# Inland Lakes Sediment Trends: Sediment Analysis Results for Five Michigan Lakes

## Final Report: 1999-2000

Cass Lake
Elk Lake
Gratiot Lake
Gull Lake
Higgins Lake

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## Acknowledgements

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## Introduction

Contaminated sediments can directly impact bottom-dwelling organisms and represent a continuing source for toxic substances in aquatic environments that may impact wildlife and humans through food or water consumption. Therefore, an understanding of the trends of toxic chemicals (e.g., polychlorinated biphenyls, Hg) accumulation in the environment is necessary to assess the current state and potential future problems of Michigan's surface water quality. A common fate of chemicals in a lake is to become deposited on the lake bottom. As this deposition occurs over time, sediments in lakes become a chemical tape recorder of the temporal trends of toxic chemicals in the environment as well as of general environmental change over time. Sediment trend monitoring is consistent with the framework for statewide surface water quality monitoring outlined in the January 1997 report prepared by the Michigan Department of Environmental Quality entitled, "A Strategic Environmental Quality Monitoring Program for Michigan's Surface Waters" (Strategy). A key goal is to measure trends in the quality of Michigan's surface waters, and one activity designed to examine these trends is the collection and analysis of high-quality sediment cores. This report details the activities and findings of the first year of the sediment trend component of the Strategy.

## Summary

Sediment cores were collected from five lakes throughout the state of Michigan, for the purpose of evaluating the spatial and temporal variations in water quality of lakes in Michigan. Sediment cores were collected from one site in each lake, dated with $^{210}$Pb and $^{137}$Cs and analyzed for a suite of metals and organic compounds. Analysis for a suite of metals rather than just target anthropogenic metals (e.g. Pb, Cu) allowed interpretations about the sources of different chemicals to be made. Selected results are as follows:

- with the exception of Cass Lake, sediment cores reached the 1800s,
- Cass Lake has a very high sedimentation rate and the sediment core only reached 1971,
- with the exception of Cass Lake, background concentrations were reached,
- although there were indications of bioturbation, records of chemical accumulation were not obscured,
- many metal accumulation rates increase from background level beginning between 1850 and 1900, increase until the 1970s and decrease to the present,
- there appear to be four major factors controlling chemical loading to the inland lake sediments: changes in watershed input, atmospheric input, biogeochemical dynamics, and direct anthropogenic input,

- changes in watershed input are strongly influenced by changes in land use (e.g. logging), and often are the primary influence on loading of aluminum, calcium, cobalt, potassium, magnesium, nickel, titanium, and vanadium,
- changes in atmospheric input are influenced by industrial sources and environmental legislation and strongly influence the loading of lead,
- biogeochemical dynamics are influenced by the redox status of the sediments, and influence trends in iron, manganese and arsenic,
- direct anthropogenic inputs include industrial activities such as mining, as well as local events, such as fertilizing, and influence the loading of cadmium, copper, chromium, lead and zinc,
- fact sheets for each lake provide further detail on specific trends of each metal.

# Methods

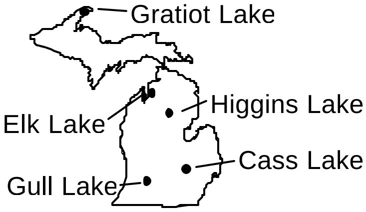

**Fig. 1.** Location of five lakes sampled in Michigan in the summer of 1999.

Further detail on all methods is presented in Appendix B. Sediment cores were collected from Cass, Elk, Gratiot, Higgins and Gull Lakes in the summer of 1999 (Fig. 1). Sediment cores were collected from the deepest portion of each lake using a MC-400 Lake/Shelf Multi-corer. Cores were described and examined for color, texture, and signs of zoobenthos and other disturbance. Cores were extruded and sectioned at 0.5 cm intervals for the top 5 cm of the core, and at 1 cm intervals for the remainder of the core.

$^{210}$Pb was measured (Freshwater Institute in Winnipeg, Manitoba, Canada) on one sub-core from each lake to determine porosity, accumulated dry mass, sedimentation rates, sediment ages and focusing factors. Results from Elk Lake were verified using $^{137}$Cs.

Sediments were frozen, freeze-dried and digested by nitric acid in a CEM-MDS-81D microwave. Standard reference material and procedural blanks were processed to test for accuracy and contamination. The concentrated-acid digests were filtered through an acid washed, distilled-deionized water (DDW) rinsed 0.40 µm polycarbonate filter. Samples were then analyzed using a Micromass Platform inductively coupled, plasma, mass spectrometer with hexapole technology (ICP-MS-HEX). Sediments were analyzed for a suite of metals and metalloids including Mg, Al, K, Ca, Ti, V, Mn, Fe, Co, Ni, Cu, Zn, As, Cd, Ba, Pb, and U.

A method is currently being developed for mercury analysis. Preliminary analyses indicated that memory effects were present, and a therefore experiments were preformed to determine a suitable rinsing technique. Because the digested sediment solutions are very concentrated, solutions are generally analyzed with a 1:10 dilution, with the standards matrix matched to the samples. However, because of the very low concentrations of mercury, and 1:10 dilution is too high. Therefore it must be determined if the matrix of the sample will suppress the mercury signal at lower dilutions. If so, a hydride generation technique will be used that removes the sample from the matrix and provides greater sensitivity.

Another sub-core was sectioned and used for analysis of organic contaminants. There was insufficient material for analysis in the topmost sediments, so the first two sections were combined, and the third and fouth sections were combined. Briefly, 40 g sediment (wet) was homogenized with ≈160 g of anhydrous sodium sulfate and extracted with methylene chloride and hexane (3:1, 400 mL) in a Soxhlet apparatus for 16 h. Sulfur was removed by treating the extracts with activated copper granules. Extracts were then concentrated and passed through a glass column packed with activated Florisil (10 g). The first fraction, eluted with 100mL hexane, contained PCBs, *p,p'*-DDE and HCB. The second fraction was eluted with 100 mL of 20% methylene chloride in hexane contained hexachlorocyclohexane (HCH) isomers (α-, β-, γ-), *p,p'*-DDD, *p,p'*-DDT and chlordane compounds, toxaphene and 16 polycyclic aromatic hydrocarbons (PAHs). The third fraction was eluted with 100 mL of 50% methanol and 50% methylene chloride contained nonylphenol, octylphenol and other polar compound. TCMX and PCB 30 were spiked as internal standards to check for recoveries of analytical procedure. Other QA/QC procedures include, matrix spikes and analytical blanks.

The fourth sub-core was frozen and stored as an archive. This will allow for further analysis, should monies become available.

## $^{210}$Pb and sedimentation rates

$^{210}$Pb analysis provides information on sediment age, rates of sedimentation, and the quality of the sediment core. Results from the five lakes showed no significant disturbance in the cores. However, results indicate that some bioturbation and mixing are present near the surface of the cores. The mixing zone is determined by plotting accumulated dry mass versus log activity of $^{210}$Pb, where the slope is related to sedimentation rates and the non-linear portion near the surface is considered the mixing zone (Fig. 2). Further descriptions of mixing processes are included below.

Cass Lake has a significantly higher sedimentation rate than the other lakes, and the oldest sediments collected are from 1971 (Table 1). Because of this, background concentrations and inventories could not be calculated for Cass Lake. The oldest sediments collected from all other lakes were from the early 1800s or older (Table 1).

