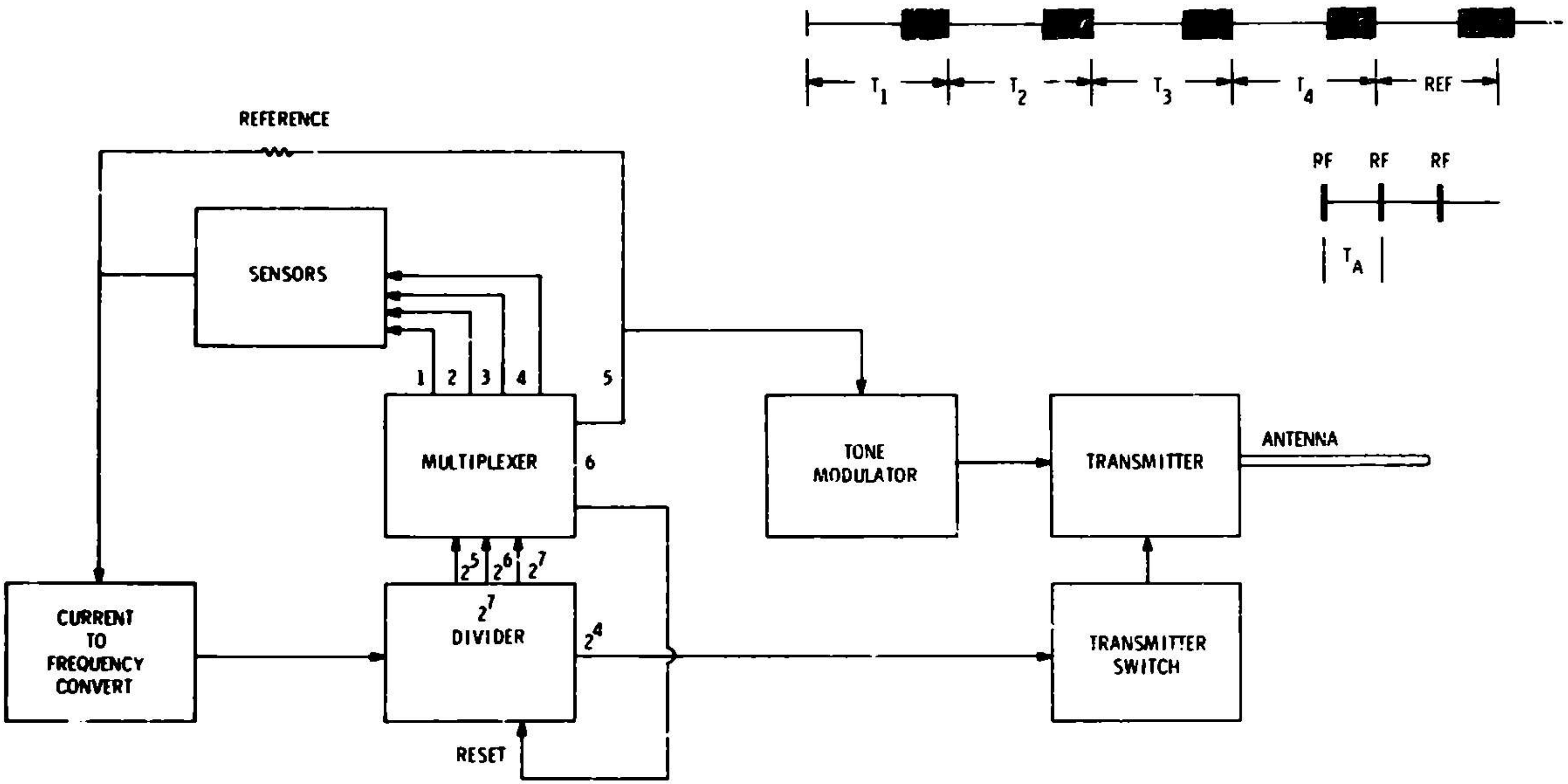

FIG. 1.--Transmitter block diagram

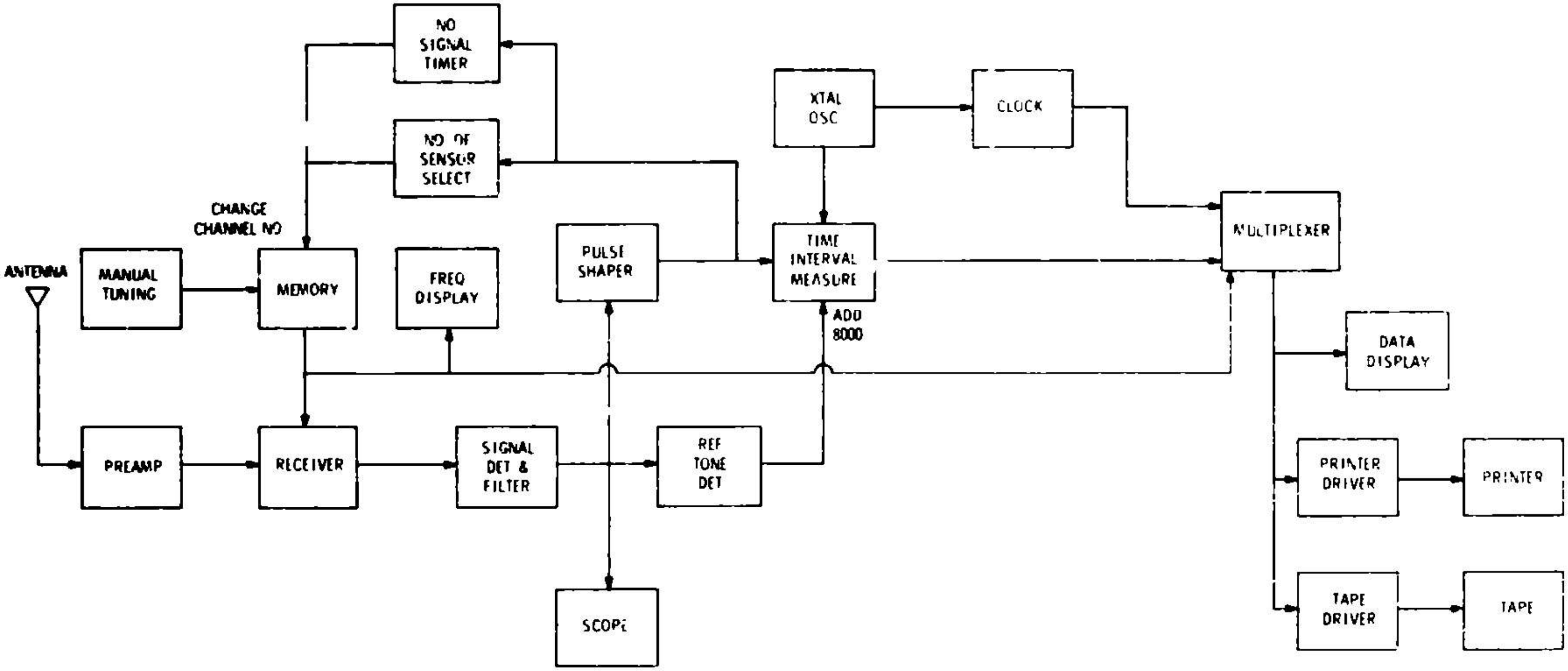

FIG. 2.--Data aquisition system block diagram

("no signal" timer) the automatic scan past "silent" channels and to dwell (data interval counter) on channels until complete data sets are obtained. The reference interval signal is processed and coded to establish the time sequence (reference tone detector). Data and reference intervals are then digitized to time intervals (time interval counter). All data (channel number, frequency, date, time, and intervals) (1) appear on a digital display; (2) may be printed (auto or manual mode); and (3) are stored on high density magnetic tape. Computer procedures are used to normalize (reference adjust), convert (to temperature units), sort, print, test, and plot data for inspection and subsequent analyses.

This system has been used in both attended and unattended modes at the Point Beach Nuclear Plant and has produced continuous temperature exposure data for plume-resident salmonids.[2] Future research and development could be initiated to (1) expand the physiological and environmental parameters of interest in fish ecology studies, and (2) adapt this system to a variety of environmental problems (e.g., in situ water temperature, current, and pollutant monitoring) particularly in situations where hard wire connections or numerous in situ recording devices are impractical.

References

