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NATURAL AND ANTHROPOGENIC FACTORS INFLUENCING  
SPATIAL AND TEMPORAL PATTERNS OF METAL  
ACCUMULATION IN INLAND LAKES

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**NATURAL AND ANTHROPOGENIC FACTORS INFLUENCING SPATIAL AND  
TEMPORAL PATTERNS OF METAL ACCUMULATION IN INLAND LAKES**

**By**

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## ABSTRACT

### NATURAL AND ANTHROPOGENIC FACTORS INFLUENCING SPATIAL AND TEMPORAL PATTERNS OF METAL ACCUMULATION IN INLAND LAKES

By

Sharon Simpson Yohn

The natural cycles of trace metals in the environment have been significantly influenced by humans, resulting in toxicological concerns for both humans and wildlife. Although environmental legislation reduced loading of some metals, humans continue to alter the environment in ever increasing ways. In order to reduce the input of metals to the environment, it is necessary to understand both current and historical sources and contaminant pathways. To help determine this, sediments were collected from 17 lakes in Michigan, USA, sediment profiles were examined and interpreted, and anthropogenic accumulation rates were correlated to characteristics of the watershed during two time periods (1970s and 1990s) to understand both natural and anthropogenic factors influencing contaminant accumulation in the sediment. Lakes record the input of contaminants from both the local watershed and from atmospheric deposition over time, and are therefore ideal for identifying sources and evaluating temporal changes.

Elements within each lake were grouped using cluster analysis based on the similarity of depth profiles, with each group representing a unique source and/or process, including terrestrial, diagenetic, anthropogenic and carbonate groups. Representative elements were chosen for each group, and these elements were used to help quantify anthropogenic accumulation rates of cadmium, copper, lead and zinc.

Cadmium, zinc and lead anthropogenic accumulation rates decreased from the 1970s to the 1990s in most lakes, probably in response to environmental legislation. Copper accumulation rates remained the same or increased over that time period for many of the study lakes, indicating that historical sources have not been reduced by environmental legislation, or that new sources have emerged.

Multivariate regression models using a maximum of two watershed characteristics to predict anthropogenic accumulation rates for each metal were determined for both time periods to provide insight into the dominant sources and pathways of these metals in the environment. Cadmium and lead accumulation rates were best predicted by characteristics that seem to represent atmospheric transport and deposition in the 1970s, including sulfate deposition rates and either average slope of the watershed or slope within a 100 m buffer of the lake. The reason for a negative correlation between slope and lead and cadmium accumulation rates is unclear, but the average slope of the watershed has a regional gradient similar to that of the overall population distribution in the state and may represent local atmospheric deposition. Copper and zinc are best predicted by population density in the 1970s. Percentage urban land cover in the watershed is the best predictor of all four metals in the 1990s, indicating that local sources are currently more important than regional atmospheric sources. Future work can now focus on identifying the specific sources of these metals that are represented by urban land cover.

## DEDICATION

**This dissertation is dedicated to my husband, Chuck Yohn,  
for his constant encouragement, support and patience.**

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Images in this dissertation are presented in color.

## CHAPTER 1 INTRODUCTION

Humans have significantly modified the natural cycle of several metals (e.g., Cd, Cu, Pb, Zn), resulting in enrichment of these metals in the environment and toxicological concerns for both wildlife and humans (Nriagu, 1978; Nriagu, 1989; Eisenreich and Strachan, 1992; Catallo et al., 1995; Sanudo-Wilhelmy and Gill, 1999). Environmental legislation, such as the Clean Air and Water Acts, reduced inputs of lead to the environment (Graney et al., 1995; Long et al., 1995; Callender and vanMetre, 1997; Callender and Rice, 2000; Simonetti et al., 2000; Mecray et al., 2001), but concentrations in the water, air and sediment remain elevated (Graney et al., 1995; Long et al., 1995; Callender and vanMetre, 1997; Mecray et al., 2001). Humans continue to alter the environment in ever increasing ways, including population growth and urban sprawl, which may result in new and emerging contaminants and sources. In order to continue reducing the loading of toxic trace metals to the environment it is necessary to understand current sources for these metals, and their pathways through the environment. Additionally, by understanding the history of contaminant inputs, it may be possible to determine how and if sources have changed over time. One technique for understating the history of trace metal inputs to a region is through the examination of sediment chronologies from multiple lakes.

An accurate record of historical chemical inputs to the lake is needed to be able to explore which processes and sources are influencing chemical loading to the environment, and how they have changed over time. Ideally, this history would be

recorded in such a way that the different sources and/or processes influencing the chemical inputs could be differentiated. Such a record exists within sediment chronologies from inland lakes (Callender and Rice, 2000), which act as collectors of metals from both the local watershed and regional atmospheric deposition. The disadvantage of sediment chronologies is that 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 (Balogh et al., 1999). However, the presented approach has four aspects that facilitate the differentiation of changes in sources and processes: data are collected for multiple elements rather than only contaminants, data are represented from large time intervals (>200 y), data are collected over a large spatial area, and data are compared to watershed characteristics that represent different sources and pathways. Although all of these approaches have been used individually (Bruland et al., 1974; Dillion and Evans, 1982; Birch et al., 1996; Heyvaert et al., 2000), this work is the first to incorporate all four.

It is necessary to quantify the rate of chemical input to a lake from anthropogenic sources to determine possible sources and pathways of contaminants using sediment chronologies. The multi-element approach allows the differentiation between *natural inputs* (inputs of metals from naturally occurring erosion or atmospheric deposition), *secondary human inputs* (increased inputs due to erosion from human activities, such as clear cutting), and *direct human inputs* (selective enrichment of certain elements due to human activities, such as lead enrichment due to the use of leaded gasoline) (Bruland et al., 1974; Johnson and Nicholls, 1988;

Ramanathan et al., 1996; Heyvaert et al., 2000; Kang et al., 2000). The examination of multiple elements also gives insight into the effects of diagenesis (Harrington et al., 1998; Brown et al., 2000), and identifying those elements that have been mobilized and represent geochemical processes rather than a history of inputs.

Sediment chronologies from multiple lakes provide information over both space and time, and provide useful insight into the history of contaminant inputs. Spatial patterns can be used to help determine if sources are controlled regionally (a spatial gradient is observed), or at the watershed scale (no spatial gradient), but provide little information about specific sources. Temporal patterns of metal accumulation can be compared to a qualitative (e.g., presence of smelters, tanneries) (Catallo et al., 1995; Spiethoff and Hemond, 1996) or a quantitative (e.g., copper mining production records) (Kerfoot et al., 1994) history of the region to understand the input of metals to the lake. Unfortunately, while in some cases the actual flux from a source is known (e.g., atmospheric flux or sewer outfall) (Bruland et al., 1974; Evans and Dillon, 1982; Johnson and Nicholls, 1988; Balogh et al., 1999), generally there is not a historical record of flux from a source.

Because the exact flux from a particular source is often unknown (e.g., input from mining), a quantifiable *watershed characteristic* that acts as an indicator of source(s) may be used instead (e.g., copper mining production records as an indicator of input from mining) (Kerfoot et al., 1994). Although this watershed characteristic does not provide the exact proportion of the input that comes from that source, use of watershed characteristics can indicate if a particular source influences chemical input into the lake at different time periods. This study will compare anthropogenic

accumulation rates from multiple lakes to watershed characteristics for two time periods (1970-1980, 1990-2000) to identify sources and pathways of metals through the environment, and evaluate changes over time. These two time periods were chosen to represent the period of intense industrial activity (1970s) and a more current time period after significant environmental legislation (1990s).

The watershed characteristics that will be examined in this study represent physical, transport, and source characteristics. The physical characteristics include lake surface area, watershed area, and watershed to lake area ratio. These parameters may give insight into the importance of atmospheric deposition; a lake with a small watershed to lake area ratio may be dominated by atmospheric deposition, whereas a lake with a large ratio may be more influenced by inputs from the watershed (Dillion and Evans, 1982).

The transport characteristics represent the pathway of metals to a lake. The presence of a source of metals will not be recorded in the lake sediments unless those metals are transported to the lake. The average slope of the watershed and K factor (measure of erodibility) were included to represent the erodibility of soils within the watershed (Detenbeck et al., 1993). Any metal deposited on the land from sources such as pesticides or fertilizers (Muhlbaier and Tissue, 1981; Rice, 1999) must be eroded before reaching the lake, and may be dependant on soil erodibility. Sulfate deposition rates were estimated to evaluate the importance of atmospheric deposition. The atmosphere can be an important pathway of metals to lakes (Winchester and Nifong, 1971; Gatz, 1975; Gatz et al., 1989; Nriagu, 1989; Callender and vanMetre, 1997; Sweet et al., 1998; Rice, 1999; Callender and Rice, 2000; Simonetti et al., 2000;

Goodarzi et al., 2001; Souch et al., 2003), but accurate estimations of deposition rates of metals for each watershed are difficult to determine. Sulfate deposition, however, has been monitored throughout Michigan (National Atmospheric Deposition Program (NRSP-3)/National Trends Network, 2003), and can be used to estimate the relative distribution of atmospheric deposition due to coal and oil burning. Both sulfate and trace metals are released with the burning of fossil fuels (Nriagu, 1989; Berner and Berner, 1996). Sulfate deposition rates will not, however, represent atmospheric deposition from other sources (e.g., copper from copper smelting, lead from the burning of leaded gasoline).

The source characteristics include Toxic Release Inventory data, population density, and land cover. Releases of toxic chemicals are required to be reported by the Emergency Planning and Community Right-to-Know Act of 1986 (EPCRA), including the location and quantity of release. These data represents point source inputs that may be unique to that lake. Watershed population density and urban land cover both represent sources related to human development, including: releases from the wear of automobile parts (Rice, 1999), automobile emissions (Callender and vanMetre, 1997; Rice, 1999), road dust (Shahin et al., 2000), wastewater, and household and yard waste (Callender and Rice, 2000). Agricultural land use represents pesticide and fertilizer use (Muhlbaier and Tissue, 1981; Rice, 1999). Forest and wetland land cover correspond to areas that should have no anthropogenic sources.

All of the characteristics are quantified on the watershed scale, but it is conceivable that sources that are closer to the lake will be more important than those

further away (Comeleo et al., 1996; Richards et al., 1996; Basnyat et al., 1999). Previous work on water quality parameters and aquatic sediments provides mixed results, with some variables predicted best with whole watershed data, and others when proximity to the waterbody was taken into account (Comeleo et al., 1996; Richards et al., 1996; Johnson et al., 1997; Basnyat et al., 1999). To address the issue of proximity, land cover, K factor, and slope were quantified in a 100 m buffer around the lake (Richards et al., 1996; Johnson et al., 1997), and land cover was weighted by the inverse of the distance to the lake along the flow path (Comeleo et al., 1996).

Previous studies found relationships between: lead and zinc concentrations in stream and reservoir sediments and population density (Callender and Rice, 2000); the sum of concentrations of mercury, copper, lead and zinc in stream sediments and population density (Rice, 1999); and metal concentrations in estuary sediments and percent urban land, point source effluent volumes, metals inputs (positive relationships) and percent area of non-forested wetlands (negative relationship) (Paul et al., 2002). These studies examine only recent relationships, rather than examining the change in patterns over time. This study will use the approach of examining spatial patterns and relationships to watershed characteristics, but also examine the changes in these relationships over time.

This study will combine the multi-element, temporal and spatial aspects of different studies performed in the past to develop a more complete understanding of what is influencing the chemical fluxes and geochemistry of lake sediments. This study is unique because it will combine all three aspects (spatial, temporal, multi-element) for metal accumulation rates and both geochemical and anthropogenic

factors landscape variables such as land use, population density, and soil erodibility. This approach will lend insight both into the factors that influence the geochemistry of lake systems, and to what degree a system is influenced by anthropogenic activities. It will also help identify sources and pathways of toxic metals in the environment.

### **Hypothesis and approach**

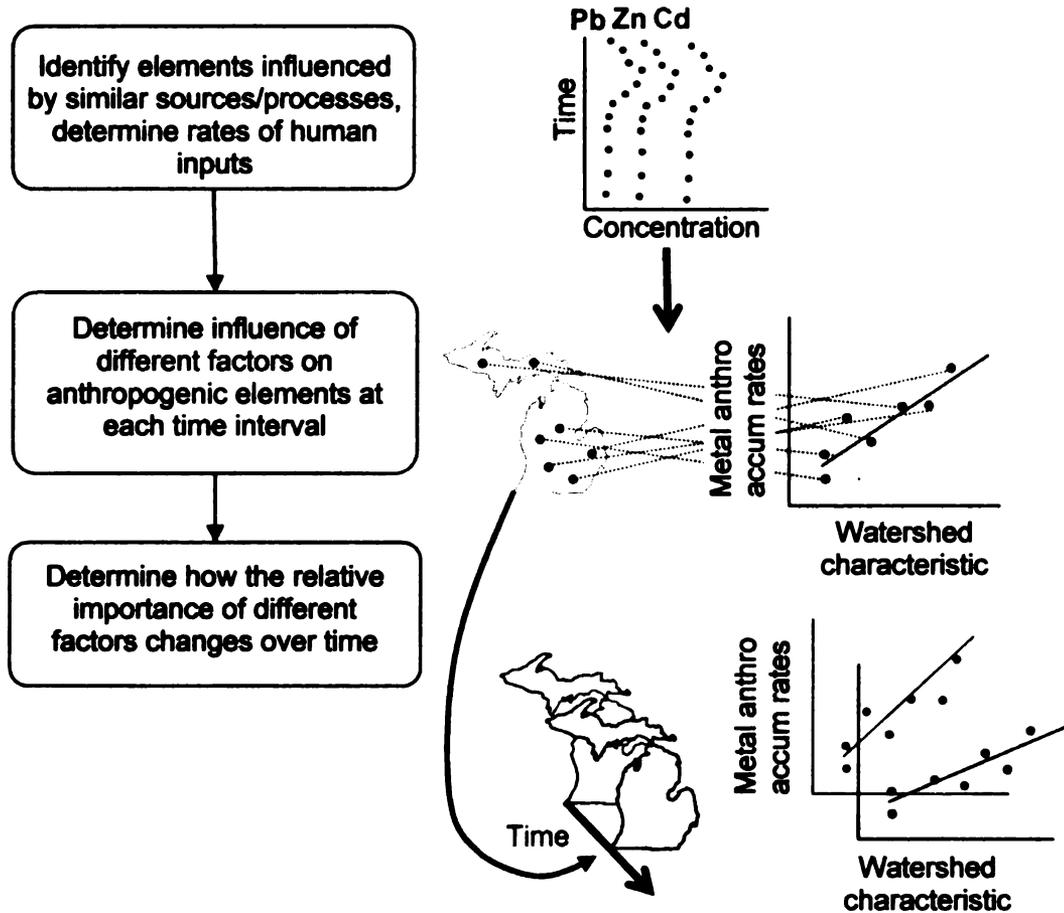
The goal of this work is to evaluate the sources for metals and their pathways through the ecosystem, and how they have changed over time by assessing the relative importance of factors influencing the rate of chemical input to lakes for different time periods. The working hypothesis is: **sources and pathways controlling metals in the environment have changed over time, and these changes should be reflected both in the spatial patterns of metal accumulation rates in lake sediments and the changing correlations between metal accumulation rates and characteristics of the lake watersheds.**

A three-step approach is used to test this hypothesis (Figure 1) and these are to:

1. Identify elements that are representative of classes. Classes are groups of elements that are influenced by the same sources and processes, and therefore can be represented by one element. Using this information, identify elements that are strongly influenced by direct human inputs and quantify anthropogenic accumulation rates.
2. Determine the influence of different watershed characteristics on accumulation rates of each of the elements shown to be dominantly influenced by anthropogenic actions at each time interval. At each time

interval, the influence of various characteristics (e.g., land use, population density) will be determined for each of these elements.

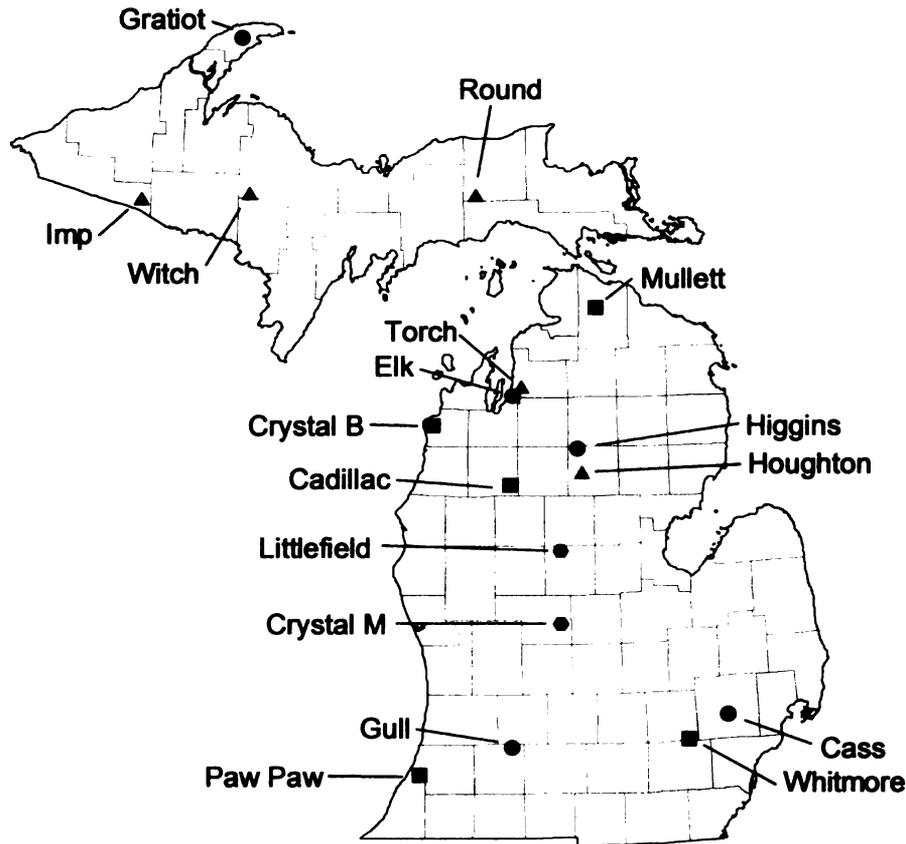
3. Examine the temporal changes in the importance of different factors.



**Figure 1.** Flow chart of research approach.

This hypothesis was investigated through the sampling of sediment from seventeen Michigan lakes (Figure 2), analysis and interpretation of metals in the sediment, and of data comparison to watershed characteristics during two time intervals (1970s and 1990s). This dissertation presents a broad scale approach to determine regional patterns, sources, and pathways of metals. It is beyond the scope of this work to describe each lake individually, but detailed descriptions of results and

additional data analysis for each of the lakes can be found in four year end reports (Simpson et al., 2000; Yohn et al., 2001; Yohn et al., 2002b; Yohn et al., 2003).



**Figure 2.** Location of lakes sampled in Michigan from 1999-2002 (● 1999, ◆ 2000, ■ 2001, ▲ 2002).

Chapter 2 describes the advantages and disadvantages of using factor or cluster analysis for grouping elements with similar depth profiles into classes (Yohn et al., in preparation-a). This chapter focuses primarily on the statistical tests using data from four representative lakes, while Chapter 3 provides the resultant groupings from the eleven lakes sampled from 1999-2001, excluding Cass Lake (Yohn and Long, in

preparation). The geochemistry and possible sources and processes influencing each class are discussed, and elements to represent each class are determined. The importance of the multi-element approach in the calculation of anthropogenic accumulation rates is also described.

Chapters 4 and 5 provide a proof of concept for steps two and three and preliminary data analysis. In Chapter 4, temporal patterns and changing spatial patterns in five Michigan lakes (sampled during 1999, Figure 2) are used to assess the importance of local and regional sources for copper and lead (Yohn et al., 2002a). Additionally, accumulation rates of lead and copper were compared to watershed population densities to further evaluate the importance of local sources. In Chapter 5 the changing source of lead and cadmium were evaluated by examining the similarity of sediment chronologies among 12 lakes (sampled during 1999-2001, Figure 2), spatial patterns of lead and cadmium accumulation for three time periods (1925-1935, 1965-1975, and 1985-1995), and the relationship between lead and cadmium accumulation rates in the sediment and watershed population densities for those three time periods (Yohn et al., 2004).

Lead inputs to inland lakes are the focus of Chapter 6, as well as the relationship between lead anthropogenic accumulation rates and characteristics of the watersheds (Yohn et al., in preparation-b). The accumulation rates of lead to 16 lakes (excluding Witch Lake) were compared to the characteristics of the watershed (e.g., population density, land cover), and multiple regression was used to determine which parameters best predict the rate of metal inputs. This chapter includes a comparison of two time periods, 1970-1980 and 1990-2000. These time periods differ from Chapter

5 because of the availability of land cover data. Witch Lake was excluded due to the local influence of mining on this lake.

Chapter 7 includes an analysis of copper, cadmium, and zinc. These elements have been shown to be primarily controlled by human actions (Chapters 1 and 2) and are discussed in a similar manner as lead in Chapter 6. This section is separated from the previous chapter in order to keep Chapter 4 at publishable length, but contains similar methods of data interpretation, and compares the same two time periods.

A summary and synthesis of the study is presented in Chapter 8. Additionally, this section discusses recommendations for the approach and direction of future work, and the transferability of this approach to other locations.

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## CHAPTER 2 THE USE OF MULTIVARIATE STATISTICS FOR THE INTERPRETATION OF SEDIMENT CHRONOLOGIES

### **Introduction**

Sediment chronologies have long been used to understand both natural and human influences on the environment (Edgington and Robbins, 1976; Kerfoot et al., 1994; Graney et al., 1995; Kolak et al., 1998; Khim et al., 1999; Lamoureux, 1999). While earlier studies often focused on specific chemicals of environmental concern, such as lead and cadmium (Iskander and Keeney, 1974; Dillion and Evans, 1982; Evans and Dillon, 1982; Johnson and Nicholls, 1988), the increased ability for multi-elemental analysis (e.g., inductively coupled plasma technology) has led to the simultaneous examination of a large number of elements in lake sediments (Kerfoot and Robbins, 1999; Sanei et al., 2001; Tuncer et al., 2001; Manta et al., 2002). The analysis of a suite of elements may provide insight into the geochemical processes occurring within the lake sediment and help clarify sources for different elements.

While the analysis of many elements may provide for a better understanding of the lake system, it also leads to large quantities of data which may be difficult to interpret. For example, the analysis of 25 elements in a sediment core vertically sectioned into 50 samples leads to over 1,200 individual data points. Because the data set is large, many investigators are using multivariate statistics to examine structure in the data that can aid in interpreting results (Kerfoot et al., 1994; Tuncer et al., 2001; Manta et al., 2002).

Multivariate statistics are typically used for initial data analysis to determine which elements follow similar trends over time in the sediment core, with the ultimate objective of using elemental behavior as an indicator for source (Kerfoot et al., 1994; Sanei et al., 2001; Tuncer et al., 2001). Similar vertical (e.g., temporal) trends are a good indication that a particular suite of elements may originate from the same source (e.g., aluminum from clay), or are influenced by the same process (e.g., erosion). Therefore, grouping elements with similar trends based on a statistical technique is useful because it reduces the number of individual trends to interpret, and may lend insight into the important sources or processes influencing that assemblage based on the elements found in the group. A group of elements may contain element(s) with well known sources (e.g., aluminum from natural terrestrial inputs such as clay); thus, other less studied elements in that group (e.g., vanadium) may be considered to be influenced by the same source and/or process (Manta et al., 2002). Additionally, a group may contain a suite of elements that matches the loading history of a particular point source, such as mining (Tuncer et al., 2001).

It is possible to determine which elements follow similar temporal trends by visual comparison of each trend. However, as the number of variables increases, it becomes more difficult to group each element, and more likely that not all relationships will be correctly identified. The potential benefit of using multivariate statistics to interpret sediment chronologies involving multi-element data sets is clear. What is less apparent is which multivariate technique is the most appropriate to use, the potential for incorrect interpretation, and what methodology should be used within each technique (e.g., should ranked or “raw” data be used?). Both factor and cluster

analysis have been used for sediment chronologies (Kerfoot and Robbins, 1999; Manta et al., 2002), with little discussion as to which technique is more appropriate to use or what the relative merits of the two approaches are. Additionally, each statistical technique has different options. For example, factor analysis could include principal component analysis or common factor analysis, and the starting point for the analysis could be a correlation matrix calculated using a parametric method (e.g., Pearson's product moment correlation coefficient) or a nonparametric method (e.g., Spearman's correlation coefficient). Different distance measures and clustering algorithms may be used for cluster analysis. As the use of multivariate statistics to interpret sediment chronologies increases, it is useful to describe and compare the statistical decision-making processes used so that results may be compared among studies. The results of earlier studies that have employed statistical techniques, such as factor and cluster analysis, to reduce sediment chronology data were generally reported with little description of the decision making processes involved (Kerfoot et al., 1994; Sanei et al., 2001; Tuncer et al., 2001). Consequently, it is difficult for other investigators to reproduce the analyses that might aid in the development of a consistent set of protocols so that comparable interpretations can be made among studies.

Therefore, we have chosen four lakes from the Michigan Inland Lakes Trend Monitoring Program ([http://www.michigan.gov/deq/0,1607,7-135-3313\\_3686\\_3728-32365--,00.html](http://www.michigan.gov/deq/0,1607,7-135-3313_3686_3728-32365--,00.html)) that represent a variety of lake conditions to illustrate the impact of the choice of statistical technique (either factor analysis or cluster analysis) along with the associated decision-making processes on the interpretation of sediment chronologies. The four lakes are a subset of 17 lakes for which sediment cores were

collected and analyzed for 18 elements. Statistical analyses were used for the purpose of choosing a representative element for each source/process grouping, and identifying elements that have been influenced by human inputs. For factor analysis, results from principle component and common factor analysis were compared, and for cluster analysis three clustering algorithms (Ward's, average, and single linkage) were examined. For both statistical methods, we explore the effect of outliers on the resulting groups. For all methods, the resulting groupings were visually checked for internal consistency.

The overall goal of this paper was to suggest a statistical technique and decision making processes for grouping elements in sediment chronologies with similar profiles, so that the proposed method may be tested in other regions and modified if necessary. It is inevitable that the use of multivariate statistics for this purpose will continue to increase, and it is essential for these statistics to be reported consistently. This paper also continues to explore the influences on the geochemical associations of chemicals in the environment.

### **Methods and Procedures**

In this section the procedures for the lake coring and geochemical analyses are described. Also, methods for identifying outlier points are outlined. In addition, a relatively comprehensive review of the two primary statistical methods, factor analysis and cluster analysis, is provided. We felt that a relatively lengthy description of these methods was necessary as many readers may not be aware of some of the important aspects and assumptions of these methodologies. Furthermore, an understanding of

the methods is required to provide context for our recommendations on the future use of these methods in interpreting sediment chronologies.