Two models were used to date the sediments, the constant flux, constant sedimentation rate model (CF:CS) (and a modification of this method, the segmented CF:CS), and the constant rate of supply model (CRS). The CF:CS model assumes a constant flux of $^{210}$Pb to the sediment and a constant rate of sedimentation over some period of time. Generally, the rate of sedimentation is assumed to stay the same throughout the length of the core (Fig. 2, CF:CS), but the segmented CF:CS (SCF:CS) model may be used if there is a clear change in sedimentation rate (Fig. 2, SCF:CS) (Heyvaert et al., 2000). The CRS model also assumes constant flux of $^{210}$Pb to the sediment, but does not assume that the sedimentation rate remains the same. Instead, the CRS model determines a different sedimentation rate between each depth. Some authors prefer the CRS model, finding that it gives more insight into changes in sedimentation rates (Fritz et al., 1993; Gottgens et al., 1999). However, the CRS method is particularly vulnerable to noisy data, as errors are propagated to date assignments (Heyvaert et al., 2000). There is no consensus as to which model is more appropriate in all cases (Oldfield and Appleby, 1984). However, in this study, the dates calculated with the CF:CS (Gratiot, Cass and Higgins Lakes) and SCF:CS (Gull and Elk Lakes) models corresponded well with the dates from the CRS model, with the dates generally no greater than 5 years apart in sediments younger than 1900, with smaller differences in the youngest sediments. All data are graphed with CF:CS or SCF:CS calculated dates. All dates older than 1800 were determined from data extrapolation assuming constant sedimentation rates, and should be considered estimations.

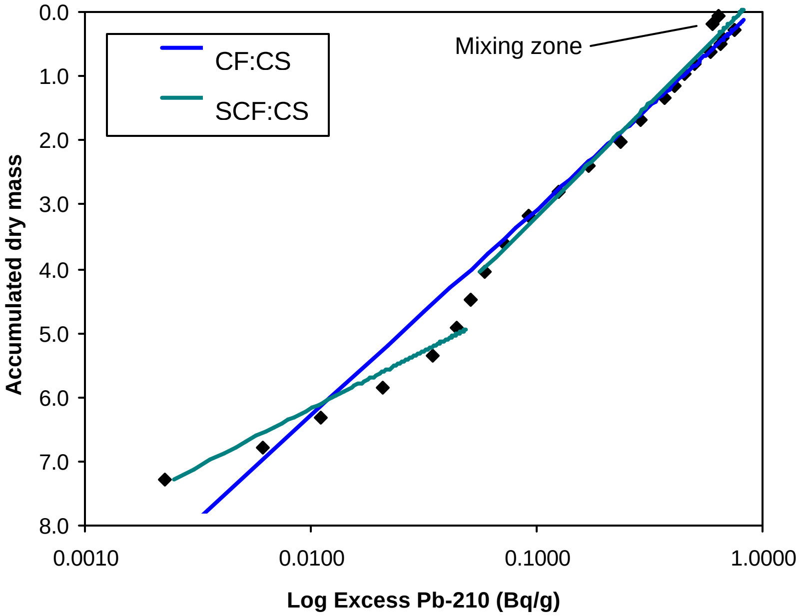

**Fig. 2.** Log of $^{210}$Pb activity (Bq/g) versus accumulated dry mass. Regression lines for the CF:CS model (blue) and the SCF:CS model are shown.

Focusing factors were determined from $^{210}$Pb data to correct for focusing, or the movement of fine-grained sediment to the deepest portion of the lake (Eisenreich et al., 1998). Focusing factors for most lakes were near two (Table 1), with the exception of Cass Lake, where the estimated focusing factor is six.

**Table 1.** Date of the oldest section, focusing factors and average sedimentation rates from sediment cores in five lakes in Michigan.

| Lake | Oldest Section (CF:CS) | Focusing Factor | Ave Sed rate ($g/m^2/y$) |
|---|---|---|---|
| Cass | 1971 | 6.00 | 3480 |
| Elk | 1279 | 2.05 | 420 |
| Gratiot | 1823 | 2.49 | 260 |
| Gull | 1496 | 1.78 | 500 |
| Higgins | 1729 | 2.02 | 240 |

## Mixing of Sediments and the Sediment Chemical Record

Resuspension of top layers of sediment and bioturbation by zoobenthos will cause the top few centimeters of sediment at the bottom of lakes to become mixed. A question that frequently arises is, “how can sediments maintain chemical trends if mixing of the top layers of sediment occurs?” It is important to understand that mixing can disturb, but not necessarily destroy the depositional record of chemical input in the sediments (Robbins, 1982; Wong et al., 1995). The degree of disturbance is a function of changes in rates of chemical inputs, the amount of bioturbation, and the sedimentation rate.

For example, in the case of no mixing and a rapid change in the amount of chemical input from high to low (Fig. 3a), there would be a sharp change in concentration recorded in the sediments (Fig 3b). If the change were slow rather than rapid (Fig. 3c), then a more gradual change in sediment concentrations would be recorded (Fig.3d).

Now, take the case in which extensive mixing occurs and that the change of rate in chemical input is slow (Fig. 3e). In this case it is possible that chemistry of the sediments in the mixed zone could be completely homogenized. At any one time the chemical concentration of the different sediment layers in the mixed zone would be the same (Fig. 3f). However, the sediments below the mixed zone would record the changes in chemical input.

The case just described is often observed for the profiles of $^{210}$Pb activity in the sediments. $^{210}$Pb is generally considered to have a constant rate of input to the sediments. Once in the sediments it is away from its source (the atmosphere), and the $^{210}$Pb decays. If mixing did not occur, then the amount of $^{210}$Pb in the sediment would decrease from the surface sediments. The rate of decrease would be a function of sedimentation rate (Fig. 3g). Because the decay rate of $^{210}$Pb can be relatively slow compared to the degree of mixing, then it is quite possible that the $^{210}$Pb activities in sediment layers of the mixed zone could be similar (Fig. 3h). In fact, the shape of the $^{210}$Pb profile in the upper sediments is one way of identifying the mixing zone.

Finally, consider the condition in which the rate of change of chemical input is relatively rapid compared to the degree of mixing (Fig. 3i). In this case, the degree of mixing is not sufficient to completely homogenize the chemical record in the sediment. Thus, the sediments in the mixed zone record changes in chemical inputs (Fig. 3j). Records of chemical change in layers of sediment in the mixed zone and no change in $^{210}$Pb activity are frequently observed in cores taken from inland lakes and large lakes (Fritz et al., 1993; Golden et al., 1993; Simick et al., 1996; Wong et al., 1995) (Fig. 3k). It should be pointed out that while the chemical record in the mixed zone would not be obscured, it would be altered. For example, if no mixing were to occur, a change in chemical inputs might look like the example shown in Figure 3l. Mixing will tend to spread out or “smear” the record and decrease the peak concentration (Fig. 3m).

In sum, while mixing tends to affect the record of chemical trends in lake sediments, it is still possible to obtain information about trends in chemical input within the mixing zone. For the lakes studied, the mixing zone is most extensive in Gratiot Lake (5 cm, which covers 8 years) and least in Elk Lake (1 cm, 4 years), with Cass, Higgins and Gull Lakes having mixing zones of ~3 cm (2, 10 and 8 years).

