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RADIOLOGICAL AND ENVIRONMENTAL RESEARCH DIVISION ANNUAL REPORT

Ecology

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FOREWORD

The calendar year 1979 has been a time of adjustment and consolidation; some programs have grown and others have been redirected as a consequence of the developing relationship with the U. S. Environmental Protection Agency. Representatives of the EPA attended the AUA review of the Ecological Sciences Section in November and were favorably impressed by the scope, sophistication, and goal-orientation of the Section's research efforts.

The tower in southern Lake Michigan collected meteorological data and air samples for a full field season in 1979. The instrumentation, largely designed and built at Argonne, was further refined to improve reliability and reduced time between servicing. A second tower will be erected and operated near the center of Lake Huron in 1980.

The analytical chemistry capability of the Section has been upgraded to meet the growing demand for trace metal analyses. One of the two x-ray spectrometers has been automated in order that this valuable analytical tool can be operated around the clock. New preconcentration methods now make it possible to measure very low concentrations of such significant pollutants as cadmium on a routine basis. With this improved technology, a simple mass-balance for the cadmium budget has been constructed, which warns of a potential hazard to the Great Lakes ecosystem, perhaps within two or three decades.

World-wide research is producing an apparent never-ending stream of hypothetical hazards to aquatic ecosystems. The general emphasis of biological research in this Section has been to devise and conduct realistic, quantitative assessments of the true magnitude of these potential threats. For example: pollutants ordinarily present in midwestern rain have been shown to be capable of causing an immediate deleterious effect on phytoplankton photosynthesis in near-surface waters; then too, although zinc is considerably less toxic to aquatic systems than cadmium, the higher concentrations of zinc present in the Great Lakes have been found to make it potentially the more immediately toxic of the two metals; and fish attracted to the plumes of warm water discharged by power plant outfalls have been shown to accumulate organic pollutants at much higher rates than fish remaining in cooler waters.

Continuing field studies on the effects of sulfur dioxide on soybeans have confirmed that significant productivity decreases occur and have shown that these losses can be predicted from dose measurements. Premature senescence and changes in photosynthetic enzyme activity have been shown to be associated with SO_2.

Research on the behavior of transuranic elements in the natural environment continues to be sponsored by DOE. Oxidation state changes are now known to be a significant factor controlling the environmental movements of these elements in aquatic systems, since some oxidation states bind tightly to sediments and others do not.

A significant event of 1979 was the departure of the Section Head, David N. Edgington, who in the fall of the year assumed new responsibilities as the Director of the Center for Great Lakes Studies at the University of Wisconsin in Milwaukee. For the past several years Dr. Edgington's scientific leadership has provided a pivot about which much of the Section's activities revolved; much of the Section's more productive research in previous years was begun on Dr. Edgington's initiative. We look forward to continuing association with him in his new assignment, and to collaborative research activities with the University of Wisconsin-Milwaukee Center.

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POTENTIOMETRIC DETERMINATION OF TOTAL CARBONATE CARBON

G. M. Arcand* and G. T. Tisue

Background and Scope

In limnological studies it is frequently necessary to determine total carbonate-carbon concentration in water. Since the number of samples may be large and the concentration can be altered markedly by temperature change, interaction with the atmosphere, and biological activity, the method used must be rapid and amenable to field use. The conventional procedure, titration of a 50 to 100 mL sample with standard acid and/or base to a given pH is not particularly accurate, specific, or convenient.[1] An accuracy of ±5% can only be achieved when (1) there is assurance that the measured pH at the end point is within ±0.2 units of the true value, and (2) the concentrations of other weak acids, weak bases, and hydrolyzable ions, e.g., iron, aluminum, and manganese, are low relative to the carbonate carbon.

An alternative procedure which uses commercially available, CO_2-selective electrodes and a high-impedance millivoltmeter (accuracy ±0.1 mV) has been investigated. There are several advantages to this approach. (1) There should be no interference due to other water constituents since the electrodes are gas sensors (the active element is isolated from the sample by a membrane impermeable to liquids). (2) The sample size can be as small as 0.5 mL. (3) A determination can be made in 15 minutes. (The advantage afforded by the small sample size is that determinations can be made readily on interstitial water.) The potential the electrode develops, E, is related to the activity, a_{CO_2}, through the Nerst relationship, $E = E' + S \ln a_{CO_2}$, where E' is a reference potential, and S is the factor that relates the measured voltage to carbonic acid concentration. The value of S is established by calibration, preferably through standard addition to each sample.

E' should be a constant, but it arises from a combination of electrode standard potentials and various junction and membrane potentials which may vary with the composition of the matrix. Changing ionic strength affects the relationship between concentration and activity. Electrode memory effects are sometimes observed. In practice, E' is found to vary.

In principle, use of a calibration curve in direct potentiometry should yield accurate results; but this approach requires that solutions of a given concentration produce the same cell potentials, irrespective of matrix and environmental variations. This condition also is not met in practice. The range of voltages for replicates can be so high as to cause the calculated concentration to vary by severalfold, a clearly unacceptable result. An alternate means of calibration is obligatory.

Progress in 1979

The CO_2 electrode was obtained from HNU Systems, Inc. It is a combination electrode requiring no separate reference electrode. The millivoltmeter was a Beckmann Model 4800 Digital pH Meter. Standard solutions were prepared from reagent grade $NaHCO_3$ and boiled deionized water. The electrode was stored in 0.01 M $NaHCO_3$ between measurements. In most cases, the first measurement following prolonged storage was anomalous. This difficulty was relieved by pre-equilibrating the electrode in a standard solution within the concentration range of the

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samples being analyzed.

To make measurements of C_T (total carbonate carbon), a 25 mL sample was pipetted into a beaker in which the electrode was mounted at a 15° angle just above a slowly spinning magnetic stirring bar. To adjust pH and ionic strength, 5 mL of 5 M NaH_2PO_4 was added. This addition brings the sample pH below 5, where >99% of C_T consists of $H_2CO_3^*$ (H_2CO_3 + CO_2 (aq.)). The maximum potential, E_1, observed over a period of several minutes, was recorded. Then 1.00 mL of a $NaHCO_3$ standard solution was added and the maximum potential, E_2, recorded. (The concentration used depends on the concentration being determined.) It is important to make the standard addition immediately after a decrease from E_1 is observed to minimize variations in ΔE (E_2 - E_1). Each unknown was followed in this manner by a standard to determine the slope to be used in calculation of the concentration. Duplicate samples were measured in all cases.

The relationship between measured potentials and concentration is given by:[2]

$$\Delta E = S \log \frac{C_X V_X + C_A V_A}{V_X + V_A + V_B} \left(\frac{C_X V_X}{V_X + V_B} \right)^{-1},$$

where, C_X is the concentration in the sample, V_X is the volume of the sample, V_B is the volume of solutions added other than the standard, C_A is the concentration of the standard added, and V_A is the volume of standard added.

To make use of this relationship, a value of C_X was estimated on the basis of the theoretical value of S, -59 mV per decade. Then, a standard solution of similar concentration was measured. (In the standard, C_X is known so that the actual value of S is calculable). This value of S was then used to calculate C_X in the unknown sample. Because a reasonable approximation to C_X can be made from the value of E_1 in the unknown, the procedure is not so tedious as it first appears.

Table 1 shows the results of some typical measurements using an addend having $C_X = 3.60 \times 10^{-3}$ M. Although E_1 varies considerably, the range of ΔE is only 0.7 mV, and the range of S is 2.1 mV per decade.

Table 1. Measurement of Nerstian slope by $NaHCO_3$ standard addition, $NaHCO_3 = 3.6 \times 10^{-3}$ M.

E_1, mV	E_2, mV	ΔE, mV	S, mV/decade
34.3	54.6	20.3	59.3
37.0	57.1	20.1	58.7
39.8	59.4	19.6	57.2
39.9	60.2	20.3	59.3

Table 2 shows typical results for a series of measurements on solutions of known concentration. The slope used was the average value from Table 1. The relative uncertainty in concentration averaged 8.3%, but in actual measurements on lake water samples the precision tended to

be better. The averages of the values reported in Table 2 agree with the known values within 3%. We consider these levels of precision and accuracy acceptable for most limnological investigations.

Table 2. Comparison of measured and known concentrations of total carbonate carbon.

E_1, mV	E_2, mV	ΔE, mV	S, mV[a]	Molarity x 10^3	
				Known	Measured
40.2	57.0	16.8	59.3	4.66	
45.4	60.6	15.2	58.7	5.30	5.09
23.6	53.3	29.7	57.2	1.90	
24.9	55.0	30.1	59.3	1.97	1.96

[a]S was measured after each sample measurement.

Table 3 gives the results obtained for samples of Lake Michigan water. Figure 1 shows values of C_T as a function of depth in the core for sediment interstitial fluid from a station in the eastern basin of Lake Erie.

Table 3. Total carbonate-carbon concentration of Lake Michigan samples.[a]

Station	Location	Depth, m	pH	C_T, 10^{-3} M
79-1	42°08'N, 87°23'W	5	7.10	1.82
		16	7.65	1.79
		30	7.53	1.92
		64	6.76	2.10
79-2	42°08'N, 86°46'W	5	8.40	2.09
79-3	41°46.5'N, 87°00'W	4	8.28	2.18
5	43°00'N, 86°22'W	4	8.36	2.18

[a]Samples obtained 23-24 June 1979.

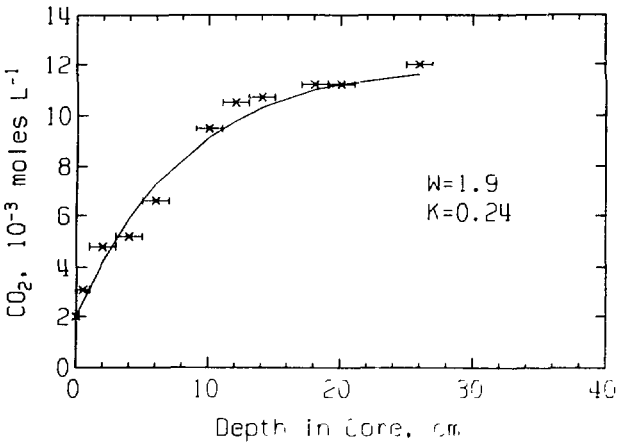

Fig. 1. Measurement of total dissolved CO_2 in sediment interstitial fluid at Lake Erie station 38.

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ELECTROLYTIC PRECONCENTRATION OF CADMIUM FOR DETERMINATION BY MASS SPECTROMETRIC ISOTOPE DILUTION ANALYSIS AND ATOMIC ABSORPTION SPECTROPHOTOMETRY*

J. Muhlbaier, C. Stevens,† D. Grazcyk,‡ and G. T. Tisue

Background and Scope

A reliable value for the present average cadmium concentration was required for construction of a budget for this element in the southern basin of Lake Michigan. However, myriad difficulties attend determinations of ultratrace amounts of heavy metals in environmental materials.[1] Contamination problems can be severe, making special sampling and handling methods obligatory. Ultrahigh purity reagents and special containers add to cost and inconvenience. Samples often require extensive chemical and physical pretreatment to remove interfering species. Even then, preconcentration is frequently necessary to bring amounts within the range of detection. These isolation and enrichment steps add to the risk of contamination and can lead to low recovery.

Preconcentration by electrodeposition offers unique advantages in dealing with these problems. The method is highly selective for metals reducible in aqueous solution, thereby essentially eliminating interference from elements in groups Ia, IIa, and VIIa of the periodic table. Because little or no chemical modification of the sample is usually necessary, the risk of contamination by impure reagents diminishes. By incorporating the working electrode directly into the sample container, one reduces greatly the risk of contamination during transfer and handling. Electrodeposition produces a concentrate of low total mass which is suitable for direct analysis by a variety of techniques, including x-ray fluorescence spectrometry,[2] atomic absorption spectrophotometry (AAS),[3,4] and mass spectrometric isotope dilution analysis (MSID).[5]

The MSID technique is an attractive one for dealing with ultratrace metal analyses because of its high sensitivity and near-absolute specificity. Perhaps its greatest advantage is the elimination of any need for quantitative recovery, once isotopic equilibration is assured. On the other hand, MSID is slow and costly, and requires a high degree of skill. MSID is perhaps best viewed as a reference method against which other simpler and less costly procedures may be evaluated.

Progress in 1979

Using MSID, we have been able to demonstrate that the preconcentration and stripping procedure described below is an efficient, but not quantitative, means of enriching Cd for subsequent determination.

We collected samples at various times and locations in the southern basin of Lake Michigan (see Table 1), using PVC samplers which enter the water closed to avoid contamination by surface microlayers. Subsamples were drained from these devices into the apparatus shown in Figure 1, then amended by the addition of 1 mL of 10% v/v Ultrex HNO_3. For MSID analyses, the acid reagent also contained 25 ng of ^{110}Cd (Oak Ridge National Laboratory, 97.12% isotopic purity).

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*A preliminary account of this work was given at the 2nd Midwest Water Chemistry Workshop, Minneapolis, Minnesota, October 1979.

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Blanks consisted either of specially purified water carried through the entire procedure (including transportation to and from the field), or of reagent-only blanks prepared just prior to analysis.

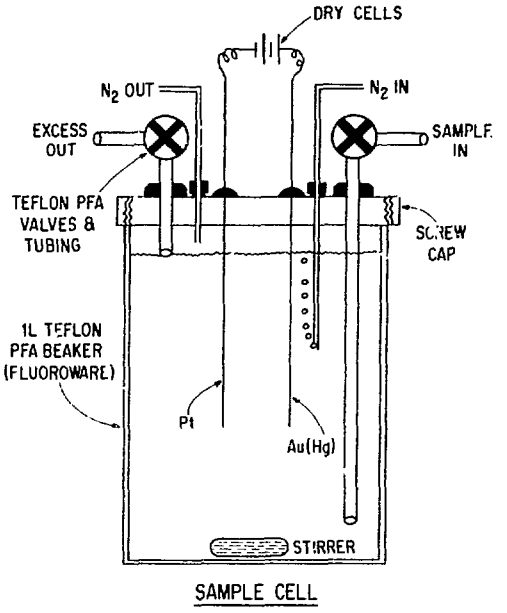

Fig. 1. Sample cell.

Although electrodeposition can be carried out readily in the field, we transported the samples to the laboratory, allowing at least 48 hours for isotopic equilibration. Allen's studies demonstrate that this interval is sufficient for added and endogenous Cd to attain equilibrium with the ligands present in lake water.[6]

With three 1.5 V dry cells connected in series across the electrodes a current of 2 to 3 mA flowed through the cell. Higher current densities lead to excessive electrolysis of water, evidenced by copious gas formation at both electrodes. During electrolysis, the solution must be purged continuously with a slow stream of N_2 or Ar to prevent accumulation on the cathode of a voluminous white solid. Mass spectrometry showed this deposit to contain large amounts of Ca, Mg, and Sr, probably deposited as oxides and suboxides. Tests showed that deposition of Cd ceased within a week. Following this interval, the cathode was removed and stripped with 200 µL of 10% v/v HNO_3 for subsequent analysis by AAS or MSID. Stripping and analysis of the anode showed that essentially all the deposited Cd was on the cathode.[4] For a 1 L sample, quantitative deposition and stripping would result in a concentration factor of 5,000.

We also used an alternate means of preconcentration that consisted simply of allowing 25 mL of sample to evaporate to dryness at room temperature in a Class 100 clean air enclosure. The residue was dissolved in 1 mL of 10% HNO_3 for direct analysis by AAS. This method is straightforward, but removes no interferences and achieves a concentration factor of only 25.

Table 1 shows the results of all our analyses by these various methods. The mean of the

Table 1. Determinations of Cd in Lake Michigan by various methods.

Collection site, date, depth	Analytical method[a]	Storage container[b]	Cd, 10^{-9} g L^{-1} mean of replicates ± 1 σ (blank corrected)
Station 5			
Jun 1978, 7.5 m	EVAP/AAS	Teflon PFA	26.0 ± 8.1
Jun 1978 60 m	EVAP/AAS	Teflon PFA	12.0 ± 4.6
Sept 1978, 8 m (depth = 63 m)	EVAP/AAS	LPE	27.3 ± 4.6
Station 78-1			
Sept 1978, 10 m	EVAP/AAS	LPE	29 5 ± 8.0
Sept 1978, 20 m	EVAP/AAS	LPE	15.9 ± 3.0
Sept 1978, 78 m (depth = 79 m)	EVAP/AAS	LPE	19.9 ± 1.2
Blanks			
Chemical[c]	EVAP/AAS	Teflon PFE	3.6 ± 4.4 (n = 16, range: ND - 9.5)
System[d]	EVAP/AAS	Teflon PFE	1.8
System[d]	EP/MSID	LPE	4.4 ± 0.7
Chemical[c]	EP/AAS	LPE	1.1 ± 0.9
System[d]	EP/MSID	Teflon PFA	ND
Chemical[c]	EP/MSID	LPE	ND
Station 18			
Jun 1978, 2 m	EVAP/AAS	Teflon PFA	45.6 ± 2
Jun 1978, 158 m	EVAP/AAS	Teflon PFA	34.0 ± 18
Sept 1978, 3 m	EVAP/AAS	Teflon PFA	18 (n = 1)
Sept 1978, 100 m	EVAP/AAS	Teflon PFA	28.0 ± 7.5
Sept 1978, 100 m (depth = 160 m)	EP/MSID	Teflon PFA	41.0 ± 6.4
Filtration Plant			
Jan 1978	EP/MSID	LPE	38.0 ± 1.0
Jan 1978	EP/AAS	LPE	24.1 ± 7.8
May 1978	EP/AAS	LPE	23.6 ± 3.9
Aug 1978	EVAP/AAS	LPE	14.5 ± 4.5
Aug 1978	EP/AAS	LPE	25.4 ± 2.0
Aug 1978	EP/MSID	LPE	29.5 ± 7.1

[a]EVAP/AAS = 25-fold concentration by evaporation, graphite furnace atomic absorptionspectrophotometry (standard additions); EP/AAS = electroplating on amalgamated Au electrode,graphite furnace atomic absorption spectrophotometry (standard additions); EP/MSID = electroplating as above, mass spectrometric isotope dilution.

[b]Teflon PFA = perfluoroalkoxy Teflon; Teflon PFE = perfluoreoethylene Teflon; LPE = linear polyethylene.

[c]Reagents, dilution water and laboratory manipulations.

[d]As in (c) above, but also including exposure to containers, collection device, and ship board manipulations.

values in the table is 26.6 x 10^{-9} g L^{-1} (±9.3), or 0.24 x 10^{-9} moles L^{-1}. The relative standard deviation of replicate analyses on individual samples by all techniques averages 22%.

The filtration plant sample of August 1978 was analyzed by all three techniques. There was no significant difference between replicate analyses by AAS and MSID following electrodeposition. With this sample, evaporative preconcentration led to a result lower by almost a factor of two. Low recovery by this technique also is indicated for the sample of September 1978 from 100 m at station 18. The filtration plant sample of January 1978 showed poorer agreement. In this case, the AAS result was 37% lower than the MSID value. However, replicate AAS analyses exhibited a large standard deviation (33% relative), making the difference between the two results barely significant at the 95% confidence interval. For preconcentration by electrodeposition, blank values varied from undetectable to several ng L^{-1}, and averaged about 2 ng L^{-1}. The observation of very low blank values in several cases suggests that further experience with the technique will yield an even lower average.

The close agreement between the AAS and MSID analyses following preconcentration by electrodeposition indicates that the electroplating and stripping steps are highly efficient if not quantitative. Therefore, the AAS technique would be the method of choice for routine use because of its greater ease and lower cost, provided additional tests indicate that reproducible recovery efficiencies are achievable in practice.