### **Geochemical analyses**

Elk, Gratiot, Gull, and Paw Paw lakes were chosen from the seventeen lakes sampled as part of the Michigan Department of Environmental Quality's (MDEQ) Inland Lakes Sediment Trend Monitoring program. They were chosen to represent a variety of lake sizes, sedimentation rates, sediment types (e.g., calcium carbonate rich and carbonate poor), and extent of human development around the lake. Sediment cores were collected from these four lakes during 1999 and 2001. Elk, Gull and Paw Paw lakes are located in the Lower Peninsula of Michigan on Pleistocene glacial deposits which are generally carbonate rich. Gratiot Lake is located in the copper rich Keweenaw area (Upper Peninsula of Michigan), part of the Canadian Shield, with little to no glacial deposits, and is calcium carbonate poor (Door and Eschman, 1970). The four lakes have very different sediment chemistries and profiles. Cores collected from Gull and Elk lakes comprise sediment deposited over several hundred years (~500 and 700 years respectively), while Gratiot Lake includes only 200 years and Paw Paw Lake 80 years of sediment history. Gull and Elk lakes are carbonate rich (300–400 g/kg Ca), while Paw Paw Lake has moderate calcium concentrations (40 g/kg Ca) and Gratiot Lake has very low calcium (2 g/kg Ca). For many elements in Gull and Elk lakes, the sediment profile is characterized by a large increase in concentration in the mid-1800s, while Gratiot and Paw Paw lakes are less dominated by one clear trend (Yohn et al., 2002b; Yohn et al., 2004).

Four replicate sediment cores from 45 to 56 cm long were taken from the deepest portion of each lake using a MC-400 Lake/Shelf Multi-corer (San Diego, CA) deployed from either the EPA Research Vessel *Mudpuppy* or the MDEQ Monitoring Vessel *Nibi*. A new set of cores was immediately taken if the cores showed any evidence of disturbance. Cores were examined and described in terms of color, texture, and signs of zoobenthos. Cores were immediately extruded and sectioned open to the atmosphere at 0.5 cm intervals for the top 5-8 cm, and at 1 cm intervals for the remainder of the core.

$^{210}\text{Pb}$  was measured on one core from each lake to determine sedimentation rates, sediment ages, and focusing factors by the Freshwater Institute in Winnipeg, Manitoba, Canada. Sediments from Gratiot and Paw Paw lakes were dated using the constant flux: constant sedimentation (CF:CS) model (Golden et al., 1993), and from Gull and Elk lakes using the segmented CF:CS model (SCF:CS) (Heyvaert et al., 2000). The use of  $^{210}\text{Pb}$  dating for these cores is discussed in detail elsewhere (Yohn et al., 2004).

Sediments for metal analysis were frozen for storage, freeze-dried and digested by nitric acid in a CEM-MDS-81D microwave (EPA Method 3051) (Hewitt and Reynolds, 1990). Standard reference material (NIST SRM 8704 Buffalo River Sediment) and procedural blanks were processed as well as three replicate digestions on two samples from each lake. The concentrated-acid digests were filtered through an acid-washed, distilled-deionized or E-pure (Barnstead International, Dubuque, IA) water rinsed 0.40  $\mu\text{m}$  polycarbonate filter (Nuclepore<sup>TM</sup>). Sediments were analyzed for a suite of metals and metalloids including magnesium, aluminum, potassium,

calcium, titanium, vanadium, chromium, manganese, iron, copper, zinc, arsenic, strontium, molybdenum, cadmium, barium, lead, and uranium in a Micromass Platform inductively coupled plasma mass spectrometer with hexapole technology (ICP-MS-HEX). Strontium data were not collected for Elk and Gull lakes, and potassium data were not collected for Paw Paw Lake.

### **Outlier analysis**

All of the data analysis techniques used in this study are sensitive to the presence of outliers (Hair, 1998). Outliers are data points significantly different from the rest of the data. Outliers may be the result of analytical/sampling errors or actually reflect unusually high or low element concentrations in the sediment. Although principal component, factor, and cluster analyses do not require data to be normally distributed (Hair, 1998), the vertical concentration data were first log-transformed since what may appear to be an outlier in the “raw” data may not be so when the data are transformed. A log transformation was chosen as geochemical data are often log-normally distributed. However, based on the Lillefors test (Wilkinson 2000), the log transformation did not significantly increase the number of elements that were normally distributed. Therefore, the original, non-transformed data were used in the statistical analyses and further examined for the presence of outliers. Data points were considered to be outliers if they were outside the outer “fence” as determined by boxplot analysis. The outer fence is defined as:

upper hinge + (3 x hspread) or

lower hinge – (3 x hspread)

where the “hinge” is the first or third quartile, and “hsread” is the distance between the hinges (SPSS 2000). This method finds data points that are far outside the range of the majority of the data, and these data may be influential when statistical analyses are performed.

Outliers were identified for all four of the lakes. Two or three samples near the surface had outlying values for several metals in Elk Lake (As, Mo, Mn, Ba, Fe). Gratiot Lake had one or two outliers for aluminum, magnesium, and chromium, Gull Lake had five outliers for arsenic, and Paw Paw Lake had four outliers for manganese, and one for barium and molybdenum.

Obviously, if outliers are due to analytical or sampling error, these data need to be removed from the data set. However, outliers that represent data accurately may be statistically influential, and one or two outlying data points could determine how an element profile groups. Consequently, it may not be appropriate to simply delete these influential points, as these points may be representative of certain processes. Our approach was to perform principal component, factor, and cluster analysis on all data for each lake and on data with the outliers removed. In addition, the statistical analyses were performed on ranked data, as the influence of outlier points is decreased when the data are ranked. Removal of outliers in Gratiot, Gull, and Paw Paw lakes did not significantly change the statistical results, or the resultant element groupings; therefore, only the results for the analyses for the “raw” and ranked data are shown below. Removal of outliers for Elk Lake did have a significant impact on the results, and results from all data types are discussed below.

## **Factor analysis**

Factor analysis (principal component or common factor analysis) is a technique used to reduce the number of variables in large data sets to a smaller number of components or factors, and is based on a correlation or covariance matrix (Klovan, 1975; Davis, 1986). Correlation, rather than covariance, should be used for datasets with variables that have greatly different ranges of values (Stenson and Wilkinson, 2000), such as sediment concentrations of elements. The resulting components or factors should represent the underlying structure of the data (Hair, 1998). The components or factors can be thought of as composite variables, which characterize more than one of the original variables and represent a common theme (Joreskog et al., 1976). For example, in our dataset, since the variables are metals, an anticipated factor is one that represents the terrestrial group of elements.

The first factor in factor analysis explains the largest amount of variance in the data, and is a linear combination of the original variables (Davis, 1986). The second factor then explains as much of the residual variance as possible, with each additional factor explaining less variance (Klovan, 1975). Factors may also be rotated to provide a more meaningful solution. In this case, the first factor does not explain the maximum possible variance; instead, a chosen number of factors are rotated to more evenly distribute the variance among factors and improve the interpretation of the factors. The *loading* of a variable on a factor is the correlation between that variable and the factor, and is a value from -1 to 1 interpreted in the same manner as a correlation coefficient (Joreskog et al., 1976). There is no agreement on what values should be considered high, moderate or low for loadings, which makes comparisons

among studies utilizing factor analysis difficult. Consensus on appropriate values or at least justification of the values chosen would facilitate the comparison of data from sediment chronology studies. Relatively high values were chosen for this study on the assumption that elements influenced by the same sources and processes will have very similar profiles and should be highly correlated. Elements with loadings greater than 0.8 (or  $< -0.8$ ) were considered to be highly loaded on a factor, and elements with loadings of 0.6-0.8 were considered to be moderately loaded. The squared loading represents the percentage of variance for that variable explained by the factor. For example, in our data we expect aluminum to load highly on a terrestrial factor, but lead to load weakly on that factor. The *eigenvalue* of a factor represents the total variance explained by that factor, and is the sum of squared loadings for a factor. If an eigenvalue of a factor is greater than one, that factor explains more variance than one variable (Hair, 1998).

For factor analysis to be an appropriate technique the variables must be correlated. A general guideline is that the correlation matrix should have a substantial number of correlations coefficients greater than 0.3 (Hair, 1998). Both a typical parametric (i.e., Pearson's) correlation coefficient and a nonparametric (i.e., Spearman's) correlation coefficient that is based on ranked data were calculated. Correlations among most of the elements within all of the four study lakes were greater than 0.3. Gull Lake had the greatest correlation among elements (98% of the possible variable pairs had values  $>0.3$  using the parametric correlation measure and 96% using the nonparametric measure), and Elk Lake had the second highest (74% and 82% for the parametric and nonparametric coefficients, respectively). The

variables were slightly less correlated for Gratiot Lake (65% and 64%), and considerably fewer variable pairs had correlations  $>0.3$  at Paw Paw Lake (48% and 48%).

Multiple factors are calculated from factor analysis, and it is not always straightforward to determine the number of factors that are meaningful. Additionally, when factors are rotated, the number of factors to rotate must be determined beforehand. There are several techniques to determine the appropriate number of factors, but the three most common are 1) retaining all factors with an eigenvalue greater than one, 2) retaining all factors that explain greater than 5% variance, and 3) using a scree test to estimate the appropriate number of factors to retain. A scree test simply involves plotting the eigenvalue for each factor versus the number of factors; the point at which the curve begins to straighten out horizontally represents the maximum number of variables to retain. The scree test typically results in more factors being retained than the other two methods (Hair, 1998). Our approach was to use factor analysis without rotation, and determine the appropriate number of factors to retain with each of the criteria individually. The factors retained by each approach were then rotated. Two additional models were also developed by retaining and rotating one more and one less number of factors. Then each of these models was examined to determine which was most appropriate.

There are several considerations when determining the most appropriate model. The total amount of variance explained should be high, but increasing the number of factors always increases the explained variance. If retaining and rotating an additional factor results in a factor with no high loadings, the solution with fewer

factors may be more appropriate, even though the total explained variance is slightly lower. Another consideration is the attainment of simple structure. The concept of simple structure is that each variable is well described by one, and only one factor, and therefore the resultant factors completely describe the underlying structure of the data set. In this case, all variables will load highly on one factor, and weakly on all other factors, and each factor will have more than one variable loaded highly on it. While complete simple structure is uncommon, the solution chosen should result in many variables being highly loaded on only one factor, rather than moderately loaded on two or more factors. The final consideration is that it should be possible to assign a meaning to each factor. For each factor, it should be considered which variables load highly or moderately on that factor, and if this combination of variables represents an underlying dimension in the data set. For example, aluminum, titanium, cobalt and vanadium may load highly on one factor, which would represent terrestrial inputs. All of these considerations must be taken into account when choosing the most appropriate solution.

As indicated earlier, each lake was also analyzed using principal component analysis. Principal component analysis takes into account all the variance among variables, which includes the common variance, specific (unique) variance, and error, while common factor analysis uses only the common variance and ignores variance unique to the variable (Davis, 1986; Hair, 1998). The communality of an element is the amount of total variance that is common with the other variables. When the communalities of most of the variables exceed 0.6, the results of common factor analysis and principal component analysis are essentially identical (Hair 1998). For all

lakes, the only elements having a communality less than 0.6 were chromium in Elk and Gratiot lakes, and titanium, arsenic, magnesium and manganese in Paw Paw Lake (Table 1). Not surprisingly, the results of the principal component analysis and common factor analysis differed little, and only the results from the common factor analysis will be discussed below.

**Table 1.** Communalities of each element for the four study lakes and Elk Lake with outliers removed.

	Gratiot	Gull	Paw Paw	Elk	Elk no outliers
Mg	0.872	0.711	0.529	0.987	0.979
Al	0.798	0.993	0.861	1.000	0.998
K	0.790	0.946		0.966	0.967
Ca	0.884	0.921	0.888	0.828	0.822
Ti	0.795	0.985	0.374	0.944	0.941
V	0.788	0.996	1.000	0.978	0.975
Cr	0.263	0.945	0.814	0.532	0.673
Mn	0.996	0.877	0.235	0.819	0.765
Fe	0.868	0.982	0.907	0.865	0.997
Cu	0.909	0.975	0.852	0.943	0.942
Zn	0.968	0.997	0.770	0.976	0.967
As	0.976	0.944	0.407	0.773	0.824
Sr	0.952		0.907		
Mo	0.394	0.847	0.854	0.638	0.232
Cd	0.870	0.942	0.910	0.773	0.835
Ba	0.930	0.946	0.544	0.971	0.908
Pb	0.933	0.930	0.796	0.944	0.930
U	0.871	0.788	0.765	0.789	0.805

### Cluster Analysis

Hierarchical cluster analysis is a grouping technique designed to maximize within group homogeneity and between group heterogeneity (Griffith and Amrhein, 1997; Gotz and Lauer, 2003). Although cluster analysis is typically used to group similar samples, it also can be used effectively to group variables (Hair, 1998). The goal of cluster analysis is to create groups of samples or variables (in this study, elements) that are similar in multi-dimensional space (Gotz and Lauer, 2003).

Similarity is based on some distance measure, such as Euclidean distance measure or correlation (Griffith and Amrhein, 1997). When clustering variables with very different ranges of values, it is most appropriate to use a correlation measure rather than Euclidean distance (Wilkinson et al., 2000). Therefore, Pearson's product moment correlation coefficient was used in the analyses described below, and the distance measure for each pair of variables for a given lake is one minus the correlation coefficient. Hierarchical cluster analysis first groups the two elements that are the most similar (closely correlated, short distance). Then the next two elements that are the most similar are clustered. This may mean that a third element is included with the first cluster, or that two new elements are clustered. This process is continued until all new elements are included in one cluster. Non-hierarchical methods, often called optimization methods, are also available. However, these methods require the number of clusters be specified before the analysis, and typically use Euclidean distance rather than correlation as the similarity metric.

While it is relatively straightforward to measure the distance between two elements, there are different methods of determining the distance between two clusters, and different clustering algorithms are used to determine which clusters are most similar. Three clustering algorithms were used in our analyses: single linkage, average, and Ward's method. All three algorithms look at all possible combinations of clusters, and determine which two are the most similar, and then join those two clusters. None of these methods allow regrouping of variables, that is, once a variable is placed in a cluster it cannot be removed. The average algorithm uses distances between the average values of clusters as a similarity measure, whereas single linkage

uses the distance from one element in one cluster to one element in another cluster, and uses those elements that are closest together. The Ward's method takes a slightly different approach, and attempts to minimize the within cluster sum of squares. Each of these methods has different biases. Ward's method is biased towards producing clusters of similar size. The average distance algorithm tends to produce clusters with similar variance. Single linkage may form long chainlike clusters where individuals in the groups may end up being dissimilar (Hair, 1998). It is common practice to apply more than one clustering procedure as a check for the stability of the groups and the existence of "natural" groupings.

#### **Assessment**

A review of previous literature revealed that multiple source and processes should be influencing depth profiles of metals in the sediments of the four lakes under study. Based on the literature, these sources and processes could be loosely categorized as terrestrial, anthropogenic, carbonate, and diagenetic. These initial definitions guided our interpretation of the statistical groupings from the factor analysis and cluster analysis procedures. Below, we describe how well the resulting groups fit these initially defined source/process groups, the potential relationships between these *a priori* identified source/process groupings, and additional groupings that may exist. In addition, these *a priori* defined groupings help to 1) cast the results of the statistical analysis in the context of widely-recognized underlying processes and 2) evaluate the physical plausibility of the resulting statistical groupings. The *terrestrial group* refers to elements influenced by clastic mineral detritus entering the lake, and, based on earlier work, is likely to include aluminum, titanium and iron,

potassium, cobalt, nickel, magnesium, sodium, scandium, and the rare earth elements (Bruland et al., 1974; Kemp and Thomas, 1976; Johnson and Nicholls, 1988; Boyle et al., 1999; Kerfoot and Robbins, 1999; Qu et al., 2001; Sanei et al., 2001; Yohn et al., 2002a). The *carbonate group* refers to elements influenced by the precipitation and dissolution of calcium carbonate in the water column and, in addition to calcium, may include strontium, magnesium, iron, manganese, and barium (Auer et al., 1996; Sanei et al., 2001). The *diagenetic group* is intended to include elements that are gained, lost, or redistributed in the deposited sediment either due to a change in the oxidation state of that metal or association with a redox influenced element, and may include iron, manganese, arsenic, molybdenum, and uranium (Cooper and Morse, 1998; Brown et al., 2000). Finally, the *anthropogenic group* refers to elements whose concentrations in the sediment have been enriched by human actions, and may include arsenic, cadmium, copper, chromium, mercury, lead, and zinc (Bruland et al., 1974; Iskander and Keeney, 1974; Lantzy and Mackenzie, 1979; Evans and Dillon, 1982; Spiethoff and Hemond, 1996).

### **Factor Analysis**

A lake by lake assessment of the efficacy of factor analysis in delineating element groups with similar profiles follows. Additionally, possible causes of the differing success among lakes are discussed. The results from the common factor analysis are discussed in the most detail, although at the end of this section these results are compared to those from factor analysis using a nonparametric correlation matrix.

### *1) Gratiot Lake*

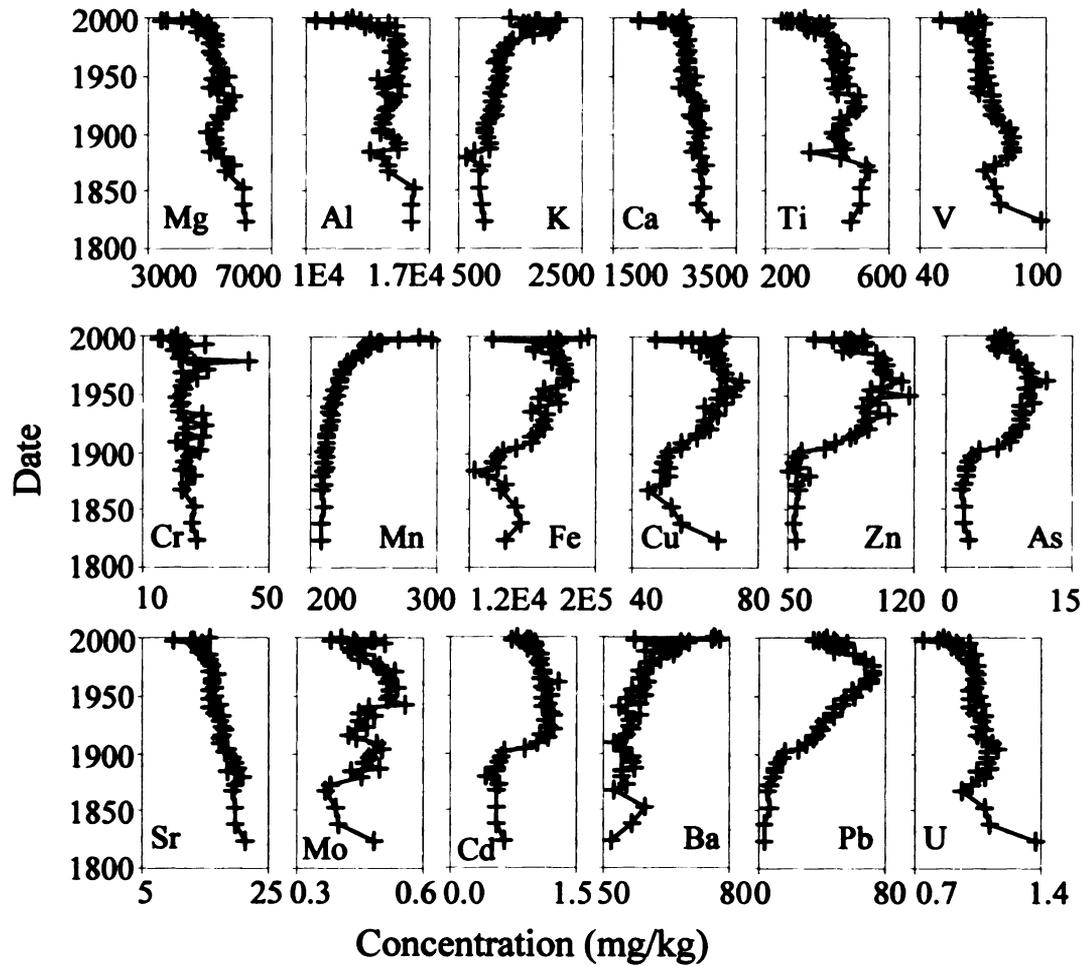
Factor analysis on sediment chronology data from Gratiot Lake resulted in three factors with variance greater than 5%, and two factors with eigenvalues greater than one (Table 2). The use of two rotated factors resulted in the greatest number of high loadings, whereas the use of a third factor resulted in one factor that was moderately loaded on only manganese and barium (Table 2). Therefore, the solution with two rotated factors was chosen as the most appropriate solution. Additionally, this solution makes some geochemical sense. Elements loading positively on Factor 1 represent terrestrial elements, and include titanium, aluminum, strontium, magnesium, calcium, uranium, and vanadium. Potassium, manganese and barium load negatively on Factor 1, and their trends are characterized by an increase in concentration near the sediment-water interface (Figure 1). This may represent diagenetic processes (Kneebone and Hering, 2000) or a diluting phase (e.g., organic matter), since these elements increase in concentration as the terrestrial elements decrease (Jaquet et al., 1982).

Elements that are highly or moderately positively loaded on Factor 2 appear to represent the anthropogenic elements (Bruland et al., 1974; Iskander and Keeney, 1974; Evans and Dillon, 1982; Spiethoff and Hemond, 1996), and include copper, arsenic, cadmium, lead, zinc and iron (Table 2). All of these elements have their highest concentrations in the 1970s and decrease until the present, and probably record the history of copper mining and smelting in the area (Figure 1). The multivariate statistics were particularly useful in identifying that iron is being influenced by anthropogenic inputs. Iron is frequently grouped with diagenetic or terrestrial

elements, but in Gratiot Lake, iron clearly follows a trend similar to the other anthropogenic elements. In this case, factor analysis allowed the identification of an unexpected anthropogenic element that otherwise may have been overlooked or misinterpreted. The identification of unexpected relationships is an advantage of using statistical methods rather than only visually evaluating the data.

**Table 2.** Factor analysis results for Gratiot Lake. “Eig” indicates the eigenvalue for the factor, “%” is the percent variance explained by each factor, and “T%” is the total percentage variance explained by the solution. Bold indicates high loading (>0.8), and italics moderate loading (0.6-0.79).

	3 factors, no rotation			3 factors, Varimax			2 factors, Varimax	
	Factor 1	Factor 2	Factor 3	Factor 1	Factor 2	Factor 3	Factor 1	Factor 2
Mg	-0.792	0.471	0.151	<b>0.922</b>	0.032	0.143	<b>0.922</b>	0.048
Al	-0.629	0.598	0.211	<b>0.867</b>	0.212	0.041	<b>0.833</b>	0.234
K	<b>0.856</b>	-0.181	0.158	-0.741	0.221	-0.439	<b>-0.842</b>	0.238
Ca	<b>-0.879</b>	0.277	0.190	<b>0.914</b>	-0.184	0.123	<b>0.906</b>	-0.164
Ti	-0.773	0.444	-0.006	<b>0.845</b>	0.033	0.283	<b>0.896</b>	0.034
V	<b>-0.859</b>	0.072	0.213	<b>0.809</b>	-0.357	0.083	0.793	-0.335
Cr	-0.348	0.365	0.093	0.488	0.150	0.046	0.479	0.162
Mn	<b>0.866</b>	-0.291	0.401	-0.725	0.103	-0.677	<b>-0.882</b>	0.147
Fe	0.681	0.570	0.283	-0.203	0.787	-0.455	-0.336	<b>0.811</b>
Cu	0.431	<b>0.827</b>	0.195	0.096	<b>0.907</b>	-0.276	0.003	<b>0.929</b>
Zn	0.551	<b>0.814</b>	-0.054	-0.087	<b>0.977</b>	-0.081	-0.109	<b>0.980</b>
As	0.517	<b>0.810</b>	-0.231	-0.117	<b>0.976</b>	0.096	-0.083	<b>0.949</b>
Sr	<b>-0.959</b>	0.075	0.164	<b>0.877</b>	-0.396	0.162	<b>0.885</b>	-0.380
Mo	0.092	0.620	0.028	0.226	0.585	-0.020	0.208	0.594
Cd	0.435	0.799	-0.208	-0.047	<b>0.926</b>	0.101	-0.015	<b>0.904</b>
Ba	0.769	-0.175	0.555	-0.542	0.143	-0.784	-0.731	0.199
Pb	0.689	0.671	-0.088	-0.279	<b>0.919</b>	-0.102	-0.299	<b>0.917</b>
U	<b>-0.829</b>	0.411	0.122	<b>0.915</b>	-0.035	0.179	<b>0.928</b>	-0.022
Eig	8.82	5.12	0.92	7.22	5.86	1.77	7.96	5.88
%	49%	28%	5%	40%	33%	10%	44%	33%
T%	82%			83%			77%	



**Figure 1.** Sediment chemical concentration (mg/kg) profiles for Gratiot Lake.

Chromium and molybdenum are the only elements that do not load highly or moderately on any factor (Table 2). This was anticipated, since these two variables have a much lower communality than all the other elements (Table 1). The low communality of chromium and molybdenum indicates that the profiles of these two elements are dissimilar to profiles of other elements in the lake sediments, and therefore were likely influenced by different sources and processes.

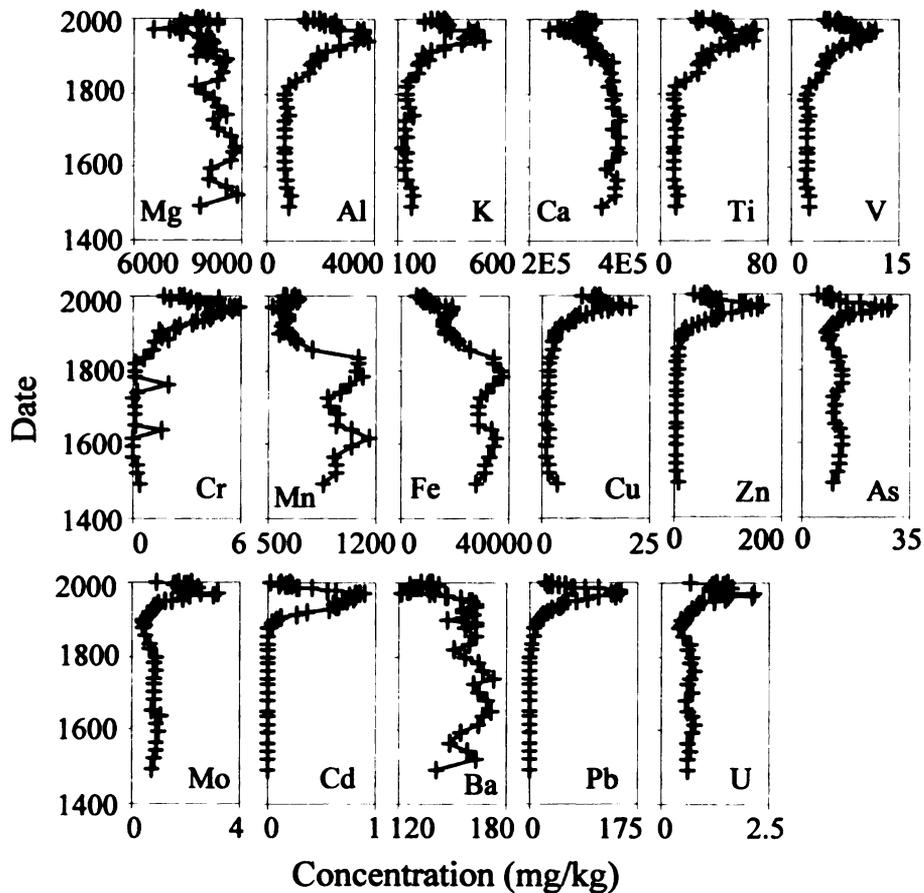
## 2) *Gull Lake*

The results of the factor analysis for Gull Lake portray a more complicated grouping of elements compared to Gratiot Lake. Three factors have eigenvalues greater than 1 and explain more than 5% of the variance (Table 3). Titanium, vanadium, chromium, copper, arsenic, molybdenum, cadmium, lead, aluminum, zinc, potassium, and uranium all load positively on the first factor and all increase in concentration in the 1900s (Figure 2) for Gull Lake. This group includes elements that are typically classified as terrestrial (e.g., Al, Ti) (Kemp and Thomas, 1976; Heyvaert et al., 2000), as well as elements that are typically anthropogenically influenced (e.g. Pb, Zn) (Sweet et al., 1998; Callender and Rice, 2000). Mg, Ca, Fe and Ba all load negatively on the first factor, but do not clearly represent any one source/process group. Only As and Ba are not well associated with Factor 1.