## Chemical Sediment Chronologies

The character of the sediment cores varied greatly between the five different lakes, due to both the local geology/soils and the trophic status of the lake. The four lakes located in the lower peninsula were rich in calcium carbonate, but varied from Cass Lake sediments, which are enriched in organic matter, and Gull and Elk Lakes, which appeared to be oligotrophic. Higgins Lake is less enriched in calcium carbonate than the other lower peninsula lakes. Gratiot Lake, located in the upper peninsula, has much lower calcium carbonate concentrations, and much higher concentrations of terrestrial elements (e.g. aluminum, iron).

Many of the metals show an increase from background levels beginning between 1850 and 1900 and often reach peak concentrations prior to this decade. Generally, chemical concentrations in the most recently deposited sediments are higher than background concentrations. Concentration profiles over time vary greatly among different metals, and among different lakes. Four major factors appear to be affecting the loading of chemicals to the lakes: changes in watershed input and within lake production, atmospheric input, biogeochemical dynamics, and direct anthropogenic input.

### Changes in watershed input and within lake production

There are two major sources of sediment in a lake: watershed (terrestrial) input and within lake production (organic and carbonate). Changes in watershed input and within lake production can affect chemical trends in two ways. First, if there is an overall increase in total sedimentation rate, but the rate of anthropogenic input remains the same, the anthropogenic input will be diluted by the increased amount of sediment, and concentrations will appear to go down. This is accounted for by examining accumulation rates (µg/cm$^2$/y), rather than concentrations. Secondly, watershed input will tend to have higher natural concentrations of metals than lake production, and changes in the proportions of these two sources can cause changes in chemical concentration trends, even if there is no change in anthropogenic input. Such changes in proportions may be due to natural (e.g. change in erosion rates due to climate change) or anthropogenic causes (e.g. increased erosion due to logging). In order to assess the effects of changing proportions of watershed input and within lake production, a terrestrial metal (e.g. aluminum) is compared to trends of other chemicals. If the trends are similar, it indicates that these processes affect the chemical.

For metals that have anthropogenic inputs, it is important to be able to differentiate the flux from anthropogenic sources and the flux from watershed sources. Typically, background accumulation rates are determined from pre-1800s samples, and are considered to remain constant throughout time (Fig 4). However, to determine a true

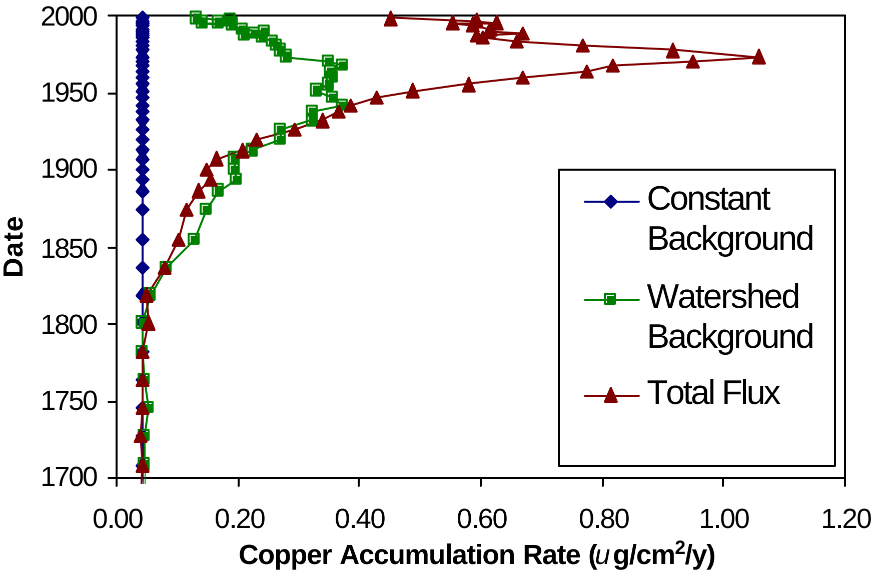

**Fig 4.** Total copper accumulation rates in Gull Lake, and background concentrations calculated with a constant value and normalized to aluminum. The amount of anthropogenic copper is the difference between total and background.

watershed background, it is necessary to use a metal:aluminum ratio. This method assumes that the metal:aluminum ratio remains the same throughout time, and a watershed background is determined for each sample separately based on the aluminum accumulation rate (Fig. 4). In this report, anthropogenic input is considered to include direct human inputs and atmospheric deposition, but does not include changing input of sediment from natural or human processes. Therefore, all graphs of anthropogenic accumulation rates have been corrected for a watershed background by normalizing to aluminum.

Elk Lake shows the most significant change in watershed input (Fig. 5). Concentrations of aluminum increase in the late 1800s until 1920, then decrease to the present, but remain above background accumulation rates. This increase in watershed input is likely due to the extensive logging and land use change in the watershed. Trends in barium, iron, potassium, magnesium, nickel, titanium, and vanadium all appear to be influenced primarily by watershed input. Plots of these metals are not shown because trends correspond to aluminum (Fig. 5). Gull Lake also shows an increase in aluminum accumulation, increasing from 1800 to 1940, remaining high until 1968, and then decreasing until the present. This trend is different than that seen in Elk Lake, but is still probably related to logging and other land use changes, including extensive development around the lake. In Gull Lake, potassium, titanium, and vanadium appear to be related to the changes in watershed input. There is no clear cause for the patterns of aluminum accumulation in Cass, Higgins and Gratiot Lakes, but they are likely related to land use changes and changes in lake productivity. In Cass Lake, cobalt, potassium, magnesium, nickel, titanium, and vanadium appear to be related to changes in watershed input; in Higgins Lake, barium and magnesium strongly correlate with aluminum, and cobalt, iron and vanadium weakly correlate; in Gratiot Lake, cobalt, magnesium, nickel and titanium strongly correlate, and vanadium and uranium correlate weakly.

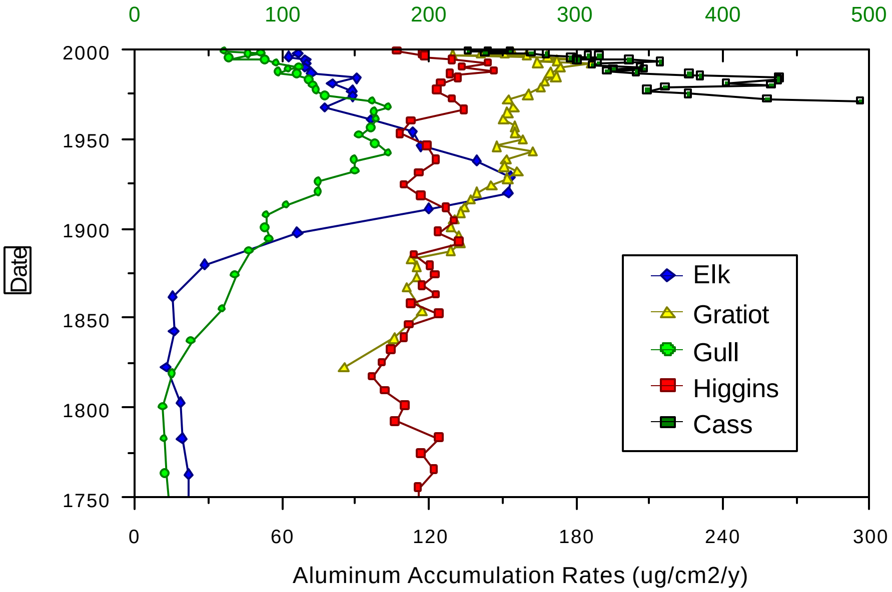

**Fig. 5.** Aluminum accumulation rates over time in five inland lakes. Cass Lake accumulation rates are plotted with the upper scale.