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FIRST ESTIMATE OF A BUDGET FOR TIN IN THE SOUTHERN BASIN OF LAKE MICHIGAN

G. T. Tisue

Background and Scope

In an earlier report, I called attention to unexpectedly high levels of tin in water and surficial sediments of Lake Michigan's southern basin.[1] Collaborators at Scripps Oceanographic Institute subsequently demonstrated[2] that the highest total tin concentrations occurred in epilimnetic water during the stratified period, and that these high concentrations were associated with the presence of di- and trialkyl tin species of anthropogenic origin. Examination of a core[1] from radiometrically dated sediments revealed that there has been nearly a 10-fold increase since 1900 in the flux of tin to the sediments of the southern basin. These discoveries raised questions about the origin, route of entry, chemical speciation, and fate of tin compounds in the Great Lakes. Using the sparse data available, I made an estimate of the tin budget in Lake Michigan. Because of the large uncertainties involved, the result can be regarded only as a guide to additional investigation.

Progress in 1979

To arrive at a budget, I compared the sum of atmospheric and tributary input estimates to an estimate of the flux of tin to the sediments. The total annual runoff from the basin's watershed is about 1.25×10^{13} L y^{-1}. Our limited measurements of total tin in the major tributaries averaged 1.1×10^{-6} g L^{-1}. Combining these values leads to an estimated input of 13.8 tons y^{-1}.

Sievering[3] reports an average Sn concentration of 9.5×10^{-9} m^{-3} in atmospheric aerosol samples from over Lake Michigan. From this value, assuming an average deposition velocity of 0.2 cm sec^{-1} and a lake surface area of 1.84×10^{10} m^2, I calculate 11 tons y^{-1} of Sn enter via dry deposition from the atmosphere.

Our limited measurements indicate the tin content of rain averages about 1×10^{-6} g L^{-1}. Annual precipitation is thought to be about 74 cm y^{-1} in the southern basin. At that rate, wet deposition from the atmosphere brings an estimated 13.6 tons y^{-1} of Sn into the lake. The total loading thus is calculated to be 38.4 tons y^{-1}. Table 1 summarizes these loading estimates and emphasizes the importance of atmospheric sources.

Table 1. Tin fluxes, southern basin of Lake Michigan.

Sources		Sinks	
Tributaries and runoff	13.8×10^6 g L^{-1} (36%)	Outflow	4.3×10^6 g y^{-1}
Atmospheric deposition: wet	13.6 (35%)	Sedimentation	68×10^6 g y^{-1}
dry	11 (29%)		
Total	38.4	Total	72.3

My estimate of the flux of Sn to the sediments (Table 1) is based on Robbins and Edgington's[4] value for the flux of Pb, and on the Sn to Pb concentration ratio in sediment. The present flux of Pb to the sediments of the southern basin is about 300 tons y^{-1}.[4] To estimate

the flux of Sn, I assumed that the Sn/Pb concentration ratio in the surface sediments at ANL station 5 reflects the average ratio for the entire basin. That ratio, 0.23, leads to an estimated Sn flux of 68 tons y^{-1}.

About 1.07×10^{13} L y^{-1} of water flows out of the basin annually. If the bulk concentration of Sn is 0.5×10^{-6} g L^{-1},[1] this outflow removes about 5 tons y^{-1} of Sn. Outflow and sedimentation together remove an estimated 73 tons y^{-1} of Sn from the southern basin. There is only approximate agreement between this value and my estimate of the input flux (38.4 tons y^{-1}). Given the uncertainties involved, closer agreement would be fortuitous. Measurements now under way will permit me to refine these estimates.

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DEPTH PROFILES OF PARTICULATE AND DISSOLVED CALCIUM, AND OF TOTAL CARBONATE CARBON, IN THE SOUTHERN BASIN OF LAKE MICHIGAN

G. T. Tisue, G. M. Arcand,* and B. M. Lesht

Background and Scope

Equilibrium calculations indicate that Lake Michigan is near or above saturation with respect to several carbonate mineral phases throughout the year.† Several factors influencing carbonate precipitation are well recognized, including temperature, pH, total dissolved carbonate carbon, and the concentrations of the precipitating cations, Ca^{++} and Mg^{++}. In theory therefore, precipitation is most likely at higher temperatures especially when the pH also rises as photosynthetic assimilation depletes dissolved CO_2. In practice, however, major uncertainties exist. Carbonate precipitation is thought to be highly episodic, and the timing and extent of these episodes at present defy prediction. In particular, one does not know either the causes or the geochemical significance of heavy precipitation events, or "whitings." Are these events simply notable for their effect on the water's optical properties, or are they important because the coprecipitation of trace elements may constitute a major mechanism for the removal of toxicants from the euphotic zone? It is also conceivable that carbonate precipitation occurs at a lower but continuous pace at other times, and that the cumulative effect of this ongoing process far outweighs that of the more dramatic whitings. It is unknown to what extent resuspension of accumulated sediments contributes particulate carbonates to the overlying water. And, since little carbonate accumulates in the permanent sediments, redissolution is clearly a feature of the annual cycle.

We have initiated a study of carbonate precipitation with the goal being to establish quantitatively the contribution of formation and sinking of autochthonous carbonate particles to the rates of clearance of adsorbed and/or coprecipitated trace elements from the lake's surface waters.[2] There has been a recent report[1] indicating that multispectral images from research satellites may permit large scale visualization of the extent and intensity of carbonate precipitation in the Great Lakes. If this approach proves feasible, it may allow one aspect of toxicant clearance to be evaluated by remote sensing on a lake-wide scale.

Progress in 1979

We made a series of measurements of dissolved and particulate calcium and carbonate carbon at various locations and depths in Lake Michigan's southern basin (Table 1). Total carbonate carbon and dissolved calcium were determined potentiometrically using species-selective

*Faculty Research Participant, Argonne Center for Educational Affairs; Idaho State University.

†Assume $C_T \cong 3 \times 10^{-3}$ M and T = 25°C. At pH = 8, the solubility of $CaCO_3$ (calcite) is $[Ca^{++}] \cong 5 \times 10^{-4}$ M. For $[Mg^{++}] = 5 \times 10^{-4}$ M, and pH = 8, $CaMg(CO_3)_2$ (dolomite) is about equally soluble, giving $[Ca^{++}] \cong 5 \times 10^{-4}$ M; but at pH = 9, dolomite is more stable than calcite, giving $[Ca^{++}] \cong 2 \times 10^{-6}$ M. At pH = 8, $Mg_4(CO_3)_3(OH)_2$ (hydromagnesite) gives $[Mg^{++}] \cong 10^{-5}$ M, and at pH = 9, $[Mg^{++}] = 3 \times 10^{-7}$ M. Average values for Lake Michigan are 8×10^{-4} M and 5×10^{-4} M, for Ca^{++} and Mg^{++}, respectively. These values indicate that, unless C_T falls drastically, higher pH values and temperatures will produce severalfold supersaturation with respect to calcite, dolomite, and hydromagnesite.

electrodes (see accompanying report). Particulate calcium was determined by x-ray fluorescence spectrometric analysis of 0.45 μm and 5 μm Nuclepore membranes through which 1 to 4 L water samples had passed. Both the filtrations and the potentiometric determinations were carried out on shipboard immediately following sample collection. In all the samples examined, >75% of the total particulate Ca was retained on the 5 μm filters, and in the near-bottom samples it was >95%. The values in Table 1 represent >5 μm material.

Table 1. Particulate calcium concentrations in Lake Michigan samples collected 23-24 July 1979.

Station designation	Collection depth, m	Particulate Ca, (5 μm membrane), 10^{-6} g L^{-1}	Temperature °C	pH	Total carbonate carbon, 10^{-3} mol L^{-1}	Dissolved Ca, 10^{-3} g L^{-1}
79-1[a]	5	25	19.0	7.10	1.82	36.3
	16	22	17.3	7.65	1.79	35.2
	30	23	7.0	7.53	1.92	35.5
	64	116		6.76	2.10	35.6
79-2[b]	5	18	17.8	8.40	2.09	35.4
	21		9.2			
	36		6.1			
	71					
79-3[c]	4		20.8	8.28	2.18	35.8
ANL-5[d]	4		16.4	8.36	2.18	36.2
ANL-18[e]	4	12	19.3			35.5
	16	16	17.3			
	24	17	8.2			
	30	22	7.0			
	40	21	6.0			
	50	21				
	75	28				
	100	33				
	125	70				
	147	138				
	150	136				
	153	116		7.45		

[a]42°08'N, 87°23'W

[b]42°08'N, 86°46'W

[c]41°46.5'N, 87°00'W

[d]43°00'N, 86°22'W

[e]42°40.5'N, 86°56.5'W

Two facts are made obvious by these data. First, particulate calcium, putatively in the form of carbonate minerals, is ubiquitous in the waters of the southern basin. Its occurrence is not limited to episodes, or whitings. However, these solids represent a quantitatively insignificant fraction (<1%) of both total calcium and total carbonate carbon present in the water column, except perhaps in near-bottom nepheloid layers. At least an order of magnitude increase in suspended carbonate mineral content would have to occur during whitings to affect materially the concentrations of dissolved Ca and total carbonate carbon.

A corollary of this conclusion is that only relatively dramatic carbonate precipitation

will be detectable by means of analyses for dissolved Ca^{++} or total carbonate carbon.

Another salient feature of the data in Table 1 is the regular logarithmic increase in particulate calcium concentration with depth. Figure 1 shows this relationship. The solid lines on the plot represent best fits to the data of the relationship:

$$C_z = C_0 \varepsilon^{mz},$$

where C_z = particulate calcium concentration at depth z, C_0 = particulate calcium concentration at the surface, ε = vertical eddy diffusivity coefficient, z = depth in the water column, $m = w_s \varepsilon^{-1}$, and w_s = Stokes settling velocity.

The slopes of these semilogarithmic plots, $m = w_s \varepsilon^{-1}$, have a mean value of 0.026 (σ = 0.009), whose inverse, 39 m, may be taken as a measure of the scale length for resuspension.[1,2] Another measure of this scale length is the half-depth, $z_{1/2}$, where $C_z = C_f/2$ (C_f = inferred value of C_z at the sediment-water interface). In our three examples the mean value of $z_{1/2}$ is 31 m (σ = 13).

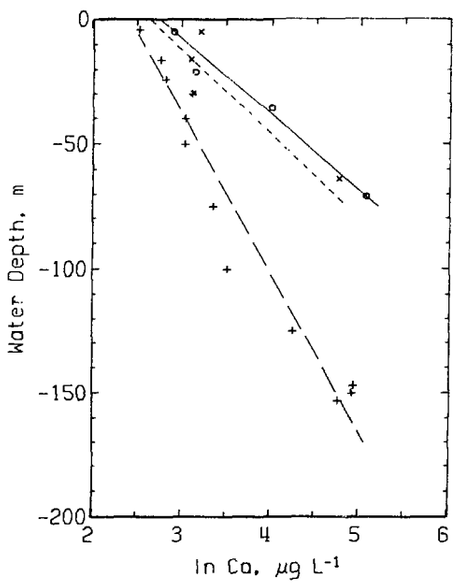

Fig. 1. Relationship of calcium concentration to water depth. x, Station 79-1, $C_z = 15.4\ e^{0.028z}$; o, Station 79-2, $C_z = 13.9\ e^{0.034z}$; +, Station 18, $C_z = 11.1\ e^{0.015z}$.

Chambers and Eadie[3] have studied seston accumulation rates as a function of depth and time of year, using fixed sediment traps. Their flux profiles are also logarithmic to a good first approximation. We calculated resuspension scale lengths, 1/m, using their data. For their stations deeper than 60 m, 1/m varied by a factor of about three, from a maximum of 56 m (±28) during April-June, to a minimum of 16 m (±10) during September-November. The average value for June-September was 23 m (±8). This seasonal variation is probably attributable to changes in the vertical eddy diffusivity for small particle settling. These changes reflect decoupling of turbulent motion in the epilimnion from the hypolimnetic waters as thermal stratification develops. In any case, the conformity of total seston accumulation rates with our estimates of

the resuspension scale length determined for particulate Ca alone is sufficiently good to suggest that resuspension plays an important role in the dynamics of carbonate mineral concentrations in the southern basin.

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HAS THERE BEEN A LONG-TERM SILICA DEPLETION IN LAKE MICHIGAN?*

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

Increased phosphorus loading over the last 30 years has caused increased diatom production. It has been suggested that the greater fixation of SiO_2 has resulted in a permanent depletion of soluble SiO_2 (from 4.5 to 1.7 mg L^{-1} between 1963 and 1976) in the water column. Since the hydraulic residence time is ~100 y almost all the silica must still be in the lake in particulate form either in the water column or in the sediments. If in the water column, the particulate SiO_2 concentration must be ~2.5 mg L^{-1}, a value far greater than measured except during the summer months. Alternatively, as the average depth is ~100 m, ~25 mg cm^{-2} amorphous SiO_2 should be in the sediments. For an average sedimentation rate of 8 to 10 mg $cm^{-2}y^{-1}$ the fraction of amorphous SiO_2 in recent sediments would be <25%. Measured fractions are almost 10-fold less in cores, representative of the depositional basins, taken in 1976. As there is no sink for lost SiO_2, questions must be raised concerning the validity of the earlier data. The concentrations of soluble reactive silica in other comparable water bodies, unaffected by phosphorus loadings, are approximately the same as those measured in Lake Michigan today.

*Abstract of paper presented at Great Lakes-80, 23rd Conference of the International Association for Great Lakes Research, Queen's University, Kingston, Ontario, 19-22 May 1980.

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A COMPUTER SIMULATION OF THE ENERGETIC EFFECTS ON BROWN TROUT THAT RESIDE IN HEATED EFFLUENTS*

W. K. Derickson,† S. A. Spigarelli, and M. M. Thommes

Background and Scope

Typically, thermal impacts on fish are considered to be insignificant by assessors, because very few data exist that document acute thermal effects in nature. This study presents data and bioenergetic simulations indicating that thermal effluents may have more of an effect on fish than previously anticipated.

An underwater telemetry system was employed to compile lengthy (up to 650 hours) thermal histories of 43 Lake Michigan brown trout during their residence in a power plant thermal plume and adjacent ambient temperature waters. Using the temperature selection (exposure) data obtained with telemetry, seasonal and annual energy budgets were computed, using equations specific to brown trout.

Progress in 1979

Energy availabilities within and outside the plume area were estimated from acoustic measurements of forage fish distribution with temperature. Caloric requirements and availabilities for plume-resident trout were compared to those of trout occupying ambient temperature waters.

Metabolic demands of plume resident trout were most elevated (relative to ambient conditions) during winter when forage was least available. Under the worst conditions (winter) trout frequenting the thermal plume had the potential for larger losses in weight and fecundity than fish residing in ambient water. Under the best conditions (e.g., moderate plume exposure and high food availability in early summer) plume-resident trout had the potential for higher gains in weight and fecundity. Over the annual cycle, trout not exposed to thermal enrichment had the greatest potential for gains in weight and fecundity.

*Abstract submitted for the 110th Annual Meeting of the American Fisheries Society, Louisville, Kentucky, 21-24 September 1980.

†Environmental Impact Studies Division, Argonne National Laboratory.

THERMAL AND SPATIAL DISTRIBUTION OF FISH IN LOCALLY HEATED AND UNHEATED AREAS OF LAKE MICHIGAN*

R. M. Goldstein,† S. A. Spigarelli, W. Prepejchal, and M. M. Thommes

Background and Scope

Some studies have suggested that fish are attracted to thermal discharges into Lake Michigan; however, actual densities and distribution patterns of fish and the interactions with factors other than temperature have not been elucidated. As a basis for evaluating the significance of thermal effects on trophic relationships, the distributional responses of fish were compared between heated and unheated areas over a two-year period. Spatial and thermal distribution and abundance of fish were determined by acoustic locator and thermal plume mapping techniques near three thermal discharges to Lake Michigan.

Progress in 1979

Echograms and temperature profiles obtained from transects along bottom contours were converted to densities of fish at (1) defined areal regions, (2) bottom depth zones, (3) water column depth strata, and (4) 1°C isotherms for comparison between plume and reference areas. The overall densities of fish often were similar at plume and reference areas. Greater inshore abundances occurred consistently at both types of areas but, at the plume areas, inshore densities occasionally differed by two orders of magnitude from one side of the discharge to the other and from the reference areas. Frequency distributions of fish density with temperature were used to determine selection and avoidance. Selected temperatures were usually at the upper end of the range of reference temperature zones sampled; and in the plume areas, usually 2° to 3°C above the highest temperature found at the reference area. In spring and fall, density distributions with temperature were unimodal at both plume and reference areas, but during summer the distributions were bimodal. Thermal distributions were related to the local abundance of alewife and smelt.

Prospects

The results of these analyses will be used to evaluate the biomass (energy) available to piscivorous fishes that are attracted to thermal effluents. Studies of thermoregulatory responses by plume-resident, piscivorous fishes show large seasonal differences in energy requirements (energetic costs of plume-residence) and these data on forage density/distribution will allow realistic evaluations of the impacts of thermal plumes on (1) growth and reproduction of salmonid fishes; (2) salmonid predation on forage species in locally heated areas; and (3) trophic transfer of toxic pollutants into the human food chain.

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*Abstract submitted for the 110th Annual Meeting of the American Fisheries Society, Louisville, Kentucky, 21-24 September 1980.

†Environmental Impact Studies Division, Argonne National Laboratory.

DEVELOPMENT OF ZOOPLANKTON COMMUNITY RESPONSES TO ADDED CADMIUM OR ZINC DURING 4-WEEK IN SITU EXPERIMENTS IN SOUTHERN LAKE MICHIGAN

J. S. Marshall, D. L. Mellinger, and J. I. Parker

Background and Scope

In 1976, we developed an in situ experimental method for studies of heavy metal effects on Lake Michigan plankton communities.[1] Our objectives were to assess the potential effects of increased concentrations of heavy metals in Lake Michigan and, ultimately, to gain a better understanding of plankton community responses to chemical stress. During 1976-1977, we studied the short-term (4- to 21-day) effects of added cadmium on the plankton community in Green Bay, Lake Michigan.[2,3] Cadmium additions as low as 0.2 µg Cd/L caused significant reductions of phytoplankton photosynthesis (indicated by dissolved oxygen measurements) and zooplankton community similarity indices. Direct effects of chronic (3-week) cadmium toxicity to the zooplankton were greatly modified by species (trophic) interactions. For example, reductions of total zooplankton density by cadmium were compounded by simultaneous reductions of phytoplankton (food) production. At the same time, populations of some zooplankton species increased at the lowest added cadmium concentrations.[2] In 1978 we studied the effects of cadmium and zinc additions, both separately and combined, on the plankton community in Green Bay. This study indicated that if Zn/Cd ratios remain >50:1 (by weight), the combined effects of increased concentrations of these metals in Lake Michigan would be primarily due to zinc alone.[4]

Progress in 1979

Two in situ experiments were conducted in the southern basin of Lake Michigan to determine and compare the temporal development of zooplankton responses to separate additions of cadmium (4 µg Cd/L) and zinc (100 µg Zn/L) over periods of 4 weeks. Quantitative analyses of the enclosed zooplankton communities (both rotifers and crustaceans) in duplicate controls (28 L polyethylene carboys), one Cd-treated enclosure and one Zn-treated enclosure, were made at weekly intervals. Dissolved oxygen and radiotracer (^{109}Cd and ^{65}Zn) concentrations in filtered (54 µm) water samples and net plankton (fraction retained by 54 µm net) from the enclosures removed from the lake each week were also measured. Field and laboratory procedures were the same as those used in our Green Bay studies.[2,3]

Preliminary results from the first of these experiments indicate that the effects of initial additions of both metals on the zooplankton (rotifers and crustaceans) tended to increase with time, although the effects of added zinc were consistently greater than those of cadmium (Figure 1). Dissolved oxygen concentrations (Table 1) also indicated more pronounced effects from added zinc than from cadmium. The mean dissolved oxygen concentration for weeks 1-4 in Zn-treated enclosures (9.8 ± 0.2 mg O_2/L) was significantly lower than that for controls (10.4 ± 0.1 mg O_2/L) whereas the average concentration of dissolved oxygen in Cd-treated enclosures (10.0 ± 0.2 mg O_2/L) is not significantly different from that for controls. Concentrations of added cadmium and zinc remaining in the water in Cd- and Zn-treated enclosures (not on enclosure walls), as calculated from specific activities of added ^{109}Cd and ^{65}Zn, did not decrease significantly during the 4-week period (Table 2). The percentages of ^{109}Cd and ^{65}Zn removed from water filtered through a 54 µm net were significantly correlated with the numbers of crustaceans per liter (Figure 2). This suggests that most of the radioisotope in net plankton was bound in the crustacean component, although some was probably also bound by

rotifers and colonial phytoplankters retained by the 54 μm net. The higher regression coefficient for ^{65}Zn than for ^{109}Cd (Figure 2) may reflect a higher plankton concentration factor for zinc, an essential trace element, than for cadmium, which is not essential.

