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RADIOLOGICAL AND ENVIRONMENTAL RESEARCH DIVISION ANNUAL REPORT

Ecology

January—December 1978

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ARGONNE NATIONAL LABORATORY, ARGONNE, ILLINOIS

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RADIOLOGICAL AND ENVIRONMENTAL RESEARCH DIVISION ANNUAL REPORT

Ecology

January through December 1978

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

Preceding Report: ANL-77-65, Part III, January-December 1977

FOREWORD

During the period covered by this report a significant change has occurred in the source of funding for two of the major programs conducted by the Ecological Sciences Section. As of 1 October 1978, sponsorship and management of our Great Lakes Research Program and of our studies of the effects of sulfur dioxide on midwestern grain crops has been transferred from the Assistant Secretary for Environment's Office of Health and Environmental Research in the Department of Energy, to the Energy Effects Division of the Office of Research and Development in the U.S. Environmental Protection Agency. This transfer is part of a major reorganization of federally funded, environmental and health effects research related to fossil fuels; the action was initiated at the direction of the Office of Management and Budget.

A significant new addition to the Great Lakes Research Program was marked by the arrival and formal acceptance of our new research vessel, the R/V Ekos. After a shakedown cruise in the Gulf of Mexico and up the Mississippi and Illinois Rivers, during which sediment cores were collected for our ongoing studies of the geochemical fate of transuranics, the Ekos arrived at Argonne in September, only a few months later than originally expected. The new vessel was formally commissioned on 25 October 1978, by Ruth C. Clusen, the Assistant Secretary for Environment of the Department of Energy. Shortly thereafter, operations on Lake Michigan were begun from our new base at the mouth of the Chicago River. Descriptions of the Ekos and its research capabilities are included in this report.

By and large, the Section's research programs have been supported in 1978 at funding levels similar to those of 1977. Results obtained in the second year of field studies of the effects of airborne concentrations of sulfur dioxide on soybeans confirm the preliminary observations of last year to the effect that significant changes in yield can occur with atmospheric concentrations of SO_2 typical of those often found near large, fossil-fuel-burning power plants; an accurate dose-response relationship is taking form. This year these studies have been expanded to include examination of the effects of acid rain occurring in concert with the impact of airborne SO_2.

As part of the Great Lakes Program's new emphasis on atmospheric input studies, a tower was erected 10 km offshore in Lake Michigan, in a location frequently downwind of the industrial areas of Chicago and northern Indiana. Measurements of atmospheric pollutant concentrations and flux-related meteorological conditions obtained over the open lake from this platform, plus measurements of trace elements collected in the water, the sediments, and the major Lake Michigan tributaries, have been combined to construct a preliminary mass balance for cadmium in the lake.

Ecological studies continue to focus on the determination of the effects of energy-related pollutants on planktonic species typical of the Great Lakes. This year also included experimental studies of the effects of enclosure size on the response of zooplankton to stress by cadmium. A new mobile field laboratory has been constructed to support studies of the effects of water temperature regimes on rates of accumulation by salmonid fishes of persistent organic contaminants such as PCB's. Present plans call for this facility to be operated near a large power plant located on the shore of Lake Michigan to examine these effects in the warm waters leaving the plant's once-through cooling system.

A variety of studies of the behavior of transuranic elements conducted in environments as diverse as the Irish Sea, Great Slave Lake, the Great Miami River, and the Great Lakes, have focused on changes in the oxidation state of plutonium, and the effects these changes have on the behavior of this important element in the aquatic environment. The development of special techniques to separate and quantify the several oxidation states of plutonium is a major step forward in improving our ability to predict the consequences of an accidental release of radioactivity to the environment.

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EFFECTS OF CHRONIC SULFUR DIOXIDE FUMIGATION ON DEVELOPMENT, YIELD, AND SEED QUALITY OF FIELD-GROWN SOYBEANS: SUMMARY OF 1977 AND 1978 EXPERIMENTS

D. G. Sprugel, J. E. Miller, P. B. Xerikos, and H. J. Smith

The primary objective of the soybean-SO_2 study[1] has been to determine the effect of sulfur dioxide fumigation on soybean yield at harvest, under field conditions. As shown in Table 1, significant yield reductions occurred at all fumigation levels used in 1977 and 1978,[2] including three plots where the SO_2 concentration during the fumigations was about 100 ppb (260 $\mu g/m^3$). These levels are considerably lower than those which have previously been thought to cause damage to soybeans. As in 1977,[3] yield reductions occurred in 1978 even where no visible damage occurred, and under conditions which did not violate U.S. Environmental Protection Agency Secondary Air Quality Standards for sulfur oxides.

Generally speaking, the amount of yield reduction caused by a series of air pollution episodes is determined by both the pollutant concentration and the duration of the exposures. For this reason time and concentration are often multiplied together to give an estimate of "dose." Where high concentrations are reached, this estimate of dose is not adequate to predict yield reduction, since short exposures (1-2 hr) to very high pollution levels (>2 ppm) may cause tissue necrosis or other permanent injury, which might not occur if the same dose were administered over a longer period of time.[4] However, at pollution levels where visible injury does not occur, dose expressed as concentration × duration is probably the most useful single predictor of yield reduction. Further studies, including exposure of field-grown plants to a single concentration of SO_2 for varying lengths of time, are needed to clarify this relationship.

For the combined 1977 and 1978 data the second-order polynomial which best expressed the relationship between yield reduction and SO_2 dose was

$$y = 0.803\,x - 0.0034\,x^2$$

where y is the yield reduction (in percent) and x is dose in ppm-hr. The squared term is significant at the 2% level. The exponential equation

Table 1. Yield reductions in soybeans subjected to varying concentrations of SO_2 in the open-air fumigation system, 1977– 1978. Values are given ± standard error.

Plot	Mean SO_2 concentration, ppm	Dose, ppm-hr	Yield, kg/ha Fumigated	Control	Yield reduction, %
1977					
Ambient	0.005–0.015	--	2566 ± 77	2577 ± 73	0.3 ± 4.2
Low	0.117	13.3	3052 ± 92	3478 ± 101	12.3 ± 4.3 ($p < 0.01$)
Medium	0.300	34.2	2482 ± 65	3140 ± 48	20.5 ± 3.1 ($p < 0.001$)
High[a]	0.790[b]	89.6	1636 ± 52	2992 ± 120	45.3 ± 3.7 ($p < 0.001$)
1978					
Low 1	0.095	6.8	2370 ± 27	2531 ± 47	6.4 ± 2.1 ($p < 0.01$)
Low 2	0.108	7.8	2256 ± 39	2379 ± 44	5.2 ± 2.5 ($p < 0.05$)
Medium 1	0.192	13.5	2191 ± 65	2494 ± 41	12.2 ± 3.1 ($p < 0.001$)
Medium 2	0.255	18.9	2008 ± 27	2485 ± 42	19.2 ± 2.0 ($p < 0.001$)
High[a]	0.362[b]	26.1	1859 ± 48	2209 ± 45	15.9 ± 3.0 ($p < 0.001$)

[a]Visible injury observed on fumigated plants.

[b]Exceeded U.S. Environmental Protection Agency Secondary Air Quality Standards for sulfur oxides.

$$y = e^{-0.0072\,x}$$

gave nearly as good a fit to the data ($r^2 = 0.983$ for the polynomial) and is much more realistic mechanistically (Figure 1). For this set of data, the dose was closely related to mean concentration during fumigation, since in each year all the plots were fumigated for the same length of time and total fumigation time did not differ greatly between 1977 and 1978. Thus it is not surprising that mean concentration during fumigation was also a good predictor of yield reduction for this set of data. The best prediction equation was

$$y = 58.6\,x\ ,$$

where y is as above and x is mean concentration in ppm. No second-order term was significant at the 25% confidence level.

To provide more detailed data on the effect of SO_2 fumigation on soybeans, individual plants from each fumigated and control plot were collected immediately before harvest in both 1977 and 1978. These plants were separated into stems, pods, and seeds and weighed individually. The only yield parameter which was consistently lower in the SO_2-treated plots was the average weight per seed, which showed a significant drop in all of the fumigated plots in 1977 and all but one plot in 1978. The number of pods and seeds per plant was lower in most of the more heavily fumigated plots in both years, but because of high within-plot variability differences were statistically significant only in the 1977 high plot. The number of seeds per pod was apparently not affected by the SO_2 treatment.

In both 1977 and 1978 bean quality was affected much less by the fumigation than bean quantity. In both years protein content was reduced slightly at the

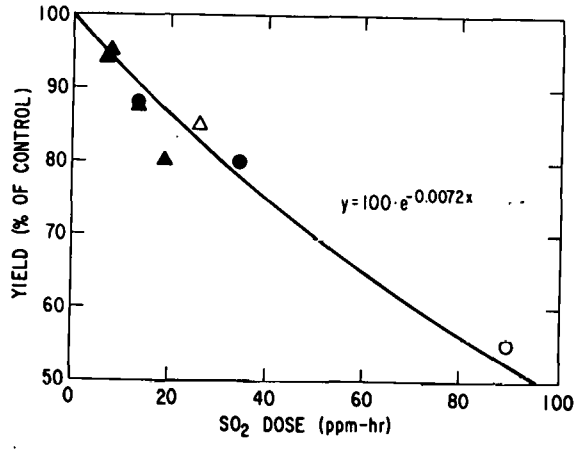

FIG. 1.--Effect of SO_2 fumigation on soybean yields in 1977 (circles) and 1978 (triangles). Open symbols indicate plots where visible damage to leaves was observed.
(ANL Neg. 149-79-144)

highest SO_2 concentration (down 2.8% in 1977 and 1.5% in 1978), while oil content was unchanged. Concentrations of the major fertilizer elements (N, P, K) were not affected by the fumigation treatment. Sulfur content of the beans increased in most of the fumigated plots, although the increase was statistically significant only in the medium and high plots in 1977 and in one of the low plots in 1978. Magnesium and boron concentrations were down 5 to 10% in the medium and high plots in both years, while zinc concentrations increased by about the same fraction in the high plots in both years. Copper, manganese, and calcium concentrations all increased in the high plot in 1977 (where tissue damage was severe and extensive), but showed no consistent pattern elsewhere.

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EVALUATION OF THE SULFUR DIOXIDE CONCENTRATION DYNAMICS FROM THE OPEN AIR FUMIGATION SYSTEM

J. E. Miller, D. G. Sprugel, P. B. Xerikos, and H. J. Smith

The open-air fumigation system (a technique used to treat field plots of crops with air pollutants) was used for the second year in 1978 in the SO_2-crop effects studies. The first report dealing with this technique indicated that the temporal fluctuation in SO_2 concentrations provided to the field plots by the system appeared to resemble actual SO_2 episodes.[1] This report summarizes the 1978 SO_2 concentration data and compares them to published information on short- and long-term SO_2 concentration variability near point sources.

In 1978 five field plots were treated with SO_2 according to the technique previously reported.[1] The frequency, duration, and mean concentration (compiled from 1 min averages at 4 min intervals) of the fumigations are summarized in Table 1. Standard deviations and standard geometric deviations are reported, although a skewness test indicated that the data are neither normally nor log-normally distributed. While log-normal statistics are commonly used with ambient air quality monitoring measurements, it has been pointed out that the data often are not log-normally or normally distributed. For this reason empirical relationships, that do not assume any particular distribution of the measurements, have

Table 1. Frequency, duration, and concentrations of SO_2 treatments of field plots in 1978. The fumigations were performed approximately three times a week from July 19 to August 27 between 10:00 and 4:00 CST.

Plot	Number of treatments	Average duration, hr-min	Arithmetic mean, ppb	Standard deviation, ppb	Geometric mean, ppb	Standard geometric deviation
Low 1	18	4-06	95	47	83	1.73
Low 2	18	4-08	108	50	96	1.67
Medium 1	17	4-08	192	84	170	1.75
Medium 2	18	4-11	255	138	217	1.85
High	18	4-14	362	188	298	2.06

been used to describe short-term and long-term variability in air pollutant concentrations.

One commonly used empirical relationship is the peak-to-mean ratio, which is the ratio of an individual measurement (usually a 5 min average) to the mean concentration for longer averaging times. Peak-to-mean ratios were generated for the 1978 data for 1, 3, and 24 hr averaging times. Cumulative frequency distributions of the ratios were tabulated and plotted as logarithmic-probabilities as illustrated for one plot in Figure 1. The data usually appeared to be log-normally distributed, except that the lower bound is one instead of zero. For this reason the peak-to-mean ratios minus one are ordinarily used in the logarithmic-probability plots.[2] The peak-to-mean ratios for all the 1978 field plots are summarized as the 5th, 50th, and 95th percentiles, along with the average of the ratios, in Table 2.

The peak-to-mean ratios for 1 and 3 hr averaging times are similar to those of published ambient SO_2 monitoring data near point sources (Table 2), indicating that the fluctuation of SO_2 concentrations in the field plots during individual fumigations closely resembles that of ambient SO_2 episodes. For 24 hr averaging times these ratios were much lower for the experimental plots than for the ambient case. It seems probable that the experimental fumigations were generally of a longer duration than the ambient episodes, since that would increase the 24 hr average and thus reduce the ratios. This difference was even more pronounced for monthly averaging times (only 2 data points per plot—data not shown) implying that the experimental plots were also treated much more frequently than the ambient

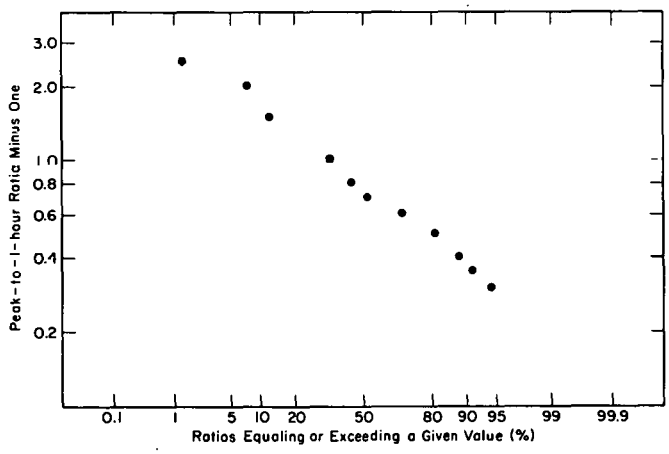

FIG. 1.--Cumulative frequency distribution of peak-to-1 hr SO_2 concentration ratios minus 1 in 1078 (Low Plot #1).

Table 2. Peak-to-mean ratios for the SO_2 fumigated field plots in 1978. The ratios are derived from the peak reading occurring during the given averaging periods.

Plot	Peak-to-1 hr ratio				Peak-to-3 hr ratio				Peak-to-24 hr ratio			
	Percentile			Av.	Percentile			Av.	Percentile			Av.
	5th	50th	95th		5th	50th	95th		5th	50th	95th	
Low 1	3.4	1.8	1.3	1.9	8.0	4.2	1.7	4.1	23	11	6.9	12
Low 2	3.1	1.7	1.2	1.9	8.6	3.9	1.6	4.1	28	12	5.1	13
Medium 1	3.2	1.6	1.3	1.8	9.1	3.3	1.4	4.0	23	12	6.0	12
Medium 2	3.7	1.8	1.2	2.0	9.1	3.5	1.8	4.2	25	11	7.8	15
High	3.8	1.8	1.3	2.0	8.9	3.8	1.6	4.1	25	11	7.9	15
Ambient values[a]	4.2	1.8	1.2	2.3	12	4.0	1.8	5.2	71	22	7.6	28

[a]Ambient SO_2 data from monitoring near point sources, taken from Ref. 2.

episodes occurred.

The conclusion that the SO_2 treatments were longer and more frequent than occurrences of episodes near point sources was not surprising, since one of the purposes of the studies was to establish the lower limit of chronic SO_2 exposure that would reduce soybean yield. Future experiments will be conducted with exposure frequencies and durations more common in areas moderately polluted with SO_2. The close agreement between the ambient and experimental peak-to-mean concentrations for 1 and 3 hr averaging times supports the contention that the fluctuations in SO_2 episodes during fumigation were similar to actual fumigations.

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YIELD RESPONSE OF FIELD-GROWN SOYBEANS TO AN ACUTE SO_2 EXPOSURE

J. E. Miller, H. J. Smith, D. G. Sprugel, and P. B. Xerikos

Plant damage from SO_2 pollution is known to occur either in response to frequent SO_2 episodes at relatively low concentrations (chronic damage) or in response to a few events at relatively high concentrations (acute damage). Either may occur in polluted areas, depending on the number, proximity, and intensity of the SO_2 sources and the meteorological conditions at the time. Results of our recent studies of chronic SO_2 fumigation of field-grown soybeans have been summarized in previous reports.[1,2] Since acute SO_2 damage does occur in certain areas, experiments were initiated in 1978 to evaluate concentration thresholds for reduction in soybean yield with intense SO_2 exposures.

A uniform area of soybeans was exposed to a gradient of SO_2 concentrations by release of the gas from a single pipe suspended over the plant canopy. The treatment technique was similar to that previously reported,[3] except that only a single 38 m long release pipe was used. The fumigation was conducted on a day having a steady wind across the pipe; and the SO_2 concentrations in the plot were monitored at intervals downwind to allow characterization of the SO_2 exposure of each row. Each of the six rows downwind from the pipe was divided into four 7 m long sections which served as replicates for a given SO_2 concentration. Control plots (twelve 7 m row sections) were established immediately upwind from the SO_2 release pipe. The plot was fumigated on August 19 between the hours of 1040 and 1500 CST. The majority of the soybeans had almost completed flowering at this time and were in the stage of early- to mid-podset.

The mean SO_2 concentrations for the fumigation period ranged from 2.0 to 0.8 ppm across the yield plot. Significant yield reductions of 15% at 2.0 ppm of SO_2 ($p < 0.025$) and 11% at 1.7 ppm SO_2 ($p < 0.0005$) were evident with an apparent yield reduction of 4.5% at 1.4 ppm ($p < 0.1$) (Figure 1). Visible injury to the vegetation occurred in all of the rows and ranged from severe chlorosis with occasional necrotic areas (2—5% of the leaf area) in the two rows immediately downwind of the SO_2 release pipe to a much milder chlorosis in the rows furthest away.

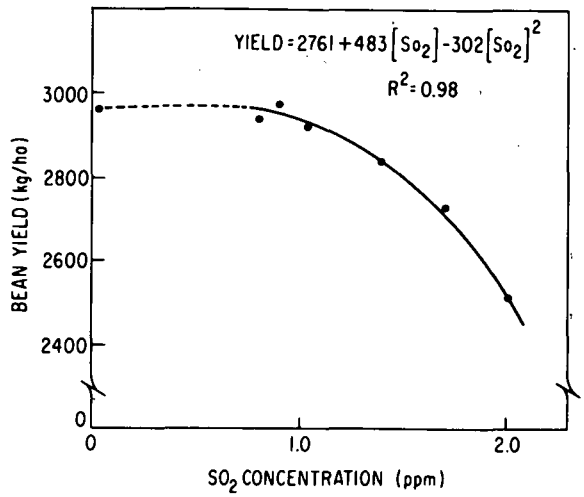

FIG. 1.--Soybean yield versus mean SO_2 concentration for a single 4 hr and 20 min fumigation. The regression equation is applicable only to SO_2 concentrations of 0.8 ppm or above.

These data suggest that the threshold for yield reduction in soybeans due to the single 260 min SO_2 exposure was approximately 1.3 to 1.5 ppm. This translates to a dose of 5.6 to 6.5 ppm-hr, which is quite similar to the lowest SO_2 dose observed to cause yield reductions in soybeans with chronic exposire to SO_2.[2] However, it is unlikely that the dose-yield relationship for chronic and acute exposures would remain the same over a wide dose range, since the two types of stress are almost certainly different. This is substantiated by the highest acute plot, where a dose of 8.7 ppm-hr caused a 15% yield reduction, compared to the chronic experiments where such a dose would cause approximately a 6% decrease.

The age of the plants when exposed to the acute SO_2 episodes is undoubtedly a very important consideration when evaluating pollutant effects. It is known that soybeans can withstand considerable stress at early developmental stages and if allowed to recover will yield as well as plants not stressed. Future experiments will be performed with plants at various ages to identify the stages of maximum sensitivity to acute SO_2 stress.

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A HISTOLOGICAL STUDY OF SOYBEANS INJURED BY EXPOSURE TO SULFUR DIOXIDE

P. M. Irving, D. J. Martinson, and J. E. Miller

In the past, the evaluation of SO_2 effects on crop growth or yield has been primarily based on the degree of visible damage to the vegetation. However, it is now known that crop yields may be reduced by exposure to sulfur dioxide without accompanying visible damage,[1] thereby making it difficult to relate this effect to crop loss. Therefore, a technique for quantifying both visible and hidden damage to crop plants after exposure to SO_2 would be extremely useful. A preliminary histological study of soybean leaves exposed to SO_2 gas was undertaken to examine the possibility that a microscopic determination of cell death is related to SO_2 exposure and crop yield.

Soybean leaf tissue samples were collected from two field plots which had been exposed to a gradient of acute SO_2 concentrations by a procedure described in this report[2] and from a plot receiving chronic SO_2 exposure.[3] The first acute fumigation took place on July 27, 1976, and leaf samples were taken from the third and fourth nodes three days after fumigation. The second plot was fumigated on August 19, 1978, and samples from the fifth node were taken nine days after the fumigation. The chronic plot was fumigated during four of the ten days prior to sampling, with an average SO_2 concentration of 218 ppb for 4½ hr/day. After preservation in a fixative, the leaf samples were dehydrated in a progressive series of alcohol solutions and then embedded in paraffin. The paraffin blocks were sectioned at 10 μm intervals and the sections were then stained with fast green and safranin dyes by a procedure in which differential absorption and destaining provided a clear distinction between living and dead cells.

