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ARSENIC IN LAKE LANSING, MICHIGAN

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ARSENIC IN LAKE LANSING, MICHIGAN

By

Ted Randall Batterson

A DISSERTATION

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1980

ABSTRACT

ARSENIC IN LAKE LANSING, MICHIGAN

By

Ted Randall Batterson

Lake Lansing, Michigan was treated with sodium arsenite for control of aquatic macrophytes in 1957. Two 2.5 m sediment cores from deep portions of the lake basin were analyzed for total As in 5 cm increments. Seventeen to 20 $\mu g\ g^{-1}$ dry weight occurred in lower portions of the cores, and this was taken as background. Both cores had maxima of 330-340 $\mu g\ g^{-1}$ at depth interval 0.15-0.30 m. These peaks were taken to represent contamination from weed treatment in 1957. The rate of decrease in recently deposited sediments predicted that concentrations near background would exist in surficial sediments in the deep portions of the basin by 1989.

One hundred ten samples of the upper 7 cm of littoral sediments were taken along transects. Concentrations two to six times background occurred over 85-90% of the sediment surface.

An arsenic mass balance budget was constructed for the lake for the interval June 1978 to June 1979. This showed that the lake lost more arsenic than it received annually.

Internal loading of the water column from the sediments was occurring.

A laboratory experiment was conducted to obtain predictions of arsenic expected in the lake as a result of interaction between contaminated sediments and the water column. Since sediments in the well aerated littoral, as well as those from the periodically anaerobic hypolimnion were contaminated, aerobic and anoxic treatments were compared. When lake water over sediments was aerated, total As of 5-25 µg per liter were observed over an 89 day experimental period. Arsenic (V) averaged greater than As(III); 8.6 and 7.4 $\mu g\ l^{-1}$ respectively. Total phosphorus was monitored, and remained at 15-41 $\mu g\ l^{-1}$. In anoxic treatments, total arsenic rose in the water to a maximum of 117 $\mu g\ l^{-1}$ in 35 days. Although As(V) was present (<32 $\mu g\ l^{-1}$), the increase was due principally to As(III). It reached a maximum of 75 $\mu g\ l^{-1}$ on day 35. Sulfide was detected in the anoxic chambers after day 35. In its presence, As(III) steadily decreased from its maximum, presumably precipitated as a sulfide. With this decrease in progress, the anoxic chambers were aerated on day 58. Arsenic (III) rose, while As(V) dropped over a 24 hour period. Oxidation of sulfide was implicated in the former case; oxidation of iron and subsequent precipitation of As(V) with compounds of ferric iron was proposed to explain the latter. Following this initial response to aeration, As(III) steadily declined. It was apparently oxidized to As(V) and removed with ferric iron. At the end of 89 days, As(III), As(V), and total As approached the initial concentrations and relative proportions. Phosphorus rose with the onset of anaerobic conditions. Not responding to the presence of sulfide, it continued to increase beyond day 35, and until the chambers were aerated. It then declined toward pretreatment levels. Since classical studies have shown such a decline to be associated with ferric iron, it appears that As(V) and phosphate compete for iron as anoxic systems are aerated.

Concentrations of arsenic observed in the lake fit expectations from the experimental work. Aerated littoral and epilimnetic water was found to be 5-25 μg total As 1^{-1}. Concentrations on the order of 100 μg 1^{-1} were observed in anaerobic hypolimnetic waters; however, concentrations that high were not the rule. Currents associated with summer storms periodically erode the metalimnion of this shallow lake. Except for infrequent summer periods, sulfide or ferric iron tend to limit total As in the hypolimnion to a concentration of 20-30 μg 1^{-1}.

DEDICATION

To my parents

ACKNOWLEDGMENTS

I would like to express my most sincere thanks to Professor Clarence D. McNabb who unceasingly offered guidance and inspiration during this endeavor.

Thanks are also extended to my other committee members, Drs. Niles R. Kevern, Kenneth W. Cummins, and Peter G. Murphy.

My fellow graduate students, G. Douglas Pullman, Robert P. Glandon, Frederick C. Payne, and George W. Knoecklein deserve thanks for their many contributions to this work.

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INTRODUCTION

Arsenic is a metalloid that exists in a variety of chemical, biochemical, physical, and geochemical forms. It is widely distributed in nature and can be found in all environmental substrates. It ranks 47th in the order of occurrence for elements in the earth's crust, constituting 5×10^{-4} percent (Kipling, 1977). Though it occasionally occurs in the free state, most arsenic is found in nature in a combined form. Minerals of which arsenic is a major constituent are arsenides, sulfarsenides or oxides of heavy metals such as silver, copper, nickel, lead, gold, and iron. Arsenopyrite (FeAsS) is the most abundant ore mineral (Onishi, 1969). Orpiment (As_2S_3) and realgar (AsS) are other important minerals and are products of volcanic sublimation or deposits from hot springs. Onishi and Sandell (1955) discussed the geochemical cycling of arsenic and conclude that volcanic exhalations and hot springs have been the main source of the element now present in sediments and sedimentary rocks. Soil values, resulting from the weathering of parent rock material, range from 1 to 40 ppm As (Vinogradov, 1953 reported in Woolson, 1977); most soils average 6 ppm As (Bowen, 1966). The arsenic content of coals varies greatly, probably reflecting the difference in where it was formed. Coal ash from the

Virginias averaged 140 ppm As while elsewhere 8000 ppm As has been reported (Onishi, 1969; Kipling, 1977).

Seawater values ranged from 0.15 to 6.0 μg As l^{-1} with an average value of 2 μg As l^{-1}. Various river waters ranged in value from 0.2 to 25.0 μg As l^{-1} (Onishi, 1969). Hot springs that are rich in bicarbonates frequently contain elevated arsenic levels, ranging from 130 to 1000 μg As l^{-1} (Woolson, 1975). Ritchie (1961) reports that hot springs in New Zealand had values of arsenic as high as 8500 μg As l^{-1}. Lake waters display a wide range of values; from 0.1 to 243,000 μg As l^{-1} (Onishi, 1969; Woolson, 1975; Schroeder and Balassa, 1966). Lakes typically have values less than 10 μg As l^{-1}; Durum, et al. (1971) report that 79% of the 727 samples they collected from surface waters of the United States were below this level.

Excluding areas of volcanic activity or thermal springs, high concentrations of this element in either the water or sediments are usually the result of anthropogenic activity. The application of arsenical herbicides and pesticides, smelting and mining operations, and burning of fossil fuels have been the major sources of contamination (Shapiro, 1971; Kobayashi and Lee, 1978; Lis and Hopke, 1973; Walsh and Keeney, 1975; Crecelius, 1975; Wagemann, et al., 1978; Aston, et al., 1975). In the upper Great Lakes States, man has purposely introduced arsenicals into aquatic systems as a means of controlling aquatic macrophytes. Minnesota's records show that between 1956 and 1969 over 408,233 kg of sodium arsenite were added to lakes to kill rooted aquatic plants. In New York State, about 38,555 kg of this compound was used from 1961 to 1966 (Shapiro, 1971). In a twenty year period beginning in 1950, Wisconsin's public waters received 741,495 kilograms of arsenic (Lueschow, 1972).

Ferguson and Gavis (1972) have proposed that an arsenic cycle may exist in stratified lakes. In those basins that have accumulated a substantial arsenic burden from human sources, this cycle could be quite dramatic. Arsenic in aquatic systems has an interesting and unusually complex chemistry; oxidation-reduction, ligand exchange, adsorption-desorption, and precipitation reactions can all take place (Ferguson and Gavis, 1972). It can occur in numerous oxidation states (+5,+3,+1,0,-1,-3) and in inorganic and organic configurations. Exchanges between compartments of the water column and sediments are affected by diffusion, mixing by currents, and biological activity (Ferguson and Gavis, 1972; Wood, 1974).

The dynamics of anthropogenic arsenic in lakes have not been well documented. A recent study by Kobayashi and Lee (1978) reported on the accumulation of arsenic in sediments of five Wisconsin lakes treated extensively with sodium arsenite. A maximum of 659 μg As g^{-1} dry weight was found in surface sediments. Core samples showed a progressive decrease in concentration in lower sediment layers. Ten parts per million As by dry weight were found in deep portions of cores. They took this to be background. They did not report data for the overlying water columns. Lis and Hopke (1973) studied Chautauqua Lake, New York. They reported elevated levels (43.4 μg As l^{-1}) of dissolved arsenic in the water column. They hypothesized that these resulted from the slow release of arsenic from sediments that became enriched as a result of large-scale sodium arsenite treatment during the period 1955 to 1963. In a later report on the concentration and distribution of arsenic in the sediments of this lake, Ruppert, et al. (1974) attempted to support this contention. However, the hypothesis remained unsubstantiated since they did not measure inputs of arsenic from streams, seepage, and atmospheric fallout. Crecelius (1975) described geochemical cycling of arsenic in Lake Washington. He found elevated sediment concentrations; greater than 200 ppm As dry weight. However, the water column was at the low end of the freshwater range of concentrations, averaging 1.6 ppb As. Arsenic contamination was attributed to a copper smelter 35 km upwind of the lake. Lake Washington does not typify most arsenic treated lakes of the Great Lakes States since its deep water does not become anaerobic and strongly reducing during the year.

Lake Lansing, Michigan was chosen for this study. It is a productive, shallow lake of glacial origin. An historical record of treatment with sodium arsenite for weed control was available. The lake had received a single treatment in 1957. The hypolimnion of the lake was known to become anaerobic and reducing in nature during the summer. The objectives of the investigation were: (1) to establish the historical perspective of the arsenic treatment by studying sediment cores, (2) to construct hydrologic and arsenic budgets to evaluate the impact of treatment on today's arsenic cycle, (3) to describe the surficial sediment distribution of arsenic, and (4) to conduct a laboratory experiment that would predict the arsenic concentration in the water column as a result of sediment-water exchange.

THE STUDY SITE

Lake Lansing is located in Ingham County, Michigan. It was created by the natural processes of glacial scouring and recession. The lake lies in the LaGrange moraine of the glacial front known as the Saginaw Lobe (Martin, 1955). Deposits of a sand-gravel-clay soil were left during the retreat of Pleistocene glaciers (U.S. Army Corps of Engineers, 1970). The lake has a low relief watershed of 842 hectares. It has a surface area of 1816×10^3 m^2, volume of 4124×10^3 m^3, mean depth of 2.3 m, and a maximum depth of 10 m. Bathymetry is presented in Figure 1 showing the division of the lake into a north and south basin. Depth-area and depth-volume curves are presented in Figures 2 and 3 respectively. The littoral zone of the lake extended to the 3 m depth contour. Seventy-nine percent of the surface area of the lake lies over this zone, while the pelagial region constitutes the remaining 21%. The lake has a single outlet that discharges only in the spring. Besides precipitation on the surface, water enters the lake via six intermittent surface streams and three street drains (Figure 1). The retention time has been calculated to be 19.5 years.

During the 1940's and 1950's, fishing quality in Lake Lansing was progressively declining apparently due to

Figure 1. Morphometric map of Lake Lansing, Michigan showing transects, inflows, outflow, and areas treated with sodium arsenite in June 1957 (stippled).

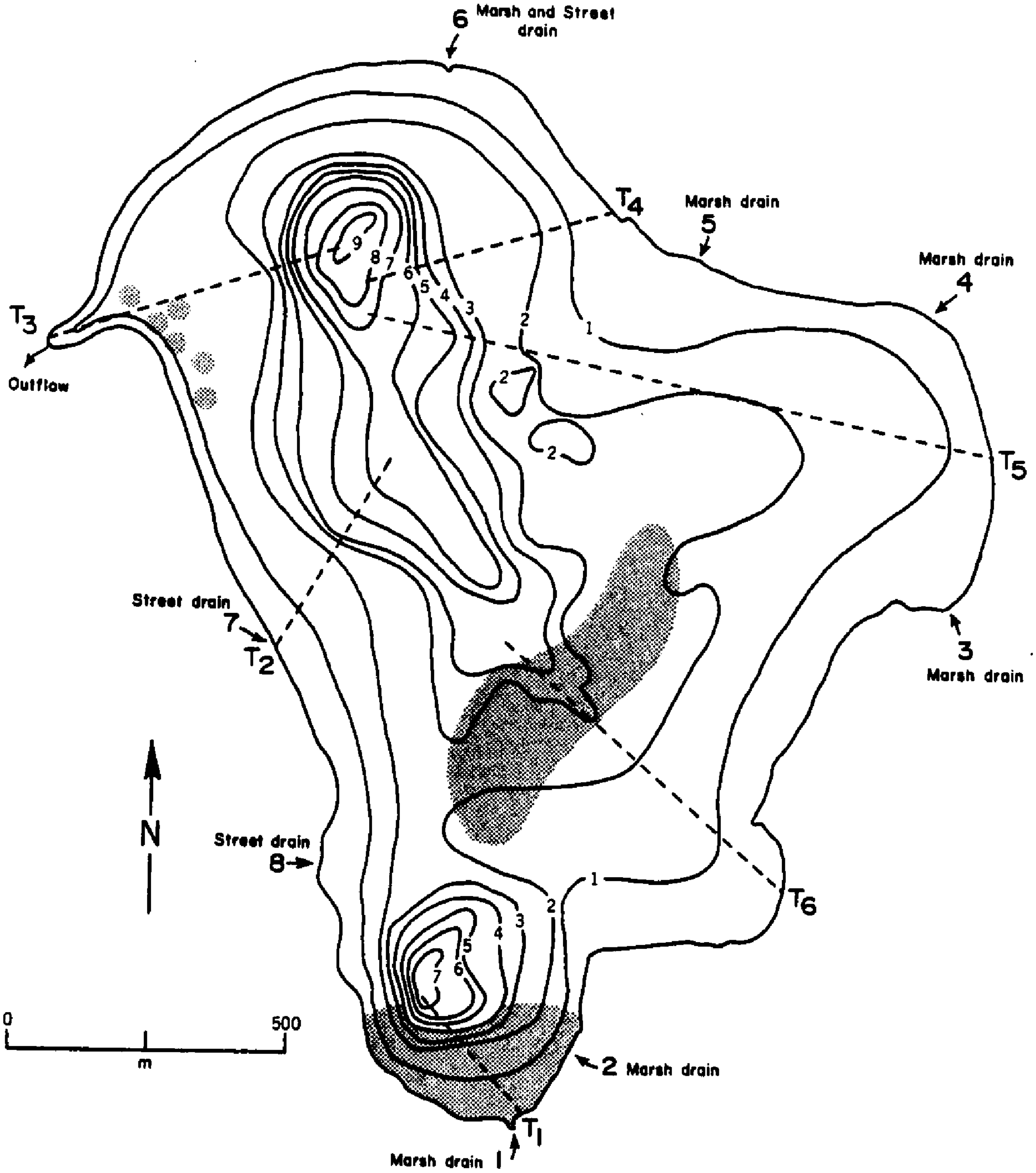

6 Marsh and Street drain
T4
Marsh drain 5
Marsh drain 4
T3
Outflow
9
8
7
6
5
4
3
2
1
2
2
T5
Street drain 7
T2
3 Marsh drain
N
Street drain 8
1
2
3
4
5
6
7
T6
0
500
m
2 Marsh drain
T1
Marsh drain 1

Figure 2. Depth-area curves for the upper 5 m of Lake Lansing, Michigan above and for the two deep holes of the lake below.