## Regional atmospheric input

Atmospheric input appears to be the major source of lead to inland lakes in Michigan. Indications that the primary source of a chemical to the environment is atmospheric deposition are 1) similarities in accumulation trends and 2) similar anthropogenic inventories (see explanation below).

For lead, accumulation trends follow the same pattern among lakes (Fig. 6), with accumulation rates increasing to the 1970s then decreasing to the present. The similar shape of the profiles indicates the common regional source of atmospheric deposition. The decrease in accumulation rates after the 1970s is related to environmental legislation and the subsequent removal of lead from gasoline (Eisenreich et al., 1986; Evans and Dillon, 1982; Graney et al., 1995).

Anthropogenic inventories are a measure of the total amount of contaminant input by humans per unit area (µg/cm$^2$) from the present till background concentrations are reached (Fig. 7). If atmospheric deposition is the major source of a chemical to lakes, then anthropogenic inventories should be the same in all lakes or show a regional pattern that reflects the distribution of sources of chemicals to the atmosphere. Inventories of lead among inland lakes sampled show a regional north-south trend (Fig. 8). The highest inventory is in Gull Lake, which is located relatively close to Chicago, and the lowest inventory is in Gratiot Lake, which is located relatively far away from any sources of lead to the atmosphere. This regional pattern is consistent with

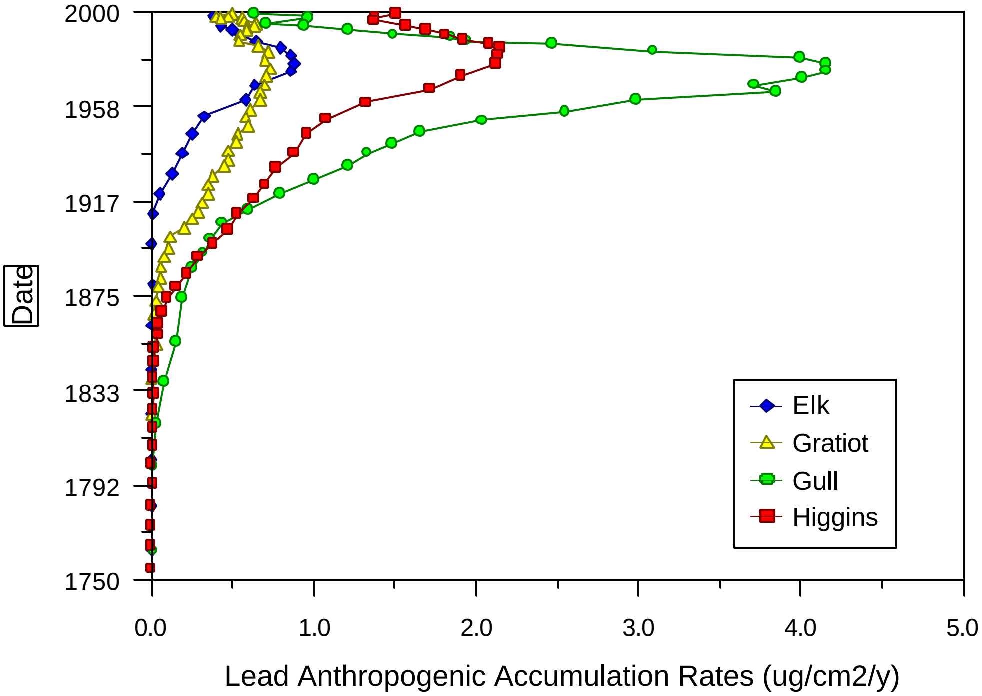

**Fig. 6.** Anthropogenic accumulation rates (ug/cm$^2$/y) for lead in four lakes. Accumulation rates have been corrected for focusing and for background accumulation.

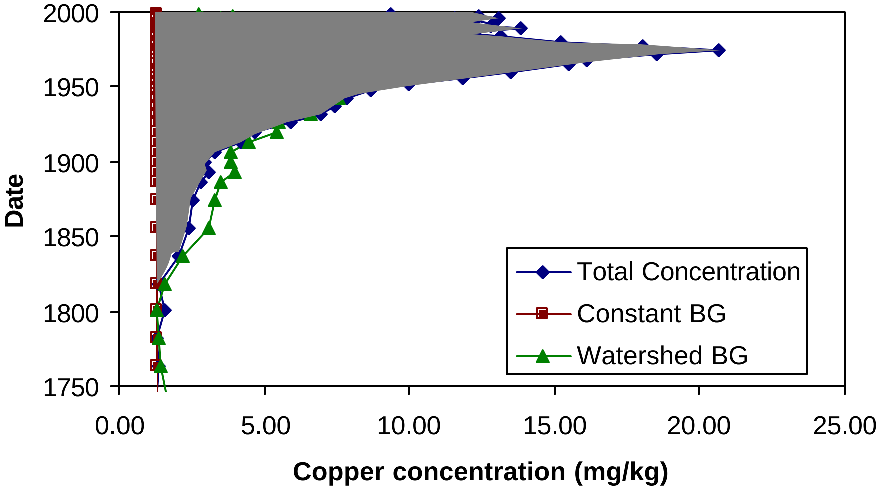

**Fig. 7.** Visual representation of anthropogenic inventory of copper in Gull Lake. The anthropogenic inventory is represented by the area between the total concentration curve and the background concentration curve. This also demonstrates the importance of using the watershed background. The inventory with watershed correction is represented in green, while the inventory calculated using the constant background would include the green and red area.

results from Lake Michigan, with the highest loading of lead occurring in the south basin (Edgington and Robbins, 1976). Additionally, the watershed inventories for the inland lakes range around the average inventory for Lake Michigan (Long et al., 1995).

Atmospheric deposition is also potentially a source for other chemicals, such as copper, cadmium and zinc. As more data are collected, it may be possible to differentiate which additional elements are being influenced by atmospheric deposition.

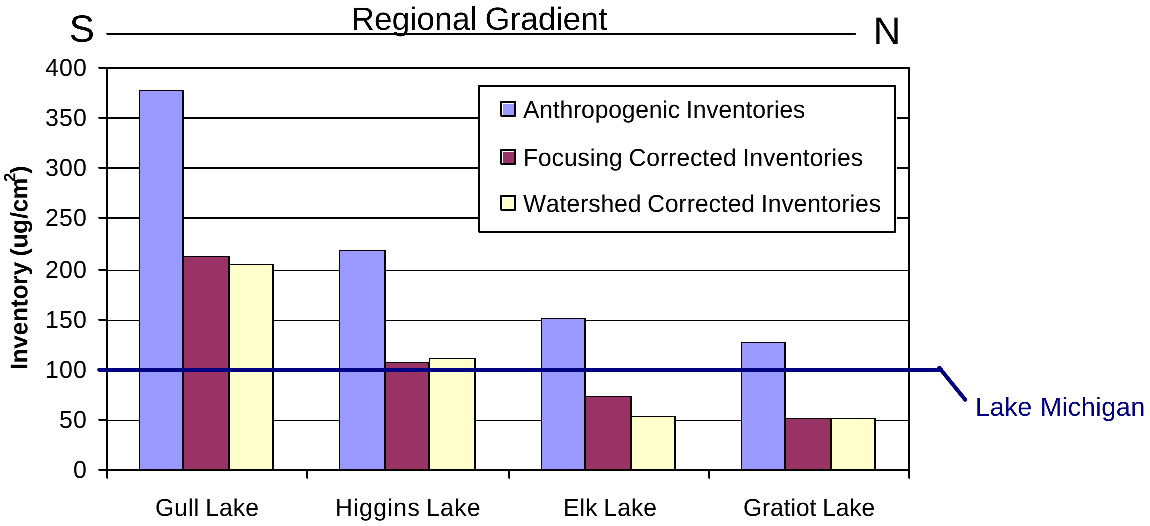

**Fig. 8.** Anthropogenic inventories for lead for five lakes in Michigan. Anthropogenic inventories and focusing corrected anthropogenic inventories were calculated with a constant background concentration. Watershed corrected inventories were calculated with a varying background, and were also corrected for focusing. The focusing corrected inventory for Lake Michigan is shown for comparison (Long et. al., 1995). In addition to showing the regional trends in lead inventories, this figure shows the importance of correcting for the watershed background and focusing factors.