The results from the first acute fumigation experiment indicated that leaf samples had been taken too early for the total effects of the SO_2 exposure to be observed. Although there were slightly more dead cells in plants exposed to the SO_2 than in the untreated plants, only the epidermal cells showed significantly higher damage. However, the second fumigation experiment showed that mesophyll cells are much more susceptible to SO_2 exposure. The results (Figure 1)

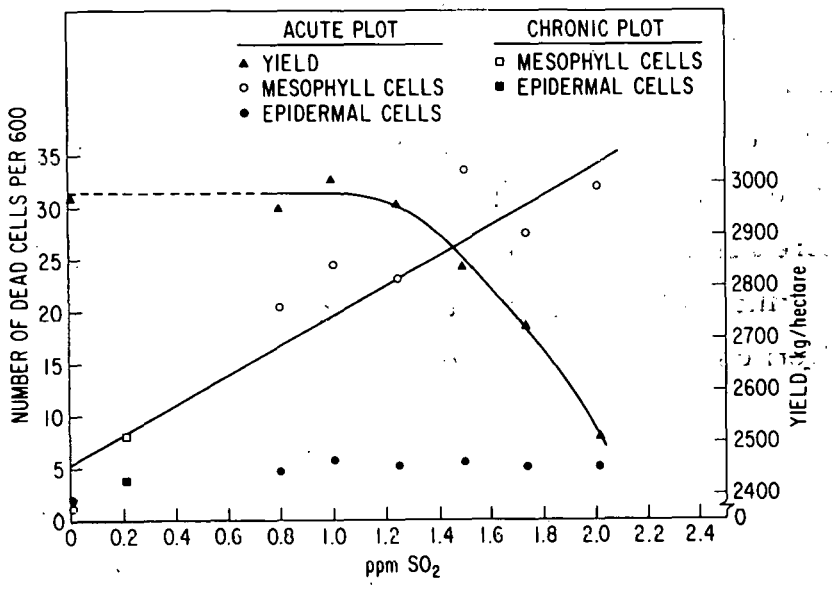

FIG. 1.--Relationship between yield and leaf cell death of soybeans exposed to acute and chronic levels of SO_2.

show significant cell death in all cell types exposed to SO_2 although only 1% of epidermal cells were killed, while 3 to 6% of mesophyll cells were killed. Apparently the epidermal cells, probably guard cells in particular, are affected immediately by toxic concentrations of SO_2 gas, while mesophyll cells do not die until at least 3 days after a lethal exposure.

The number of dead mesophyll cells is highly correlated ($r = 0.9209$) with SO_2 concentration. A constant number of dead epidermal cells occurred at all SO_2 concentrations, while both palisade and spongy meosphyll tissue exhibited increasingly larger numbers of dead cells as the SO_2 concentration increased. Apparently the number of susceptible epidermal cells is limited, while mesophyll tissue can continue to be damaged with increased SO_2 exposure. Significant reductions in seed yield occurred only at the two highest SO_2 exposure levels although cell death was observed at all treatment levels (Figure 1).

Although no visible damage occurred in the chronic SO_2 exposure plot, significant numbers of dead cells were observed, and yield was decreased by 20%. Again, nearly one percent of the epidermal cells were affected, while in this case, only 1.3% of the mesophyll cells were killed. Four times as many spongy mesophyll cells were affected as compared to palisade meosphyll cells.

Gaseous sulfur dioxide enters plant leaves principally through open stomata. The gas may then dissolve on wet cell walls, diffuse into the cell and cause toxic

effects if not quickly metabolized. The greater effect seen in spongy mesophyll cells as compared to the palisade mesophyll may be due to the loosely arranged organization of spongy cells which provides a greater surface area for absorption.

Although more data are required, the results from this preliminary investigation suggest that yield decreases will occur in soybeans when approximately 3.5 to 4% of the leaf cells are killed by SO_2 exposure during an acute episode and that cell death also results from chronic SO_2 exposures, even though visible damage is not observed.

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AN ESTIMATE OF MINIMUM SO_2 DEPOSITION VELOCITIES IN THE OPEN-AIR FUMIGATION SYSTEM

D. G. Sprugel, J. E. Miller, P. B. Xerikos, and H. J. Smith

One of the more important parameters in modeling pollutant transport and effects is the "deposition velocity" of the pollutant, which is defined as the vertcal flux rate of the pollutant divided by the ambient concentration. The deposition velocity may be thought of as the rate at which the absorbing surface cleans the pollutant out of the air. That is, if the deposition velocity of a pollutant is 0.5 cm sec^{-1}, then one might imagine that the surface is completely removing the pollutant from a layer of air 0.5 cm thick each second, with the "clean" layer immediately replaced by a fresh polluted layer. The rate of pollutant deposition is, of course, important in interpreting the pollutant effects on exposed plants, as well as in modeling long- and short-range pollutant transport and fate.

Deposition velocities are controlled by a variety of atmospheric and biological factors, including wind speed, atmospheric stability, height and structure of the plant canopy, and stomatal resistance of the vegetation. Most estimates of deposition velocities to vegetated surfaces have been made using micrometeorological techniques,[1] but it is also possible to estimate the uptake of sulfur dioxide by measuring the increased sulfur content of plants exposed to elevated pollutant levels. During the summer of 1978 this method was used to make an estimate of the deposition velocity for the soybean field plots exposed to SO_2 in the open-air fumigation system.[2,3]

SO_2 exposure of the field plots was begun on July 20, 1978. On July 31, after 4 fumigations, the above-ground portions of 8 plants were collected from each of the fumigated and control plots within the study field.[3] The sampling was repeated on August 22, after 15 fumigations. These plants were dried and weighed and then analyzed for sulfur content by the Soil and Plant Analysis Laboratory of the University of Wisconsin at Madison. The individual plant weights and sulfur contents of the tissues were used to estimate the total sulfur content of the plants in each plot. In the July 31 samples only the plants in the plot exposed to the highest levels of SO_2 had sulfur levels significantly above those

of the plants in the adjacent unfumigated plot; however, by August 22 all four plots showed elevated sulfur levels compared to their respective controls. It was assumed that the sulfur levels in the unfumigated plants represented normal uptake from the soil and ambient air, and that the difference between the sulfur levels in the control plots and the fumigated plots represented uptake of SO_2 added to the atmosphere during the fumigations. These uptake values were then compared with the known SO_2 levels during the fumigations to estimate deposition velocities to the fumigated plants (Table 1).

The deposition velocity estimates in Table 1 range from 0.5 to 0.9 cm sec^{-1} which is lower than the range generally found under similar conditions by micrometeorological methods. Typical values over rapidly growing fields of agricultural crops are in the range 1.0 to 1.5 cm sec^{-1}, and numerical modelers often use 1.0 cm sec^{-1} as a convenient mean value for all atmospheric and environmental conditions.[1] However, the values given in Table 1 represent minimum estimates

Table 1. Estimates of SO_2 deposition from two sampling dates in the open-air fumigation system.

	Plot (date)				
	High (7/31)	Low-1 (8/22)	Low-2 (8/22)	Medium (8/22)	High (8/22)
S content, g/m^2					
Control	0.78	1.47	1.60	1.60	1.35
Fumigated	0.97	1.61	1.74	2.23	2.11
Difference (SO_2 uptake)	0.19	0.14	0.14	0.63	0.76
SO_2 exposure before sampling date					
Time, hr	18.3	59	59	59	59
Mean concentration ppm	0.309	0.093	0.103	0.252	0.352
Estimated deposition velocity cm/sec	0.71	0.54	0.49	0.90	0.78

for a number of reasons. We have measured only the sulfur retained by the plants fairly late in the growing season, and SO_2 which is taken up early in the season may be lost again in several ways. Some SO_2 is converted to H_2S and released again as a gas, and some may be leached from the leaves as sulfate. Excess sulfur may also be lost in abscised leaves, or translocated to the roots (which we did not sample). Some SO_2 is undoubtedly taken up by the soil surface, and this also would not appear in our estimates of deposition velocity. Finally, SO_2 taken up by the leaves may have substituted for some of the sulfur which would normally be taken up from the soil, and thus reduced root uptake. If this were true, then the fumigated plants would have absorbed more SO_2 than we estimated, since we are equating atmospheric uptake only to the sulfur "excess" in the fumigated plants. Notwithstanding these qualifications, this alternative methodology represents a useful check on the more traditional techniques for estimating deposition velocities of air pollutants.

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THE EFFECTS OF ACID PRECIPITATION ALONE AND IN COMBINATION WITH SULFUR DIOXIDE ON FIELD-GROWN SOYBEANS

P. M. Irving and J. E. Miller

The potential hazards of acid precipitation to ecosystems in the northeastern area of the United States has been and is continuing to be investigated, while little work is being done concerning its effects on systems more common to the Midwest. In view of the increasing prevalence of acid precipitation in this region, a study was undertaken in 1977 to determine its effects, and possible interactions with SO_2, on soybeans, an economically important crop in the Midwest. The results of the first year of field experiments appeared previously,[1] and this report summarizes the findings to date.

Field-grown soybeans were exposed to acid (∿ pH 3.1) or control (∿ pH 5.3) precipitation simulants in sulfur dioxide fumigated and unfumigated field plots as described previously.[1,2] The precipitation simulants, which closely approximated the physical and chemical characteristics of natural rainfall, were applied every 5 to 7 days in July and August with a total of 34 cm applied in 1977 and 45 cm in 1978. Sulfur dioxide fumigations of approximately 4 hr duration were performed 24 times in 1977 and 17 times in 1978, resulting in average SO_2 concentrations of 0.79 ppm and 0.19 ppm, respectively.

No statistically significant effects of the acid or control simulants, nor interactions with SO_2, were found on seed yield in either year, although the plots receiving both precipitation simulant and SO_2 had significantly lower yields (12 to 46%) than plots receiving only precipitation simulant (Table 1). In 1977 the seed yields were slightly lower in both the fumigated and unfumigated acid-treated plots, when compared to the appropriate controls, while in 1978, yields in the unfumigated, acid-treated plots were somewhat higher. It is interesting to note that the weights of individual seeds were consistent with the yield differences; in 1978 the seed weight in the acid precipitation plot was significantly different from that in plots both with control precipitation and no precipitation. This suggests that the acid treatment in 1978 did, in fact, have an effect on productivity as reflected seed growth.

Table 1. Seed yield of soybeans exposed to acid precipitation alone and in combination with sulfur dioxide.[a]

	Kg/hectare		Grams/seed	
	1977	1978	1977	1978
Control precipitation	2535	2610	0.1693	0.1518
No precipitation	2447	2509	0.1705	0.1478
% change N.P.	4 (n.s.)	4 (n.s.)	-1 (n.s.)	3 (n.s.)
Acid precipitation	2436	2661	0.1660	0.1572
No precipitation	2714	2479	0.1722	0.1488
% change N.P.	-10 ($p < 0.10$)	7 ($p < 0.10$)	-4 (n.s.)	6 ($p < 0.025$)
% change C.P.	-4 (n.s.)	2 (n.s.)	-2 (n.s.)	4 ($p < 0.05$)
Control precipitation-SO_2	1443	2082	0.1309	0.1516
No precipitation-SO_2	1535	2220	0.1310	0.1491
% change N.P.-SO_2	-6 (n.s.)	-6 (n.s.)	0 0	2 (n.s.)
Acid precipitation-SO_2	1312	2233	0.1207	0.1513
No precipitation-SO_2	1473	2162	0.1310	0.1454
% change N.P.-SO_2	-10 (n.s.)	3 (n.s.)	-8 (n.s.)	4 ($p < 0.05$)
% change C.P.-SO_2	-9 (n.s.)	7 (n.s.)	-8 ($p < 0.10$)	0 (n.s.)

a) SO_2 exposure of 0.79 ppm in 1977 and 0.19 in 1978.
N.P. = no precipitation.
C.P. = control precipitation.

While the statistical significance of the data varied for individual sampling dates, the rate of photosynthesis of leaves in 1978 was usually higher in both the control and acid-treated plots than in the untreated plots (Table 2). These results suggest the possibility that the photosynthesis rates were stimulated in precipitation-treated plots by the availability of additional water or nutrients. Sulfur dioxide apparently reduces the photosynthetic rate (Table 2, column 3). However, acid precipitation modifies this effect. The chlorophyll content of the leaves was higher in the unfumigated acid-treated plants, while plants fumigated with sulfur dioxide showed an apparent reduction in chlorophyll (Table 2).

Although visible damage was not apparent in any of the plots, a histological study revealed significant increases in the number of dead leaf cells in all plots, compared to untreated controls, except the one exposed to control precipitation alone (Table 3). It is interesing that the proportion of dead

Table 2. Photosynthetic rate and chlorophyll content of soybeans exposed to acid precipitation alone and in combination with sulfur dioxide as compared to untreated plants.

	Control precipitation	Acid precipitation	Control precipitation-SO_2	Acid precipitation-SO_2
Photosynthesis		% Difference		
8/03/78	11 (n.s.)	36 ($p < 0.001$)	2 (n.s.)	7 ($p < 0.025$)
8/13/78	4 ($p < 0.001$)	2 (n.s.)	-6 (n.s.)	9 (n.s.)
8/19/78	17 ($p < 0.1$)	22 ($p < 0.1$)	7 ($p < 0.001$)	20 ($p < 0.05$)
8/31/78	38 ($p < 0.001$)	22 ($p < 0.05$)	9 (n.s.)	32 ($p < 0.025$)
Chlorophyll		% Difference		
8/03/78	6 ($p < 0.05$)	13 ($p < 0.025$)	7 ($p < 0.1$)	2 (n.s.)
8/13/78	0.9 (n.s.)	5 (n.s.)	0	-1 (n.s.)
8/30/78	0.5 (n.s.)	0.8 (n.s.)	-16 ($p < 0.1$)	-13 ($p < 0.1$)
9/06/78	10 (n.s.)	78 ($p < 0.025$)	- 3 (n.s.)	-17 (n.s.)

Table 3. Number of dead leaf cells per 600.

	Untreated	Unfumigated		Fumigated	
		Control precipitation	Acid precipitation	Control precipitation	Acid precipitation
Palisade mesophyll	1.32	0.53 (n.s.)	3.66 ($p < 0.05$)	3.36 ($p < 0.05$)	11.46 ($p < 0.01$)
Spongy mesophyll	1.16	1.04 (n.s.)	5.12 ($p < 0.001$)	12.70 ($p < 0.001$)	21.44 ($p < 0.001$)
Epidermal	1.54	2.42 (n.s.)	4.76 ($p < 0.001$)	3.70 ($p < 0.001$)	6.04 ($p < 0.001$)

mesophyll cells of plants exposed to acid precipitation and sulfur dioxide combined was more than the additive effects of each applied singly.

The occurrence of toxic effects due to these pollutants depends on the rate at which they enter the plant and their distribution within the tissues. Plant growth may, however, be stimulated by the nutrients present in acid rain as

suggested by the chlorophyll experiments and seed weight data. Similarly low levels of SO_2 may stimulate growth as reported by Cowling et al.[3] In 1978, 14 kg of sulfur per hectare were added to the plots receving the acid simulant, more than enough to fertilize a deficient field as compared to the 0.17 kg of sulfur added to the control plots. Soil analyses of the field plots showed reduced levels of sulfur at the end of the growing season in the control plots but no depletion in the acid-treated plots. Addition of pollutants at concentrations or rates greater than can be metabolized by the plant may result in toxic effects such as the increased cell death and the yield decreases (in the SO_2-fumigated plots) seen in this study.

Acid precipitation may produce effects on plants ranging from beneficial to harmful depending on environmental conditions and exposure rates. Positive plant response to the fertilization effects may or may not be overcome by the negative response to stress.

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RAINFALL ACIDITY AT ARGONNE

P. M. Irving

Acid precipitation is an increasingly prevalent feature of human-induced change in the earth's chemical environment. Studies show that the incidence of acid rain (pH < 5.5) is spreading from the northeastern section of the United States to the south and west with some intensification in the northeast. In order to assess the potential effects of acid precipitation on the agricultural ecosystems of the Midwest, studies were undertaken to characterize the chemical properties of the natural precipitation of this area and to assess the effects of acid precipitation on soybeans. This report presents the results of the precipitation chemistry study.

Rain samples from 100 precipitation events were collected at Argonne National Laboratory from April through October in 1977 and April through September in 1978 and during July and August 1978 at the sulfur dioxide-acid precipitation field investigation site about 26 miles southwest of Argonne. Wet deposition, only, was collected with a large Plexiglass hemisphere supported atop a 4 liter polyethylene collection bottle. This apparatus collected one liter of sample for each millimeter of rainfall. The collector was thoroughly rinsed with deionized water before each precipitation event, and samples were analyzed within 24 hr after collection.

During the two years of collection, the pH of individual rains varied from 3.25 to 7.20. In 1977, the weighted calculated pH value obtained by averaging the hydrogen ion concentrations of sampled precipitation (322 mm rain), was 4.13, while in 1978 a total of 474 mm of rain had a calculated pH value of 4.09. Monthly pH values were lower in the spring and early summer as shown in Figure 1. A similar seasonal pattern in acidity has been reported for the northeastern United States[1] and is probably the result of seasonal differences in sulfur and nitrogen deposition.

Sulfate concentrations of the precipitation samples (analyzed according to the procedure described by Seils and Tisue in "X-Ray Spectrometric Determination of Sulfate in Natural Waters" submitted to Adv. X-Ray Anal.) varied

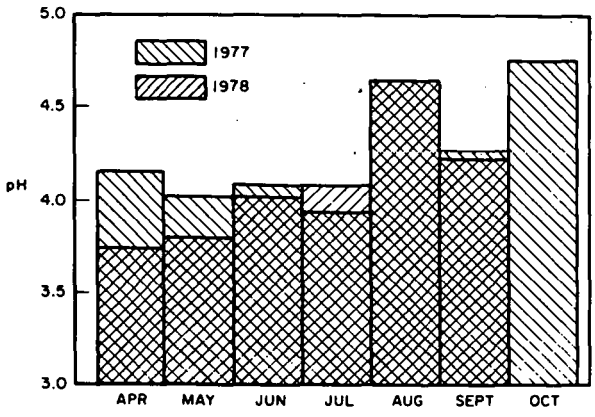

FIG. 1.--Monthly precipitation weighted pH values.

from 7 to 154 μmol/liter with a precipitation weighted average of 43, and were significantly correlated ($p \leq 0.01$) with hydrogen ion concentrations ($r = 0.434$). The lack of a high degree of correlation between hydrogen ion concentration and sulfate concentrations suggests the importance of the contribution of nitrates and ammonia to the acidity of precipitation. Although H_2SO_4 may have dominated precipitation chemistry in the past, recent data[2] show that nitrate concentrations are increasing and are sometimes equal to or greater than the sulfate concentrations.

To further characterize the chemical composition of the precipitation samples, which may contain both fully dissociated strong acids and incompletely dissociated weak acids, acid/base titrations were performed. Figure 2 shows a representative titration curve and a plot of Grans' function, which is a measure of the amounts of hydrogen ion remaining in a sample after addition of known amounts of hydroxide ion. Total acidity (A_T) was determined as the equivalent amount of NaOH needed to raise the pH of the sample to 9.0. The intersection of the Gran's plot with the x axis gives the total moles of hydroxide required to neutralize the strong acid (SA) component of the samples. The differences between A_T and SA in the samples indicated the presence of weak acids having concentrations which varied from sample to sample but did not contribute substantially to the observed pH values. A weak acid can, however, contribute to biological adicification, as in the case of ammonium ion, which can be exchanged for hydrogen ion by plants and soil microorganisms and thus cause soil acidification. The values for strong acid concentration were signficantly correlated ($p \leq 0.01$) with the measured

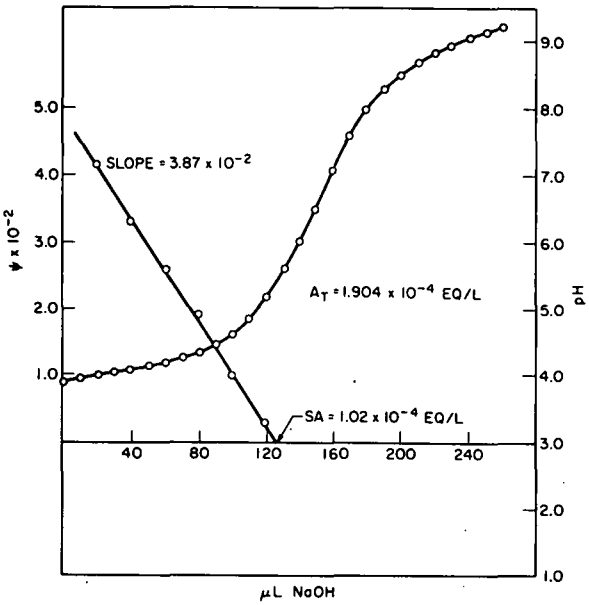

FIG. 2.--Titration of rain water sample (30 June 1978) with 4.0×10^{-2} M NaOH according to pH and according to Gran's function [$\psi = (V_i + V)10^{-\Delta pH}$]. Measured pH = 3.85; calculated pH = 3.80. A_T = total acidity; SA = strong acid component.

hydrogen ion concentrations of the samples (r = 0.520).

The results of this study indicate that precipitation in the Midwest is acidic and that the low pH values are due to the presence of strong acids. Additional information on rain chemistry is desirable in order to predict and interpret its effects on biological systems.

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INDUCTION OF VISIBLE INJURY IN CHAMBER-GROWN SOYBEANS EXPOSED TO ACID PRECIPITATION

P. M. Irving

The determination of threshold concentrations of pollutants that cause visible injury to plants is usually an initial step of documentation of pollution effects. Visible injury has been observed in a number of plant species exposed to acid precipitation at pH values of 3.2 and less. However, response thresholds have not been established, especially with regard to the quantity of acid rain of a given pH that produces visible injury. Therefore, a preliminary investigation was undertaken to determine such thresholds for soybeans.

Chamber-grown soybean plants were exposed, ten weeks after germination, to acid (pH 3.0) and control (pH 5.4) precipitation simulants having ionic compositions similar to natural rain. Eight groups of plants were exposed to a range in quantities of precipitation (0.65 to 9.35 cm) within a four day period. Natural precipitation at Argonne (1978) ranged from 0.03 to 5.2 cm per event. The rainfall rate of the simulants (2.7 cm hr^{-1}) was in the upper range of natural rates.

Although visible damage was not observed in any of the plants receiving the control simulant, two types of injury, necrotic lesions and chlorotic areas, occurred in leaves treated with the acid simulant. The results, given in Table 1, indicate that necrotic lesions may occur in young soybean leaves after exposure to as little as 2 cm of acid rain (pH 3.0) when applied at high exposure rates. All treated plants showed necrotic damage after exposure to 7 cm of acid simulant applied in 3 consecutive days.

Necrotic injury was first observed 3 days after the initial exposure in at least one plant from all but the lowest acid exposure level. The injury initially appeared as yellow lesions on leaves of the third node. These lesions eventually became ivory colored and then brown. A second type of injury was observed 10 days after the final exposure in 40% of the plants receiving the three highest precipitation quantities, and appeared as chlorotic areas on leaves at nodes just below those exhibiting the necrosis. Tissue destruction due to the necrotic injury never exceeded 5% of the area of damaged leaves, while chlorotic areas

Table 1. Number of soybean plants exhibiting visible injury after exposure to acid precipitation.

Group	Exposure dates (Dec. 1978)	Simulant exposure cm	Simulant exposure min	% of plants exhibiting: Necrosis	% of plants exhibiting: Chlorosis
1	21	0.65	15	0	0
2	21	1.91	44	20	0
3	21–22	3.46	80	70	0
4	21–22	4.59	106	100	0
5	21–23	5.67	124	80	0
6	21–23	6.97	154	100	40
7	21–24	8.23	179	100	40
8	21–24	9.35	205	100	40

covered up to 25% of affected leaves. The percent tissue destruction to the entire plant, however, was negligible, even at the extremely high exposure levels. The extent of leaf destruction due to the acid rain simulant should not directly reduce photosynthetic rates of the plant as a whole, although individual leaves having large chlorotic areas may have had reduced rates.