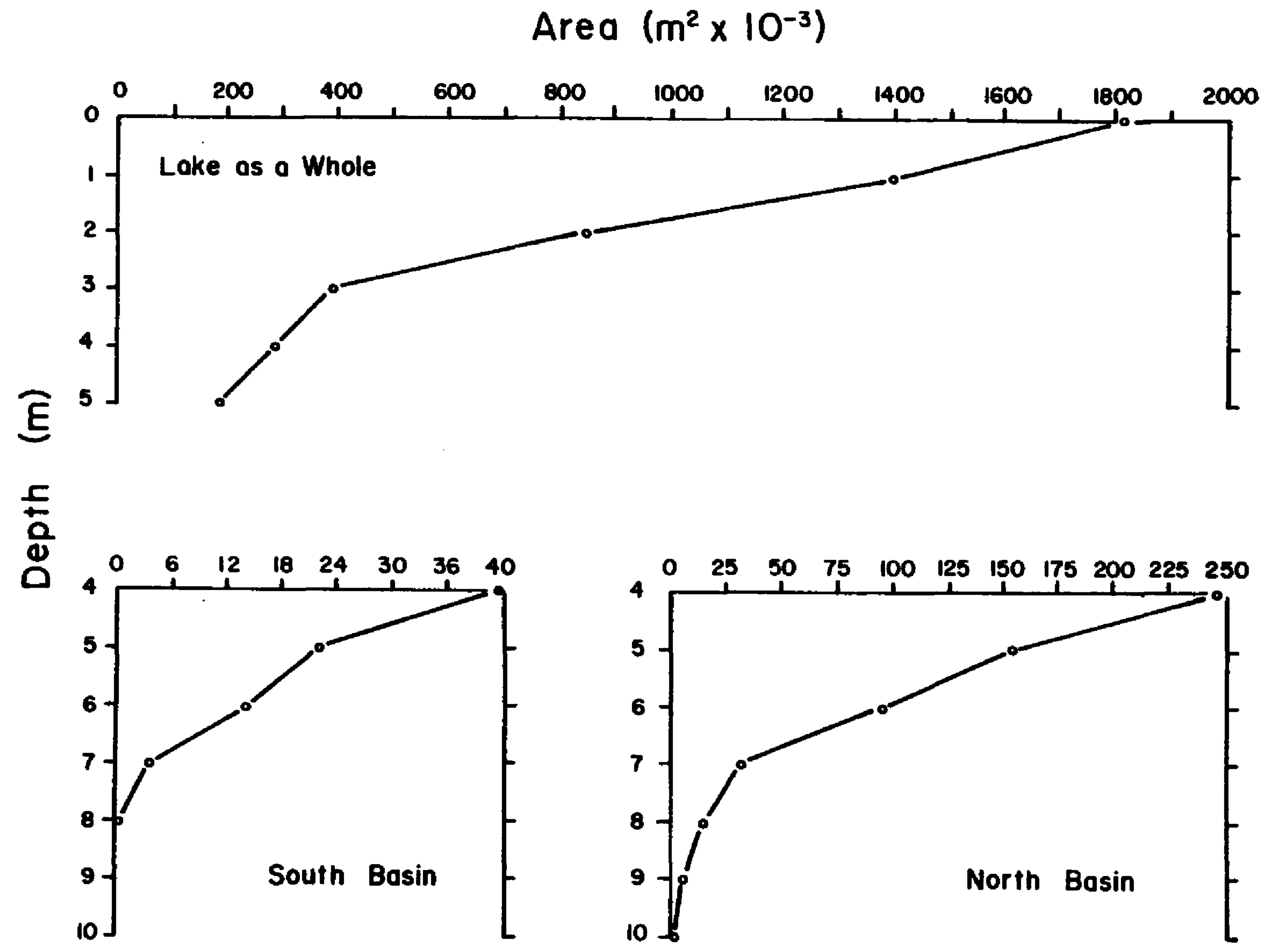
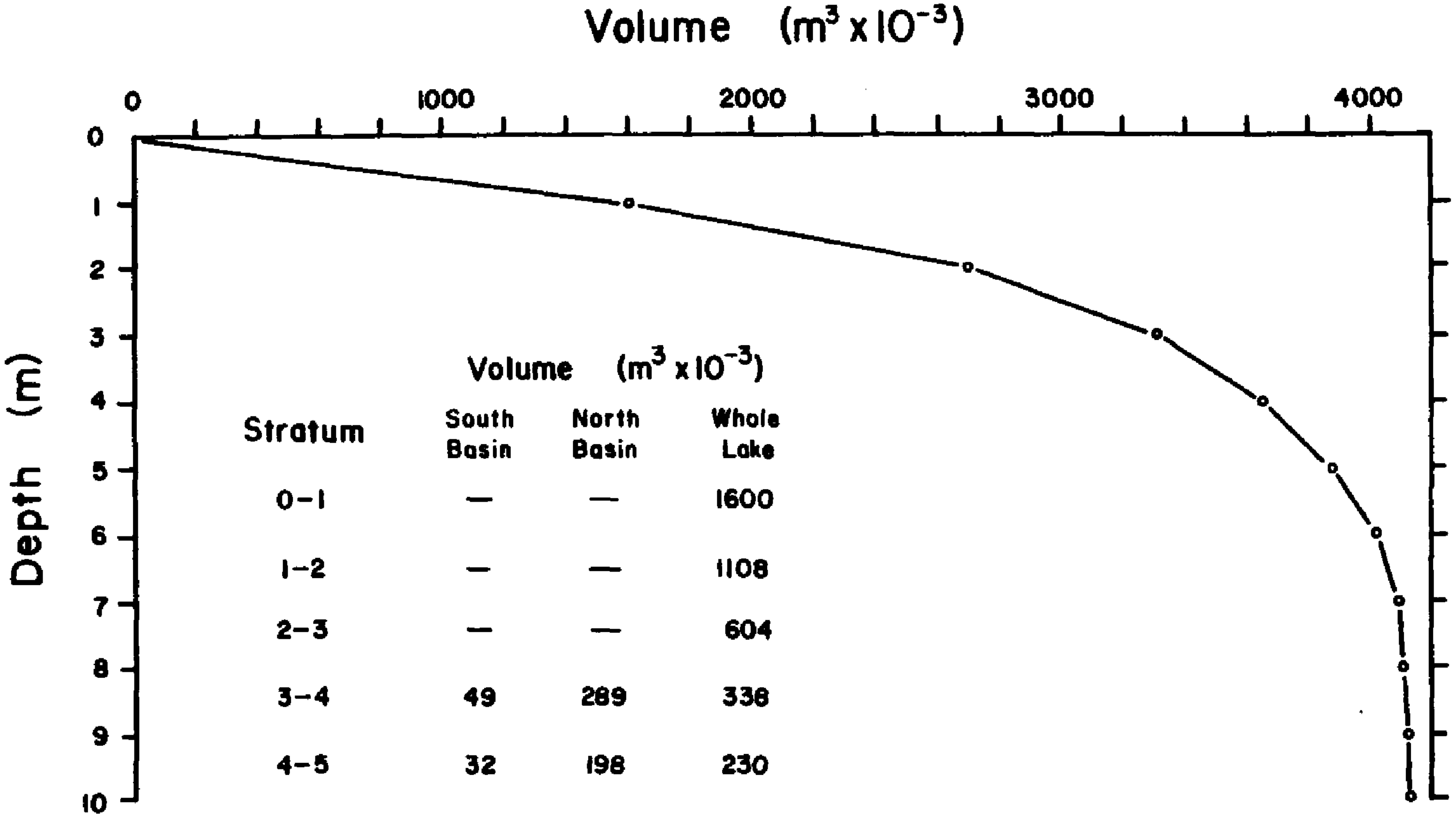

Area (m^2 x 10^{-3})
Depth (m)
Lake as a Whole
0
200
400
600
800
1000
1200
1400
1600
1800
2000
0
1
2
3
4
5
South Basin
0
6
12
18
24
30
36
40
4
5
6
7
8
9
10
North Basin
0
25
50
75
100
125
150
175
200
225
250
4
5
6
7
8
9
10

Figure 3. Depth-volume curve for Lake Lansing, Michigan with tabled volumes for strata of the two deep holes and the lake as a whole.



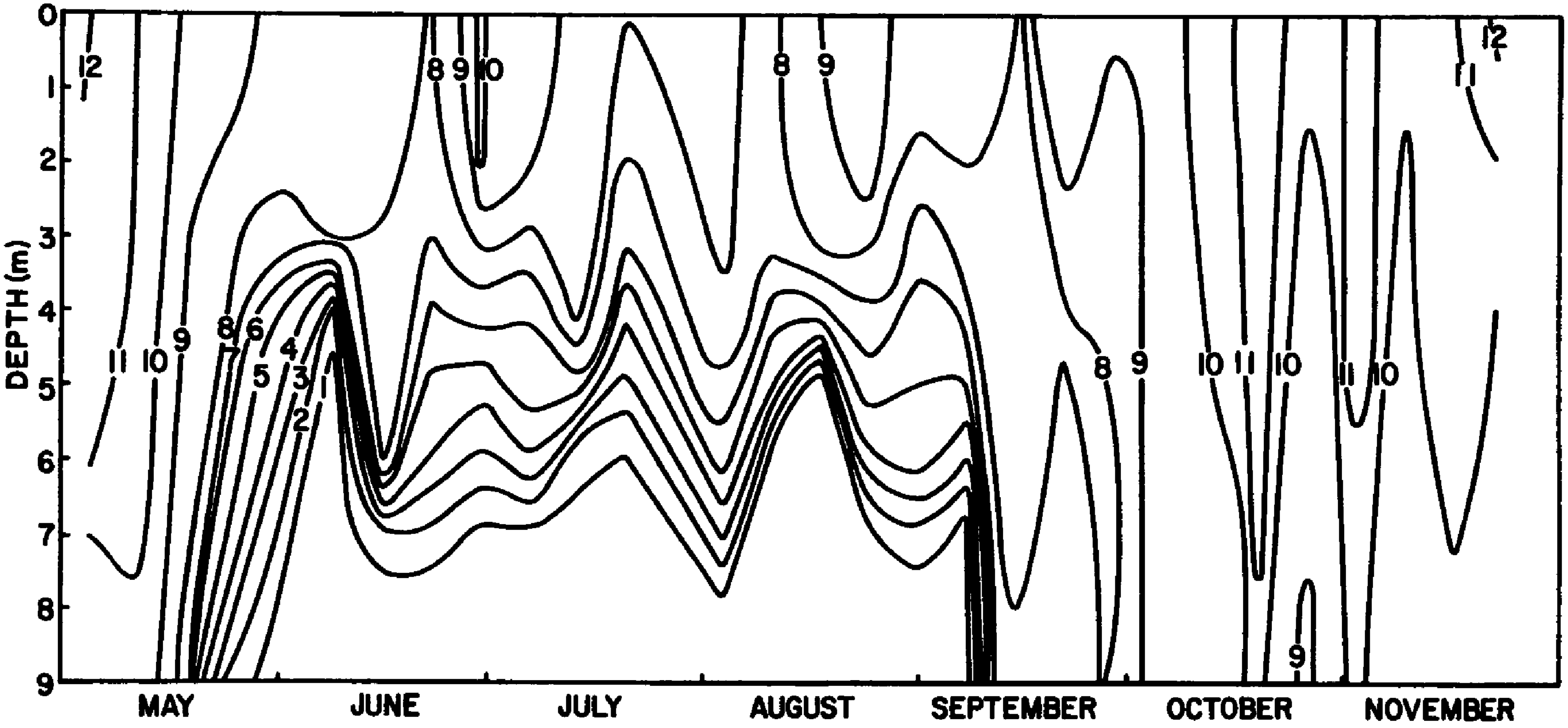
Volume ($m^3 \times 10^{-3}$)

Stratum	South Basin	North Basin	Whole Lake
0-1	—	—	1600
1-2	—	—	1108
2-3	—	—	604
3-4	49	289	338
4-5	32	198	230
5-6	18	123	141
6-7	8	61	69
7-8	1	24	25
8-9	—	8	8
9-10	—	1	1

increased biomass of aquatic vegetation (Roelofs, 1958). To reverse or halt this declining trend, the lake was treated to erradicate dense growths of submersed macrophytes. Sodium arsenite was selected because of its relative low cost, effectiveness in eliminating nuisance weeds, its apparent harmlessness to either large or small fish, and its failure to exterminate or seriously diminish the supply of natural foods (Mackenthun, 1950). Approximately 20 hectares (11% of the surface area) of the lake, were selected for treatment (cf. Figure 1). Those areas were treated in June 1957 by personnel from the Fish Division of the Michigan Department of Conservation. They used 3785 liters of sodium arsenite ($NaAsO_2$) which contained 1 kg l^{-1} arsenic trioxide (As_2O_3). This treatment resulted in an arsenic input of 2920 kg. This is the only documented application of arsenicals to this lake.