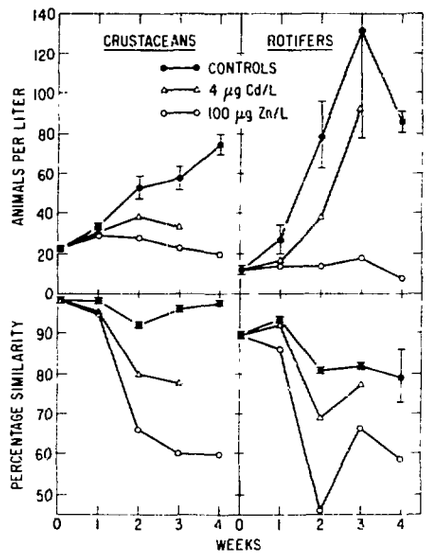

Fig. 1. Effects of initial additions of 4 μg Cd/L and 100 μg Zn/L on numbers of animals per liter and percentage similarity index for crustacean zooplankton and planktonic rotifers after in situ incubations in Lake Michigan of one to four weeks.

Table 1. Dissolved oxygen concentrations (mg O_2/L) in Cd- and Zn-treated enclosures and controls 1-4 weeks after additions of 4.0 μg Cd/L or 100 μg Zn/L (12 June-10 July 1979).

Week	Controls	Cd-treated	Zn-treated
1	10.3 (2)[a]	10.2 (1)	10.0 (1)
2	10.8 (2)	10.1 (1)	10.5 (1)
3	10.1 (2)	9.7 (1)	9.6 (1)
4	10.4 (3)	--	9.0 (1)

[a]Number of enclosures.

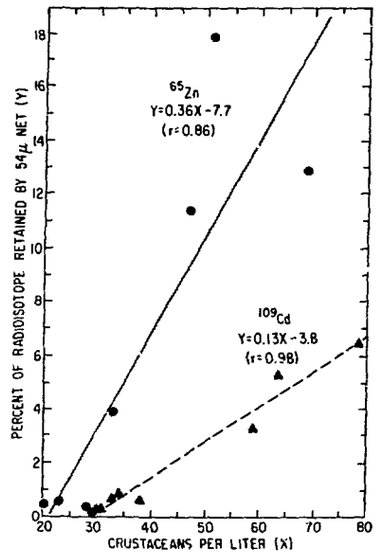

Fig. 2. Relationships between percentages of ^{65}Zn and ^{109}Cd retained by a 54 μm net and numbers of crustaceans per liter.

Table 2. Added cadmium and zinc concentrations (μg/L) in Cd- and Zn-treated enclosures 1-4 weeks after additions of 4.0 μg Cd/L or 100 μg Zn/L (12 June - 10 July 1979).

Week	μg Cd/L	μg Zn/L
1	3.8 (1)[a]	104 (1)
2	4.2 (1)	106 (1)
3	3.1 (1)	86 (1)
4	--	86 (1)

[a]Number of enclosures.

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SEASONAL VARIATIONS OF ZOOPLANKTON POPULATIONS IN AN ISOLATED BAY AND OPEN AREAS OF ELA 382 DURING 1978 AND 1979

D. L. Mellinger, J. S. Marshall, and D. F. Malley*

Background and Scope

An oligotrophic, Precambrian Shield lake in the Experimental Lakes Area of Canada was selected as the site for a long-term project to study the fates and effects of added pollutants on aquatic communities. This project is directed by personnel of the Department of Fisheries and Oceans, Freshwater Institute, Winnipeg, Manitoba. In the spring of 1978, the large southwestern bay (3 ha) was isolated, by means of a sea curtain, from the rest (32 ha) of ELA Lake 382. Zooplankton samples were collected in the isolated bay and open lake at approximately weekly intervals during the summer and fall of 1978.[1] These data provide a basis for assessing the effects of isolation on the zooplankton community of the bay as well as establishing pretreatment seasonal population trends.

Progress in 1979

During 1979, the bay in the southeastern corner of the lake was added to the weekly sampling routine (Figure 1). This region (uncurtained bay) is more closely comparable, in terms of average depth, to the isolated (curtained) bay than the open lake. The major taxa of rotifers and crustacean zooplankton enumerated in 1978 (14 dates) and 1979 (11 dates) are shown in Figures 2 and 3, respectively.

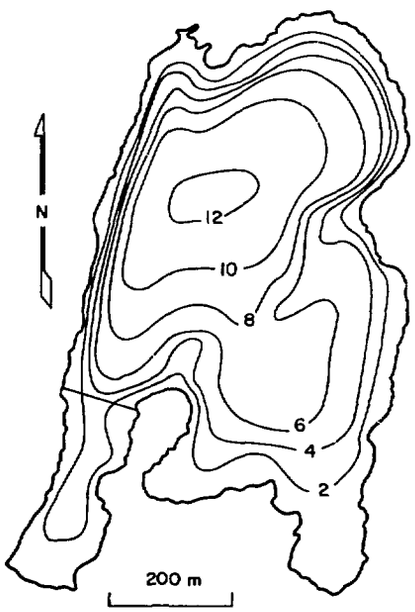

Fig. 1. Bathymetric chart of ELA Lake 382. The solid line across the mouth of the southwestern bay indicates the position of the sea curtain.

*Department of Fisheries and Oceans, Freshwater Institute, Winnipeg, Manitoba, Canada.

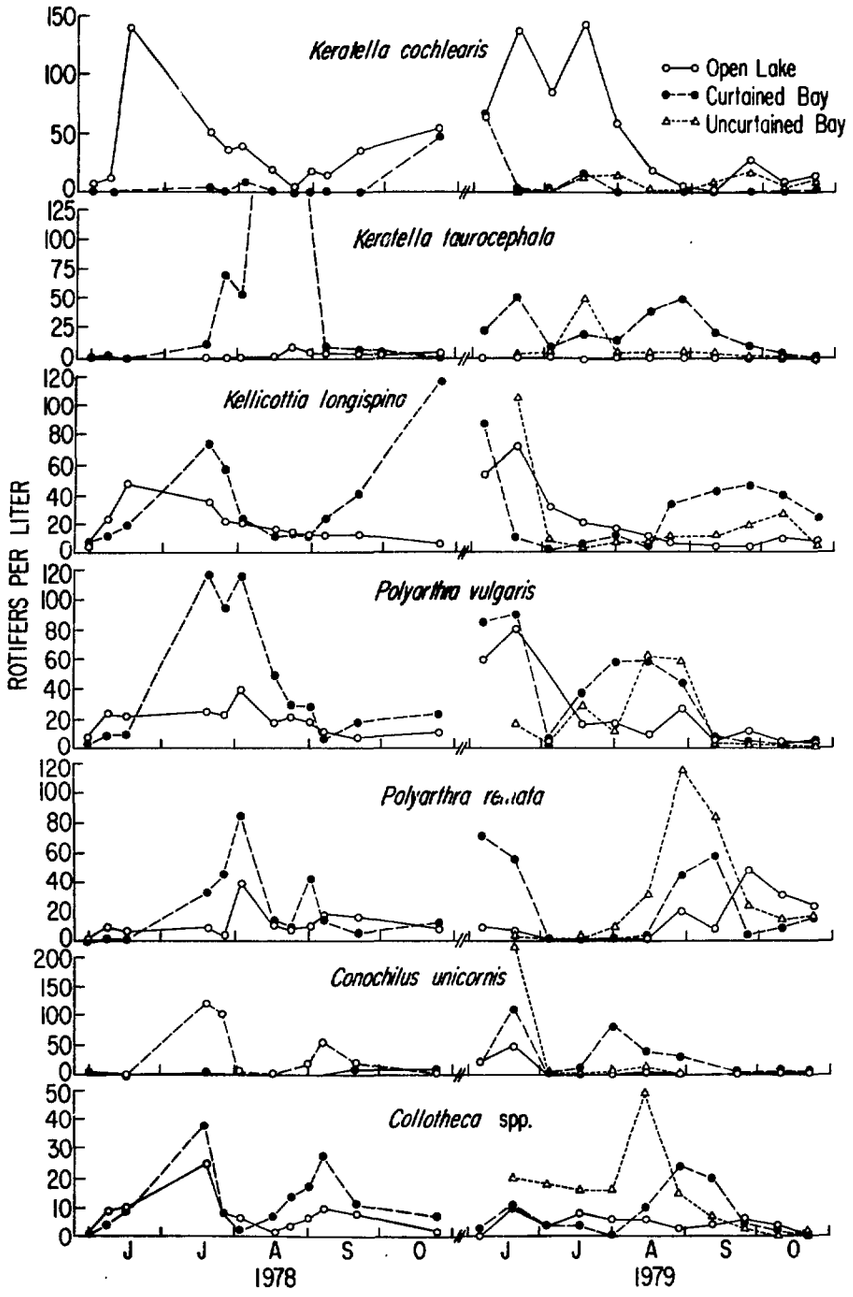

Fig. 2. Seasonal distributions of the major species of rotifers (number/L) in ELA Lake 382.

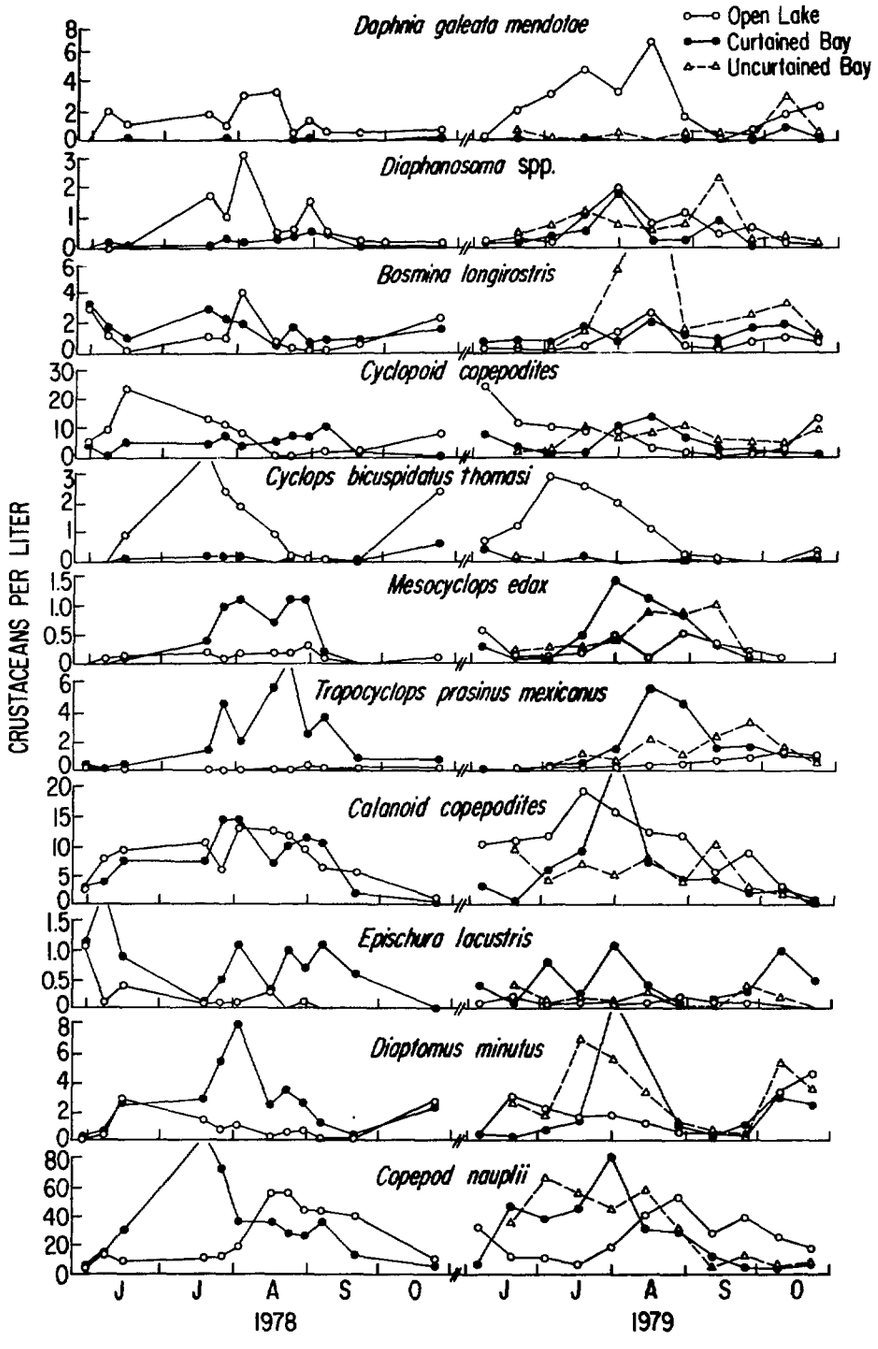

Fig. 3. Seasonal distributions of various categories of crustacean zooplankton (numbers/L) in ELA Lake 382.

Within the rotifer community, the temporal distribution patterns of some taxa were quite variable. For example, Keratella taurocephala achieved a concentration or greater than 400 animals/L in the curtained bay during August 1978 compared to 50 animals/L during the same period in 1978. This degree of variation is not surprising since these organisms have great reproductive capacity which enables them to respond quickly to favorable conditions. In contrast to K. taurocephala, K. cochlearis exhibited very similar seasonal patterns in both years although this species had a markedly higher density in the open lake than it did in the bays. While differences of various rotifer populations in the three regions were apparent during 1979, the mean densities of total rotifers were not significantly different: curtained bay, 144 ± 31; uncurtained bay, 139 ± 32; open lake, 128 ± 31 animals/L ($\bar{x}$ ± S.E.).

The temporal patterns seen within the crustacean community tend to be more consistent than they are for the rotifer community. Clearly, certain crustacean species achieved higher densities in one region than they did in the other two. Holopedium gibberum and Daphnia galeata mendotae had consistently lower densities in the curtained bay than in the uncurtained bay or the open lake. The densities of Bosmina longirostris, on the other hand, were similar in the curtained bay and the open lake while in the uncurtained bay, a population pulse occurred during August 1979 that was not evident in the other two regions. Cyclops bicuspidatus thomasi adults were found mainly in the open lake during the sampling period while Mesocyclops edax and Tropocyclops prasinus mexicanus were present in greater concentrations in the bays. Calanoid copepods represented a major portion of the crustacean community in all three regions. In 1979, the mean densities of crustaceans (exclusive of nauplii) in the curtained bay, uncurtained bay, and open lake were 18 ± 5, 22 ± 3, and 26 ± 3 animals/L ($\bar{x}$ ± S.E.), respectively.

Using a similarity index, percentage similarity (PS), to compare the curtained bay with the uncurtained bay on ten dates during 1979 yielded a mean PS of 53.2 ± 3.0 for rotifers and 69.3 ± 4.8 ($\bar{x}$ ± S.E.) for crustaceans. The open lake-curtained bay comparison for 1979 produced a mean PS of 41.2 ± 4.4 for rotifers and 61.1 ± 3.9 for crustaceans. These 1979 open lake-curtained bay means are not significantly different from those of 1978, 44.8 ± 3.3 for rotifers and 54.2 ± 2.3 for crustaceans.

The data collected to date suggest that the zooplankton community of the curtained bay continued to be similar to that of the rest of the lake. Although there were differences in the timing and intensity of the pulses of various species, the population trends in the two bays were generally quite similar during 1979.

Reference

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EFFECTS OF FOX RIVER WATER ON PHYTOPLANKTON PHOTOSYNTHESIS AND ZOOPLANKTON POPULATIONS IN GREEN BAY

J. I. Parker, J. S. Marshall, D. L. Mellinger, and C. W. Kennedy

Background and Scope

The effects of incremental additions of filtered Fox River water on phytoplankton and zooplankton from central Green Bay were investigated in an in situ time-series experiment during 5-21 August 1979. We were invited to cooperate in the experiment by The University of Michigan, Great Lakes Research Division. The overall goal of the experiment was to determine the influence of nutrient and pollutant-rich Fox River water on the plankton community in Green Bay. Our purpose in joining this effort was to evaluate the utility of a new in situ plankton bioassay technique[1] for the detection of both stimulating and inhibiting effects on the plankton community. The plankton community bioassay has been used successfully to document the effects of added toxic trace elements. However, its capabilities in detecting the effects on the plankton community by a natural mixture of pollutants (Fox River water) has not been tested.

Progress in 1979

We collected the Fox River water samples to be used for treatment at Green Bay, Wisconsin, and filtered them through a 0.2 μm Gelman pleated filter. We collected Green Bay samples from a depth of 4 m at station A located 17.5 km northeast of Menominee, Wisconsin. We decanted bay water into 8 L polyethylene carboys and treated them with either 0.0, 0.1, 1.0, 5.0 or 10% (v/v) additions of filtered Fox River water. The effects of dilution were normalized among all samples by adding the appropriate amount of filtered bay water to produce the same dilution ratio in each carboy. Three arrays of 15 carboys each were deployed at the station of bay water collection. The four treated and one control carboy were incubated at 3.0, 4.5, and 6.0 m below the surface. One array was retrieved for analysis each day for three consecutive days (6-8 August 1979) and a fourth carboy array was prepared and deployed for a two-week incubation period (6-21 August 1979) After retrieval of an array, sufficient water was decanted from each carboy for analyses of algal photosynthesis, chlorophyll a, micronutrients, and phytoplankton and zooplankton community structure parameters.

The rate of algal photosynthesis measured daily in bay water samples ranged between 40 and 50 mg $C/m^3 \cdot hr$. The carboys treated with various additions of Fox River water showed a marked stimulation of algal photosynthesis compared to the control carboys, with progressively greater rates at each successively higher treatment level. The effect became particularly distinctive by the third day when the rates were distributed sequentially according to treatment level (Figure 1). The separation between the treated and control samples became less obvious at 16 days after treatment and the stimulating effects of the Fox River water additions appeared to wane.

The average densities of total rotifers (Table 1) in carboys treated with 0.1 to 5.0% additions of filtered Fox River water were significantly higher than those for the controls (Figure 1). Whereas, the average densities of total crustaceans showed no significant differences (Figure 1). The increase of rotifers could have been caused by something in the filtered Fox River water at the time it was added or subsequently secreted by phytoplankton as a result of their stimulated photosynthesis. It seems less likely that the increased rotifer population could have responded to an increased phytoplankton cell population in only three days.

Table 1. Average densities of rotifers (#/L) in enclosures treated with different additions (% volume) of filtered (0.2 μm) Fox River water after 3 days of in situ incubation in northwestern Green Bay, Lake Michigan, August 1979.