Unlike Gratiot Lake where an orthogonal rotation of the factors resulted in a larger number of high loadings and a clearer interpretation of the element groupings, rotation of either two or three factors for Gull Lake did not improve the interpretation. Compared to the unrotated solution, the rotated factors were shifted toward the Ba and As variables, when viewed in variable space, and the loadings for most of the other variables decreased in magnitude. An oblique rotation would likely improve the interpretation, however oblique methods require an *a priori* subjective decision on the size of the angle between factors making them more difficult to use.

**Table 3.** Factor analysis results for Gull Lake. “Eig” indicates the eigenvalue for the factor, “%” is the percent variance explained by each factor, and “T%” is the total percentage variance explained by the solution. Bold indicates high loading (>0.8), and italics moderate loading (0.6-0.79).

	3 factors, no rotation			3 factors, Varimax			2 factors, Varimax	
	Factor 1	Factor 2	Factor 3	Factor 1	Factor 2	Factor 3	Factor 1	Factor 2
Mg	<i>-0.781</i>	0.195	0.252	-0.323	<i>-0.680</i>	-0.380	-0.419	<i>-0.720</i>
Al	<b>0.900</b>	0.247	0.348	<b>0.890</b>	0.182	0.409	<b>0.920</b>	0.298
K	<b>0.916</b>	0.200	0.258	<b>0.830</b>	0.263	0.433	<b>0.891</b>	0.363
Ca	<b>-0.931</b>	0.227	0.057	-0.563	<i>-0.707</i>	-0.322	-0.568	<i>-0.778</i>
Ti	<b>0.930</b>	0.174	0.300	<b>0.867</b>	0.271	0.399	<b>0.891</b>	0.380
V	<b>0.970</b>	0.162	0.169	<i>0.797</i>	0.357	0.483	<b>0.889</b>	0.452
Cr	<b>0.961</b>	0.102	0.106	<i>0.739</i>	0.420	0.472	<b>0.833</b>	0.505
Mn	<b>-0.804</b>	0.197	-0.438	<b>-0.841</b>	-0.412	-0.009	-0.605	-0.509
Fe	<i>-0.732</i>	0.523	-0.416	<i>-0.740</i>	<i>-0.616</i>	0.236	-0.390	<i>-0.642</i>
Cu	<b>0.943</b>	-0.245	-0.158	0.496	0.769	0.371	0.545	<b>0.825</b>
Zn	<b>0.979</b>	0.142	-0.135	0.580	0.500	<b>0.641</b>	<b>0.803</b>	0.565
As	<i>0.640</i>	0.585	-0.438	0.180	0.115	<b>0.948</b>	<i>0.653</i>	0.181
Mo	<b>0.816</b>	-0.113	-0.410	0.241	<i>0.705</i>	0.540	0.470	<i>0.702</i>
Cd	<b>0.898</b>	0.366	0.036	<i>0.674</i>	0.224	<i>0.661</i>	<b>0.917</b>	0.304
Ba	<i>-0.647</i>	<i>0.673</i>	0.274	-0.163	<b>-0.959</b>	-0.001	-0.014	<b>-1.000</b>
Pb	<b>0.942</b>	0.036	-0.202	0.494	0.584	0.587	<i>0.695</i>	<i>0.637</i>
U	<b>0.825</b>	-0.043	-0.326	0.316	<i>0.626</i>	<b>0.545</b>	<i>0.534</i>	<i>0.642</i>
Eig	12.75	1.60	1.38	6.59	5.05	4.09	8.13	6.06
%	75%	9%	8%	39%	30%	24%	48%	36%
T%	92%			93%			84%	

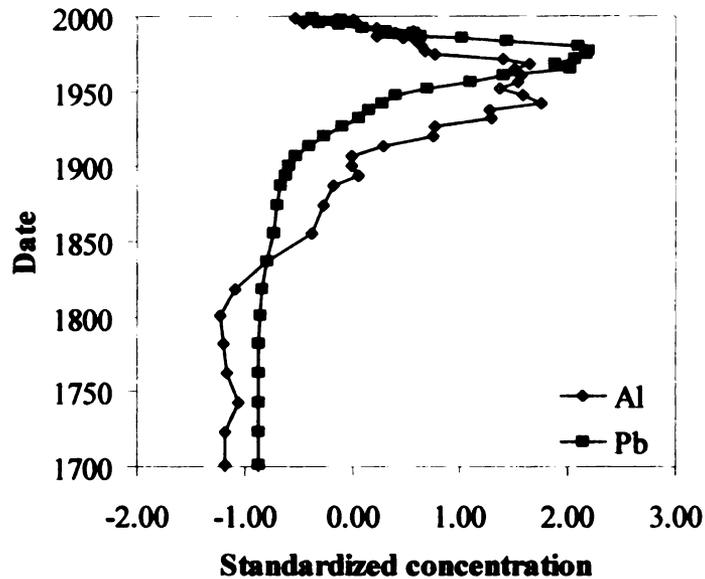


**Figure 2.** Sediment chemical concentration (mg/kg) profiles of Gull Lake.

The impact of the time period encapsulated by the sediment core on the ability of factor analysis to distinguish between important sources and processes in the post-settlement period is also evident from the results for Gull Lake. Whereas the sediment age for Gratiot Lake extended back only approximately 200 years, the sediments for the Gull Lake core were deposited over approximately 500 years. Consequently, there were considerably more data points for the pre-settlement period compared to the post-settlement period for Gull Lake. As a result, the pre-settlement period had a greater influence on the factor analysis results, making it difficult to distinguish

between different processes in the post-settlement period. To illustrate, the standardized profiles of an element that is most often linked to terrestrial inputs to a lake (Al) and an element that has dominant anthropogenic sources (Pb) were compared (Figure 3).

Although these two elements loaded highly on the same factor, there are clear differences between the two elements in the post-settlement period, with concentrations of aluminum increasing and peaking earlier than lead. The



**Figure 3.** Standardized concentrations of aluminum and lead in sediments of Gull Lake.

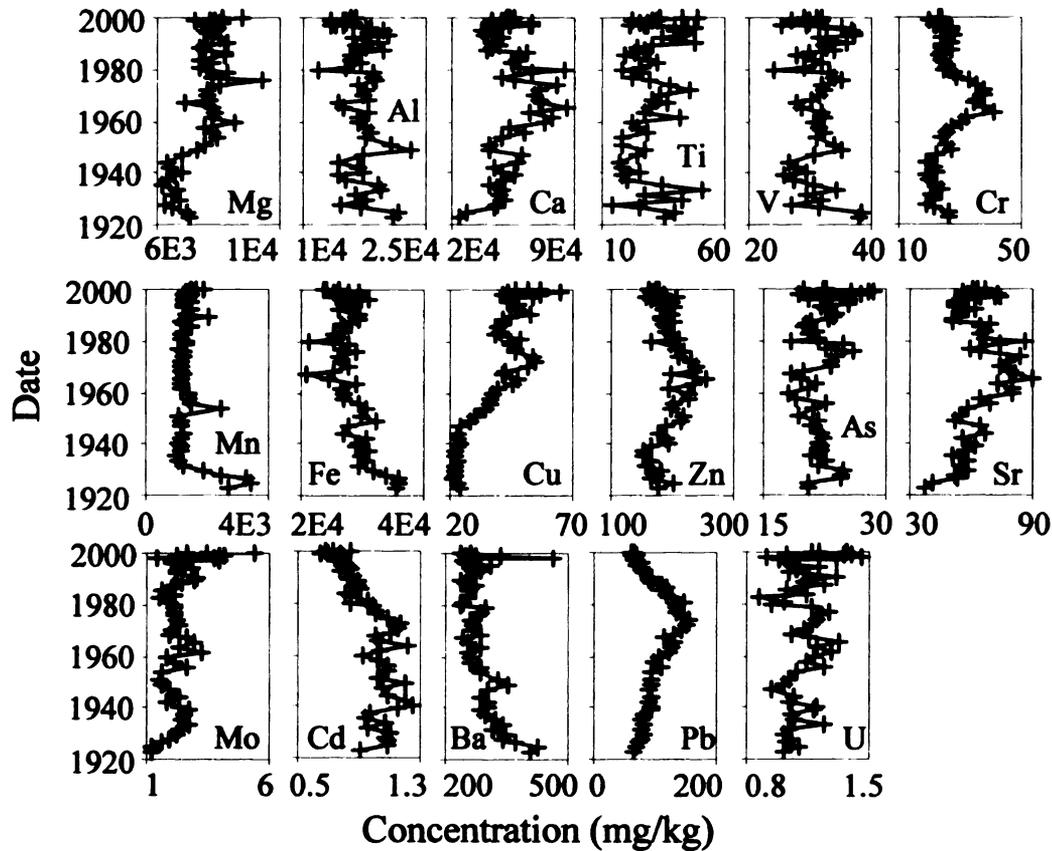
increases in aluminum concentration correspond with increases in the overall sedimentation rate, likely due to high erosion rates related to the extensive clear cutting in the area. Lead, on the other hand, is more related to atmospheric deposition from sources such as coal burning and leaded gasoline (Eisenreich et al., 1986; Graney et al., 1995; Yohn et al., 2002a). This comparison indicates that while factor analysis can successfully group elements with similar overall profiles, identifying relatively minor differences, especially in the post-settlement period when there are fewer data points, is difficult and may result in important source/process groups to be missed.

### 3) Paw Paw Lake

The unrotated solution for Paw Paw Lake had four factors with eigenvalues greater than one, all of which explain more than 5% of the variance (Table 4). The unrotated and rotated solutions (using either four or three retained factors) have many moderate loadings (0.6-0.8), and several elements that only load weakly on factors. The larger number of weak loadings compared to the solutions for Gratiot and Gull Lakes reflect the lower communalities for several of the elements (Mg, Ti, As, and Ba) at Paw Paw Lake (Table 1). This suggests that element profiles in Paw Paw Lake are less similar to each other compared to the other lakes (Figure 4). Additionally, the factors for Paw Paw Lake are difficult to interpret in terms of the *a priori* defined source/process groups. When four factors are rotated, the first factor appears to be a terrestrial factor, but contains only two elements (V-Al). The second factor includes chromium, lead and zinc, typically anthropogenic elements, as well as calcium and strontium, which are generally influenced by calcium carbonate deposition. Factor 4 may represent diagenetic elements (Mo-U-As), but Factor 3 is difficult to interpret (Cd-Fe, and negatively loaded on Cu).

**Table 4.** Factor analysis results for Paw Paw Lake. “Eig” indicates the eigenvalue for the factor, % is the percent variance explained by each factor, and “T%” is the total percentage variance explained by the solution. Bold indicates high loading (>0.8), and italics moderate loading (0.6-0.79).

	4 factors, no rotation				4 factors, Varimax rotation				3 factors, Varimax rotation		
	Factor 1	Factor 2	Factor 3	Factor 4	Factor 1	Factor 2	Factor 3	Factor 4	Factor 1	Factor 2	Factor 3
Mg	0.490	0.160	0.459	-0.228	0.326	0.383	-0.502	0.155	-0.057	0.385	0.577
Al	-0.445	0.700	0.415	-0.014	<b>0.798</b>	0.154	0.444	-0.060	<b>0.889</b>	0.307	0.030
Ca	<b>0.863</b>	0.164	-0.313	0.136	-0.495	0.749	-0.261	0.120	-0.683	0.640	0.023
Ti	-0.009	-0.002	0.582	-0.188	0.503	-0.085	-0.297	0.163	0.275	-0.036	0.526
V	-0.402	0.516	0.725	-0.217	<b>0.993</b>	0.003	0.115	0.000	<b>0.895</b>	0.161	0.374
Cr	0.509	0.703	0.226	-0.095	0.355	<b>0.822</b>	-0.109	0.017	0.110	<b>0.858</b>	0.248
Mn	-0.455	-0.151	0.068	0.029	0.127	-0.424	0.196	-0.022	0.278	-0.387	-0.088
Fe	-0.685	0.374	0.083	0.539	0.316	-0.171	<b>0.858</b>	0.205	0.658	-0.086	-0.291
Cu	0.693	-0.200	0.573	-0.060	0.131	0.259	-0.734	0.479	-0.347	0.200	<b>0.864</b>
Zn	0.353	<b>0.800</b>	0.063	-0.032	0.309	<b>0.808</b>	0.119	-0.082	0.198	<b>0.861</b>	0.013
As	-0.022	-0.100	0.390	0.494	0.121	-0.099	0.113	0.608	0.112	-0.108	0.312
Sr	<b>0.903</b>	0.145	-0.260	0.058	-0.453	0.752	-0.354	0.102	-0.698	0.647	0.094
Mo	0.396	-0.638	0.376	0.385	-0.250	-0.208	-0.443	0.743	-0.444	-0.301	0.590
Cd	-0.058	0.760	-0.367	0.440	-0.034	0.578	0.757	-0.040	0.254	0.571	-0.507
Ba	-0.686	0.249	-0.081	0.066	0.267	-0.274	0.591	-0.221	0.591	-0.180	-0.413
Pb	0.544	0.679	-0.198	0.027	-0.029	<b>0.883</b>	0.070	-0.100	-0.126	<b>0.883</b>	-0.121
U	0.425	-0.111	0.489	0.577	0.017	0.192	-0.147	<b>0.840</b>	-0.157	0.118	0.532
Eig	4.81	3.70	2.52	1.39	2.94	4.19	3.24	2.05	3.97	4.03	2.83
%	28%	22%	15%	8%	17%	25%	19%	12%	23%	25%	17%
T%	73%				73%				65%		



**Figure 4.** Sediment chemical concentration (mg/kg) profiles of Paw Paw Lake.

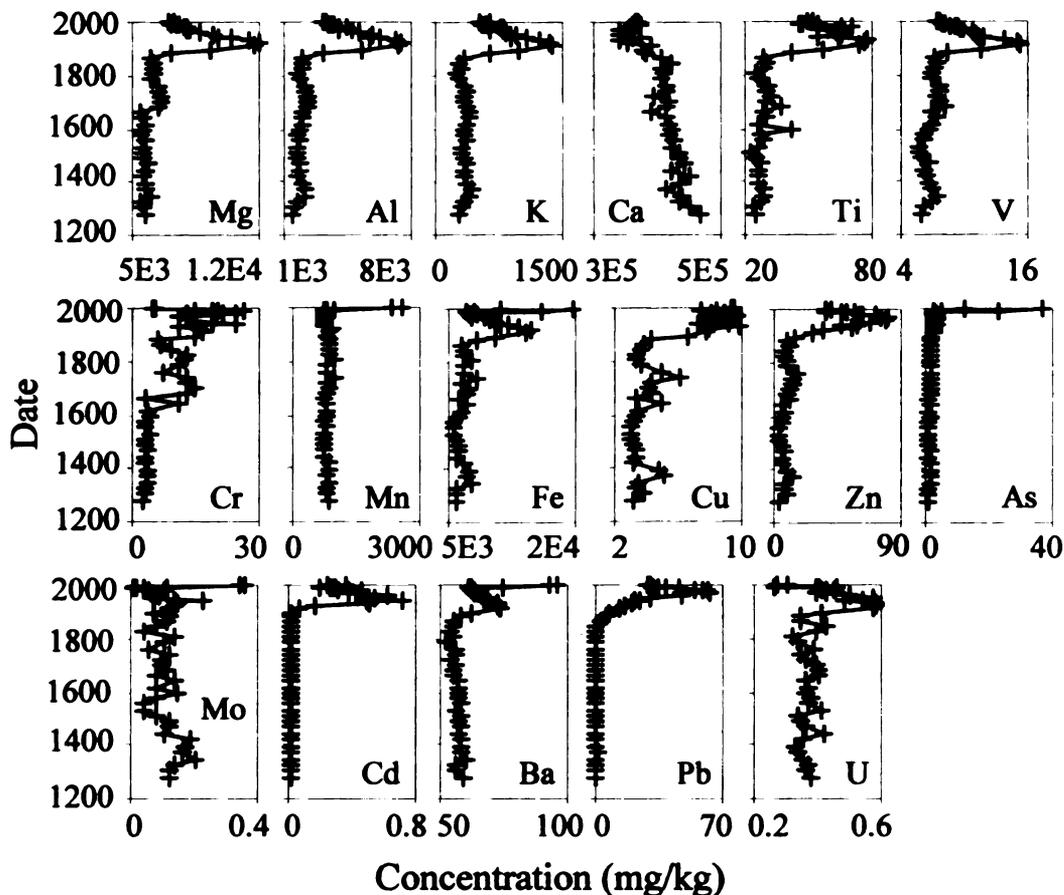
#### 4) Elk Lake

Three factors with eigenvalues greater than one and explaining greater than 5% variance were found for Elk Lake (Table 5). The unrotated solution shows a high degree of simple structure with all elements having high or moderate loadings on the first two factors. Rotating two factors changes the interpretation only slightly. Interpretation of both the unrotated and rotated two-factor solutions indicates that the factor analysis is separating elements that have high concentrations at the surface (Mn, Fe, As, Mo, and Ba) from those that do not (Figure 5). When three factors are rotated, the elements that had loaded highly of the first factor of the two-rotation solution are

now distributed among two factors (Factor 1 and Factor 3), and the elements with high surface concentrations remain grouped together on Factor 2. Even though the two factor solution has a high degree of simple structure, the three factor solution is more interpretable in terms of the *a priori* defined physical processes and appears to be the more appropriate solution. Factor 1 can be interpreted as representing the terrestrial elements (Ti-V-Al-Mg-K-U), whereas the elements that load positively on Factor 3 (Cu-Cd-Pb-Zn) represent anthropogenic elements. Ca loads negatively on Factor 3 and represents the carbonate group. The elements associated with Factor 2 (As-Mo-Mn-Ba-Fe) may be associated with diagenesis.

**Table 5.** Factor analysis results for Elk Lake. “Eig” indicates the eigenvalue for the factor, “%” is the percent variance explained by each factor, and “T%” is the total percentage variance explained by the solution. Bold indicates high loading (>0.8), and italics moderate loading (0.6-0.79).

	All data						Outliers removed				
	3 factors, no rotation			3 factors, Varimax			2 factors, Varimax		3 factors, Varimax rotation		
	Factor 1	Factor 2	Factor 3	Factor 1	Factor 2	Factor 3	Factor 1	Factor 2	Factor 1	Factor 2	Factor 3
Mg	<b>0.922</b>	0.178	0.326	<b>0.914</b>	0.117	0.371	<b>0.931</b>	0.064	<b>0.938</b>	0.314	-0.023
Al	<b>0.949</b>	0.186	0.256	<b>0.891</b>	0.105	0.443	<b>0.966</b>	0.062	<b>0.930</b>	0.358	0.076
K	<b>0.914</b>	0.156	0.325	<b>0.902</b>	0.135	0.366	<b>0.918</b>	0.083	<b>0.943</b>	0.271	0.071
Ca	<b>-0.881</b>	-0.020	0.226	-0.485	-0.173	<i>-0.750</i>	<b>-0.857</b>	-0.203	<i>-0.567</i>	<i>-0.692</i>	-0.145
Ti	<b>0.966</b>	0.096	0.028	<i>0.730</i>	0.162	0.620	<b>0.966</b>	0.152	<i>0.797</i>	<i>0.546</i>	0.086
V	<b>0.874</b>	0.234	0.398	<b>0.943</b>	0.063	0.289	<b>0.893</b>	0.003	<b>0.953</b>	0.247	-0.072
Cr	<i>0.677</i>	0.211	-0.172	0.431	-0.053	0.586	<i>0.710</i>	-0.032	0.488	<i>0.646</i>	-0.133
Mn	0.159	<b>-0.891</b>	0.024	-0.133	<b>0.894</b>	0.036	-0.075	<b>0.911</b>	-0.009	-0.257	<b>-0.836</b>
Fe	<i>0.745</i>	-0.491	0.261	0.551	<i>0.700</i>	0.266	0.596	<i>0.653</i>	<b>0.975</b>	0.136	-0.165
Cu	<b>0.928</b>	-0.128	-0.257	0.454	0.321	0.795	<b>0.863</b>	0.355	<i>0.603</i>	<i>0.757</i>	0.075
Zn	<b>0.865</b>	0.106	-0.464	0.346	0.050	<b>0.924</b>	<b>0.846</b>	0.119	0.444	<b>0.840</b>	0.253
As	0.322	<b>-0.808</b>	-0.126	-0.090	<b>0.835</b>	0.261	0.106	<b>0.863</b>	0.487	<i>0.763</i>	0.066
Mo	0.099	<i>-0.743</i>	0.275	0.029	<i>0.776</i>	-0.184	-0.090	<i>0.725</i>	0.212	-0.410	-0.140
Cd	<b>0.828</b>	0.043	-0.292	0.411	0.127	<i>0.766</i>	<b>0.808</b>	0.168	0.521	<i>0.663</i>	0.352
Ba	<i>0.695</i>	<i>-0.693</i>	0.090	0.347	<b>0.854</b>	0.350	0.498	<b>0.850</b>	<b>0.894</b>	0.283	0.168
Pb	<i>0.767</i>	0.035	-0.595	0.171	0.073	<b>0.954</b>	<i>0.725</i>	0.157	0.270	<b>0.906</b>	0.193
U	<i>0.652</i>	0.529	0.289	<b>0.803</b>	-0.293	0.242	<i>0.761</i>	-0.335	<b>0.840</b>	0.246	0.200
Eig	10.00	3.23	1.49	5.91	3.64	5.18	9.46	3.64	8.38	5.07	1.11
%	59%	19%	9%	35%	21%	30%	56%	21%	49%	30%	7%
T%	87%			86%			77%		86%		



**Figure 5.** Sediment chemical concentration (mg/kg) profiles of Elk Lake.

As shown earlier, the outlier analysis for Elk Lake identified 2-3 points near the surface as outliers for several variables (As, Mo, Mn, Ba, Fe). Factor analysis on the Elk Lake data with influential outlying data points removed resulted in a considerably different interpretation. When three factors are rotated, Factor 2 no longer simply represents those elements with high surface concentrations. Rather it can now be interpreted as the anthropogenic factor, and includes the same elements as were previously associated with Factor 3, as well as arsenic. Barium and iron now

load highly on the terrestrial factor (Factor 1), and Factor 3 contains only manganese. Molybdenum does not load highly or moderately on any factor.

The choice between the solution from the factor analysis with all data points and that with outlier points removed is not clear, and analysis both with and without outliers may be necessary. Visual inspection of Figure 5 indicates that the overall profiles of arsenic, molybdenum, manganese, barium and iron are dissimilar. However, because all of these elements had high concentrations at the surface, they were grouped together when all data points were included in the factor analysis. While this may be appropriate because all of these elements have likely been influenced by diagenetic processes, additional insight on the behavior of the elements was gained by also analyzing the data with those influential points removed.

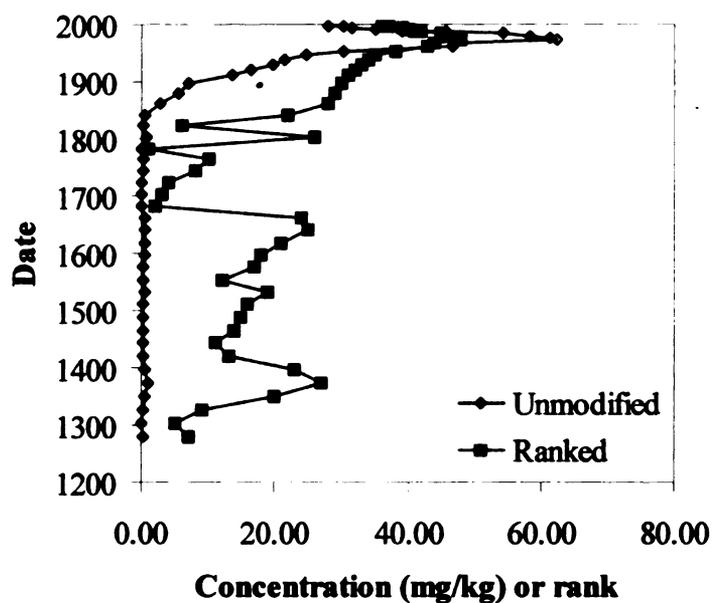
#### *Factor Analysis of Ranked Observations*

Factor analysis was also used on a Spearman's correlation coefficient matrix. Spearman's correlation coefficient is similar to Pearson's product moment correlation coefficient, except that it is performed on ranked data. Using ranked data reduces the influence of outliers and may be more appropriate for sediment chronologies. When data are ranked, the lowest concentration data point for each element is assigned the number 1, the second lowest number 2, and so forth. If two data points have the same concentration of an element, both data points are assigned the average of the two ranks (e.g., if the 5<sup>th</sup> and 6<sup>th</sup> lowest concentrations have the same value, both will be assigned the value of 5.5) (SPSS 2000).

For all lakes, using a Spearman's correlation matrix (i.e., ranked data) for factor analysis did not result in clearer element groupings compared to using the

standard Pearson's product moment correlation matrix (i.e., "raw" data). Overall, the results for the factor analysis using the ranked data were similar to those when applied to the "raw" data, except that the loadings were generally lower. Ranked data reduces the influence of large changes in concentration, and also increases in the importance of small changes in concentration. For Elk and Gull lakes in particular, many elements have multiple samples with similar concentrations (e.g., all lead concentrations older than 1800 have similar

concentrations), and minor changes in these concentrations become magnified when using ranked data (Figure 6). Because of this, the terrestrial and anthropogenic elements were not differentiated using ranked data in Elk



**Figure 6.** Unmodified concentrations (mg/kg) and ranked values of lead in sediments of Elk Lake.

Lake, but were differentiated when the original observations were used to calculate the correlation matrix. Therefore, with sediment chronology data and the types of questions asked here, it may be more appropriate to apply factor analysis to parametric rather than nonparametric correlation matrices. In other situations or questions, this may not be true (e.g., Wayland et al., 2003). When using parametric correlation

coefficients, it is essential to identify possible outliers using boxplot analysis and to perform statistical analyses with and without these points.

### *Summary*

Overall, factor analysis is effective for differentiating groups of elements with broadly similar profiles, but not for identifying small differences among profiles, especially if the differences are confined to a time period (e.g., post-settlement) for which there are few data points. Factor analysis was particularly successful for Gratiot Lake, where there were a small number of groups with very distinct profiles. Factor analysis was less successful in categorizing elements when correlation was small from a number of the element profiles (e.g., Paw Paw Lake), when the differences between profiles is confined to a short segment of the profile (e.g., Gull Lake), or when outlier/influential points are present (e.g., Elk Lake).