Lake Lansing is typically covered with ice from early December to mid-March. Anaerobic conditions have not been observed in the lake during recent winters. Dissolved oxygen during the growing seasons of 1978 and 1979 is shown in Figures 4 through 7. Stratification was established in May 1978 and persisted through September of that year. In 1979, stratification set-up temporarily in the south basin in May but did not persist until June. Summer stratification of this lake is typically disrupted by high winds. These tend to come from the southwest and west, often in the company of rainstorms. The fetch of the south basin in relation to

Figure 4. Depth-time diagram of dissolved oxygen isopleths (mg l^{-1}) from the north basin deep hole, Lake Lansing, Michigan, 1978.


DEPTH (m)
0
1
2
3
4
5
6
7
8
9
MAY
JUNE
JULY
AUGUST
SEPTEMBER
OCTOBER
NOVEMBER
12
11
10
9
8
7
6
5
4
3
2
1
8
9
10
8
9
8
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11
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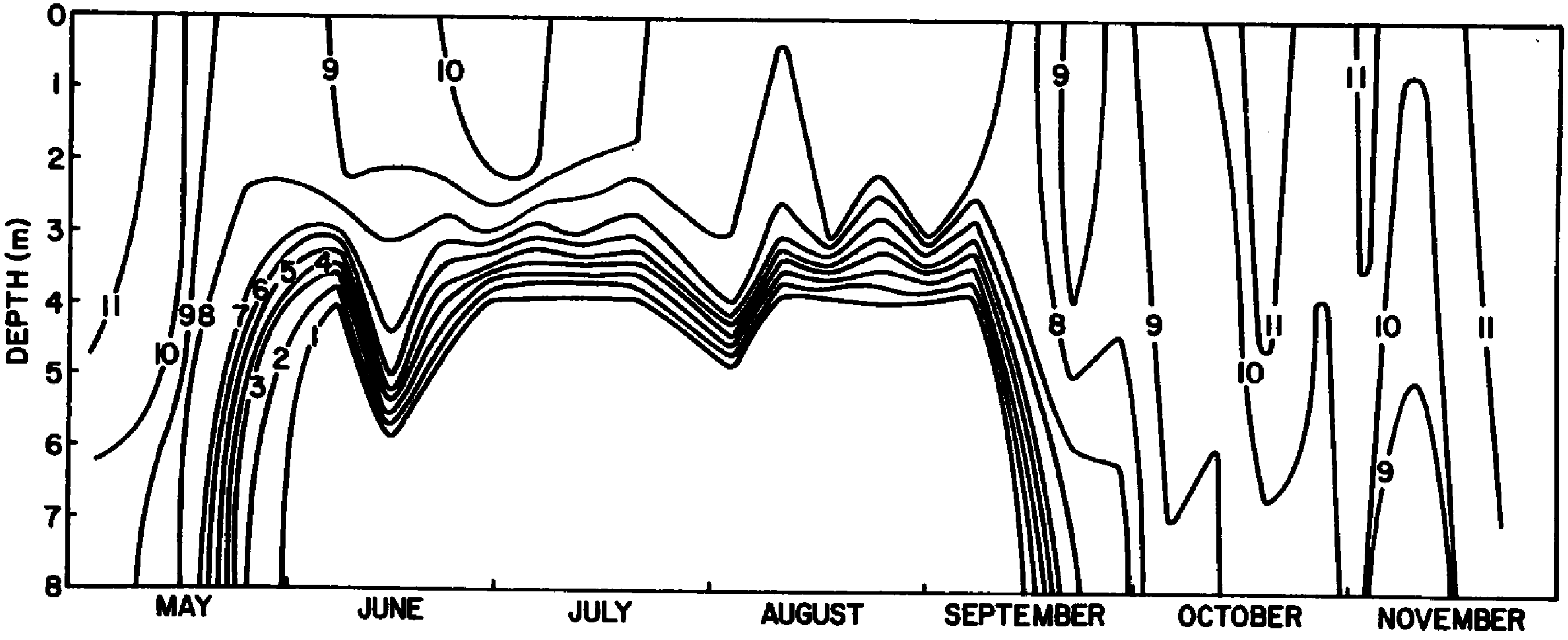
11
10
9
12
11

Figure 5. Depth-time diagram of dissolved oxygen isopleths (mg l^{-1}) from the south basin deep hole, Lake Lansing, Michigan, 1978.



DEPTH (m)
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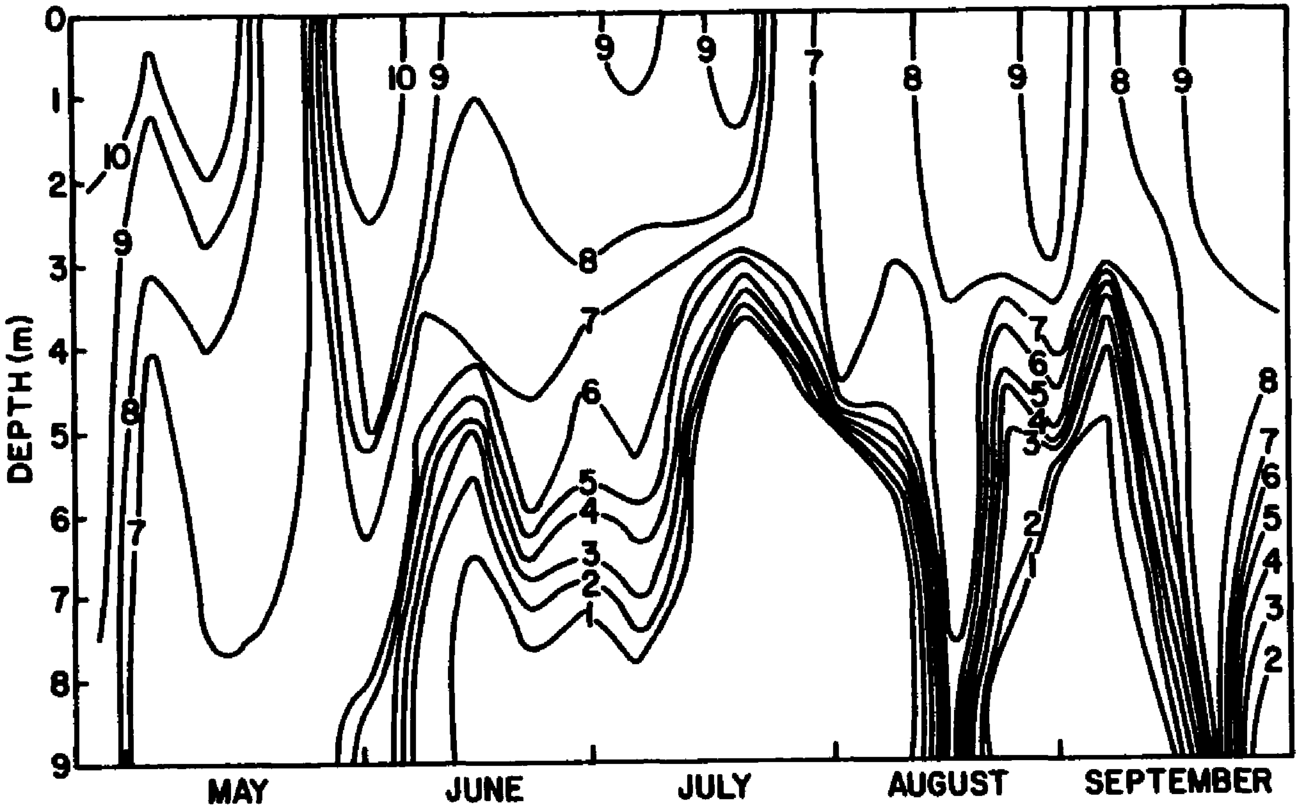
Figure 6. Depth-time diagram of dissolved oxygen isopleths (mg l^{-1}) from the north basin deep hole, Lake Lansing, Michigan, 1979.



0
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2
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6
7
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9
DEPTH (m)
MAY
JUNE
JULY
AUGUST
SEPTEMBER
10
9
8
7
10 9
9
9
7
8
9
8 9
8
7
6
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4
3
2
1
7
6
5
4
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2
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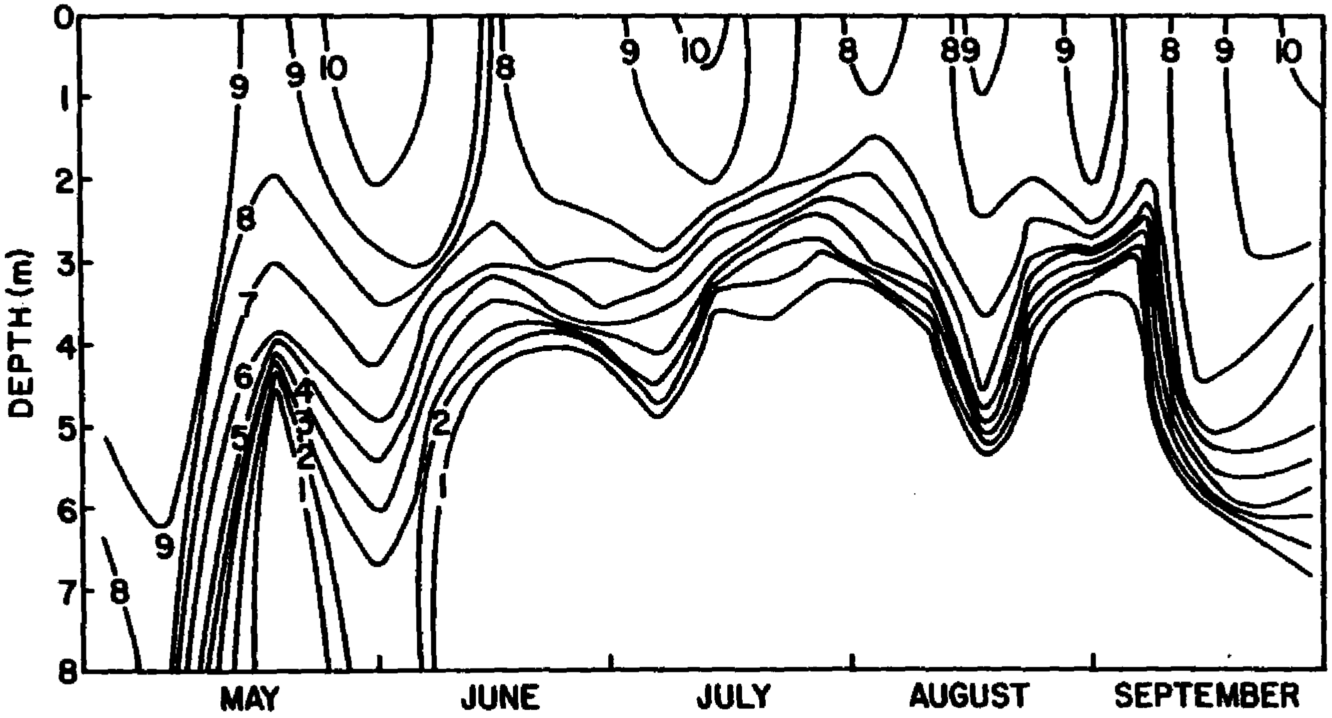
4
3
2

Figure 7. Depth-time diagram of dissolved oxygen isopleths ($mg\ l^{-1}$) from the south basin deep hole, Lake Lansing, Michigan, 1979.


DEPTH (m)
0
1
2
3
4
5
6
7
8
MAY
JUNE
JULY
AUGUST
SEPTEMBER
9
9
10
8
9
10
8
8
9
9
8
9
10
8
7
6
5
4
3
2
2
1
1
9
8

these winds is much shorter than that of the north basin. Hence, wind-related disruption of stratification is more frequent in the north basin. These impacts of winds can be seen in Figures 4 through 7 as the downward displacement of oxygen isopleths. With this pattern of circulation, hypolimnetic water temperature is relatively high in Lake Lansing. It ranged between 13° and 17° C during the summers of 1978 and 1979. Surface water temperatures were in the range of 22° to 26° C during that time.

MATERIALS AND METHODS

Sediment cores from the deep portions of Lake Lansing were taken to establish the degree of arsenic contamination due to weed treatment in 1957. Two sites were selected for sampling. They were from the deepest portion of the north and south basins. These sediments were extremely loose and unconsolidated. They were sampled by freezing the sediments onto the exterior surface of tubing which extended from the water surface and penetrated the sediments a known distance. Lengths of two inch o.d. thin-walled aluminum electrical conduit were used which were threaded and joined by couplings.