Species	0% n = 3	0.1% n = 3	1.0% n = 3	5.0% n = 3	10.0% n = 3
Keratella cochlearis	28 ± 14[a]	81 ± 11	47 ± 4	84 ± 9	49 ± 8
K. crassa	56 ± 6	61 ± 6	55 ± 6	52 ± 8	61 ± 4
K. earlinae	1 ± 1	15 ± 1	18 ± 4	21 ± 4	8 ± 5
Trichocerca multicrinis	17 ± 2	18 ± 6	25 ± 0	18 ± 6	21 ± 1
T. cylindrica	1 ± 1	1 ± 1	0	1 ± 1	0
T. porcellus	0	0	0	0.3 ± 0.3	0
Ascomorpha ecaudis	8 ± 1	11 ± 1	13 ± 2	15 ± 3	9 ± 6
Asplanchna priodonta	5 ± 4	5 ± 5	13 ± 3	11 ± 4	16 ± 2
Synchaeta stylata	0	0	0	0	1 ± 1
Ploesoma spp.	1 ± 1	1 ± 1	1 ± 1	0.3 ± 0.3	1 ± 1
Polyarthra vulgaris	340 ± 86	370 ± 68	570 ± 19	502 ± 84	379 ± 33
P. major	51 ± 6	81 ± 10	89 ± 15	118 ± 7	64 ± 9
P. euryptera	2 ± 1	3 ± 3	1 ± 1	1 ± 1	1 ± 1
P. remata	31 ± 6	46 ± 9	45 ± 8	76 ± 11	54 ± 9
Pompholyx sulcata	6 ± 1	3 ± 1	7 ± 3	3 ± 1	1 ± 1
Filinia longiseta	2 ± 0	0	4 ± 1	1 ± 1	3 ± 1
Concochilus unicornis	13 ± 8	24 ± 11	18 ± 4	10 ± 0	16 ± 3
Collotheca mutabilis	1 ± 1	7 ± 1	3 ± 2	3 ± 1	3 ± 1
Brachionus cf. angularis	0	0	0	0	1 ± 1
Total rotifers	588 ± 89	736 ± 86	919 ± 20	923 ± 106	706 ± 29

[a]mean ± standard error for n enclosures.

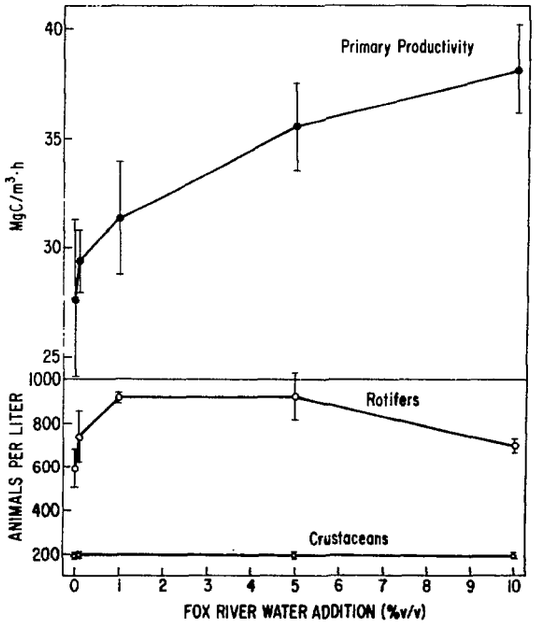

Fig. 1. Dose response relationship of total crustaceans and rotifers and algal primary productivity to incremental additions of Fox River water, measured on day three.

The dissolved nutrient concentrations in the Fox River water were 0.5 µmol/L orthophosphate-P, 62 µmol/L SiO_4-Si, and 2.5 µmol/L NO_3-NO. At the start, the dissolved nutrient concentrations in the Green Bay station were 0.165 µmol P/L, 12.4 µmol Si/L, and 2.0 µmol N/L. The additions of Fox River water provided incremental increases in the concentration of silicon measured in the treated carboys (Figure 2). The nitrate levels were not measurably affected by the treatment additions. The total P available in the carboys was increased by the treatment addition, but no increase was measurable. This was likely due to rapid luxury uptake of P by algae within the first few hours after the treatment additions. The rapid decline in P from the beginning of the experiment to day 3 and the downward trend in silicon levels of the treated samples from day 1 through day 3 suggests that both nutrients were being utilized by the phytoplankton community (Figure 2). The concommitant increases in algal photosynthesis supports the conclusion that Fox River water inputs to Green Bay have a substantial impact on the rate of algal photosynthesis and the ambient algal crop.

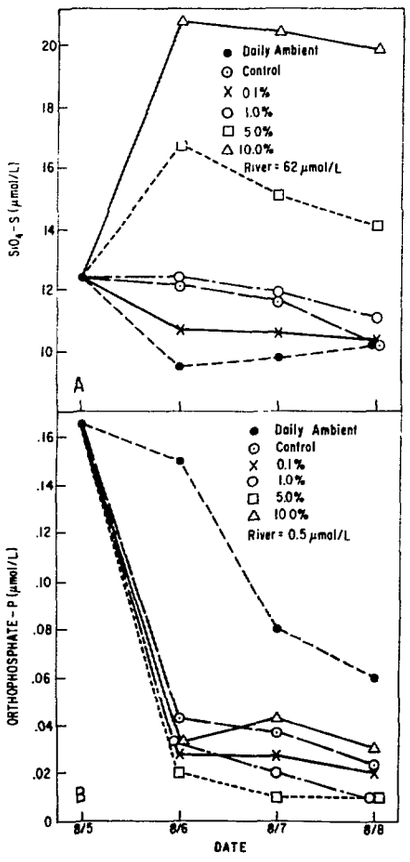

Fig. 2. Daily changes of dissolved silicon and phosphorus among the treated and control carboys, and the bay water (ambient) at station A.

The geographical extent of an affected zone in Green Bay was assessed by making a continuous measurement of chlorophyll a, and suspended solids during a surface water transect (2 m below the surface) from Green Bay, Wisconsin, to the incubation station. It showed an abrupt decline in both variables at 15 km north of the mouth of the Fox River (Figure 3). These observations suggest that during this period approximately one-third of the southern arm of Green Bay is heavily impacted by nutrient enrichment from the Fox River.

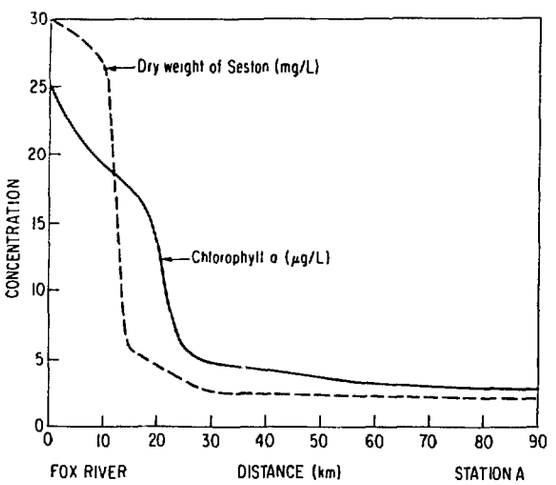

Fig. 3. Surface water transect of the chlorophyll a concentration and dry weight of total seston from the mouth of the Fox River to the in situ incubation station A.

Prospects

Further funding for the experiment has been obtained by The University of Michigan, and our continued cooperation has been requested. Since the response by crustaceans was inconclusive in the first 3-day experiment, the length of future tests will be at least one week and a 25% v/v Fox River water treatment will be added.

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EFFECTS OF ATMOSPHERIC PRECIPITATION ON PRIMARY PRODUCTIVITY IN LAKE MICHIGAN*

J. I. Parker, G. T. Tisue, C. W. Kennedy, and C. A. Seils

We tested the effects of incremental additions (0.1-50.0% v/v) of atmospheric precipitation on algal primary productivity (^{14}C) in Lake Michigan water samples. We used wet deposition in experiments I, III , and IV, and a melted snow core in experiment II. A significant reduction in productivity occurred in experiments I-III. No significant difference occurred in experiment IV, but carbon uptake was greater than in the control samples and this precipitation sample appeared to simulate productivity. Phosphate, nitrate, and ammonia levels in the precipitation samples exceeded the lake water averages by factors of 10, 2 and 50, respectively. Silicon levels in precipitation were lower than in the lake water by a factor of 5. Addition of precipitation reduced pH very little, while alkalinity was dramatically reduced. Zn, Cu, Pb, Ni, Cd, and Sn levels in the precipitation samples greatly exceeded the lake water averages. These observations suggest that atmospheric precipitation contains constituents such as nutrients and toxic trace elements that competitively interact to either stimulate or depress algal photosynthesis.

*Abstract of a paper presented at the Great Lakes-80, 23rd Conference of the International Association for Great Lakes Research, Queen's University, Kingston, Ontario, 19-22 May 1980.

HISTORICAL INPUTS OF AIRBORNE POLLUTANTS IN CAROLINA BAY LAKES

B. L. Proctor and D. N. Edgington

Background and Scope

Current and anticipated nuclear industry necessitates determination of baseline data for environmental monitoring programs for the Barnwell Nuclear Fuel Plant and airborne pollutants in general. Undisturbed Carolina Bay Lakes are ideal regional pollution monitors. They are primarily rain fall collectors with very restricted drainage basins. There is minimal surface runoff due to the high permeability of the surface soils. Also the bays are generally located in highly leached soils.[1-3]

The purpose of this preliminary study was to determine the concentrations of Ni, Pb, ^{137}Cs, ^{210}Pb, and $^{239,240}Pu$ in vertical sediment cores from several Carolina Bay Lakes on or near the Savannah River Laboratory and the Barnwell Nuclear Fuel Plant (Figure 1).

Progress in 1979

A series of sediment cores was collected along the NW-SE axis in four Carolina Bay Lakes. These cores were analyzed for several heavy metals[4] and radionuclides.[5,6]

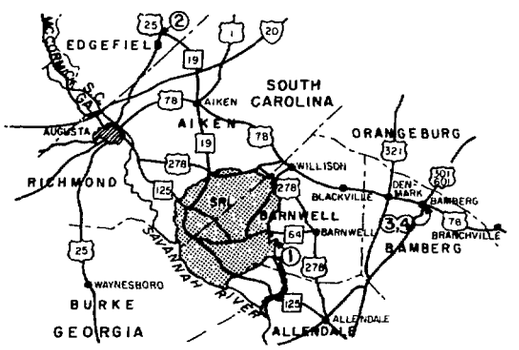

Fig. 1. Carolina Bay Lakes near the Savannah River Laboratory (SRL) and the Barnwell Nuclear Fuel Plant. 1, Thunder Bay, SRL; 2, Trenton Airport Pond, Trenton, S.C.; 3, Clear Lake, Bamberg, S.C.; 4, Little Clear Pond, Bamberg, S.C.

The vertical concentrations of Ni, Pb, Zn, ^{137}Cs, ^{210}Pb, and $^{239,240}Pu$ in sediments collected from the center of each Carolina Bay Lake are presented in Table 1. The sedimentation rates calculated from the radionuclide profiles are presented in Table 2.

Table 1. Vertical concentrations in sediments collected from the center of each Carolina Bay Lake.

Depth	μg/g (dry)			pCi/g (dry)		fCi/g (dry)
cm	Ni	Pb	Zn	^{137}Cs	^{210}Pb	$^{239,240}Pu$
Thunder Bay						
1	70	200	182	2.4	1.6	71
2	70	200	220	5.4	0.95	83
3	50	98	309	3.89	1.3	129
4	57	159	156	1.4	0.93	150
5	80	248	94	--[a]	0.54	68
6	57	107	71	--	0.2	1.8
7	80	134	98	--	ND[b]	2.0
8	71	111	90	--	ND	1.9
9	61	95	65	ND	ND	lost
10	--------lost--------			ND	0.24	1.3
14	47	74	55	ND	ND	ND
18	57	95	68	ND	0.134	ND
Trenton Airport Pond						
1	167	236	247	6.84	3.9	167
2	98	298	217	3.58	1.8	189
3	87	134	133	2.1	1.1	143
4	73	117	121	--	0.79	95
5	54	148	153	--	0.21	45
6	47	118	103	--	ND	lost
7	53	122	109	--	ND	12.3
8	49	118	100	--	ND	6.5
9	43	121	94	--	ND	5.0
10	41	117	87	--	ND	4.0
15	48	87	67	ND	ND	ND
20	47	93	66	ND	ND	ND
Cedar Lake						
1	120	233	228	5.05	5.9	68
2	85	200	208	3.86	2.8	94
3	70	125	90	2.9	1.49	121
4	67	166	118	--	0.92	167
5	61	107	51	--	ND	5.2
6	71	125	55	--	ND	2.1
7	62	96	46	--	ND	ND
8	53	94	44	ND	ND	ND
9	53	93	50	ND	ND	ND
10	66	111	51	ND	ND	ND
18	71	97	55	ND	0.083	ND
Little Clear Pond						
1	97	198	227	13.6	5.4	72
2	88	202	200	3.16	3.2	68
3	47	78	83	2.98	2.7	98
4	59	88	72	2.27	1.6	117
5	53	179	163	1.65	1.0	134
6	42	93	87	1.03	0.17	45
7	56	101	72	--	ND	72
8	55	97	59	--	ND	5.9
9	53	82	63	--	ND	ND
10	58	88	67	--	ND	ND
15	53	89	65	ND	0.097	ND
20	58	78	62	ND	0.089	ND

[a]Not detected.

[b]ND = not determined.

Table 2. Sedimentation rates for Carolina Bays (cm/yr).

	^{210}Pb	^{137}Cs	$^{239,240}Pu$
Thunder Bay		0.15	0.192
Trenton Pond	0.07	0.115	0.384
Clear Lake	0.09	0.115	0.23
Little Clear Lake	0.07	0.23	0.301

The chemical profiles in these Carolina Bay Lakes are complex and difficult to interpret. However these data suggest:

1. The root mat in Thunder Bay and Trenton Airport Pond appears to be a selective filter. Ni, Pb, Zn, and $^{239,240}Pu$ are concentrated in the root mat but are also found deeper in the sediment column. Cesium-137 appears to be restricted to the root mat.
2. It is possible there is a downward mobilization of $^{239,240}Pu$ in these sediments. This radionuclide is found 4 to 6 cm deeper in the sediment column than ^{137}Cs (with or without a root mat).
3. The heavy metal concentrations in these sediments are higher than expected for this region of the United States. It is possible that the heavy metals are being concentrated in these sediments by some mechanism.

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UPTAKE AND TRANSFER OF ^{65}Zn BY THE PLANKTON COMMUNITY IN A MIDWESTERN POND

D. L. Schulze* and J. I. Parker

Background and Scope

The processes of biogeochemical cycling of trace elements in aquatic ecosystems are poorly known and difficult to investigate. There is a need for appropriate experimental techniques to investigate the role and importance of biota in the uptake, transfer and fate of toxic trace elements in aquatic systems. As an initial step in meeting this need, we investigated the processes and time trends of zinc incorporation by a phytoplankton community and the transfer of zinc to the zooplankton community. An in situ time-series experiment was conducted using the natural assemblages of phytoplankton and zooplankton from a 0.8 ha pond (maximum depth 8 m) located on the Argonne National Laboratory site.

Progress in 1979

A 4 x 2 array of 13 L glass bottles was prepared and treated with the radiotracer ^{65}Zn for in situ incubation in the pond. The first two bottles were prepared to investigate the importance of food alone in the transfer of zinc to zooplankton. These bottles were filled with 0.45 µm filtered pond water, spiked with 52 µCi as a carrier-free zinc chloride solution and inoculated with the natural assemblage of phytoplankton. The phytoplankton inoculum was prepared by screening out the zooplankton from a 13 L water sample with 85 µm Nitex netting and then retaining the phytoplankton by filtration on 28 µm Nitex netting. These operationally defined phytoplankton (28 to 85 µm) were then backwashed into the bottles with 0.45 µm filtered pond water. These two bottles were incubated in situ for 48 hours prior to the beginning of the time-series experiment to ensure ^{65}Zn labelling of the phytoplankton. After 48 hours the phytoplankton were removed with 28 µm Nitex netting, gently washed in 0.45 µm filtered pond water and decanted into two new bottles containing the zooplankton inoculum in 0.45 µm filtered pond water. The zooplankton inoculum was operationally defined as particles >85 µm and was prepared by filtering 13 L of pond water through 85 µm Nitex netting and then backwashing the animals into the bottles with 0.45 µm filtered pond water.

To investigate the importance of direct sorption of zinc by zooplankton from the water a second pair of bottles was filled with 0.45 µm filtered pond water, inoculated with zooplankton and spiked with sufficient ^{65}Zn to produce a concentration of 1 µCi/L. A third pair of bottles was prepared similarly, but the phytoplankton inoculum was also added to investigate the competition for ^{65}Zn in the water by phytoplankton and zooplankton. Two control bottles were filled with whole pond water and spiked similarly with the ^{65}Zn. All bottles were deployed in the pond, and incubated continuously for 12 days. Sampling began immediately after deployment and continued at elapsed time intervals of 10, 18, 28, 40, 48, 64, 88, 160, 234, and 282 hours.

The phytoplankton community of the pond was relatively simple and consisted primarily of Peridinium spp. and Certium spp., although Rhizoclonium spp., Staurastrum sp., and Fragilaria were present. The zooplankton community consisted of mainly Keratella sp., but Bosmina sp. and copepods were present. A pond water sample passed through 85 µm Nitex netting was most

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efficient at retaining the zooplankton without significant retention of phytoplankton. The 28 μm Nitex netting showed the best retention of the phytoplankton in the filtrate from the 85 μm filtration.

Since the zooplankton may ingest particles from both the 0.45 to 28 μm and 28 to 85 μm particle size categories, the uptake values in these categories were summed and subsequently referred to as particles <85 μm. The maximum uptake of ^{65}Zn among all treatments throughout the experiment occurred in this category.

The uptake by <85 μm particles in the control bottles ranged from 18 to 36.5% of the added ^{65}Zn, and uptake in the bottles treated with labelled phytoplankton was similar (11 to 43%). The smallest particles in this size range accounted for most of the uptake. Uptake by the <85 μm categories in the filtered water treatment (Figure 1B) and filtered water plus phytoplankton treatment (Figure 1D) showed less than 2.5% uptake throughout the experiment.

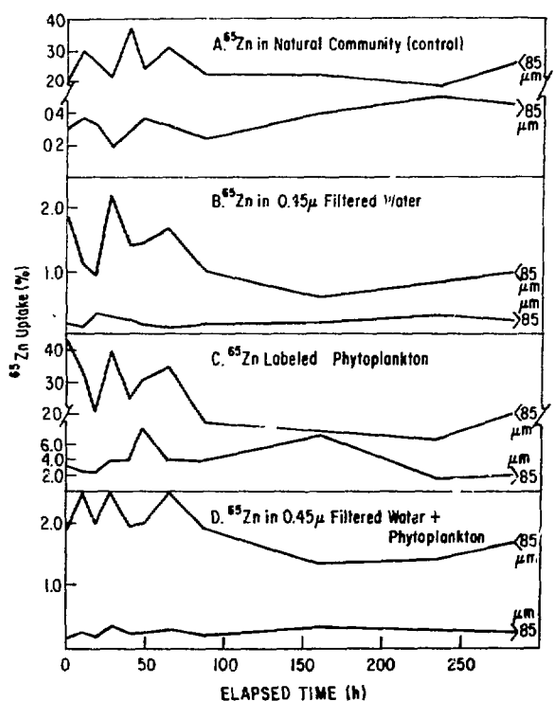

Fig. 1. Uptake of ^{65}Zn by zooplankton (>85 μm) and phytoplankton (<85 μm) exposed to different sources of ^{65}Zn.

During the first 4 days of incubation <85 μm particles showed dramatic oscillations in ^{65}Zn sorption and transfer. Maximal oscillation occurred in the control bottles and labelled phyto-

plankton bottles, and there appears to be a diurnal rhythm with maximal uptake during daylight hours and loss during darkness (Figure 1). This may be related to periods of algal photosynthesis and respiration. Following this period these fluctuations appear less intense as an equilibrium distribution of ^{65}Zn among the particles is approached.

The zooplankton category (>85 μm) contained the least zinc. The time-series plot of percent uptake by the zooplankton compared to uptake by <85 μm particles showed an inverse relationship, supporting the contention that zinc is transferred from the <85 μm particles to zooplankton by ingestion. Evidence of the importance of food as a transfer pathway occured in samples treated with ^{65}Zn labelled phytoplankton (Figure 1C). In these bottles a reduction in labelled small particles was followed by a simultaneous increase in labelled zooplankton and zooplankton uptake of ^{65}Zn was about an order of magnitude greater than in all other treatments. Zinc-65 uptake by zooplankton in the bottles containing 0.45 μm filtered water only (Figure 1B) and in the bottles containing 0.45 μm filtered water plus unlabelled phytoplankton (Figure 1D) was minimal among all treatments. These observations suggest that although sorbtion of ^{65}Zn by zooplankton occurs, the transfer through the food chain pathway is more important.