The plants were observed for four weeks after exposure to the simulants and no additional damage was noted. New growth, including flower and pod formation, appeared normal.

This preliminary study suggests that high exposures of rain at the lower range of pH values that occur naturally, are needed to produce significant visible damage.

THE NEW RESEARCH VESSEL, EKOS

G. P. Romberg, R. W. Dana, and R. M. Williams

The increase in Great Lakes research programs at ANL has been accompanied by an increase in requirements for ship time. Typically, vessels were chartered from universities which required conforming to rigid schedules laid out far in advance. This situation gave little opportunity to have cruises coincide with specific lake events (e.g., upwelling or plankton blooms) or to reschedule cruises when scheduled time was lost because of rough lake conditions. Also, the mooring locations of these vessels and their slow cruising speeds required a substantial amount of nonproductive traveling time for each cruise. These limitations, coupled with planned increases in ship usage, prompted the Radiological and Environmental Research Division to examine the feasibility of operating a fast research vessel to be based in Chicago and committed to our research needs.

Fast research vessels are a relatively new concept and have become popular for coastal oceanographic research. The common crew boat used extensively in the Gulf Coast offshore oil industry has been conveniently adapted for this purpose. The semiplaning hull design of these vessels yields cruising speeds of between 15 and 25 knots, while the wide beam, hard chine and low profile ensure stability and a low center of gravity. The large open afterdeck offers a convenient work platform, and cabin space normally used for personnel seating provides a spacious scientific laboratory.

After considerable internal discussion to determine our vessel requirements and careful use of external consultants, it was concluded that a modified crew boat should be built to our specifications.

The vessel, named R/V Ekos , is 58 feet long with a 16.5 foot beam. Propelled by twin diesels for high speed and good maneuverability, the Ekos has a maximum speed of 19 mph with a cruising (14 mph) range of 400 miles. The crew boat design provides a large laboratory (12' × 16' × 8') complete with wet tray, laboratory sinks and ample counter space. A large hatch in the laboratory roof permits heavy experimental equipment to be easily installed and removed. The afterdeck is equipped with a crane-winch combination for handling heavy equipmen..

FIG. 1.--The R/V Ekos . (ANL Neg. 301-78-192)

The pilot house is equipped with marine radio, radar, depth sounder, automatic direction finder, gyrocompass with autopilot, and Loran C navigation.

ANL took possession of the Ekos in September 1978 in New Orleans and the trip to ANL provided the initial shakedown, as well as a working cruise. Water and sediment samples from the Gulf of Mexico, the Mississippi River, and many of its tributaries were collected to examine the extent of plutonium distribution in the Mississippi-Ohio River systems.

In Chicago, the Ekos is conveniently moored just inside the Chicago River locks to Lake Michigan. The principal attribute of the Ekos is fast access to experimental stations in southern Lake Michigan. Since September, the Ekos has been used extensively as our Great Lakes research moved into a new phase of intensive study of pollutant inputs, transfer and effects. Only extreme lake ice conditions (> 6") in late winter prevented regular sampling on Lake Michigan. The many advantages of having such a versatile research vessel will result in a more comprehensive and unified Great Lakes Research Program.

FIELD LABORATORY FOR IN SITU CONTAMINANT STUDIES WITH FISH

G. P. Romberg, W. Prepejchal, and M. M. Thommes

Laboratory experiments provide the most controlled method for studying the kinetics of pollutant accumulation by fish. However, the results of such studies are of little value unless experimental conditions such as water quality, food, activity, and photoperiod simulate actual environmental conditions. With these factors in mind a 12' × 50' housetrailer has been outfitted as a mobile field laboratory for conducting in situ studies to determine the effect of thermal plume residence on the uptake of pollutants by Lake Michigan fish. Tests are being conducted with brown trout because this important species exhibits extended thermal plume residence.[1]

The field laboratory has been set up near a coal-fired power plant (Edgewater Plant, Sheboygan, Wisconsin), where a continuous supply of Lake Michigan water is obtained by submersible pumps placed in the intake and discharge structures. Backup pumps are installed in each location, and are activated by an electronic controller unit that monitors line pressure. The controller also operates electronic vent and drain valves which empty all external supply lines when there is a power outage or double pump failure that would allow the lines to freeze in subzero winter temperatures. The supply lines are covered with one-half inch of foam insulation to minimize the change in water temperature between the pumps and the laboratory. Inside the laboratory paired distribution lines supply water to nine 800 L cylindrical tanks. Flow is regulated to provide an exchange of water in each tank every 2 hr (66 L/min).

Figure 1 summarizes the exposure conditions in each of the nine tanks. Five temperature regimes will be used in conjunction with the three different sources of food. Temperatures in the intake and discharge tanks are allowed to fluctuate naturally to a maximum of 20°C. In two treatments temperature is varied between intake and discharge conditions to approximate frequency distributions of body temperature determined by field studies on plume-resident brown trout.[2] In one of these tanks the water flow is programmed to simulate continuous plume residence, while in the other tank it simulates intermittent plume residence. The

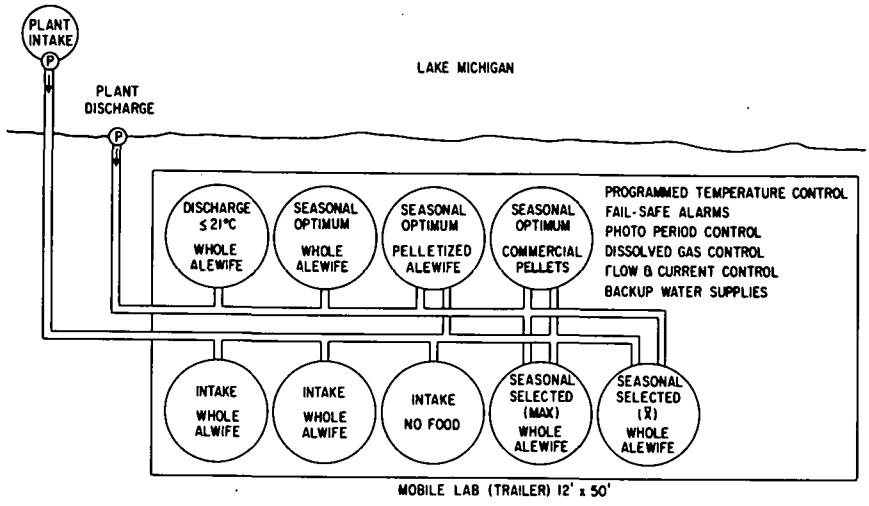

FIG. 1.--Schematic of the mobile field laboratory set up at the Edgewater Plant, Sheboygan, Wisconsin, showing the temperature conditions and food supplied to each fish tank.

fifth condition provides constant temperature exposure at seasonal optimum temperatures allowing our results to compared with studies conducted at constant temperatures.

Figure 2 illustrates how a temperature controller unit utilizes various water supplies to regulate tank temperature toward a central set point. Typically a supply of ambient intake or discharge water is sufficient to maintain tank temperature between the primary upper (UL_1) and lower (LL_1) limits. If tank temperature exceeds the primary limits, then the supply is switched to chilled intake or heated discharge water at the secondary limits of UL_2 and LL_2, respectively. Should tank temperature exceed the maximum boundary limits of LL_3 and UL_3, the controller shuts off all supply water and sounds an alarm.

Controller units for the two tanks receiving cycled temperatures have been modified so the specific set temperature is automatically varied over time according to a programmed 24 hr schedule. This schedule is adjusted monthly to provide a frequency distribution of exposure temperature similar to that observed in the field studies. The temperature and operating mode of each tank are monitored using a data acquisition/storage system that records the data on a computer-compatible magnetic tape.

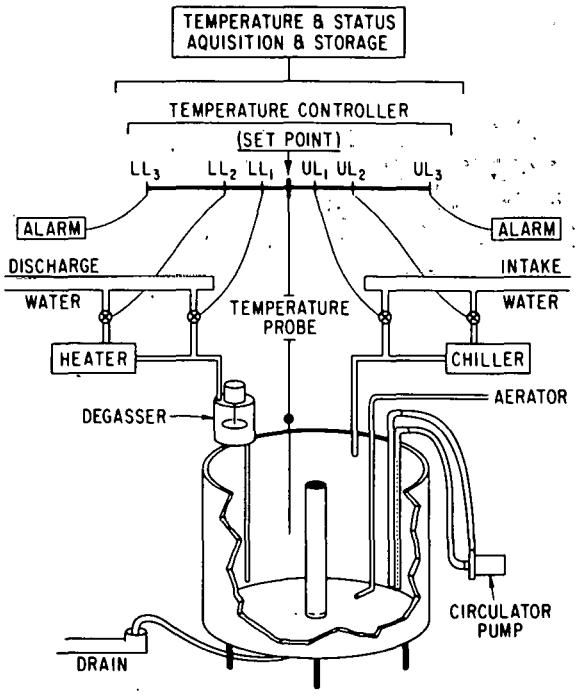

FIG. 2.--Schematic of water flow, temperature control, and water conditioning apparatus on each fish tank.

Other components of the tank system include a degassification unit that reduces levels of supersaturated dissolved gases in discharge water. In this unit incoming water falls onto a spinning disc and disperses into a fine spray that equilibrates rapidly with a supply of ambient air pumped through the chamber. To promote convective mixing in the tank, degassed discharge water is introduced near the bottom and intake water enters near the top. Further mixing is accomplished with a circulation system that pumps water through a vertical diffuser head to create a tank current (1 fps) similar to that in near-field plumes. A hinged tank cover isolates fish from external disturbances and allows natural photoperiod to be simulated with a light source mounted in each lid.

Food serves as a secondary variable, with most fish fed to satiation twice daily on a diet of frozen alewife or pelletized fish food. Alewife represent the natural food of brown trout in Lake Michigan, and a large collection was made in the Sheboygan area. The two pelletized diets represent the type of food that would normally be used in hatchery or aquaculture operations, and differ only in their source of fish protein. Uptake of pollutants directly from water is being

determined by maintaining some fish under starvation conditions.

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TEMPERATURE SELECTION BY BROWN TROUT RESIDING IN A THERMAL DISCHARGE AREA

S. A. Spigarelli and M. M. Thommes

Brown trout (Salmo trutta) are common occupants of thermal discharge areas and are frequently caught by sport fishermen at shoreline discharge sites on Lake Michigan.[1] Determinations of temperature selection by this species under field conditions are requisite to an analysis of temperature effects and provide a means of validating or disproving predictions based on laboratory studies of temperature selection. Since 1972, we have developed and used three independent methods to estimate temperature selection by fish occupying heated discharges: (a) a temperature-integrating fish tag;[2] (b) measurement of fish body temperatures immediately after capture from a thermal plume;[3] and (c) underwater telemetric monitoring of fish responses to plume temperatures.[4] The purpose of this report is to summarize and compare the results obtained by each method.

Temperature-integrating fish tags were placed on 376 brown trout collected at the Point Beach Nuclear Power Plant between 1973 and 1974, and 20 recaptured tags were analyzed to determine mean exposure temperatures for each fish. Body temperatures of 339 brown trout were measured immediately after their capture from the thermal discharge area at Point Beach between August 1972 and October 1973. Occupied water temperatures and internal body temperatures of 44 plume-resident brown trout were monitored using radiotelemetry between October 1975 and October 1977.

Results from these studies show that brown trout select intermediate plume temperatures during each season and only select their final preferred temperature (17—18°C) in summer when maximum ambient temperatures occur (Table 1). However, the seasonal selected temperatures (mean or mode) consistently exceed mean intake (T_i) temperatures by 3 to 10°C, indicating elevated acclimation by plume-resident fish. Maximum increases in body temperature ($T_b - T_i$) occur during seasons with low ambient temperatures, i.e., behaviorally-controlled increases in body temperature are inversely related to natural water temperatures.

Table 1. Summary of data on seasonal temperature selection by brown trout residing in thermal plumes (°C).

Season	Year	Method	N	Mean T_i	Mean T_d	Mode T_b	Mean T_b	$(\bar{T}_b - \bar{T}_i)$ ΔT_b
Spring	1973	C.S.	202	6.5	13.9	12—13	12.3	+5.8
	1976—1977	T	1985	7.6	17.2	14	12.2	+4.6
Summer	1973	C.S.	77	13.0	22.2	18	17.2	+4.2
	1977	T	1480	8.0	20.9	15	15.9	+7.9
Fall	1973	C.S.	60	10.9	20.0	15	15.9	+5.0
	1973	TLD	10	12.6	20.8	--	16.1	+3.5
	1974	TLD	10	8.5	17.8	--	14.7	+6.2
	1975—1977	T	6703	8.9	17.9	12	13.8	+4.9
Winter	1975, 1977	T	4806	1.6	20.3	12	10.9	+9.3

C.S. = creel census
T = telemetry
TLD = temperature-integrating tag
T_i = intake temperature
T_d = discharge temperature
T_b = fish body temperature

A similar pattern of temperature selection is exhibited by rainbow trout in thermal plumes.[5]

The relationship between water temperature and fish body temperature for each period of study is shown in Figure 1. Although the mean intake temperatures ranged from 1 to 15.3°C, mean fish body temperatures for the same periods ranged from 10.4 to 17.6°C, indicating the importance of behavioral thermoregulation. Temporal changes in selected temperatures (mean body temperatures) reflected changes in water temperature, but the increases in fish body temperatures $(T_b - T_i)$, solid lines in Figure 1, were inversely related to water temperature, i.e., fish ΔT_b was greatest in winter when water temperatures were lowest and was least in summer and fall when ambient temperatures were relatively high for

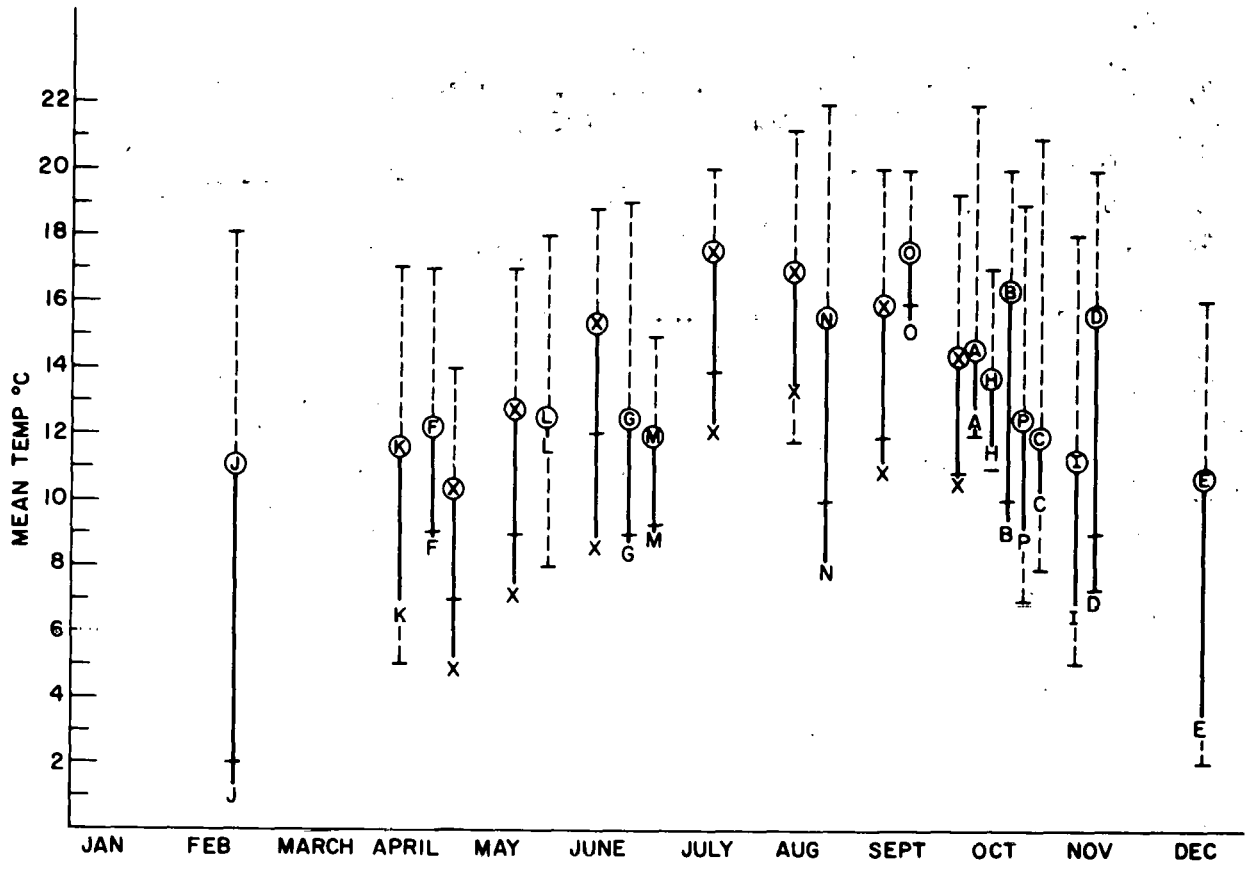

FIG. 1.--Mean fish body temperatures (O) during telemetry periods (A—P) and creel census periods (X). Mean intake temperatures designated as uncircled letters. Solid line represents mean increase (ΔT) in body temperature for each period. Ranges of fish body temperatures are shown between horizontal lines for each period.

those seasons. These findings are very significant because inshore densities of forage fishes are very low in winter and spring, and very high in summer and fall, indicating (1) probable energetic deficiencies for plume-resident trout from December—April, and (2) greatly increased forage consumption from June—November.[6]

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ORGANIC CONTAMINANTS IN THERMAL PLUME RESIDENT BROWN TROUT

G. P. Romberg and S. Bourne*

Previous research has quantified the seasonal temperature selection patterns of brown trout residing in thermal discharges,[1] and has indicated probable changes in pollutant uptake by these fish.[2] Therefore, a pilot study was conducted to identify possible contaminants accumulated by thermal plume-resident fish in Lake Michigan. Brown trout were maintained in tanks receiving intake and discharge ($\leq 21°C$) water from a power plant and were fed a diet of frozen alewife. Fish were sampled over a period of 127 days in order to estimate uptake rates and equilibrium levels for toxic organic and inorganic materials occurring in Lake Michigan fish and water. Experimental fish and natural samples were analyzed to determine the distribution of contaminants in various tissues and the corresponding pollutant levels in similar size brown trout from Lake Michigan. This report summarizes the quantitative analyses for the major organic contaminants.

Analyses were performed by four independent laboratories. In order to allow a comparison of our analytical results with routine contaminant monitoring studies of Lake Michigan, the Great Lakes Fishery Laboratory (GLFL, Ann Arbor, Michigan) measured PCB and DDE levels in whole brown trout (test fish) and alewife used as food in the pilot study. High precision analysis of PCB's was performed by the Argonne Analytical Chemistry Laboratory (ACL/CEN) to estimate variability among fish. A general qualitative screening (GC/MS) is being conducted to identify other organic contaminants in test brown trout. Quantitative analysis for chlorinated pesticides and PCB's in selected fish tissues was contracted to Raltech Scientific Services (RSS).

Analytical procedures were similar at the four laboratories, with some variation in methods of sample cleanup and use of reference standards. Samples

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Table 1. Concentrations of chlorinated organic pollutants in brown trout and alewife.

Sample	Type	Condition location	LAB	Lipid (% wet)	PCB	DDE	DDD	DDT	Dieldrin	Heptachlor epoxide	Oxy-chlordane
Brown trout	whole	hatchery	RSS	6.00	0.09	0.03	0.01	N.D.	0.02	N.D.	N.D.
			GLFL	7.40	<0.2	0.04					
			ACL		0.16						
		15 d[a]	GLFL	7.0	0.89	0.23					
			ACL		0.92						
		127 d	RSS	9.11	2.99	1.31	0.19	0.17	0.18	0.04	0.05
Alewife	whole	Point Beach	RSS	2.13	1.30	0.45	0.06	0.08	0.12	0.02	0.01
			GLFL	3.6	3.21	0.74					
			ACL		4.13						
Brown trout	muscle	hatchery	RSS	3.22	0.07	0.02	N.D.	N.D.	N.D.	N.D.	N.D.
		15 d	RSS	3.98	0.27	0.11	N.D.	N.D.	0.04	0.01	N.D.
			ACL	5.56	0.41						
		41 d	RSS	5.00	1.04	0.68	0.05	0.07	0.08	0.01	0.02
			ACL	3.85	0.92						
		127 d	RSS	4.39	1.39	0.57	0.05	0.06	0.07	0.01	0.02
			ACL	6.39	2.26						
		41/86[b]	RSS	4.26	1.44	0.62	0.07	0.09	0.08	0.02	0.02
			RSS	5.90	1.76						
		Point Beach	RSS	4.72	1.20	0.43	0.07	0.06	0.06	0.01	N.D.
		Sheboygan	RSS	3.30	2.74	0.88	0.04	0.05	0.04	0.02	N.D.
Brown trout	liver	41/86	RSS	5.63	1.49	0.47	0.07	0.05	0.08	0.01	0.01
	kidney		RSS	8.02	3.17	1.34	0.19	0.14	0.18	0.04	0.05
	gill		RSS	10.20	3.69	1.53	0.23	0.18	0.22	0.03	0.05
	caeca		RSS	16.10	5.12	2.11	0.35	0.29	0.33	0.08	0.09

Table 1. Cont.

Sample	Type	Condition location	LAB	Alpha-chlordane	Gamma-chlordane	Cis-nanochlor	Trans-nanochlor	Hexachloro-benzene	Alpha HCB
Brown trout	whole	hatchery	RSS	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
			GLFL						
			ACL						
		15 d	GLFL						
			ACL						
		127 d	RSS	0.07	N.D.	0.08	0.13	0.01	0.02
Alewife	whole	Point Beach	RSS	0.04	0.05	0.06	0.06	N.D.	N.D.
			GLFL						
			ACL						
Brown trout	muscle	hatchery	RSS	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
		15 d	RSS	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
			ACL						
		41 d	RSS	N.D.	0.02	0.03	0.05	N.D.	N.D.
			ACL						
		127 d	RSS	0.02	N.D.	0.03	0.05	N.D.	N.D.
			ACL						
		41/86	RSS	0.02	N.D.	0.05	0.06	N.D.	N.D.
			RSS						
		Point Beach	RSS	0.03	0.02	0.03	0.05	N.D.	N.D.
		Sheboygan	RSS	0.02	0.02	0.02	0.04	N.D.	N.D.
Brown trout	liver	41/86	RSS	0.02	0.01	0.04	0.04	N.D.	N.D.
	kidney		RSS	0.06	N.D.	0.08	0.10	0.01	0.02
	gill		RSS	0.07	N.D.	0.09	0.15	0.01	0.02
	caeca		RSS	0.12	N.D.	0.13	0.25	0.02	0.03

[a] 15 d = 15 days at intake temperature.