## Biogeochemical Dynamics

Some elements, because of their geochemical properties, can be remobilized after they have been deposited in the sediments. Elements such as arsenic, iron and manganese are less soluble in an oxidizing environment, but may move into the porewater in a reducing environment, such as anoxic sediments. Once the elements move into the porewater, they can move through the sediment column and obscure the original record of deposition. It is important to be able to differentiate which trends are due to remobilization, and which are due to changes in loading, particularly for arsenic, which has known anthropogenic sources. This can be accomplished by comparing arsenic trends to iron and manganese. If arsenic trends are similar to iron and manganese, those trends are interpreted as being due to remobilization. Arsenic trends that differ from iron and manganese trends may be related to changes in arsenic loading.

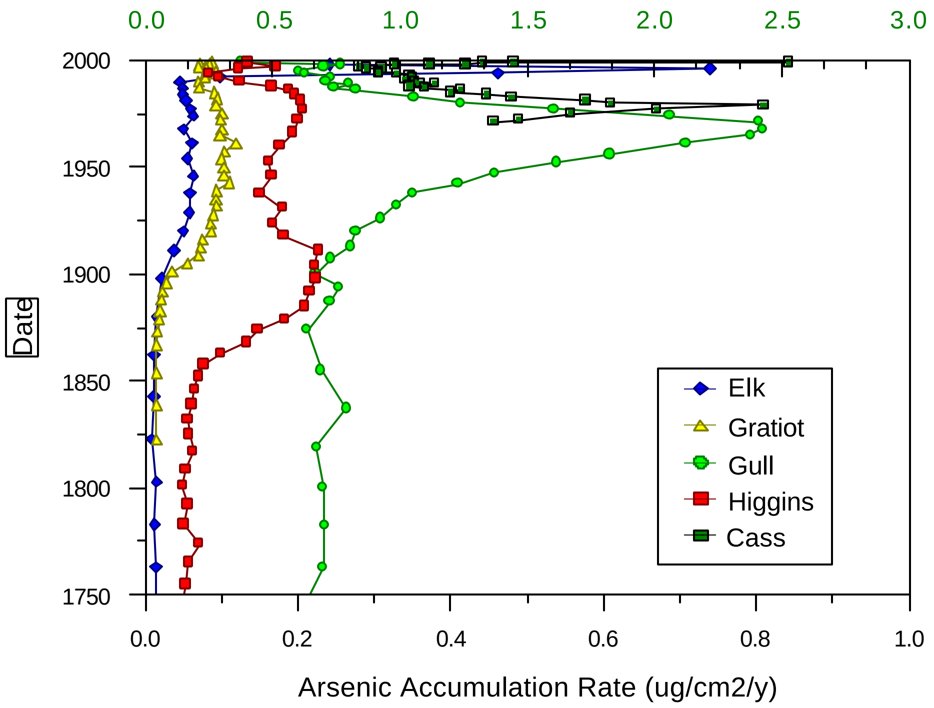

**Fig. 9.** Arsenic accumulation rates in five inland lakes in Michigan. Cass Lake accumulation rates are plotted on the upper scale.

Through the comparison of iron, manganese and arsenic trends, it was determined which peaks were influenced by remobilization, and which were caused by increased loading of arsenic. In Elk Lake, the surface peak in arsenic (Fig. 9) is due to remobilization, but a smaller increase from the 1900s to 1970 may be related to increased loading. Arsenic peaks in the 1600s and late 1700s in Gull Lake appear to be caused by remobilization (not shown), while the peak around 1970 is probably due to increased loading of arsenic (Fig. 9). Arsenic trends in Cass Lake and Higgins Lake appeared to be strongly influenced by remobilization, while trends in Gratiot Lake appear to be primarily related to changes in arsenic loading (Fig. 9).

Besides obscuring the record of deposition, remobilization cause concentration peaks in the sediment unrelated to changes in inputs. Because these concentration peaks can occur near the surface, they may be an environmental health concern. To date, only one major contaminant (arsenic) has exhibited this phenomenon. The problem is that changes in the input of arsenic may not alleviate this buildup of arsenic.

## Direct Anthropogenic Input

The accumulation rates of cadmium, chromium, copper and zinc increase above background levels, and do not appear to be related to the three other factors influencing chemical loading (watershed input / within lake processes, atmospheric deposition, and biogeochemical dynamics), indicating that the increased loading is related to direct anthropogenic input. As described above, loading of arsenic is also influenced by direct anthropogenic inputs. Generally, anthropogenic accumulation begins around the 1900s, increases until around the 1970s then decreases to the present. Within each lake, trends in As, Cd, Cu and Zn tend to be similar, but the shapes of the trends vary among lakes.

Major anthropogenic sources of these elements include (Reimann and Caritat, 1998):

Arsenic: Coal combustion, ore smelting, pig and poultry sewage, phosphate fertilizers, insecticides and fungicides.

Cadmium: Coal combustion, smelters (esp. copper and zinc), iron and steel mills, electroplating, fertilizers, traffic (tire wear and exhaust), sewage sludge and wastewater, waste incineration.

Chromium: Chemical industry, steel works, electrometallurgy, copper smelting, combustion of natural gas, oil and coal, sewage sludge, waste incineration and some P fertilizers.

Copper: Copper mining and smelting, other non-ferrous smelters, plastic industry, steel works, agriculture, sewage sludge (pig farming).

Zinc: Zinc smelters, combustion, traffic (wear of tires), wastewater, sewage sludge.

Accumulation rates for Cass Lake are higher than the other lakes, however, because background concentrations were not reached, it is not possible to determine anthropogenic accumulation rates. Because of this, Cass Lake data are not included on the following graphs. See Appendix A for data.

In Elk Lake, accumulation rates for arsenic, cadmium, copper and zinc all begin increasing in the late 1800s (Figs. 9-13). Arsenic, cadmium and zinc begin to decrease in the late 1960s to early 1970s, while copper accumulations rates remain elevated until the present. Elk and Gratiot Lakes tend to have the lowest accumulation rates, except for comparatively higher accumulation rates of chromium in Elk Lake. In Gratiot Lake, accumulation of arsenic, copper, cadmium and zinc all follow the same trend, and are likely related to nearby smelting and mining. Cadmium, copper, and zinc accumulation patterns were similar in Higgins Lake, showing either a decrease in accumulation or a slower rate of increase from the 1930s-1950s, and then increasing again until the 1980s. Accumulation rates in Higgins Lake were generally higher than Elk and Gratiot Lakes, but lower than Gull Lake, with the exception of cadmium accumulation rates that were almost equal to Gull Lake. Gull Lake showed similar trends in all five elements, which are similar to the trends seen in Higgins Lake.