Once at the site from which a sediment sample was to be taken, the water depth was measured. Added to this was the length of sediment desired. Sections of tubing were then selected which would exceed that length by several feet to provide for excess tubing above the water. It was imperative that all joints were water-tight; silicone sealant was applied to the threads to accomplish this. The first section was stoppered and lowered into the water. Additional lengths were added until the stoppered end was just above the sediment surface. The last section was attached and then the lower end was carefully pushed into the sediments to the appropriate depth. After insertion into the sediments, pelletized dry ice was added to the tube from the end extending above the water surface. The amount added was enough to freeze the sediments as well as a small portion of water above the sediment-water interface. Replenishment of dry ice was maintained at a rate to offset sublimation. Thirty minutes after the initial addition of dry ice the samples were retrieved. As the tube was raised out of the water the sections were uncoupled down to the frozen sample. That portion was then lifted out of the water and placed in a vertical postion. As the sample was removed from the sediments, the amorphous zone between frozen and unfrozen portions was smeared, thus disrupting the sediment's original position along the length of the tube. Once out of the water, this outer disrupted layer was stripped away. After that, the sample was wrapped in plastic and the tube repacked with dry ice for transportation back to the laboratory. Once there, the dry ice was removed from the tube and replaced with warm water. Conducted heat melted the sediments that were contiguous with the exterior of the tubing allowing for the tube to be pulled free. The frozen sample was then cut into 5 cm sections. These doughnut-shaped pieces were rinsed thoroughly with ion-free water and then individually placed in labeled plastic bags. There were two reasons for the rinsing: to wash away any contamination that might be the result of the sectioning process or the sediments being in contact with the aluminum tube, and to remove internal and external smeared layers.

The frozen samples were then dried in a Napco Model 630 forced air drying oven at 70° C for 72 hours. The sample was then ground by mortar and pestle to a powder. From each of the well-mixed ground samples approximately one gram of sediment was removed and dried at 105° C for 24 hours. The sample was then introduced into a tared 2 dram polyvial and weighed. These vials had previously been acid washed. After weighing, the polyvials were heat-sealed and taken to Michigan State University's nuclear reactor facility for neutron activation analysis. For each group of samples that was irradiated there was included three standards for quantifying the analyses. Two of the standards were obtained from the National Bureau of Standards and prepared for introduction to the polyvials per their instructions. These were Standard Reference Material 1645 (River Sediment) and 1571 (Orchard Leaves). The other standard was a 2.0 ml solution containing 150 micrograms As ml^{-1}.

A Triga Mark I nuclear reactor was used for irradiation. Twenty sediment samples and three standards were introduced into a 40 position specimen rack that was rotated during irradiation to establish uniform flux for all sample positions. Sixteen to twenty hours following irradiation (allowing for the partial decay of ^{24}Na activity), the samples were counted for 1000 seconds live-time with a 76.2 cm^3 active volume Ge(Li) detector having a relative efficiency of 15% and an energy resolution of 1.8 keV FWHM at the 1.333 MeV photopeak of ^{60}Co. The source-to-detector geometry was kept constant for all counts and the detector resolution was sufficient to completely resolve the ^{76}As peak (559 keV) and the adjacent peak of ^{82}Br (554 keV). The gamma-ray spectrum from each sample and standard was analyzed by a Canberra Series 80 multi-channel analyzer. This analyzer computes the peak net area which is the number of counts in a peak that are above an average background level. Corrections for decay between counting time of the samples and standards were made. The mass of arsenic in the samples was derived from the time-corrected counts of the standards.

Surficial sediment samples were collected from varying water depths along six transects (cf. Figure 1). These permanent transects were selected such that they crossed over the major sediment types of the lake. Transects 1 and 6 were located over fibrous peat; transects 2 and 3 over fine organic ooze; and transects 4 and 5 over sand mixed with fine organic particles (Siami, 1979). Since most of these sediments are loose and flocculent, typical dredging devices were not employed. Instead, a 5.7 cm i.d. clear acrylic tube that was 7 cm long was used for sampling. The samples were obtained by cautiously swimming down to the sediment surface, slowly inserting the open-ended tube into the sediments, stoppering first the top and then the bottom, and then returning to the water surface. Samples were then dispensed into labeled zip-locked plastic bags and stored in a cooler prior to transport to the laboratory. Five samples from four water depths were taken along each of the six transects.

These surficial sediment samples were analyzed by neutron activation analysis according to the procedures described above.

An annual hydrologic budget for the lake was constructed from measurements of inputs (marsh drains and street drains of Figure 1), outflow, precipitation and evaporation, and net seepage. This budget covered the period June 20, 1978 to June 18, 1979. The methods used at Lake Lansing for measuring discharge from marsh drains and street drains have been described by Glandon, et al. (in press). Discharge of the outfall was measured three times per week from the onset of flow (April 27,1979) to cessation (June 1, 1979). Water leaving the lake passed through a concrete control structure. Discharge was calculated by measuring stage height and applying this to a U.S.G.S. approximation formula for a rectangular weir (U.S.D.I., 1967). Stage height measurements were recorded for the lake throughout the study. These were measured in relation to the southeast edge of the sill of the dam which had been measured to be at 259.6 m above mean sea level. At this stage height, the surface area of the lake was calculated to be 1816 x 10^3 m^2. When the elevation exceeded 259.6 m, natural banks of the lake and retaining walls resulted in a nearly vertical rise (rather than lateral) of the water. Therefore, the surface area of the lake remained unchanged for stage heights that exceeded this elevation. For those stage heights less than 259.6 m, the surface area was calculated from the depth-area curve of Figure 2.

Discharge (m^3) measurements from the marsh drains, street drains, and outfall were converted to changes in lake level by dividing those values by the average surface area of the lake for the interval in question. Precipitation and evaporation data were collected at the weather station located on the South Farm of Michigan State University, approximately 9 km from the lake. The net atmospheric effect on the water budget was determined for intervals of interest by the difference between precipitation and evaporation (mm). The net atmospheric effect for an interval was added to the change in stage height that could be accounted for in that interval by the discharge of input and the outflow. The residual change in lake level for the interval was taken to be the result of seepage. Multiplying that residual by the corrected surface area for that interval gave the net volume (m^3) gain or loss due to seepage. The water budget thus developed was used with measurements of arsenic concentrations to estimate the annual mass arsenic budget for the lake.

Glandon, et al. (in press) have described the methods used at Lake Lansing for collecting and compositing representative water samples from the discharge of marsh drains, street drains, and the lake's outflow. A discharge-proportional scheme was used to make up composite samples for arsenic analyses. Composite samples from these sources were preserved with 2 ml concentrated HNO_3 per liter and were refrigerated until analyzed.

Atmospheric arsenic loading was determined by placing triplicate lexan containers in a fabricated stand one meter above the surface of the lake and 50 m from the western shore in the south basin. The containers were 23 cm deep and had a surface area of 0.26 m^2 each. Prior to placement, the containers were successively washed and rinsed with 1:1 HNO_3, 1:1 HCl, and ion-free water. Six liters of deionized water were then poured into each container, rinsing the inside surface well. One liter from each container was withdrawn. These three liters were then mixed together; a one liter sample was withdrawn, preserved with 2 ml concentrated HNO_3 and refrigerated until analysis. This sample represented the beginning of an interval. "Beginning" sample containers were then carried to the field and exchanged for "finishing" containers, those that had been exposed for a period of time. By having water in the containers, the lake surface which would be receiving atmospheric fallout was simulated. The interval exposure was varied to maintain water in the containers, but to prevent overflowing, depending on the precipitation-evaporation balance. Typically the exposure period was two weeks. The "finishing" containers were returned to the laboratory where all internal surfaces were scraped down with an acid-washed rubber spatula. Water in the containers was washed around to rinse the surfaces. Water from all containers was combined, the volume measured, and then mixed. From the well-mixed composite, one liter of water was withdrawn, preserved with acid and refrigerated. This sample represented the end of the exposure period.

The atmospheric arsenic input to the surface area of the lake was calculated from the following equation:

$$As = \frac{\{(C_f \times V_f) - (C_b \times V_b)\}}{S_{sa}} \times L_{sa}$$

where As = mass of arsenic input during the interval in question:

C_f, C_b = concentration of total arsenic in the "finishing" and "beginning" containers, respectively:

V_f, V_b = volume of water in the "finishing" and "beginning" containers, respectively;

S_{sa} = total surface area of the containers;

L_{sa} = average corrected (for changes in stage height) surface area of the lake for that interval.

Lake water for arsenic determinations was collected by a PVC Kemmerer bottle and composited into three samples; littoral and upper pelagial water, and two lower pelagial waters, one representing the north basin and the other the south basin. The littoral and upper pelagial water was composited from samples taken at mid-depth from the 0.5, 1.5, 2.5, and 3.75 m depth contours on each of six transects (cf. Figure 1), and from those same depths over both basin's deep holes. The volumes of water for the composite, representing each of 32 sampling sites, were in proportion to the volume of water in the zones of the lake that the samples represented. The north basin lower pelagial water sample was composited from volumes of water from 5.5, 6.5, 7.5, and 8.5 m in proportion to the volumes of the 5-6, 6-7, 7-8, and greater than 8.0 m strata of the north basin of the lake. The south basin lower pelagial water was composited from volumes of water from 5.5 and 6.5 m in proportion to the volumes of the 5-6 and greater than 6 m strata of the south basin of the lake. A one liter sample from each of the three composites was preserved with HNO_3 and refrigerated until analyzed.

All water samples were analyzed for total arsenic by atomic absorption spectrophotometry. The method employed was the gaseous hydride evolution technique as described in *Standard Methods for the Examination of Water and Wastewater, 14th Edition* (APHA, 1976). Following analyses, estimates of arsenic in the seepage component of the annual budget were made. A net volume loss from the lake due to seepage in an interval was multiplied by the average littoral and upper pelagial arsenic concentration for that interval on the assumption that seepage from the lake occurred through sediments in the shallows of the basin (cf. McBride and Pfannkuch, 1975; Dunst and Beauheim, 1979). If a net seepage gain occurred in the basin over an interval of the year, that volume was multiplied by the average arsenic concentrations in the marsh drains at low flow. The relief of the watershed of Lake Lansing predicts that seepage to the lake comes predominately through the marshes to the north and east of the basin (cf. Winter, 1978).

A laboratory experiment was designed to evaluate the interaction between the water column and sediments of the lake.

Sediments were collected from the deep portion of the south basin using an Ekman dredge. These were homogenized. Five, 38 liter capacity metal containers, lined with 3 mil polybags were filled with the mixture to a depth of 5 cm. This resulted in a 835 cm^2 sediment surface and a remaining capacity in the containers of approximately 35 liters. A sediment sample was removed from each unit and analyzed for arsenic by neutron activation with techniques previously described. The units with sediments were then exposed to the atmosphere for five days. After that, they were filled with water taken from near the surface of the lake over the deep portion of the south basin. The water was carefully layered over the sediment in an attempt to minimize the disruption and suspension of material. All units were aerated and placed in a 15° C water bath. This temperature was the summer time average for water overlying deep basin sediments.

The experimental units had lids that were slightly convex, creating an air space between the top of the water and the lid. A gasket and silicone sealant afixed the lid to the container. Lids were fitted with small diameter inflow and outflow gas ports, and a large diameter sampling port. Suspended from the inflow gas port was a diffusor stone that hung below the water surface. The other end of this port was connected to a manifold with various gas sources.

One unit was randomly selected and aerated during the experiment. The other four units were subjected to a period of anoxia and then aerated. The sampling procedure consisted of first withdrawing water for arsenic and phosphorus determinations. After that, *in situ* measurements of temperature, dissolved oxygen, and pH were taken. Temperature and dissolved oxygen were measured with a YSI Model 54A D.O. meter and probe. Hydrogen ion concentration was determined by using a Corning Model 6 portable pH meter with an Orion Model 91-25 epoxy combination probe. After the initial sampling, the four anoxic units were purged with 99.9% N_2. Then all ports were sealed. Following *in situ* measurements, the anoxic units were briefly purged with N_2 to expel any intrusion of O_2 that might have resulted during the sampling procedure. This filled the head-space above the water with N_2 as well. At the end of 58 days, the four anoxic units were aerated for the remainder of the experiment (89 days). During the period of aeration, sampling continued.

Water samples were analyzed for total phosphorus, arsenic (III), arsenic (V), and total arsenic. Total phosphorus concentrations were determined colorimetrically using the single reagent-ascorbic acid method on unfiltered, persulfate digested samples (APHA, 1976). Before the addition of the color reagent, all samples and standards were subjected to a reducing reagent to eliminate arsenate interference (Johnson, 1971). Water for arsenic determinations was preserved with 1 ml concentrated HCl and analyzed by atomic absorption spectrophotometry. The gaseous hydride technique described above was employed. Speciation was accomplished by the fact that only As(III) is effectively converted to hydride (Aggett and

Aspell, 1976). Therefore, aliquots of the sample were treated differently. One was analyzed directly to determine the As(III) content. Another was subjected to KI, a mild reductant, which converts As(V) to As(III). The difference between the first and second determination yields the amount of As(V) present. A third aliquot is digested by using HNO_3 and H_2SO_4, converting all forms of arsenic present to the As(V) state, then treated with KI. This analysis represents the total arsenic. Subtracting the sum of the As(III) and As(V) values from this final analysis yields the amount of organic arsenic present.

