

Assessing environmental change through chemical-sediment chronologies from inland lakes

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Abstract

This paper examines the hypothesis that the spatial pattern of metal accumulation rates in inland lake sediments provides insight into the causes of the historical and continued loadings of contaminants to the environment. To address this, copper and lead accumulation rates in the Great Lakes' watershed were studied. A multi-element approach was used, in which many non-toxic chemicals were measured along with the toxic chemicals of interest, rather than a target-specific approach. The multi-element approach also allowed for assessing the environmental state of the lake with respect to its surrounding watershed. Sediment cores were collected from the deepest portion of five Michigan inland lakes, sectioned, metals extracted by nitric acid, microwave digestion and leachates analysed for 26 metals using an inductively coupled, plasma, mass spectrometer with hexapole technology. Sedimentation rates, ages and focusing factors were calculated via ²¹⁰Pb. Dasymeric mapping was used to estimate population distributions in lake watersheds. Watershed area was estimated from digital elevation data using Arc/INFO (ESRI, Redlands, California). The data show that as loadings from dominant (regional) sources decrease (e.g. atmospheric deposition in the case of lead), new patterns provide insight into causes for continued contaminant loadings (e.g. population density). The data also show the universal response of the watersheds to the onset of the anthropogenic loadings of lead but not that of copper. Individual watersheds had different onset times for anthropogenic copper loadings. Recent lead loadings to the environment can be related to population density, and those of copper reflect, in part, a spatial pattern that is similar to the regional pattern for lead during the mid-1970s. As this pattern for lead could be related to a regional gradient of lead concentrations in atmospheric deposition, the same relation cannot be made for copper. The cause for this spatial pattern for copper is not clear.

Key words

chronologies, metals, population, sediments.

INTRODUCTION

The environment is being altered because of changes in population growth and distribution (e.g. creation of mega cities), the use of chemicals (e.g. pesticides) and land use (e.g. transition of agriculture to urban). Thus, the following questions are asked: (i) what is the current state of the environment?; (ii) what is the cause of the current state?; (iii) what are emerging and lingering issues?; and (iv) what are the future trends? Changes in the accumulation rates or loadings of metals to lakes over time are recorded in the sediments (Jaquet *et al.* 1982), making sediment

chronologies an extremely useful approach to answering these questions (Hermanson 1998).

This paper examines changes in lead and copper accumulation rates (via sediment chronologies) to the Great Lakes' region, where regulatory measures have worked to decrease loadings of these as well as several toxic chemicals. Because loadings for many of these chemicals are not at background levels, influences on and sources for these chemicals need to be determined. Major anthropogenic sources for lead include coal combustion, ore smelting (lead and zinc), waste incineration, leaded gasoline combustion and for copper, copper mining and smelting, other non-ferrous smelters, plastic industry, steel works, agriculture, and sewage sludge (pig farming; Reimann & Caritat 1998). Important sources for lead and copper in the Great Lakes' basin are leaded gasoline and mining, respectively.

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Sediment chronologies from large lakes (e.g. >1000 km²) are often used to address environmental issues, but these chronologies typically integrate the contaminate accumulation signal from a large area that might be at a scale too coarse to address the problem stated above. On the other hand, studying the chemical sediment chronology of one inland lake (e.g. <100 km²) provides important information about a particular lake; however, the sources influencing one lake might or might not have the same effect on another lake. The results cannot necessarily be generalized to other lakes in the region and, thus, sediment chronologies from multiple inland lakes that are spatially located over a region are an excellent compliment to those from the large lakes. Inland lakes record information on a local scale that can be compared to other inland lakes on a larger spatial scale. Most spatial studies of lakes have only examined recent data (Johnson & Nicholls 1988; Boyle *et al.* 1999; Callender & Rice 2000), rather than examining the change in patterns over time, as we do in this study.

Interpreting and comparing sediment chronologies from inland lakes offer certain challenges. In particular, terrestrial inputs from the watershed, anthropogenic inputs from the watershed and atmosphere, and autochthonous materials are deposited together in one mixed record, making it difficult to differentiate the relative importance of each different source (Edgington & Robbins 1976; Balogh *et al.* 1999). To address this problem, we measure not only the toxic chemical(s) (the target specific approach) of interest such as lead (Iskander & Keeney 1974; Dillion & Evans 1982; Spiethoff & Hemond 1996), but also many non-toxic chemicals such as aluminium and barium (the multi-element approach). The multi-element approach is integral to understanding patterns of metal accumulation within a lake (Bruland *et al.* 1974; Johnson & Nicholls 1988; Ramanathan *et al.* 1996; Heyvaert *et al.* 2000; Kang *et al.* 2000). The multi-element approach allows for the determination of current contaminant levels and historical loading trends, predicting future changes in chemical loadings, detecting new and emerging issues, understanding diagenesis and the influences of terrestrial input from the watershed, differentiating terrestrial inputs from anthropogenic inputs (e.g. Kemp & Thomas 1976; Harrington *et al.* 1998; Brown *et al.* 2000). Thus, this pilot study combines the spatial, temporal and multi-element aspects of different studies performed in the past (e.g. Birch *et al.* 1996; Bruland *et al.* 1974; Dillion & Evans 1982; Heyvaert *et al.* 2000) to develop a more complete understanding of what is influencing the chemical fluxes and geochemistry of lake sediments.

This study not only examines spatial patterns of metal accumulation rates, but also the changes in spatial patterns

over time. Our hypothesis is that the spatial pattern of chemical accumulation rates provides insight into the causes of the historical and continued loadings of contaminants to the environment. It is developed around the following: (i) environmental regulations are typically put in place to address dominant contaminant sources whose influences are typically at regional scales; (ii) spatial and temporal patterns of chemical loadings from dominant influences/sources most likely obscure the patterns from less dominant sources such as those that might operate at the watershed scale; (iii) as loading from the dominant sources are reduced, the effect of less dominant influences/sources on the spatial patterns of contaminant accumulation rates might be revealed; and (iv) the newly detected patterns will provide insight into the underlying causes for the continued loading of the contaminants to the environment.

By understanding changes in the importance of different sources and processes over time, it might be possible to determine the influences and efficacy of environmental legislation. In addition, this approach will help us to understand what sources and processes are influencing contaminant accumulation rates of individual lakes. This is important because it has been shown that contaminants can have an adverse effect on the zoobenthos (Catallo *et al.* 1995), and that sediments might provide a continuous source of toxic metals to the aquatic environment (Spiethoff & Hemond 1996). This information can help policy-makers by indicating which sources of contamination are the most significant.