[b] 41/86 = 41 days at intake and 86 days at discharge temperatures.

analyzed at the GLFL laboratory were processed as follows: (1) blending; (2) extraction on a column with 10% ethyl acetate in hexane; (3) gel permeation cleanup; (4) silica gel cleanup; (5) detection by gas chromatography with electron capture detector (GC/EC); (6) quantification against mixed PCB standards (Aroclor 1248, 1254, 1260). At the ACL laboratory a florosil column cleanup was substituted for steps 3 and 4 in precision PCB measurements. The Raltech Laboratory substituted florosil cleanup for step 3 and used a single PCB standard (Aroclor 1254). Samples prepared by ACL for general organic screening were extracted with ethyl acetate (step 2) and measured by GC/mass spectroscopy after step 3.

In general, the quantitative results from the three laboratories were in agreement for experimental trout, but not for PCB's in Lake Michigan alewife (Table 1). The higher values reported by GLFL and ANL may be related to differences in the PCB standards. Variability in PCB concentrations in fish (muscle) increased with time as did variability in fish growth (Table 2).

In addition to PCB's a total of 12 chlorinated hydrocarbons (or derivatives) were detected in fish samples (Table 1). All but two of these compounds were detected in the alewife used as food for brown trout. Concentration of these compounds generally increased in brown trout muscle over the 127 days exposure period, and showed no sign of attaining equilibrium. Since these brown trout were from a hatchery whose fish would normally be released into Lake Michigan, these results indicate the possible rates of accumulation and levels of contamination that may occur when these fish are introduced into the lake.

The similarity in PCB levels between intake (127 d) and discharge (41/86 d) conditions may be the result of inadequate food supply at higher discharge temperatures. Final pesticide levels in test fish were approximately equal to the levels measured in similar sized brown trout collected near the pilot study area (Point Beach, Wisconsin) and the present study area (Sheboygan, Wisconsin). However, PCB levels in the muscle of brown trout collected from the Sheboygan area were nearly twice as high as levels in brown trout from Point Beach. This difference is likely to be the result of higher PCB concentration in the Sheboygan area of Lake Michigan.

Table 2. Variability in growth rate, lipid content, and muscle PCB levels in brown trout exposed to intake or discharge temperatures

Exposure, days	Δ wt, g	Lipid, %	PCB, ppm
15[a]	30	5.94	0.50
	30	6.37	0.43
	30	4.35	<0.4
	30	5.56	0.41 (est)
41[a]	50	3.25	1.02
	70	5.23	0.97
	80	4.16	1.00
	30	2.75	0.68
	57	3.85	0.92 ± (0.16)
127[a]	175	6.32	1.65
	160	6.32	3.68
	665	8.61	2.44
	700	3.87	1.77
	135	6.81	1.75
	367	6.39	2.26 ± (0.85)
41[a]/86[b]	165	8.79	2.02
	170	6.73	3.17
	70	5.61	1.57
	115	3.71	0.98
	105	4.67	1.07
	125	5.90	1.76 ± (0.89)

[a]Intake

[b]Discharge

Without exception, the pyloric caecum of brown trout contained the highest concentration of lipids, PCB's and chlorinated pesticides. This organ is actively involved in the digestive process and has been reported to be a site of high accumulation of organic pollutants.[3]

Gill and kidney samples contained lower concentrations of contaminants than the caecum, while liver and muscle values were lowest. The high levels of

chlorinated organics in gills could indicate significant direct uptake from Lake Michigan water as proposed in a recent study.[4] Other work has indicated that direct uptake via the gills accounts for less than 3% of total uptake.[5]

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SORPTION OF CADMIUM AND ITS EFFECT ON GROWTH AND THE UTILIZATION OF INORGANIC CARBON AND PHOSPHORUS OF TWO FRESHWATER DIATOMS*

H. L. Conway and S. C. Williams†

Cadmium was rapidly sorbed by Asterionella formosa and Fragilaria crotonensis during the first 5 to 10 min of exposure (0.05 to ∿9 µg Cd L^{-1}), followed by a hyperbolic increase in the cellular cadmium content as a function of time. Results obtained from experiments conducted in the light and dark, experiments using live and dead populations, and cellular site location studies imply that the sorption of cadmium by A. formosa is partially an active process; but for F. crotonensis it appears to be passive. Populations of A. formosa exhibited a corresponding decrease in the growth rate as the ambient cadmium concentration was increased from ∿ 2 to ∿ 9 µg L^{-1}. In contrast, the growth rate of F. crotonensis was unaffected at levels ranging from ∿ 0.05 to ∿ 9 µg Cd L^{-1}. The utilization of inorganic carbon by A. formosa was unaffected at ∿4 µg Cd L^{-1}, but reduced 45% at ∿9 µg Cd L^{-1}. The utilization rates of carbon and phosphorus by F. crotonensis were reduced at the lower cadmium concentrations and enhanced at the highest.

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INFLUENCE OF OXIDATION STATE ON THE SORPTION OF PLUTONIUM BY FRESHWATER DIATOMS

D. M. Nelson, C. W. Kennedy, and H. L. Conway

Plutonium can exist in aqueous media in any of four oxidation states (III, IV, V, or VI). In the Irish Sea,[1] Lake Michigan, and a series of Canadian lakes,[2] plutonium has been shown to be present in solution as a mixture of oxidized (V + VI) and reduced (III + IV) forms with up to 90% in the oxidized form. There is a striking difference in the adsorption of these two plutonium species onto suspended particulate matter, the adsorption of the reduced form being about 1000 times higher than that of the oxidized form. Biological as well as physical uptake could be influenced by the oxidation state of the available plutonium. In this study biological uptake was investigated using two common freshwater diatom species.

Four experiments were completed using populations of Asterionella formosa and Fragilaria crotonensis which were exposed to both oxidized and reduced plutonium. The experimental procedure consisted of mixing a sample of unialgal population (obtained from a steady-state chemostat) with synthetic Lake Michigan water containing ^{237}Pu tracer in the required form. These batch cultures had initial diatom biomasses of 0.7 to 2.3 mg (dry)/liter and doubling times of 25 to 30 hr. Subsamples were drawn from these cultures and analyzed for cellular ^{237}Pu activity, population cell volume,[3] and the concentration and oxidation state of the plutonium. In all experiments the plutonium concentration was about 10^{-12} M with greater than 95% of the plutonium in th specified oxidation state.

The time-dependent sorption of plutonium is plotted in Figure 1 and can be described by a hyperbolic function $BR = \frac{BR' \cdot t}{K+t'}$, wher BR is the bioaccumulation ratio (cpm per gram of dry cells) · (cpm per gram of water)$^{-1}$ at time t (hours), BR' is the value of BR at infinite time, and K is the time necessary for BR to equal BR'/2.

The bioaccumulation ratios were large in both species for both oxidation states. The BR measured in three of the experiments was somewhat less than the BR of $\sim$ 25,000 observed in natural mixed diatom populations collected from Lake

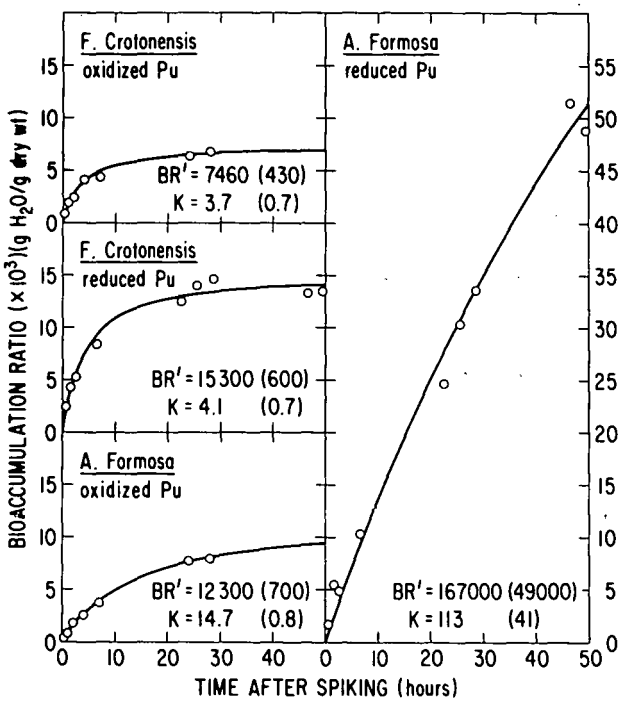

FIG. 1.--Bioaccumulation ratio versus time for A. formosa and F. crotonensis. The standard deviation for BR' and K, in parentheses, was calculated using the statistical methodology of Cleland.[5]

Michigan.[4] No explanation is available for the extremely large BR exhibited by A. formosa, for reduced plutonium. The long time constant (several times longer than the doubling time) argues against this being due to direct metabolism by the diatom.

The fractions of plutonium assimilated into the cells, the silica frustule, and the organic coating of the frustule were established at the end of each experiment. These fractions were separated by ultrasonic disruption followed by uv irradiation. From the data in Table 1 it is seen that although plutonium in both oxidation states distributes throughout the cell, the oxidized form appears to cross the cell wall more rapidly than the reduced form. The plutonium found within the cells subsequent to the administration of the oxidized form was largely reduced, suggesting that cells may act as a reducing agent for plutonium in nature.

Table 1. Cellular location of ^{237}Pu activity in Asterionella formosa and Fragilaria crotonensis, expressed as a percentage of total cellular activity.

Cell fraction	Pu IV		Pu VI	
	Asterionella formosa	Fragilaria crotonensis	Asterionella formosa	Fragilaria crotonensis
Cell contents	12	25	41	56
Organic coating of frustule	61	47	46	26
Frustule	27	28	13	18

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EXPERIMENTAL STUDIES OF STRESS IN FRESHWATER PLANKTON COMMUNITIES USING DIFFERENT ENCLOSURE TECHNIQUES*

J. S. Marshall, D. L. Mellinger, and D. L. Saber†

Structural and functional responses of plankton communities to cadmium stress were studied during 1977 in Lake Michigan using small-volume (8 L) completely sealed enclosures, and in Canada's Experimental Lakes Area (ELA) Lake 223 using large-volume (1.5×10^5 L) open-surface enclosures. In Lake Michigan the effects of cadmium additions in the 0 to 5 µg Cd/L range on total numbers of microcrustaceans were greater in "light" versus "dark" or in shallow versus deep epilimnetic incubations. Measurements of dissolved oxygen suggest that this interaction with light (depth) was an indirect effect due to cadmium's reduction of photosynthesis. Zooplankton density and species diversity were not significantly affected within 21 days by additions of less than 1.6 µg Cd/L, whereas community similarity was reduced by 0.2 µg Cd/L and apparently would be detectably reduced by additions as low as 0.05 to 0.1 µg Cd/L. In the ELA Lake 223 experiment, the effect of an initial cadmium addition in zooplankton density progressively increased with time up to 31 days and then decreased, probably due to decreasing cadmium concentrations in the water. The reduction of community similarity by cadmium addition was similar to that observed in the Lake Michigan experiments.

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EFFECTS OF ENCLOSURE ON A LAKE MICHIGAN ZOOPLANKTON COMMUNITY

J. S. Marshall and D. L. Mellinger

An in situ experiment was conducted to determine the responses of a zooplankton community in northern Green Bay, Lake Michigan, to enclosure for 3 to 6 weeks in polyethylene carboys of different volumes (4, 8, 20, and 50 L). One carboy of each size for each of four depths (4, 5, 6, and 7 m) was filled with epilimnetic water and suspended at the designated depths on July 11, 1978. Those at 4 and 7 m were removed after 3 weeks, and those at 5 and 6 m were removed after 6 weeks. Enclosure effects on the zooplankton were indicated by the degree of community similarity [coefficient of community (CC) and percentage similarity (PS)] between samples from the enclosures and the open lake after 3 and 6 weeks of in situ incubation. Enclosure effects were also indicated by the average densities of total crustacean zooplankton as well as the populations of different species of zooplankton. Preliminary analysis of the results indicates that there was no significant effect of enclosure volume (4—50 L), although depth (m) and duration of incubation (3 to 6 weeks) had several significant effects on the zooplankton. Reductions of average CC and PS after 3 weeks were similar to those observed in 1977 experiments in Lake Michigan and were no greater than those in a much larger enclosure (1.5×10^5 L) in a small Canadian lake.[1] The average values of CC after 6 weeks of enclosure were significantly lower than those after 3 weeks, whereas the average values of PS were not significantly reduced further after 6 weeks. There were several significant differences between the average densities of specific zooplankton populations in the lake and the carboys after 3 or 6 weeks, but the average density of total zooplankton in enclosures as 4 to 5 m was not significantly different from that in the lake after either 3 or 6 weeks.

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EFFECTS OF ENCLOSURE ON ZOOPLANKTON IN A LARGE BAY OF ELA LAKE 382

D. L. Mellinger and J. S. Marshall

A large (3 ha) bay of ELA Lake 382 was isolated from the rest of the lake on May 26, 1978. The main purpose of this long-term project is to study the effects of added cadmium on the biota of this bay. Following enclosure, zooplankton samples were collected in the bay and open lake with 153 μm nets at approximately weekly intervals during summer and fall of 1978. These data provide a baseline for comparison with the results of future stress experiments and for making a preliminary assessment of the effects of enclosure on the zooplankton community of the bay.

The density of crustacean zooplankton (animals/L) in the bay was very similar to that of the open lake immediately following enclosure. Average densities for the period, June through October, were not significantly different between the bay and lake (22.6 ± 2.9 (S.E.) and 24.4 ± 3.6 (S.E.)). The largest differences occurred during early summer when the density of the bay was lower than that of the open lake. The bay-lake percentage similarity (PS) on the first sampling date (4 days after enclosure) was 67.0. The mean PS for 12 dates was 54.3 ± 2.3 (S.E.).

The species composition of the two zooplankton communities was the same except for the absence of Holopedium gibberum, Daphnia pulex, and Orthocyclops modestus in the bay samples. Some differences in species composition are to be expected since the depth of the bay (maximum, 3 m) is considerably less than that of the open lake (maximum 12 m). Bosmina longirostris was the only abundant cladoceran in the bay, while there were usually several abundant species of Cladocera present in the open lake. The copepod community of the bay was similar to that of the open lake although Tropocyclops prasinus and Diaptomus minutus represented a larger proportion of the bay community than they did of the open lake. These data suggest that the bay was qualitatively rather similar to the open lake during the first summer and fall of enclosure.

PLANKTON RESPONSES TO CADMIUM ADDITIONS IN SMALL ENCLOSURES IN CANADA'S EXPERIMENTAL LAKES AREA LAKE 382

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

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Two in situ experiments were conducted to determine the short-term (3 weeks) effects of cadmium on the plankton community in ELA Lake 382. A large (3 ha) bay was isolated by a curtain in May 1978 for a future study on the effects of added cadmium (tentatively) on the enclosed ecosystem. In each experiment, a pair of 25 L polyethylene carboys for each of six incubation depths (2.5, 3.0, 3.5, 4.0, and 5.0 m) were filled with epilimnetic water. Cadmium (1 µg Cd/L) was added to one of each pair of carboys, leaving the other as a control. Experiment 1 was initiated on August 9 and terminated on August 30, and experiment 2 was initiated on August 30 and terminated on September 19. At the end of each experiment the zooplankton were removed and preserved in 4% formalin. At the end of experiment 1, the concentration of dissolved oxygen in each carboy was measured with a YSI oxygen meter.

Responses of the ELA Lake 382 plankton community to additions of 1 µg Cd/L were similar to those in small (8 L) enclosures in Lake Michigan or a much larger enclosure (1.5×10^5 L) in ELA Lake 223 after three weeks.[1] The average reduction of total crustacean density was 17%, which is close to the value predicted for 1 µg Cd/L (14%) from a regression curve for Lake Michigan data. The average value of percentage similarity for the zooplankton communities in Cd-treated carboys was within the 95% confidence limits for values predicted from Lake Michigan data.[1] The average percentage reduction of dissolved oxygen concentrations caused by 1 µg Cd/L in the ELA Lake 382 enclosures was also close to the value predicted from Lake Michigan data.[1]

Reference

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AN IN SITU EXPERIMENTAL METHOD FOR TOXICOLOGICAL STUDIES ON NATURAL PLANKTON COMMUNITIES*

J. S. Marshall and D. L. Mellinger

During 1976 and 1977 we developed and tested a new in situ method for toxicological studies on natural plankton communities using small-volume (8 and 25 L) enclosures. Effects of enclosure for 4 to 21 days on the plankton in northern Green Bay, Lake Michigan, were studied in connection with cadmium addition experiments. In situ incubations in opaque enclosures or in translucent ones at depths > 8 m caused large changes in zooplankton community structure, as measured by two similarity indices, coefficient of community (CC) and percentage similarity (PS), whereas incubations in translucent enclosures at 3 to 8 m caused relatively small changes. The effect of cadmium additions (0—5 μg Cd/L) on total zooplankton abundance in translucent enclosures at 3 to 5 m was significantly greater than those at 6 to 8 m. This interaction between cadmium and light (depth) was probably due to a reduction of phytoplankton photosynthesis, as indicated by changes in dissolved oxygen (DO) concentrations. Zooplankton abundance was not significantly affected by < 1.6 μg Cd/L, whereas DO and PS were significantly reduced by ≧ 0.2 μg Cd/L. Values of PS for zooplankton communities in large-volume (1.5×10^5 L) enclosures in a small Canadian lake 3 weeks after cadmium addition were within 95% confidence limits from the results of 3 week experiments in Lake Michigan.

*Abstract of a paper presented at the 3rd Symposium on Aquatic Toxicology, American Society for Testing and Materials, New Orleans, Louisiana, 17—18 October 1978.

PRELIMINARY OBSERVATIONS OF THE EFFECTS OF RAINWATER ADDITION ON LAKE MICHIGAN PHYTOPLANKTON PRIMARY PRODUCTIVITY

J. I. Parker

Atmospheric precipitation in the southern basin of Lake Michigan contains a variety of pollutants such as acids, trace elements, and phosphates. Their concentration in rainwater samples usually exceeds the concentration in the lake water, and there is no doubt that deposition from the atmosphere is one of the major sources of pollutants to Lake Michigan.[1] Murphy and Doskey[2] report that approximately 18% of the annual phosphorus budget in the lake is provided by atmospheric inputs. Deposition of atmospheric pollutants in the lake can increase their concentration in the surface layer, and prior to their dilution some of these pollutants could affect the surface water plankton.

The rate of phytoplankton primary production may be increased by phosphate additions from rain or reduced by toxic trace elements in the rain. Hypothetically then, the co-occurrence of a phytoplankton bloom (when production rates are maximal) and a "dirty" rainfall event could increase or decrease the quantity of organic matter produced. This could substantially alter annual producitivy rates since greater than half of the annual productivity occurs during bloom periods in the spring and fall.

To test this hypothesis a series of experiments are being conducted to measure the change in primary production rate (^{14}C uptake) in water samples containing the natural assemblage of Lake Michigan phytoplankton treated with various additions of filtered rainwater. In September 1978, a pilot experiment for this series was completed, and the results are summarized in Figure 1. All production values presented have been corrected for dilution. The average primary production rate among the control samples was 5.5 mg $C/m^3 \cdot h$. The production rates in samples treated with 0.1 and 1.0% (by volume) rainwater were not measurably different from the rates in the control samples. Samples treated with 5.0% rainwater showed production rates that averaged approximately 10% higher than those of the control samples, while an increase to 10% rainwater resulted in productivity levels equal to those of the control samples. However, further

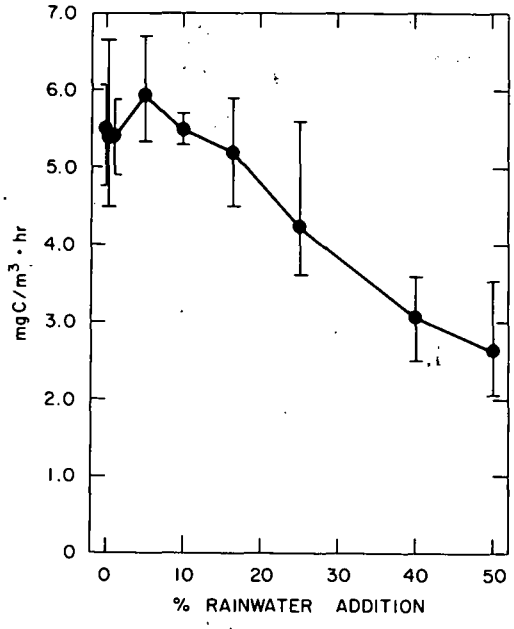

FIG. 1.--Mean primary production rate of phytoplankton exposed to serial additions of acidic rainwater.

incremental additions of rainwater progressively reduced primary production, and the rate in the 50% rainwater treatment averaged < 50% of the rate in the control samples.

These preliminary findings suggest additions of rainwater less than 10% stimulate primary production. Phosphates in the rainwater may be the stimulating agent. Phosphorus is one of the limiting nutrients for many freshwater phytoplankton, and phosphate additions to natural assemblages of Lake Michigan phytoplankton have been shown to stimulate primary productivity.[3] Toxic constituents, such as trace elements or changes in pH caused by acidic pollutants in the rainwater, may be responsible for the observed reductions in productivity rate at higher dilution ratios. It appears that the stimulating effect of low-level rainwater additions are masked by the toxic effects of rainwater additions in excess of 10%.

Further experimentation will be conducted throughout the 1979 field season to evaluate these observed trends. Tests will be conducted in late winter using melted snow as the treatment. In addition, other field tests will be done before, during, and after the spring and fall phytoplankton blooms to document the response by phytoplankton in a variety of physiological states and environmental conditions.

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SOURCES OF PLUTONIUM TO THE GREAT MIAMI RIVER

G. E. Bartelt, C. W. Kennedy, and C. M. Bobula III

An important objective of our study of the plutonium isotope, ^{238}Pu, in the Great Miami River watershed has been to determine the contribution of various sources to the total ^{238}Pu transported by the river. Periodic discharges of industrial wastewater from Mound Laboratory from 1973 to 1975 have released approximately 20 mCi of ^{238}Pu each year to the Great Miami River.[1--3] Changes in the wastewater treatment system in 1976 have reduced the annual discharge to less than 3 mCi/year.[4] However, despite this sevenfold reduction of plutonium in the wastewater discharge, the annual flux of ^{238}Pu down the river has remained relatively constant and is approximately 10 times greater than can be accounted for by the reported effluent discharges (Table 1). Therefore, other sources of the ^{238}Pu in the Great Miami River exist.

A second possible source of plutonium is the resuspension of sediments enriched by earlier wastewater releases and deposited in the river.[6] However,

Table 1. Annual flux of ^{238}Pu at Franklin, Ohio.

Date	^{238}Pu concentration,[a] fCi/L	Annual flux,[b] Ci
1974	19.4 ± 0.9	0 .041
1975	14.6 ± 1.1	0 .031
1976	12.1 ± 0.8	0 .026
1978	20.3 ± 2.1	0 .043

[a] Average concentration of ^{238}Pu on suspended sediment. This value is used to approximate the total plutonium per liter because over 95% of the plutonium is associated with particulate material.[5] The ± value is 1 σ counting error.