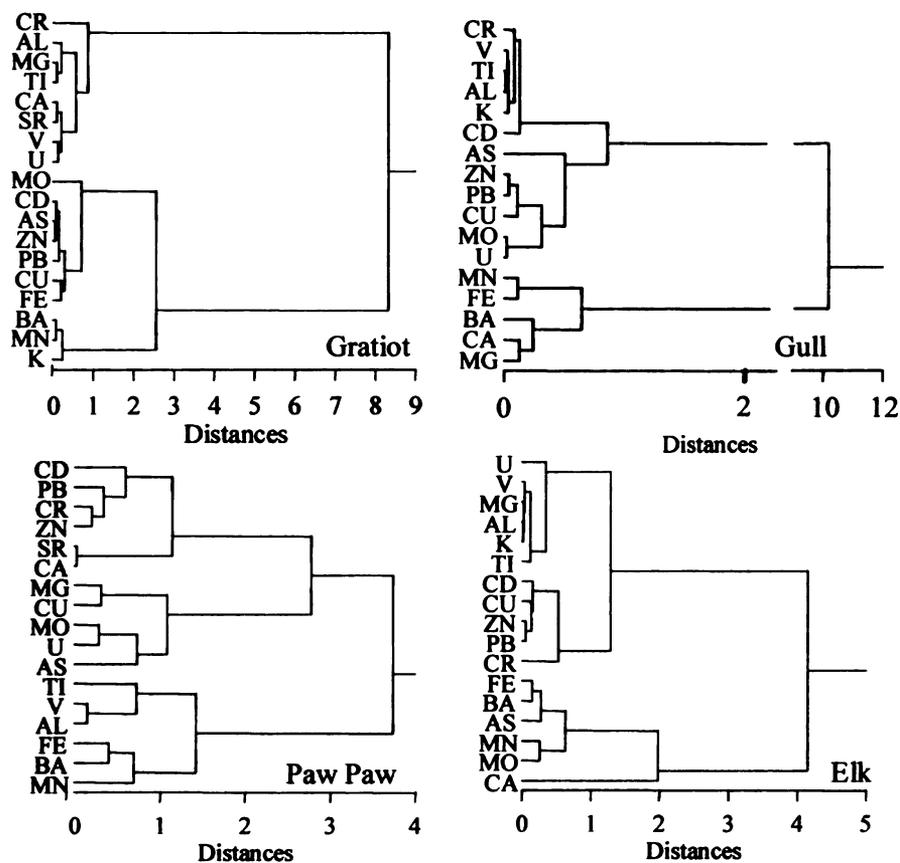
One difficulty in using factor analysis for sediment chronologies is that the processes influencing metal inputs to lakes are temporally related to each other. For example, the majority of human disturbance in North America has occurred since the 1850s. This disturbance can influence both terrestrial elements (e.g., through land use change, such as clear cutting) (Davis, 1976) and direct human inputs (e.g., atmospheric deposition of lead from leaded gasoline, cadmium from smelting) (Iskander and Keeney, 1974; Johnson and Nicholls, 1988; Kada and Heit, 1992; Callender and Rice, 2000; Heyvaert et al., 2000). While these are clearly different sources and processes influencing the two groups, the processes are temporally related, and therefore are not always well differentiated by factor analysis (e.g., Gull Lake). While it is possible to use a non-orthogonal rotation technique that allows

factors to correlate (e.g., Oblimin), it is then necessary to determine what extent of correlation to allow among the factors. As an alternative to factor analysis, the use of cluster analysis to group elements was explored on the same dataset.

### **Cluster analysis**

Results from the three clustering algorithms were similar to each other for all of the lakes, therefore, only results using the most common method, Ward's, are shown, with any differences in element clusters among the methods discussed.

The cluster tree for Gratiot Lake is shown in Figure 7. The cluster tree is read left to right, where the horizontal lines represent similarity (reported as distance) and the vertical lines show when two elements or clusters have been joined. A long horizontal line before two clusters are joined indicates that there is a long distance between the two clusters, or that they are relatively dissimilar. Hierarchical cluster analysis does not create definite groups; instead, the number of groups is determined by the user. A common approach is to consider where there is a large increase in distance before two groups are combined (a long horizontal line to the left of the vertical line joining the clusters). This indicates that the groups are relatively dissimilar, and perhaps should be considered separate. For example, in Gratiot Lake, three clusters might be chosen and interpreted as, K-Mn-Ba (diagenetic group), Fe-Cu-Pb-Zn-As-Cd-Mo (anthropogenic group), and the last including the remainder of the elements (terrestrial group). However, molybdenum and chromium are still fairly dissimilar to their groups (anthropogenic and terrestrial). To make the final decision of which elements belong in which groups, standardized profiles (z-scores) for each



**Figure 7.** Cluster trees for sediment chronologies for four Michigan lakes. Ward's clustering algorithm and Pearson's correlation were used.

element in a group are plotted together, and examined for similarity. The investigator then must judge if the profiles are similar enough for those elements to be included in a group. This decision should be based on how similar the elements need to be based on the purpose of the study. In the case of Gratiot Lake, molybdenum is dissimilar to the rest of the anthropogenic group, while chromium is similar to the terrestrial group, with the exception of one unusual point. Therefore, chromium was grouped as a terrestrial element, while molybdenum was left unclassified (Table 6). This is slightly

different than the results of factor analysis, where neither chromium nor molybdenum was placed in a group.

**Table 6.** Final groupings for each element in the four study lakes, and for Elk Lake with outliers removed (Elk OR). T = terrestrial, A = anthropogenic, C = carbonate, D = diagenetic. D1 and D2 indicate separate diagenetic groups. A – indicates that data were not collected for that element.

	Gratiot	Elk	Elk OR	Gull	Paw Paw
Mg	T	T	T	C	
Al	T	T	T	T	T
K	D	T	T	T	–
Ca	T	C	C	C	C
Ti	T	T	T	T	T
V	T	T	T	T	T
Cr	T			T	A
Mn	D	D		D1	
Fe	A	D	T	D1	
Cu	A	A	A	A	A
Zn	A	A	A	A	A
As	A	D	A		D2
Sr	T	–	–	–	C
Mo		D		D2	D2
Cd	A	A	A		A
Ba	D	D	T	C	
Pb	A	A	A	A	A
U	T	T	T	D2	

The final groupings of the elements based on cluster analysis and the examination of standardized profiles for Gratiot Lake are very similar to the groups determined by factor analysis, therefore either approach provides the same information. However, the same is not true for Gull Lake (Figure 7). Cluster analysis can differentiate smaller differences in profiles, and therefore distinguish the source/process groups in Gull Lake.

The first group of elements in Gull Lake is the terrestrial elements, including vanadium, titanium, aluminum, potassium, chromium and cadmium (Figure 7).

Cadmium and chromium are the last two elements to be included in this cluster, and have been found to have anthropogenic inputs in other lakes (Kemp and Thomas, 1976; Johnson and Nicholls, 1988; Kada and Heit, 1992). Since part of the purpose of this type of study is to identify elements that have been influenced by human inputs, further investigation into the sources of cadmium and chromium may be warranted, such as the examination of cadmium to aluminum ratios (Bruland et al., 1974; Koelmans, 1998; Tuncer et al., 2001). However, the similarity of the trends of cadmium and chromium to the terrestrial elements suggests that these elements are more influenced by terrestrial inputs than direct anthropogenic inputs.

The anthropogenic elements are lead, copper and zinc (Figure 7), and a diagenetic group includes molybdenum and uranium. Manganese and iron form a second diagenetic group, while barium, calcium and magnesium form the carbonate group. Although Mn-Fe and Ba-Ca-Mg could be considered one cluster (Figure 7), and have profiles that are similar overall (e.g., lower concentrations in the 1900s) (Figure 2), the two groups are distinctly different when plotted together, and probably represent different sources and/or process groups of diagenetic and carbonate.

The decision making processes used above was utilized for Paw Paw and Elk lakes, and the resultant groups are shown in Table 6. Paw Paw Lake had six different groups, including terrestrial (Al-Ti-V), anthropogenic (Cd-Pb-Cr-Zn), carbonate (Ca-Sr), and two diagenetic groups (Mo-U-As and Fe-Ba-Mn) (Figure 7). The last grouping included only copper and magnesium. The reason for the similar profiles between these two elements is unclear. In Paw Paw Lake, factor analysis resulted in moderate loadings and poor delineation of groups of elements. Cluster analysis, in

this case, provides more information about the similarities among element profiles than factor analysis.

Elk Lake has only four clear groupings: terrestrial (U-V-Ti-Mg-Al-K), anthropogenic (Cd-Zn-Pb-Cu), diagenetic (Mn-Mo-Fe-As-Ba) and carbonate (Ca) (Figure 7). These groupings are similar to those found with factor analysis. Removal of the influential outliers from the dataset results in regroupings of elements that are also similar to factor analysis. Iron and barium group with the terrestrial elements, and arsenic with the anthropogenic elements. Although molybdenum, manganese and calcium cluster together, there is a relatively large distance before they are clustered, indicating that the profiles are not very similar.

For all four lakes results from the three clustering algorithms were generally very similar, which suggests that the groups were distinct from each other, and not an artifact of the technique used. The use of more than one algorithm was useful to test if the solution is robust. Elements that change groups with different algorithms typically do not fit well into any group, and should be considered individually, rather than placed in a group.

Overall, cluster analysis was successful in grouping elements with similar profiles. The use of hierarchical cluster analysis shows which elements are the most similar within groups, and which elements fit the group more poorly and perhaps should be considered individually. For exploratory data analysis, this information is particularly useful for interpreting possible sources and/or processes that influence different elements.

## **Discussion**

Factor analysis identified elements with broadly similar profiles, and the resultant groups were consistent with visual examination in two of the four lakes. In the remaining two lakes, subtle differences in the depth profiles were important for differentiating source/process groups (e.g., terrestrial and anthropogenic in Gull Lake), but were not identified by factor analysis. In the last 200 years, humans have influenced the terrestrial, anthropogenic, and possibly carbonate groups. As a result, the broad depth patterns in the sediment of these groups often correlate with each other, and may be difficult to differentiate with orthogonal factor analysis. Accepting results from factor analysis without examination of the profiles may lead to missing subtle but important differences among profiles, and therefore lead to incorrect interpretations. Oblique rotation, which allows factors to be correlated to each other, should be considered if factor analysis is used for grouping sediment profiles. It appears to make little difference if principal component analysis or factor analysis is used when analyzing sediment chronologies, as long as there is a high degree of communality.

Cluster analysis, though typically used for grouping samples, was useful for determining element groupings. One possible advantage of cluster analysis for the grouping of variables is that, unlike factor analysis, this technique does not attempt to create factors that are uncorrelated. Additionally, hierarchical cluster analysis not only creates groups, but also shows which elements are the most similar, and may allow for additional interpretation of data. Cluster analysis objectively determines the similarity

of element profiles, and provides the framework for determining which elements belong in each source/process group.

Outliers generally appeared to be “true” data, and needed to be considered in the interpretation of sediment chronologies. Often these outliers represented the modification of historical deposition records due to diagenetic processes, and it was helpful to interpret these profiles both with and without the outliers present.

Regardless of the statistical approach used, a difficulty in differentiating source/process groups is that humans have significantly influenced sediment chronologies in North America for only 150-200 years, but sediment cores may represent a much longer time period (e.g., Gull and Elk lakes). It may be difficult to separate out both natural processes and human processes in sediment cores that encompass hundreds of years, and have relatively few samples during the last 150 years. For example, in Gull Lake it was difficult to differentiate terrestrial and anthropogenic inputs. Possible approaches to avoid this issue include: 1) truncating the core, 2) “edit” the core by deleting some of the pre-settlement data points to make the number of pre and post settlement points more equal in number, 3) run statistical analyses on the entire core and then separately on the post settlement portion. Regardless of the approach used, it is important to be careful when comparing groups from lakes with large differences in the time periods captured by the cores.

While it would be ideal to have a statistical technique to objectively group elements that were controlled by the same sources and/or processes, with no additional judgment required to define these groups, it is unlikely that this will occur in a system as complex as lake sediments. A close examination of each element will always be

necessary for the correct interpretation of sediment chronology data. However, multivariate statistical analysis provides an important framework for data analysis, and helps facilitate the task of interpreting profiles of a large number of elements and greatly reduces the possibility of important relationships not being identified.

### **Comments and recommendations**

We suggest the following approach to the analysis of multivariate data. First, potentially influential points need to be identified using boxplot or some other analysis. If these points can be attributed to analytical error, such as an unusual point in only one element, then they should be removed from the data set. If influential points represent the data, further analyses and interpretations should be done with and without these points to determine their influence. Next, perform cluster analysis on the dataset using correlation as the distance measure. The standardized profiles for elements in each possible group should be plotted together to visually check their similarity. The confirmation of the groupings by actual examination of the profiles is essential; without this step the potential for incorrect groupings is high, regardless of the statistical technique used. Finally, if the core encompasses a very long span of time, it may be truncated around 1800 (for cores collected in North America), and the recent sediments evaluated again to identify subtle differences in cores during the time period of human influence. The resultant element groupings from these steps can then be interpreted to provide an understanding of the geochemistry of the sediments and history of inputs to the lake.

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### CHAPTER 3

## THE IMPORTANCE OF THE MULTI-ELEMENT APPROACH FOR INTERPRETING SEDIMENT HISTORIES

### **Abstract**

Sediment chronologies are often used to provide a history of anthropogenic inputs to lakes and their surrounding watersheds. However, analysis of only target elements (e.g., lead, arsenic) may lead to incorrect interpretations and quantification of human inputs to lake sediments. This study uses sediment cores collected from eleven lakes in Michigan, U.S.A., to determine a minimum suite of elements for environmental monitoring of anthropogenic inputs using sediment chronologies.

Cluster analysis was used to group elements with similar profiles, and a representative element was chosen from each group. Groupings were similar, but not identical among lakes. A suite of six elements in addition to those elements directly influenced by anthropogenic inputs was selected to represent terrestrial inputs (aluminum and titanium), diagenesis (iron, manganese and molybdenum), and carbonate deposition (calcium). The use of these six elements allowed the differentiation of anthropogenic and diagenetic influences on arsenic by comparison to the diagenetic elements. Additionally, results from determination of anthropogenic inputs using normalization to a terrestrial element were different from using a constant background, indicating the importance of assessing terrestrial inputs. This suite of elements should be considered the minimum analysis needed to provide sufficient information for an environmental monitoring program using sediment chronologies.

## Introduction

Lake sediments act as recorders of events that occur both within the watershed and the region, and can provide a history of events such as forest fires, logging, and urbanization. This is particularly useful because the water column of most lakes have not been monitored over long periods of time, making the historical record found in the sediments an important tool for environmental monitoring.

The application of sediment chronologies to environmental monitoring is most useful if a quantifiable record of human inputs to a lake can be determined. To do this, it is necessary to distinguish between *natural inputs* (inputs of metals from naturally occurring erosion or atmospheric deposition), *secondary human inputs* (increased inputs due to erosion from human activities, such as clear cutting), and *direct human inputs* (selective enrichment of certain elements due to human activities, such as lead enrichment due to the use of leaded gasoline). Increasing erosion within a watershed will cause additional inputs of metals such as lead and cadmium to a lake, but these metals are not selectively enriched compared to other terrestrial elements such as aluminum (Heyvaert et al., 2000). Therefore, it is useful to differentiate direct human inputs which enrich certain metals (e.g., lead, cadmium), from increased erosion.

A further complication in the interpretation of sediment chronologies is the potential mobilization of metals after deposition (early diagenesis), which may obscure the depositional record (McKee et al., 1989). While some elements that have significant human sources (e.g., lead) are relatively unaffected by diagenesis, others, such as arsenic, are more likely to be influenced by diagenetic processes (Brown et al.,

2000). It is critical to be able to identify when a sediment profile of an element represents a history of inputs to the lake, and when it represents post-depositional processes.

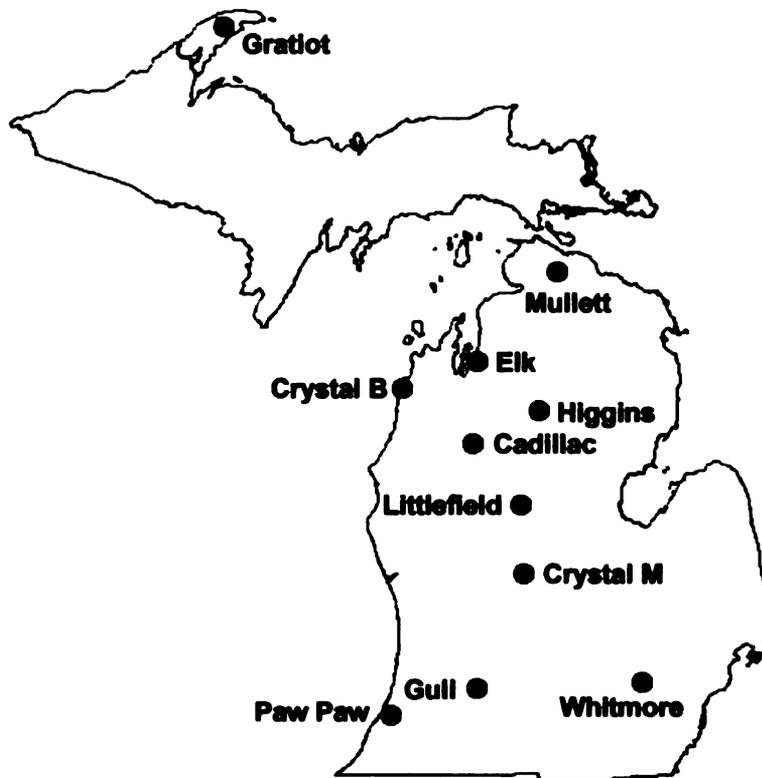
As a result of these complications in the interpretation of sediment chronologies, it may be necessary to analyze more than only elements with known human sources to be able to quantify direct human inputs. When analyzing inorganic contaminants in water, it is well known that there is a minimum suite of parameters that must be quantified (e.g., major anions and cations, temperature, pH) to model the water and understand the behavior of trace elements (Garrels and Thompson, 1962; Long and Saleem, 1974). It is possible that there is a comparable set of elements to be measured that are necessary to understand the history of trace element deposition in the sediment. The following hypothesis will be explored: there is a relatively small set of elements, in addition to elements of interest (e.g., lead, arsenic), which are necessary to identify and quantify direct anthropogenic inputs to inland lakes and to interpret depositional patterns. To explore this hypothesis, elements with similar profiles will first be grouped in each lake using cluster analysis to determine if there are elements that are consistently representative of each group. Secondly, we will investigate if it is necessary to analyze additional elements to interpret and quantify anthropogenic inputs. Specifically, the importance of diagenetic and terrestrial elements will be investigated.

## Methods

Sediment cores were collected from eleven lakes throughout Michigan from 1999 to 2001: Elk, Gratiot, Higgins, Gull, Crystal M, Littlefield, Cadillac, Crystal B, Mullett, Paw Paw and

Whitmore lakes

(Figure 1). Lakes in the Lower Peninsula of Michigan are located on Pleistocene glacial deposits, which are generally carbonate rich. Gratiot Lake is located in the copper rich Keweenaw area



**Figure 1.** Location of eleven study lakes in Michigan.

(Figure 1), part of the Canadian Shield, with sparse glacial deposits in this area (Door and Eschman, 1970). The lakes vary greatly in surface area and depth and were chosen for sampling based on depth, location, and accessibility. Lakes reflect a gradient of human disturbance, from areas of high development to relatively remote lakes.

A set of four replicate sediment cores from 40 to 58 cm long were taken from the deepest portion of each lake using a MC-400 Lake/Shelf Multi-corer (San Diego, CA) deployed from either the U.S. Environmental Protection Agency Research Vessel *Mudpuppy* or the Michigan Department of Environmental Quality Monitoring Vessel

*Nibi.* A new set of cores was immediately taken if the cores showed any evidence of disturbance. Cores were examined and described in terms of color, texture, and signs of zoobenthos. Cores were immediately extruded and sectioned open to the atmosphere at 0.5 cm intervals for the top 5-8 cm, and at 1 cm intervals for the remainder of the core.

$^{210}\text{Pb}$  was measured on one sub-core from each lake at the Freshwater Institute in Winnipeg, Manitoba, Canada, under the direction of Paul Wilkinson, to determine sedimentation rates, focusing factors, and sediment ages. Three different models were used to extract dates from  $^{210}\text{Pb}$  data; the constant flux, constant sedimentation model (CF:CS) (Golden et al., 1993), the segmented CF:CS (SCF:CS) (Heyvaert et al., 2000), and the constant rate of supply model (CRS) (Sanchez-Cabeza et al., 2000).

For all models, sediment deeper than the presence of excess  $^{210}\text{Pb}$  cannot be dated. Dates older than this were determined by extrapolation, using the assumption that sedimentation rates remain constant below this depth. For the CF:CS, and SCF:CS model, the sedimentation rate in the lower portion of the core was used to extrapolate dates. For the CRS model, the average sedimentation rate in the last five samples with quantifiable excess  $^{210}\text{Pb}$  was used. The sedimentation rate chosen to use for extrapolation has a significant effect on the resulting dates, and all dates older than 1850 should be considered estimations.

Sediments for metals analysis were frozen for storage, freeze-dried and digested by nitric acid in a CEM-MDS-81D microwave (EPA Method 3051) (Hewitt and Reynolds, 1990). Standard reference material (NIST SRM 8704 Buffalo River Sediment) and procedural blanks were processed as well as three replicate digestions

on two samples from each lake. The concentrated-acid digests were filtered through an acid-washed, distilled-deionized or E-pure (Barnstead International, Dubuque, IA) water rinsed 0.40  $\mu\text{m}$  polycarbonate filter (Nuclepore). Sediments were analyzed for a suite of metals and metalloids including Mg, Al, K, Ca, Ti, V, Cr, Mn, Fe, Cu, Zn, As, Sr, Mo, Cd, Ba, Pb, and U using a Micromass Platform inductively coupled plasma mass spectrometer with hexapole technology (ICP-MS-HEX), with a concentric nebulizer for sample introduction.

All statistics were performed using SYSTAT 10 (SPSS, 2000). Boxplots were used to identify outliers for each element for each lake, and were considered to be outliers if they were outside the outer fence (SPSS, 2000; Yohn et al., in preparation). Elements were grouped by hierarchical cluster analysis on standardized data. Three clustering algorithms were used, Ward's, average and single linkage, to test the robustness of the solution. Clusters were chosen based on the examination of standardized profiles (Yohn et al., in preparation).

## **Results and discussion**

### **$^{210}\text{Pb}$ and dating**

$^{210}\text{Pb}$  profiles varied greatly among lakes, with some lakes having relatively log linear decay, others showing abrupt changes in sedimentation rate, and others appearing to have gradual shifts in sedimentation rate. Because of this, sedimentation rates and ages in each lake were determined using the constant flux, constant sedimentation model (CF:CS) (Golden et al., 1993), the segmented CF:CS (SCF:CS) (Heyvaert et al., 2000), and the constant rate of supply model (CRS) (Oldfield and Appleby, 1984; Sanchez-Cabeza et al., 2000), and then the models were evaluated to

ascertain which was the most appropriate for each lake based on the location of the  $^{137}\text{Cs}$  peak and the stable lead peak (Table 1) (Yohn et al., 2004).

**Table 1.** Characteristics of 11 Michigan study lakes and selected data determined from  $^{210}\text{Pb}$  analysis, including sampling year, lake surface area, lake depth (depth of the water column above the coring location), model used for dating, the approximate mixed depth, the average sedimentation rate, the focusing factor (FF), and the oldest section in the core.

Lake name	Year sampled	Lake surface area (km <sup>2</sup> )	Lake depth (m)	Dating model	Approx mixed depth	Sed rate (g/m <sup>2</sup> /y)	FF	Oldest section
Cadillac	2001	4.7	8	CRS	14 cm	117	1.7	1829 <sup>a</sup>
Crystal B	2001	39	50	CRS	4 cm	624	2.9	1516 <sup>a</sup>
Crystal M	2000	2.9	17	CRS	6 cm	465	1.7	1732 <sup>a</sup>
Elk	1999	31	59	SCF:CS	1 cm	337	2.1	1279 <sup>a</sup>
Gratiot	1999	5.8	24	CF:CS	5 cm	255	2.5	1823 <sup>a</sup>
Gull	1999	8.2	34	SCF:CS	3 cm	404	1.8	1496 <sup>a</sup>
Higgins	1999	39	41	CF:CS	3 cm	232	2.0	1729 <sup>a</sup>
Littlefield	2000	0.7	21	Pb		444	2.0 <sup>b</sup>	1732 <sup>a</sup>
Mullett	2001	67	36	SCF:CS	4 cm	801	3.6	1708 <sup>a</sup>
Paw Paw	2001	3.7	28	CF:CS	3 cm	828	2.7 <sup>c</sup>	1923
Whitmore	2001	2.7	20	SCF:CS	6 cm	556	2.8 <sup>c</sup>	1887

a. Estimated dates based on extrapolation.

b. A focusing factor could not be calculated for Littlefield Lake, so the average focusing factor of all lakes sampled previously (except Cass Lake) was used.

c. Estimated focusing factors based on extrapolation.

$^{210}\text{Pb}$  in the sediments of Littlefield Lake has an unusual profile, with the lowest  $^{210}\text{Pb}$  activities in the middle of the core, and could not be dated using  $^{210}\text{Pb}$  (Yohn et al., 2004). It is unlikely that an error in core collection would cause this altered  $^{210}\text{Pb}$  profile. This profile indicates that deposition of sediment at the sampling site was disturbed either by natural or human processes. Dates for this lake were estimated through the shape of the stable lead profile. The sample with the highest concentration of lead was assigned a date of 1972, and the sample where background

concentrations were reached was assigned a date of 1850. Sedimentation rates were calculated from these dates and ages were estimated for each section (Yohn et al., 2004).

### **Outlier analysis**

Although cluster analysis does not require data to be normally distributed, this technique is sensitive to the presence of outliers (Hair, 1998; Yohn et al., in preparation). Outliers are data with values in one or more variables that are significantly different from the rest of the data, and may represent analytical/sampling errors, or accurately reflect concentrations in the sediment. If outliers are present due to analysis or sampling error, these data should clearly be removed. However, even outliers that represent data accurately will be statistically influential, and one or two outlying data points may determine how an element factors or clusters. It is not appropriate to simply delete these influential points, as these points may be representative of certain processes. Therefore cluster analysis was performed on all data for each lake and on data with outliers removed.

Outliers were present in nine of the eleven lakes. Two or three samples near the surface were outliers for several metals in Elk Lake (As, Mo, Mn, Ba, Fe), and this lake was analyzed both with and without these outliers present. Mullett (As, Mn, Ba) and Higgins (Ba, Mn) lakes also had high concentrations near the surface of some elements. Removal of these points did change results slightly. Results using all data will be reported, but the effect of the outliers will be discussed. In Crystal M Lake, titanium and molybdenum each had one high outlier. These data appeared to be

analysis error, and Crystal M Lake was analyzed without these samples. Outliers in Gratiot Lake were present for aluminum (2 samples) and chromium (one sample), and in Gull Lake for arsenic (five samples). However, removal of these data had little impact on analysis, therefore all data were used. Crystal B, Cadillac, Paw Paw and Whitmore lakes also had one to three outliers, but removal of these data had no significant effect on the groupings, therefore all data were used.

### **Element grouping**

Elements that have similar temporal trends in a sediment core are probably influenced by similar sources and processes (Kemp and Thomas, 1976; Sanei et al., 2001). Elements with similar profiles can be grouped using cluster analysis (Yohn et al., in preparation). If these groups of elements remain consistent among lakes, it would be possible to choose one element to represent each group, and reduce the number of elements analyzed without loss of information. Elements in the study lakes were divided into groups with similar profiles and groups were categorized as terrestrial, anthropogenic, diagenetic or carbonate. Elements that had profiles dissimilar to other elements were not grouped. The category that each group was assigned to was based on the expected sources or processes influencing the suite of elements in that group.