At the watershed scale, communities surrounding the lake potentially influence chemical loading to lakes. These communities often do not contribute much in the way of industrial contamination, but do act as sources of contamination to the lake via household and yard wastes, storm drains, construction activities and materials, and traffic. For example, Callender and Rice (2000) found a relationship between fluxes of lead and zinc to lakes and population density. By comparing known contaminant-accumulation rates to population densities of each watershed, it might be possible to evaluate impacts of the local community. The shores of inland lakes across the US are a preferred location for many homes and cottages, and many of these residents are concerned about the health of their lake. By establishing a correlation between population density and heavy-metal contaminants, it is possible to demonstrate to residents that they do influence the health of the lake. This might result in actions such as allowing less development around the lakes, or updating sewer systems, which would decrease metal loading to the lake.

METHODS

Sediment cores were collected from Cass, Elk, Gratiot, Higgins and Gull Lakes in the State of Michigan, USA, during 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 (Ocean Instruments, San Diego, CA, USA), which takes four replicate cores and is designed to collect the flocculent material at the sediment-water interface. If the cores showed any evidence of disturbance, a set of new cores was immediately taken. Cores were described and examined for colour, texture and signs of zoobenthos. Sediment was extruded from the cores and sectioned at 0.5-cm intervals for the top 5–8 cm of the core, and at 1-cm intervals for the remainder of the core. An extruding device was designed for this study to facilitate the extrusion in remote areas (i.e. no electrical or hydraulic power is needed) and allows for precise sampling of the flocculent material at the sediment-water interface. Samples were stored in the field on ice in acid-washed plastic jars.

Upon return to the laboratory, sediments were frozen until they could be freeze-dried and digested by nitric acid in a CEM-MDS-81D microwave (CEM, Matthews, North Carolina; Hewitt & Reynolds 1990). 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- μ m polycarbonate filter (Nuclepore; Whatman, Clifton, New Jersey). Samples for mercury analysis were preserved with a gold chloride solution (final concentration 200 p.p.b. Au). Samples were then analysed using a Micromass Platform inductively coupled, plasma, mass spectrometer with hexapole technology (ICP-MS-HEX; Micromass International, Manchester, UK). Sediments were analysed for a suite of metals and

metalloids including magnesium, aluminium, potassium, calcium, sodium, titanium, vanadium, manganese, iron, cobalt, nickel, copper, zinc, arsenic, cadmium, barium, lead, lithium, selenium, scandium, phosphorus, boron, rubidium and uranium. Solutions were generally analysed by direct injection with a 1:10 dilution, with the standards matrix matched to the samples; typically adjustments were made for high calcium concentrations. In some cases, magnesium, calcium and potassium were analysed via flame atomic absorption spectrometry (Perkin Elmer 5100PC; Wellesley, Massachusetts).

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

All spatial data were collected from secondary sources, and were in or were converted into the Michigan GEOREF coordinate system: oblique Mercator projection, datum NAD83, spheroid GRS 1980. Sources and type of data included: (i) digital elevation map (DEM) of Michigan, US Geological Survey (Aichele, pers. com.), DEM data was in 30 m² grid size raster data, 1:24 000 scale (ii) census tract data: Michigan Maps and Information, Topologically Integrated Geographic Encoding and Referencing (TIGER) database (<http://www.crs.msu.edu/db/welcome.html>), data were imported as polygon coverages with census tracts, population data from 1990 were used, and were downloaded for each county; (iii) state ownership data: Michigan Department of Natural Resources spatial data library (<http://www.dnr.state.mi.us/spatialdatalibrary>), data were imported as polygon coverages and included data for state owned mineral rights, and state owned surface rights; and (iv) lake data: Michigan Department of Natural Resources spatial data library (<http://www.dnr.state.mi.us/spatialdatalibrary>), data were imported as shape files with lake identification, lake type and other data.

Watersheds were delineated around each of the five lakes of interest. All watersheds were delineated with the WATERSHED command in Arc/INFO.

To determine population densities within the watershed, it was essential to estimate as accurately as possible where people were living within the census tract. Therefore, dasy-metric mapping was used to estimate population distribution. Areas that are state owned (surface or fee rights) or areas covered by lakes were considered as non-livable areas. It was assumed that the population was evenly distributed throughout the remaining livable area within each census tract.

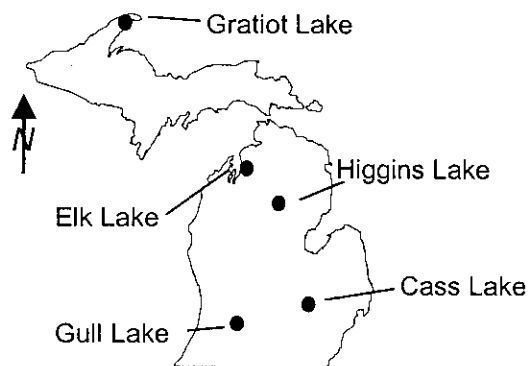


Fig. 1. Location of lakes sampled in Michigan, USA. For reference, the Greater Chicago metropolitan/industrial area is located southwest of Gull Lake.

Anthropogenic accumulation rates of heavy metals were plotted versus population density, and correlation analysis was performed using a best fit, least squares regression line. R^2 and P -values were calculated, with the slope being considered significantly different than zero if $P < 0.05$.

RESULTS AND DISCUSSION

Sedimentation rates and focusing

^{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).

Cass Lake had a significantly higher sedimentation rate than the other lakes, and the oldest sediments collected were 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 later (Table 1).

Three 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 might be used if

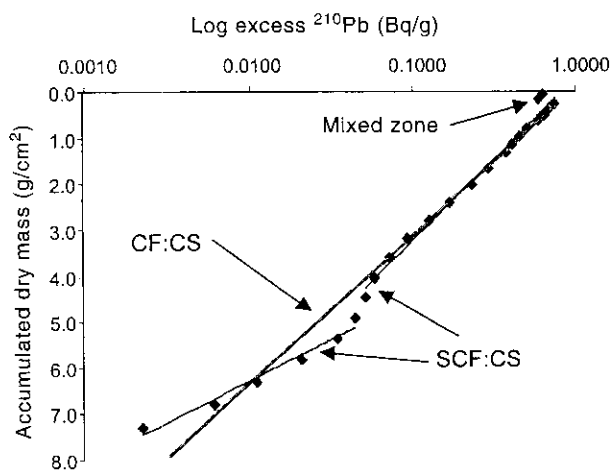


Fig. 2. Log ^{210}Pb activity (Bq/g) versus accumulated dry mass (g/cm^2). Regression lines for the constant flux : constant sedimentation (CF:CS) model and the segmented constant flux : constant sedimentation (SCF:CS) model are shown.