ACCUMULATION OF TOXIC POLLUTANTS BY BROWN TROUT EXPOSED TO VARIOUS TEMPERATURES IN LAKE MICHIGAN

S. A. Spigarelli, M. M. Thommes, W. Prepejchal and D. A. Warner

Background and Scope

Previous studies of thermoregulation by fishes residing in thermal effluent areas have shown significant increases in body temperatures and acclimation states over fishes residing in ambient temperature areas.[1] Brown trout (Salmo trutta) are common occupants of thermal effluents and are caught in large numbers by fishermen at shoreline discharge sites on Lake Michigan.[2]

Thermoregulatory behavior of brown trout residing in thermal effluent areas was monitored using underwater radiotelemetry. Selected temperatures of this species consistently exceeded ambient temperature by 3 to 10°C.[3] The increased temperature dose to plume-resident fish could result in increased accumulation of toxic pollutants (i.e., those with long biological half-times) since energy requirements (uptake via food) and metabolic rates (direct uptake) are a function of temperature. A controlled experiment was designed to test this hypothesis and to estimate the accumulation of biologically active pollutants by fish that reside in thermal effluents.

A field laboratory[4] was constructed and sited at a power plant (Sheboygan, Wisconsin) using Lake Michigan water for once-through cooling. Heated (thermal discharge) and unheated (intake) Lake Michigan water was circulated and mixed in the laboratory to simulate three temperature conditions: ambient temperature, seasonal thermoregulatory patterns of brown trout (cycled), and constant optimal temperature (~13°C). Brown trout used in this experiment were obtained from the Wisconsin Department of Natural Resources (Wild Rose Hatchery) stock regularly planted in Lake Michigan. Fish were fed (ad libitum, twice per day) diets of (1) whole alewife collected from the Sheboygan area; (2) pelletized food used in the Wisconsin hatchery; or (3) pellets duplicating the Wisconsin dry formula, but with Lake Michigan alewife meal substituted for commercial fish meal.

Progress in 1979

An experiment was initiated in April 1979 in which 45 preweighed brown trout from the hatchery were held at each of the combined temperature-food treatments. Test fish were sampled in a time-series starting with day 0 and ending at 57 days of exposure. Samples of whole fish and selected tissues were wrapped in aluminum foil and stored at 0°C until analyzed. Preliminary analyses for PCBs (expressed as 1:1:1 mixture aroclor 1248:1254:1260) and trace elements were made on selected samples to indicate the focus of more extensive future analyses.

PCBs

The results of preliminary PCB analyses are shown in Figure 1. Brown trout obtained from the hatchery contained an average of 0.15 ppm PCB on a whole body, wet weight basis, an average caecum concentration of 0.94 ppm, and an average muscle concentration of <0.1 ppm. The three foods used in the experiment contained 2.52 ppm (whole alewife), 1.20 ppm (pelletized alewife), and 0.18 ppm (Wisconsin pellets). After 57 days, exposure to 13°C, a 6-fold increase in muscle concentration of PCBs was observed in fish fed whole alewife (tank 7) compared to those fed Wisconsin pellets (T_5). Assuming minimal contribution of PCBs from Wisconsin pellets (hatchery fish were in "equilibrium" with their diet) and similar direct uptake from water between 13°

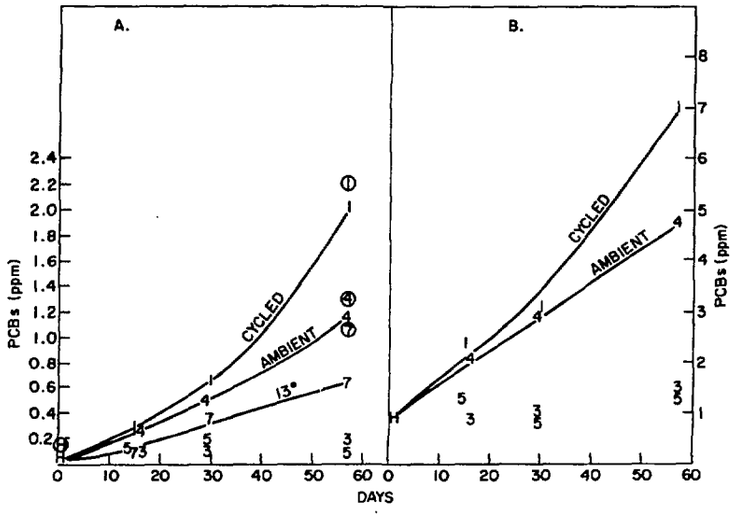

Fig. 1. PCB concentrations (ppm wet wt) in experimental fish exposed to different temperatures and diets: 1, thermoregulatory cycle and alewife food; 3, ambient temperature and no food; 4, ambient temperature and alewife food; 5, constant 13°C and hatchery pellets; 7, constant 13°C and alewife food. Panel A: concentrations in whole fish ((1)) and muscle (1). Panel B: concentrations in caeca. Points connected by eye.

treatments, the results indicate that direct accumulation of PCBs from water is much less important than accumulation via food. A similar comparison between fish given an alewife diet (T_4) and those starved (T_3) at ambient temperatures yielded a concentration ratio of 8:1. These results indicate that direct uptake of PCBs (bioconcentation) accounts for <15% of the total uptake by brown trout in Lake Michigan. However, these preliminary data are only indicative of relative contributions since fish growth and food consumption under each treatment will be analyzed and factored into the determination of uptake routes and rates.

Analyses of PCB concentrations in fish fed whole alewife and held under three temperature conditions indicate a significant effect of temperature. After 57 days fish exposed to simulated thermoregulatory cycles (T_1) had PCB concentrations ~1.7 times the concentration in fish exposed to ambient temperatures (T_4) and twice the concentration of fish held at constant 13°C (T_7). PCBs in fish (whole and muscle) held under the thermoregulatory cycle had nearly equaled the concentration of PCBs in alewife diet while concentrations in fish exposed to ambient temperatures would require ~115 days to equal the diet concentration, assuming a linear extrapolation with time. PCB concentrations in whole brown trout captured in the Sheboygan area of Lake Michigan ranged from 3.6 to 5.5 ppm. Other recent analyses of brown trout from this area indicate a range of 5 to 14 ppm on a whole body basis.[5] Assuming a linear increase from 57 days, PCB concentrations in fish exposed to the thermoregulatory cycle would equal Lake Michigan values in >100 days, while those in fish exposed to ambient temperatures would require >175 days. Under such conditions, brown trout exposed to the selected temperature cycles for long periods could accumulate PCB concentrations as much as 5 ppm higher than those inhabiting

ambient temperatures.

The ratios of PCB concentrations in caeca to those in whole fish may be indicative of the growth rate of brown trout, since an apparent inverse relationship was found. The highest caeca-to whole fish ratios (~6) occurred in hatchery fish on day 0, intermediate values (~4) were found in fish that grew ~30% (ambient temperatures), and the lowest values (~3) occurred in fish that grew ~60% (thermoregulatory cycle). If this relationship is substantiated on further analyses, it may be indicative of (1) a labile pool of PCBs being mobilized and redistributed during rapid growth or (2) different sites of deposition of incoming PCBs depending upon the growth status of the animal or the uptake route.

Trace Elements

Lyophilized samples of fish were heated to 500°C overnight and the ash was digested in concentrated HNO_3. Cu and Zn were determined by atomic adsorbtion spectrophotometry (AAS) in an air-acetylene flame using the standard conditions recommended by the manufacturer. No interferences could be detected by the method of standard additions. The concenrations of Pb and Cd in the digested ash were below the range detectable by conventional AAS. These elements were determined using a graphite furnace atomizer, following temperature programming cycles optimized for each element. To obtain valid results, all determinations were performed by the method of standard additions. The elements in the blanks were either undetectable or significantly less than the amounts being determined. Replicate analyses of NBS Standard Reference Bovine Liver agreed with the accepted values within their published uncertainties.

Preliminary results of trace element analyses from this experiment and from the available literature are given in Table 1. Values reported for Lake Michigan fish prior to 1972 were approximately: <1 μg/g Cu, <16 μg/g Zn, <0.2 μg/g Cd, and <0.3 μg/g Pb. Analyses since 1977 by ANL and others indicate: (1) a small increase in Cu and Cd, (2) a substantial increase (>5-fold) in Zn, and (3) a possible decrease in Pb concentrations in Lake Michigan fishes. Bioconcentration ratios (fish/H_2O) in 1979-1980 are on the order of 10^3 for Cu, Zn, and Cd, and $<10^3$ for Pb. Biomagnification ratios indicate little or no increase in concentration of these metals among consumer (fish) trophic levels.

An unexpected result of the analysis was the indication that brown trout stocked in Lake Michigan (raised in the Wisconsin hatchery) have whole body concentrations of Cu and Pb that equal or exceed those of brown trout collected from Lake Michigan. The diet used in the hatchery (Wisconsin dry pellets) is relatively high in Cu and Pb compared to the alewife diet eaten by trout in Lake Michigan.

Increased temperature may have the effect of increasing whole body concentrations of Cd and decreasing those of Cu and Pb. Although numerous studies have shown direct relationships between temperature and uptake of heavy metals, the differences in metal concentrations between the hatchery diet and the natural alewife diet probably complicated the temperature effect; i.e., concentrations of Cu, Cd, and Pb in whole hatchery fish were less than concentrations in the hatchery diet, while that of Zn was higher in whole fish than in the diet. Thus, a probable condition of "equilibrium" between hatchery fish and their diet is altered when fish are stocked in Lake Michigan and begin using foods that contain lower concentrations of Cu, Cd, and Pb and higher concentrations of Zn.

Table 1. Summary of past and present data on Cu, Zn, Cd, and Pb concentrations in Lake Michigan fishes (ppm, wet weight).

Sample type	Date	Cu	Zn	Cd	Pb	Ref
Alewife 1968	1968	0.7	16.2	0.05	--	6
Alewife 1970	1970	--	--	0	0.1	7,8
Alewife 1979	1979	0.8-1.2	25-56	0.08-0.1	0.03-0.1	ANL
Alewife 1979	1979	0.5-1.5	--	<0.2	<5.0	9
Salmon muscle	1968	0.4	3.7	0.15	--	6
Trout/salmon	1970	--	3.2-4.1	--	--	7
Brown trout	1970	--	--	0	0.25-0.3	7,8
Fish muscle	1971	ND	9.0	--	--	10
Lake trout	1972	--	~11	--	--	11
Lake trout	1977-78	--	25-68	--	--	11
Brown trout	1979	1.0-1.1	22-30	0.01-0.02	0.03-0.04	ANL
Brown trout	1979	1.3-4.5	--	<0.2	<5.0	9
Lake Michigan H_2O[a]	1980	1.5×10^{-3}	5.0×10^{-3}	0.02×10^{-3}	0.1×10^{-3}	12
Bioconcentration[b]	1979-80	1×10^{3}	4×10^{3}	1×10^{3}	4×10^{2}	
Biomagnification[c]		~1	<1	<1	~1	
Hatchery diet	1979	16.7	14.3	0.17	0.87	ANL
Hatchery brown trout	1979	2.5-3.5	19-32	0.003-0.02	0.06-0.07	ANL
Alewife diet	1979	0.8-1.2	25-56	0.08-0.1	0.03-0.1	ANL
Ambient temperature	1979	3.1-12.4	14-26	0.006-0.02	0.02-0.3	ANL
Cycled temperature	1979	1.8-2.8	19-24	0.02-0.32	0.02-0.05	ANL

[a]Offshore.

[b]Whole fish/H_2O.

[c]Trout/alewife.

Prospects

The initial results for PCBs indicate (1) the definite potential for increased accumulation of lipophilic contaminants by fish that are exposed to elevated temperatures; and (2) the importance of the trophic pathway in PCB accumulation and transfer. A significant fraction of each Lake Michigan salmonid population (excluding lake trout) is attracted to thermal outfalls during some period of the year, and the most significant impact of this exposure may be alterations in the uptake and tissue distribution of lipophilic contaminants. Also, fish samples from this experiment offer a unique opportunity to identify the most significant toxicants in the Lake Michigan food chain, and to characterize the pathways of transfer for each, i.e., bioconcentration vs. biomagnification.

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SIMULATIONS OF THE IMPACT OF WATER INTAKES ON SELECTED FISH POPULATIONS IN LAKE MICHIGAN

S. A. Spigarelli, M. M. Thommes, and A. Jensen*

Background and Scope

In response to the thermal (316a) and water intake (316b) sections of Public Law 92-500, numerous site-specific environmental studies were performed by the electric utilities that use Lake Michigan water. Invariably, the site-specific demonstrations showed a multitude of effects ranging from subtle effects of heated effluents to large numbers of fish killed by entrapment. When viewed independently even the largest power plants were judged to cause minimal impacts in an ecosystem the size of Lake Michigan.

An alternative approach to the determination of cooling-system impacts is to utilize the site-specific data bases in a combined or system-wide assessment. This approach was taken by ANL in a study sponsored by the Enforcement Division, Region V, U.S. Environmental Protection Agency. The impacts of all water intakes were assessed in terms of projected reductions in standing stocks and yields of three fish populations in Lake Michigan: alewife (Alosa pseudoharengus), smelt (Osmerus mordax), and yellow perch (Perca flavescens). The potential for impacts was indicated by the following: (1) approximately 260% of the total inshore volume of Lake Michigan is withdrawn by all water intakes (full capacity flow) in one year and the total withdrawal rate will increase; (2) very large numbers of immature and adult fishes are entrapped and killed by water intakes; and (3) the fish community of Lake Michigan is highly dynamic with large temporal fluctuations in the populations of naturally reproducing forage species and steadily increasing populations of non-reproducing predatory salmonids; i.e., the natural feedback controls on predator/prey ratio are no longer functional in Lake Michigan. The ecological status of the alewife population has reversed completely in the last decade, going from a very abundant nuisance (exotic species) to an immensely valuable and critical forage species that supports the massive stocks of salmonid predators (~12 million per year) introduced to Lake Michigan. The smelt population serves as a secondary forage base, but at present this species cannot support a large predator population. Alewife, smelt and yellow perch are important to the commercial fishery, and smelt and perch are highly prized sport fishes. For these reasons, it is very important to estimate fish mortalities and population impacts associated with water intakes and to develop a resource allocation strategy and a mitigation strategy, if necessary.

Fish impingement and entrainment data were collected by utilities preparing 316(b) demonstrations and were assembled in a computer data base and analyzed by ANL. Estimates were made of the annual (1975) losses of adults, eggs and larvae at 16 sampled power plant intakes and at all other water intakes on Lake Michigan. These estimates were used as the data base for mathematical simulations or projections of impact on each of the three fish populations. Two models commonly used in fisheries research were applied to (1) describe the dynamics of the affected fish populations, (2) estimate stock biomass, and (3) simulate the impacts of present and increased water withdrawals. A dynamic pool model and a surplus production model independently projected very similar results.

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Progress in 1979

This project was completed in 1979 and a draft report[1] was submitted to the U.S. Environmental Protection Agency. A summary of the results is given in Table 1.

Table 1. Results of simulation of impacts on three fish populations in Lake Michigan.

Estimates for 1975	Alewife	Rainbow smelt	Yellow perch	
	Lake Michigan total	Lake Michigan total	Lake Michigan total	Green Bay
Maximum impingement, kg	2.10×10^6	1.86×10^4	1.31×10^4	5.00×10^3
Maximum egg entrainment, number	7.39×10^{10}	6.15×10^8	4.81×10^7	1.20×10^7
Maximum larval entrainment, number	1.31×10^9	8.28×10^7	3.26×10^6	2.40×10^6
Standing stock biomass, kg				
Surplus production model	2.06×10^8	2.53×10^7	1.07×10^7	5.21×10^6
Dynamic pool model	2.37×10^8	2.47×10^7	1.00×10^7	-
U.S. Fish & Wildlife Service	1.22×10^8	1.37×10^7	-	-
Percent reduction in standing stock				
Impingement	2.45	0.46	-	-
Entrainment	0.41	0.30	-	-
Impingement + Entrainment	2.86	0.76	0.28	0.61
Maximum sustainable yield, kg	3.00×10^7	2.50×10^6	7.42×10^5	3.50×10^5
Percent reduction in MSY				
Impingement	3.42	0.71	-	-
Entrainment	0.56	0.46	-	-
Impingement + Entrainment	3.98	1.18	0.47	1.03

An important result of this study is the estimation of the standing stocks (biomass) of alewife, smelt, and yellow perch populations in Lake Michigan. Previous estimates by the U.S. Fish and Wildlife Service[2] have been based on annual sampling in selected regions of Lake Michigan, but these estimates were known to be low. Our estimates for alewife and smelt are approximately twice those previously reported, and our estimates for yellow perch are the first for Lake Michigan and Green Bay. In 1975, the apparent population biomass ratios were: alewife/smelt ≅ 8/1 and alewife/perch ≅ 19/1, while the ratios of impinged biomass were: alewife/smelt ≅ 113/1 and alewife/perch ≅ 160/1. The large differences between lakewide abundance and impingement ratios are a reflection of the distribution patterns of these species; i.e., alewife are more vulnerable to water intakes because this species occupies shallow inshore waters more frequently than the other species.

The estimated impacts of the lakewide losses of alewife, smelt, and yellow perch at water intakes are relatively low at present rates of withdrawal (e.g., 3% reduction in standing stock and 4% reduction in yield of alewife). The projected reductions in standing stock biomass of alewife are shown in Figure 1. Application of the average impingement and entrainment coefficients in the simulation resulted in a significantly lower rate of decrease in the population

compared to application of the maximum coefficient. Nonflow-related factors such as water intake location and design also affect alewife impingement and entrainment rates. In general, water intakes located on the western and southern shores of Lake Michigan, and all canal intakes experience relatively high rates of fish entrapment. As an example, a canal intake sited on the western shore of Lake Michigan or on Green Bay would impinge alewife at a rate 10 times that of another intake type sited on the northeastern shore.

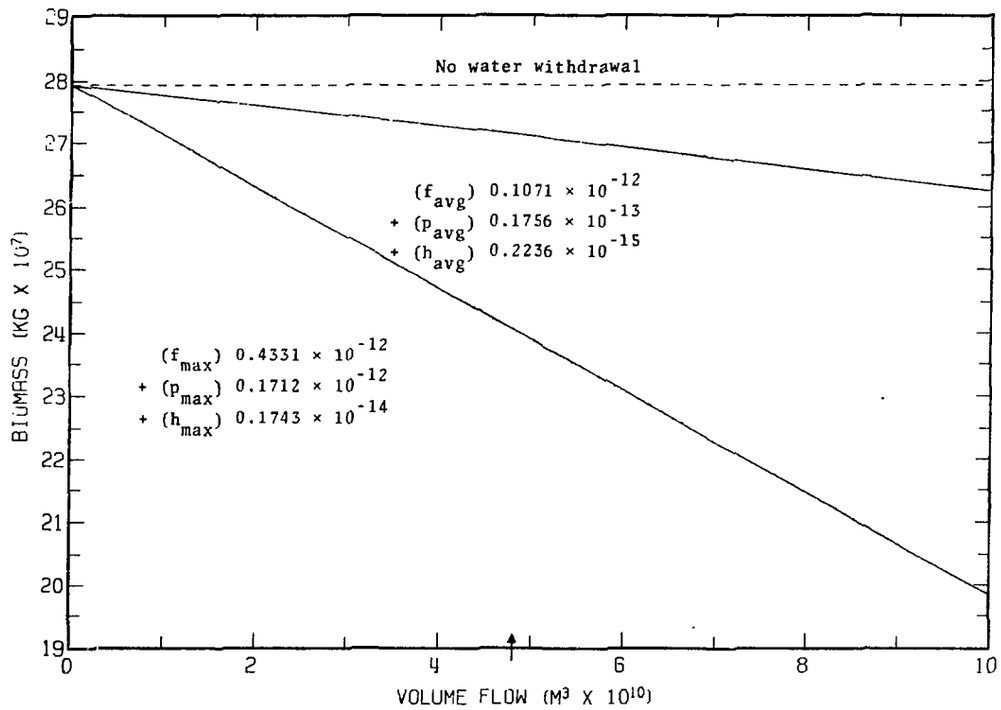

Fig. 1. Combined entrainment and impingement impact of increased water withdrawal on biomass of alewife in Lake Michigan (1975). (Arrow indicates total design flow for all water intakes in 1975.) Average (f_{avg}) and maximum (f_{max}) impingement and entrainment coefficients (p, eggs; h, larvae) for 16 sampled intakes.