The elements classified as terrestrial in the study lakes generally include titanium, vanadium, aluminum, magnesium, chromium and potassium, and sometimes uranium, barium and iron (Table 2). Changes in the inputs of terrestrial elements, which are those that are influenced by the amount of allochthonous non-organic

material entering the lake, may be caused by increased erosion by natural (e.g., forest fires) or human processes (e.g., clear cutting) (Davis, 1976). Gratiot Lake, the only lake sampled in the Upper Peninsula of Michigan, includes calcium in the terrestrial elements. Gratiot Lake is the only non-carbonate rich lake where calcium may be more influenced by terrestrial inputs than calcium carbonate dynamics.

**Table 2.** Classification of elements into terrestrial (T), carbonate (C), diagenetic (D, D1,D2),and anthropogenic (A, A1, A2). Use of A2 indicates there was more than one group of anthropogenic elements in the lake. Use of D1, D2 notation indicates that there was more than one group of diagenetic elements in the lake. Unclassified elements did not fit clearly into a group, and elements classified twice appear to be influenced by both classes. A (-) indicates that data were not collected for this element. Lakes include Gratiot (Grat), Elk, Gull, Higgins (Hig), Littlefield (Lit), Crystal M (CrM), Cadillac (Cad), Crystal B (CrB), Mullett (Mul), Paw Paw (Paw), and Whitmore (Whit). OR indicates that outliers were removed.

	Elk											
	Grat	Elk	OR	Gull	Hig	Lit	CrM	Cad	CrB	Mul	Paw	Whit
Ti	T	T	T	T		T		T		T	T	T
V	T	T	T	T			T	T	T	T	T	T
Cr	T			T			T		T	T	A	T
Cu	A	A	A	A	A			A	A	A	A	A2
As	A	D	A	A,D2	D1	D1	D1	D		D	D	
Mo		D		D2	D1	D1	D2				D	D
Cd	A	A	A		A	A	A	A	A	A	A	A1
Pb	A	A	A	A	A	A	A	A	A	A	A	A1
Al	T	T	T	T	T	T	T	T	T	T	T	T
Zn	A	A	A	A	A		A	A	A	A	A	A1
Sr	T	-	-	-	C	C	C	C	C	C	C	C
Mg	T	T	T	C	T	C, T				T		
K	D	T	T	T	T	T	T		T	-	-	-
Mn	D	D		D1	D2	D2	D1	D		D		
Ba	D	D	T	C	D2	D2		C	C	D		T
Ca	T	C	C	C	C	C	C	C	C	C	C	C
Fe	A	D	T	D1		D1		D	T	D		
U	T	T	T	D2	D1	D1	D2	T				D

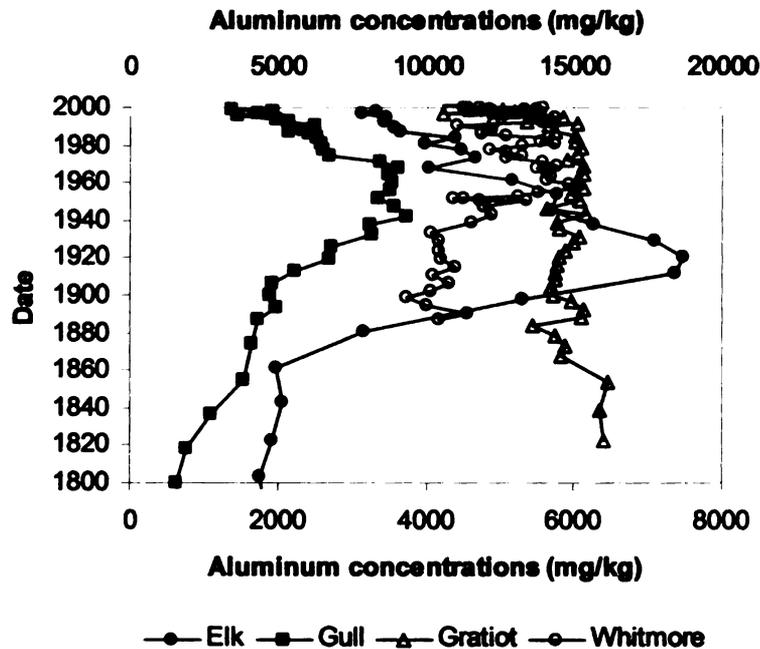
The terrestrial groupings are relatively similar among lakes (Table 2) and to results from previous studies (Kemp and Thomas, 1976; Qu et al., 2001; Sanei et al., 2001; Tuncer et al., 2001) despite a large variation of profiles among lakes (Figure 2).

Aluminum is grouped with the terrestrial elements in all the lakes, suggesting it may be considered representative of this group.

Titanium, vanadium, and potassium are clustered with the terrestrial inputs in

all but one or two lakes, and may also be considered representative.

The carbonate cluster includes calcium and strontium, and sometimes magnesium and barium (Table 2). This portion of the sediment is most often thought to be influenced by calcium carbonate deposition and therefore tends to have low concentrations of most metals (Auer et al., 1996; Sanei et al., 2001). In many of the lakes (Elk, Gull, Higgins, Crystal M, and Mullett Lake), calcium is negatively correlated to aluminum ( $r = -0.746$  to  $-0.801$ ). These lakes are carbonate rich, and



**Figure 2.** Sediment aluminum concentration profiles (mg/kg) of four lakes representing the diversity of concentrations and profiles found among the study lakes. Gratiot and Whitmore lakes have significantly higher aluminum concentrations, and are plotted on the upper x-axis.

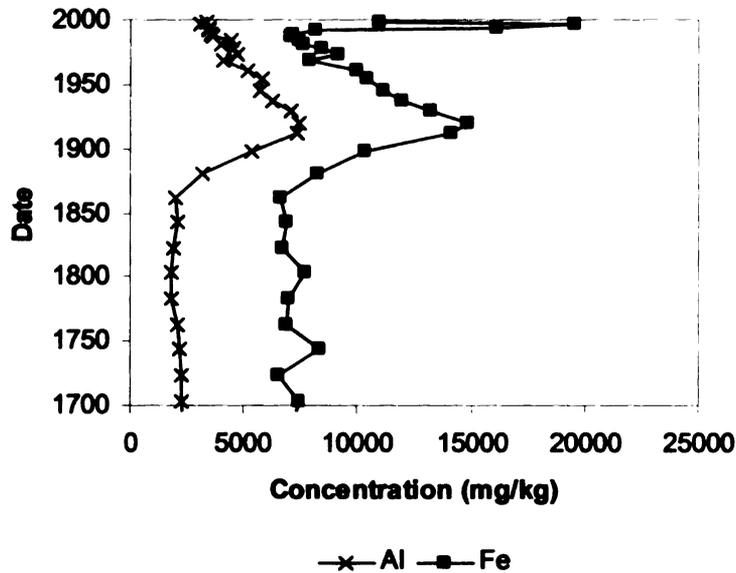
increases in the amount of carbonate would dilute the concentration of the terrestrial elements (Jaquet et al., 1982). Calcium is the most representative element of this group (Table 2).

Diagenetic processes are apparent in all of the lakes, but the behaviors of elements are not consistent among lakes. Molybdenum, uranium, iron, manganese, barium, and arsenic all appear to be influenced by diagenetic processes in some of the lakes (Table 2). In some lakes there are two diagenetic groups, the first including molybdenum and uranium, and the second iron, barium and manganese. However, in other lakes, all of these elements have similar profiles. Arsenic in some lakes behaves similarly to molybdenum, and in other lakes arsenic profiles are similar to iron or manganese. However, despite the dissimilar behaviors, it appears that molybdenum, iron and manganese represent all the diagenetic groups for the study lakes (Table 2).

Lead profiles are influenced dominantly by anthropogenic inputs in all of the study lakes, and zinc, copper and cadmium in the majority of lakes (Table 2). These elements are enriched in lake sediments due to human actions and may enter lakes from atmospheric deposition or from point source inputs within the watershed (Bruland et al., 1974; Iskander and Keeney, 1974; Evans and Dillon, 1982; Spiethoff and Hemond, 1996; Kerfoot and Robbins, 1999). Chromium concentrations in the sediment are only influenced dominantly by anthropogenic inputs in Paw Paw Lake. There are also anthropogenic inputs of arsenic in Gratiot, Elk and Gull lakes, and iron in Gratiot Lake. Extensive copper mining and smelting occurred near the Gratiot Lake watershed, possibly providing a source for iron to the lake.

Anthropogenic elements from each lake did cluster together, despite the fact that the sources for each metal may be different (e.g., copper from copper smelting emissions, or lead from leaded gasoline). Most of these profiles increase from the early 1900s to the 1970s, and decrease to the present. The overall pattern of industrial growth combined with few environmental regulations in the early 1900s, the implementation of environmental legislation in the 1970s (Eisenreich et al., 1986; Callender and vanMetre, 1997), along with the decline of some major industries (e.g., steel production, copper mining) (Kerfoot et al., 1994; Perkins et al., 2000) may lead to the overall similarity in the profiles of the anthropogenic metals, despite differences in sources.

Outliers in Elk, Higgins and Mullet lakes are the result of a large increase in concentration near the sediment surface, probably due to primary and secondary diagenetic processes (Elk Lake: Mo, Ba, Mn, Fe, As; Higgins Lake: Mn, Ba; Mullett Lake: As, Mn, Ba). The removal of outliers in Higgins and Mullet lakes shows that some elements are grouped only because of high concentrations near the surface. In Higgins Lake, manganese and barium are no longer grouped together when outliers are removed. In Mullett Lake, manganese, barium and iron are still grouped after the removal of outliers, but the profile of arsenic is dissimilar. The removal of outliers in Elk Lake allows some interpretation of the original sources and processes influencing the inputs of elements that are affected by diagenesis. After the removal of outliers, iron and barium cluster with the terrestrial elements. Examination of the profiles indicates that iron and barium have profiles very similar to the terrestrial elements, except for the increase in concentration at the surface due to diagenesis, indicating that



**Figure 3.** Sediment aluminum and iron concentration profiles (mg/kg) in Elk Lake.

elements, except for the high concentrations near the surface.

Despite the dissimilarity of element profiles among lakes, the placement of elements into source/process groups is consistent enough to choose representative elements for each of these groups. Aluminum is the most representative of the terrestrial elements, calcium of the carbonate group, and iron, manganese, and molybdenum represent the diagenetic group. This group of elements is the minimum suite necessary, in addition to any anthropogenically influenced elements of interest, to represent terrestrial inputs, carbonate deposition and diagenetic processes.

### **Identification and quantification of human inputs**

Element groupings are similar among lakes, and it is possible to select representative elements to characterize source/process groups. When modeling contaminants in water, the analysis of all the major constituents is necessary to

these two elements are influenced by both terrestrial inputs and diagenetic processes (Figure 3). Similarly, the concentration profile of arsenic is very similar to the anthropogenic

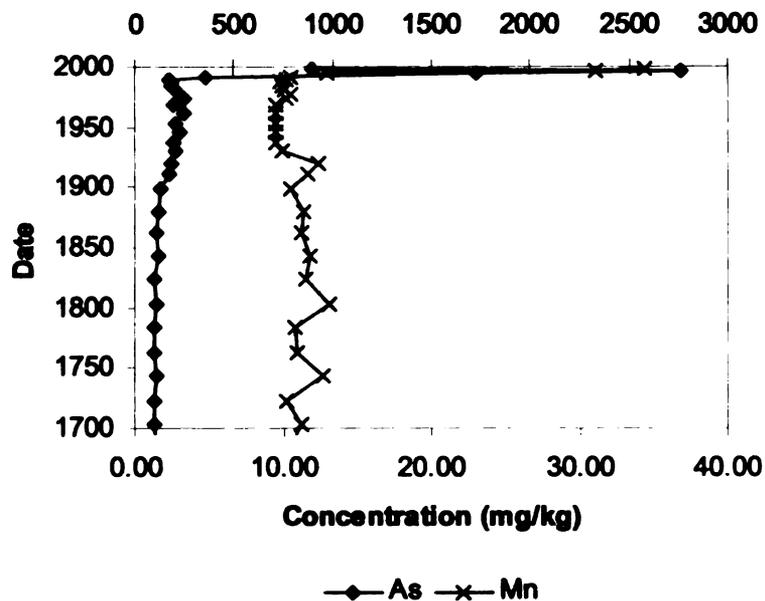
understand the behavior of the contaminant. Similarly, it may be necessary to analyze elements representing each source/process group to understand histories of contaminant inputs in the sediment. In particular, the analysis of diagenetic elements may be necessary to understand arsenic profiles, and the analysis of terrestrial elements to differential natural, secondary and direct human inputs.

Arsenic is an element of particular interest, as both anthropogenic inputs and diagenetic processes influence arsenic (Harrington et al., 1998). In order to monitor the anthropogenic inputs of arsenic using sediment chronologies, it is essential to be able to differentiate early diagenesis from anthropogenic inputs. In this study, we assume that if arsenic follows a trend similar to an element that is known to be influenced by diagenetic processes and not anthropogenic inputs, it may be concluded that arsenic is being influenced by diagenesis. If arsenic patterns are dissimilar to diagenetic elements, it is possible that arsenic patterns are due to anthropogenic inputs.

It is clear from the results of the cluster analysis that arsenic concentration profiles in the sediment may be altered by diagenetic processes, and often cannot be interpreted simply as anthropogenic inputs. Diagenetic processes may cause profiles that, for example, have a peak in arsenic concentrations near the sediment water interface, such as Elk Lake (Figure 4). This pattern could easily be interpreted as an increase in human inputs, however, the same pattern is seen in iron, manganese, barium, and molybdenum, indicating that the high concentrations at the surface are more likely a result of diagenetic processes (Figure 4). This demonstrates the need to analyze for some diagenetic elements to interpret arsenic profiles. In all lakes where arsenic is influenced by diagenesis, it has a similar trend to iron, manganese or

molybdenum (Table 2). There are clear anthropogenic inputs of arsenic in only three lakes (Gratiot, Elk and Gull), and Elk and Gull lakes are also influenced by diagenesis.

Quantification of a terrestrial element



**Figure 4.** Arsenic and manganese sediment concentration profiles in Elk Lake. Both elements show a large concentration increase near the surface, probably due to diagenetic processes.

may also be necessary to understand and measure direct human inputs. Unlike organic contaminants (e.g., DDT), metals are present naturally in sediments, complicating the determination of anthropogenic inputs. Metals such as lead and copper will enter the lake from both direct anthropogenic sources and terrestrial inputs, and in order to calculate the amount of human inputs, it is necessary to determine the terrestrial inputs. While humans can influence terrestrial inputs (e.g. increased erosion due to land use change), these inputs are still of natural geological material, and should be differentiated from direct anthropogenic inputs (e.g., atmospheric and point source inputs).

There are two techniques used in determining natural or background concentrations. The first approach, the constant background technique, is to use the average concentration in sediments that were deposited before significant human

influence (Callender and Rice, 2000). This technique works on the assumption that the concentration of an element due to natural inputs remains the same throughout the depth of the core. This constant background concentration is subtracted from the total to determine the anthropogenic concentration.

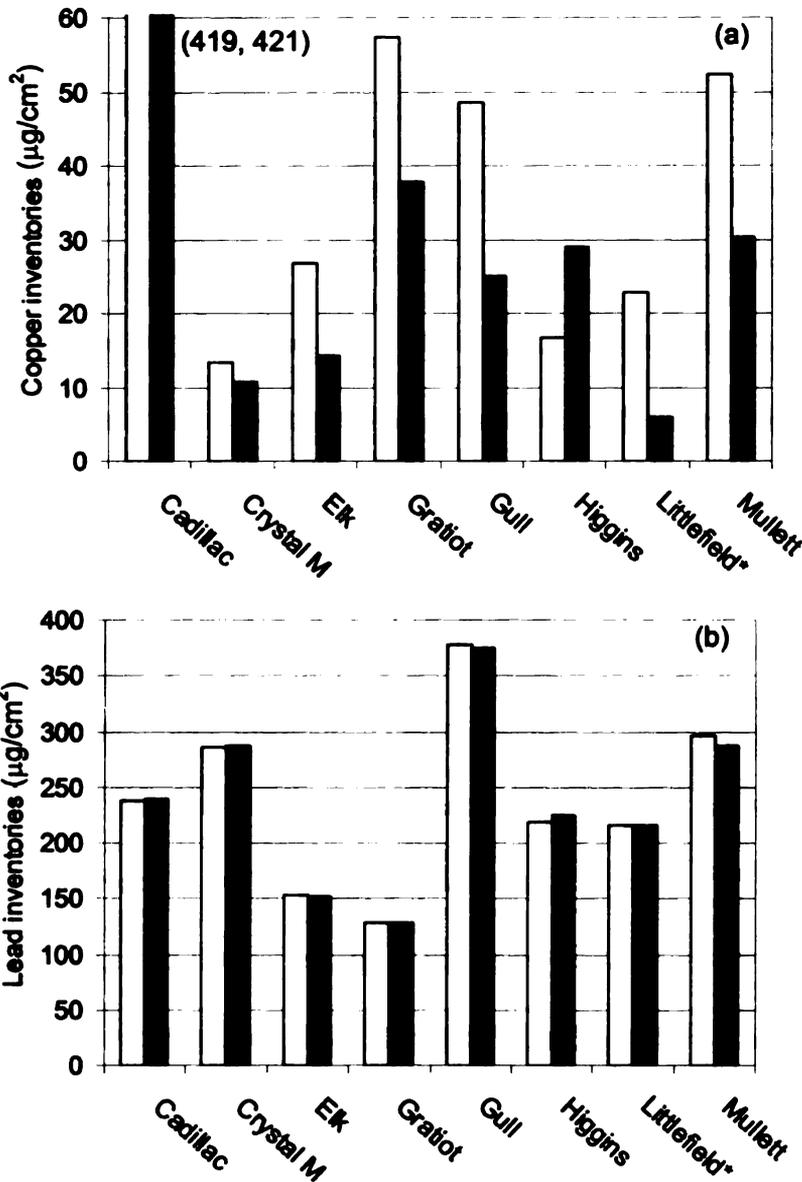
A second method, the watershed correction technique, uses normalization to a terrestrial element to determine anthropogenic inputs. This technique assumes that the concentration of a metal remains the same in the terrestrial inputs from the watershed, but the amount of terrestrial input may vary over time. Since the concentration of elements is assumed to remain the same in the terrestrial inputs, it follows that the natural ratios of elements remain the same throughout the core. The ratio of an anthropogenic element (e.g., lead), and an element not influenced by direct human inputs (e.g., aluminum, iron or scandium) is determined in the pre-anthropogenic sediments (Bruland et al., 1974; Koelmans, 1998; Tuncer et al., 2001), and the concentration due to human inputs is calculated separately for each depth using the equation:

$$M_S^T - \left( \frac{M_{BG}^T}{Al_{BG}^T} \times Al_S^T \right) = M_S^{Anthro}$$

- $M_S^T$  Total concentration of the anthropogenic metal of interest in sample S
- $M_{BG}^T$  Total concentration of anthropogenic metal of interest in background sample
- $M_S^{Anthro}$  Anthropogenic concentration of metal of interest in sample S
- $Al_{BG}^T$  Total aluminum concentration in background sample
- $Al_S^T$  Total aluminum concentration in sample S

If the constant background technique is sufficient to determine anthropogenic inputs, then the analysis of terrestrial elements is not necessary in order to monitor elements such as lead (Heyvaert et al., 2000). However, if there are large changes in concentration of terrestrial elements over time, the use of the watershed correction technique may be more appropriate (Kemp and Thomas, 1976; Johnson and Nicholls, 1988), and the analysis of a terrestrial element necessary. Differences in anthropogenic inventories for lead and copper calculated with a constant background and normalizing to aluminum were examined to determine if the analysis of terrestrial elements is necessary. Anthropogenic inventories are a measure of the total amount of contaminant input by humans per unit area ( $\mu\text{g}/\text{cm}^2$ ) from the present until background concentrations are reached (Golden et al., 1993).

The importance of the calculation method used depends both on the lake and the element (Figure 5). Among lakes the difference between the two calculation methods is greater for lakes like Elk and Gull, which have large shifts in the amount of terrestrial inputs. For all lakes, the relative difference between the constant background methods and the watershed correction technique are much higher for copper than lead (Figure 5). This is because there is sufficient anthropogenic lead input to make the natural inputs relatively insignificant. As a result, the method used to calculate natural inputs has little effect on the determination of human inputs. Copper anthropogenic inputs are much lower than those of lead (Figure 5), with the exception of Cadillac Lake, making the calculation of these inputs more sensitive to the background value used. Copper sulfate was added to Cadillac Lake to control swimmer's itch, and caused the highly elevated copper concentrations. Overall, lakes



**Figure 5.** Focusing corrected anthropogenic inventories of (a) copper and (b) lead calculated using the constant background (white) and watershed correction technique (black). Inventories for copper in Cadillac Lake were above the scale. \*The focusing factor of Littlefield Lake was estimated.

with large shifts in terrestrial inputs (e.g., Gull and Elk lakes) and anthropogenically influenced elements that are not highly enriched are the most sensitive to the background calculation technique.

For many of the lakes, the use of aluminum normalization changes the results for copper significantly (Figure 5a).

Therefore, in order to quantify direct human

inputs to a lake it is essential to quantify a terrestrial element. Aluminum consistently groups with the terrestrial elements in the study lakes, and is the most representative of this group, but titanium and vanadium also frequently represent the terrestrial elements and may be considered representative.

## **Conclusions**

When determining anthropogenic inputs from sediment chronologies, it is necessary to evaluate terrestrial inputs and diagenetic processes as well as inputs of anthropogenic metals. We suggest a suite of six elements in addition to elements known or suspected to have human inputs that will represent the minimum analysis needed to evaluate temporal trends and quantify direct anthropogenic inputs. These are aluminum and titanium which represent the terrestrial elements; iron, manganese and molybdenum to represent diagenetic processes; and calcium to represent carbonate deposition. Although aluminum appears to be sufficient to evaluate terrestrial inputs, the analysis of a second terrestrial element would help validate the results. Analysis of terrestrial elements is necessary when calculating anthropogenic inputs, and also acts as an indicator of the amount of erosion and sediment input from the watershed (Davis, 1976). Three elements are necessary to monitor diagenesis, because elements respond differently in various lake environments. These three elements appear to be sufficient because, in the study lakes, arsenic always behaves similarly to one of these elements when it is influenced by diagenesis. While the analysis of calcium is not necessary to calculate anthropogenic inputs, analysis of this element gives insight into the important processes of calcium carbonate deposition. These six elements, in addition to elements with known anthropogenic sources, should be considered the minimum number of elements needed to interpret patterns of human inputs when using sediment chronologies.

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## CHAPTER FOUR

**Yohn, S.S., Long, D.T., Fett, J.D., Patino, L.C., Giesy, J.P. and Kannan, K., 2002.  
Assessing environmental change through chemical-sediment chronologies from inland  
lakes. *Lakes & Reservoirs: Research and Management* 7, 217-230.**

**CHAPTER 4**  
**ASSESSING ENVIRONMENTAL CHANGE THROUGH CHEMICAL SEDIMENT**  
**CHRONOLOGIES FROM INLAND LAKES**

**Abstract**

This paper examines the hypothesis that the spatial pattern of metal accumulation rates in inland lake sediments provides insight into the cause(s) for the historical and continued loadings of contaminants to the environment. To address this, copper and lead accumulation rates in the Great Lakes watershed are studied. A multi-element approach was used, in which many non-toxic chemicals are measured along with the toxic chemicals of interest, rather than a target specific approach. The multi-element approach also allows 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 analyzed for 26 metals using an inductively coupled plasma mass spectrometer with hexapole technology. Sedimentation rates, ages and focusing were calculated via  $^{210}\text{Pb}$ . Dasymeric mapping was used to estimate population distributions in lake watersheds. Watershed area was estimated from digital elevation data using Arc/INFO.

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.

### **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, questions are asked such as what is the current state of the environment, what is the cause of the current state, what are emerging and lingering issues, and what are 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 Zn), 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 and de Caritat, 1998). Important sources for lead and copper in the Great Lakes basin are leaded gasoline and mining, respectively.

Sediment chronologies from large lakes (e.g.,  $> 1,000 \text{ km}^2$ ) are often used to address environmental issues, but these chronologies typically integrate the contaminate accumulation signal from a large area, which may be at a scale too coarse to address the problem stated above. On the other hand, studying the chemical sediment chronology of inland lakes (e.g.,  $<100 \text{ km}^2$ ) provides important information about a particular lake, however the sources influencing one lake may or may 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 and Nicholls, 1988; Boyle et al., 1999; Callender and 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 and 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 and Keeney, 1974; Dillion and Evans, 1982; Spiethoff and Hemond, 1996), but also many non-toxic chemicals such as aluminum 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 and Nicholls, 1988; Ramanathan et al., 1996; Heyvaert et al., 2000; Kang et al., 2000). The multi-element approach allows: for determining 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 and 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., Bruland et al., 1974; Dillion and Evans, 1982; Birch et al., 1996; 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 cause(s) for the historical and continued loadings of contaminants to the environment. It is developed around the following:

- environmental regulations are typically put in place to address dominant contaminant sources whose influences are typically at regional scales,

- **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,**
- **as loading from the dominant sources are reduced, the effect of less dominant influences/sources on the spatial patterns of contaminant accumulation rates may be revealed, and**
- **the newly detected patterns will provide insight into the underlying causes(s) for the continued loading of the contaminants to the environment.**

**By understanding changes in the importance of different sources and processes over time, it may 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 may provide a continuous source of toxic metals to the aquatic environment (Spiethoff and 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 may be possible to evaluate impacts of the local community. The shores of inland lakes across the United States 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 may result in actions such as allowing less development around the lakes, or updating sewer systems, which would decrease metal loading to the lake.

### Methods

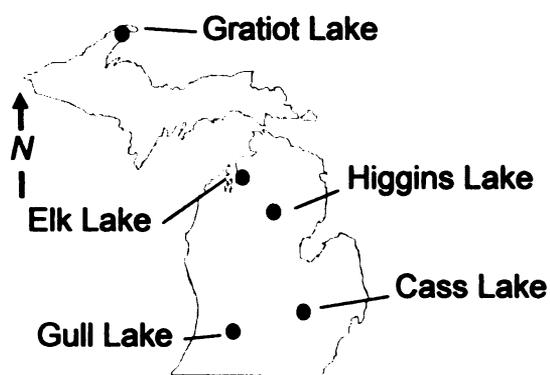
Sediment cores were collected from Cass, Elk, Gratiot, Higgins and Gull Lakes in the State of Michigan, USA during the summer of 1999 (Figure 1). Sediment cores

were collected from the deepest portion of each lake using a MC-400 Lake/Shelf Multi-corer, 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 color, texture, and signs of zoobenthos.

Sediment was extruded from the cores and sectioned at 0.5 cm intervals for the top 5



**Figure 1.** Location of lakes sampled in Michigan, U.S.A. For reference the Greater Chicago metropolitan/industrial area is southwest of Gull Lake.

to 15 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<sup>™</sup> microwave (Hewitt and Reynolds, 1990). Standard reference material (Buffalo River SRM 2704) 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 (Nucleopore<sup>™</sup>). Samples for Hg analysis were preserved with a gold chloride solution (final concentration 200 ppb Au). Samples were then analyzed using a Micromass Platform<sup>™</sup> inductively coupled plasma mass spectrometer with hexapole technology (ICP-MS-HEX). Sediments were analyzed for a suite of metals and metalloids including magnesium, aluminum, 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 analyzed 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 analyzed via flame atomic absorption spectrometry (Perkin Elmer 5100PC<sup>™</sup>).