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 & 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 most recently deposited sediments. All data were 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.

Another factor that needed consideration in interpreting the data is sediment focusing. This is the process by which fine-grained sediment and associated contaminants are redistributed laterally by currents and episodic storm events from shallow nearshore (erosional) regions to more quiescent (depositional) areas (Davis & Ford 1982; Eisenreich *et al.* 1998). Sediment focusing occurs in different intensities in lakes, making it difficult to compare chemical concentrations, trends, and rates of accumulation among lakes. However, a focusing factor can be used to account for this sediment movement. For example, the total mass of an anthropogenically derived contaminant in a sediment core is known as the inventory of the contaminant. Dividing by a focusing factor, the inventory can be corrected for the amount of sediment focusing that has occurred at the collection site. The focusing factor (FF) is calculated as the ratio of the integrated ^{210}Pb inventory

Table 1. Date of the oldest section (date), focusing factors (FF) and average sedimentation rates (rate) from sediment cores in five lakes in Michigan, USA

| Lake | Date | FF | Rate ($\text{g}/\text{m}^2/\text{year}$) |
|---------|------|-------|--------------------------------------------|
| 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 |

*estimated

measured in the sediment to the expected inventory from ^{210}Pb deposition from the atmosphere (15.5 pCi/cm^2 ; Golden *et al.* 1993), as shown in equation 1:

$$\text{FF} = \frac{^{210}\text{PB inventory}}{15.5 \text{ pCi/cm}^2}$$

Focusing factors for most lakes were near two (Table 1), with the exception of Cass Lake, where the estimated focusing factor is six.

Chemical-sediment chronologies

There are two major sources of sediment in a lake: watershed (terrestrial) input and within-lake production (organic and carbonate), and these sources appeared to vary greatly among 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 differed in the amount of organic matter. Cass Lake sediments were enriched in organic matter and tending toward a eutrophic state, and Gull and Elk Lakes appeared to be oligotrophic, and were poor in organic matter. 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. aluminium, iron).

Because of these differences, chemical sediment chronologies based on absolute concentrations could not be compared among the lakes. For example, if over time 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 concentration patterns in the sediment core will appear to go down. This problem is accounted for by examining accumulation rates ($\mu\text{g/cm}^2/\text{year}$), rather than concentrations.

To determine anthropogenic accumulation rates for metals, background concentrations (typically estimated from pre-1800s samples) are subtracted from total concentrations for each sediment increment. It is generally considered that these background concentrations/accumulation rates remain constant throughout time (Fig. 3). However, watershed inputs 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 might be due to natural (e.g. change in erosion rates due to climate change) or anthropogenic causes (e.g. increased erosion due to logging).

For example, Elk Lake shows the most significant change in watershed input (Fig. 4), as seen by the increase in the accumulation rate of aluminium from the late 1800s until 1920, then the decrease to the present. Aluminium accumulation rates still remain above background accumulation rates. This increase in watershed input is likely due to the extensive logging and land use change in the watershed (Davis 1976; Dearing *et al.* 1987). Trends in barium, iron, potassium, magnesium, nickel, titanium and vanadium all appear to be influenced primarily by watershed input in Elk Lake. Gull Lake also shows an increase in aluminium 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

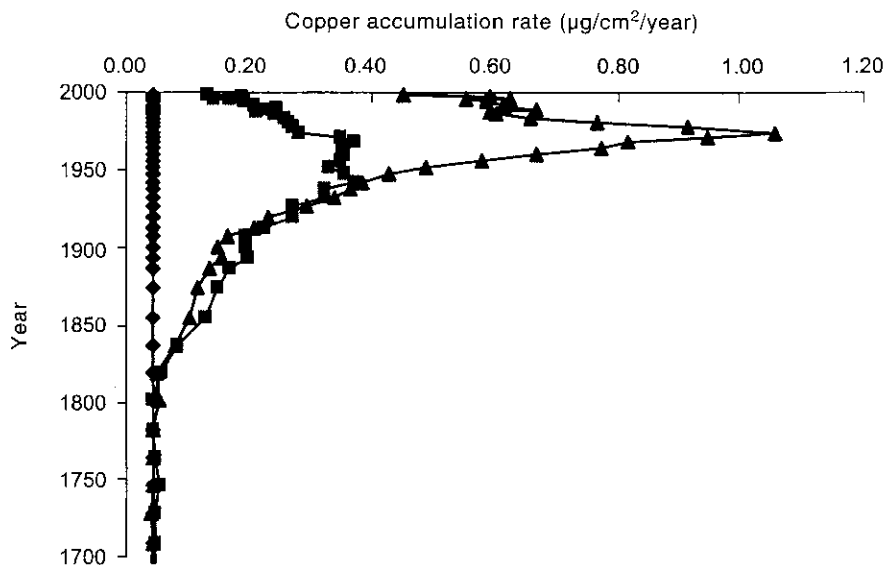


Fig. 3. Copper accumulation rates (Δ) total and (\blacklozenge) pre-1800 background values) and watershed (aluminium corrected) background values (\blacksquare) for Gull Lake. The rate of anthropogenic copper accumulation would be the difference between total and background.

probably related to logging and other land-use changes, including extensive land 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 aluminium 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 aluminium, and cobalt, iron and vanadium weakly correlate; in Gratiot Lake, cobalt, magnesium, nickel and titanium strongly correlate, and vanadium and uranium correlate weakly. It is clear that a variety of elements might be used to characterize inputs to a lake from the watershed, but aluminium appears to be the most consistent indicator.