RESULTS

The arsenic concentrations for the deep sediment samples are presented in Figures 8 and 9. In the north basin, the maximum value occurred at a depth of 0.25-0.30 m and was 337 μg As g^{-1} dry weight; in the south basin it occurred at 0.15-0.20 m and was 335 μg As g^{-1} dry weight. From these maximum concentrations there was a rapid decrease with depth, and then a gradual decline with some minor fluctuations to a concentration of 17 to 20 μg As g^{-1} dry weight. This range is taken as the natural background concentration for sediments in deep portions of this basin.

The similarity in the shapes of the curves for the arsenic distribution with depth in the north and south basins is striking. The data lead to the conclusion that peak concentrations were the result of the 1957 sodium arsenite treatment. Based on that assumption, the sedimentation rate in the north basin calculates to be 1.1 cm yr^{-1}; in the south basin the estimate is 0.7 cm yr^{-1}. The difference in sedimentation rates could be a function of the ratio of catchment area to basin area. That ratio is markedly smaller for the south basin.

An annual hydrologic budget was developed for Lake Lansing to serve as the basis for an arsenic mass balance

Figure 8. The distribution of arsenic in a sediment core from 9 m in the north basin of Lake Lansing, Michigan, July 13, 1979.

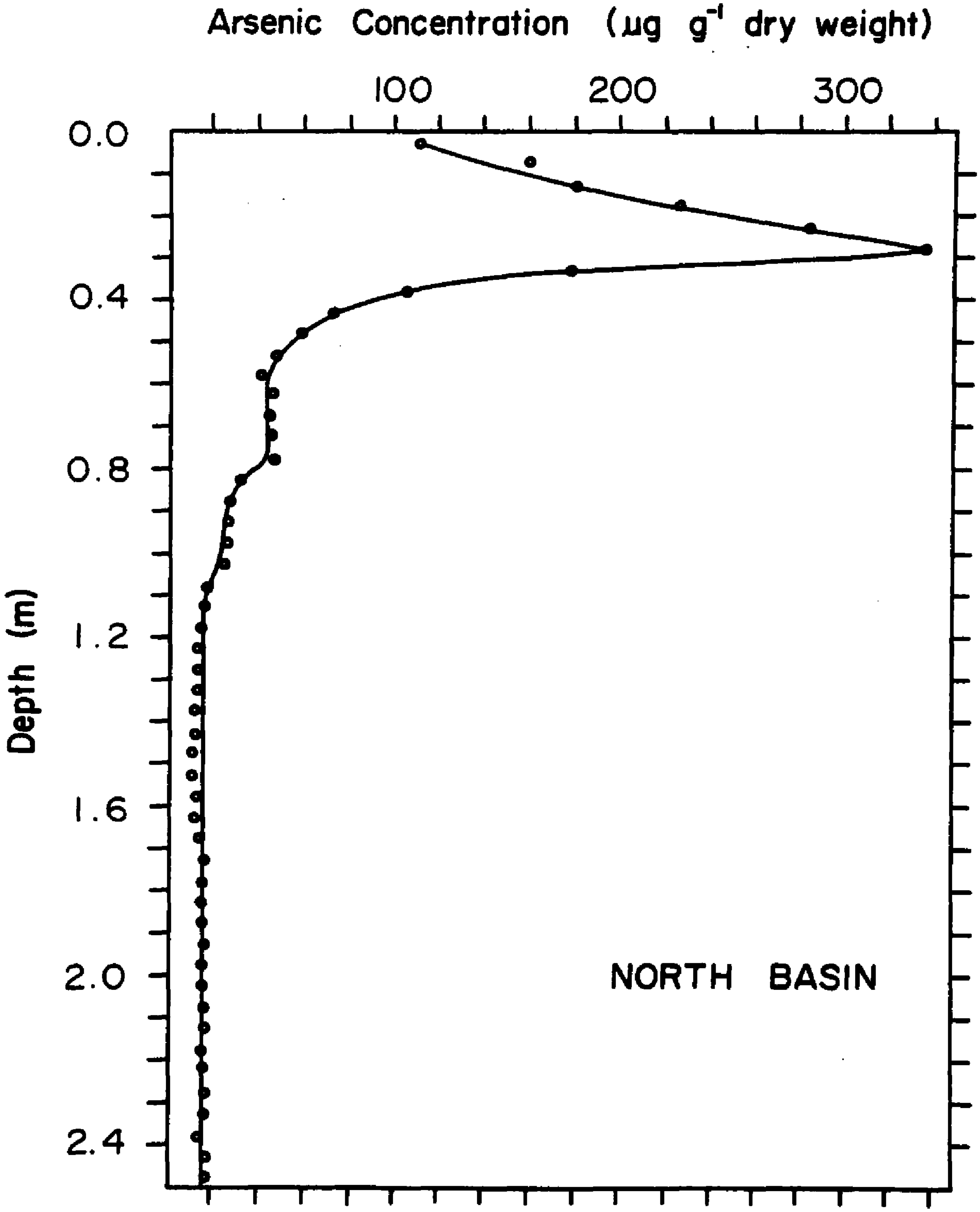
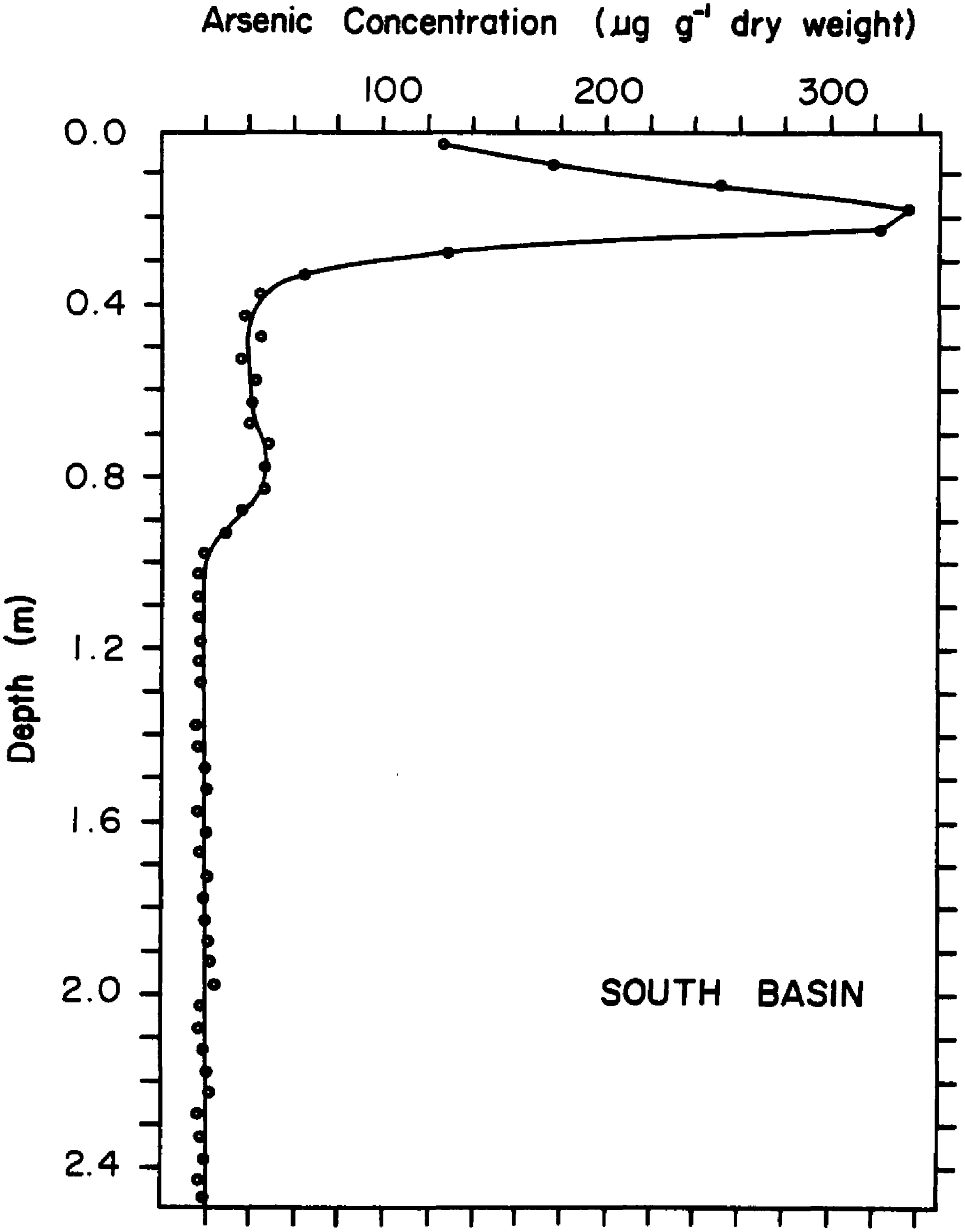

Arsenic Concentration (µg g⁻¹ dry weight)
100
200
300
Depth (m)
0.0
0.4
0.8
1.2
1.6
2.0
2.4
NORTH BASIN

Figure 9. The distribution of arsenic in a sediment core from 7 m in the south basin of Lake Lansing, Michigan, July 13, 1979.


Arsenic Concentration (µg g⁻¹ dry weight)
100
200
300
0.0
0.4
0.8
1.2
1.6
2.0
2.4
Depth (m)
SOUTH BASIN

estimate for the lake. The data are summarized in Table 1. It shows that the lake did not discharge through the overflow structure during the summer, fall or winter. The only overland flow input during those seasons was from street drains as a result of rain or snow melt. The discharge from street drains was relatively small, constituting 0.5% of the annual overland discharge to the lake. Net losses to the atmosphere and seepage were the major components of the water budget in summer and fall. Evapotranspiration from extensive lake-side marshes undoubtedly contributed to high rates of net seepage loss in the dry summer and fall of 1978. Net losses of water from the lake in summer and fall resulted in a drop of the lake surface below the elevation of the outlet dam.

Winter during the year of study was relatively wet. Precipitation on the watershed in this season was held as snow; there was virtually no melt in this particular winter. Seepage loss appears to have continued to recharge the deficit in the groundwater accrued from the previous summer and fall. With the onset of spring, overland flow from marsh drains, and seepage, and to a lesser extent discharges from street drains, gradually brought the surface of the lake to the sill of the outlet dam. By late April, outflow occurred and continued to early June.

The seasonal patterns of overland flow and changes in lake level measured in this study were, by our observation, typical for the basin during recent years. Lake level

Table 1. Seasonal aspects of the annual hydrologic budget of Lake Lansing, Michigan. Tabled values are in units of m^3.

	Atmosphere		*Overland Flow*		*Seepage*
Interval	Precipitation minus Evaporation[1]	Marsh Drain Discharge	Street Drain Discharge	Outlet Discharge	Net Gain or Loss
Summer 6/20/78-8/28/78	-251849	0	+ 543	0	-131620
Fall 8/28/78-11/6/78	- 6969	0	+ 630	0	- 58018
Winter 11/6/78-2/8/79	+194290	0	+ 178	0	- 72631
Spring Runoff 2/8/79-4/23/79	+ 5390	+402909	+ 639	0	+199440
Runoff-Outflow 4/23/79-6/18/79	-127119	+145429	+1011	-212491[2]	- 3632
TOTALS	-186257	+548338	+3001	-212491	- 66461

1. Evaporation was calculated using a pan coefficient of 0.7. During certain periods of the year (late fall and early spring) water in the evaporation pan froze while the lake surface remained open. Values for those periods were estimated by extrapolating data from just prior to or immediately following that phenomenon. During the winter, precipitation was taken as the water content of snow or ice. Water losses through sublimation from ice and snow were taken to equal water gained from condensation; net evaporation was taken as zero.

Table 1. Continued.

2. Outflow began in the interval 4/25-4/27/79 and stopped in the interval 5/30-6/1/79.

records of the U.S.G.S. suggest that the seasonal patterns of 1978-79 have existed for at least three decades. From the water budget, the turnover-time for Lake Lansing (lake volume divided by annual discharge) was calculated to be 19.5 years. The long residence time promotes retention in the basin of arsenic introduced during weed treatment of the lake in 1957.

The hydrologic budget was used to generate an annual arsenic budget for Lake Lansing. Whether this contaminated lake was functioning as a sink or a source of arsenic was the question of primary interest. Arsenic in the discharge of marsh drains, street drains, and the outflow from the lake were measured and applied to discharge data such that Appendix Tables 1, 2, and 3 resulted. Measurements for atmospheric loading are given in Table 4 of the Appendix. Appendix Table 5 presents data on seepage. A summary of the annual arsenic budget is given in Table 2.

Atmospheric loading and the discharge of drains contributed nearly the same amounts of arsenic to the lake annually. Street drains, while discharging 0.5% of the water, carried 2.5% of the arsenic flowing overland to the basin in a year. The totals of Table 2 show that the annual arsenic loading was less than discharge to the downstream environment in the spring of the year. In addition, there was a loss of arsenic from the lake by seepage. Thus, Lake Lansing serves as a source rather than a sink for arsenic. This can only occur as a result of internal loading of the water column with arsenic from surficial sediments.

Table 2. Seasonal aspects of the annual arsenic budget of Lake Lansing, Michigan. Tabled values are in units of g total arsenic.