1. W. Prepejchal, J. Haumann, and S. A. Spigarelli, Developments in underwater radiotelemetry and preliminary fish tracking in thermal plumes, Radiological and Environmental Research Division Annual Report, January-December 1974, ANL 75-3, Part III, pp. 128—132.
2. W. Prepejchal, M. M. Thommes, S. A. Spigarelli, and G. P. Romberg, Temperature selection and avoidance behavior of salmonids, this report.

AUTOMATED BEHAVIORAL BIOASSAY SYSTEM

T. L. Beitinger, W. Prepejchal, and J. Haumann*

In cooperation with the ANL Electronics Division, we have designed and constructed an instrumentation system to determine temperature avoidance, preference, and regulation by adult salmonid fishes. This design features a temperature gradient over time instead of the spatial gradients of classical temperature preference research. The experimental approach allows an individual fish to serve as a "living thermostat" to regulate its body temperature by controlling the temperature of its environs. Miniaturized radiotransmitters, attached to the fish, are used to monitor both environmental and internal body temperatures. These transmitters are similar in design to our field transmitter but considerably smaller, owing to reduced power (battery) required for short transmission distances. An ANL designed microprocessor controls the complex functions of equipment operation, and data acquisition and transformation. In addition to the hard copy data output from an input-output printer interfaced to the microprocessor, data are stored on digital cassettes for subsequent computer analyses.