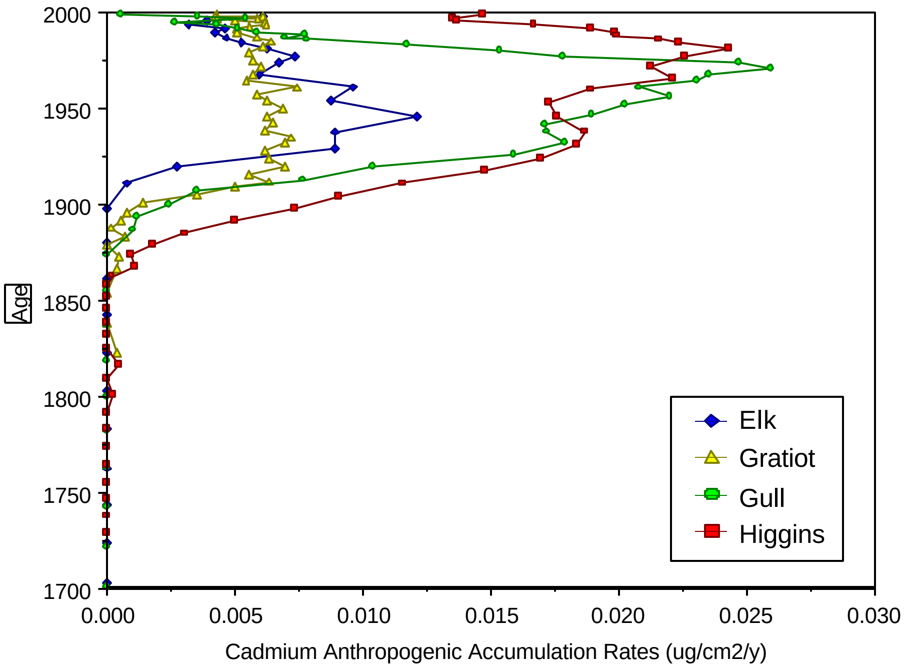

**Fig. 10.** Anthropogenic accumulation rates for cadmium. Rates have been corrected for focusing and background accumulations.

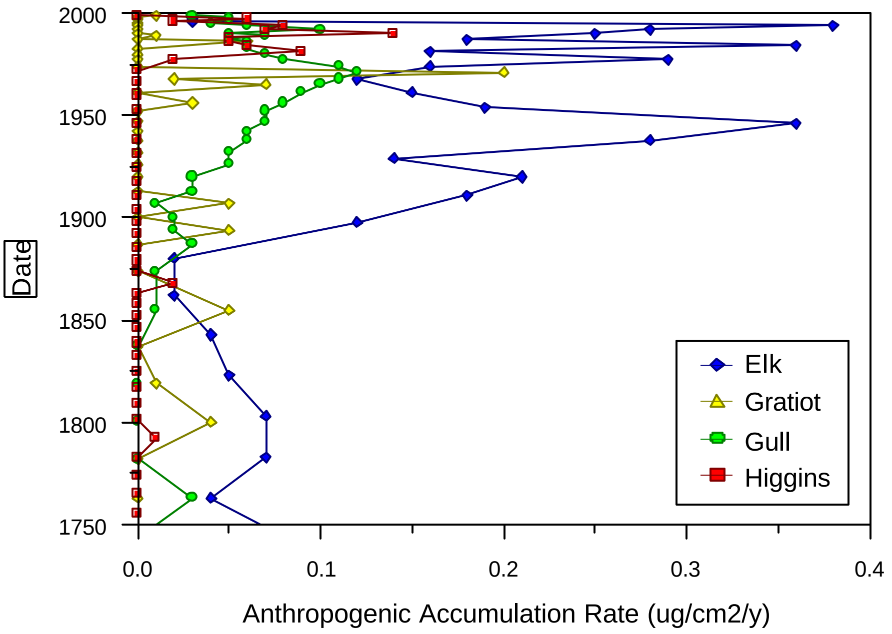

**Fig. 11.** Anthropogenic accumulation rates of chromium. Rates have been corrected for focusing and background accumulations.

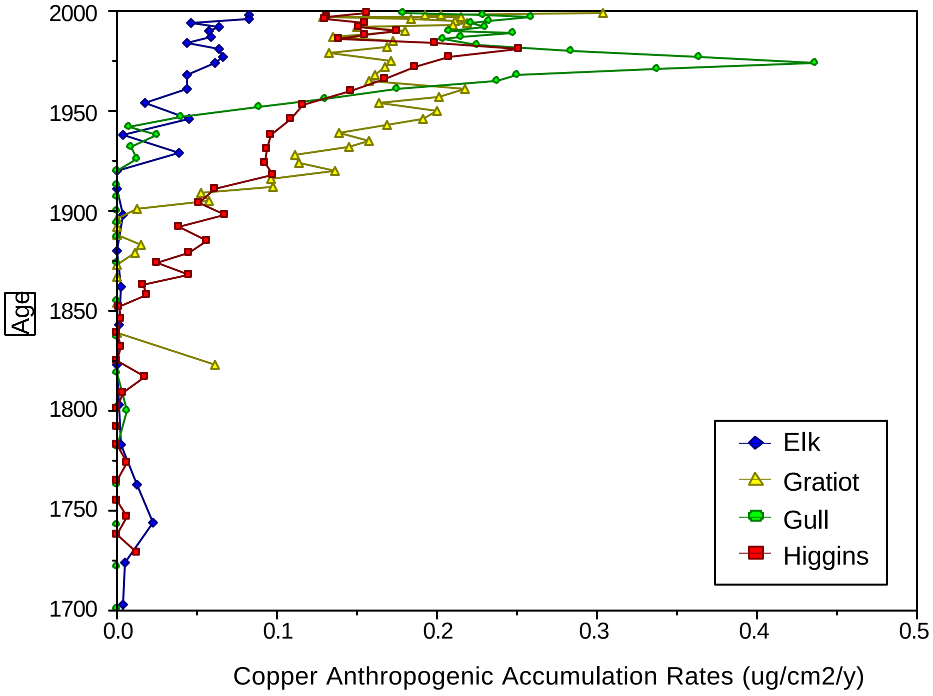

**Fig. 12.** Anthropogenic accumulation rates for copper. Rates have been corrected for focusing and background accumulation.