By comparing selected metals to aluminium, it might be possible to assess the effects of the changing proportions of watershed inputs and within lake production on the metal concentrations in the sediment. This method assumes that the metal : aluminium ratio of material washed in from the watershed remains the same over time (Bruland *et al.* 1974). A watershed background is determined for each sample separately based on the aluminium accumulation rate. The watershed background metal concentration is estimated by multiplying the aluminium concentration in the sediment times the average metal/aluminium ratio for pre-1800 sediments. Using this approach, 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. Anthropogenic accumulation rates have been calculated using equation 2:

$$FCAccum_i (\mu\text{g}/\text{m}^2 \text{ yr}) = (C_i \times W_j \times 10^4) / FF_j$$

where $FCAccum_i$ = focusing corrected sediment accumulation rate for i^{th} metal at j^{th} lake, C_i = watershed background corrected concentration of i^{th} metal in the sediment ($\mu\text{g}/\text{g}$) at j^{th} lake, W_j = mass sedimentation rate ($\text{g}/\text{cm}^2 \text{ year}$) in j^{th} lake based on ^{210}Pb dating, FF_j = sediment focusing factor for j^{th} lake.

Figure 5(a,b) shows the changes in the focusing corrected anthropogenic sediment accumulation rates over time for lead and copper, respectively. Although, watershed corrections could not be made for Cass Lake because the cores only reached the 1970s, Cass Lake is included for relative comparisons.

Significant anthropogenic accumulations for lead in all of the lakes begin around 1875. Concentrations peak around the mid-1970s in all of the lakes. Concentration peaks are highest for Cass Lake followed in order by Gull, Higgins, Elk and Gratiot lakes. Anthropogenic accumulation rates for lead in the lakes are decreasing to the present.

Patterns for the temporal changes of copper accumulation in the lakes are not as regular as they are for lead. Anthropogenic copper accumulation begins earliest in Higgins Lake (1850) and most recently in Gull (1940) and Elk (1930) lakes. Significant accumulations began in Gratiot Lake around 1900. Patterns of peaks in copper accumulation rates are not as regular as they are for lead. Accumulation rates in Gull, Higgins and possibly Elk

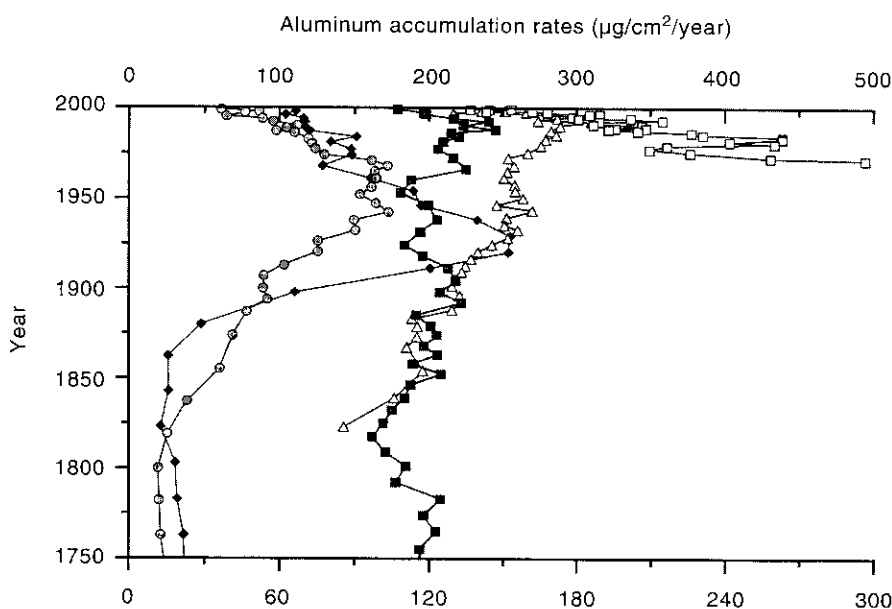


Fig. 4. Aluminium accumulation rates over time in five inland lakes. For Cass Lake accumulation rates, use the upper scale, for all other, use the lower scale. y, Year. (\blacklozenge) Elk; (\blacktriangle) Gratiot; (\bullet) Gull; (\blacksquare) Higgins; (\blacksquare) Cass.

peaked around the mid-1970s. Copper accumulation rates in Gratiot Lake were highest around the late 1950s and also in recent times. Cass Lake had the highest over-all rates while those of Higgins, Gull and Gratiot lakes were similar. Elk had the lowest accumulation rates for copper.

The coincidence of the peak accumulation rates for lead suggests that a regional source has influenced the anthropogenic loading of lead, but such a conclusion is not clear for copper, which might be a combination of both regional sources and local influences. The relative magnitudes of the peak concentrations for lead in the mid-1970s is consistent with a regional gradient for lead deposition from the

atmosphere. Concentrations might be expected to be higher to the south (influence from the greater Chicago area, for example) and lower to the north (Eisenreich *et al.* 1986). Such a regional gradient is not apparent for copper since Gull, Higgins, and Gratiot lakes appear to have similar accumulation rates.

To gain further insight into the patterns of the anthropogenic accumulation rates for lead and copper, the data from Fig. 5 were re-plotted in Fig. 6(a,b). In these plots, the accumulation rates determined from each increment were normalized to the highest accumulation rate in the particular core. Such plots allow the exploration of how the