	Atmosphere	*Overland Flow*			*Seepage*
Interval	Loading	Marsh Drain Discharge	Street Drain Discharge	Outlet Discharge	Net Gain or Loss
Summer 6/20/78-8/28/78	121	0	5	0	-2598
Fall 8/28/78-11/6/78	122	0	2	0	-1474
Winter 11/6/78-2/8/79	216	0	<1	0	- 899
Spring Runoff 2/8/79-4/23/79	170	645	6	0	+ 339
Runoff-Outflow 4/23/79-6/18/79	199	248	9	2426	- 542
TOTALS	828	893	22	2426	-5174

A study was undertaken to establish the amounts of arsenic in the surficial sediments of the basin. The results are given in Figure 10. Values for the two deepest portions of the lake are from the 0.00-0.05 m layer of the sediment cores portrayed in Figures 8 and 9. The remaining values represent the mean of five samples taken at each site. The standard deviation of these averaged 15% of the mean.

It can be seen from Figure 10 that only the wave washed northeast shore of the lake had concentrations that could be considered in the range of background values. The level of arsenic elsewhere was two to six times higher than the pre-weed treatment concentrations observed in deep portions of the cores shown in Figures 8 and 9. These data demonstrate that arsenic contamination occurs in 85-90% of the surficial sediments. The highest concentrations were found in the deep portions of the north and south basins.

A laboratory experiment was conducted to obtain an approximation of the concentration of arsenic to be expected in the water column over contaminated sediments of the lake. The sediments used in the experimental units were obtained from the deep portion of the south basin. The mean sediment value for all units was 288 μg As g^{-1} dry weight. The dissolved oxygen in the aerobic treatment averaged 9.0 mg l^{-1}; in the anoxic treatment it averaged 0.4 mg l^{-1} for the first 58 days and 8.7 mg l^{-1} after aeration. The mean temperature in all units for the duration of the experiment was 14.8° C. The data for arsenic in the water columns of the experimental units is given in Table 6 of the Appendix.

Figure 10. Concentrations of arsenic ($\mu g\ g^{-1}$ dry weight) in the surficial sediments of Lake Lansing, Michigan, June 1979.

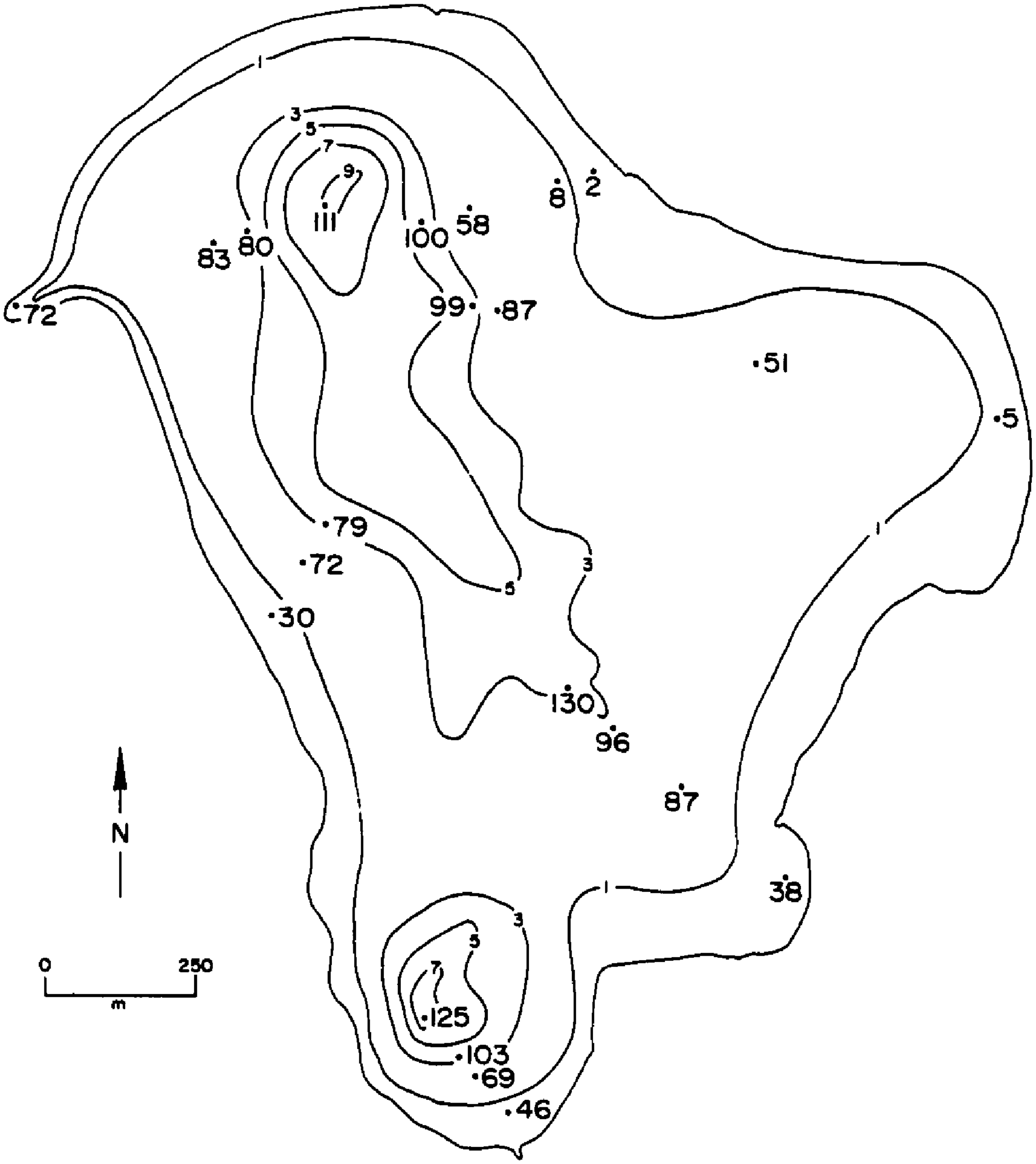
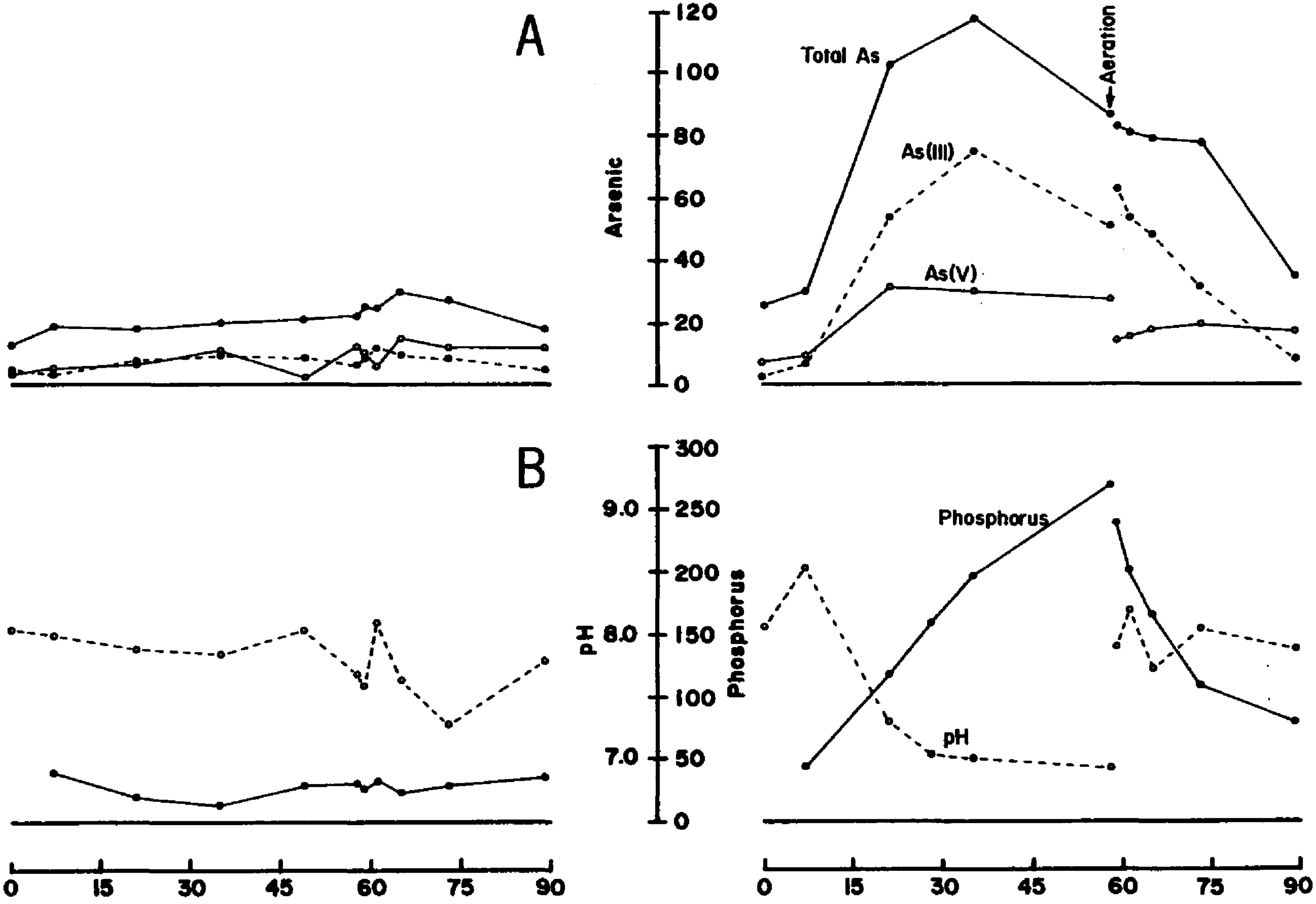

1
3
5
7
9
111
100
58
8
2
83
80
72
99
87
51
5
79
72
30
130
96
87
38
125
103
69
46
N
0
250
m

Figure 11 shows the results of the experiment; individual points for the *righthand series* represent the mean of four units. The aerobic treatment (*lefthand series*) shows only minor changes for the parameters measured. Arsenic values (μg As l^{-1}) with the range followed by the mean were: total arsenic, 13.9-30.0, 21.7; arsenic (III), 3.4-12.0, 7.4; arsenic (V), 2.9-15.0, 8.6. Total phosphorus (μg PO_4-P l^{-1}) ranged from 15-41, with a mean value of 29. The pH ranged from 7.3 to 8.1. The anoxic treatment showed marked variations. Total arsenic began at 25.5 μg As l^{-1} and increased slowly for the first seven days. Between day seven and 21 it showed the greatest rate of increase; thereafter the rate declined. The maximum value of 117.0 μg As l^{-1} was reached on day 35. From that peak concentration, there was a steady decrease for 14 days; this continued at approximately the same rate for an additional 14 days after aeration. The greatest decrease occurred during the last 16 days of the experiment. The final total arsenic concentration was 35.0 μg As l^{-1}. Arsenic (III) displayed the same general trend as total arsenic during the anoxic portion of the experiment. The initial As(III) value was 2.5 μg As l^{-1} and maximized at 74.8 μg As l^{-1} on day 35. After an initial increase following aeration, As(III) showed a fairly constant decrease for the remainder of the experiment, ending at 8.1 μg As l^{-1}. Arsenic (V) began at 7.1 μg As l^{-1} and increased slowly during the first seven days. Between days seven and 21 it increased the greatest amount, reached its maximum on day

Figure 11. Variation in the chemical composition of water overlying deep water sediments from the south basin of Lake Lansing for 89 days in experimental tanks. *Lefthand series*: aerated treatment; *Righthand series*: anoxic treatment, aerated on day 58. A, arsenic concentrations for the (III), (V), and total forms in μg l^{-1}; B, pH and concentrations of total phosphorus in μg l^{-1}.


A
B
Arsenic
0
20
40
60
80
100
120
Total As
As(III)
As(V)
Aeration
pH
Phosphorus
7.0
8.0
9.0
0
50
100
150
200
250
300
0
15
30
45
60
75
90

21 (31.1 μg As l^{-1}), then it remained relatively constant until aeration. Aeration caused a significant decline in As(V). It slowly increased thereafter, reaching a final value of 17.4 μg As l^{-1}. Total phosphorus behaved differently from arsenic by continually increasing throughout the low oxygen period. Phosphorus began at 44 and reached 271 μg PO_4-P l^{-1} on day 58. Following aeration, there was initially a rapid decrease which lessened with time. On day 89 the total phosphorus was 81 μg PO_4-P l^{-1}. The pH rose during the first week of anoxic conditions; daily N_2 purging during this interval drove off free CO_2 formed by respiration. After that, the units were purged only at sampling times. The pH declined to 7 by day 28 and remained near that value until day 58. Aeration caused a significant increase in pH, perhaps by the liberation of free CO_2.

The experimental sediments contained a somewhat elevated arsenic concentration as compared to the surficial sediments of Figure 10. Nevertheless, the results of the laboratory experiment suggest that concentrations of <30 μg As l^{-1} would be expected in the water column of the lake, if the water column over contaminated sediments were predominately aerobic. Additionally, concentrations on the order of three to four times higher would be expected if the water column over those same sediments were anoxic for three or more weeks. These expectations for the lake would hold if external loading to the water column (stream discharge, atmospheric loading, and seepage) were small or negligible. That was the case for Lake Lansing. The maximum external loading occurred during the interval 2/8/79 to 4/23/79, delivering 821 g of arsenic. Mixed and held in the volume of the lake, this amount of arsenic would result in a concentration increase of 0.2 μg As 1^{-1}. Loading in other intervals of the year had a substantially smaller impact on concentration in the water column.

Data for the total arsenic in the different compartments of Lake Lansing are presented in Table 3. A range of concentrations on the order of 5-25 μg As 1^{-1} was observed for all water strata excluding 7/31/78. On that date, total arsenic was 87 and 115 μg As 1^{-1} for the lower pelagial water in the north and south basins, respectively.