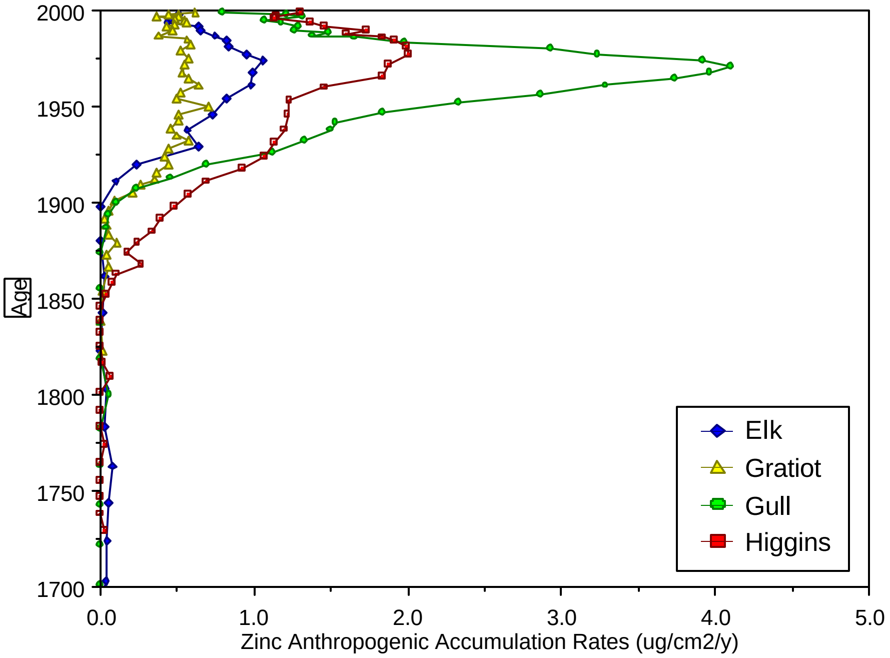

**Fig. 13.** Anthropogenic accumulation rates for zinc. Rates have been corrected for focusing and background accumulation.

# Organic Contaminants

Concentrations of organic contaminants are generally highest in Cass Lake, and lowest in Gratiot Lake (Table 2, Figs. 14-17). Concentrations in the older sediments (1-2 cm) are generally higher than those in the most recently deposited sediments (0-1 cm) for total pesticides and DDTs (Figs. 16-17). However, this is not true for total polychlorinated biphenyls (PCBs) and total polyaromatic hydrocarbons (PAHs) (Figs 14-15). Cass and Elk Lakes have higher concentrations of PCBs in the most recent sediments, and Cass, Higgins and Elk Lakes have higher concentrations of PAHs in surface sediments.

Because of the limited data, and because it was necessary to combine samples, these results should be interpreted carefully. The increase of PCBs in Cass Lake, and PAHs in Higgins and Elk Lake are small, and may not be significant compared to changes throughout the sediment core. The increase in PCBs in Cass and Elk Lake and PAHs in Cass Lake do appear to be significant.

It is important to consider that the top section from Elk Lake includes four years of deposition, making it impossible to determine if levels of PCBs are currently increasing, were increasing and are now decreasing, or if some input event occurred within these four years. PCBs are not currently produced in the United States, and sources include the disposal of transformers and capacitors, and most significantly, redistribution of PCBs already in the environment (ATSDR, 1993).

Cass Lake also shows an increase in the concentration of PAHs in the sediments. PAHs are produced by incomplete combustion from sources including vehicles, heating and power plants, industrial processes, and open burning (VanMetre et al., 2000). Increased concentrations of PAHs in urban areas have been shown to relate to patterns of traffic density (VanMetre et al., 2000). The increased concentrations in surface sediments of Cass Lake may reflect increased vehicle use in the area, although there is insufficient data for definitive conclusions.

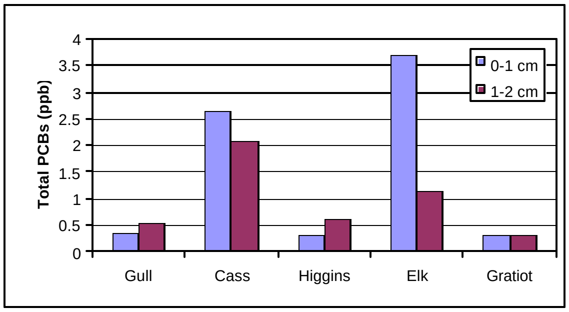

**Fig. 14.** Concentrations of total PCBs from 0-1 and 1-2 cm depth in five lakes in Michigan.

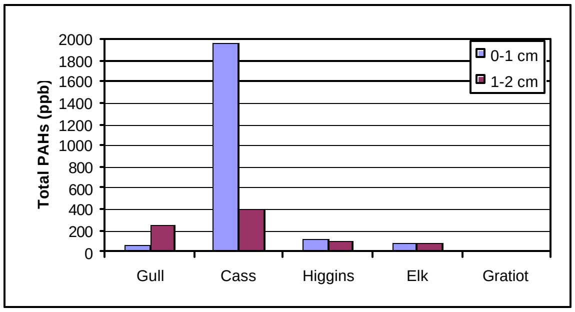

**Fig. 15.** Concentrations of total PAHs from 0-1 and 1-2 cm depth in five lakes in Michigan.

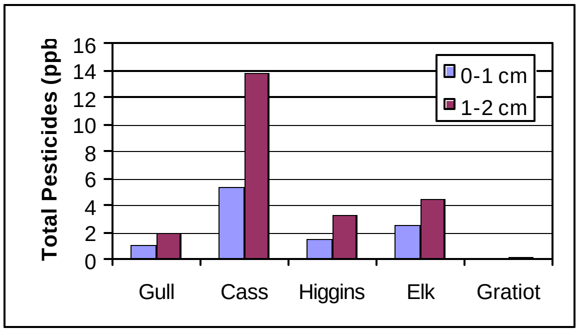

**Fig. 16.** Concentrations of total pesticides from 0-1 and 1-2 cm depth in five lakes in Michigan.

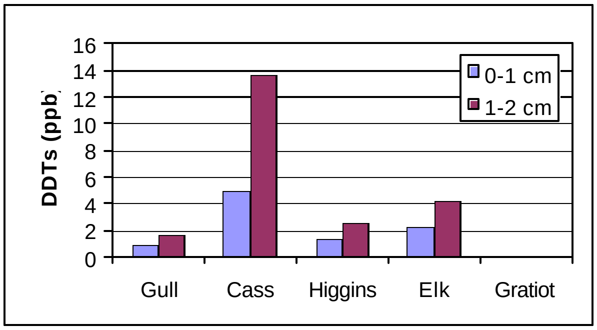

**Fig. 17.** Concentrations of DDTs from 0-1 and 1-2 cm depth in five lakes in Michigan.

**Table 2.** Summary of results from organic contaminant analysis. Concentrations are in parts per billion (ng/g wet sediment).