During the past year, we converted a general-use laboratory into a "wet-lab" facility. Central in the development of this facility was the construction of an aeration-filtration water treatment system to eliminate excess iron from our well-water supply. We have held adult salmonids in the laboratory for as long as 6 months with no apparent deleterious effects.

---

*Electronics Division

IMPROVEMENTS IN TLD TEMPERATURE TAG CALCULATIONS

G. P. Romberg and W. Prepejchal

Fade characteristics of TLD temperature tags approximate a hyperbolic function of the form $1/S = 1/S_0 + m_T t$ with a linear relationship between $\ln(m_T)$ and $1/T_{°K}$, where S = TL signal at time (t), S_0 = initial TL signal, and m_T = rate of TL change, which is a function of absolute temperature ($T_{°K}$).[1] Establishment of these relationships makes it possible to determine average temperature exposures and discharge residence times mathematically rather than by the previously used graphic technique.[2]

Predicted 1/S values are provided by a computer program which yields a listing of the 1/S values for hourly increments of increasing discharge residence time. Also listed are the discharge and intake temperatures used for each calculation and the combined average temperature. Constant temperature exposure required to produce a given 1/S value is calculated by solving for T in the equation describing fade characteristics.

Correlations between observed and predicted values of 1/S and average temperature are illustrated in Table 1 for discharge control tags used in the 1974 fish tag study. Since temperature exposure is calculated from total change in TL signal, accuracy improves as total fade increases over time at higher temperatures. At an exposure of about 17 C, approximately 500 and 1000 hours are required to obtain respective error terms of ± 0.1 C and ± 0.5 C in calculated average temperature. For an exposure at 25 C, these times will decrease to approximately 200 and 500 hours, respectively. Due to asymmetry in the TLD fade response, the calculated average uniform temperature value (which assumes a constant temperature exposure) will typically be slightly higher than the true average temperature exposure.

Maximum possible discharge residence time, which assumes the lowest discharge temperature exposure, is determined by the number of hourly discharge temperatures used to calculate a 1/S value equal to the measured tag value. This procedure was verified using a tag recovered from a fish known

Table 1. Measured and predicted values of 1/S and average temperature exposure for control tags in the discharge flume.

Elapsed Time (hr)	Measured 1/S Value	Predicted 1/S Value	Calculated Average Uniform Temperature[a]	Measured Average Discharge Temperature
143	270.9 ± 8[b]	266.1	17.1 ± 3.3[c]	14.4
311	306.4 ± 10	296.5	18.7 ± 1.3	16.7
491	318.6 ± 10	324.1	16.8 ± 1.0	17.0
820	374.1 ± 12	376.8	17.4 ± 0.7	17.2
982	401.2 ± 12	402.8	17.5 ± 0.5	17.3

(a) Calculated using measured 1/S value.
(b) Error corresponding to a 3% error in the mean TL signal (S).
(c) Error caused by uncertainty in 1/S.

to have been confined within the discharge flume for the entire tag period. The measured 1/S value after 525 hours of actual discharge residence was 322.9 ± 10 compared to a predicted value of 329.0. This indicated a residence time of 484 ± 69 hours or 92 ± 13% of the total tag time. Measured average temperature exposure was 16.9 C compared to a calculated average uniform temperature exposure of 16.7 ± 1.0 C.

The mathematical treatment of TLD temperature tag data is superior to a graphic technique; the results indicate the need for improving standard error of the mean TL signal.

References

1. G. P. Romberg and W. Prepejchal, Characteristics of temperature-sensitive fish tags used in 1974, Radiological and Environmental Research Division Annual Report, January-December 1974, ANL-75-3, Part III, pp. 155–160.
2. G. P. Romberg and W. Prepejchal, Temperature sensitive (TLD) fish tags: Improvements in technique, Radiological and Environmental Research Division Annual Report, January-December 1973, ANL-8060, Part III, pp. 120–126.

PUBLICATIONS BY THE STAFF OF THE ECOLOGY SECTION IN THE PERIOD JANUARY THROUGH DECEMBER, 1975

Journal Articles, Book Chapters, Etc.

T. L. Beitinger, J. J. Magnuson, W. H. Neill, and W. R. Shaffer, Behavioural thermoregulation and activity patterns in the green sunfish, Lepomis cyanellus, Anim. Behav. 23, 222–229 (1975).