Table 3. Concentrations of total arsenic (μg As l^{-1}) in Lake Lansing, Michigan.

Date	*Littoral & Upper Pelagial Water*	*Lower Pelagial Water*	
		North Basin	South Basin
7/17/78	17.0	24.0	14.0
7/31	26.0	87.0	115.0
8/14	19.0	21.8	14.7
8/28	22.0	24.0	19.0
10/9	19.6	18.7	18.5
10/23	17.5	17.6	15.5
11/6	14.9	13.9	13.1
1/24/79	11.0	11.0	
2/8	11.7	11.0	11.3
4/23	9.0	8.9	7.2
5/7	10.0	10.5	11.2
5/21	16.3	3.4	14.2
6/18	10.7	12.0	11.2
7/2	23.0	5.6	11.1
7/16	18.4	19.2	22.2
7/30	23.0	23.9	22.5
8/13	11.2	16.2	19.4
8/27	5.4	17.0	21.0
9/17	10.0	8.0	8.7

DISCUSSION

The amount of data on the concentrations of arsenic in sediments of lakes is rather extensive. Seydel (1972) reports Lake Superior surface sediments as ranging from 2.8-5.4 ppm As while Lake Michigan sediments ranged from 7.2-28.8 ppm As. She used Lake Superior as a comparison to Lake Michigan assuming the former to be relatively unpolluted. Walters, et al. (1974) found a core from Lake Erie to be greatly enriched with mercury and copper but not with arsenic; they reported a maximum of 2.5 ppm. Galloway and Likens (1979) reported on atmospheric enhancement of metal deposition to sediments of Woodhull Lake, New York. They do not include arsenic as one of those being enriched; the core had values of 3.12 to 10.4 mg As kg^{-1}. Ruppert, et al. (1974) took 98 sediment grab samples from Chautauqua Lake, New York and compared those to two bedrock and soil samples from that area. They concluded that the arsenic values of the lake sediments were not from natural sources but were the result of sodium arsenite treatment during the period 1955-1963. Arsenic concentrations for 96 of the samples ranged from <0.5-58.75 ppm, while two other samples had values of 140 and 306 ppm As. The mean for all samples was 22.1 ppm. Wagemann, et al. (1978) report sediment arsenic concentrations for five lakes in the vicinity of Yellowknife, Northwest Territories, Canada. Two of those lakes, Kam and Keg, were known to be contaminated with arsenic as a consequence of gold mining activities. Ten sediment grab samples (top 0-20 cm) ranged from 6 to 3500 ppm As by dry weight. Three other lakes in the same area were chosen as reference lakes for the study; they had sediment concentrations which ranged from 19-105 ppm As. Kobayashi and Lee (1978) studied 15 sediment cores from five Wisconsin lakes that had been extensively treated with sodium arsenite for weed control. Surface sediment concentrations (to 5 cm depth) ranged from 10 μg As g^{-1} in Lake Mendota to 659 μg As g^{-1} in the south bay of Big Cedar Lake. Typically concentrations were less than 300 ppm As. In all of the cores, arsenic concentration fell to 10 ppm or less at depths below anthropogenic influence. Arsenic concentrations for 14 surface sediments (0-1 cm) from Lake Washington ranged from 15-210 ppm As; these averaged 81 ppm (Crecelius, 1975). Five sediment cores showed generally higher concentrations of arsenic near the surface. It decreased with depth to the background concentration of about 10 ppm As.

From the above, it is apparent that the concentration that constitutes anthropogenic arsenic contamination in lake sediments is site specific. The data for the cores in Lake Lansing show background to be in the range of 17-20 μg As g^{-1} dry weight. Contamination of the lake in 1957 was reflected in the elevated arsenic concentrations in the upper 0.5 m of cores; the maximum concentrations which occur there (over 330 ppm As) are 18 times greater than background. In the depth interval between background and peak concentrations associated with weed treatment, there was a slight but distinct elevation of arsenic content in both cores that were studied. While this increase (cf. Figures 8 and 9) may be due to the downward migration of arsenic that was applied to the lake, it should be noted that the initial rise from background can be correlated in time with early immigration and commercial development of the drainage basin. In particular, coal-burning locomotives began to move along the rail route less than 100 m from the south shore of the lake in 1878 (Raphael, 1958). The watering-station located there was a regular stop. Implicating arsenic from the coal of these trains as the primary cause for the rise from background would require a mean sedimentation rate of approximately 1 cm per year; based on the data, this is not an unrealistic estimate. Further, sediments in the south basin of the lake rose from background to higher concentrations at that time than did sediments in the more remote north basin. Superimposed on that arsenic that may have fallen out from early coal-fueled locomotives, was whatever contribution that may have been made from the volcanic ash of Krakatoa that erupted in 1883.

The data from the deep sediment cores can be used to predict how much longer it will take for the surficial sediments of those areas to once again reach background levels (17-20 ppm As). Using the calculated sedimentation rates for the two basins, Table 4 was constructed. From these data linear regression equations were derived for each of the

Table 4. Sediment arsenic concentrations with depth and the number of years since the sodium arsenite treatment in 1957. Years since treatment based on sedimentation rates of 1.1 cm yr^{-1} for the north basin and 0.7 cm yr^{-1} for the south basin.

	North Basin		*South Basin*	
Depth (cm)	Total As ($\mu g\ g^{-1}$)	Years since treatment	Total As ($\mu g\ g^{-1}$)	Years since treatment
0-5	111	22	125	22
5-10	160	18	175	15
10-15	181	14	251	7
15-20	226	10	335	0
20-25	284	6		
25-30	337	0		

basins.

North basin: $\hat{y} = 337 - 10.3(x);\ r^2 = 0.99$

South basin: $\hat{y} = 326 - 9.5(x);\ r^2 = 0.99$

where $\hat{y}$ is the arsenic concentration in μg As g^{-1} and x is the number of years since treatment. The predicted time to reach background levels would be 31 years in the north basin and 32 years in the south basin (assuming constant sedimentation rates). This means that by the late 1980's the contamination from treatment would be ameliorated in those deep water areas. However, this does not imply that the water column will no longer be affected by the herbicide contamination after this date. This prediction can not be applied to the surficial shallow water sediments since the sedimentation rate in these areas is unknown. These contaminated sediments could continue to serve as a source of arsenic to the water column long after its amelioration in the deep basins.

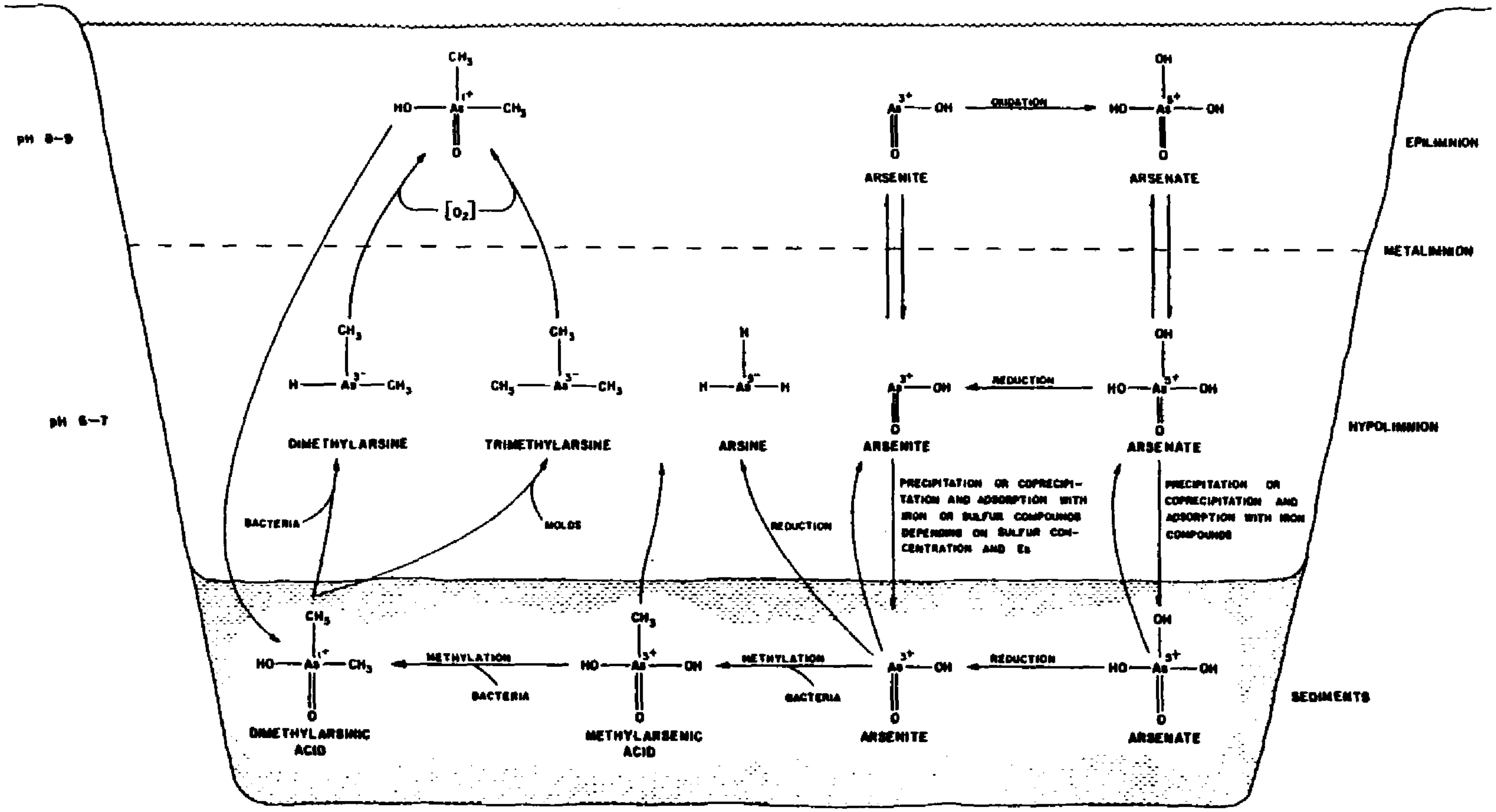
Surficial sediments of the lake, excluding the near northeast shore, showed arsenic burdens of two to six times the background level. They also showed, in nearly all cases, an increase in concentration with increasing depth of the lake water. These samples were taken from a variety of sediment types. The lowest concentrations were found in the shallow region of the lake's northeast shore. Prevailing winds during the open-water season arise from the southwest, blowing across the long axis of the lake. Fine-grained organic particles are swept by wave action away from the northeast shoreline leaving an area of sand. The greatest flux of seepage is thought to occur in this highly permeable area as well. This in conjunction with wave-generated currents could be important in moving arsenic from the shore.

Crecelius, et al. (1975) and Ruppert, et al. (1974) found the highest concentrations of arsenic in sediments that were predominated by sand. However, they both conclude that arsenic is more highly correlated with smaller particle sizes than sand. Those disparities as well as the findings here suggest that arsenic concentrations are not necessarily a function of sediment type. In Lake Lansing, the distribution of arsenic in surficial sediments appears to be a function of where it was placed during weed treatment and its transport by currents to deeper portions of the lake.

Annual mass balance budgets for arsenic in lakes are scarce in the literature. Using procedures for input-output estimates similar to the procedures used in this study, Crecelius (1975) concluded that the sediments of Lake Washington trapped 55% of the annual arsenic input. The lake served as a sink for the element. Conversely, the annual budget for Lake Lansing showed that internal loading of the water column from the sediments resulted in an annual loss from the lake that was greater than the sum of the inputs. Concentrations of arsenic in water exiting Lake Lansing, controlled by rates of sediment-water column exchange, were an order of magnitude higher than concentrations in input water thus accounting for the imbalance.

A proposed cycle for arsenic in a stratified lake is presented in Figure 12 (Ferguson and Gavis, 1972; Wood, 1974). Transformations include oxidation-reduction and ligand

Figure 12. A proposed cycle for arsenic in a stratified lake (modified from Ferguson and Gavis, 1972; Wood, 1974).


pH 8–9
EPILIMNION
METALIMNION
pH 6–7
HYPOLIMNION
SEDIMENTS
[O2]
ARSENITE
OXIDATION
ARSENATE
DIMETHYLARSINE
TRIMETHYLARSINE
ARSINE
ARSENITE
REDUCTION
ARSENATE
PRECIPITATION OR COPRECIPITATION AND ADSORPTION WITH IRON OR SULFUR COMPOUNDS DEPENDING ON SULFUR CONCENTRATION AND Eh
PRECIPITATION OR COPRECIPITATION AND ADSORPTION WITH IRON COMPOUNDS
BACTERIA
MOLDS
REDUCTION
DIMETHYLARSINIC ACID
METHYLATION
BACTERIA
METHYLARSENIC ACID
METHYLATION
BACTERIA
ARSENITE
REDUCTION
ARSENATE

exchange. Transfers from solution to solid phases and vice-versa are shown. The lefthand side of the figure depicts organoarsenical pathways; the righthand side shows inorganic interconversions. Methylation of arsenic compounds is thermodynamically unfavorable in water and can only occur by biological mediation (Ferguson and Gavis, 1972). However, the presence of these forms is not precluded by biological activity since both methylarsenic acid (MAA) and dimethylarsenic acid (DMA) are synthesized pesticides and may be in natural waters as a result of agricultural and home use. Measurements of ambient concentrations of organoarsenicals have been limited by the lack of appropriate speciation methodologies that are economically and routinely feasible (Holm, et al., 1979). Detection of gaseous arsines is difficult since they can be rapidly oxidized; dimethylarsine burns spontaneously in the air (Peoples, 1975). Braman and Foreback (1973) were the first to report methylated arsenicals in natural waters. They reported values from four small lakes in and around Tampa, Florida that ranged from 0.5 to 0.22 ppb for MAA and 0.15 to 0.62 for DMA (cacodylic acid). They concluded that the MAA was generally present in smaller concentrations than DMA since it was only an intermediary in the methylation sequence. DMA, unless subjected to bacterial oxidation (since it is extremely resistant to chemical oxidation), was thought to be very persistent in natural waters. Braman (1975) has reported a lake value of 0.14 ppb for trimethylarsine. The reactions and cycling of these organoarsenicals in freshwater systems has yet to be thoroughly investigated.