[b] The annual flux was calculated using a mean annual flow rate at Franklin of 67 m^3/s.[6]

in the distance from the effluent discharge point to Franklin, our major sampling site (9.7 km), there appear to be few areas where large accumulations of sediment could occur. Spring floods thoroughly scour the river, removing temporary sediment beds. Two spring flood cycles have occurred since the wastewater discharge of plutonium was reduced in 1976. Therefore, it seems improbable that resuspension of earlier sediment deposits would continue to be a significant contributor to the annual flux of plutonium.

A much more likely source is the continuing erosion of soil from a canal and stream system contaminated with ∿ 5 Ci of ^{238}Pu,[7] which connects directly to the river 6.9 km upstream from Franklin. Results from samples analyzed in 1978 show the average concentration of ^{238}Pu in suspended sediments from the canal to be approximately 10^3 times greater than suspended sediment concentrations in the river and wastewater effluent (Table 2). This agrees with previously reported concentrations of ^{238}Pu in suspended sediments from the canal ranging from 10^3—10^5 times higher than suspended river sediments.[8] Thus the main contributor to the total amount of plutonium transported by the Great Miami River would appear to be highly enriched sediment from the canal, which is eroded into the river where it is then diluted by uncontaminated sediments.

Table 2. Concentrations of ^{238}Pu in suspended sediment samples.

Location	Concentration, fCi/L
Canal	15,500 ± 800
Wastewater discharge	11,200 ± 800
Great Miami River at Franklin	20.3 ± 2.1

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PLUTONIUM REMOVAL AND DIURNAL VARIATIONS OF SUSPENDED SEDIMENT CONCENTRATIONS IN THE GREAT MIAMI RIVER

C. M. Bobula III, C. W. Kennedy, and G. E. Bartelt

Studies of the biogeochemical behavior of atmospherically deposited ^{238}Pu and $^{239,240}Pu$ indicate that the transport and removal of plutonium from terrestrial ecosystems is mediated primarily by erosional and sediment discharge processes.[1,2] Effluent release experiments conducted downstream of the industrial outfall at Mound Laboratory have demonstrated that ^{238}Pu which enters the aquatic environment as dissolved waste is rapidly adsorbed by suspended solids in the effluent pulse (dissolved phase/particulate phase distribution ratio, $D_{w/s} \cong 1.0$) and that the dissolved/particulate distribution of ^{238}Pu between release events $\cong 5 \times 10^{-2}$.[3] Reasonable estimates of the annual transport of $^{239,240}Pu$ based upon long-term discharge and sediment loading data have been reported for a large subwatershed in the upper reaches of the Great Miami River Basin.[2] In this report we discuss data which characterize the short-term variability of suspended particulate transport downriver of a canal system contaminated with ^{238}Pu. With the exception of literature which reports on fluctuations of stream microflora and benthic invertebrate populations, little information concerning diurnal trends in the suspended loads of lotic systems is currently available.

Suspended sediment concentrations were determined 5.0 river miles downstream of the Great Miami River-drainage canal confluence near Franklin, Ohio, during two consecutive 24 hr periods (9—11 July 1978). Identical procedures were followed during a single 24 hr period (12—13 July) near Trenton, Ohio, 15.0 river miles downstream. Water samples collected at 1 to 2 hr intervals in midstream at half-depth were filtered through preweighed 0.45 μm Millipore filters. Dry weights of the filtered residue were determined. Concentrations of total organic particulates in the dry residue represent weight losses after ignition of the filtered solids at 500°C. Incident solar radiation was continuously monitored to characterize the relationship between light stimulus and fluctuations of suspended organic material concentrations.

Trends in diurnal variation of the suspended sediment at the two sampling sites were very similar and are represented by data from Franklin (Figure 1). The cyclic response of suspended organics (including benthic algae, diatoms, plankters, and allochthonous drift) to sunlight has been observed by others;[4—6] diurnal variation in drift is related to the light and dark periods, usually with peaks at dawn and dusk in mid to late summer. Our data for the Great Miami River show daily concentration maxima at dawn and dusk (0600 and 2000 hours) and a daily concentration minimum in late morning (1000—1200 hours). Hynes has attributed bimodal peaks in phytoplanktonic drift to the active production of oxygen and the division of diatoms during optimal light conditions which make them buoyant and more likely to be swept away. Negative phototaxic behavioral patterns in benthic fauna may lessen the chances that animals will be entrained by the current during daylight hours.[7]

Diurnal variations of the inorganic particulate loads of rivers and streams during periods of near-constant discharge have been less widely studied. Hourly discharge measurements 7.1 river miles upstream from Franklin at Miamisburg (range: 1195—1018 cfs) and 24.5 river miles downstream from Franklin at Hamilton (range: 1473—1290 cfs) indicated a gradually decreasing trend in flow over our two day sample collection period.[8] The observed daily fluctuations of

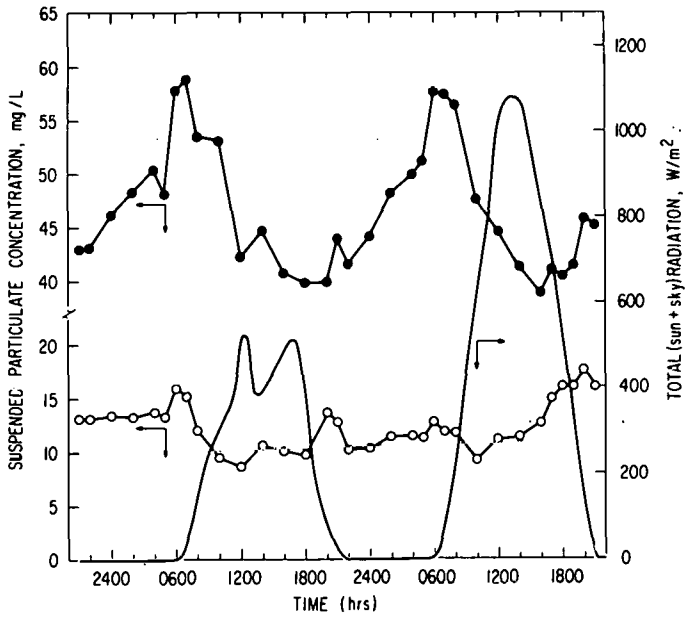

FIG. 1.--Diurnal variations of suspended load in the Great Miami River near Franklin, Ohio. Inorganic particulates (ash wt.), ·-· ; organic particulate (ash-free dry wt.), o-o; total incident radiation, —.

inorganic particulate concentration, therefore, are not solely a function of changes in river discharge. It is probable that industrial and municipal effluents introduced to the Great Miami River upstream of our sampling site directly increase the inorganic particulate load or resuspend previously deposited riverbed sediments into the water column. It is also possible that daily maximums of inorganic suspended load result, in part, from the resuspension of riverbed sediment by bottom-feeding fish and other benthic organisms. Large carp Cyprinus carpio, and suckers Catostomus commersoni, were particularly active between 0500 and 0600 hours both days.

Ash wt/dry wt ratios for filtered solids at Franklin varied approximately 16% each day with maximum values occurring at 0800 hours and minimum values at 1800—1900 hours (Figure 2). Changes in both the absolute and proportionate amount of the inorganic component of suspended load material may significantly affect estimates of the transport of plutonium and other radionuclides in aquatic systems. Studies of the sedimentary phase distribution of plutonium in Lake Michigan sediments have indicated that approximately 95% of the plutonium in these sediments is associated with a sodium citrate-sodium dithionite extractable mineral fraction.[9] The remaining ∿ 5% is extractable from organic components (principally humic and fulvic acids) in 0.1 N sodium hydroxide. Hence, it is conceivable that the daily 14 to 17% variability of particulate material phase composition shown in Figure 2 causes cyclical variations in the plutonium concentration of suspended solids transported by the river.

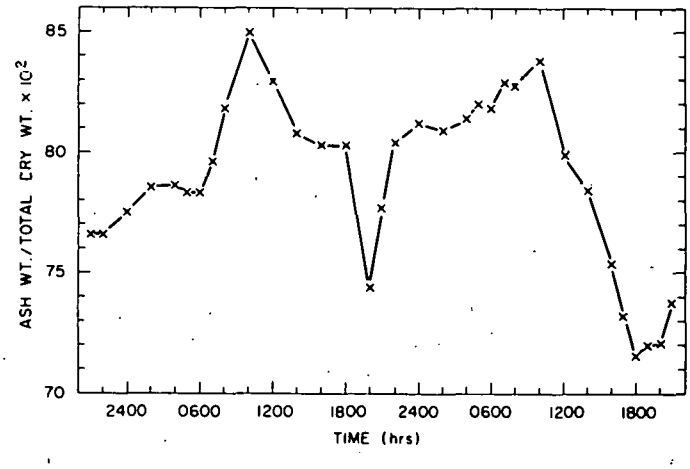

FIG. 2.--Ash wt/total dry wt ratio of filterable particulates (> 0.45 μm) near Franklin, Ohio.

Although the processes governing short-term sediment discharge rates in lotic systems are not fully understood, our preliminary results characterize the nature of diurnal suspended load variability and its potential significance for plutonium transport estimates for the Great Miami River.

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ION EXCHANGE SEPARATION AND RADIOCHEMICAL DETERMINATION OF URANIUM

K. A. Orlandini

A method has been developed for the determination of uranium at the submicrogram level by alpha spectrometric-isotopic dilution in soil, sediment, water, and biota. The uranium is separated from most of the other elements by making the solution 0.4 M in nitric acid and 1.6 M in aluminum nitrate and passing it through a column containing a strongly basic anion exchange resin.[1] In this system the distribution ratio of uranium is very high, > 1000, whereas those for most other elements are very low, < 1. As a consequence, uranium can, in a single operation, be selectively separated from solutions having (1) relatively large volumes and (2) relatively high concentrations of those constituents that would otherwise interfere with the determination of uranium.

Sample Preparation and Discussion of Technique

Ordinarily, solid samples are ashed at 500 C to destroy organic material and then leached or dissolved with strong acids such as hydrochloric, nitric, and hydrofluoric. Refractory substances are dissolved by means of high temperature fusion.[2] The concentration of actinide elements, including uranium, from a large water sample is facilitated by evaporation, co-precipitation or absorption techniques. ^{232}U is added at the dissolution stage as the isotopic diluent to monitor chemical recovery of the naturally occurring isotopes.

Solutions containing uranium derived from preparative steps are evaporated to near dryness and redissolved in a minimum volume of 2 M nitric acid. In order to promote the formation of the uranyl nitrate anion complex, aluminum nitrate is added to the dilute acid sample. It is convenient to add the aluminum salt as a 2 M solution (which has previously been passed through an anion exchange column to remove uranium contamination) so that the final solution is 0.4 M in nitric acid and 1.6 M in aluminum nitrate. This solution is passed through a Biorad AG 1-X8, 100 to 200 mesh ion exchange column.[1] The column is washed first with a solution of the same composition (to remove elements such as iron)

and then with 9 M hydrochloric acid; the uranium is eluted from the column with 0.1 M hydrochloric acid-0.01 M hydrofluoric acid. The uranium is electroplated onto stainless steel[3] and assayed alpha spectrometrically. Uranium recovery averages 60% with a range of 50 to 95%.

The 9 M hydrochloric acid wash removes the aluminum that was a major constituent of the preceeding wash solution and the thorium that may have been present in the sample. Thorium is strongly adsorbed onto Dowex-1 from strong nitrate media. Both of these elements will, if present, be electrodeposited along with the uranium. The aluminum will degrade the spectrum; the thorium is an interference in the uranium determination as the energy of the alpha particle from ^{230}Th (4.68 MeV) is very close to that from ^{234}U (4.77 MeV).

Uranium can also be eluted from the column with 5 M HNO_3. This has the advantage over 9 M HCl of effecting a separation from plutonium, but the disadvantage of requiring a much larger volume of wash. Plutonium is an interference in samples where it is also being determined and ^{242}Pu is an isotopic diluent. The energies of the ^{234}U and ^{242}Pu alpha particles are 4.77 and 4.90 MeV, respectively.

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PLUTONIUM IN FRESH WATER

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

The concentrations of plutonium and thorium in a group of freshwater lakes having a wide variety of limnological characteristics have been reported previously.[1] Included in that report were values for such parameters as pH, alkalinity, conductivity, and the concentrations of chloride and sulfate. Since then the concentrations of uranium, the Pu(VI)-to-Pu(IV) concentration ratios in these waters, and the concentrations of plutonium, thorium, and uranium in suspended sediment, have been determined (Table 1). The small differences between some of the values in this table and those reported previously are the result of a change in the method used to calculate concentrations from the data obtained in alpha spectrometric assays.

At present strong correlations between the plutonium, thorium, or uranium concentrations and the limnological parameters, pH and alkalinity, appear to exist. A series of laboratory experiments are in progress to determine whether the systematic trends suggested by the field data can be duplicated using Pu tracers in known oxidation states and various amorphous oxide substrates.

An important conclusion that can be drawn from the plutonium data is that the rate at which the plutonium concentrations decrease is slow in relation to man's temporal scale. In Lake Michigan and Great Slave Lake where the volume-to-surface area ratios are relatively high, several percent of the plutonium that entered is still dissolved in the water. In Lake Michigan, the only system for which there are reliable data, the decrease in the concentration in the period 1971 to 1978, if there had been no additional input from the atmosphere, would have been only a factor of about two. Even in the shallow lakes, where the ratio of the amount of sediment to the volume of water is relatively large, the amount of plutonium dissolved in the water is about 0.1% of the amount that entered. The process that appears to control the rate at which plutonium is being removed from the water is adsorption onto suspended solids and their incorporation in the fixed sediment. The process which might increase the rate of removal at higher concentration levels as well as establish an upper limit for the plutonium

concentration, is precipitation. These processes are discussed below.

There is an obvious correlation between the eutrophic level of a lake and the plutonium oxidation state ratio. The decreases in the values in going from oligotrophic to eutrophic lakes appears to be due to increases in the concentrations of natural ligands. The formation of Pu(IV)-ligand complexes in solution may decrease the affinity of the solids for Pu(IV), the form that is strongly adsorbed, and shifts the Pu(IV)-Pu(VI) redox equilibrium toward the reduced form. (Complexing ligands interact much more strongly with Pu(IV) than they do with Pu(VI). That there may be decrease in adsorption onto solids with increasing eutrophic levels is suggested by the thorium data, if one excludes the data for Christie Bay and the Main Basin of Great Slave Lake. It is noteworthy that the oxidation state ratio in the several parts of Great Slave Lake is correlatable with the degree of eutrophication. From McLeod Bay to Christie Bay to Main Basin the VI/(V ratio goes from 3 to 0.6 to less than 0.1.

Virtual Plutonium Concentration in Natural Waters

It appears that the plutonium that is now in these lakes is either dissolved in the water or adsorbed onto the surfaces of suspended solids and that a state of equilibrium exists between these phases. The rate at which the plutonium concentration in the water decreases is therefore totally dependent on the rate at which the suspended solids are transferred out of the system.

In the event of a major intrusion of soluble plutonium into a lake, it appears that the solubility of some plutonium compound could limit its concentration in the water. With increasing concentration, the point will be reached where this plutonium compound will precipitate. In water of a particular composition, this compound will have, in comparison with all other plutonium compounds, the lowest solubility. The oxidation state of the plutonium in this compound will very probably be IV. In near neutral media Pu(IV) compounds are generally far less soluble than those of Pu(V) or Pu(VI).

Consideration of the magnitudes of the thorium concentrations in the waters of these lakes and of the processes that appear to be controlling them provides insight about what the fate of plutonium would be should there be a

major intrusion into a body of freshwater. Thorium and Pu(IV) are very close chemical analogs, and hence the factors which control the concentrations of thorium would be expected to play comparable roles in controlling the concentrations of plutonium. It appears that Pu(IV) rather than Pu(VI) will control plutonium behavior since the adsorption onto suspended solids of U(VI), the analog of Pu(VI), is much lower than that of either Pu(IV) or Th(IV). As the concentrations of thorium, 4×10^{-12} to 1×10^{-9} M are many orders of magnitude higher than those that would be predicted on the basis of the solubility of some compound such as Th(OH), XH_2O, it is apparent that there are constituents of these waters which interact with thorium in a way that forestalls the formation of this and other highly insoluble compounds.

The phenomenon that determines the concentration of thorium is its adsorption from the water onto suspended sediments and the incorporation of these solids into fixed sediments, not the solubility of some thorium compound. The concentrations of thorium in the surface and ground waters entering these lakes are less than their saturation values (the ratios at which thorium-bearing minerals dissolve are extremely slow), and the solubilities of thorium compounds in these waters are much less than they are in the lake waters. Thus the annual input of thorium from surfaces and ground waters is equal to both the annual transfer from the water to suspended sediments and the annual transfer of suspended sediments to permanent burial. That the solubility of a thorium compound has not been exceeded is shown by the concentrations of thorium above and below the chemocline in ELA-241, the lake with the highest thorium concentrations. Below the chemocline, where there are no oxides of iron and manganese (the solids that adsorb thorium), the thorium concentration is a factor of 10 higher than it is above the chemocline. The concentration at which a thorium compound would precipitate could be orders of magnitude higher than those that now exist in these lakes. A plutonium concentration of 1×10^{-9} M, (the thorium concentration below the chemocline in ELA-241), corresponds to a ^{239}Pu activity level of 25 pCi/mL. This is factor of five higher than the MPC for plutonium in drinking water.

Table 1. Concentrations of plutonium, thorium and uranium in natural waters, distributions onto suspended solids, and the plutonium oxidation state ratios.

Lake	Concentration, mL^{-1}			Distribution ratio $\times 10^{-4}$			Pu oxidation state ratio (VI/IV)
	Pu ($\times 10^{17}$)[a]	Th ($\times 10^{11}$)[b]	U ($\times 10^{10}$)[a]	Pu	Th	U	
Oligotrophic							
Michigan	3.0	0.4	3.4	200	100	0.4	4
GSL McLeod Bay[c]	3.7	2.1		50	100		3
Clear	4.6	21	1.3	300		0.08	7
Mesotrophic							
Last Mountain	4.5	3.5	22	10	20	0.03	1.5
GSL Christie Bay[c]	2.9	0.6		20	400		0.6
Katherine	2.8	5.6		40	4	0.5	0.3
Lake of the Woods	2.4	5.6	0.9	60	60	2	0.3
ALEA	7.4	21	31	3	10	0.02	0.2
Eutrophic							
ELA 661	44	57	1.1	4	2	1	<0.02
GLS Main Basin[c]	1.5	1.4		20	400		<0.1
ELA 241							
Surface	29	60	2.9	8	3	20	<0.04
9 meters[d]	48	110	10	3	2	2	<0.05
11 meters[d]	220						<0.01

a) The relative error of these values is ±10%.
b) For the values greater than 2.0, the relative error is ±10%. For the values less than 2.0 the standard error is ±0.2.
c) Great Slave Lake
d) Iron and manganese oxides formed an exposure to air were the bulk of the solids.

It cannot be concluded from the thorium concentrations in these waters that comparable plutonium concentrations could be sustained. The fact that the solubility of $Pu(OH)_4 \cdot XH_2O$ is 10 orders of magnitude lower than that for $Th(OH)_4 \cdot XH_2O$ suggests the plutonium concentrations that could be sustained are much lower than those for thorium, i.e., the water constituents which enhance solubility would not be as effective. There is evidence, albeit limited, that plutonium concentrations many orders of magnitude higher than fallout levels (about 10^{-17} M) can be sustained. The concentration of the isotopic diluent, ^{242}Pu, which is used in the analytical methods, has been as high as 10^{-13} M for protracted periods in freshwater samples and the concentrations of ^{239}Pu has been as high as 10^{-12} M in water taken from the Irish Sea. The plutonium in these samples appeared to be in true solution.

It is axiomatic that the concentration of plutonium in the water of a particular lake will be limited by the solubility of a particular plutonium compound, and there is a suggestion from the information in the preceeding paragraphs that the magnitude of these limits for most natural water could be as high as or higher than the MPC for drinking water. Furthermore, it appears that the principal chronic pathway of plutonium to man is his diet and that the constituent of his diet that is the major source of plutonium is drinking water. As there is a possibility that the concentrations in drinking water will be limited by solubility to values that are less than MPC, it is important that the solubilities in natural waters be determined and the factors that govern them be identified.

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PLUTONIUM IN THE GREAT LAKES*

M. A. Wahlgren, J. A. Robbins,† and D. N. Edgington

Since 1971, measurements of plutonium concentrations have been made annually in Lakes Michigan and Ontario and at less frequent intervals in the other Great Lakes. The concentrations of plutonium in the water column have decreased only slightly during the 7 years of measurement. The residence times for plutonium in the lakes have been estimated by simple time-concentration models. The apparent sinking rates for plutonium are found to be essentially constant in all the Great Lakes, suggesting that the basic processes which control the concentrations of dissolved plutonium are similar, despite considerable differences in chemical, biological, and physical characteristics of the lakes. Analyses of plutonium in water, suspended solids, material from sediment traps, and sediment cores, show that considerable resuspension of previously sedimented material into the hypolimnion occurs throughout a major part of the year. A mechanism is proposed to account for the seasonal cycling of plutonium in the epilimnion of Lake Michigan. Recent studies show that plutonium in Lake Michigan (and in the Irish Sea) exists primarily in the water column as Pu VI and on the sediments as Pu IV. In order to understand the long-term geochemical and biological behaviors of plutonium in aquatic environments better, further study of the limnological factors which control the chemical forms of plutonium is required.

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*Summary of a chapter in Transuranic Elements in the Environment, U. S. Department of Energy publication TID-22800, in press.

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^{239,240}Pu IN LAKE MICHIGAN: 1971—1978

M. A. Wahlgren, D. M. Nelson, K. A. Orlandini, and E. T. Kucera

The plutonium concentration data presented in recent annual reports has consisted primarily of results from studies of short-term variations, i.e., the annual plutonium cycle conducted at Lake Michigan station ANL-5, 12 km SW of Grand Haven, Michigan. While the water depth of 67 m at this station is nearly equal to the mean lake depth of 84 m, the mean annual concentration of plutonium in the water column at ANL-5 might differ from far-offshore regions because of its proximity to major tributaries and a high sedimentation band near the eastern shore. The results from lakewide sampling cruises during 1972,[1] 1973,[2] and 1976[3] show that samples taken from offshore stations during the spring convective mixing period and from the hypolimnion during early summer can be utilized to estimate the mean annual concentration of plutonium in the lake. In this report, mean annual concentrations of total plutonium in unfiltered water from far offshore (> 30 km) stations for the period 1971 through 1977, and from station ANL-5 (1975 through 1978) are summarized to establish the long-term trend in plutonium concentration in Lake Michigan.