If the reductions in standing stock biomass and in yield to the fishery are evaluated as though no other stresses are placed on these fish populations, the impacts of present water withdrawals are small. Alternatively, if the other estimable sources of mortality are considered (i.e., predation, fishing and water withdrawal) the mortality of alewife and smelt at water intakes can be viewed as a significant additional impact on forage populations that may already be stressed by unchecked predation.

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ACCELERATED SENESCENCE IN SOYBEANS EXPOSED TO SULFUR DIOXIDE

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

Background and Scope

Little is known about the mechanistic effects responsible for the productivity decreases in plants exposed to sulfur dioxide (SO_2). Some of our previous work[1] as well as that of others[2] has suggested that senescence is accelerated in field-grown plants fumigated with SO_2. In this study, we attempted to relate parameters indicative of premature senescence, such as, chlorophyll degradation during leaf aging, rate of leaf drop, and seed weight with SO_2 dose to soybeans.

Progress in 1979

Field plots of soybeans (Glycine max cv. S-1492) were intermittently exposed to a regime of SO_2 concentrations and doses using a technique previously described[3] (Table 1). Leaf chlorophyll concentrations at the 4th and 8th nodes were determined spectrophotometrically five times between late August and early September. A count of leafless nodes per plant was made in early September to estimate leaf drop. Individual plants were harvested on 8 October to determine weight per seed and total seed weight at each node.

Table 1. Sulfur dioxide concentration dose and exposure schedule in plots used for senescence study, 1979.

Plot	$[SO_2]$ ppm	Number of exposures	Total exposure, hr	Dose ppm·hr
1	0.27	17	63.2	17.1
	0.34	17	63.2	21.5
2	0.20	10	36.6	7.3
	0.25	10	36.6	9.2
3	0.26	7	23.2	6.0
	0.26	7	23.2	6.0
4	0.04	18	57.4	2.3
	0.04	18	57.4	2.3

The preliminary results indicate that chlorophyll degradation was more rapid during senescence in plants exposed to SO_2 at all but the lowest SO_2 concentration (0.04 ppm). Significant differences in chlorophyll concentration of SO_2-exposed plants compared to control plants were first observed (31 August) at the highest exposure doses (21.5 and 17.1 ppm·hr) in leaves at the 8th node. At the final sampling date (11 September) chlorophyll content was significantly lower in leaves at the 4th and 8th nodes of fumigated plants that received SO_2 doses ranging from 6.0 to 21.5 ppm·hr (plots 1, 2, and 3) as compared to ambient controls. An apparent recovery in the rate of chlorophyll degradation was also observed in plot 1 after a four-day period of no fumigation in late August.

A count of the leafless nodes per plant on 10 September indicated leaf drop was accelerated in the rows receiving the highest SO_2 exposures in plots 1, 2, and 3 (83 to 29.0 ppm·hr dose),

with the largest differences observed at the highest SO_2 doses.

Total seed yield was found to be 9% less in the SO_2 fumigated plants in plot 1 ($p < .05$) and 5% less in the fumigated plants in plot 2 ($p < .025$) as compared to ambient controls.[4] There were no significant yield differences in plot 3; inadequate control plots prevented the determination of yield differences in plot 4.

The harvest of individual plants in plot 1 indicated a lower dry weight per seed in the fumigated plants that received the highest SO_2 dose (21.5 ppm·hr) as compared to ambient controls. When the seeds were separated into groups consisting of the top four nodes, middle four nodes, and bottom eight nodes, it was noted that dry weight per seed was 6 to 10% lower than controls in each group. Since most of the assimilate from a leaf moves into the pod at the axil of that leaf in a soybean plant,[5] our results indicate that SO_2 affects pod fill at all nodes.

These results suggest that senescence is accelerated in soybeans exposed to SO_2 and that this effect may be partially responsible for the decreased yields through decreased seed size observed at the highest SO_2 concentrations. It is interesting to note that chlorophyll degradation and leaf drop occurred to a lesser degree at lower SO_2 doses without accompanying yield decreases.

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STRONG AND WEAK ACIDS IN PRECIPITATION AT ARGONNE, 1979

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Background and Scope

With the current awareness of the conversion of gaseous air pollutants to acidic species and their simultaneous long-range transport, emphasis has been placed on pH electrode measurements of wet deposition samples since damage to vegetation and aquatic systems may result from acidic deposition. The electrode measurements are usually reported as reflecting the acidity of the samples and are used to calculate hydrogen ion (H^+) deposition. Unfortunately, the use error resulting from the of measured pH to estimate H^+ concentration in low ionic strength samples (such as rainwater) may be as much as 50%.[1] In order to eliminate the errors associated with measuring pH with an electrode in precipitation solutions of low ionic strength, acidity was determined by titrating precipitation samples with a base, allowing calculation of strong acid (A_S), weak acid (A_W), and total acid (A_T) concentrations.

Progress in 1979

Precipitation was collected on an event basis using a Battelle automatic, wet deposition collector. Samples were microtitrated with standardized NaOH (~0.02 M) in a CO_2-free atmosphere to pH 9.5. Total acidity of the sample was determined as the equivalent amount of base (NaOH) needed to achieve a pH value of 9.5. The concentration of the A_S component was determined using a function modified according to Gran,[2] which measures potentiometrically the amount of hydrogen ions left in a sample after addition of known amounts of hydroxide ions. A plot is made of the function Ψ as the ordinate and V_B as abscissa:

$$\Psi = (V_S - V_B)10^{(pH - pH_i)}$$

where V_S is the volume of sample, V_B is the volume of added base, pH is the value corresponding to V_B-values, and pH_i is the initial pH value obtained. For strong acids the relationship is linear, and the point of equivalence occurs at the volume of NaOH required to reduce the stochiometric H^+ concentration to zero. Extrapolation of the relevant pseudolinear portion of the plot to the abscissa will indicate the A_S concentration. The absolute value of the electrode pH does not affect the shape of the plots, thus eliminating errors.

The difference between A_T and A_S is the weak acid (A_W) concentration. To determine whether there were dissociated weak acids present, some of the samples were back-titrated with H_2SO_4 to pH 3.0 after neutralization with NaOH to pH 5.0. The results were plotted using the -log C_{HX} as the ordinate and the corresponding pH for the abscissa, where C_{HX} is the concentration of H^+ added in moles/liter. Deviation from the linearity indicates the pK of the dissociated weak acid at the point of deviation.

Wet deposition of acid is summarized on a monthly basis in Table 1. The weighted average H ion concentration based on A_S of the precipitation sampled in this study was 0.938 x 10^{-4}eq L^{-1}, which results in a calculatd pH value of 4.03. Weighted pH values from electrode measurements of precipitation during spring and summer at Argonne in 1977 and 1978 were 4.13 and 4.09, respectively;[3] the corresponding values calculated from A_S were 4.24 and 4.19.

Table 1. Deposition of strong, weak and total acids in single precipitation events summarized by monthly weighted means, May-September 1979.

Months 1979	Number of events	Precipitation quantity cm	Deposition 10^{-7} eq cm^{-2} A_S	A_W	A_T
May 2	1.62	1.55	6.03	7.58	
June 7	2.82	1.90	12.98	14.90	
July 4	5.92	9.66	13.60	16.96	
Aug 9	13.00	8.81	46.95	55.77	
Sept 1	0.10	0.08	0.32	2.46	
Σ 23	23.46	22.00	79.88	97.67	

Regression analyses indicated that neither precipitation amount nor duration were significantly correlated with acidity concentrations. The acid back-titrations indicated the presence of dissociated weak acids having pK values from 3.8 to 4.1 in some of the samples.

This work will be expanded in the future to determine the relationship between precipitation chemistry, meteorological conditions, and air quality.

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SO_2 EFFECTS ON SOYBEAN YIELD: DOSE-RESPONSE RELATIONS FROM 1979 FIELD STUDIES

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

Background and Scope

In previous studies of SO_2 effects on the yield of soybeans performed in 1977 and 1978 field plots were treated for 18 or 24 days during the growing season (4 to 5 hr/day) with mean SO_2 concentrations ranging from 0.09 to 0.79 ppm.[1] Significant yield reductions were found with all treatments and the yields were highly correlated with the total applied dose (concentration x time of exposure) as well as the mean treatment concentrations.[2] From a practical standpoint the dose-yield relationship is the most attractive to use for making crop loss assessments since the dose incorporates both the exposure concentrations and the total time of exposure. However, it is clear that there must be limits to the use of this type of relationship. For example, there was a difference between the dose-yield relationship for a single acute SO_2 exposure and that for the aforementioned chronic exposures.[3] In the 1978 and 1979 experiments the range in SO_2 doses was primarily a function of the treatment concentrations, and thus it was uncertain if the yield effects were more dependent on the SO_2 concentration or the total accumulated dose. The following experiments, in which both exposure concentrations and time of exposure were varied, were performed during the 1979 field season to examine further the use of the dose concept to predict yield reductions.

Progress in 1979

Three field plots of soybeans (Glycine max Merr., cv. S-1492), each consisting of sixteen 7-meter row sections, were intermittently treated with SO_2 between July 23 and September 10, 1979, by an open-air fumigation technique similar to that previously described.[1] The three plots were treated at different frequencies resulting in variable total exposure times as shown in Table 1. The SO_2 exposure technique also generated different mean SO_2 concentrations for each row segment within a plot (Table 1). Thus a range in doses due to variation in the total time of exposure as well as the concentration was obtained.

Table 1. Treatment variables for SO_2 fumigated field plots of soybeans in 1979.

Plot	Number of treatments	Total treatment time, hr	Range of mean $[SO_2]$, ppm	Range of total applied dose, ppm·hr
1	17	63.2	0.173-0.458	10.9-28.9
2	10	36.6	0.151-0.357	5.5-13.1
3	7	23.2	0.186-0.520	4.3-12.1

The soybean yield data from the 1977 and 1978 experiments was best expressed as the exponential relationship $y = a\,e^{bx}$, where y is the soybean yield as a percent of the control values, and x is either the mean applied SO_2 concentration (ppm) or the total applied dose (ppm·hr). Exponential curves were fitted to the 1979 yield data as a function of SO_2 dose, mean SO_2 concentration, and the total time of treatment for the three plots separately as well as plots 1

and 2, and plots 1, 2, and 3 combined (Table 2). A significant relationship between soybean yield and SO_2 dose was found in all cases but plots 1 and 3 alone. The coefficients of determination (r^2) were much lower in 1979 than in previous years apparently owing to greater intra-plot variability. Thus, the lowest SO_2 doses causing significant yield reductions in 1979 were approximately 10 ppm·hr. The exponential relationship between yield and SO_2 concentration was also significant in plot 2 and plots 1 and 2 combined. However, the dose was clearly superior to concentration when the data from all three plots were combined indicating the obvious importance of relating yield to both the SO_2 concentration and the total time of exposure. The exponential equation for yield as a function of time of exposure was also significant for all three plots combined which is not unexpected since the highest doses resulted from the longer periods of treatment.

Table 2. Exponential curve functions ($y = a\ e^{bx}$) for soybean yields as a function of SO_2 dose (ppm·hr), SO_2 concentration (ppm), and total time of exposure (hr). Yields are expressed as a percentage of the respective plot controls.

		Yield vs. dose			Yield vs. $[SO_2]$			Yield vs. time		
Plot	df	a	b	r^2	a	b	r^2	a	b	r^2
1	15	101.5	-6.5×10^{-3}	0.13	101.6	-0.41	0.13			
2	15	109.5	-1.6×10^{-2}	0.47[a]	109.4	-0.57	0.46[a]			
3	15	95.4	-2.3×10^{-3}	3.1×10^{-3}	95.4	0.05	0.003			
1,2	31	101.7	-6.8×10^{-3}	0.23[a]	106.5	-0.53	0.25[a]	101.8	-1.8×10^{-3}	0.10
1,2,3	47	101.4	-6.5×10^{-3}	0.19[a]	99.1	-0.18	0.03	101.1	-1.7×10^{-3}	0.11[b]
1977,1978	129	100.0	-7.2×10^{-3}	0.93[a]	100.0	-0.71	0.93[a]	--		

[a]Significant at $p < 0.01$.

[b]Significant at $p < 0.05$.

The exponential equations for the combined dose-yield data from plots 1 and 2 or plots 1, 2, and 3 agree fairly well with those for the combined 1977 and 1978 experiments (Table 2). For example, a dose of 10 ppm-hr would predict 5%, 5% or 7% yield reductions, respectively. This is noteworthy in that the soybean cultivar "Wells" was used in 1977 and 1978 while S-1492 was used in 1979 indicating that the SO_2 sensitivity of the two cultivars was probably similar and that the data from the three years of study may be considered collectively. Also, the 1979 experiments seem to substantiate the hypothesis that the SO_2 dose can be used to predict SO_2-induced soybean yield losses within certain bounds of SO_2 concentrations and duration of exposure. The three years of experiments encompass an SO_2 concentration range of 0.09 to 0.79 ppm and a duration of exposure of 23 to 114 hours, and it is not at all certain that the dose-yield relationship would hold beyond these bounds. Of particular importance in this regard is the documented stimulation of plant growth at low SO_2 concentrations. Therefore, it is suggested that this type of data not be extrapolated above or below the experimental bounds of SO_2 concentration and duration of exposure. Future work will continue to define the proper application of these relationships.

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NITRATE REDUCTASE AND RIBULOSE-1,5-DIPHOSPHATE CARBOXYLASE ACTIVITY FROM LEAVES OF SO_2-TREATED AND UNTREATED SOYBEANS

J. E. Miller, P. B. Xerikos, H. J. Smith, and K. Albrecht*

Background and Scope

Previous studies have established that bean yield of field-grown soybeans may be reduced by atmospheric SO_2 concentrations that do not cause obvious symptomatic injury to the vegetative tissues.[1] Detection of these subtle effects by analysis of the tissues for specific sulfur species is not feasible because of the rapid incorporation of SO_2 into the normal sulfur pool of the plant. Also, the small increment of sulfur added to the tissues as a result of the pollution episodes often precludes total sulfur measurements as an indicator of a harmful SO_2 dose. For these reasons we have initiated work to determine if physiological measurements can be useful indicators of SO_2 stress. Previous work by our group has indicated that gross photosynthesis rates of soybeans may be altered by SO_2 doses that may potentially reduce yield but do not visibly injure the tissues.[2] However, the gross photosynthesis rates of the SO_2-treated tissues usually return to control rates shortly after termination of the SO_2 treatment. Some measurement of a residual or carryover effect would be more useful as an indicator of SO_2 stress since SO_2 pollution events are typically episodic.

Progress in 1979

In the 1979 field season preliminary experiments were performed to determine the response of two key enzymes in soybean leaf tissues, nitrate reductase (NR) and ribulose-1,5-diphosphate carboxylase (RuDPC), to SO_2 fumigations. The activity of NR previously has been shown to be very responsive to stress[3] (e.g., water stress), while RuDPC has been shown to be activated by long-term SO_2 treatment in vivo[4] although it may be competitively inhibited with respect to $HCO_3^=$ by sulfite in vitro.[5] Soybean leaf tissue samples (the most recently expanded leaves) were periodically collected throughout the growing season from field plots which were periodically treated with SO_2 and from nearby control areas. Bean yields in the SO_2 treated plots were 9% less than from the control plots. The NR activity was determined with a standard procedure which measures the production of nitrite from nitrate by leaf discs submersed in an anaerobic incubation medium.[3] RuDPC activity was estimated by measuring the incorporation of $^{14}CO_2$ into acid stable products in a cell-free extract prepared from the leaf tissues.[4]

In July and early August NR activity was reduced as much as 48% during treatment with approximately 0.3 ppm SO_2, and the reductions were still evident in leaf tissues sampled the day following the SO_2 treatments. However, in mid- to late August similar SO_2 treatments caused no significant effects on NR activity, and the NR rates in the control tissues were reduced to as little as 16% of the rates in July. The lower NR activity and lack of response to the SO_2 treatment was ascribed to an unseasonably cold and wet period starting in mid-August which probably adversely affected gas uptake rates and the overall metabolism of the leaf tissues.

The activity of RuDPC was apparently stimulated by treatment with ~0.3 ppm SO_2 in early August. This stimulation was observed during fumigations and also on nonfumigation days, indicating a residual effect. In mid- to late August the RuDPC activity was consistently lower in tissues from the SO_2 treated plots compared to the controls. The RuDPC activity in the control

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tissues did not show the decline in mid-August that was observed for NR.

These experiments indicate that NR and RuDPC activities do not show promise as specific indicators of SO_2 stress. While NR activities were reduced by SO_2 treatments in late July and early August, no SO_2 effects could be detected in late August. Also, NP activity was apparently overly responsive to other variables such as temperature, light intensity, and temperature. The activity of RuDPC in response to SO_2 was likewise inconsistent in that a stimulation was found in early August and an inhibition in mid- to late August. Future studies of this type will deal with physiological measurements more closely related to sulfur metabolism in an attempt to identify processes that respond more specifically to SO_2 stress.

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PLUTONIUM CONCENTRATION IN NATURAL WATERS - ITS RELATIONSHIP TO SEDIMENT ADSORPTION AND DESORPTION

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Background and Scope

The evidence obtained to date on the behavior of fallout plutonium in Lake Michigan suggests that its adsorption onto solids is a reversible process, i.e., an adsorption-desorption equilibrium exists between the plutonium dissolved in the water and that associated with suspended solids and unconsolidated sediments. During the past decade the changes in its concentrations in these solids and the water have been small. Establishing whether or not the adsorption is reversible is important, for if it is, the concentration of plutonium in the water will be fixed by the concentration of plutonium in the unconsolidated sediments. Since sediment consolidation and burial in many natural systems is a very slow process, the decrease in plutonium concentration in the water will be dependent entirely on the rate at which this process occurs.

One way of testing the possible reversibility of plutonium adsorption on sediments is to equilibrate natural sediments containing plutonium with water which does not contain plutonium. If adsorption is a reversible process the concentration of plutonium in the water after equilibration should be the same as the concentration in the water originally in contact with the sediments. Since the concentration of plutonium in Lake Michigan sediments is quite low, experiments using these sediments as the plutonium source are not practicable. Experiments which are, are those between Lake Michigan water and sediments having a much higher plutonium concentration. This report describes experiments in which Lake Michigan water was used to extract plutonium from sediments contaminated 10 years ago by ^{238}Pu. These sediments are from a section of the Miami-Erie canal near the Mound Laboratory containing ~1000 pCi/g of ^{238}Pu.

Progress in 1979

In one experiment 0.1 g portions of the sediment were extracted by dispersing them in 1000 mL portions of filtered (0.45 μm) Lake Michigan water and stirring for 0.2, 1, 2, 4, and 8 days. The sediment was separated from the water by filtration, and the filtrates were analyzed for their ^{238}Pu content. The amounts of plutonium in the water corresponded to 0.83, 0.96, 1.23, 1.53, and 1.45% of the plutonium initially in the sediment, suggesting that equilibrium was established in less than a week.

In another set of experiments, the amounts of sediment were varied between 0.015 and 5.5 g/L. Although the fraction of plutonium which was extracted decreased from 5.5% to 0.022% as the sediment concentration was raised, the distribution ratio between the sediments and the water remained constant at 1×10^6 L/kg.

To establish what fraction of the plutonium on the sediment could be removed by extraction with Lake Michigan water, portions of the sediment were repeatedly extracted with 1000 mL portions of water, with each extraction period being 4 days. In experiment A the amount of sediment was 0.1 g and in experiment B it was 0.01 g. After each extraction the phases were separated by filtration, the sediment was added to a fresh portion of water, and the filtrates were analyzed. From the amounts of plutonium initially on the sediments and the amounts of plutonium

in the filtrates, the percent plutonium extracted and the sediment-to-water distribution ratio were calculated. These data were presented in Table 1.