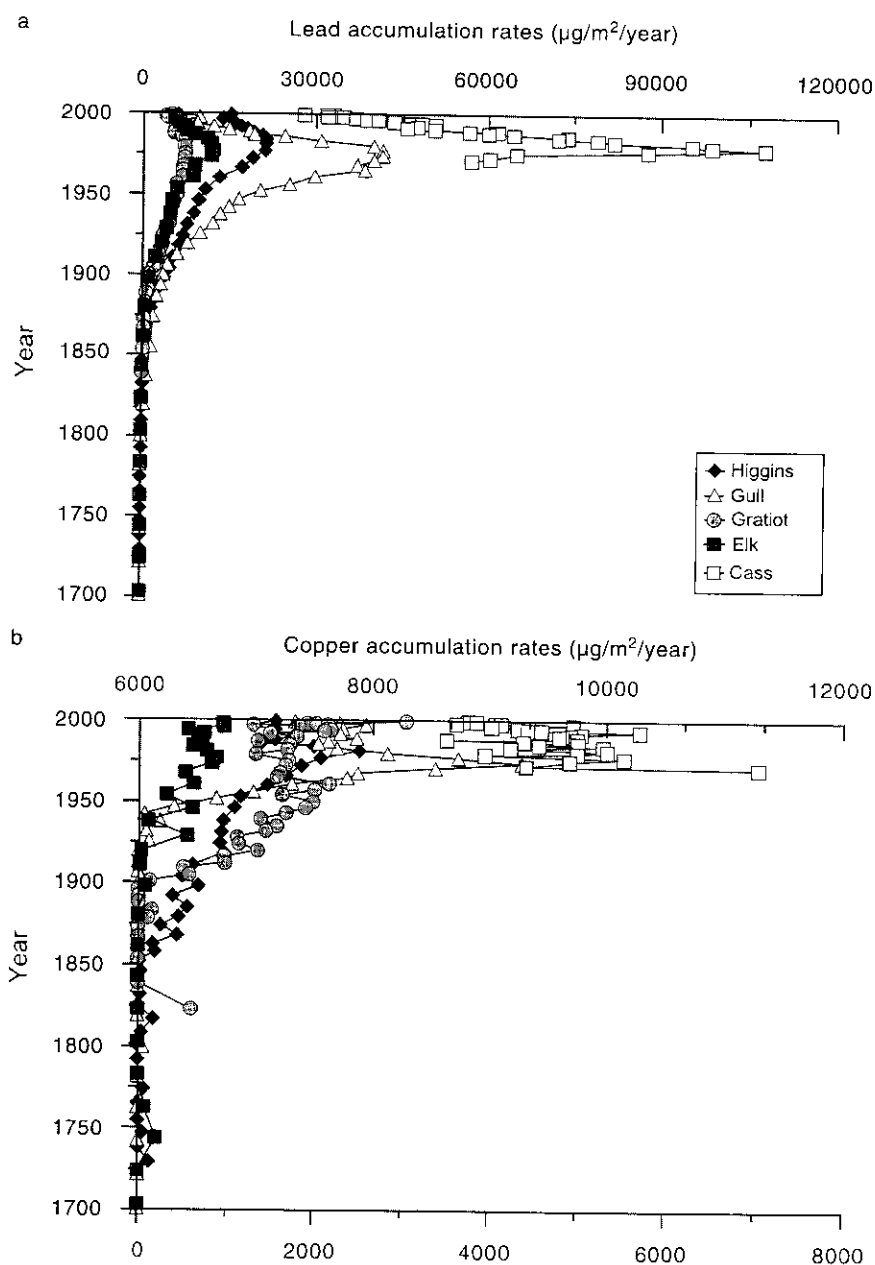


Fig. 5. Metal accumulation rates for study lakes. (a) Lead, (b) copper. The top axis in part b is for Cass Lake only.

temporal trends of the accumulation rates compare among the lakes. For example, if the source for contaminant was the same over a region, the trajectories for the change in accumulation rates among the lakes should overlap.

As might be expected, the peak accumulation rates for lead reach the normalized value of one in the mid-1970s (Fig. 6a). The graph clearly shows the time of onset of the anthropogenic additions of lead to be the same among the lakes. Furthermore, except for Gratiot Lake, all of the lakes had a similar pattern of increase to the peak rates in the mid-1970s and their trajectories overlap. The difference in Gratiot Lake might be due to contribution of lead from

smelting operations or the influence of bioturbation, which can smear the sediment record (Robbins 1982). However, the decreasing trajectories in lead accumulation rates after the peak were not the same among the lakes. It can be seen in recent sediments that Gull Lake has returned to rates 15% of the peak with the other lakes following the order Cass (25%), Elk (45%), Higgins (70%) and Gratiot (70%).

Figure 6(b) more clearly shows how the timing for the onset of copper accumulations in the lakes differed. Additionally, once anthropogenic accumulations of copper begin, the rates of increase among the lakes were not as similar as they are for lead. Elk, Cass, Higgins and Gull