The results presented in Table 1 show that the mean annual concentration in the water column is similar at ANL-5 and at offshore stations and has decreased at the rate of only 6% per year during the period 1972 through 1978. The nearly constant concentration indicates that steady-state equilibria exist between plutonium inputs to the lake and the loss of plutonium from the water column. The estimated annual tributary input of ~ 0.1 Ci y^{-1} total (particulate and dissolved) plutonium[4] cannot at present play a major role in maintaining the water column inventory of plutonium (~ 2.4 Ci) and is probably exceeded by outflow from the lake, i.e., 5×10^{13} L $y^{-1} \times 0.6$ fCi L^{-1} or ~ 0.15 Ci y^{-1}. Therefore, the loss to the sediments must be nearly equal to the mean annual atmospheric input of 0.7 to 0.8 Ci, and the application of a very simple steady-state model[5] to the system yields a plutonium residence time estimate of 3 y. This estimate is in reasonable agreement with the value of 2.4 y computed using a much more rigorous approach.[4]

Table 1. Mean annual concentrations of $^{239,240}Pu$ in unfiltered Lake Michigan waters.[a]

	$^{239,240}Pu$, fCi L^{-1}	
Year	Offshore	ANL-5
1971	0.97 ± 0.16 (6)	
1972	0.80 ± 0.10 (14)	
1973	0.77 ± 0.11 (5)	
1974	0.73 ± 0.10 (4)	
1975	0.62 ± 0.10 (4)	0.74 ± 0.12 (12)
1976	0.63 ± 0.12 (9)	0.63 ± 0.10 (10)
1977	0.58 ± 0.06 (6)	0.56 ± 0.15 (8)
1978		0.52 ± 0.03 (5)

[a]The values given are the means and standard deviations of the mean for (n) measurements. The data for 1971 are taken from Malestkos[10] and for the following years includes both published and unpublished data from Argonne measurements.

For the computer simulation of the time-dependence of plutonium concentrations in the Great Lakes,[4] the conventional assumption was made that no exchange of plutonium between aqueous and solid phases could occur. For Lake Michigan the model predicted greater year-to-year variations and a considerably faster rate of decline than observed in field measurements. These findings are consistent with an earlier hypothesis[6] that the surficial sediment pool of plutonium may exert a significant role in maintenance of the concentration of dissolved plutonium in Lake Michigan.

The addition of plutonium oxidation state spikes to both raw and filtered Lake Michigan water has shown that Pu IV is rapidly taken up by suspended particulates ($K_d \sim 10^6$), while Pu VI remains in solution. These results are consistent with field observations of the behaviors of the geochemical analogs Th and U,[7] and with the results of a few direct measurements of the $^{239,240}Pu$ IV and VI content of suspended particulate and sediment floc in Lake Michigan. In filtered Lake Michigan water, concentrations of spiked ^{242}Pu near 10^{-14} M in both

the IV and VI oxidation states apparently remained in solution for 30 days, which strongly suggests that the solubility of plutonium species, per se, does not at present limit the concentration ($\sim 10^{-17}$ M) of dissolved $^{239,240}Pu$ in the lake. The concentration of dissolved Th in Lake Michigan is $\sim 10^{-12}$ M; thus ^{239}Pu may be soluble up to the limit of $\sim 10^{-12}$ M permitted in drinking water. Other spiking experiments in filtered and dialyzed Lake Michigan water show that constituents within the colloidal-sized fraction are capable of slow reduction of the Pu VI spike and inhibit the oxidation of Pu IV.

These observations suggest the existence of an active redox cycle for Pu in Lake Michigan. In this cycle, Pu IV atoms in solution are continually taken up by particulate materials but may be oxidized within microzones of the particles such as freshly deposited manganese coatings[8] and also in solution by agents such as dissolved oxygen. In turn, the concentration of Pu VI in solution may be limited by reaction with reducing constituents of the colloidal-sized fraction (or decomposer organisms such as bacteria or fungi, which might have been present after filtration) and with planktonic organisms in the environment to produce Pu IV and thus maintain the cycle.

It has been pointed out by Patalas that the annual biological production may vary by factors of 100 or more between temperate and northern lakes.[9] From the observations of similar concentrations of dissolved plutonium in Lake Michigan and various comparison lakes,[7] it follows that biological scavenging and other transient events such as calcite formation and settling have little or no effect on the long-term rate of removal of dissolved plutonium to the lake sediment sink.

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DETERMINATION OF PLUTONIUM OXIDATION STATE IN LARGE VOLUMES OF NATURAL WATER

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A method has been developed to determine the relative concentrations of the lower and upper oxidation states of plutonium in large volumes of natural water. It is based on the classical lanthanum fluoride procedure in which Pu(III) and Pu(IV) are separated from Pu(VI) and most of the other sample constituents by sequential precipitations of lanthanum fluoride. The first precipitation is carried out in the presence of Cr(VI), which oxidizes Pu(III) to Pu(IV) and Pu(V) to Pu(VI). Pu(IV) is carried on the first precipitate; Pu(VI) is reduced to Pu(III) by Fe(II) and is hence carried on the second precipitate. The plutonium fractions are separated from lanthanum by dissolving the precipitates in an aluminum nitrate-nitric acid solution, passing this solution through a Dowex-1 anion exchange column, washing the column with strong nitric acid, and eluting the plutonium from the column with a dilute hydrochloric acid-hydrofluoric acid solution. The fractions are electrodeposited onto planchets, and the depositions are assayed alpha spectrometrically. The isotopic diluents, ^{242}Pu in the IV state and ^{236}Pu in the VI state, as well as nitric acid and dichromate are added at the time the samples are taken. All the other operations can be performed in the laboratory at a later date. The period from the time a sample is taken to the time the laboratory work is performed may be as long as 30 days.

The values obtained for the Pu(VI)-to-Pu(IV) concentration ratio when Lake Michigan water was analyzed by the lanthanum fluoride method agreed with those obtained by an independent method. This was the nitric acid anion exchange procedure which was modified to accommodate 50 L samples. The sample was spiked with ^{242}Pu(IV) and ^{236}Pu(VI) and was made 7 M in HNO_3; 100 g of Dowex-1 resin was added, and the phases equilibrated by prolonged stirring. The resin, which had adsorbed the Pu(IV), was separated from the solution and washed with 7 M HNO_3, and the plutonium was eluted with 0.1 M HCl-0.01 M HF. This solution and the one obtained by combining the 7 M HNO_3 solutions were evaporated to small volumes. The plutonium fractions were electrodeposited and

assayed alpha spectrometrically.

There was agreement of the sums of the concentrations of ^{239}Pu(IV) and ^{239}Pu(VI) determined by these two methods; these sums also agreed with the values obtained by the method customarily used to determine total plutonium concentration: the addition of a single isotopic diluent, reduction of the plutonium to the III state with sulfite, coprecipitation with calcium fluoride, separation of the plutonium by nitric acid-anion exchange, electrodeposition of the plutonium, and alpha spectrometric assay.

The agreements between the values for the Pu(VI)-to-Pu(IV) ratios and amongst the values for the total plutonium concentration suggest that (1) the ^{239}Pu dissolved in the water is ionic or readily converted by the reagents that are added, and (2) the forms present in the water are either in the IV and VI oxidation states or in states that are rapidly converted to these states. If this situation did not exist, isotopic exchange between the two forms of ^{239}Pu and their respective isotopic diluents would probably not occur, and the values obtained by the several methods would not be consistent.

The method was evaluated by analyzing samples of water from Canadian lakes having a wide variety of limnological characteristics.[1] The lanthanum fluoride separations were made about 30 days after the samples were taken. From the ^{236}Pu-to-^{242}Pu activity ratios obtained in the alpha spectrometric assays of the Pu(IV) and Pu(VI) fractions, it was found that the degree of oxidation of ^{242}Pu(IV) ranged from 8 to 48% and the degree of reduction of ^{236}Pu(VI) ranged from 2 to 16%. The ^{236}Pu-to-^{242}Pu activity ratios provided the means for correcting the ^{239}Pu-to-^{242}Pu and ^{239}Pu-to-^{236}Pu ratios obtained in the alpha spectrometric assays to the times the samples were taken, and hence for calculating the amounts of ^{239}Pu(IV) and ^{239}Pu(VI) that were present at that time. In all cases, the magnitudes of the corrections were such that the accuracy of the Pu(IV)-to-Pu(VI) concentration ratios were not appreciably different from those which would have been obtained had the analyses been carried out immediately after the samples were taken.

The method was also evaluated by adding nitric acid, dichromate and the isotopic diluents to a group of identical water samples from Lake Michigan and

performing the separation procedure after 1, 10, 20, and 30 days. The Pu(VI)-to-Pu(IV) concentration ratios and the sums of these concentrations were in agreement. In the solution that stood for 30 days, 30% of the ^{242}Pu(IV) had been oxidized and 2% of the ^{236}Pu(VI) had been reduced.

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SEDIMENT TRAP METHODOLOGY

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The processes by which dissolved pollutants from atmospheric or tributary inputs are deposited in local regions of the bottom sediments of Lake Michigan are known only in part. Settling particulate material must play a major role in these processes, but sediment traps have been used only rarely in the Great Lakes. This circumstance arose not only because of previously unresolved questions on the collection efficiency of various trap designs but also the problem of loss of arrays of submerged equipment following severe storms on large lakes. The trap and mooring designs developed during the plutonium study in Lake Michigan are presented, and the experience with their use is summarized.

The traps used were right circular cylinders, as recommended by Pennington.[1] Under quiescent conditions, the sediment traps, like rain gauges, collect settling material with 100% efficiency. In the presence of wind-driven currents, both under and over collection can occur. Under collection is the result of vortex action that resuspended previously collected material: over collection is the result of material being deposited behind a barrier that is analagous to a snow fence. In an earlier report,[2] it was shown that the collection of sedimenting material per unit of trap area was independent of variations in the ratio of diameter to trap height, within a limited range. Additional field experiments have been carried out which confirm this conclusion. During stratified conditions, the collection efficiency has been found to be essentially constant for height-to-diameter ratios from 4 to 9 and diameters from 4 to 16 cm. The collection efficiency during the more turbulent conditions of convective mixing was similar but passed through a maximum at a height-to-diameter ratio of 5, and this value is suggested as the standard ratio for traps for Lake Michigan use. The results of the field studies of collection efficiency are in good agreement with those of a recent flume study by W. D. Gardner at Columbia University, Lamont, in which collection efficiencies very near 100% were demonstrated for similar traps.

The mooring arrangement is an adaptation of the U system often used in current-meter studies. The base of the U consists of two anchors (75 kg each) that are several hundred meters apart and interconnected by a line. One upright segment of the U is formed by a vertical array of sediment traps on a line attached to one of the anchors. This line is kept taut by a submerged float (50 kg displacement), located 5 meters below the surface (to minimize the effects of wave action on the experimental array). A loose line is, in turn, attached to a small surface marker buoy. This line is used to hoist the array aboard ship for servicing. The other upright segment of the U is a line attached to the second anchor which is supported by a floating radar reflector. The reflector serves to locate the array under conditions of poor visibility and to permit recovery when the small surface marker buoy is lost. The spacing of the traps in our experiments was such that samples could be taken of the particulates formed in surface water and of bottom sediments that might be suspended by wave action. (Their locations were 10, 20, 30, 50, and 80 m below the surface and 2, 4, 8, 16, and 32 m above the bottom.)

The settling particulate material consists of two basic types of material, (a) resistant mineral material of terrestrial origin which may spend long periods of time in the water column and (b) transient materials such as calcite and biogenic detritus. Biota and biogenic detritus may be lost during the collection interval owing to decomposition within the trap. The use of preservatives in the trap led to two problems: the collection of biota may exceed 100% if premature death occurs in the overlying water due to diffusion of preservative from the trap, and alteration of some minerals such as calcite by the preservative may occur in the trap. For these reasons, pairs of traps with and without preservatives are used at each depth sampled. These experiences have shown that the collection of settling particulate material is a useful supplement to more conventional samples in the study of processes occurring in the lake and that with a relatively simple experimental array, sediment traps can be maintained and serviced even in the mid-lake region of Lake Michigan.

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ESTIMATION OF THE CONTRIBUTION OF "SEDIMENT" TO THE CONCENTRATIC OF PLUTONIUM IN NET PHYTOPLANKTON SAMPLES

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Early studies at Argonne showed that net plankton samples taken during the spring diatom bloom exhibited wet weight concentration factors (CF's) for plutonium of five to ten thousand, and it was recognized that occluded mineral material might contribute to the apparent concentration of the net plankton samples. The contribution was believed to be minor since microscopic examination of many samples indicated little contamination by mineral particulates, and a strong correlation between the plutonium concentration factor and the silicon content of the samples was observed.[1] Some more recent experimental studies which tend to support the original conclusion are summarized as follows.

The ratio of ^{241}Am to ^{239}Pu in material from sediment traps in the water column during the spring convective mixing period has been found to be 2.0 ± 0.02, while the ratio in plankton samples is 0.06 ± 0.02, i.e., much more similar to the ratio in filtered water (0.03 ± 0.01) than to that in suspended sediments.[2] This result suggests an upper limit of 10% for the sediment contribution to the diatom samples. The contribution to samples of littoral organisms, benthic invertebrates, and zooplankton samples may be somewhat higher, since the ^{241}Am:^{239}Pu ratios were 0.12 ± 0.06, 0.12 ± 0.05, and 1.10 ± 0.03, respectively. Alternatively, the higher ratios could be explained if the CF for dissolved ^{241}Am is greater than that for dissolved plutonium, as appears to be the case for suspended sediments.

Selective extraction of plutonium from net plankton samples was attempted. Acetone washings of a "damp-dried" net plankton sample were used to remove surface coatings, which should wash away at least some occluded mineral grains. This treatment removed only ∿ 1% of the plutonium content of the sample. Extraction of a net plankton sample with citrate-dithionite removed < 50% of the plutonium, while a similar extraction from a suspended-sediment sample removed ∿ 95%. A part of the extraction from plankton may be due to disruption of the cells during extraction.

Phytoplankton samples, which have CF's of 10,000, typically contain 10% ash content (primarily amorphous silica). Relative to the plankton ash, the CF then becomes 100,000 or about one-third that observed for ashed material from sediment traps or from filtration of suspended particulates in the 0.45 to 30 μm size range. Thus, if the diatoms contained little or no plutonium, the ash from the sample would have to contain approximately one-third mineral sediment to yield an apparent plankton CF (wet weight) of 10^4. An experiment has been carried out where a net phytoplankton sample and a suspended-solids filter from the same surface water station were dried, ashed, and inspected microscopically. The amorphous silica was removed from both samples by sodium carbonate extraction for comparison of mineral ash content. This comparison showed that the plankton ash contained no more than ∿1% of the mineral grains which constituted > 50% of the ash of the suspended particulate sample. Thus, it can be conservatively estimated that mineral sediments contribute less than 10% of the plutonium content of the plankton sample.

These results are consistent with the conclusions expressed in the earlier studies that the observed concentration factors for net plankton samples indicate considerable uptake of dissolved plutonium by phytoplankton, and that diatoms exhibit significantly higher concentration factors than other algae or their predators.

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PRELIMINARY EDDY-CORRELATION MEASUREMENTS OF MOMENTUM, HEAT AND PARTICLE FLUXES TO LAKE MICHIGAN

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The atmosphere is one of the most important sources of pollutants deposited in the Great Lakes. Significant amounts of airborne particulate material are transported from nearby land areas and transferred to the water surface by turbulent transfer processes in the lower atmosphere. To calculate the total amount of potentially harmful substances entering the lakes by this route, rates of dry and wet deposition must be determined for various pollutant particle sizes and pollutant chemical conditions. This will require an improved understanding of the processes of aerosol particle formation, atmospheric transport and diffusion, and small (submicron) particle removal from the atmosphere at the air-water interface. The latter can be investigated by intensive, short-term experimental evaluations of particle fluxes, and a study of this kind is the subject of this preliminary report.

The information sought during the short-term experiments deals with the resistance r_{sp} to the transfer of particles through the thin air layer (i.e., the laminar sublayer) in immediate contact with the water surface. By measuring the total vertical flux F_p of particles with eddy-correlation techniques several meters above the surface and calculating the equivalent, total aerodynamic resistance r_a beneath the point of measurement, r_{sp} can be determined indirectly. In simplified terms, we can write

$$r_{sp} = \bar{p}/F_p - r_a \quad , \tag{1}$$

where $\bar{p}$ is the pollutant concentration at the height of measurement. The quantity $F_p/\bar{p} \equiv v_d$ is the so-called deposition velocity, a useful concept but one which often causes confusion since many authors tend to ignore the fact that the definition implicitly includes the height at which F_p and $\bar{p}$ are measured. At any rate, this number can be multiplied by a concentration to obtain a measure of the vertical flux. While most efforts to model particulate deposition deal with v_d rather than r_{sp}, it should be remembered that v_d is not an intrinsic property of the atmosphere-air system, but rather a derived quantity that is specific to

the type of contaminant. The purpose here is to address the proper parameterization of v_d from field measurements of r_{sp}, which is not yet well understood for particles in the air layer over water surfaces.

Mostly as a result of theoretical and wind-tunnel studies over smooth surfaces, values of v_d for submicron particles are often assumed to be quite small, near 0.1 cm s^{-1}, corresponding to values of r_{sp} near 10 s cm^{-1}. Very limited work has been devoted to evaluating v_d directly in the field by measurement of fluxes over water surfaces. Indirect, mass-balance methods have been used to obtain values of v_d near 0.4 cm s^{-1} over the North Atlantic. This result has been inferred from the rate at which pollutants are apparently removed along trajectories of identifiably polluted air.[1] A variety of wind speeds and wave conditions were probably encountered.

The major structural features of the air-water interface are the waves, whose extent and nature are primarily determined by wind speed and fetch. Even up to large wind velocities the surface roughness of large water bodies is quite small, compared to that of most land surfaces. A significant and unique alteration in the air-water interface occurs when wind speeds are sufficient for whitecaps to form, for then the boundary between air and water begins to become less distinct. In these conditions, the simple concept of a single thin layer of air whose transfer properties determine r_{sp} may not be valid. Thus, field measurements aimed at parameterizing v_d must take place during a wide range of wind speeds, including conditions associated with an aerodynamically-smooth surface on the one extreme, to a spray-generating rough water surface on the other.

Preliminaty Results

A preliminary set of momentum, heat and particle flux measurements have been taken from a tower located 10 km offshort in southwestern Lake Michigan near Chicago (see Figure 1). The measurements utilize the eddy-correlation instruments developed by the Atmospheric Physics Section, and extensively used over many different surfaces.[2] Present plans are to use this equipment on the offshore tower during 3 or 4 short field experiments during the 1979 season.

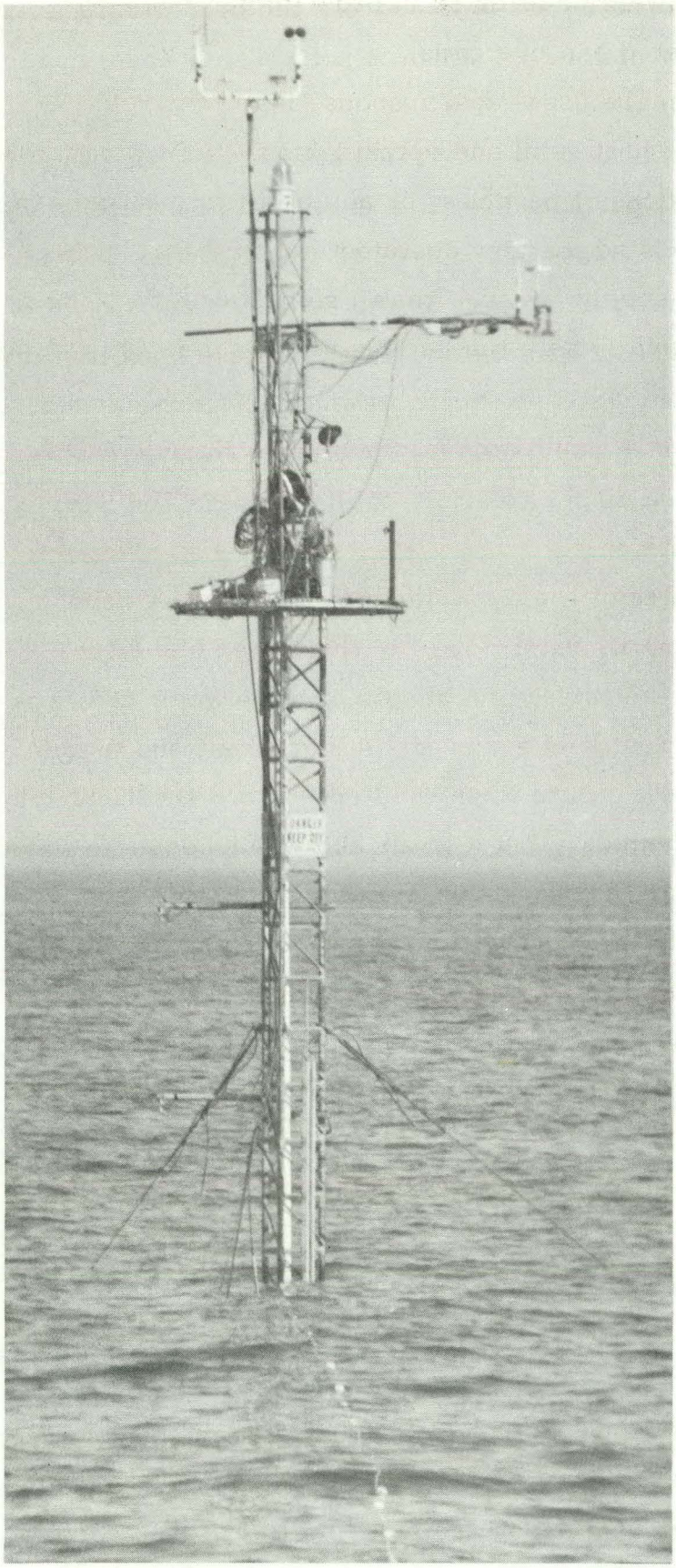

FIG. 1.--Meteorological tower (10 m height) located in southwestern Lake Michigan.

These preliminary measurements were undertaken in order to determine the types of problems to be encountered and overcome.

The eddy-correlation technique uses rapid response instrumentation to measure turbulent fluctuations of horizontal and vertical wind velocity, temperature, humidity, local concentrations of particles, or any other contaminants of interest. At present the system is not battery operated and therefore requires a ship to be anchored nearby to supply power. Analog signals are transmitted via multiconductor cable to the ship, where the various covariances (eddy fluxes) are computed and recorded.

The preliminary measurements consisted of momentum, heat and particle fluxes as measured by $\overline{u'w'} = u_*^2$, $\overline{w't'} = H/\rho C_p$, and $\overline{w'p'} = F_p$, where u', w', t', and p' are the turbulent fluctuations of horizontal wind velocity, vertical wind velocity, temperature and particle concentration (0.1 to 1 μm diameter). respectively, and the overbars represent about 20 min of time averaging.

Table 1 lists the results obtained. Since the period of measurement in early November 1978 was characterized by very light winds (1—2 m s^{-1}), only very small fluxes to and from the aerodynamically smooth water surface were recorded. Of principal interest are the particle deposition velocities. The 2 hr average deposition velocity was experimentally indistinguishable from zero, but the series of 20 min averages show the water surface to be intermittently either

Table 1. Eddy-correlation measurements from a Lake Michigan tower on 2 November 1978.