$^{210}\text{Pb}$  was measured (Freshwater Institute in Winnipeg, Manitoba, Canada) on one sub-core from each lake to determine sedimentation rates, sediment ages and focusing factors. Results from  $^{210}\text{Pb}$  analyses were verified in selected lakes using  $^{137}\text{Cs}$ .

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:

- **Digital Elevation Map (DEM) of Michigan:** United States Geological Survey (Aichele, pers. com.). DEM data was in 30 m<sup>2</sup> grid size raster data, 1:24,000 scale.
- **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.
- **State Ownership Data:** Michigan Department of Natural Resources spatial data library ([www.dnr.state.mi.us/spatialdatalibrary](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.
- **Lake Data:** Michigan Department of Natural Resources spatial data library ([www.dnr.state.mi.us/spatialdatalibrary](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, dasymetric 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.

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  $p < 0.05$ .

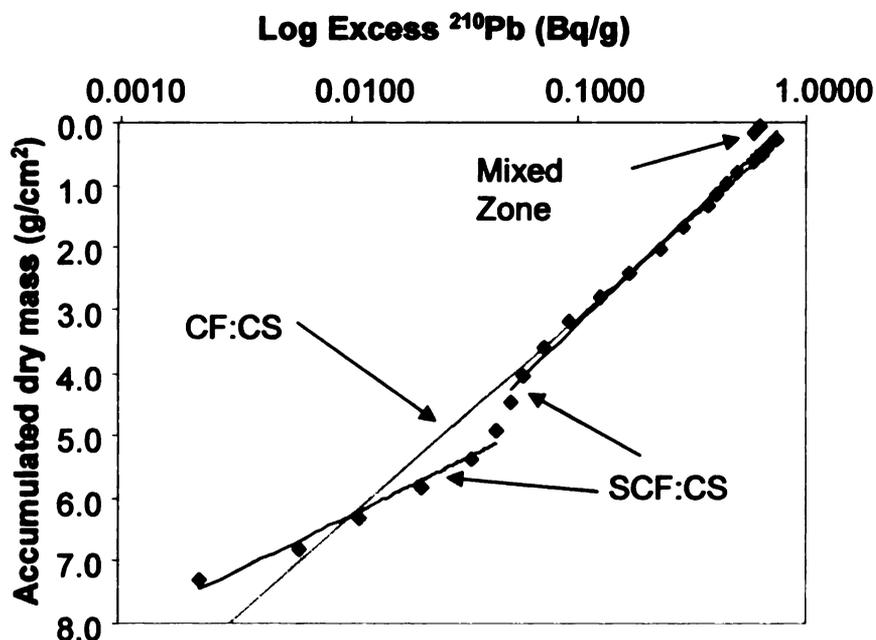
## **Results and Discussion**

### **Sedimentation rates and focusing**

$^{210}\text{Pb}$  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  $^{210}\text{Pb}$ , where the slope is related to sedimentation rates and the non-linear portion near the surface is considered the mixing zone (Figure 2).

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).



**Figure 2.** Log <sup>210</sup>Pb activity (Bq/g) versus accumulated dry mass (g/cm<sup>2</sup>) in Elk Lake. Regression lines for the CF:CS (constant flux-constant sedimentation) model and the SCF:CS (segmented constant flux-constant sedimentation) model are shown.

**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 (g/m <sup>2</sup> /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

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  $^{210}\text{Pb}$  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 (Figure 2, CF:CS), but the segmented CF:CS (SCF:CS) model may be used if there is a clear change in sedimentation rate (Figure 2, SCF:CS) (Heyvaert et al., 2000). The CRS model also assumes constant flux of  $^{210}\text{Pb}$  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 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 and 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  $^{210}\text{Pb}$  inventory measured in the sediment to the expected inventory from  $^{210}\text{Pb}$  deposition from the atmosphere (15.5 pCi  $\text{cm}^{-2}$ ; from Golden et al., 1993):

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

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

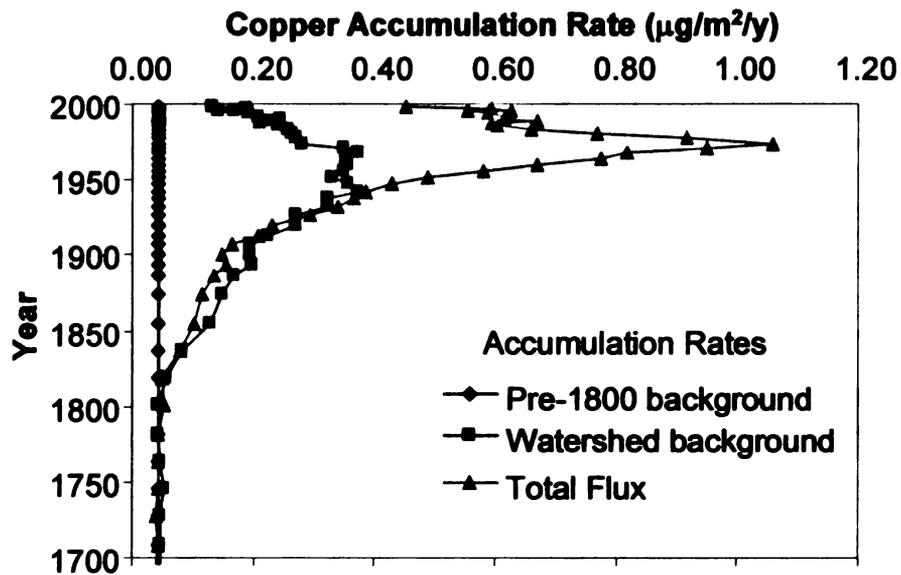
## **Chemical sediment chronologies**

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. aluminum, 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 ( $\mu\text{g}/\text{m}^2/\text{y}$ ), rather than concentrations.

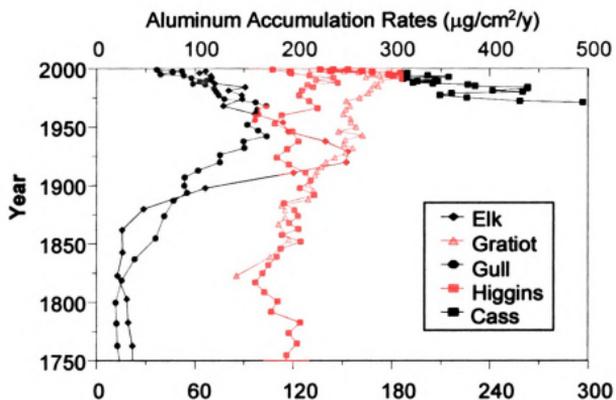
To determine anthropogenic accumulation rates for metals, background concentrations (typically estimated from pre-1800s samples) were subtracted from total concentrations for each sediment increment. It is generally considered that these background concentrations/accumulation rates remain constant throughout time

(Figure 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 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).



**Figure 3.** Copper accumulation rates; total, pre-1800 background values, and watershed (aluminum corrected) background values for Gull Lake. The rate of anthropogenic copper accumulation would be the difference between total and background.

For example, Elk Lake shows the most significant change in watershed input (Figure 4) as seen by the increase in the accumulation rate of aluminum from the late 1800s until 1920, then the decrease to the present. Aluminum 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,



**Figure 4.** Aluminum accumulation rates over time in five inland lakes. For Cass Lake accumulation rates use the upper scale, for all other used the lower scale.

and vanadium all appear to be influenced primarily by watershed input in Elk Lake.

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 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 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. It is clear that a variety of elements might be used to characterize inputs to a lake from the watershed, but aluminum appears to be the most consistent indicator.

By comparing selected metals to aluminum, it may 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:aluminum 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 aluminum accumulation rate. The watershed background metal concentration is estimated by multiplying the aluminum concentration in the sediment times the average metal/aluminum ratio for pre 1800s 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 the following equation:

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

$FCAccum_j^i$  = focusing corrected sediment accumulation rate for  $i^{\text{th}}$  metal at  $j^{\text{th}}$  lake,

$C_j^i$  = watershed background corrected concentration of  $i^{\text{th}}$  metal in the sediment

( $\mu\text{g}/\text{g}$ ) at  $j^{\text{th}}$  lake,

$W_j$  = mass sedimentation rate ( $\text{g}/\text{cm}^2 \text{yr}$ ) in  $j^{\text{th}}$  lake based on  $^{210}\text{Pb}$  dating,

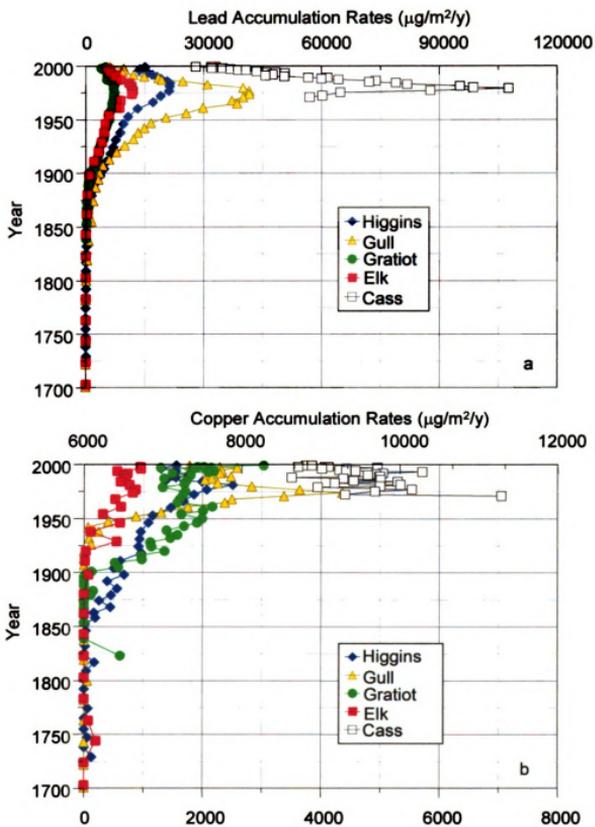
$FF_j$  = sediment focusing factor for  $j^{\text{th}}$  lake

Figures 5a and b are graphs of 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 middle 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 begin in Gratiot Lake around 1900. Accumulation rates in Gull, Higgins and possibly Elk peak around the mid 1970s. Copper accumulation rates in Gratiot Lake were highest around the late 1950s and also in recent times. Cass Lake has the highest over all rates while those of Higgins, Gull, and Gratiot lakes are similar. Elk has 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 a regional source 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

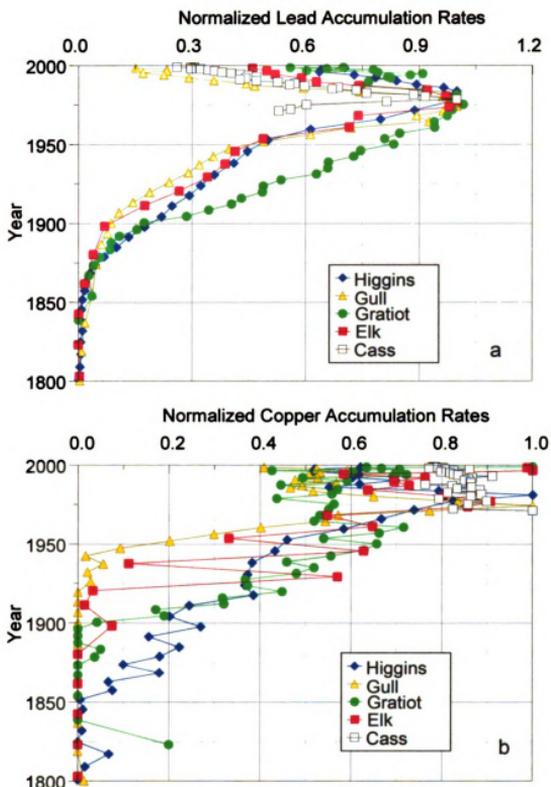


**Figure 5.** Graphs showing the metal accumulation rates for study lakes a. lead, b. copper. The top axis in b. is for Cass Lake only.

the atmosphere. Concentrations might be expected to be higher to the south (influence from the great 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 Figures 5a and b were replotted in Figures 6a and b, respectively. 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 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 (Figure 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 have a similar pattern of increase to the peak rates in the mid 1970s and their trajectories overlap. The difference in Gratiot Lake may be due to contribution of lead from smelting operations or the influence of bioturbation, which can smear the sediment record (Robbins, 1982). The decreasing trajectories in lead accumulation rates after the peak are not the same among the lakes, however. 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.** Graphs showing the metal normalized rates for study lakes. Accumulation rates are normalized to the highest value in a core. a. lead, b. copper.

Figure 6b 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 lakes have 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 is 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 is related to environmental legislation and the subsequent removal of lead from gasoline (Evans and 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.

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 ( $\mu\text{g}/\text{cm}^2$ ).

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

where:

$\text{Inv}_i$  = focusing corrected inventory for  $i^{\text{th}}$  metal in the sediment core ( $\mu\text{g}/\text{cm}^2$ ),

$\text{Csed}^*$  = watershed background corrected concentration of metal in sediment ( $\mu\text{g}/\text{g}$  dry wt.),

$\phi$  = porosity,

$\rho$  = sediment dry density ( $\text{g}/\text{cm}^3$ ),

$d$  = thickness of sediment increment (cm),

$i$  = number of depth increment, and

$\text{FF}_j$  = focusing factor at  $j^{\text{th}}$  core site.

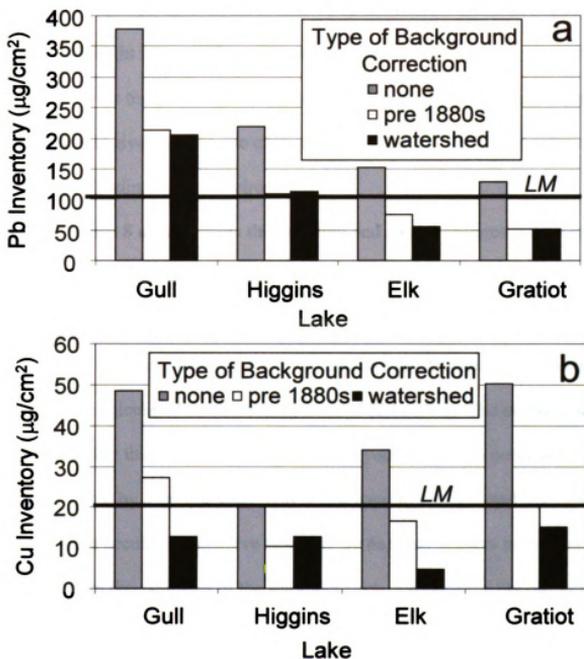
If atmospheric deposition is the major source of a chemical to lakes, then focusing and watershed corrected anthropogenic inventories should be the same in all lakes or show a regional pattern that reflects the distribution of sources of chemicals to the atmosphere. If inventories for a contaminant are different among all lakes and no

regional trend is evident, then local sources dominant contaminant loadings in the lakes. Regional patterns in inventories could indicate the roles of land use in contaminant loadings.

The anthropogenic inventories of lead (Figure 7a) among sampled inland lakes are 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 is 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 and Robbins, 1976). Figure 7a 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 (Figure 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 may 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.



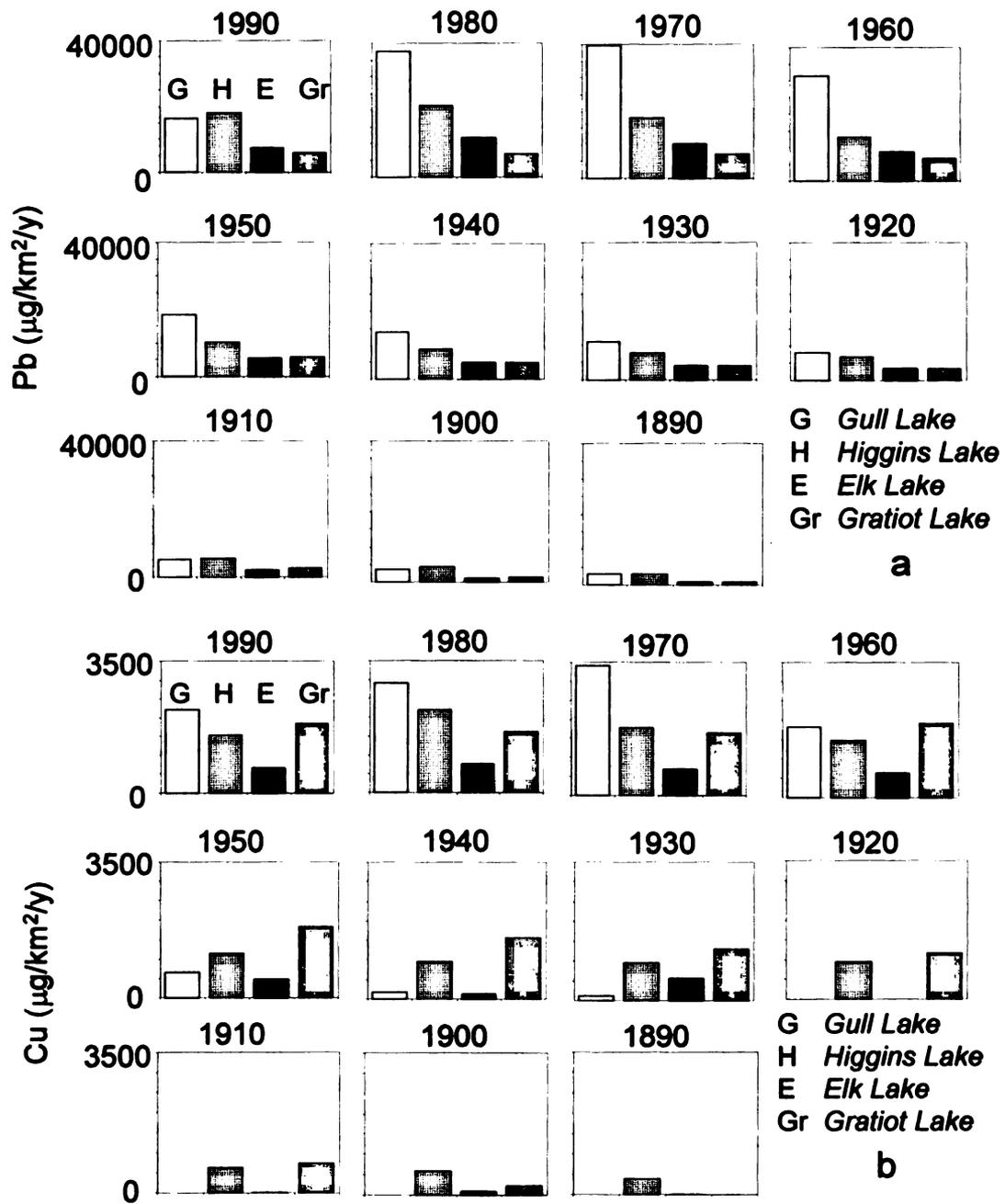
**Figure 7.** Graphs showing the metal inventories as a function of background correction for study lakes: a. lead, b. copper. Lake Michigan (*LM*) values for lead are from Long et al. (1995) and for copper from Kolak et al. (1999).

## **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 may however give insights into changes in regional and watershed influences on lead and copper loadings to the environment.

Figures 8 a and b show 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 ten-year period, five years before and five 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 1) a particular year may not be represented by a sample taken and would have to be estimated from the shape of the sediment accumulation curve (e.g., Figure 6a), and 2) 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



**Figure 8.** Graphs showing decadal metal accumulation rates for study lakes; a. lead, b. copper.

the north is evident. By the 1930s, the pattern is well developed and is 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 are similar. Higgins Lake in 1990 has the highest rate of lead accumulation.

In contrast, no clear pattern emerges for copper accumulation until 1960s (Figure 8b). Prior to that time Higgins Lake and eventually Gratiot Lake had the highest rates of accumulation. In 1960, copper accumulation in Gratiot remains high, however, an accumulation pattern similar to lead is seen for Gull, Higgins, and Elk lakes. Gull has the highest rates of copper accumulation and Elk the lowest. Although the rates are slightly lower, this pattern remains in 1990.

We interpret 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 lake represent a regional influence, the cause of this influence 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 and 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 km<sup>2</sup> (Table 2), and populations ranged from 7 to 5,830 with

population densities of 0.4 to 946 people/m<sup>2</sup>. 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.

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

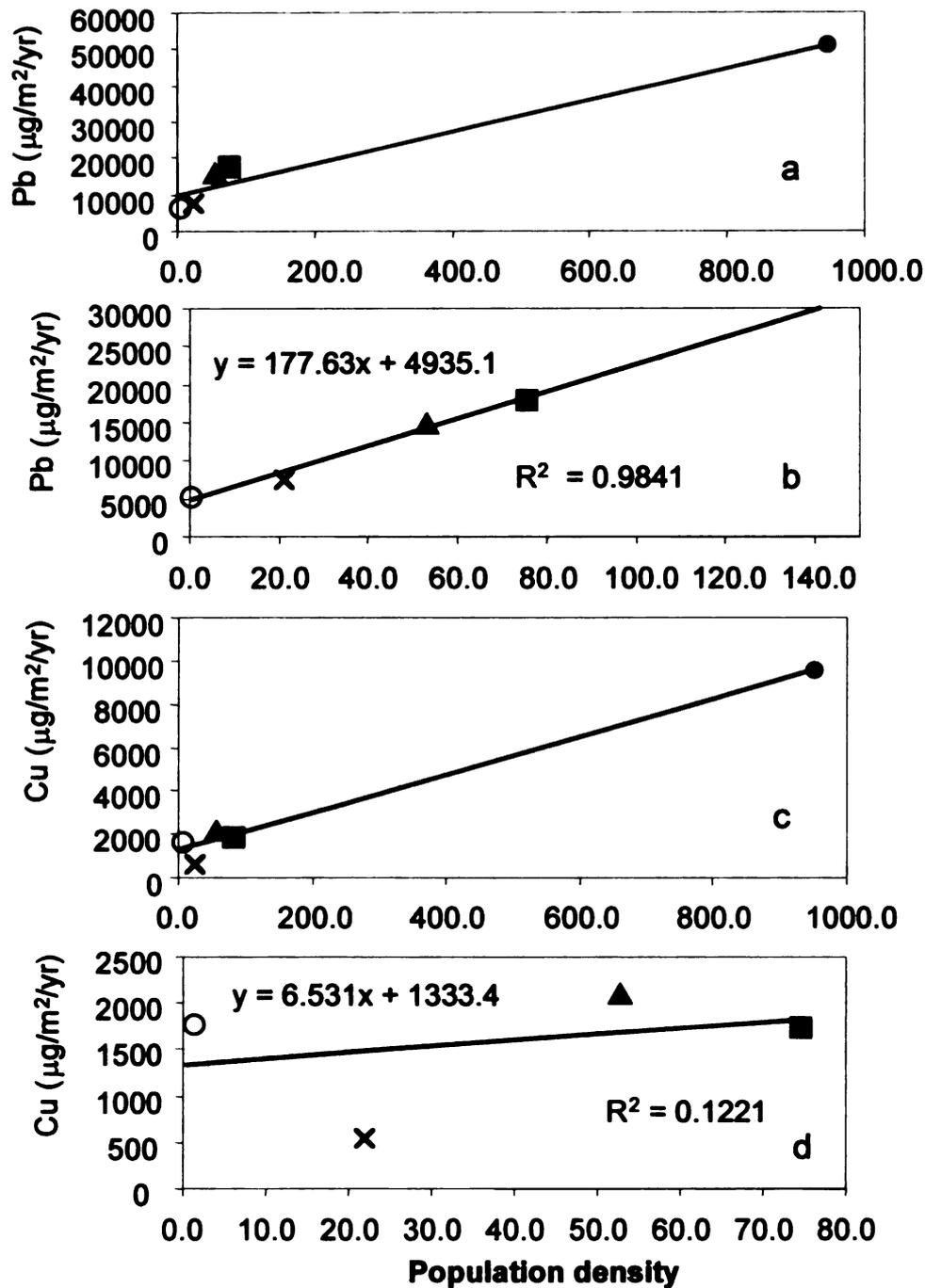
<b>Watershed</b>	<b>Watershed area (km<sup>2</sup>)</b>	<b>Watershed population</b>	<b>Population density (per km<sup>2</sup>)</b>
<b>Cass Lake</b>	11.6	5830	946
<b>Elk Lake</b>	120.8	1280	20
<b>Gratiot Lake</b>	26.3	7	0.4
<b>Gull Lake</b>	14.7	326	52
<b>Higgins Lake</b>	116.5	2561	75

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 may be significant around some of the lakes (e.g., Gratiot Lake population may increase almost tenfold, B. Hay, pers. com., 2000). However, the results still do 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 Figures 9 a, b, c, d). In Figure 9a, all five lakes are included and the trend of the data clearly show that there is a relationship between population density and lead accumulation rate, but this relationship does not appear to be linear. Cass Lake, near Detroit, has the highest population density and highest rate of lead accumulation. Recent lake sediments have been highly disturbed by waste additions from a treatment plant, perhaps causing the unusually high sedimentation rates found for the lake. The non-linearity between Cass Lake and the other lakes may be related to underestimated population densities in the other four lakes, to a non-linear relationship between population density and accumulation rate, or to additional sources of lead and copper not related to population density present in some of the lakes. Replotting the data without Cass Lake (Figure 9b) shows that there is a linear relationship between population density and lead accumulation rate. The intercept (e.g., zero population density) of about  $5,000 \mu\text{g}/\text{m}^2/\text{yr}$  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 (Figure 9 c, 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 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.



**Figure 9.** Graphs showing the 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 symbols: (●) Cass, (■) Higgins, (▲) Gull, (X) Elk, (○) Gratiot.

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 may 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 may 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 and Evans, 1982; Evans and Dillon, 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 and zinc in five reservoirs located along a rural-urban gradient.

### **Summary**

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 accumulation rates provides insight into the cause(s) for the historical and continued

loadings of contaminants to the environment. The data show 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.

### **Acknowledgements**

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## CHAPTER 5

**Yohn, S.S., Long, D.T., Fett, J.D. and Patino, L.C., 2004. Regional versus local influences on lead and cadmium loading in the Great Lakes region. *Appl. Geochem.* 19, 1157-1175.**

**CHAPTER 5**  
**REGIONAL VERSUS LOCAL INFLUENCES ON LEAD AND CADMIUM**  
**LOADING TO THE GREAT LAKES REGION**

**Abstract**

Environmental legislation has reduced the anthropogenic loadings of lead and cadmium to the Great Lakes region over the last three decades. However, the accumulation rates of these metals still remain above background values. Because environmental legislation was targeted at major sources (e.g., lead in gasoline) whose influence on the environment was on a regional scale, local sources (e.g., watershed scale) for the metals may now play a more significant role. The relative importance of regional versus local scale influences on metal inputs to the environment is poorly understood. In this study, sediment chronologies of lead and cadmium were examined from 12 inland lakes that cover the broad geographic area of the State of Michigan. These chronologies were compared temporally and spatially and to watershed population densities and metal production records to gain an understanding of local and regional influences on metal inputs to the Great Lakes region. Results show that anthropogenic lead loading during the 1930s and 1970s was dominated by regional sources, such as coal burning and use of leaded gasoline. Current loadings are now more related to local influences such as watershed population densities, rather than atmospheric deposition. Anthropogenic cadmium loadings to the Great Lakes region have been dominated by both regional and local sources over time. Lead may also have shown the influence of local sources over time, if the influence of emissions from gasoline had not been present. This work shows that lead and cadmium loadings in

the Great Lakes region are strongly related to watershed population densities, however, the specific sources and pathways for the metal cycling are unclear.