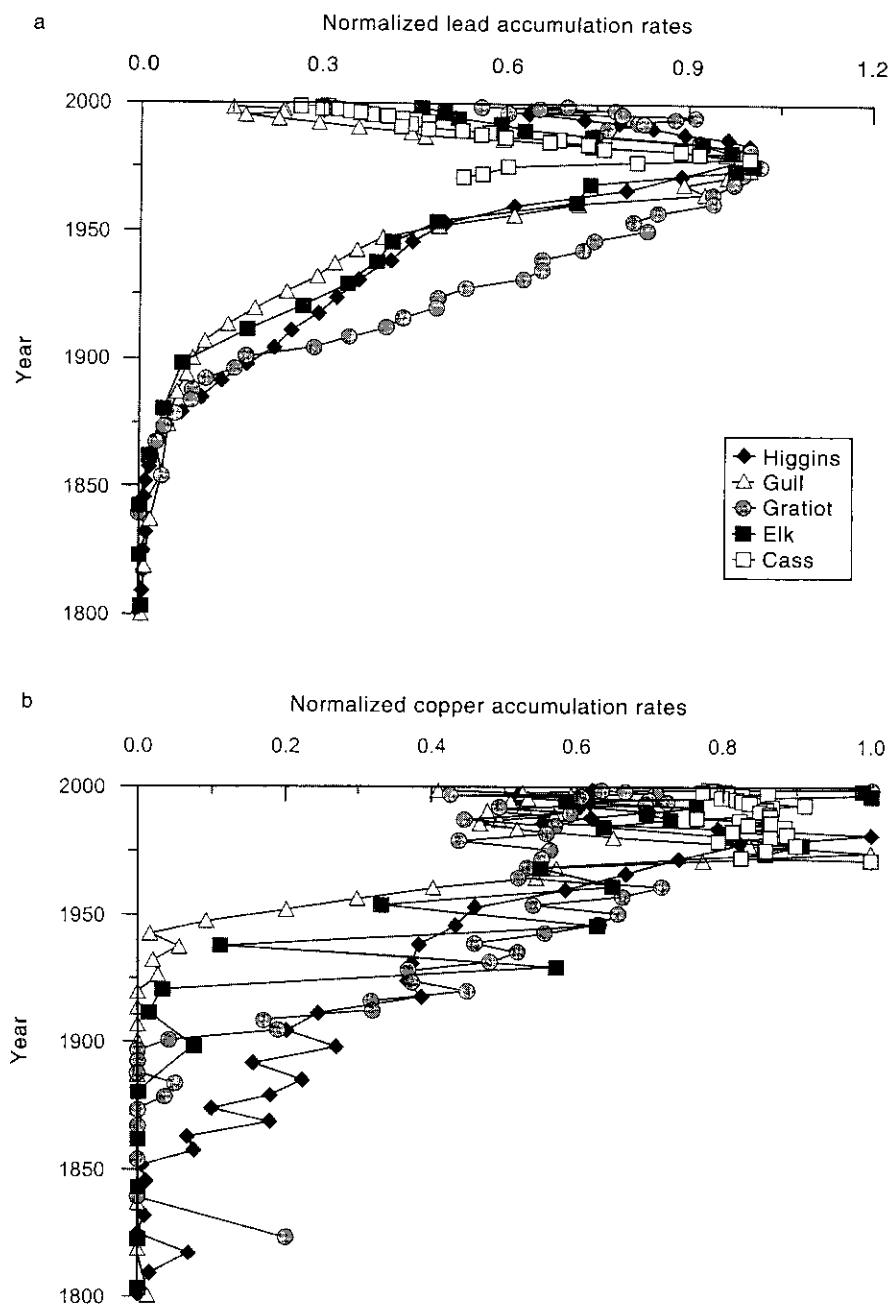


Fig. 6. Metal normalized rates for study lakes. Accumulation rates are normalized to the highest value in a core. (a) Lead, (b) copper.

lakes had peaks in accumulation rates in the mid-1970s. Elk Lake accumulation rates in recent sediments remain similar to peak rates, unlike Cass, Higgins and Gull Lakes. Post mid-1970s, there was very little similarity in the rates of change for copper accumulation among the lakes. For example, Gull Lake has returned to 40% of the peak with the other lakes following the order Higgins (62%), Cass (78%), Elk (99%), Gratiot (100%).

For lead, the overlapping peak concentrations and trajectories of the temporal change of accumulation prior to the mid-1970s further supports a regional source for loadings in this portion of the Great Lakes. The consistent onset of the occurrence of anthropogenic lead implies a rapid distribution from the source. These observations are consistent with the atmosphere as being the dominant source for lead prior to the mid-1970s. The decrease in accumulation rates after this time was related to environmental legislation and the subsequent removal of lead from gasoline (Evans & Dillon 1982; Eisenreich *et al.* 1986; Graney *et al.* 1995). The lack of overlap of the normalized accumulation trajectories after the mid-1970s is consistent with the hypothesis that the source for lead in the environment is changing from regional influences to more local or watershed scale influences.

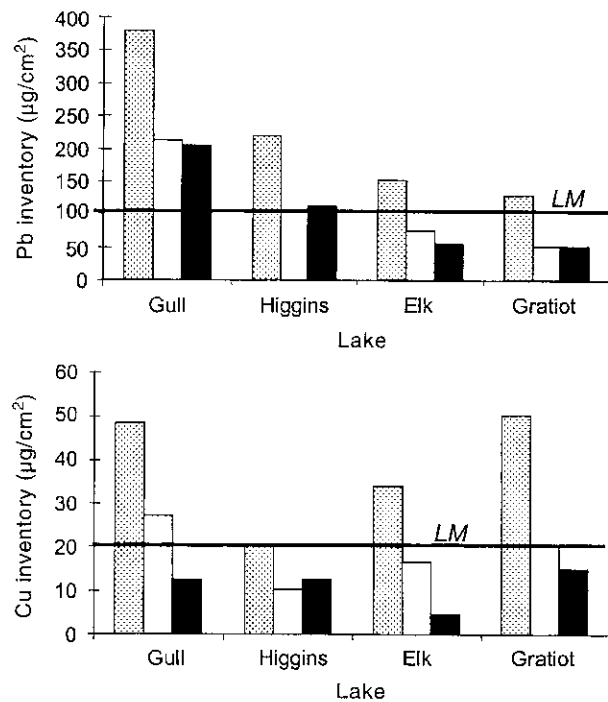


Fig. 7. Metal inventories as a function of background correction for study lakes. (a) Lead, (b) copper. Lake Michigan (LM) values for lead are from Long *et al.* (1995) for copper from Kolak *et al.* (1999). (■) none; (□) pre-1880s; (▨) watershed.

Although atmospheric deposition has been suggested as a source for copper (Eisenreich *et al.* 1986), the temporal relationships of the accumulation trajectories are not as consistent with the hypothesis as they are for lead. The impact from humans on copper loadings to the environment is clear, but a regional source does not appear to be evident from the above analysis.

Anthropogenic inventories

To further examine the role of the atmospheric influence on lead and copper accumulations in the sediment of the lakes, focusing corrected anthropogenic inventories were compared. Anthropogenic inventories are a measure of the total mass in a core of contaminant input by humans per unit area ($\mu\text{g}/\text{cm}^2$), as shown in equation 3:

$$\text{Inv}_i (\mu\text{g}/\text{cm}^2) = (\sum_i [\text{Csed}^* \times ((1-\phi) \times \rho \times d)]) / \text{FF}_j$$

where Inv_i = focusing corrected inventory for i^{th} metal in the sediment core ($\mu\text{g}/\text{cm}^2$), Csed^* = watershed background corrected concentration of metal in sediment ($\mu\text{g}/\text{g}$ dry weight), ϕ = porosity, ρ = sediment dry density (g/cm^3), d = thickness of sediment increment (cm), i = number of depth increment, and FF_j = focusing factor at j^{th} core site.

If atmospheric deposition is the major source of a chemical to lakes, then focusing and watershed corrected 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. If inventories for a contaminant are different among all lakes and no regional trend is evident, then local sources dominate contaminant loadings in the lakes. Regional patterns in inventories could indicate the roles of land use in contaminant loadings.

The anthropogenic inventories of lead (Fig. 7a) among inland lakes sampled were not equal, indicating that if the atmosphere was the source for lead, then the lead concentrations in the atmosphere were not well mixed. The highest inventory is in Gull Lake, which is located relatively close to the greater Chicago area, and the lowest inventory was in Gratiot Lake, which is located relatively far away from major sources of lead to the atmosphere. This regional north-south trend is consistent with results from Lake Michigan, with the highest loading of lead occurring in its south basin nearest Gull Lake and lowest in the northern basin near Elk Lake (Edgington & Robbins 1976). Figure 7(a) also shows the influence of correcting the inventory value by using either pre-1800 background metal concentrations or watershed background concentrations to determine anthropogenic concentrations in the sediments.