| | Elk 1 | Elk 2 | Gratiot 1 | Gratiot 2 | Cass 1 | Cass 2 | Higgins 1 | Higgins 2 | Gull 1 | Gull 2 |
|---|---|---|---|---|---|---|---|---|---|---|
| cm depth[1] | 0-1 | 1-2 | 0-1 | 1-2 | 0-1 | 1-2 | 0-1 | 1-2 | 0-1 | 1-2 |
| Age[2] | 1997 | 1993 | 1999 | 1998 | 1999 | 1999 | 1998 | 1995 | 1999 | 1996 |
| Total polychlorinated biphenyls (PCBs)[3] | 3.70 | 1.14 | 0.31 | 0.31 | 2.63 | 2.09 | 0.32 | 0.61 | 0.36 | 0.53 |
| Octylphenol | <10 | <10 | <10 | <10 | <10 | <10 | <10 | <10 | <10 | <10 |
| Nonylphenol | <100* | <100* | <10 | <100* | <10 | <10 | <10 | <10 | <100* | <100* |
| Total polyaromatic hydrocarbons (PAHs) | 76 | 74.7 | <1 | 1.1 | 1967 | 402 | 119 | 99.3 | 65.6 | 245.8 |
| Naphthalene | <1 | <1 | <1 | <1 | <1 | <1 | <1 | <1 | <1 | <1 |
| Acenaphthylene | 2.3 | <1 | <1 | <1 | <1 | <1 | <1 | <1 | <1 | <1 |
| Acenaphthene | <1 | <1 | <1 | <1 | <1 | <1 | <1 | 2.2 | <1 | <1 |
| Fluorene | <1 | <1 | <1 | <1 | <1 | <1 | <1 | <1 | <1 | <1 |
| Phenan/Anthra | <1 | <1 | <1 | <1 | 601 | 46 | 5.5 | 3 | 1 | 11.9 |
| Fluoranthene | 21.3 | 20.2 | <1 | <1 | 296 | 162 | 41.2 | 30.6 | 23.9 | 76.8 |
| Pyrene | 15.9 | 15.2 | <1 | <1 | 230 | 194 | 5.3 | 14.6 | 10.8 | 48.3 |
| Benzo[a]anthracene | 6.3 | 6 | <1 | <1 | 85 | <1 | 4.3 | 7.0 | 4.4 | 18.2 |
| Chrysene | 14.8 | 14.3 | <1 | 1.1 | 199 | <1 | 26.9 | 21.6 | 12.4 | 43 |
| Benzo[b]fluoranthene, B[k]F | 7.8 | 8 | <1 | <1 | 120 | <1 | 20.5 | 6.5 | 7.4 | 15.5 |
| Benzo[a]pyrene | 7.6 | 8.6 | <1 | <1 | 189 | <1 | 15.6 | 13.7 | 5.8 | 27.3 |
| Indeno[123cd]pyrene, D[ah]a | <1 | 0.3 | <1 | <1 | 102 | <1 | <1 | <1 | <1 | 4.8 |
| Benzo[ghi]perylene | <1 | 2 | <1 | <1 | 145 | <1 | <1 | <1 | <1 | <1 |
| Total Pesticides | 2.55 | 4.46 | 0.03 | 0.07 | 5.39 | 13.86 | 1.53 | 3.20 | 0.98 | 1.97 |
| Hexachlorobenzene (HCB) | 0.21 | 0.07 | ND | ND | 0.07 | 0.08 | 0.05 | 0.46 | 0.01 | ND |
| Hexachlorohexanes (HCHs) | 0.11 | 0.17 | ND | ND | 0.25 | ND | 0.04 | 0.08 | ND | ND |
| a-BHC | 0.03 | 0.17 | ND | ND | ND | ND | ND | 0.01 | ND | ND |
| b-BHC | 0.08 | ND | ND | ND | 0.19 | ND | 0.03 | 0.07 | ND | ND |
| g-BHC | ND | ND | ND | ND | 0.06 | ND | ND | ND | ND | ND |
| d-BHC | ND | ND | ND | ND | ND | ND | ND | ND | ND | ND |
| CHLs | ND | 0.02 | ND | ND | 0.21 | 0.16 | 0.03 | 0.09 | 0.05 | 0.23 |
| g-chlordane | ND | 0.01 | ND | ND | 0.13 | 0.10 | 0.02 | 0.05 | 0.04 | 0.16 |
| a-chlordane | ND | 0.01 | ND | ND | 0.08 | 0.07 | 0.01 | 0.03 | 0.01 | 0.08 |
| DDTs | 2.22 | 4.20 | 0.02 | 0.05 | 4.86 | 13.61 | 1.41 | 2.57 | 0.91 | 1.72 |
| p,p' DDE | 2.06 | 2.33 | 0.01 | 0.03 | 2.32 | 2.55 | 1.05 | 2.02 | 0.75 | 1.22 |
| p,p' DDD | 0.09 | 1.18 | ND | 0.02 | 2.42 | 10.99 | 0.36 | 0.55 | 0.15 | 0.49 |
| p,p' DDT | 0.06 | 0.70 | ND | ND | 0.12 | 0.07 | ND | ND | ND | 0.01 |

1. The first two slices were combined (cm 0-1), and the third and fourth slices (1-2 cm), due to insufficient sample mass for analysis.
2. Since samples were combined[1] each analysis covers a range of years. The median age is presented for each of the combined samples.
3. Data for PCB congeners are given in Appendix A.

## Minimum sampling frequency

There are three major factors that should be considered when determining how often to resample a lake. The first factor is the minimum depth of new sediment that must be deposited to definitively determine a trend. Only sampling 1.0 cm (two 0.5 cm samples) may not be sufficient to determine a trend. Four samples (2.0 cm) should provide enough data to reliably determine a trend. Therefore the minimum amount of time between sampling will be determined by the sedimentation rate, and the length of time needed to deposit 2.0 cm of new sediment (Table 3).

**Table 3.** Minimum number of years needed to deposit approximately 2 cm of new sediment for five inland lakes in Michigan.

| Cass | Elk | Gratiot | Gull | Higgins |
|---|---|---|---|---|
| 1 y | 10 y | 2 y | 4 y | 6 y |

The second factor that needs to be taken into account is the cost effectiveness of the sampling schedule. For example, it may be most cost effective to sample every five years, in which case Cass, Gratiot and Gull Lakes may be sampled every five years. However, Higgins and Elk would be sampled on a different schedule, because their minimum time between sampling is greater than five years.

Finally, this sampling schedule may be readjusted if the DEQ considers any of the lakes to be a high priority. Factors affecting this may include land use changes around the lake, sediment data, water quality data or other sources. If there are environmental concerns about any of the lakes, they should be sampled with greater frequency, and those lakes of less concern can be sampled at greater intervals.

## Future work

A high priority is completing the method for accurate analysis of mercury, and an addendum to this report will be added after the mercury levels for these lakes are determined.

Over the next 4-5 years six to ten additional lakes will be sampled each year. A research vessel specifically constructed for sampling inland lakes will be used for this sampling. This boat will allow lakes with lower quality boat launches to be sampled, increasing the range of lakes that can be sampled.

Identification of the 30-40 lakes that will comprise the sediment trend monitoring program is a priority. These lakes will be identified based on accessibility, limnological character, geographic location, airshed location, and watershed characteristics.

Tin (possible anthropogenic contaminant), phosphorous (a measure of trophic level), and boron (a potential indicator of wastewater input) will be added to the suite of elements analyzed on the ICP-MS. Continued analysis of a full suite of elements will allow for additional geochemical fingerprinting, and a better understanding of sources of different chemicals to the environment. In order to better understand the influence of biogeochemical dynamics and to identify the effects of remobilization of metals, porewater will be collected at different depths throughout the sediment core. As funds become available, older sediments may be analyzed for organic chemicals, and the suite of organic chemicals that are analyzed may be expanded.

As data from additional lakes are collected, it will be possible to perform more detailed spatial analysis. For example, a more detailed regional pattern of atmospheric lead deposition may be determined. It may also be possible to better understand the importance of atmospheric deposition for other anthropogenic elements such as copper and zinc.

Sediment chemistry is one component of the DEQ's overall strategy. The first year of this program has proven the feasibility of collecting high quality sediment cores. The sediment trend monitoring component of the program will consist of approximately 30-40 lakes, with return frequencies appropriate to each lake based on sedimentation rates calculated from the first visit. The first time a lake is sampled, the entire core will be analyzed, as was done for these five lakes, to determine background concentrations and historical trends. In the future, only the uppermost sections of the core will be analyzed for metals, as this would represent the sediment deposited since the first visit, and would enable evaluation of recent trends. It would still be necessary to perform full $^{210}$Pb analysis to determine the age of the recent sediment.

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Appendices available upon request