### **Introduction**

Over the last three decades significant progress has been made in reducing the levels of metals released to the environment. This reduction of metal inputs has been recorded in lake sediments. For example, the removal of lead from gasoline has significantly reduced lead concentrations in lake sediments (Graney et al., 1995; Callender and vanMetre, 1997). However, despite the reduction of major contaminant sources, concentrations of contaminant metals in sediments, air and water still remain above natural levels (Sanudo-Wilhelmy and Gill, 1999; Simonetti et al., 2000a; Alfaro-De la Torre and Tessier, 2002).

Even as point sources for metals are regulated and emissions from these sources decline, humans continue to alter the environment in ever more significant ways (e.g., urban sprawl) which will have unknown impacts on metal inputs to the environment. Therefore it is essential to understand metal loadings to both assess the effects of environmental legislation, and to determine the emerging sources for metal pollution. This study compares patterns of metal accumulation in inland lakes over space and time to try to determine the current and historical influences on lead and cadmium loadings to the Great Lakes region. Michigan has a surface area of approximately 151,586 km<sup>2</sup>, extends seven degrees of longitude and six degrees of latitude (Encyclopædia Britannica Premium Service, 2003), and has a large number of lakes, making it an ideal location for this study.

Humans have significantly altered the global cycles of both lead and cadmium (Graney et al., 1995; Simonetti et al., 2000a; Alfaro-De la Torre and Tessier, 2002). Atmospheric levels of lead have been enriched significantly in North America from the mid-1800s to the present (Shahin et al., 2000). Lead isotope ratios in the Great Lakes area have been used to show that the major source of lead to the atmosphere in the early 1900s was coal burning, from 1930-1980 leaded gasoline was dominant, and current sources are mixed and less clear (Graney et al., 1995). In the United States, automobile emissions to the atmosphere in 1993 were only 1% of those in 1970 (Bollhofer and Rosman, 2001). Lead also has local sources, and may be found in wastewater effluents and stormwater runoff (Callender and Rice, 2000). Sources for cadmium to lakes have been less extensively studied. Known sources to the environment include both regional sources (e.g., coal combustion, smelters, steel mills) and local sources (e.g., tire wear, sewage sludge and wastewater) (Reimann and de Caritat, 1998). Lead and cadmium are of particular interest because these elements are known health hazards for both humans and wildlife (Catallo et al., 1995; Callender and vanMetre, 1997), and are present in concentrations above the threshold concentration level (below this concentration toxic effects are unlikely to occur: MacDonald et al., 2000) in several of the study lakes (Yohn et al., 2002).

A common approach to understanding factors that influence contamination loading to the environment is to study one lake closely (Bruland et al., 1974; Evans and Dillon, 1982; Johnson and Nicholls, 1988; Balogh et al., 1999). However, while the extensive study of one lake over time provides important information about that particular lake, the results cannot necessarily be generalized to other lakes in the

region. To create a more general model of factors influencing metal input to lakes, multiple lakes can be sampled, and the influence of a particular source determined over space (Yohn et al., 2002). These studies usually examine only contemporary effects (Johnson and Nicholls, 1988; Boyle et al., 1999; Callender and Rice, 2000), rather than examining the change in patterns over time. Our study examined spatial patterns, as well as the changes in those spatial patterns over time.

The dominant sources for contaminants to the environment are often difficult to determine, but spatial and temporal deposition patterns may show if the input of a metal was locally or regionally influenced. If a contaminant is regionally influenced, it must have an atmospheric pathway which allows the metal to move beyond the local watershed. Deposition will be controlled by the distribution of sources in the region, rather than by the presence of the source in the local watershed. A metal with locally influenced inputs is affected dominantly by sources within the watershed.

Knowing if inputs of a contaminant are locally or regionally influenced can be useful for policy makers. Reducing inputs of a metal that is regionally influenced requires legislation on the state or federal level (e.g., reduction of emissions from automobiles), while a metal that is locally influenced may be effected by county and municipal governments or lakes associations (e.g., reduction of pesticides used on lawns bordering the lake). However, once it is known if a metal is locally or regionally influenced, it is also desirable to determine sources for that metal to the environment. Ideally, the actual flux from a particular source is known (e.g., atmospheric flux or sewer outfall) (Bruland et al., 1974; Evans and Dillon, 1982; Johnson and Nicholls, 1988; Balogh et al., 1999). Unfortunately, this information is

rare, and therefore a quantifiable factor that acts as an indicator of that source(s) may be used instead (e.g., copper mining production records as an indicator of input from mining) (Kerfoot et al., 1994). Although this factor does not provide the exact proportion of the input that comes from that source, use of the factor can indicate if a particular source influences chemical input into the lake at different time periods.

Our approach was to first determine if inputs of lead and cadmium were locally or regionally influenced by examining sediment chronologies from multiple lakes over time. If sediment chronologies from multiple lakes have very similar patterns over time (e.g., concentrations increase from background at similar times and peaks occur at the same time) then inputs of that metal are regionally influenced. Secondly, spatial patterns can be examined for different time intervals. If deposition of a metal is regionally influenced then all lakes should have similar inputs, or a spatial gradient should exist. If lakes in close proximity have very different inputs, this implies that the metal is influenced by sources within each watershed (locally influenced).

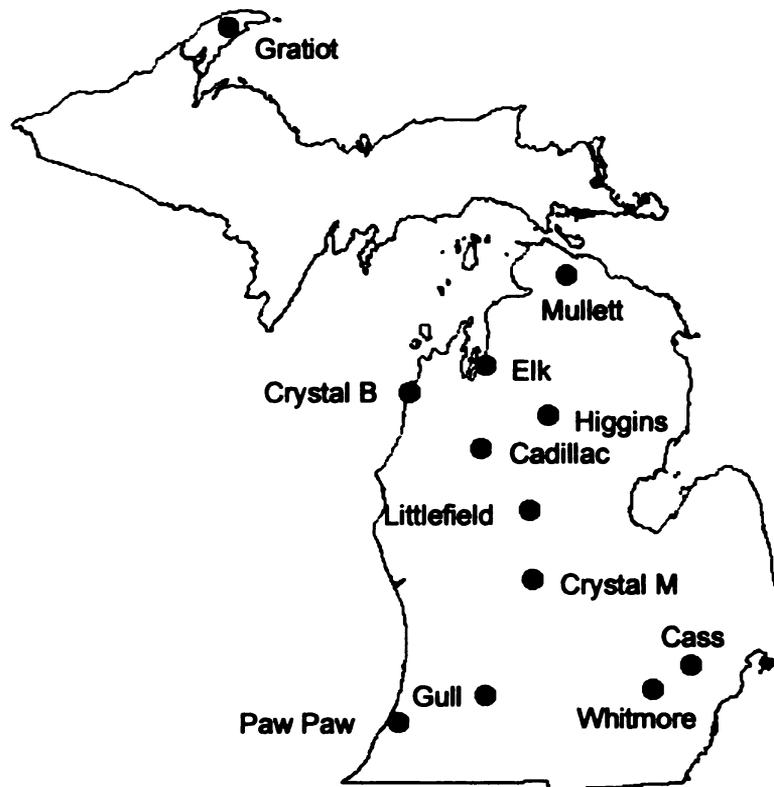
Finally, we compared two factors which represent possible sources to the environment: watershed population densities and industrial production records. Population densities are representative of multiple sources, including sewage and storm water discharge, yard waste and other local inputs (Callender and Rice, 2000). Population densities are also positively correlated to traffic density (Callender and Rice, 2000), and may be representative of sources related to automobiles and highways (e.g., tire wear, auto emissions, road maintenance). National production records (e.g., production of leaded gasoline, or smelter production of cadmium) provide an estimation of the patterns of output from these industries. They do not

report how much of a metal is released into the environment, but if patterns of production are similar to depositional patterns, this may be a good indication of source.

An important assumption in using sediment cores as records of environmental change is that the chemicals of interest are not remobilized and redistributed in the sediment after deposition. For example, because of its oxidation-reduction properties, iron can be highly redistributed in the sediment and changes in vertical concentration often do not reflect changes in input (Kneebone and Hering, 2000). On the other hand, elements such as lead and cadmium are much less influenced by such processes, and therefore we will assume that concentrations of cadmium and lead reflect changes in inputs.

### **Methodology**

Sediment cores were collected from twelve lakes throughout Michigan from 1999 – 2001 (Figure 1, Table 1). Lakes in the Lower Peninsula of Michigan are located on Pleistocene glacial deposits, which are generally carbonate rich, whereas Gratiot Lake is located in the Upper Peninsula on part of the Canadian Shield, with little to no glacial deposits in this region (Door and Eschman, 1970). The lakes vary greatly in surface and watershed area (Table 1), and were chosen based on depth, location, and accessibility. Lakes were also chosen to represent a broad range of human disturbance, from areas of high development (e.g., Cass Lake) to relatively remote lakes (e.g., Gratiot Lake).



**Figure 1.** Lakes sampled in Michigan, USA. For reference, Gary, Indiana and Chicago, Illinois are located to the southwest of Michigan.

**Table 1.** Characteristics of 12 Michigan study lakes. Lake depth is the depth of the water column above the coring location.

Lake	Location (county)	Year sampled	Lake surface area (km <sup>2</sup> )	Lake depth (m)	Watershed area (km <sup>2</sup> )	Watershed to lake area ratio
Cadillac	Wexford	2001	4.7	8	48	10.2
Cass	Oakland	1999	5.2	37	9.1	1.8
Crystal B	Benzie	2001	39	50	106	2.7
Crystal M	Montcalm	2000	2.9	17	12	4.1
Elk	Grand Traverse	1999	31	59	217	6.9
Gratiot	Keweenaw	1999	5.8	24	31	5.3
Gull	Kalamazoo	1999	8.2	34	61	7.4
Higgins	Roscommon	1999	39	41	108	2.8
Littlefield	Isabella	2000	0.7	21	17	22.9
Mullett	Cheboygan	2001	67	36	718	10.7
Paw Paw	Berrien	2001	3.7	28	30	8.0
Whitmore	Washtenaw/ Livingston	2001	2.7	20	5.6	2.0

Four replicate sediment cores from 40 to 58 cm long were taken from the deepest portion of each lake using a MC-400 Lake/Shelf Multi-corer (Ocean Instruments, San Diego, CA) deployed from either the EPA Research Vessel Mudpuppy or the Michigan Department of Environmental Quality Monitoring Vessel Nibi. If the cores showed any evidence of disturbance, a new set of cores was immediately taken. The cores were described and examined for color, texture, and signs of zoobenthos. Cores were immediately extruded and sectioned at 0.5 cm intervals for the top 5-8 cm, and at 1 cm intervals for the remainder of the core.

$^{210}\text{Pb}$  was measured on one core from each lake to determine sedimentation rates, sediment ages and focusing factors (Freshwater Institute in Winnipeg, Manitoba, Canada). Sediments dates and accumulation rates were calculated using three models: the constant flux: constant sedimentation model (CF:CS) (Golden et al., 1993), the segmented CF:CS (SCF:CS) (Heyvaert et al., 2000), and the constant rate of supply model (CRS) (Appleby and Oldfield, 1978). The evaluation of the models is described in the results section.

Sediments for metals analysis were frozen for storage, freeze-dried and digested with nitric acid in a CEM-MDS-81D microwave (CEM, Matthews, NC; EPA Method 3051). Standard reference material (NIST RM 8704 Buffalo River Sediment) and procedural blanks were processed. Three replicate digestions were performed on two samples from each lake. The concentrated-acid digests were filtered through an acid-washed, distilled-deionized water (DDW) rinsed 0.40  $\mu\text{m}$  polycarbonate filter (Nuclepore). Samples were then analyzed using a Micromass Platform inductively

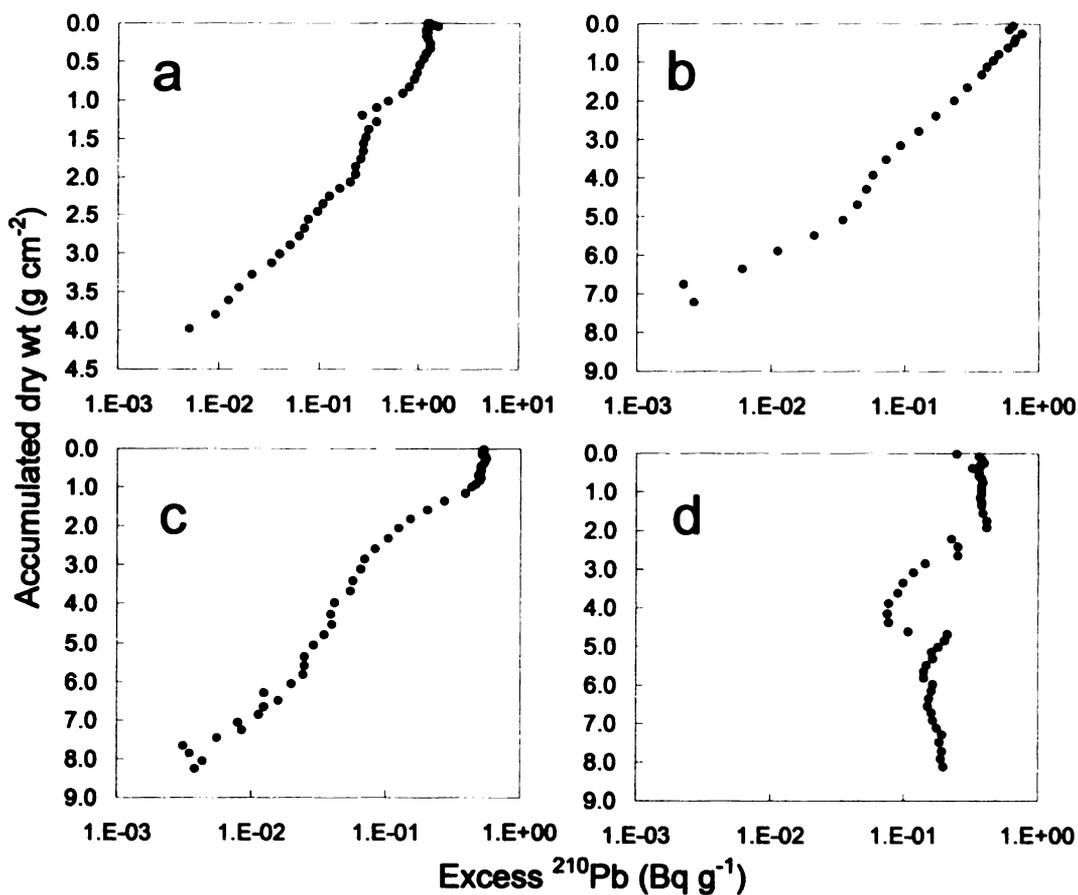
coupled plasma mass spectrometer with hexapole technology (ICP-MS-HEX), using a concentric nebulizer for sample introduction. Due to high concentrations of calcium in the extracts from some lakes (2,000 mg/kg in solution), all standards were matrix matched with calcium concentrations similar to those in the extract. Indium and bismuth were used as internal standards. Sediments were analyzed for a suite of metals and metalloids, including Mg, Al, K, Ca, Ti, V, Cr, Mn, Fe, Cu, Zn, As, Sr, Mo, Cd, Ba, Pb, and U. Reproducibility of the reference material for all elements was better than 15% relative standard deviation, and recovery of cadmium and lead were greater than 90%. Recoveries of other elements (e.g. aluminum) were much lower (20%), due to the use of partial digestion.

Spatial data were collected from secondary sources, and were in, or were projected into the Michigan GEOREF coordinate system: oblique Mercator projection, datum NAD83, spheroid GRS 1980. Sources for data included the United States Geological Survey, Michigan Maps and Information (TIGER base data), and Michigan Department of Natural Resource's spatial data library. The digital elevation models (DEMs) used to delineate watersheds were obtained from the Shuttle Radar Topography Mission (SRTM) dataset. Census data at the township scale were used for population density calculations. Population data were collected from 1870-1990. Watersheds were delineated in the same manner as described in Yohn et al., 2002. Production data were collected from the Minerals Yearbook, United States Department of the Interior, and included data available from 1859-1999.

## Results and discussion

### $^{210}\text{Pb}$ results

The most recently deposited sediment in a lake may be disturbed, or mixed, by resuspension of sediment or bioturbation by zoobenthos. The depth of the mixed zone in lake sediments can be inferred from the depth in which the  $^{210}\text{Pb}$  activity remains relatively constant. While mixing rates are sufficient to homogenize  $^{210}\text{Pb}$ , other chemicals are often not homogenized (Golden et al., 1993; Simpson et al., 2000). Mixed zones for the study lakes were less than 6 cm deep, with the exception of Cadillac Lake. Cadillac Lake had a very deep mixed zone, with the top 14 cm having



**Figure 2.**  $^{210}\text{Pb}$  activity (Bq/g) profiles for Gratiot (a), Elk (b), Crystal M (c) and Littlefield (d) lakes.

relatively constant  $^{210}\text{Pb}$  activities (Figure 2). Cadmium and lead were not homogenized in the mixed zones of the study lakes.

Three different models were used in this study to date sediment cores using unsupported  $^{210}\text{Pb}$  activities, the constant flux constant sedimentation model (CF:CS) (Golden et al., 1993), the segmented CF:CS (SCF:CS) (Heyvaert et al., 2000) and the constant rate of supply model (CRS) (Appleby and Oldfield, 1978; Sanchez-Cabeza et al., 2000). Sedimentation rates in each lake were determined using all models possible for that lake, and then the models were evaluated to ascertain which was the most appropriate to use in determining sediment ages. There is no consensus as to which model is more appropriate in all cases (Oldfield and Appleby, 1984), and several factors were considered when choosing a model. Visual examination of the  $^{210}\text{Pb}$  profile gave some insight into the most appropriate model to be used. The CRS model is more appropriate for lakes with large mixing zones, and the SCF:CS or CRS models are more appropriate for lakes with clear changes in sedimentation (Heyvaert et al., 2000). Additionally, this study uses two other indicators to determine the most appropriate model to use: profiles of cesium-137 ( $^{137}\text{Cs}$ ) activity and stable lead concentration profiles.  $^{137}\text{Cs}$  is an artificial radionuclide that was produced by atmospheric testing of nuclear weapons in the late 1950s and early 1960s, with peak fallout occurring in the early 1960s (Walling and Qingping, 1992). The second indicator is the stable lead peak. Stable lead has an historical pattern of deposition that is very consistent among lakes, with lead concentrations increasing from the mid-1800s to the early to mid-1970s, and decreasing to the present. The peak in lead concentrations in the mid-1970s due to the removal of lead from gasoline is consistent

enough to use for dating verification (Callender and vanMetre, 1997; Alfaro-De la Torre and Tessier, 2002).

Gratiot, Higgins, Cass and Paw Paw Lakes all showed a log-linear decay of  $^{210}\text{Pb}$  over depth (Figure 2a), suggesting that sedimentation rates remained constant over time. These lakes were dated using the CF:CS model. Cass Lake had a very high sedimentation rate, and the oldest section in the collected core was only 1971 (Table 2). Mullett, Whitmore, Gull and Elk Lakes also had a log-linear decay of  $^{210}\text{Pb}$ , but one or more breaks in the slope were present (Figure 2b). This implies that sedimentation rates changed over time in these lakes, and therefore they were dated using the SCF:CS model. The CRS model was most appropriate for Crystal M, Crystal B and Cadillac Lakes (Figure 2c).

$^{210}\text{Pb}$  in the sediments of Littlefield Lake did not show a log-linear decay with depth, and could not be dated using  $^{210}\text{Pb}$  (Figure 2d). It is unlikely that an error in core collection would cause this  $^{210}\text{Pb}$  profile, but rather this profile indicates that the sediment or process of deposition was somehow disturbed. Although dating with  $^{210}\text{Pb}$  is not feasible for this lake, we attempted to estimate dates through the examination of the stable lead profile. The sediment sample with the highest concentration of lead was assigned the date of 1972 (Eisenreich et al., 1986). The amount of sediment deposited from the sample with the highest lead concentration to the surface (year 2000) was determined ( $\text{g}/\text{m}^2$ ), and divided by 28 years (1972-2000) to obtain a sedimentation rate of  $692 \text{ g}/\text{m}^2/\text{y}$ . With this sedimentation rate applied to the entire core, the peak in lead occurred at the appropriate time, but lead concentrations decreased towards background much earlier than in other cores.

Therefore a separate sedimentation rate was determined from 1972-1850, where the date 1850 was assigned to a sample with low lead concentrations. Lead concentrations begin to increase from background near 1850 in Michigan lakes (Simpson et al., 2000), which is similar to values found in Ontario lakes (Blais and Kalff, 1995). This sedimentation rate (252 g/m<sup>2</sup>/y) was used to date the lower section of the core (from 1972 to 1733).

**Table 2.** Selected data determined from <sup>210</sup>Pb analysis, including the model used for dating, the approximate mixed depth, the average sedimentation rate, the focusing factor (FF), and the oldest section in the core.

	Model	Approximate mixed depth	Sedimentation rate (g m <sup>-2</sup> y <sup>-1</sup> )	FF	Oldest section
Cadillac	CRS	14 cm	117	1.7	1829 <sup>a</sup>
Cass	CF:CS	3 cm	3480	6.0 <sup>c</sup>	1971
Crystal B	CRS	4 cm	624	2.9	1516 <sup>a</sup>
Crystal M	CRS	6 cm	465	1.7	1732 <sup>a</sup>
Elk	SCF:CS	1 cm	337	2.1	1279 <sup>a</sup>
Gratiot	CF:CS	5 cm	255	2.5	1823 <sup>a</sup>
Gull	SCF:CS	3 cm	404	1.8	1496 <sup>a</sup>
Higgins	CF:CS	3 cm	232	2.0	1729 <sup>a</sup>
Littlefield	Pb	NA	444	2.0 <sup>b</sup>	1732 <sup>a</sup>
Mullett	SCF:CS	4 cm	801	3.6	1708 <sup>a</sup>
Paw Paw	CF:CS	3 cm	828	2.7 <sup>c</sup>	1923
Whitmore	SCF:CS	6 cm	556	2.8 <sup>c</sup>	1887

a. Estimated dates based on extrapolation.

b. A focusing factor could not be calculated for Littlefield Lake, so the average focusing factor of all lakes sampled previously (except Cass Lake) was used.

c. Estimated focusing factors based on extrapolation.

Comparison among lakes of sediment chronology data is complicated by the process of sediment focusing, which is the tendency of fine-grained sediment to move towards the deepest portion of the lake. This process can be accounted for through the use of a focusing factor. The focusing factor (FF) was calculated by dividing the

actual  $^{210}\text{Pb}$  inventory in each lake (Kada and Heit, 1992) by the expected  $^{210}\text{Pb}$  inventory (Golden et al., 1993).

$$\text{FF} = \frac{\text{actual } ^{210}\text{Pb inventory}}{\text{theoretical } ^{210}\text{Pb inventory}}$$

Focusing factors were calculated for each of the study lakes in Michigan, and ranged from 1.7 to 6.0 (Table 2). The focusing factors for Cass, Whitmore and Paw Paw Lakes were estimated using extrapolation to calculate the inventory of excess  $^{210}\text{Pb}$ , since supported  $^{210}\text{Pb}$  levels were not reached. A focusing factor could not be calculated for Littlefield Lake, so the focusing factor was estimated by taking the average of the focusing factor of all lakes sampled previously, excluding Cass Lake.

## **Temporal patterns**

### *Lead*

Lead concentrations vary considerably among the twelve study lakes (Figure 3), but the profiles are very similar in shape (Figure 4). All lakes increase from background concentrations in the mid-1800s and peak between 1973 and 1981. The similarity of trends in the study lakes indicates that lead was regionally influenced until the 1980s. This is further corroborated by the similarity of the profiles among lakes in this study to other lakes in the Great Lakes region (Graney et al., 1995; Alfaro-De la Torre and Tessier, 2002; Outridge et al., 2002). However, rates of decrease in concentration from the peak to the present differ among study lakes. There has been little documentation of this phenomenon for multiple lakes at this spatial scale.

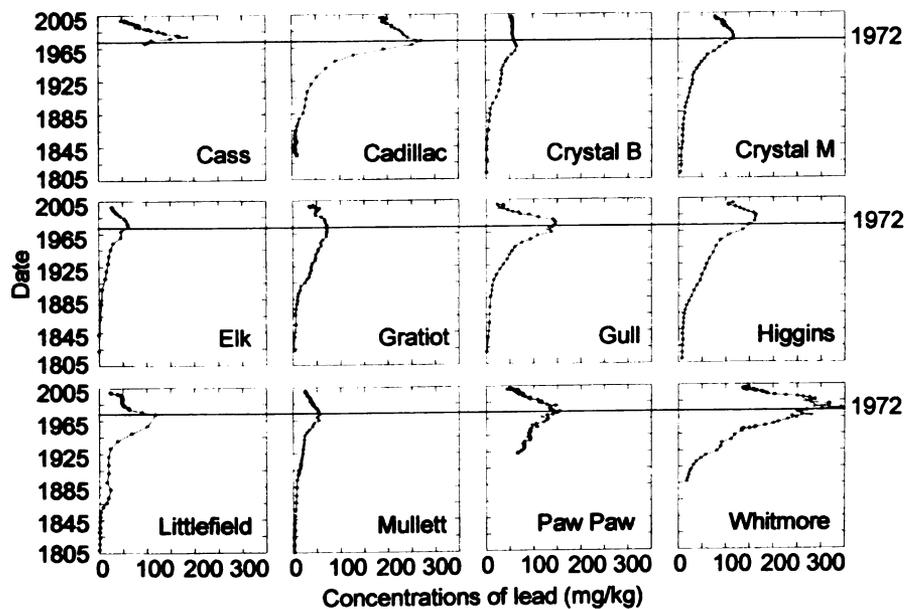


Figure 3. Lead concentrations (mg/kg) over time in 12 Michigan lakes.