Table 1. Extraction of ^{238}Pu from Miami-Erie canal sediments with filtered Lake Michigan water.

Experiment A			Experiment B[a]		
Equilibration	Percent extracted[b]	Distribution ratio, mL/g	Equilibration	Percent extracted[b]	Distribution ratio, mL/g
1	1.6	0.9×10^6	1	6.0	1.7×10^6
2	1.5	1.0×10^6	2	4.9	2.4×10^6
3	1.4	1.0×10^6	3	5.8	2.2×10^6
4	1.5	1.0×10^6	4	5.6	2.4×10^6
5	1.5	1.0×10^6	5	5.7	2.6×10^6
6	1.8	0.8×10^6	6	4.1	4.0×10^6
7	2.0	0.7×10^6	7	4.0	4.5×10^6
8	1.8	0.8×10^6	8	4.0	4.8×10^6
9	1.7	0.9×10^6	9	3.1	6.8×10^6

[a]The mass of particles being extracted was adjusted for a 8% loss during each filtration.

[b]Percentages are based on the calculated amount of ^{238}Pu on the sediment after the preceeding extraction.

The consistency of the values obtained in experiment A indicates that equilibrium was established in each extraction. In experiment B the decrease in percent plutonium extracted with the number of the extraction indicates that equilibrium was not established. The reason would appear to be that the time required to establish equilibrium progressively increases as the percentage of plutonium extracted increases. The important finding in experiment B was that nearly 35% of the plutonium was extracted from the sediment.

An important feature of the extraction of plutonium from these sediments is a change of oxidation state which occurs during extraction. The plutonium on the particles was determined to be almost entirely (>98%) in the reduced form (oxidation states III or IV) as measured by lanthanum fluoride precipitation. The dissolved plutonium, in contrast, was primarily (80 to 90%) in the oxidized form (oxidation states V or VI). The fraction of the dissolved plutonium present in the oxidized form in these experiments was the same as that observed for the ambient plutonium in Lake Michigan.

Since the soluble plutonium in these experiments was largely in the oxidized form, two additional experiments were carried out to test the effect of an added oxidizing agent. Chlorine at concentrations of 10 and 100 ppm (generated by the addition of sodium hypochlorite) was used. Duplicate 0.1 g sediment samples were extracted for two successive four day periods. At the lower chlorine concentration 23% of the plutonium was in the first extract and 25% in the second. At the higher concentration 63% was in the first extract and 21% (of that initially present) in the second, indicating almost complete removal of plutonium from the sediment.

From these observations, it is apparent that most of the plutonium which is associated with these sediments is bound by adsorption and that this plutonium is in equilibrium with the pluto-

nium dissolved in the water. As a consequence the conclusion is drawn that the adsorption of plutonium onto sediments will, in the event of an intrusion into a system, markedly reduce the initial plutonium concentration in the water; but after the equilibrium has been established, any further reduction in plutonium concentration can only occur by the removal of sediments from the system.

IDENTIFICATION OF PU(V) IN NATURAL WATERS

D. M. Nelson and K. A. Orlandini

Background and Scope

We have previously shown[1,2] that in many natural waters either Pu(V) or Pu(VI) is the dominant oxidation state of the plutonium in solution. The standard oxidation state separation which we used, lanthanum fluoride precipitation, distinguishes between plutonium which is in the reduced forms (III or IV) and that which is in the oxidized forms (V or VI). However, no information is gained regarding which member of each pair is actually present.

It is important to establish which of the oxidized forms is present since the geochemical behaviors of the two states are very probably different. If the oxidized form in water is the VI state, then the known geochemical behavior of natural uranium (VI) can be used to help predict the behavior of this plutonium. However, if the stable form is the V state, then predictions based upon the behavior of uranium (VI) could be seriously in error.

The relative stabilities of Pu(V) and Pu(VI) are difficult to predict since the redox potential of the Pu(V):Pu(VI) couple in neutral solution is within the range of estimated potentials for natural waters. An experimental technique capable of distinguishing Pu(V) from Pu(VI) is, therefore, needed. This technique must not use materials likely to alter the oxidation state of the ambient plutonium, should give clean separations, and should be capable of handling the large sample volumes needed in environmental samples. Adsorption onto a chemically inert substrate appeared to be the approach that would most easily meet these requirements.

Progress in 1979

Several solid substrates were evaluated to establish whether Pu(V) and Pu(VI) could be distinguished by their adsorption properties. The adsorption characteristics of these solids were measured in solutions of known pH with plutonium in known oxidation states. The nuclide used was ^{237}Pu. The Pu(VI) stock solution was prepared by electrolytically oxidizing a solution of Pu(IV) in 0.8 M HNO_3 at a platinum electrode. Experiments using Pu(VI) were normally done in the presence of 10^{-5} M MnO_4^- ion to ensure that the plutonium was not reduced during equilibration. The Pu(V) stock solution was prepared by electrolytically oxidizing a solution of Pu(IV) in 1.0 M HCl at a platinum electrode. The evolution of Cl_2 gas during the electrolysis reduced the final acidity to ~0.1 M. The oxidation state purity of these solutions was established using the procedure reported below.

Two materials were found to have significantly different adsorption characteristics for the V and VI states. The first, silicic acid, (Mallinckrodt, 100 mesh, powder) which is added as the solid, adsorbs Pu(VI) much more strongly than Pu(V). The second, calcium carbonate, which is formed in situ, adsorbs Pu(V) more strongly than Pu(VI).

Differential adsorption on silicic acid has previously been used[3] to separate Np(V) from Np(VI) in near neutral solution. The adsorption characteristics which we measured for Pu(V) and Pu(VI) are presented in Figure 1 where the distribution ratios, K_d, are plotted as a function of pH. It can be seen that a very clean separation is possible at the pH of most natural waters, 6 to 8. Since both Pu(III) and Pu(IV) are also strongly adsorbed in this pH range, the only plutonium oxidation state remaining in solution should be Pu(V).

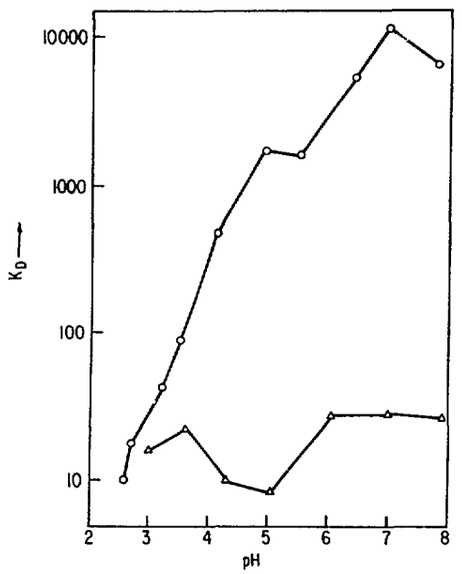

Fig. 1. The distribution ratio, K_d, of plutonium between silicic acid and 0.001 M $NaHCO_3$; Δ, Pu(V); o, Pu(VI). The pH was adjusted by adding HCl.

During the neptunium study it was noted that a strong oxidizing agent was needed to maintain the VI state. We have observed similar behavior for plutonium. This suggests that Pu(VI) is reduced to Pu(V) either by the silicic acid or by some component of the water. A series of experiments was, therefore, conducted to distinguish between these possibilities. Pu(VI) tracer was added to both Lake Michigan water and 0.01 M bicarbonate solution and, at various times after the additions, subsamples were removed and equilibrated for 2 minutes with silicic acid (10 g/L). The results of these experiments, some of which are shown in Figure 2, indicate that the degree of reduction is not a consequence of contact with silicic acid. They indicate that Pu(VI) is rapidly reduced to Pu(V) in these waters. When a trace of permanganate ion is present, there is no decrease in adsorption with time, i.e., no reduction occurs.

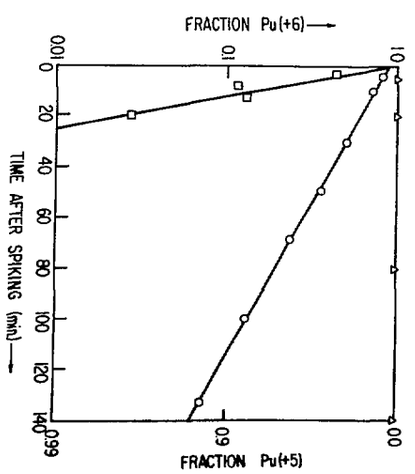

Fig. 2. Conversion of Pu(VI) to Pu(V) after introduction into pH 8 solutions. □, 0.01 M $NaHCO_3$; o, Lake Michigan water; Δ, Lake Michigan water + 10^{-5} $KMnO_4$.

The silicic acid separation technique was then applied to freshly collected samples of water from the Irish Sea and Lake Michigan to determine the oxidation state of the ambient plutonium. Pairs of filtered water samples were processed from each location. One sample from each pair was analyzed using the rare earth fluoride technique to separate the plutonium (III and/or IV) from the plutonium (V and/or VI). The other sample was equilibrated with silicic acid (10 g/L). The silicic acid was removed by filtration and the filtrate was then analyzed using the rare earth fluoride procedure. The concentations of oxidized plutonium remaining in solution after equilibration with silicic acid were 128 fCi/L for the Irish Sea sample and 0.47 fCi/L for the Lake Michigan sample. These compare with oxidized plutonium concentrations of 101 fCi/L and 0.41 fCi/L for the untreated replicates. The total plutonium concentrations in the samples as determined by a ferric hydroxide preconcentration procedure were 129 and 0.42 fCi/L. Since the oxidized plutonium was not measurably adsorbed by silicic acid, it appears that the oxidized form of plutonium in the water of both the Irish Sea and Lake Michigan is the V state. To verify that hexavalent actinides were strongly adsorbed during these extractions, uranium analyses were performed on the Lake Michigan water before and after the silicic acid treatment. About 95% of the uranium was adsorbed.

Recent experiments using $CaCO_3$ precipitation support the finding of the silicic acid technique. Tracer experiments indicate that Pu(V) and Pu(IV) are carried on $CaCO_3$ (>75%) while Pu(VI), like U(VI), is not (<7%). Precipitation is accmplished by increasing the Ca^{++} concentation to 200 mg/L and raising the pH to ~9 with sodium hydroxide. The carbonate is that naturally present in the water. The resulting $CaCO_3$ precipitate is separated, dissolved in nitric acid and the plutonium analyzed by the lanthanum fluoride method. Using this technique we have shown that the oxidized form of plutonium in Lake Michigan is coprecipitated with $CaCO_3$ while the uranium remains in solution. These experiments support the conclusion that the oxidized form of plutonium in Lake Michigan is Pu(V).

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PLUTONIUM OXIDATION STATES IN THE IRISH SEA

D. M. Nelson and M. B. Lovett*

Background and Scope

It has become apparent that oxidation state is an important factor influencing the environmental behavior of plutonium. We have previously shown[1] that plutonium in seawater exists in at least two oxidation states, a reduced state (either III or IV) which is strongly bound to sediments and an oxidized state (either V or VI) which is weakly bound. The degree to which plutonium is removed from the oceans and ultimately its geochemical fate is, in part, governed by (1) the relative abundances of the reduced and oxidized states, and (2) the extent to which these forms adsorb onto sediment, i.e., their distribution ratios.

The plutonium entering the Irish Sea from the operations of the British Nuclear Fuels Ltd. reprocessing plant at Windscale provides an excellent opportunity for the study of these processes. This relatively constant, point source is particularly useful in studies of the spatial and temporal changes in oxidation state which may occur after plutonium is introduced into the sea. Initial measurements, made during the summer of 1977, established that 70 to 90% of the plutonium in filtered seawater collected near the Windscale discharge was in an oxidized form. A more extensive set of samples, collected during September of 1977 indicated a similar oxidation state distribution existed throughout the Irish Sea at that time.

Progress in 1979

During 1979 the analysis of two additional sets of water samples collected from throughout the Irish Sea during May of 1978 and April of 1979 were completed. This work was done in cooperation with the Fisheries Radiobiological Laboratory (FRL), Lowestoft, England. The samples were collected during their routine monitoring cruises. Argonne's measurements of plutonium oxidation states complement the FRL measurements of ^{137}Cs and of total plutonium, both dissolved and particulate, in seawater. Since ^{137}Cs is not lost significantly from seawater, changes in the ^{137}Cs to plutonium ratio after release provide the means to calculate the fraction of plutonium remaining in solution.

As before, the fractions of plutonium in the reduced and oxidized forms were established using the rare earth fluoride precipitation technique. The measurements of total plutonium obtained by summing the concentrations found in the reduced and oxidized forms were in excellent agreement with the total plutonium concentrations measured on replicate samples at FRL.

The results from these two latest sampling periods confirm the observations made during 1977. As shown in Figure 1, the fraction of the dissolved plutonium present in the oxidized form during each of these sampling periods is independent of plutonium concentration. Also, since the total plutonium concentration is correlated with the time elapsed since the plutonium was introduced, the fraction in the oxidized form does not change appreciably between a week and a year after introduction. The constancy of this data set suggests that a redox equilibrium is established very shortly after the plutonium is introduced into the sea and that the position of this equilibrium is independent of time, plutonium concentration, and location in the Irish Sea.

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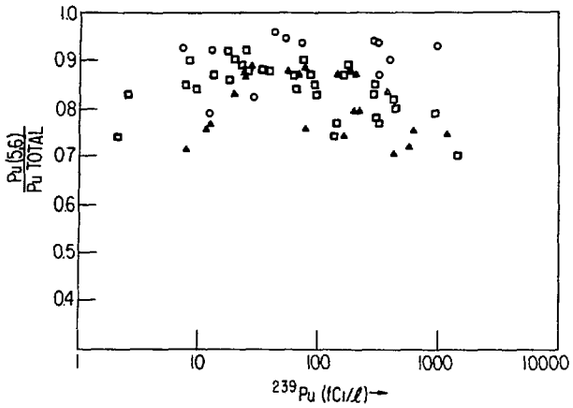

Fig. 1. The fraction of dissolved plutonium present in the oxidized form in the Irish Sea. o, September 1977; Δ, May 1978; □, April 1979).

The fraction of the Windscale plutonium which has remained in solution, relative to ^{137}Cs, has varied between 5 and 8% during the period 1974-1978. Since ~85% of this soluble plutonium has now been shown to be in the oxidized form, we estimate that ~5% of the plutonium released from Windscale leaves the area in solution as Pu (V or VI). To determine the origin of this oxidized plutonium, we collected samples of the material being discharged from Windscale for two months prior to the May 1978 sampling trip. Analysis of these samples showed that prior to release no more than 1% of the plutonium was in the oxidized form. Most, and possibly all, of the oxidized plutonium found in the Irish Sea must therefore have been oxidized after its release. This, again, supports the idea that the plutonium oxidation state in the Irish Sea is controlled by an active redox equilibrium.

The oxidation state of plutonium adsorbed to suspended particulate matter was originally determined by difference from replicate samples of filtered and unfiltered water. More accurate measurements have now been made using a technique in which the plutonium is leached from the particles after they are collected on a filter. Using this new technique we now estimate that <1% of the plutonium adsorbed to inorganic paticles is in the oxidized form. Hence, the distribution ratio for the oxidized form onto inorganic particles is at least 1000 times lower than the distribution ratio for the reduced form.

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REMOVAL OF FALLOUT PLUTONIUM FROM THE MISSISSIPPI RIVER WATERSHED

D. M. Nelson and J. O. Karttunen

Background and Scope

The processes which remove plutonium from land and transport it to the sea are of fundamental importance in assessing the potential impact of any plutonium releases which might occur in the nuclear power industry. The mechanisms and rates by which this removal occurs can be established through studies of fallout plutonium. This fallout was uniformly deposited over wide areas and the time and magnitude of the input are well documented. Studies of removal on the scale of a large watershed are possible.

We have previously investigated plutonium removal from the watershed of the Miami River above Sidney, Ohio,[1] and from two small watersheds in the same area.[2] The results confirmed particle transport as the dominant mechanism for plutonium removal. In the Miami River more than 90% of the plutonium was on suspended solids; the concentration on these solids was slightly higher than that for typical agricultural soils in the area. This indicated a preferential transport of the smaller soil particles since they have a somewhat higher plutonium concentration than the bulk soil.[3] The yearly removal of plutonium from the upper Miami River watershed was estimated to be ~0.05% of that which had been deposited. These studies covered a small geographical area and, because of the nature of the watersheds, little could be learned about historical removal rates.

Progress in 1979

These studies have now been expanded to include the watershed of the Mississippi. Samples of filtered water and suspended particulate matter were collected from the Mississippi and several of its major tributaries. The plutonium concentrations were measured in these samples as well as in core samples collected offshore from the Mississippi delta in areas where the sedimentation rates are high. The core samples were also analyzed for ^{210}Pb content.

Concentrations of $^{239,240}Pu$ in the filtered water samples averaged 0.22 fCi/L with a range of 0.04 to 0.37 fCi/L for the 15 samples. There was no apparent geographical pattern to the data nor was there a correlation between the concentration of plutonium in solution and the amount of suspended particulate matter in the water. The plutonium concentrations are quite similar to those we have preivously found in the upper Miami River and the Grand River (Michigan). Using the average concentration of 0.22 fCi/L and the average flow of the Mississippi (5×10^{14} L/year) we calculate the annual transport of dissolved plutonium to be ~0.1 Ci. Since the total plutonium deposition on the Mississippi watershed has been ~6000 Ci (2 mCi/km^2 $\times$ 3×10^6 km^2), the annual removal of dissolved plutonium is approximately 0.002% of the total inventory.

The plutonium concentration on the suspended solids averaged 9.5 fCi/g with a range of 4.1 to 18 fCi/g. Again there was no obvious geographical pattern nor was the plutonium concentration on the solids correlated with the amount of suspended solids in the water. The average distribution ratio (activity per kg of solids/activity per liter of water) of 5×10^4 observed here was somewhat lower than that for Lake Michigan ($\sim 4 \times 10^5$). The amount of plutonium on solids being transported annually by the Mississippi is calculated to be ~3 Ci (9.5 pCi/g $\times$ 3×10^{14} g/year). This is a factor of 30 higher than the amount dissolved in the

water and again emphasizes the importance of suspended particles in plutonium transport. The current annual removal of plutonium from the Mississippi watershed is ~0.05% of the total inventory, quite similar to that observed previously for the upper Miami.

The analysis of the sediment cores lead to several unexpected observations. Firstly, the plutonium concentrations (26 to 44 fCi/g) in the surface layers from all six of the cores were substantially higher than the concentrations measured on suspended particles in the river. This could be a consequence of particle sorting after the particles enter the ocean. However, the mean surface concentration of 36 fCi/g is 2 to 3 times higher than the concentrations observed for the smallest particle size range (<2 μm) separated from midwestern agricultural soils.[3] An alternative explanation is that the suspended particles adsorb additional plutonium from the ocean water before settling to the bottom. If this is the case, the cores contain information about past plutonium concentrations in the ocean as well as about past transport down the Mississippi and we must be careful not to misinterpret the data.

The historical record of plutonium accumulation in these sediments, as revealed in profiles of concentration vs. depth, shows little change during the past 20 years. Either the inputs were fairly constant or the differences have been obscured by biological mixing after deposition. Comparisons of the ^{210}Pb and $^{239+240}Pu$ profiles support the idea that significant biological mixing occurs in this area. Plutonium was detected in several of the cores at depths well below what could be expected on the basis of ^{210}Pb dating. There is no indication, in these cores, that the amount of plutonium transported by the Mississippi was ever substantially higher than it is today.

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AMERICIUM IN FRESHWATER SYSTEMS

K. A. Orlandini

Background and Scope

Concern about the behavior and ultimate fate of americium in the environment is a consequence of the high toxicity of the principal nuclide, ^{241}Am, and the large amounts formed in nuclear fuels. At present the principal source of environmental americium is ^{241}Am, from the decay of ^{241}Pu (15 y), one of the fallout plutonium nuclides. Its concentration in environmental water is exceedingly low, and in fact prior to 1979 attempts to determine concentrations in some freshwaters (e.g., Lake Michigan) were unsatisfactory because of limited sample size (50 L) and the low concentration. For studies of the biogeochemical behavior of americium in natural aquatic systems the measurement of the concentration ratio (concentration ratio = concentration in solids/concentration in water) is important since adsorption onto solids is probably the dominant factor in controlling the americium concentration in most natural water systems.