The inorganic interconversions shown in Figure 12 (Ferguson and Gavis, 1972) suggest that arsenite, As(III), tends to be oxidized to arsenate, As(V), in aerobic epilimnetic water. In this portion of a lake, arsenate is most likely to exist as the anion, $HAsO_4^{2-}$ (Ferguson and Gavis, 1972). Chemically similar to phosphate, it can be adsorbed, occluded or precipitated with hydrous ferric oxides. Thus ferric iron may control arsenate solubility in oxic portions of a lake basin. Wagemann (1978) has predicted that barium, chromium, and copper could also form insoluble metal complexes with arsenic. He feels that barium is the most convincing candidate capable of holding arsenic to rather low concentrations under pH and Eh conditions of aerated freshwaters. Presently, studies of arsenic and barium in natural waters are too few to provide an assessment of his theoretical predictions.

Figure 12 suggests that turbulent dispersion and convection can transport some of the arsenate and metal complexes into an oxygen-depleted hypolimnion. Once there, reduction of these compounds is likely to take place in the water or on the surface of anaerobic sediments. Depending on the pH, Eh, iron and sulfur concentrations within these lower strata, arsenite, insoluble arsenic sulfides or ferrous arsenic sulfides could result. Ferguson and Anderson (1974) report that at low Eh in the presence of sulfide (S^{2-}), As(III) should be effectively removed from the water column as insoluble sulfides. Arsenic (V) is not similarly affected.

Mortimer (1941,1942) has demonstrated the importance of the aerated microzone at the sediment-water interface in controlling the release of phosphorus, iron, and sulfur to the water. In his experiment, the release of iron and phosphorus increased markedly as oxygen was depleted at the sediment surface and the redox potential decreased. This was explained by the reduction of ferric iron in complexes holding phosphate. Ferrous iron and phosphate appeared in the water column simultaneously. As the Eh continued to fall, sulfate concentrations decreased. Sulfate is reduced to sulfide at a substantially lower Eh than the reduction of ferric to ferrous iron (Hutchinson, 1957). Once the Eh has fallen low enough for sulfide production, ferrous sulfide can be formed which is exceedingly insoluble at neutral or alkaline pH (Wetzel, 1975). It appears that considerable quantities of iron and sulfur were lost to the sediments as FeS in his system. As these events proceeded, the concentration of phosphate continued to rise. A companion sediment-water system was aerated to provide a comparison in his experiment. His results are relevant to this study, since he demonstrated the control exerted by ferric iron on the migration of phosphate across an aerated sediment surface. The control of sulfides on ferrous iron concentration in anaerobic water overlying sediments was supported by his data.

The model of Figure 12 and the work of Mortimer and others regarding the cycles of iron, sulfur, and phosphorus can be used to develop an hypothesis regarding the results of the laboratory experiment obtained in this study. Arsenic here was dominated by inorganic species; an organic fraction was detected by the analytical procedures used. Arsenic and phosphorus did not increase over time in water above an aerated sediment surface. In anoxic treatment chambers both increased. The dramatic increase in total arsenic was due principally to an increase in As(III), derived either directly from the sediments or from the reduction of As(V). It is proposed that ferric iron controlled solubility of arsenic and phosphorus in the aerated water-sediment system; reduction to ferrous iron allowed release to the water column in the anoxic treatment. Sulfide accumulated in low oxygen chambers as anoxia persisted. Hydrogen sulfide was first noted by odor on day 35. The increase in sulfide concentration was expected to lag in time behind ferric iron reduction because of lower Eh optima for its accumulation. The arsenic maximum of day 35 was depressed thereafter by the formation of insoluble compounds of As(III) and sulfide. Predicted by the hypothesis, phosphorus continued to increase in water of the anoxic treatment units until they were aerated.

Aeration after 58 days caused dramatic changes in the concentrations of inorganic arsenic species and phosphorus in anoxic chambers. The initial rise in As(III) is ascribed primarily to the oxidation of sulfides to sulfates and concomitant release of As(III). The initial rapid decline in As(V) is assigned to its complexing and precipitation with newly formed hydrated ferric oxides. The oxidation of ferrous to ferric iron is extremely rapid in the near neutral pH range of these waters (Stumm and Morgan, 1970). Phosphorus was likely removed from the system by the same mechanism in the manner of the work of Mortimer (1941,1942). Wauchope (1975) studied the affinities of ferric hydroxides for arsenate and phosphate, and showed a greater affinity for the former. The total arsenic declined gradually as aeration continued; As(III) was slowly converted to As(V) and removed in combination with ferric iron. Phosphorus slowly declined by removal with this compound as well.

Data from the laboratory experiment led to expectations regarding levels of arsenic to be observed in water of the lake. With periods of three to five weeks of anaerobiosis in the hypolimnion of the north and south basins, arsenic concentrations on the order of 100 $\mu g\ l^{-1}$ were predicted, depending on the availability of the sulfide ion. An abundance of sulfide or periodic aeration of the hypolimnion during high winds in spring or summer were expected to depress the concentration. Ferric iron control on solubility was predicted for the latter case. Thermal and oxygen stratification of the lake were periodically disrupted during the summers of this study. Data from the field are not sufficient to sort out the proposed control on arsenic concentrations in the hypolimnions due to sulfide and ferric iron. That conditions of stable anaerobiosis similar to those observed in the laboratory did in fact exist in the hypolimnions in July of 1978 was suggested by observed concentrations near 100 μg As 1^{-1} at the end of that month.

The epilimnion-littoral region of Lake Lansing and the water column at overturn had arsenic concentrations on the order of 5-25 μg 1^{-1}. Anaerobic conditions did not develop in the lake during the winter of this study; the arsenic concentration was in the mid-portion of the range at that time. These results were expected from the laboratory work with sediments held under aeration. However, the substantial portion of As(III) in the aerobic treatment would not be predicted from the model in Figure 12. This result is similar to the findings in seawater, in which the thermodynamically unfavorable arsenite occurs at concentrations above those that would be expected (Johnson, 1972; Johnson and Pilson, 1975; Andreae, 1979). These findings have been explained as the consequence of biologically mediated reactions in which arsenate (V) is reduced to arsenite (III). Brunskill, et al. (in press) working in freshwater found that little or no reduction of arsenate occurred under aerobic conditions and rapid algal growth. This is contrary to the results of Johnson and Burke (1978), who found a reduction of arsenate during marine phytoplankton blooms. It is clear that this inconsistency and certain aspects of the proposed arsenic cycle in lakes awaits experimental results that will provide clarification.

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APPENDIX

Table A-1. Arsenic inputs from marsh drains during 6/20/78 to 6/18/79.

Interval	Discharge (m^3)	Total As concentration (g As m^{-3})	Total As input for interval (g As)
6/20/78 - 2/8/79	0	-	0.0
2/8/79 - 4/23/79	402909	0.0016	644.7
4/23/79 - 5/7/79			
4/23-4/27	17470	0.0016	28.0
4/27-5/7	79886	0.0020	159.8
5/7/79 - 5/21/79			
5/7-5/11	17004	0.0020	34.0
5/11-5/21	23734	0.00086	20.4
5/21/79 - 6/18/79			
5/21-6/8	7266	0.00086	6.2
6/8-6/18	0	-	0.0

Table A-2. Arsenic inputs from street drains during 6/20/78 to 6/18/79.

Interval	Discharge (m^3)	Total As concentration (g As m^{-3})	Total As input for interval (g As)
6/20/78 - 7/5/78	176	0.0092[1]	1.6
7/5/78 - 7/17/78	0	-	0.0
7/17/78 - 7/31/78	104	0.0092	1.0
7/31/78 - 8/14/78	118	0.0092	1.1
8/14/78 - 8/28/78	145	0.0092	1.3
8/28/78 - 10/9/78	479	0.0023[2]	1.1
10/9/78 - 10/23/78	81	0.0023	0.2
10/23/78 - 11/6/78	70	0.0023	0.2
11/6/78 - 1/24 79	178	0.0023	0.4
1/24/79 - 2/8/79	0	-	0.0
2/8/79 - 4/23/79	639	0.0092	5.9
4/23/79 - 5/7/79	477	0.0092	4.4
5/7/79 - 5/21/79	292	0.0092	2.7
5/21/79 - 6/18/79	242	0.0092	2.2

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1. Average of six storms that occurred during the spring and summer.

2. Average of six storms that occurred during the fall.

Table A-3. Arsenic losses from the outflow during 6/20/78 to 6/18/79.

Interval	Discharge (m^3)	Total As Concentration (g As m^{-3})	Total As output for interval (g As)
6/20/78 - 4/23/79	0	-	0.0
4/23/79 - 5/7/79	106574	0.0111	1183.0
5/7/79 - 5/21/79			
5/7-5/11	39104	0.0111	434.1
5/11-5/21	61448	0.0121	743.5
5/21/79 - 6/18/79			
5/21-6/8	5365	0.0121	64.9
6/8-6/18	0	-	0.0

Table A-4. Arsenic inputs to the lake surface from atmospheric bulk fallout.

Interval	Number of days in interval	Rate of As input (g As day^{-1})	Total As input for interval (g As)
6/20/78 - 7/5/78	15	1.748[1]	26.2
7/5/78 - 7/17/78	12	1.748	21.0
7/17/78 - 7/31/78	14	1.748	24.5
7/31/78 - 8/14/78	14	1.748	24.5
8/14/78 - 8/28/78	14	1.748	24.5
8/28/78 - 10/9/78	42	1.748	73.4
10/9/78 - 10/23/78	14	1.748	24.5
10/23/78 - 11/6/78	14	1.748	24.5
11/6/78 - 1/24/79	79	2.302[2]	181.9
1/24/79 - 2/8/79	15	2.302	34.5
2/8/79 - 4/23/79	74	2.302	170.3
4/23/79 - 5/7/79	14	9.565	133.9
5/7/79 - 5/21/79			
5/7-5/18	11	1.524	16.8
5/18-5/21	3	1.544	4.6
5/21/79 - 6/18/79			
5/21-5/23	2	1.544	3.1
5/23-6/18	26	1.558	40.5

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[1] Average value for nine intervals from 6/18/79 to 11/14/79.

[2] Average value for 13 intervals from 4/25/79 to 11/14/79.

Table A-5. Net gain or loss of arsenic due to seepage during 6/20/78 to 6/18/79.

Interval	Seepage (m^3)	Total As concentration[1] (g As m^{-3})	Total As gain or loss for interval (g As)
6/20/78 - 7/5/78	-41768	0.0195	-814.5
7/5/78 - 7/17/78	-21759	0.0195	-424.3
7/17/78 - 7/31/78	-39589	0.0195	-772.0
7/31/78 - 8/14/78	-30272	0.0195	-590.3
8/14/78 - 8/28/78	+1768	0.0017	+3.0
8/28/78 - 10/9/78	-72011	0.0208	-1497.8
10/9/78 - 10/23/78	+13933	0.0017	+23.7
10/23/78 - 11/6/78	0	0.0017	0.0
11/6/78 - 1/24/79	-44147	0.0130	-573.9
1/24/79 - 2/8/79	-28484	0.0114	-324.7
2/8/79 - 4/23/79	+199440	0.0017	+339.0
4/23/79 - 5/7/79	+14528	0.0017	+24.7
5/7/79 - 5/21/79	+27240	0.0017	+46.3
5/21/79 - 6/18/79	-45400	0.0135	-612.9

1. Since lake sampling did not begin until 7/17/78, an average value of six 1978 littoral and upper pelagial water column concentrations was applied to intervals from 6/20/78 to 8/14/78. When the lake was gaining water from seepage (a positive value), an average value from the total arsenic concentrations of the marsh drains was used. All other values represent the mean littoral and upper pelagial water column concentrations of the interval in question.

Table A-6. The various forms of arsenic in the water of the experimental units (μg As l^{-1}).

	Aerobic Treatment				*Anoxic Treatment*			
Day	As(III)	As(V)	Organic	Total	As(III)	As(V)	Organic	Total
0	4.5	2.9	6.5	13.9	2.5	7.1	16.0	25.5
7	3.4	5.3	10.3	19.0	6.7	9.6	13.5	29.8
21	7.6	6.1	4.3	18.0	53.5	31.3	17.3	102.0
35	9.0	11.0	0.0	20.0	74.8	29.8	12.5	117.0
58	6.0	12.0	4.0	22.0	51.0	27.3	8.3	86.5
59[1]	8.0	10.0	7.0	25.0	62.5	14.5	5.5	82.5
61	12.0	6.0	7.0	25.0	53.3	15.3	12.0	80.5
65	9.4	15.0	5.6	30.0	48.0	17.8	12.7	78.5
73	8.6	12.0	6.4	27.0	31.3	19.3	27.3	77.8
89	4.6	12.0	1.4	18.0	8.1	17.4	9.6	35.0

[1] After the sampling on day 58 the anoxic units were aerated for the remainder of the experiment.