Time (CST)	u_*, cm/s	σ_w, cm/s	H, w/cm²	v_d, cm/s
1200—1220	3.9	7.4	2.0	0.032
1220—1240	5.0	10.9	3.9	-0.023
1240—1300	7.2	12.3	7.3	0.021
1300—1320	6.1	10.5	6.4	-0.059
1320—1340	3.5	9.4	3.0	0.017
1340—1400	1.5	6.8	1.8	-0.009
				Av. = 0.004 ± 0.015

a source or a sink for small particles. All the fluxes listed in Table 1 are probably underestimates, due to the poor response of the mechanical wind sensors in the extremely light winds then present. Nevertheless, the deposition velocity estimates are certainly within a factor of two of the actual values, so that an estimate of zero for v_d appears valid under these near-calm conditions.

Discussion

This preliminary effort to measure particle fluxes using eddy-correlation procedures over water is, in one sense, only a feasibility study. To continue measurements in 1979, some improvements in the arrangement of instrumentation at the tower will be needed, but these will not be discussed here. The main result is that v_d is near zero for very light winds. This finding has an impact on the feasibility of methods sometimes proposed to measure the particle fluxes. One category of these methods is gradient or bulk methods. Perhaps a bulk method can be applied if particle concentration and wind speed are measured at a single height and air-water virtual temperature differences are also measured. However, this requires techniques for estimating r_{sp} which are not yet fully developed. Similarly, the prospects for successfully using in-air, gradient measurements of particle concentration to infer values of the vertical flux, without some implicit assumption on r_{sp} (through a choice of a transfer coefficient), seems very poor. That is, with deposition velocities of 0.1 cm s^{-1} or less, which now appear likely during light winds, the concentration gradients would be exceedingly small. This can be shown by a few simple calculations.

One approach to relating concentration differences to fluxes in the surface boundary layer is via the equation

$$\bar{p}_2 - \bar{p}_1 = F_p/(ku_*)[\ln (z_2/z_{1-} + \bar{\psi}_1 - \bar{\psi}_2] \quad , \tag{2}$$

where $\bar{p}_2$ is measured at height z_2, $\bar{p}_1$ is measured at z_1, $k = 0.4$ is the von Karman constant, and $\bar{\psi}_1$ and $\bar{\psi}_2$ are stability-dependent functions at the two heights. Replacing F_p with $v_d\bar{p}_2$ results in

$$(\bar{p}_2 - \bar{p}_1)/\bar{p}_2 = v_d/(ku_*)[\ln(z_2/z_1) + \bar{\psi}_1 - \bar{\psi}_2] \, . \tag{3}$$

Consider the case of measurements taken across a twofold increase in height ($z_2 = 2z_1$) with near neutral conditions ($\bar{\psi}_1 = 0$, $\bar{\psi}_2 = 0$) and where the remaining unknowns on the right-hand side of Eq. 3 would be typically, $u_* = 15$ cm s^{-1} and $v_d = 0.1$ cm s^{-1}. Then the particle concentration difference ratio on the left of Eq. 3 is

$$(\bar{p}_2 - \bar{p}_1)/\bar{p}_2 = 0.012 .$$

Thus, about a 1% accuracy in the measurements of mean concentrations is needed in this case just to determine the direction of the flux. If 1% is the standard error on individual mean concentration measurements, then about 100 measurements are needed to achieve a 10% accuracy in the flux measurements $(1\%/100)^{\frac{1}{2}}$ = 0.1%, or 10% of the concentration difference. Similarly, it can be shown that if v_d is near 1 cm s^{-1}, then concentration differences are on the order of 10% of $\bar{p}$, and each short-term calculation of the fluxes should be accurate to near 10%.

In conclusion, on occasion when v_d is small, as the present data indicate for light winds, individual difference measurements cannot be expected to give good estimates of the particle fluxes unless the accuracy of each mean measurement is 0.1% or less. This is not possible with instruments now available because of zero-drift problems, which, significantly, are not serious sources of error when the same equipment is used in eddy-correlation and high-frequency techniques.

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DEVELOPMENT OF A BATTERY OPERATED DATA ACQUISITION SYSTEM FOR ATMOSPHERIC AND LIMNOLOGICAL RESEARCH

R. M. Williams, J. R. Haumann, and R. V. White

In assessing the needs for pollutant transport studies in the Great Lakes Research Program it was immediately evident that an automatic data acquisition system for remote operation was required. Evaluation of the atmospheric input contribution to Great Lakes pollutants requires long-term, relatively frequent measurements of meteorological parameters from stations located over the open lake; investigating the physics of sedimont resuspension at the sediment water interface has higher frequency, shorter-term requirements. The overlapping data acquisition requirements of these two tasks defined a set of specifications for a remote data acquisition system. Commercially available systems were found to be inadequate to meet the requirements for flexibility and cost. Therefore, the system was developed at ANL in cooperation with the Electronics Division.

The basic requirements were: (1) capacity: 32 channels; (2) resolution: 12 bits (1 part in 4096); (3) sample rate: 41 hr to 0.050 sec (0.02 sample hr^{-1} to 20 sample sec^{-1} per channel); (4) operation modes: continuous, burst and conditional; (5) record mode: instantaneous and mean; (6) duration: > 2 weeks or until the cassette is full.

System Description and Operation

To meet these requirements a battery powered system has been developed that utilizes micropower analog and digital circuitry to reduce power consumption and microprocessor capability to achieve flexibility. As shown schematically in Figure 1, the system consists of three packages: the analog sensors, the battery pack, and the data acquisition system (DAS).

Analog signals are transmitted through a muticonductor cable to the DAS analog signal conditioning circuits, where the comparatively low-level, analog signals are amplified to the 0 to 5 VDC level for compatibility with the analog-to-digital converter. A matrix program board allows selection of correspondence between analog and digital channels; a single analog channel may go to several

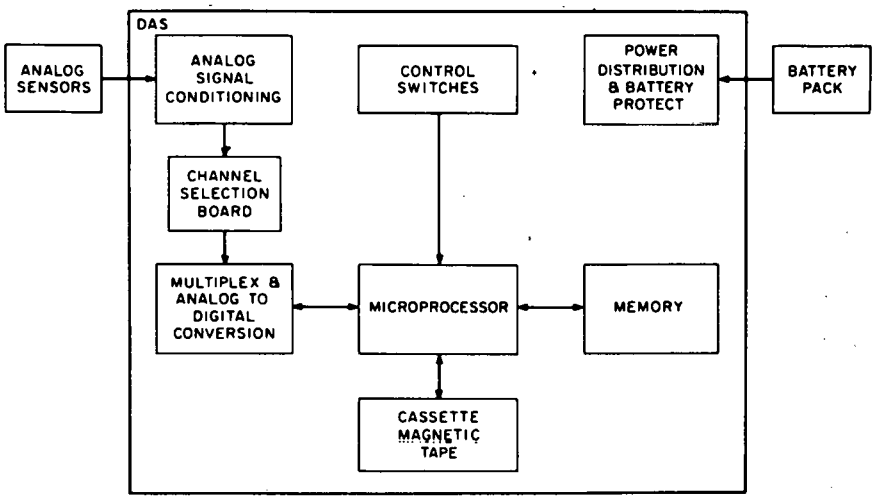

FIG. 1.--Battery operated data acquisition system schematic (DAS).

digital channels if desired. From this point, the microprocessor takes control

The DAS is built around the RCA 1802 CMOS microprocessor (μP), operating with a basic synchronizing clock rate of 0.050 s. Control switches are initially set to program the desired μP operation. The following parameters are input to the μP through the control switches.

Sample rate 1 : 1 to 99 synchronizing clock pulses per sample scan.

Sample rate 2 : binary multiple of rate 1.

Total number of channels sampled.

Number of channels sampled at rate 1.

Number of channels sampled at rate 1 but mean-recorded at rate 2.

Burst mode, number of scans on.

Burst mode, duty cycle.

Channel number.
Initiation level.
Number of samples for average.
Sampling mode and logic.
} 3 conditional channels

Real time clock initialization.

Delay time before sampling starts.

magnetic tape identification code.

After setting the control switches and inserting a 300' or 450' digital cassette magnetic tape, the μP program is started. The μP loads the control

switch information into memory and onto tape, waits the appropriate delay (as set by the control switch) and then begins operation. Operation basically consists of (a) sampling the selected analog channels at the selected sampling rates, (b) converting the analog levels to digital format, and (c) storing the result in a temporary memory. This sequence continues until the temporary memory is nearly full, whereupon the μP directs that these data be dumped and recorded on the magnetic tape, with no pause in data acquisition.

Two types of data can be recorded. The instantaneous value of the analog signal can be sampled at either rate 1 or rate 2, and recorded. Additionally selected channels can be sampled at rate 1, with only their mean values recorded at rate 2. For example, 900 values sampled once per second can be averaged and recorded every 15 min.

There are three modes of operation: sampling and recording can be (1) continuous, (2) occur in bursts with a set duty cycle, or (3) occur conditionally in bursts with a duty cycle determined by information contained in any of three input channels. Continuous sampling operates until one of the following: the cassette is full, the DAS is manually stopped, or the battery is disconnected. The burst mode can be programmed by control switch settings so that sampling is carried out for a preselected number of rate-2 cycles and then shut down for another preselected number of rate-2 cycles. For example, the system can take samples for 5 minutes and then shut down for the remaining 55 min of the hour before resuming.

The conditional sampling mode is the most powerful and makes good use of the computing capability of the μP. Up to three channels can be selected for comparisons to determine whether data storage should occur. An initiation level for each channel is preset with the control switches. The μP operates in the continuous sampling mode at rates 1 and 2 but does not store any data for recording until the initiation levels are exceeded on one or more of the three comparison channels. The initiation level for each channel may be compared to (a) the instantaneous value, (b) the running average, or (c) the running variance of the channel. Comparison results can then be either logically AND-ed or OR-ed to determine the resultant operation. Once storage is conditionally started it will

be stopped when the comparison fails against one-half of the initiation level. Conditional sampling is most advantageous for examining intermittent events but requires some knowledge of appropriate initiation levels of interest.

The DAS is packaged in a 10" diameter by 24" long PVC cylinder, the latter an acceptable material for use in air or shallow water. In deep water, aluminum or stainless steel will be needed. The package contains an aluminum frame to support a 21 printed circuit card section for analog signal conditioning, 3 printed circuit digital cards, the cassette recorder, and other items.

Power is supplied from an external battery pack which consists of 50 A-hr @ +8 V, 5 A-hr @ -8V, and 5 A-hr @ +14 V supplies. The batteries are rechargeable, sealed lead-acid cells (Gates Energy Products). A battery protection circuit contained in the DAS shuts down operation if the battery supply voltage falls below the critical level. This insures that the battery pack will not be damaged by an excessive discharge and thus will retain full capacity for its rated life.

DEVELOPMENT OF A WIND-DIRECTION CONTROLLED AEROSOL SAMPLING SYSTEM

R. M. Williams and R. V. White

In support of programs designed to estimate atmospheric pollutant inputs to the Great Lakes, an aerosol sampling system has been developed and installed to obtain gross information concerning atmospheric pollutant concentrations in the nearshore region of Lake Michigan off Chicago. The system consists of three Hi-Volume air samplers (Sierra Instruments Model 305) with flow controllers, wind speed, and direction indicators (R. M. Young Model 6001), and a recording and controlling package. At present the system is set up at the 68th Street water intake facility operated by the City of Chicago, approximately 4 km offshore.

The Hi-Volume air samplers (nominal flow rate 40 SCFM-68 $m^3 hr^{-1}$) are individually controlled so as to operate only when the wind is coming from a preselected direction sector. The controller compares the output of the wind direction sensor (0—3.6 VDC) to preselected upper and lower voltage limits which correspond to the three sectors to be surveyed. If the comparison is satisfactory a relay is actuated and power is supplied to the particular Hi-Volume air sampler designated to sample air from the corresponding wind direction sector. A selectable delay of between 0 to 20 seconds requires the wind direction comparison to be satisfied for this period before the sampler is activated, thus eliminating problems with fluctuating wind directions near the upper and lower limits. Digital logic is employed to allow the controller to operate through the output discontinuity inherent in wind direction sensors at the 0°/360° position.

The controlling package includes a strip chart recorder, which continuously records the wind speed and direction, as well as a signal to indicate which sector (or sectors) is operating. Table 1 in the following report[1] shows a sample of the information obtained with the system.

Reference

1. R. M. Williams and J. Muhlbaier, Preliminary findings of wind-direction controlled aerosol sampling over Lake Michigan, this report.

PRELIMINARY FINDINGS OF WIND-DIRECTION CONTROLLED AEROSOL SAMPLING OVER LAKE MICHIGAN

R. M. Williams and J. Muhlbaier

A wind-direction controlled aerosol sampling system consisting of three Hi-Volume air samples and described in the preceding article[1] has been operated at Chicago's 68th Street water intake facility (4 km offshore) since August 1978. Wind sectors selected were : A (135° to 180°), B (200° to 270°), and C (345° to 070°); these sample air from Gary-Indiana Harbor, Chicago, and open-lake areas, respectively. To date, prevailing winds have resulted in Sector C operating approximately twice as often as sector A, and sector B operating approximately twice as often as C. Filter samples using Whatman 41 filter paper are collected approximately weekly or until at least 1000 m^3 of air are sampled. Timers on the controlling system limit the total sampling time of each filter to a maximum of 24 hr (approximately 1600 m^3).

Filters are initially analyzed for inorganic trace elements by x-ray fluorescence, a technique which supplies fairly rapid analysis of many elements without destruction of the sample. Elements present at very low concentrations, such as cadmium, are subsequently analyzed by atomic absorption. In 1978 approximately 50 filters were analyzed for Fe, Pb, Mn, Zn, Br, Se, and Cd.

Results of these initial studies are given in Table 1 in terms of monthly averages for each sector for the five months since sampling commenced. The concentrations obtained here correspond closely with those reported by Fingleton[2] for a similar study conducted over Lake Michigan. The results clearly indicate that the air from sector A (i.e., from the Gary-Indiana Harbor area) is the most polluted, except for the automobile exhaust-related pollutants Pb and Br, which are high in the air from Chicago (Sector B). As expected, air which has blown over a long fetch of open lake from the NNE (Sector C) is very clean. Enrichment factors relative to crustal abundance were also calculated using Fe as the reference element. Mn showed no enrichment, thus indicating a crustal source; Zn, Pb, Br, Se, and Cd showed respectively increasing enrichment factors as might be expected from their relative volatility and large anthropogenic sources.

Table 1. Monthly average aerosol concentration (ng/m^3), 1978.

Month		Mn	Fe	Zn	Se	Br	Cd	Pb
Aug	A	90	3350	335	4.0	45	8.5	310
	B	60	1950	200	4.5	140	2.5	440
	C	34	1300	74	3.6	14	1.5	110
	Av.	61	2200	200	4.0	66	4.2	290
Sept	A	138	6350	540	3.1	52	3.0	450
	B	62	2100	170	5.2	115	1.5	395
	C	NB	440	NB	ND	3.8	2.0	22
	Av.	67	2960	237	2.8	57	2.1	290
Oct	A	210	7300	645	9.0	74	2.5	580
	B	37	1360	170	5.7	120		370
	C	3	480	6	3.5	9.0	ND	40
	Av.	83	3050	270	6.1	6.7		330
Nov	A	94	4950	300	9.0	100		470
	B	8.7	1370	130	8.3	85		290
	C	10	510	15	4.4	23		110
	Av.	38	2280	150	7.2	69		290
Dec	A	90	3550	410	2.1	60		410
	B	64	910	66	1.3	74		260
	C	16	220	90	ND	27		80
	Av.	57	1560	190	1.1	54		250

Note: A = 135° to 180°
B = 200° to 270°
C = 345° to 070°

NB = not above blank value.
ND = not detected.

Pairwise collection coefficients were calculated to check internal consistency of the data. Since Fe and Mn are each primarily crustally derived, while Pb and Br occur because they are gasoline additives, these pairs should be highly correlated. In fact, these pairs exhibited correlations of 0.95 and 0.93, respectively. In contrast, the coefficient for Fe and Br was only 0.60, indicating little correlation as expected.

Sampling and analysis will continue for at least one year with additional elements to be analyzed using a wavelength spectrometer. To date, only minimal data interpretation has been attempted since the data collection is only partially completed. Future analysis will include determination of the effects of air-water temperature difference and wind speed upon the rates at which pollutants are deposited upon the lake surface. In addition, the data will be examined for the influence of lake breeze circulations.

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TIN IN THE WATERS, SEDIMENTS, AND TRIBUTARIES OF LAKE MICHIGAN'S SOUTHERN BASIN: A PRELIMINARY STUDY

T. Tisue and C. A. Seils

Tin is an element whose biogeochemistry has been little studied. Perhaps owing to analytical difficulties, tin is seldom measured in environmental samples. Consequently, the magnitudes of its natural and anthropogenic fluxes are ill-defined; its sources and sinks are largely uncharacterized. Yet its use in the metallurgical and chemical process industries is extensive. Tin compounds, especially organotin derivatives, are found as biocides in a variety of formulations and as antioxidants in common plastics, notably PVC. Total tin usage in the U.S. was 200,000 metric tons in 1977.

For some time we have been investigating the use of ammonium pyrollidine-dithiocarbamate (APDC) as a reagent for concentrating trace elements from natural waters prior to their determination by x-ray fluorescence spectrometry. Tin is among the elements to which this procedure proved applicable in Lake Michigan.[1] Additional results for both surface waters and the southern basin's two major tributaries appear in Table 1. Although sparse, the data indicate higher Sn concentrations in late autumn river runoff than in samples taken in the spring, and higher levels in coastal samples (station 5) than those taken further offshort (stations 18 and 19).

These concentrations are much higher than those reported for coastal marine samples[2] or small Florida lakes and springs.[3] To test whether these high tin levels were associated with corresponding increases in the tin content of bottom sediments, we analyzed a core from station 5. The core was collected in September 1978 using a 3" gravity corer, sectioned in 1 or 2 cm intervals at 40°C under N_2, and squeezed hydraulically to express the interstitial fluids. Analyses of the pore waters for Sn and other metals will appear subsequently.

The individual core sections were lyophilized and ground to a fine powder in a Spex Mill (glass ball, plastic vial). This material was either pressed into a pellet for direct examination by x-ray fluorescence, or leached in 1 to 3 g quantities with 20 mL 10% aqueous HCl for 10 days at room temperature. Trace

Table 1. Tin in Lake Michigan and tributaries.

Sample	Net Sn K_α, counts/10^3 s	Sn, μg L^{-1} [from 10^{-3} x net counts/10^3 s = (1.06 x μg Sn) - 0.05]
Station 5, 9/6/77 3 m, 1 L	13,432	12.6[a]
Station 5, 9/6/77 10 m, 0.3 L	5,470	17.0[a]
Station 18, 9/8/77 3 m, 1 L	572	0.5[a]
Station 19, 9/6/78 3 m, 0.35 L	884	2.3[a]
Grand River 6/8/77, 0.213 L	(152)	<2.0[b]
Grand River 12/15/77, 0.245 L	943	3.4
St. Joseph River 6/10/77, 0.249 L	(37)	<1.8[c]
St. Joseph River 12/19/77, 0.252 L	825	2.9

[a] 3 σ detection limit for a 1 L sample was 0.45 μg.

[b] 3 σ detection limit for 0.213 L sample.

[c] 3 σ detection limit for 0.249 L sample.

elements were precipitated from the leachate by the addition of an equal volume of freshly prepared 2 wt. % aqueous APDC. The precipitate formed with APDC was collected on a membrane filter, washed, dried in air, and mounted for x-ray fluorescence analysis.

Sn K x-rays were excited in both the pellets and precipitates with a Sn secondary source which was in turn irradiated with a W-anode x-ray tube operated between 2 and 20 mA at 70 keV. The response of the instrument was

calibrated using Sn standards prepared by treating solutions of known Sn concentration with APDC in the manner described for the sediment leachates, or by using pellets from sections whose Sn content had been determined by V. Hodge[4] using the method of Hodge et al.[2] Figure 1 shows the results of these analyses.

The limit of detection for Sn by both direct x-ray examination of the APDC precipitation technique corresponded to a concentration of about 10 ppm in the dried sediment. This limitation restricted useful analyses to those core sections from depths above 10 cm. Figure 1 compares our results to those obtained by V. Hodge[4] on a subsample of a box core he obtained at station 5 (smooth curve). Because our present methods of calibration are approximate, we have normalized our results to the value Hodge reports for the 0 to 1 cm core section, thus allowing a comparison of the trends in both samples.

The two sets of analyses are in qualitative agreement. The agreement is acceptable considering that (1) the cores were obtained at different times using different devices, (2) only our cores were squeezed prior to analysis, and (3) the Sn was assayed by entirely different methods.

The striking fact revealed by the sediment analyses is the sharp increase in tin content in the more recent deposits. We may take Hodge's value of 2 ppm

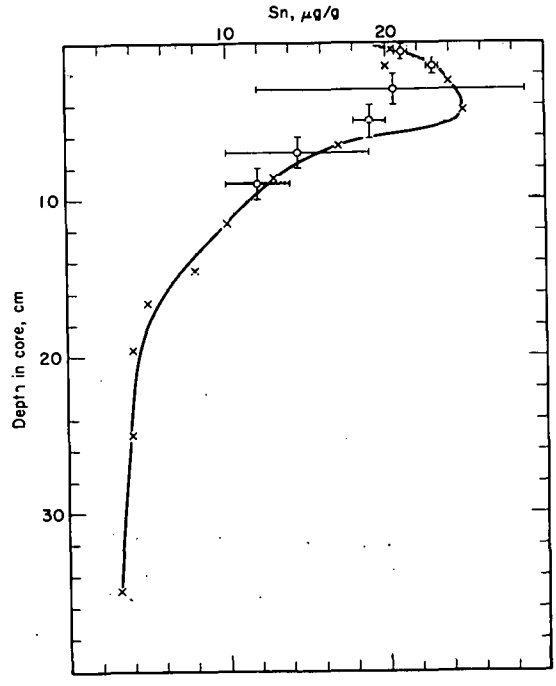

FIG. 1.--Tin concentration profile at station 5. V. Hodge,[4] X; ANL analyses, o.

in the 50 to 60 cm section as representative of tin fluxes in precultural times (the sedimentation rate at station 5 is 0.2 to 0.4 cm/yr). If one assumes that the Sn profile is largely unperturbed by diagenetic processes, the Sn concentrations in the upper core sections indicate that current fluxes are an order of magnitude higher than those in the precultural period. This degree of anthropogenic perturbation of geochemical fluxes is matched in Lake Michigan sediments only by the element Pb.

This result points to the need for more extensive investigation of the present flux of Sn to Lake Michigan, its sources, and its potential for effecting changes in the lake's ecosystem.