Available information on americium in freshwaters and freshwater systems has been scant.[1-3] An effort has, therefore, been made to obtain a more complete description of americium behavior in freshwater systems by determining ^{241}Am concentrations in water and sediments.

Progress in 1979

In 1979 large volume samples (>300 L), collected from Lake Michigan, were analyzed using improved separation techniques to determine the ^{241}Am concentration accurately. By utilizing sequential procedures the radiometric measurement of americium and other actinide elements (e.g., plutonium, thorium, uranium) can be carried out on the same sample. Americium and the other actinides are separated and purified by ion exchange and solvent extraction techniques before the assay for ^{241}Am and ^{243}Am (the isotopic diluent) by alpha spectrometry.

Five large samples of filtered Lake Michigan water have now been analyzed for ^{241}Am content by combining the americium fractions saved from samples having uniform plutonium concentrations. Two composites from 1975, one collected in the spring when the lake was well mixed and the other collected from near the bottom later in the year, had ^{241}Am concentrations of 0.013 ± 0.002 fCi/L. Two composites from autumn of 1976, one from the hypolimnion and one from the epilimnion yielded ^{241}Am concentrations of 0.011 ± 0.001 and 0.0030 ± 0.0006 fCi/L, respectively. The lower concentration of ^{241}Am in the surface waters during the autumn corresponds with a depletion of plutonium from 0.44 to 0.09 fCi/L for these samples.This suggests that americium, like plutonium,[4] undergoes a seasonal cycle characterized by a depletion in the surface waters in the autumn. The concentration of ^{241}Am in a 600 L sample collected in December 1979 was 0.010 ± 0.001 fCi/L showing that any overall decrease in ^{241}Am concentration in Lake Michigan during the past 5 years has been slight.

Americium was also measured in three basins of Great Slave Lake (Canada, N.W.T.) and yielded concentrations of 0.035, 0.08, and 0.08 fCi/L. In lakes or bogs where the acidity and organic matter are high, ^{241}Am appears to be significantly more soluble. The Okeefenokee Swamp (Georgia) and Lake 661 (Experimental Lakes Area, Canada) had concentrations of 0.3 and 0.9 fCi/L, respectively.

These more accurate ^{241}Am measurements now allow the concentration ratio onto sediments to be estimated. The average ^{241}Am concentration observed for fine-grained Lake Michigan sediments is ~40 fCi/g yielding a concentration ratio of ~4 x 10^6. This value is quite comparable to the concentration ratio for quadravalent plutonium observed in Lake Michigan. The three basins of Great Slave Lake show a similar correspondence between the concentration ratios of ^{241}Am (1.4 x 10^5, 2.3 x 10^5, and 3.9 x 10^5) and those of $^{239}Pu(IV)$(1.7 x 10^5, 2.0 x 10^5, and 5.1 x 10^5). We have also observed a correlation between Pu(IV) and americium concentration ratios in the Irish Sea.[5] This indicates that the processes which remove americium from the water are similar to those which remove Pu(IV).

In midwestern top soils (plowed layer) and eroded soil materials in riverine environments the concentrations of ^{241}Am are 1 to 5 fCi/g (dry) while the concentrations in the surficial sediments and suspended solids of midwestern lakes are 10 to 50 fCi/g. Sediment concentrations as high as 170 fCi/g have been observed in a southeastern U.S. aquatic system where the fallout plutonium is concentrated in the top 2 cm of sediment. The plutonium to americium activity ratios in the sediment cores of midwestern lakes are the same (within analytical error) as those in the homogenized midwestern top soils, and the mean of these ratios (4.3) is in agreement with that expected for about 16 years' accumulation of ^{241}Am from decay of the ^{241}Pu from fallout.

Characterization of the americium on sediments by means of a reductant-complexant extraction of both lacustrine (Lake Michigan) and estuarine (Buzzard's Bay, Massachusetts) sediments shows that >95% of it is associated with the "hydrous metal oxide fraction," as is plutonium.[6]

Data on the occurrence and concentration of americium in Lake Michigan biota can be found in Ref. 3.

Prospects

The adsorption of americium (and plutonium) onto particulate material in natural water systems is a function of pH, the concentrations of dissolved organic matter, and inorganic complexing agents, oxygen availability and the type of particulate material formed in or entering the aquatic system from the surrounding terrain. Studies of these factors are being conducted in both the laboratory and the field with the objective being to identify the chemical species and to characterize the state of americium (and plutonium) in natural waters.

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R/V EKOS, A RESEARCH TOOL

R. M. Williams and R. W. Dana

Background and Scope

The research vessel Ekos was purchased in 1978 with the purpose of increasing the interdisciplinary cooperation and hence effectiveness of our Great Lakes research programs. Design specifications of the vessel were the result of tradeoffs between available money and the desires of the research scientists. The initial report on the vessel's capabilities, including specifications, can be found in last year's Annual Report.

Progress in 1979

As expected the acquisition of the research vessel Ekos has provided uncomplicated access to Lake Michigan and opened new areas of research to the Laboratory. The vessel has sufficient size (58 ft) and speed (18 knots) to conduct multidisciplinary research on a one-day basis anywhere in the southern basin of Lake Michigan.

Average use between April and December was three days per week, while during the colder months trips occurred once per week. Heavy summer use is to be expected but winter operational capability is very important because of lack of data during this period. Four extended cruises involving the whole southern basin were completed. Joint cruises were conducted with scientists from SUNY-Buffalo and Illinois Institute of Technology.

Typical activities include collection of biological and chemical samples from stations accessible on day trips from Chicago. The extended southern basin cruises collect water samples and sediment cores for biological and chemical analyses. Instruments located at the 68th Street water intake crib and a research tower on the Indiana Shoals are regularly serviced. On three occasions overnight micrometeorological experiments were conducted which used the Ekos as a data gathering laboratory and power source for the instruments.

DEVELOPMENT OF A TIME-LAPSE CAMERA SYSTEM FOR BENTHIC RESEARCH

B. M. Lesht and R. V. White

Background and Scope

Photographs of the ocean floor have long been used as a tool for studying benthic processes, both physical and biological. For the most part, the purpose of such photographs (typically either single frames or a few successive frames taken with a towed camera) has been exploratory. Although some long series of bottom photographs have been made from fixed cameras, only very recently have time-lapse photographs been used in conjunction with other instruments in quantitative studies. To our knowledge, this technique has not been used previously in the Great Lakes.

The camera system described here (see Figure 1) was developed for use in the sediment resuspension program of the Great Lakes project. In its present configuration, the camera is synchronized with a recording current meter. The resulting records are used to document the frequency and intensity of sediment resuspension events and to provide data necessary for the derivation of transfer functions between current speed and resuspension for use in numerical water quality models.

Progress in 1979

Design and construction of the camera system was completed in time for field trials during the last part of the 1979 season.

The camera is a standard super 8 mm movie camera with single frame and strobe synchronization controls. It has a fairly wide-angle lense (7.5 mm), which, combined with the domed optical port on the pressure case, results in a field of view measuring 0.6 m by 0.45 m when the camera is mounted 1 m above the bottom.

Photographs are taken in groups called bursts. The number of frames exposed during each burst and the interval between bursts can be selected from 135 different combinations. The controlling circuit (intervalometer) is based on a quartz crystal clock for precise time keeping. When exposed at a typical rate, one frame every 15 minutes, a 3300 frame role of film will last over 30 days.

This system was deployed five times between July 20 and October 20 at locations in Lake Michigan and Saginaw Bay. Over 800 hours of data have been recovered, showing several instances of intense sediment resuspension.

Prospects

The recording current meter failed to operate correctly during the 1979 field tests. Efforts are under way to correlate the resuspension events recorded in Lake Michigan with wind data taken at our Indiana Shoals meterological tower.

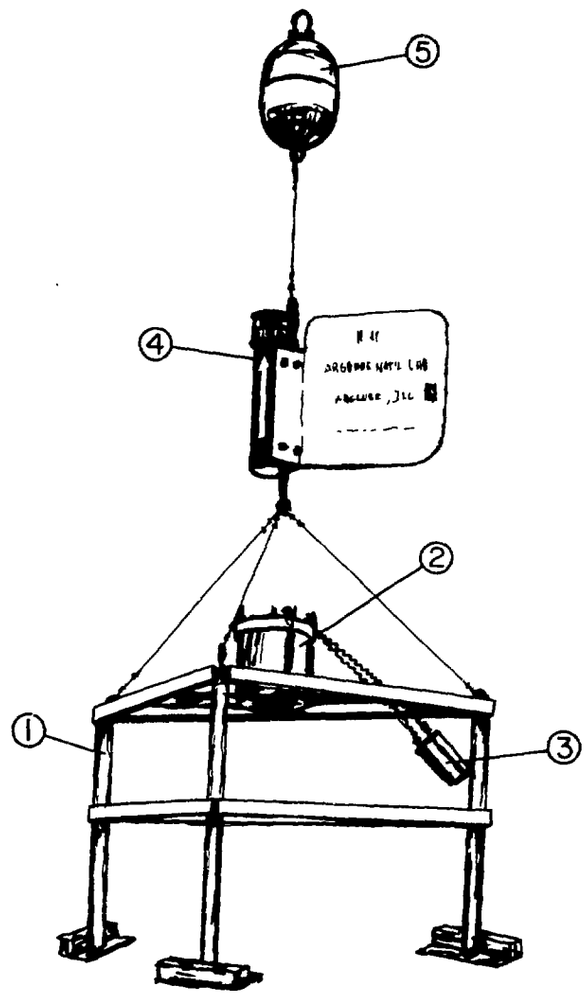

Fig. 1. Time lapse camera system showing: (1) unistrut frame; (2) pressure case containing camera, electronics, and batteries for the electronic strobe light; (3) electronic strobe light; (4) recording current meter; (5) subsurface float.

SEDIMENT RESUSPENSION PROCESSES IN THE GREAT LAKES

B. M. Lesht

Background and Scope

This program is designed to investigate physical resuspension of bottom sediments in the Great Lakes. Emphasis is placed on field experiments in which turbidity and currents near the bottom are measured for long periods of time (weeks or months) with self-contained instrument packages. The goals of this work are: (1) direct observations of resuspension events in various lake environments; (2) correlation of resuspension events with meteorological forcing; (3) determination of threshold parameters for resuspension and entrainment rates for various sediment types; and (4) coupling of threshold parameters and entrainment rates with models of lake circulation to explain existing patterns of sediment distribution and to predict likely patterns of sediment and pollutant dispersal.

Progress in 1979

As with any field-oriented program this project is equipment intensive. Therefore much of this first year's effort has been devoted to development of equipment.

Two instrument packages are currently in use. One, a time-lapse camera system (TLCS) was described in the preceding paper of this report. The other, referred to as the benthic boundary layer instrument package (BBLIP) is designed to record detailed measurements of the mean and fluctuating flow field within 1 m of the bottom. Included are relatively high frequency (0.61 Hz) samples of horizontal velocity at three levels, the direction of the mean current, and the pressure exerted on the bottom by surface waves. In addition, the water turbidity near the bottom is sampled at one-half this frequency.

Table 1. Experiment locations, 1979 Great Lakes sediment resuspension study.

Dates	Instrument	Location	Hours of data recovered
May 31 - June 21	BBLIP	Saginaw Bay 1 (43°51.2'N, 83°42.8'W)	None (pressure case flooded)
July 20-21	TLCS	Indiana Shoals (41°45'N, 87°23'W)	22 (TLCS field test)
July 31 - Aug 2	TLCS	Indiana Shoals	53
Aug 9-19	TLCS	Indiana Shoals	214
Aug 31 - Sept 18	TLCS	Indiana Shoals	226
Oct 9-22	BBLIP	Saginaw Bay (43°59.6'W, 83°37.6'W)	312
Oct 9-22	TLCS	Saginaw Bay 2	312

These systems were deployed several times during 1979. Table 1 shows the experiment locations and results. Figure 1 is an example of the data returned by the BBLIP. This plot shows the near bottom transmittance in Saginaw Bay as a function of time. The obvious drops in transmittance may be the result of local resuspension, but preliminary analysis of the current meter data suggest that the primary cause is advection of an established nepheloid layer. This layer seems to move along the bottom of the bay in a direction opposite to that of the forcing wind.

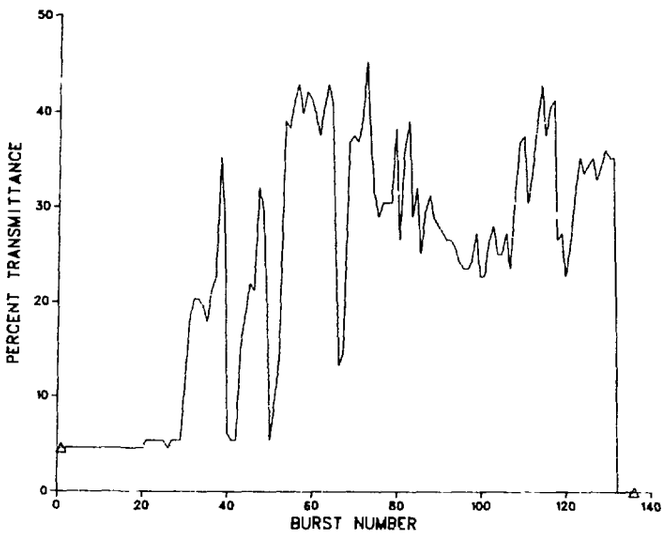

Fig. 1. Time series of transmittance 40 cm above the bottom in Saginaw Bay. Experiment was begun 9 October 1979. Bursts are two hours apart.

In addition to work on data collected this year, analysis of similar data, taken on the Atlantic inner continental shelf, is continuing. In these studies, field data are used as a basis for determining empirical threshold parameters for resuspension and entrainment rates. As an example, Figure 2 shows the observed relationship between the concentration of suspended sediment 1 m above the bottom and the rms wave orbital velocity measured at the same level for the inner continental shelf data. These data also were used to compute the values plotted in Figure 3, which shows the approximate sediment entrainment rate as a function of bottom shear stress.

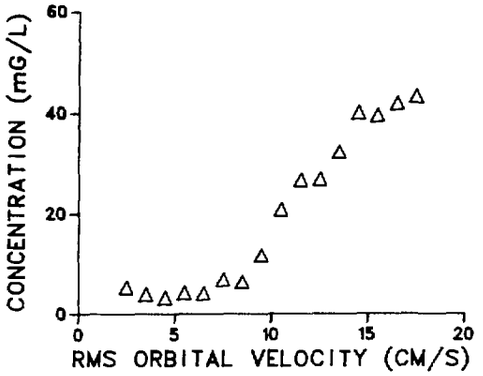

Fig. 2. *Relationship between concentration of* resuspended sediment and wave-orbital velocity 100 cm above the bottom. Data taken on the Long Island inner continental shelf.

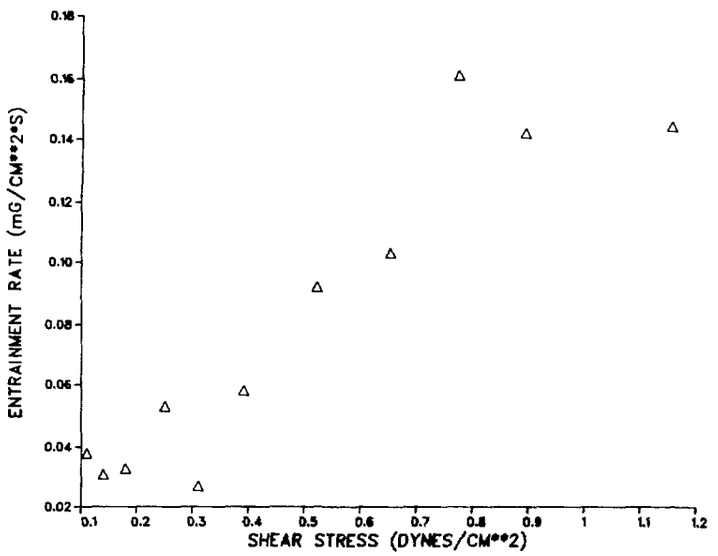

Fig. 3. Sediment entrainment rate versus estimated bottom sheer stress for Long Island inner shelf sediments. Shear stress estimated from current meter measurements.

Prospects

Analysis of the inner continental shelf data should be completed in 1980. The techniques developed during this phase of the study will be applied to the existing Great Lakes observations and to those collected in the next field season. This should enable us to make quantitative estimates of the occurrence of resuspension and the rate of entrainment of sediments at selected Great Lakes locations.

DEVELOPMENT OF A SEQUENTIAL AIR SAMPLER FOR INORGANIC ELEMENTS AND COMPOUNDS

R. M. Williams, R. V. White, and R. S. Ely

Background and Scope

The atmospheric contribution to the mass balance of contaminants entering natural bodies of water has only recently been identified as a major component. The air/water interface processes which control the transfer of particles and gases to the water are not well understood. To examine these processes successfully requires that field experiments be carried out over real surfaces under a variety of naturally occurring conditions. The long-range objective of these experiments is to parameterize the transfer processes in terms of easily determined measurements (e.g., wind speed and contaminant air concentration). In two years of existence the Great Lakes Transport Group has been developing the capabilities to achieve this objective. A system for determining trace metal air concentrations of trace metals in air blowing from three sectors has been in operation at the Chicago 68th Street water intake facility since August 1978. In addition a research tower on the Indiana Shoals in Lake Michigan has been operational from May to November since September 1978. This research tower is the primary location for determining the desired parameterization since it is small enough and is sufficiently far from land that effects of the measuring station and the coastal boundary are minimized. However, good meteorological measurements alone are not sufficient. A portable air sampler for aerosol concentration measurements under severe conditions is also necessary.

Progress in 1979

A rugged air sampler system has been developed for use from towers and buoys to gather the required aerosol concentration data under realistic conditions. In order to determine concentration variations daily, or for even shorter periods, a multiple sampler is desirable. The finished system consists of a circular plate containing 24 filters, which are sequentially rotated into the air path. The electronic control circuitry allows selection of both the sampling period (3 to 49 hours) and a delay interval before starting (1 to 29 hours). The filters are serviced by replacing the entire filter platter. At that time the number of the last filter sampled is displayed as well as the shortened sampling time for the last filter. After the 24th filter, the system is shut down to conserve power. A typical automobile battery has sufficient capacity for about 20 days' operation, while a solar panel recharging system extends operation indefinitely.

An efficient air pump is required for remote operation since batteries are the only power source. The pump selected is a Brailsford TD-4X2S pump which delivers about 3.5 L/min against a pressure drop of 2 cm Hg with a current drain of 0.12 amp @ 12 VDC (power consumption less than 1.5 watts).

The other critical part of the system is the filter for removing the inorganic particulate matter. It must have good filtering efficiency and yet not seriously restrict the airflow and it must be chemically compatible with the contaminants to be measured. The selected filter is a Teflon membrane manufactured by Ghia Corporation. At 3.5 L/min the pressure drop is less than 2 cm Hg, and yet collection efficiency for 0.1 μm particles exceeds 99%.

The filter samples are ideal for nondestructive analyses by x-ray fluorescence for many trace elements, by ion chromatography for nutrients, and by gas chromatography for particulate

organics. A modified system is now being developed for gaseous trace organics.

The first unit was operated for four months in late 1979 from the Indiana Shoals tower in southern Lake Michigan. Air, drawn from the same level that the wind speed and direction were determined (~9 m), was sampled every 8 hours. Analyses of the collected filters were delayed to await operational capability of the automated x-ray fluorescence device (early 1980).

Prospects

In 1980, inorganic air sampler units will be placed on the 68th Street crib and Indiana Shoals tower in Lake Michigan, and on the Six Fathom Bank tower in Lake Huron. In addition organic air samplers will be placed at the two tower locations. Analyses of the partial 1979 data and the 1980 data will be used to determine atmospheric dry deposition inputs of both inorganic and organic contaminants to the lakes.

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