The pattern of inventories for copper (Fig. 7b) is not similar to that of lead. Gull and Higgins lakes have similar inventories, Elk Lake the lowest, and Gratiot the highest. Gratiot Lake, however, is located on the Keweenaw Peninsula of Michigan, a region of Michigan characterized by copper-mining activities (Kolak *et al.* 1999). Although copper was not mined in the watershed of Gratiot Lake, the lake's proximity to the mining activities made it susceptible to emissions (e.g. smelters), resulting in the relatively high inventories. The lower copper inventory values for Elk Lake than Higgins and Gull lakes might indicate some form of a regional gradient similar to lead.

The watershed corrected inventories for the inland lakes are around the average inventory values in Lake Michigan for lead (Long *et al.* 1995) and copper (Kolak *et al.* 1999), and shows that the environmental record from inland lakes can be compared to the record from large lakes.

Temporal and spatial patterns of accumulation

The previous analysis indicated that both dominant (regional) and local (watershed) factors are involved in the accumulation of lead and copper in the environment and that the relative contributions of these factors have changed over time. Although spatial analysis of anthropogenic inventories is an important approach that gives insight into possible regional and watershed influences, inventories cannot be studied over time. Changes in the spatial pattern of accumulation rates over time might, however, give insights into changes in regional and watershed influences on lead and copper loadings to the environment.

Figure 8(a,b) shows the temporal and spatial changes in lead and copper anthropogenic accumulation rates in the study lakes in Michigan. Metal accumulation rates are shown for each decade, starting with 1890. The rates are averages for a 10-year period, 5 years before and 5 years after the decade. For example, the rates for 1990 are calculated as the average from 1985 to 1995. The purpose of using averages rather than the value for a particular year is that a particular year might not be represented by a sample taken and would have to be estimated from the shape of the sediment accumulation curve (e.g. Fig. 6a), and there is some degree of inaccuracy in the estimates of the sediment ages. Considering the rates of change observed in the sediment for metal accumulation, being off by only a few years can significantly affect accumulation values being compared. Using averages minimizes both of these issues.

At the onset of significant inputs of anthropogenic lead to the environment (e.g. 1890), a regional pattern of higher

accumulations rates to the south and lower to the north is evident. By the 1930s, the pattern was well developed and was maintained through to the 1980s. By 1990, however, the pattern appears to break down. Gull Lake no longer has the highest rates of lead accumulation and Gratiot and Elk were similar. Higgins, in 1990, had the highest rate of lead accumulation.

In contrast, no clear pattern emerged for copper accumulation until the 1960s (Fig. 8b). Prior to that time, Higgins Lake and, eventually, Gratiot Lake, had the highest rates of accumulation. In 1960, copper accumulation in Gratiot remained high; however, an accumulation pattern similar to lead was seen for Gull, Higgins and Elk lakes. Gull had the highest rates of copper accumulation and Elk the lowest. Although the rates were slightly lower, the pattern remained in 1990.

We interpreted the changes in the spatial and temporal patterns of lead accumulation to be due to change from more regional influences on lead loadings (e.g. atmosphere and leaded gasoline emissions) to more local influences (e.g. watershed and population density). For copper, local influences (e.g. copper mining) play a role. If the pattern of copper accumulation in Gull, Higgins and Elk lakes represent a regional influence, the cause of this influence

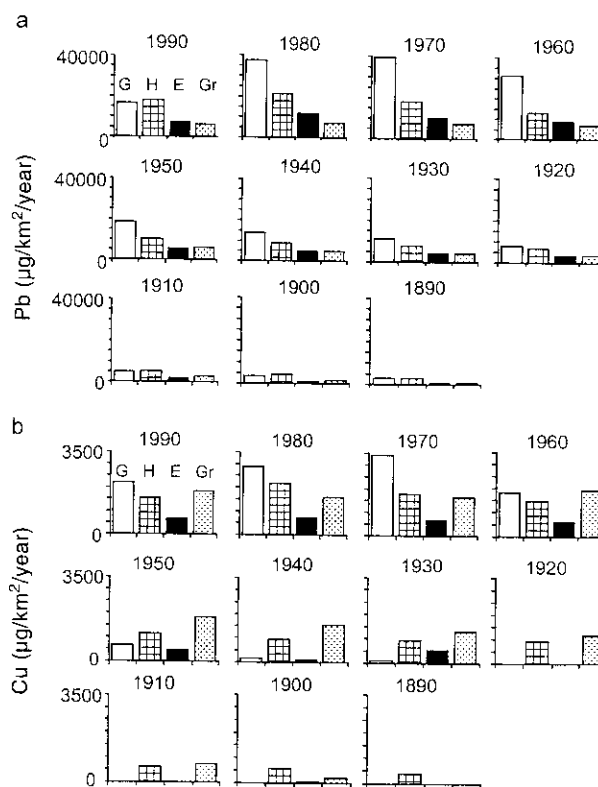


Fig. 8. Decadal metal accumulation rates for study lakes. (a) Lead, (b) copper. E, Elk; G, Gull Lake; Gr, Gratiot; H, Higgins; y, year.

Table 2. Areas, populations and population densities for watersheds of the five study lakes in Michigan

| Watershed | Watershed area (km ²) | Watershed population | Population density (per km ²) |
|--------------|-----------------------------------|----------------------|-------------------------------------------|
| Cass Lake | 11.6 | 5830 | 946.0 |
| Elk Lake | 120.8 | 1280 | 20.0 |
| Gratiot Lake | 26.3 | 7 | 0.4 |
| Gull Lake | 14.7 | 326 | 52.0 |
| Higgins Lake | 116.5 | 2561 | 75.0 |

is unclear and most likely it is not related to the atmosphere.

Population effects on lead and copper accumulation

To explore the role of watershed scale influences such as population density (e.g. Callender & Rice 2000), population densities for the watershed surrounding a lake were compared to accumulation rates within the lake. Areas in the watershed ranged from 11.6 to 120.8 km² (Table 2), and populations ranged from 7 to 5830 with population densities of 0.4–946 people/km². Because of the assumptions made in determining population within the watershed (e.g. that population is spread evenly throughout all areas that are not state owned or water), there is clearly error present in the watershed populations. The most significant source of error is likely from not accounting for the tendency of people to live near water, which would result in an underestimation of population density within the watershed.

Additional error was incurred when delineating the watersheds, particularly for lakes with little topography (e.g. Cass Lake), but this source of error was probably not significant compared with the error inherent in assuming an even distribution of people throughout each census tract. Finally, no attempt was made to account for seasonal increases in population, which might be significant around some of the lakes (e.g. Gratiot Lake population might increase almost ten-fold, Hay, pers. com., 2000). However, the results still reflect the observed relative density of population around lakes, with Cass having significantly higher development around the lake, and Gratiot Lake being the least developed.