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X-RAY FLUORESCENCE ANALYSIS OF AIR FILTERS

J. L. Muhlbaier and G. T. Tisue

A procedure has been developed for the analysis of trace metals on air particles by energy dispersive x-ray fluorescence. Air particles are collected on a 20 × 25 cm Whatman 541 filter using a high volume pump. A 3 cm square section of the filter is mounted between Mylar films in a 35 mm slide mount.

Typical spectra from blank and exposed filters are shown in Figures 1 and 2. They were obtained by counting for 1000 s, using a Mo secondary source. The x-ray tube was oporated at 70 keV with a current of 5 mA. The blank filter was obtained by placing a clean filter in the sampling apparatus with the pump off. The largest background contamination comes from Mn and Fe. Using the Mo secondary source, there is the possibility of detecting the K lines of the elements K to Sr and the L lines of Pb. The elements Mn, Fe, Zn, Br, and Pb have been measured on a routine basis. Copper is also easily detectable, but contamination from the high volume pump motor is frequently a problem.

Spectral analysis is accomplished by applying a second derivative filter across the spectrum.[1] This has the dual advantages of eliminating the slowly varying component of the background and improving the resolution. The thin specimen criterion is met with air filters, and thus the effects of x-ray absorption and particle size may be neglected.[2] The x-ray intensity is then directly proportional to the element mass. Spectral lines for most elements are sufficiently resolved that the peak areas can be compared directly to standards. One important exception is the complete overlap of the As(K_α) and the Pb(L_α) lines. However, the Pb(L_β) line is easily detectable and is free of interference in our samples. Since the ratio of the Pb(L_α) to Pb(L_β) line is constant, the degree of interference of the Pb(L_α) line can be calculated and subtracted from the As + Pb line, allowing the quantification of As.

Standards were purchased from Columbia Scientific Industries as dried deposits of standard solutions uniformly pipetted onto Whatman 541 filters. Since the substrate is the same for the standards and samples, the scattering and the absorption properties are nearly identical. The standard curves, representatives

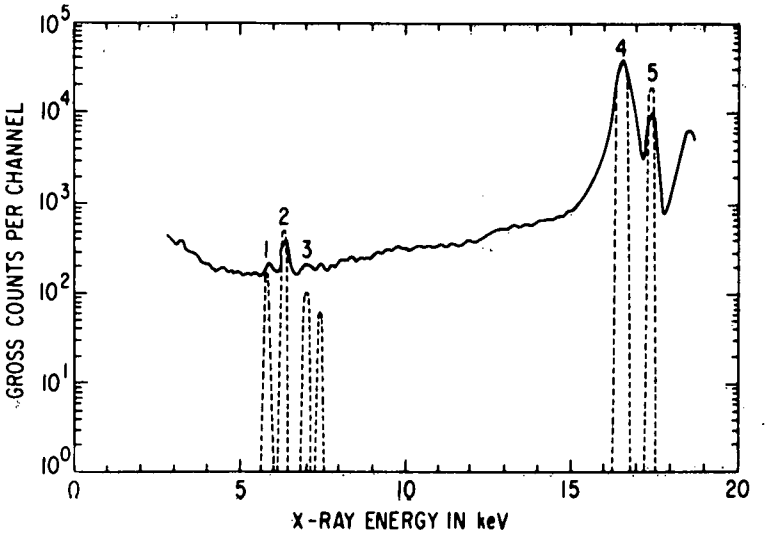

FIG. 1.--Spectrum of blank filter. The numbered peaks correspond to the following elements: (1) Mn(K_α); (2) Fe(K_α); (3) Fe(K_β); (4) Mo(K_α, incoherent); and (5) Mo(K_α, coherent).

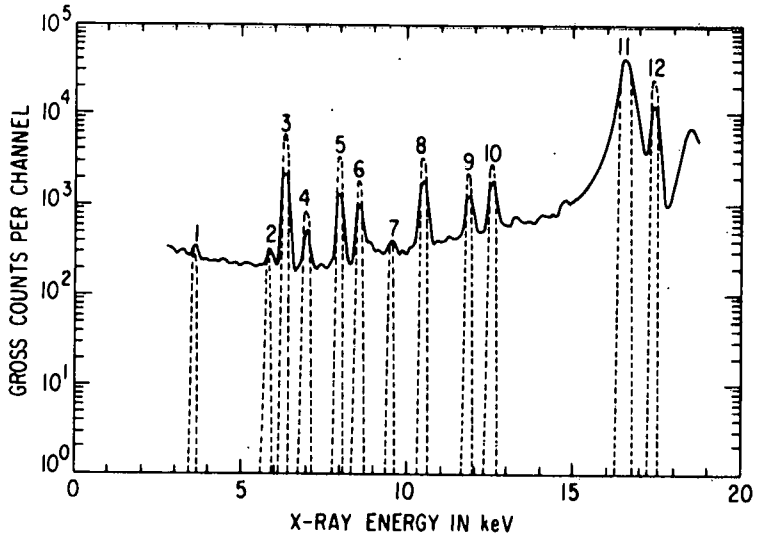

FIG. 2.--Spectrum of air filter. The numbered peaks correspond to the following elements: (1) Ca(K_α); (2) Mn(K_α); (3) Fe(K_α); (4) Fe(K_β); (5) Cu(K_α); (6) Zn(K_α); (7) Zn(K_β) + Au(L_α); (8) Pb(L_α) + As(K_α); (9) Br(K_α); (10) Pb(L_β); (11) Mo(K_α, incoherent); and (12) Mo(K_α, coherent).

of which are shown in Figures 3 to 6, are linear and pass through the origin.

Sensitivities and detection limits have been computed for several elements and are shown in Table 1. These are based on 1000 s counts of standards. The sensitivity is defined as the slope of the standard curve, in counts/sec/μg/cm^2. The sensitivity improves as the atomic number of the analyzed element approaches that of the secondary target, owing to the increasing absorption cross section.

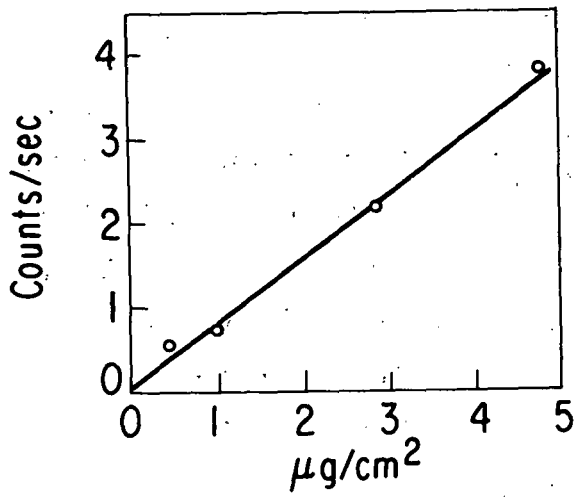

FIG. 3.--Standard curve of V.

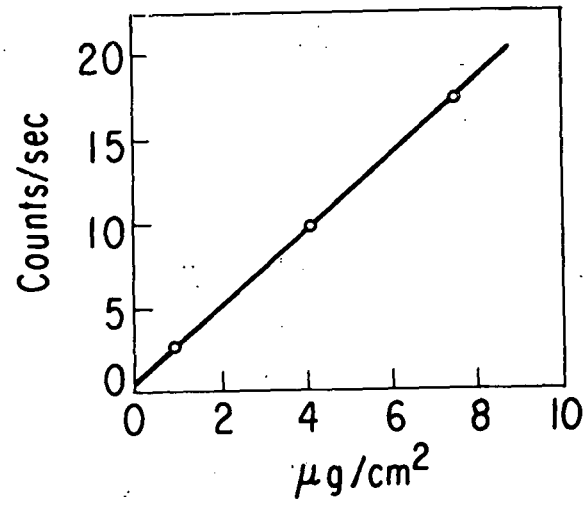

FIG. 4.--Standard curve of Mn.

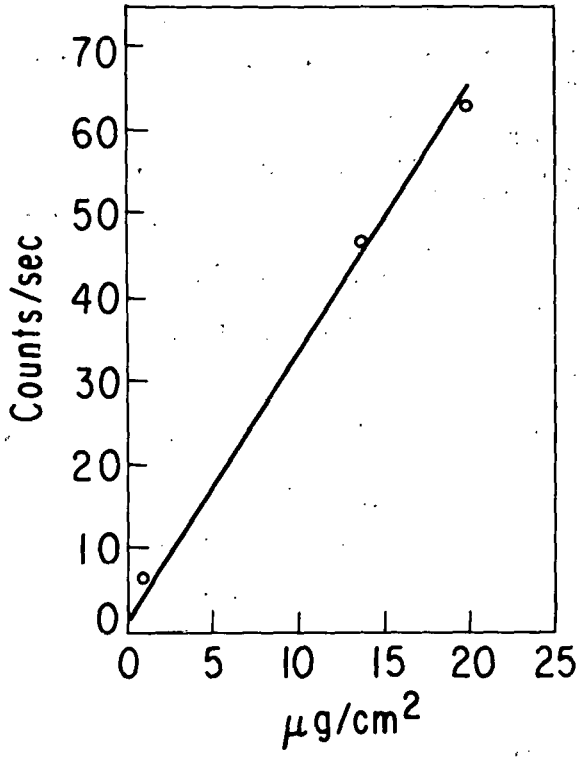

FIG. 5.--Standard curve of Fe.

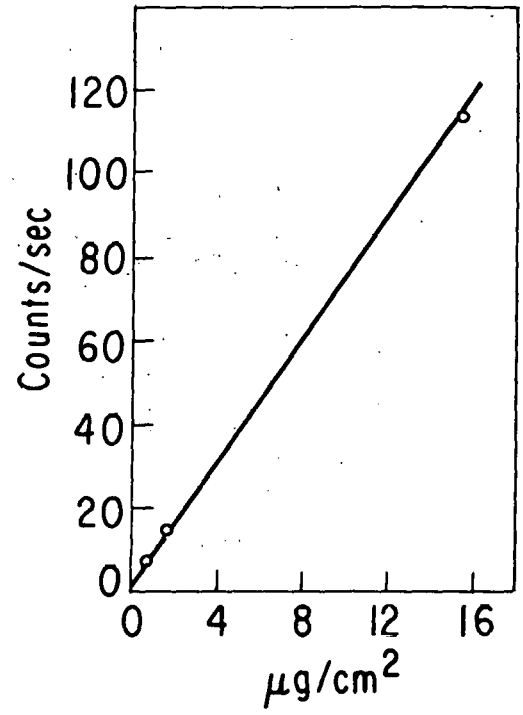

FIG. 6.--Standard curve of Zn.

Table 1. Sensitivity and detection limits for air-particles.

Element	Sensitivity, counts/sec/ $\mu g/cm^2$	Detection limit, ng/cm^2	ng/cm^3	Average concentration, ng/m^3
Ti	0.41	280	78	20[b]
V	0.79	200	76	5.5[a]
Cr	1.38	110	31	8.6[a]
Mn	2.33	75	21	55[a]
Fe	3.39	56	16	1720[a]
Co	4.90	32	9.0	12[a]
Ni	5.52	32	9.0	33[b]
Cu	7.51	31	8.7	44[a]
Zn	8.23	25	7.0	260[a]
As	13.9	14	3.9	17[b]
Se	13.7	14	3.9	2.9[a]
Br	15.3	12	3.4	9.2[a]
Pb L_β	5.7	41	11	1200[b]

[a]Ref. 3.
[b]Ref. 4.

The detection limit is defined as three times the standard deviation of the background divided by the sensitivity. Table 1 also shows the detection limit in terms of mass of the element per volume of air based on a filter area of 420 cm^2 and based on an average sampling volume of 1500 m^3. For comparison, the final column lists average air concentrations as measured over Lake Michigan[3] and Chicago.[4]

The reproducibility of duplicate measurements on our x-ray unit has been determined to be about 5%, with most of the uncertainty due to irreproducibility in positioning of the sample. Four segments of one filter were counted to test the consistency of the air filter and the analysis and data processing. The results are shown in Table 2. The precision is poor for Mn because the measurement is close to the detection limit when using the Mo secondary source. However, the other elements show precisions of better than 10%.

Table 2. Precision of analysis of 4 portions of air filter (ng/cm^2).

Mn	190 ± 140
Fe	8170 ± 660
Zn	980 ± 90
Br	900 ± 80
Pb	2420 ± 150

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X-RAY SPECTROMETRIC DETERMINATION OF SULFATE IN NATURAL WATERS*

C. A. Seils and G. T. Tisue

We have developed techniques that permit accurate and precise determination of sulfate occurring in trace amounts in natural waters. After removing interferring species by acidification and cation exchange, sulfate is precipitated with $BaCl_2$. By properly controlling precipitation and digestion conditions, the barium sulfate precipitate may be washed free of excess $BaCl_2$; very low blanks are observed. Barium sulfate is collected on 0.45 μm membrane filters in either small (6 mm diameter) or large (14 mm diameter) spot geometries. Barium is determined quantitatively by exciting its K x-rays with radiation from a holmium secondary source, which in turn is excited by radiation from a tungsten anode x-ray tube operated at 70 kV and 5 to 20 mA. The small and large spot geometries permit useful analyses on samples containing 0.1 to 2×10^{-6} moles sulfate, and 1 to 25×10^{-6} moles sulfate, respectively. Calculated detection limits lie several-fold lower in both cases, and each is precise to within less than 10% relative error. The method has been tested with rainwater, lake and spring water, interstitial fluid from Great Lakes sediments and a set of intercomparison samples circulated as part of the MAP3S program.

*Abstract of a paper presented at the 28th Annual Denver X-Ray Conference on Applications of X-Ray Analysis, University of Denver, Denver, Colorado, 1-3 August 1979; the full text will appear in Advances in X-Ray Analysis, Vol. 22.

PRELIMINARY MASS BALANCE CALCULATIONS FOR CADMIUM IN SOUTHERN LAKE MICHIGAN

J. Muhlbaier and T. Tisue

Cadmium is a relatively volatile element, one that is highly enriched on atmospheric particles relative to its average abundance in the earth's crustal rocks.* This characteristic suggests that cadmium is among those elements whose fluxes from the atmosphere are important, and perhaps comparable in magnitude to tributary inputs.[1]

Cadmium borne into the lake by both tributaries† and atmospheric particles[3] appears to be relatively soluble under oxic conditions. This property may result in heightened biological availability and also lead to a slow rate of removal on settling particles. In most areas, the surface sediments of southern Lake Michigan remain oxic to a depth of several centimeters.[4] Under these conditions, the concentration of cadmium in the interstitial fluid appears to be controlled by the solubility of cadmium carbonate, rather than the far less soluble cadmium sulfide found under anoxic conditions.[5] This situation creates the possibility that cadmium returns from the sediments to the water column by diffusion and/or resuspension.

The present concentration of cadmium dissolved in Lake Michigan is so low that to sample, handle, and measure it challenges the state of the art. Present concentrations in offshore waters are < 30 ng L^{-1}.[6] However, cadmium is very toxic to aquatic organisms, and Marshall[6] has shown that even levels below 100 ng L^{-1} can affect natural zooplankton communities adversely. Thus, despite the ultratrace amounts now present, it is important to know whether cadmium concentrations are likely to increase, and if so, at what rate.

Our approach to answering this question is to compare the sum of input rates from the major sources to the sum of removal rates to the major sinks.

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*We measured an average enrichment factor for Cd of 340 in 22 samples of airborne particulate matter collected over Lake Michigan.

†The average ratio of dissolved to suspended loads in the rivers we sampled was 2.0. See also Ref. 2.

As sources we considered rain and snow, dry deposition from the atmosphere, shore erosion, tributaries, and runoff from the land; as sinks, natural outflow sedimentation.

To establish the present concentration of cadmium in Lake Michigan, we collected and analyzed twelve samples from various locations in the southern basin. The average value for cadmium in these samples was 26×10^{-9} g L^{-1} ($N = 12$, $\sigma = 8.5$, range: 11 to 46×10^{-9} g L^{-1}). These values were substantiated by a separate determination using mass spectrometric isotope dilution.

Cadmium Input

Rain Water

Twenty-nine rain events were sampled with a Battelle automatic rain collector at ANL during the period March to September 1978. The rain was frozen until it could be analyzed by graphite furnace atomic absorption spectrophotometry (GFAA). The average cadmium concentration weighted according to rainfall amount was 0.32 ppb.* The range of values was 0.07 to 1.1 ppb.

The average total annual precipitation over Lake Michigan is about 29.2 inches or 74 cm.[7] Assuming a surface area over the southern basin of 1.8×10^4 km^2, approximately 1.33×10^{13} L of precipitation falls on the lake surface each year. If one takes the average concentration of cadmium in rain at ANL to be representative of precipitation falling on the lake, wet deposition accounts for a cadmium input rate of 4.3×10^6 g/yr.

Dry Deposition

Particles were collected from large volumes of air on 20 × 25 cm Whatman 541 filters at the 68th Street water intake crib. A quarter of each filter was leached into 0.1 N nitric acid and analyzed by GFAA using the method of Janssens and Dams.[8] Four portions of the same filter showed the method to have a precision of ∿7%. The average airborne cadmium concentration from the analysis of 28 filters collected between August and November was 1.9 ng/m^2. The values

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*The precipitation-weighted average is given by: $\Sigma C_i \times Q_i / \Sigma Q_i$, where C_i is the Cd concentration and Q_i is the amount of rain for each event.

ranged from 0.43 to 5.0 ng/m^3.

Estimates of the dry deposition velocity of cadmium to the lake surface vary from 0.1 cm/sec in the summer to 0.5 cm/sec in the winter. The annual average is probably close to 0.2 cm/sec.[9] This latter value leads to a dry deposition rate over the southern basin of 2.2×10^6 g/yr, or about half the rainwater input rate. Because cadmium is predominately on the surface of atmospheric particles, it is probably very accessible to leaching and therefore, easily placed in solution.[3] The total atmospheric contribution from wet and dry deposition is thus predicted to be 6.5×10^6 g/yr.

Shoreline Erosion

Approximately 1.0×10^{13} g/yr of material is expected to erode from the shoreline into the southern basin.[10] The average crustal cadmium concentration is 0.1 µg/g according to Wedepohl.[11] These values lead to an erosion contribution of 1.0×10^6 g/yr. This will be an overestimate if sand with low trace metal levels is the predominant material washed into the lake.

Tributaries

Water was collected from the major tributaries in the spring and fall of 1978. These samples were filtered immediately after collection using 0.45 µm membranes to separate the soluble portion from suspended solids. The soluble portion was analyzed by GFAA. The suspended solids were leached in 0.1 N HNO_3 and analyzed by GFAA. The soluble inputs are listed in Table 1. The concentration value for Burns Ditch was taken from the work of Wahlgren et al., who used spark source mass spectrometry.[12] The uncharted runoff figure is calculated from a total discharge to the whole lake of 3.84×10^{13} L/yr, or 1.28×10^{13} L/yr into the southern basin.[13] The difference between this value and the known river discharge is referred to as uncharted runoff. An intermediate concentration of 0.09 ppb is assigned to it.

The cadmium on suspended solids is summarized in Table 2. The total estimated input from tributaries is 3.1×10^6 g/yr, or about one-half the atmospheric input rate. This indicates that atmospheric sources of cadmium to Lake Michigan are indeed quite important.

Table 1. Tributary inputs of soluble cadmium.

Sampling site	Tributary flows 10^{11} L/yr	Cd concentration, μg L^{-1} Spring 1978	Fall 1978	Cd input, 10^5 g/yr
St. Joseph	30.4	0.08	0.10	2.73
Kalamazoo	11.6	0.07	0.07	0.81
Grand	30.0	0.19	0.095	4.3
Muskegon	17.0	0.05	0.06	0.94
Burns Ditch	1.2	0.40[a]		0.48
Milwaukee	3.4	0.25		0.85
Uncharted	31	0.09[b]		2.8
	125			12.9

[a]Ref. 13.
[b]Estimated concentration.

Table 2. Tributary inputs of cadmium on suspended solids

Sampling site	Cd concentration, μg L^{-1} Spring 1978	Fall 1978	Cd input, 10^5 g/yr
St. Joseph	85	140	3.4
Kalamazoo	65	60	0.73
Grand	130	740	13
Muskegon	17	8	0.21
Milwaukee	100	—	0.34
			17.7

Cadmium Removal

Outflow

One removal mechanism for cadmium is the outflow of lake water. If the total volume of the lake is assumed to remain constant, the outflow will equal the sum of runoff plus rainfall minus evaporative losses. The runoff amounts to 1.25×10^{13} L/yr. The rainfall is 74 cm annually and the evaporative losses amount to about 84 cm a year. For the southern basin the net outflow is calculated to be 1.07×10^{13} L/yr. The cadmium concentration in lake water has been

measured at 0.016 ppb, leading to a predicted net outlfow rate for cadmium of 2.8×10^5 g/yr.

Sedimentation

The rate of removal of cadmium by sedimentation was estimated using the sediment deposition rates proposed by Edgington and Robbins.[14] They found an average cadmium concentration of 3.0 ppm in the upper centimeter of 41 cores collected in the southern basin.[15] The sedimentation calculations are shown in Table 3. Rather than take an average sedimentation rate for the entire basin, we adopted Edgington and Robbins' values for the areal extent of sedimentation rates lying within a given range, multiplied each by the value 3.0 ppm, and summed the products to obtain the total annual cadmium deposition. Sedimentation accounts for the removal of 3.75×10^6 g/yr of cadmium. This may be an underestimate if the top centimeter of sediment covers a large time span and the deposition rate is rapidly increasing. However, the average concentration in precultural sediment was 1.5 ppm so the cadmium deposition does not appear to be increasing rapidly.

Balance

The sources and sinks of cadmium in southern Lake Michigan are summarized

Table 3. Loss of cadmium to sediments

Mean mass sedimentation rate, $g/cm^2/yr$ [a]	Area of southern basin affected[a] 10^{13} cm^2	Total Cd flux, 10^7 g/yr [b]
0.0	10.6	0
0.01	0.5	0.015
0.006	3.5	0.063
0.015	1.6	0.072
0.030	1.2	0.108
0.050	0.5	0.075
0.070	0.2	0.042
		0.375

in Table 4. According to this estimate, cadmium is being added to Lake Michigan two to three times faster than it is being removed. This suggests that cadmium is accumulating in the water column. Assuming a maximum concentration of 0.026 ppb cadmium at present in the lake and a volume of 1600 km^3, the cadmium in the water column in the southern basin is 42×10^6 g. If the net accumulation of cadmium is 6.5×10^6 g/yr, the approximate doubling time of cadmium is 7 yr. Owing to its toxicity, apparent buildup of cadmium in Lake Michigan may be cause for concern.

Table 4. Mass balance of cadmium.

Sources		Sinks	
Rain	4.3×10^6 g/yr	Outflow	0.28×10^6 g/yr
Dry	2.2	Sedimentation	3.8
Erosion	1.0		4.08
Tributaries	1.3		
Suspended	1.8		
	10.6		

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