T. L. Beitinger, Diel activity rhythms and thermoregulatory behavior of bluegill in response to unnatural photoperiods, Biol. Bull. 149, 98–108 (1975).

T. L. Beitinger and J. J. Magnuson, Influence of social rank and size on thermoselection behavior of bluegill (Lepomis macrochirus), J. Fish. Res. Board Can. 32, (11), 2133–2137 (1975).

D. N. Edgington, J. C. Ritchie, and J. A. Robbins, Comments on the paper "Use of rivers to predict accumulation in sediment of radionuclides discharged from nuclear power plants" by P. Plato, Health Phys. 29, 429–431 (1975).

D. E. Leydon, T. A. Patterson, and J. J. Alberts, Preconcentration of x-ray fluorescence determination of copper, nickel, and zinc in sea water, Anal. Chem. 47, 733–735 (1975).

J. Miller and D. E. Koeppe, Effects of inorganic anions on swelling, respiration, and phosphorylation in corn mitochondria, Physiol. Plant. 34, 153–156 (1975).

J. E. Miller, J. J. Hassett, and D. E. Koeppe, The effect of soil properties and extractable lead levels on lead uptake by soybeans, Comm. Soil Sci. Plant Anal. 6, 339–347 (1975).

J. E. Miller, D. E. Koeppe, and J. J. Hassett, The effect of soil lead sorption capacity on the uptake of lead by corn, Comm. Soil. Sci. Plant Anal. 6, 349–358 (1975).

J. A. Robbins and D. N. Edgington, Determination of recent sedimentation rates in Lake Michigan using ^{210}Pb and ^{137}Cs, Geochim. Cosmochim. Acta 39, 285–304 (1975).

J. E. Schindler and J. J. Alberts, An investigation of the role of organic materials in freshwater systems, Verh. Internat. Verein. Limnol. 19, 2201–2206 (1975).

M. A. Wahlgren and D. M. Nelson, Plutonium in the Laurentian Great Lakes: Comparison of surface waters, Verh. Internat. Verein. Limnol. *19*, 317–322 (1975).

Contributions to Conference Proceedings and Miscellaneous Reports

D. N. Edgington and J. A. Robbins, The application of natural and fallout radionuclides to studies of sedimentation in Lake Michigan, Proc. 2nd Int. Conf. on Nuclear Methods in Environmental Research, U.S. ERDA Report CONF-740701, pp. 443–458 (1975).

D. N. Edgington and J. A. Robbins, The behavior of plutonium and other long-lived radionuclides in Lake Michigan. II. Patterns of deposition in the sediments. Proc. IAEA Symp. on Impacts of Nuclear Releases into Aquatic Environment, Helsinki, Finland, 30 June–4 July 1975, Int. Atomic Energy Agency, Vienna, pp. 245–260 (1975).

J. O. Karttunen, USAEC Report No. HASL-294, Cs-137 in Various Chicago Foods, pp. III-2–III-5, July 1, 1975.

J. S. Marshall, B. J. Waller, and E. M. Yaguchi, Plutonium in the Laurentian Great Lakes: Food chain relationships, Abstracts of papers, XIX Congr. Int. Assoc. Limnol., Winnipeg, 22–29 August 1974, p. 134 (1975).

R. W. Miller, J. E. Schindler, and J. J. Alberts, Mobilization of mercury from freshwater sediments by humic acid, *Mineral Cycling in Southeastern Ecosystems*, F. G. Howell, J. B. Gentry, and M. H. Smith, Eds., 1–3 May 1974, August, Georgia, CONF-740-513, pp. 445–451 (1975).

S. A. Spigarelli, Behavioural responses of Lake Michigan fishes to a nuclear power plant discharge, Proc. IAEA Symp. on Environmental Effects of Cooling Systems at Nuclear Power Plants, Oslo, Norway, August 26–30, 1974. Int. Atomic Energy Agency, Vienna, pp. 479–498 (1975).

M. A. Wahlgren and J. S. Marshall, The behaviour of plutonium and other long-lived radionuclides in Lake Michigan. I. Biological transport, seasonal cycling and residence times, Proc. IAEA Symp. on Impacts of Nuclear Releases into the Aquatic Environment, Helsinki, Finland, 30 June–4 July 1975. Int. Atomic Energy Agency, Vienna, pp. 227–243 (1975).

M. A. Wahlgren and J. S. Marshall, Distribution studies of plutonium in the Great Lakes, Proc. 2nd Int. Conf. on Nuclear Methods in Environmental Research, U.S. ERDA Report CONF-740701, pp. 267–275 (1975).