Population densities for each watershed in 1990 are plotted against 1990 accumulation rates for lead and copper in Fig. 9. In Fig. 9(a), all five lakes are included and the trend of the data clearly show that there is a relationship between population density and the lead-accumulation rate, but this relationship does not appear to be linear. Cass Lake, near Detroit, had the highest population density and highest rate of lead accumulation. Recent lake sediments have been highly disturbed by waste additions from a

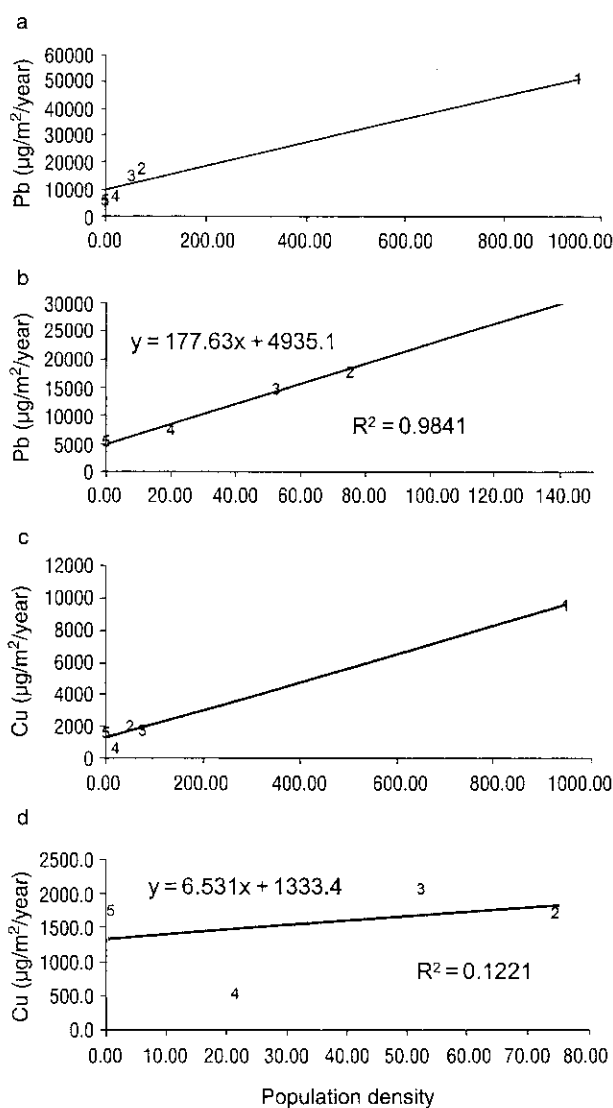


Fig. 9. Metal accumulation rates versus watershed population densities for study lakes. (a) Lead with Cass Lake, (b) lead without Cass Lake, (c) copper, (d) copper without Cass Lake. Lake numbers: (1) Cass, (2) Higgins, (3) Gull, (4) Elk, (5) Gratiot.

treatment plant, perhaps causing the unusually high sedimentation rates found for the lake. The non-linearity between Cass Lake and the other lakes might be related to

underestimated population densities in the other four lakes, to a non-linear relationship between population density and the accumulation rate, or to additional sources of lead not related to population density present in some of the lakes. Re-plotting the data without Cass Lake (Fig. 9b) showed that there is a linear relationship between population density and the lead-accumulation rate. The intercept (e.g. zero population density) of approximately $5000 \mu\text{g}/\text{m}^2/\text{year}$ for lead accumulation might be considered the current regional lead accumulation rate.

Accumulation rates of copper exhibited a different pattern, with Gratiot Lake appearing to have a higher than expected accumulation rate (Fig. 9c,d). These high rates again show the importance of the local copper mining activities and, therefore, the higher input rate not related to population density would be expected. Overall, there is no clear relationship between the 1990 population density and copper 1990 accumulation rates.

Because of the error present in the population-density estimations, and because of the small sample size of five lakes, great care must be taken in interpreting the data. It is crucial to realize that because Cass Lake has a significantly higher population density and significantly higher rates of heavy-metal input, it is possible to have statistically significant results when there appears to be little correlation between population density and accumulation rates for the other four lakes. Therefore, although preliminary conclusions might be drawn from these data, further samples are needed to verify the results.

The rates of input of lead, but not copper, to inland lakes in Michigan are related to population density within the watershed. The relationship might be due to a direct relationship between the two factors (e.g. lead in sewage where the amount of sewage would be directly related to the number of people), or due to an indirect relationship (e.g. population related to amount of industry or road density).

Whether the relationship is direct or indirect, the results indicate that local processes are important in the current chemical loading to lakes. This supports the earlier conclusion that the dominant source for lead has changed in the last decade from regional atmospheric sources to more localized sources (Dillion & Evans 1982; Eisenreich *et al.* 1986). These results are similar to the results of Callender and Rice (2000), who found a relationship between population density and concentrations of lead in five reservoirs located along a rural-urban gradient.

DISCUSSION AND CONCLUSIONS

Lead and copper concentrations in sediment cores from five inland lakes in Michigan were studied to test the hypothesis that the spatial pattern of chemical accumu-

lation rates provides insight into the causes for the historical and continued loadings of contaminants to the environment. The data showed that the loadings of lead and copper to the environment are generally decreasing from historic high loadings in the mid-1970s, but have not decreased to background values. However, the data do show that as loadings from dominant (regional) sources for chemical loadings decrease (e.g. atmospheric deposition in the case of lead), new patterns provide insight into causes for continual contaminant loadings (e.g. population density).

The data also show the universal response of the watersheds to the onset of the anthropogenic loadings of lead, but not that of copper. Individual watersheds had different onset times for anthropogenic copper loadings. The magnitude of recent loadings of lead to the environment can be related to population density. The magnitude of recent copper loadings reflect, in part, a spatial pattern that is similar to the regional pattern for lead during the mid-1970s. This pattern for lead could be related to a regional gradient of lead concentrations due to atmospheric deposition, but the same relation cannot be made for copper. The cause for this spatial pattern for copper is not clear.

Finally, it is clear that sediment chronologies provide important insights into contaminant loadings to the environment over various temporal and spatial scales. We also suggest that using an approach that combines both spatial and temporal analysis gives the most robust information about the history and current state of chemical loadings to the environment.

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