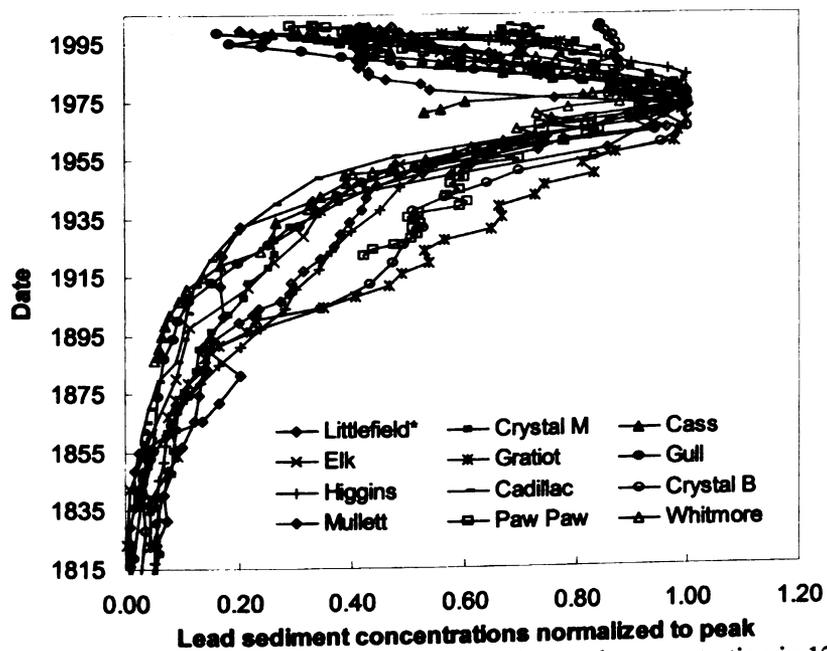
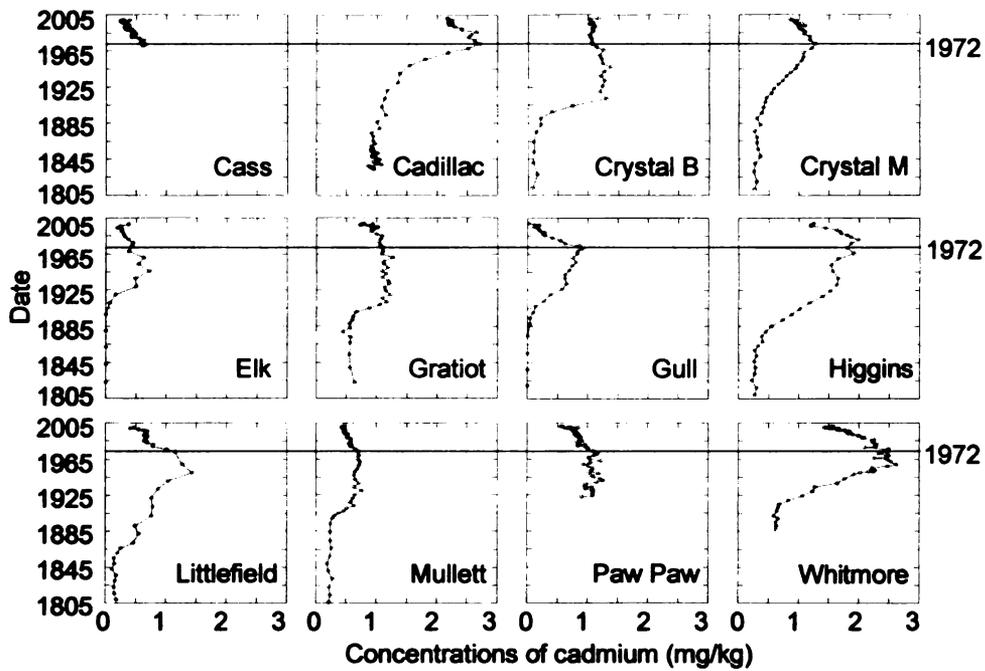


Figure 4. Lead concentrations normalized to peak concentration in 12 Michigan lakes.

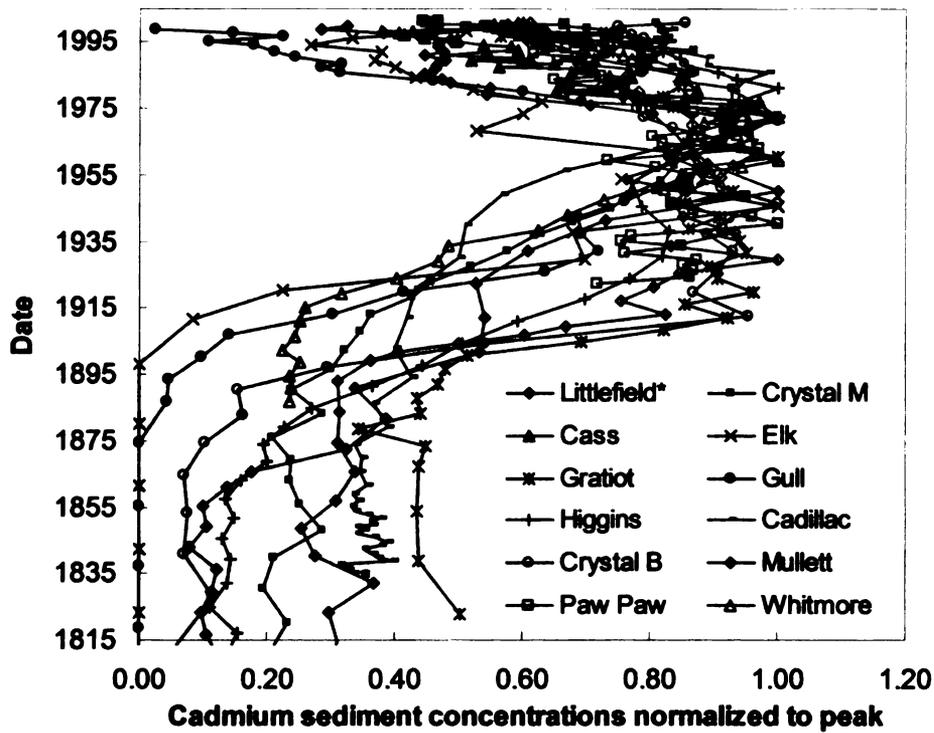
There are several possibilities for the differing rates. Mixing of the sediment and focusing can cause broadening of contaminant peaks (Crusius and Anderson, 1995), and different amounts of focusing and/or mixing could cause the differences in the profiles among lakes. However, the increasing trend is very similar among lakes, despite differences in within lake processes, indicating that these explanations in themselves are not sufficient. Another possibility is that the input of lead is decreasing at similar rates among lakes, but input rates of a diluting component of the sediment (e.g., production of organic matter, calcium carbonate) are different among some lakes. Profiles of lead accumulations rates, which should account for the effects of dilution, were examined among lakes, but rates of decrease still differed among lakes. The difference in decreasing rates of lead may also be caused by a shift from regional to local influence. Local sources for lead may be point sources within the watershed, or the input of soils that have enriched lead concentrations due to current and historic atmospheric deposition.

### *Cadmium*

Patterns of deposition and possible sources for cadmium to lake sediments have not been as extensively studied as lead. Similar to lead, cadmium profiles also increase from background levels, peak in the subsurface and decrease to the present (Figure 5). The pattern of cadmium deposition in the study lakes is similar to the cadmium profile found in another lake in the region (Lake Tantare in Quebec, Canada: Alfaro-De la Torre and Tessier, 2002). However, despite the overall similar trend,



**Figure 5.** Cadmium concentrations (mg/kg) over time in 12 Michigan lakes.



**Figure 6.** Cadmium concentrations normalized to peak concentration in 12 Michigan lakes.

profiles are not as similar among lakes as they are for lead profiles (Figure 6). Unlike lead, cadmium concentrations in the sediments increase from background at different times among lakes, and peak at different times. The overall shape of the cadmium profiles in study lakes and Lake Tantare implies regional human perturbation of the cadmium cycle, however, the differences among the profiles indicate that cadmium has been locally influenced much more than lead.

### **Spatial patterns**

Further insight into influences on lead and cadmium loadings in the region were obtained by examining the spatial patterns of focusing-corrected anthropogenic accumulation rates. If lead or cadmium inputs are regionally influenced, then accumulation rates should be the same in all lakes or show a regional pattern that reflects the distribution of sources for these elements to the atmosphere. If accumulation rates differ greatly in nearby lakes, or no regional gradient exists, then the deposition of that metal may be inferred to be locally influenced. A metal with locally influenced inputs will probably also be atmospherically deposited, but if local influences are dominant, they could obscure the regional pattern.

The portion of the anthropogenic elemental abundances of lead and cadmium in the sediment was determined by normalizing to a relatively inert element (aluminum). Normalization corrects for changing proportions of terrestrial inputs and diluting phases (e.g., calcium carbonate) (Bruland et al., 1974; Kemp and Thomas, 1976; Callender and vanMetre, 1997; Koelmans, 1998; Tuncer et al., 2001; Alfaro-De la Torre and Tessier, 2002). For most lakes, the metal to aluminum background ratio

was calculated as the average ratio of all samples older than 1800. However, sediment cores taken from Whitmore and Paw Paw Lakes were not deep enough to reach background sediments (oldest sections were 1887 and 1923, respectively). Therefore, background metal to aluminum ratios in these lakes were estimated from Higgins Lake, which had the similar concentrations of selected major sediment components (e.g., aluminum and calcium) to both Paw Paw and Whitmore Lakes. Background concentrations were not calculated for Cass Lake, because the sediment core from Cass Lake only reached 1971. Because such a small time interval was sampled, and because Cass Lake had a sedimentation rate much higher than any other lake, we did not feel that it was reasonable to estimate anthropogenic inputs.

Focusing corrected anthropogenic accumulation rates were calculated using the equation (Wong et al., 1995):

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

$FCAccum_j^i$  = focusing corrected sediment accumulation rate for  $i^{\text{th}}$  metal at  $j^{\text{th}}$  lake,

$C_j^i$  = watershed background corrected concentration of  $i^{\text{th}}$  metal in the sediment ( $\mu\text{g}/\text{g}$ ) at  $j^{\text{th}}$  lake,

$W_j$  = mass sedimentation rate ( $\text{g}/\text{cm}^2\text{yr}$ ) in  $j^{\text{th}}$  lake based on  $^{210}\text{Pb}$  dating,

$FF_j$  = sediment focusing factor for  $j^{\text{th}}$  lake

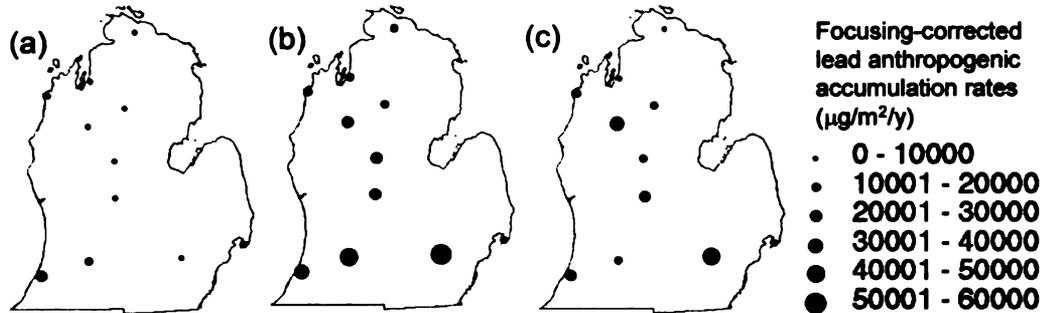
Spatial patterns were examined over three time intervals: 1925-1935 (1930), 1965-1975 (1970) and 1985-1995 (1990). The early industrial period is represented by 1930, the period of peak anthropogenic inputs by 1970 (e.g., Figures 3,5), and 1990 represents recent deposition. Focusing-corrected anthropogenic accumulation rates

were averaged over a decade to correspond to population density data (decadal census data). Using decadal averages also accounts for samples (0.5 or 1 cm sections of sediment) including deposition from varying numbers of years among lakes. For example, the sample with the highest concentration of lead in Elk Lake includes sediment deposited from 1972-1976, and in Gull Lake this sample includes 1975-1979. Averaging over a longer time period rather than attempting to choose one comparable sample from each lake reduces the influence of the varying time intervals.

### *Lead*

In 1930, the two lakes with the highest lead accumulation rates, Paw Paw and Gull lakes, are in the southwest corner of Michigan (Figure 7a). The other study lakes have relatively low anthropogenic accumulation rates ( $<10,000 \mu\text{g}/\text{m}^2/\text{y}$ ). Rates have increased in all lakes in 1970, and lakes in southern Michigan continue to have the highest values (Figure 7b). Lead accumulation rates in Whitmore Lake, near Detroit, increased more than other lakes. In both the 1930s and the 1970s there was a general trend of higher accumulation rates in the south and decreasing northwards. This regional trend has also been seen in the Great Lakes, with higher atmospheric deposition and sediment concentrations in southern than northern Lake Michigan (Edgington and Robbins, 1976; Eisenreich, 1980). In 1990 the regional gradient is no longer apparent (Figure 7c). Accumulation rates of lead in Gull and Paw Paw Lakes decreased substantially, and no longer had rates higher than lakes further north. Furthermore, some lakes that are in relatively close proximity had very different accumulation rates (e.g., Littlefield and Cadillac). Lead accumulation rates for

Gratiot Lake remained below 10,000  $\mu\text{g}/\text{m}^2/\text{y}$  for all three time intervals, and are not shown in Figure 7.



**Figure 7.** Average lead focusing-corrected anthropogenic accumulation rates ( $\mu\text{g}/\text{m}^2/\text{y}$ ) for: (a) 1925-1935, (b) 1965-1975, (c) 1985-1995. Cass Lake is not shown because anthropogenic accumulation rates could not be calculated. Gratiot Lake and the Upper Peninsula are not shown; Gratiot Lake has an accumulation rate between 0 – 10000  $\mu\text{g}/\text{m}^2/\text{y}$  for all time periods.

The regional gradient present in 1930 and 1970 suggests that lead is regionally influenced. Many studies have shown that the atmosphere is an important pathway for lead (e.g., Edgington and Robbins, 1976; Evans and Dillon, 1982; Eisenreich et al., 1986; Outridge et al., 2002), and Graney, et al., (1995) suggest from isotope data that lead emissions to the atmosphere were influenced by both coal burning and leaded gasoline in the 1930s and dominantly by leaded gasoline in the 1970s. The general population distribution in Michigan decreases towards the north, therefore, sources for lead to the atmosphere such as coal burning stoves or automobiles would be expected to produce the regional gradient seen in 1930 and 1970. Furthermore, prevailing winds are predominantly from the southwest in this region (Landis et al., 2002), and may have carried atmospheric lead into Michigan from the extensive steel mills in and

around Gary, Indiana (Souch et al., 2003), and the large population center of Chicago, Illinois. This may account for the higher lead accumulation rates in Paw Paw and Gull Lakes in 1930 and 1970, but is unlikely to be the only contributor of lead to Michigan lakes. Sources impacting lead inputs in 1990 are less apparent, but the lack of spatial gradient indicates that lead has become more locally influenced as regional sources (e.g., leaded gasoline) have declined.

Atmospheric deposition has been estimated from measurements and modeling in the Great Lakes region (Eisenreich and Strachan, 1992; Hoff et al., 1996; Sweet et al., 1998; Simonetti et al., 2000b; Alfaro-De la Torre and Tessier, 2002), making it possible to compare atmospheric deposition rates of lead to anthropogenic accumulation rates in lake sediments. Accumulation rates in the study lakes are all significantly higher than measures of total atmospheric deposition within the region (Table 3), indicating another source for lead in addition to atmospheric deposition. There appears to still be a regional gradient of atmospheric deposition in 1990, with the lowest rates of deposition measured in the north, over Lake Superior, and higher rates measured over Lake Michigan (Eisenreich and Strachan, 1992; Sweet et al., 1998). If this gradient is ignored, we can estimate from the literature the average rate of atmospheric deposition to this region ( $\sim 1700 \mu\text{g}/\text{m}^2/\text{y}$ ), and use this to evaluate the approximate percentage of the lead input to each lake from atmospheric deposition (estimated atmospheric deposition from the literature / anthropogenic accumulation in lake sediments; Table 3), with the remaining portion being due to local sources. All lakes have less than 50% of lead inputs contributed from atmospheric deposition, with Gratiot Lake having the highest atmospheric component ( $\sim 30\%$ ), and Cass, Cadillac

**Table 3.** Summary of lead and cadmium accumulation rates in this study (average 1985-1995) and accumulation rates measured in the sediment, atmospheric deposition, and snowpack from previous studies. Data from this study are focusing-corrected anthropogenic accumulation rates, data from other studies are total accumulation rates. Percent atmospheric is the estimated percent of the sediment accumulation rate due to atmospheric deposition, with the parenthetical values in the first line representing the estimated rate of atmospheric deposition ( $\mu\text{g}/\text{m}^2/\text{y}$ ) used in the calculation.

Location	Medium	Accum rate $\mu\text{g}/\text{m}^2/\text{y}$		% atmospheric	
		Pb	Cd	Pb	Cd
This study 1985-1995				(1700)	(100)
Cass*	sediment	55000	220	3%	45%
Elk	sediment	8900	60	18%	167%
Gratiot	sediment	4900	50	33%	200%
Gull	sediment	18000	70	9%	143%
Higgins	sediment	15000	170	11%	59%
Crystal M	sediment	26000	210	6%	48%
Littlefield	sediment	17000	100	9%	100%
Cadillac	sediment	34000	240	5%	42%
Crystal B	sediment	12000	210	13%	48%
Paw Paw	sediment	25000	130	6%	77%
Whitmore	sediment	45000	340	4%	29%
Mullett	sediment	9200	80	17%	125%
Lake Tantare, Canada <sup>a</sup>	sediment		61		
L. Superior, 1993-1994 <sup>b</sup>	atmospheric	1500	460		
L. Superior <sup>c</sup>	atmospheric	817	148		
L. Michigan, 1993-1994 <sup>b</sup>	atmospheric	1600	450		
L. Michigan <sup>c</sup>	atmospheric	1747	153		
L. Erie, 1993-1994 <sup>b</sup>	atmospheric	1800	490		
L. Huron <sup>d</sup>	atmospheric	1700	110		
L. Ontario <sup>d</sup>	atmospheric	2200	140		
Eastern Ontario, 1998 <sup>e</sup>	snowpack	720-1800	60-140		
Northeast USA, 1998 <sup>e</sup>	snowpack	140-340	25-60		

\* Accumulation rates for Cass Lake are total (not anthropogenic) focusing corrected accumulation rates.

a. Headwater lake in an ecological reserve in Quebec, Canada (Alfaro-de la Torre and Tessier, 2002).

b. Sweet et al., 1998

c. Eisenreich and Strachan, 1992

d. Hoff et al., 1996

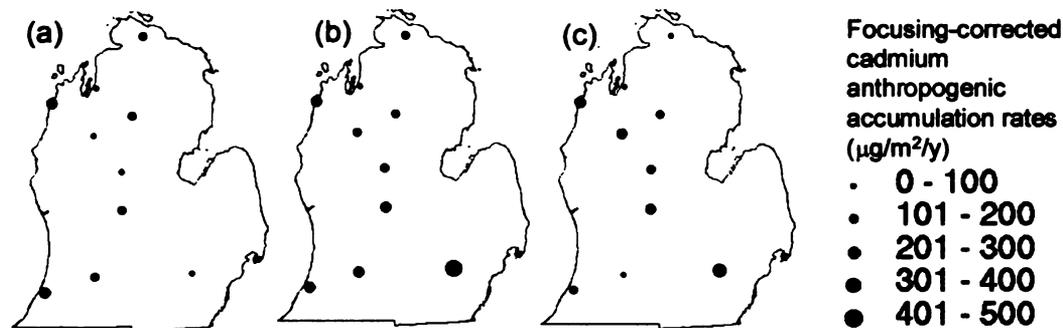
e. Simonetti et al., 2000b

and Whitmore Lakes having the lowest ( $\leq 5\%$ ). These three lakes are all located in relatively highly developed areas, while Gratiot Lake is in a more remote location. Some of the difference in the estimation of the percentage of total inputs due to atmospheric deposition among lakes is probably due to a regional atmospheric gradient. Atmospheric deposition rates are probably lower than estimated in the north (e.g., near Gratiot Lake), causing an overestimation of the contribution from the atmosphere. However, even if the lowest deposition rate ( $817 \mu\text{g}/\text{m}^2/\text{y}$ , Eisenreich and Strachan, 1992) for the northern region of the state is used, atmospheric deposition still accounts for a portion in Gratiot Lake (17%) which is greater than that of the urban lakes. From these data it can be inferred not only that lead is locally influenced in 1990, but also that the relative contribution of atmospheric deposition varies among lakes. This may account for varying rates of decrease in lead sediment concentrations among lakes that was described above.

### *Cadmium*

As might be anticipated from the results shown in Figure 8, spatial patterns of cadmium deposition over time are less evident than lead. The regional trend of higher accumulation rates in the south that was present for lead is absent for cadmium over all time intervals. Similar to lead, in 1930 Paw Paw Lake has the highest accumulation rates, but unlike lead, Crystal B Lake also has relatively high accumulation rates. In 1970 the southern lakes have high accumulation rates of cadmium, with Whitmore Lake having the highest accumulation rate. However, lakes further north (e.g., Crystal B) also have high accumulation rates. In 1990, cadmium

accumulation rates in Gull and Paw Paw have decreased significantly, and Whitmore, Crystal M, Cadillac and Crystal B Lakes have the highest rates, resulting in a spatial pattern that is similar to lead in 1990. A regional gradient does not exist in 1990, but those lakes with relatively high cadmium accumulation rates also have high values for lead. Accumulation rates of cadmium remain low ( $<100 \mu\text{g}/\text{m}^2/\text{y}$ ) in Gratiot Lake throughout all time intervals.



**Figure 8.** Average cadmium focusing-corrected anthropogenic accumulation rates ( $\mu\text{g}/\text{m}^2/\text{y}$ ) for: (a) 1925-1935, (b) 1965-1975, (c) 1985-1995. Cass Lake is not shown because anthropogenic accumulation rates could not be calculated. Gratiot Lake and the Upper Peninsula are not shown; Gratiot Lake has an accumulation rate between 0 – 100  $\mu\text{g}/\text{m}^2/\text{y}$  for all time periods.

Relatively high accumulation rates of cadmium in Gull and Paw Paw Lakes in 1930 and 1970 may have been influenced by the Gary / Chicago area (Souch et al., 2003), but except for the direct influence of this area there appears to be no regional trend in cadmium accumulation rates. This suggests that the primary influence on cadmium is local contributions. There was probably also atmospheric deposition of cadmium in these time periods, but the overall spatial pattern of deposition is locally influenced. The decrease in accumulation rates in Gull and Paw Paw Lakes in 1990

suggests a decrease in the influence of atmospheric contaminants from this urban region. It is unclear what is locally influencing cadmium inputs to lakes in this region.

From atmospheric deposition rates in the region (Eisenreich and Strachan, 1992; Hoff et al., 1996; Sweet et al., 1998; Simonetti et al., 2000b; Alfaro-De la Torre and Tessier, 2002), it may be inferred that cadmium loadings were greatly influenced by atmospheric deposition in 1990 (Table 3). Rates of atmospheric deposition of cadmium range from approximately 100 – 150  $\mu\text{g}/\text{m}^2/\text{y}$ , if data from Sweet et al., (1998) are excluded. Atmospheric deposition rates reported by Sweet et al. (1998) in the Great Lakes region are higher than both anthropogenic and total accumulation rates in our study lakes, and are significantly higher than other estimations of atmospheric deposition (Eisenreich and Strachan, 1992; Hoff et al., 1996; Simonetti et al., 2000a), and therefore are not included in this analysis.

Five of the study lakes have cadmium accumulation rates equal to or lower than the rate of atmospheric deposition estimated from the literature (Table 3,  $\sim 100 \mu\text{g}/\text{m}^2/\text{y}$ ), indicating that accumulation rates calculated from lake sediments underestimate cadmium deposition, or that rates of atmospheric deposition are overestimated. Despite this discrepancy, these data suggest that cadmium inputs to five of the study lakes were influenced primarily by atmospheric deposition (Elk, Gratiot, Gull, Littlefield and Mullett Lakes, accumulation rates  $\leq 100 \mu\text{g}/\text{m}^2/\text{y}$ ). Five other study lakes are probably locally influenced, all with accumulation rates  $> 200 \mu\text{g}/\text{m}^2/\text{y}$  (Cass, Crystal M, Cadillac, Crystal B, and Whitmore Lakes). Higgins and Paw Paw Lakes have intermediate accumulation rates (170 and 130  $\mu\text{g}/\text{m}^2/\text{y}$ ), and with the discrepancies in the data, it is difficult to determine the influence of local

inputs on these two lakes. Overall, atmospheric deposition is a more significant source for cadmium than lead.

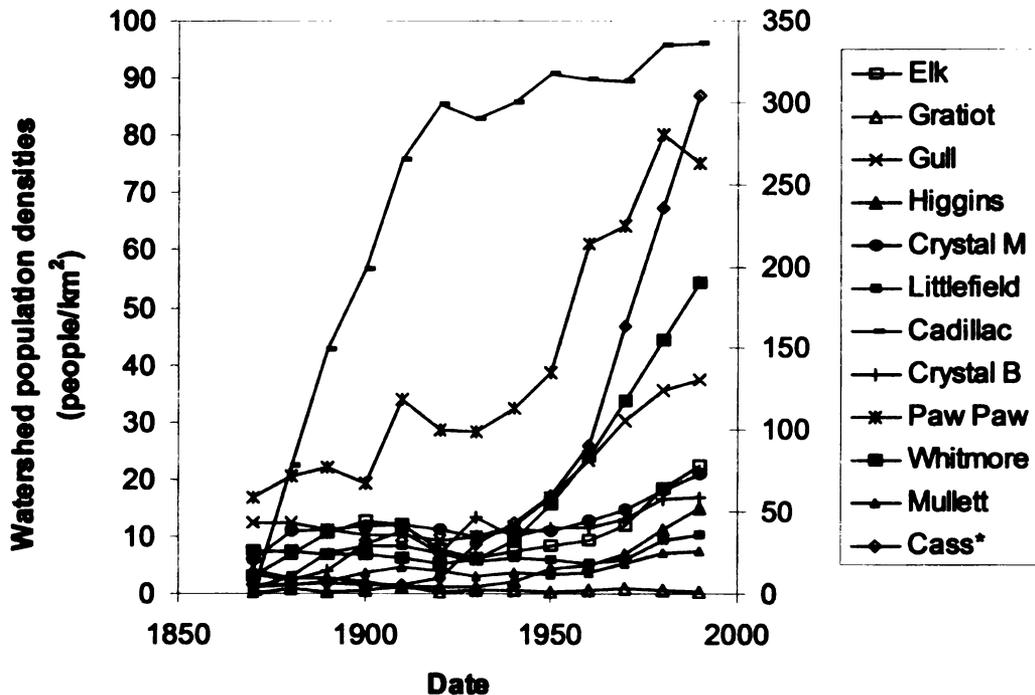
The similarity of the spatial pattern of lead and cadmium in 1990, with Whitmore, Crystal M, Cadillac and Crystal B Lakes having higher accumulation rates (Figure 7c, 8c), suggests that sources for cadmium and lead may have been the same for some lakes, or may be related to similar processes (e.g., population growth within the watershed). Those lakes that are most influenced by local sources for lead (Cadillac, Whitmore, Cass and Crystal M) are also influenced for cadmium (Table 3). Spatial patterns may have been dissimilar in 1930 and 1970 because major atmospheric sources were present for lead and not cadmium (e.g., leaded gasoline). These regional sources for lead may have masked any local influences.

### **Population density**

The examination of spatial and temporal patterns of cadmium and lead provide insight into the relative importance of local and regional influences on cadmium and lead loading to the environment, as well as determine if the patterns are consistent with specific sources suggested in the literature. These interpretations may be further tested by the comparison of accumulation rates of metals in the sediment to watershed population densities. Although humans themselves are not sources for metals, many human activities do release metals to the environment, and population density values can serve as an approximate indicator for these sources. Population density has been related to sewage and storm water discharge, yard waste and other local inputs

(Callender and Rice, 2000), as well as sources related to automobiles and highways (e.g., tire wear, auto emissions, road maintenance) (Rice, 1999).

Watershed population densities for most lakes have increased over time, with greater rates of increase after the 1940s (Figure 9). The highest rates of watershed



**Figure 9.** Watershed population densities (people/km<sup>2</sup>) over time. \*Cass Lake is plotted on the right y-axis scale.

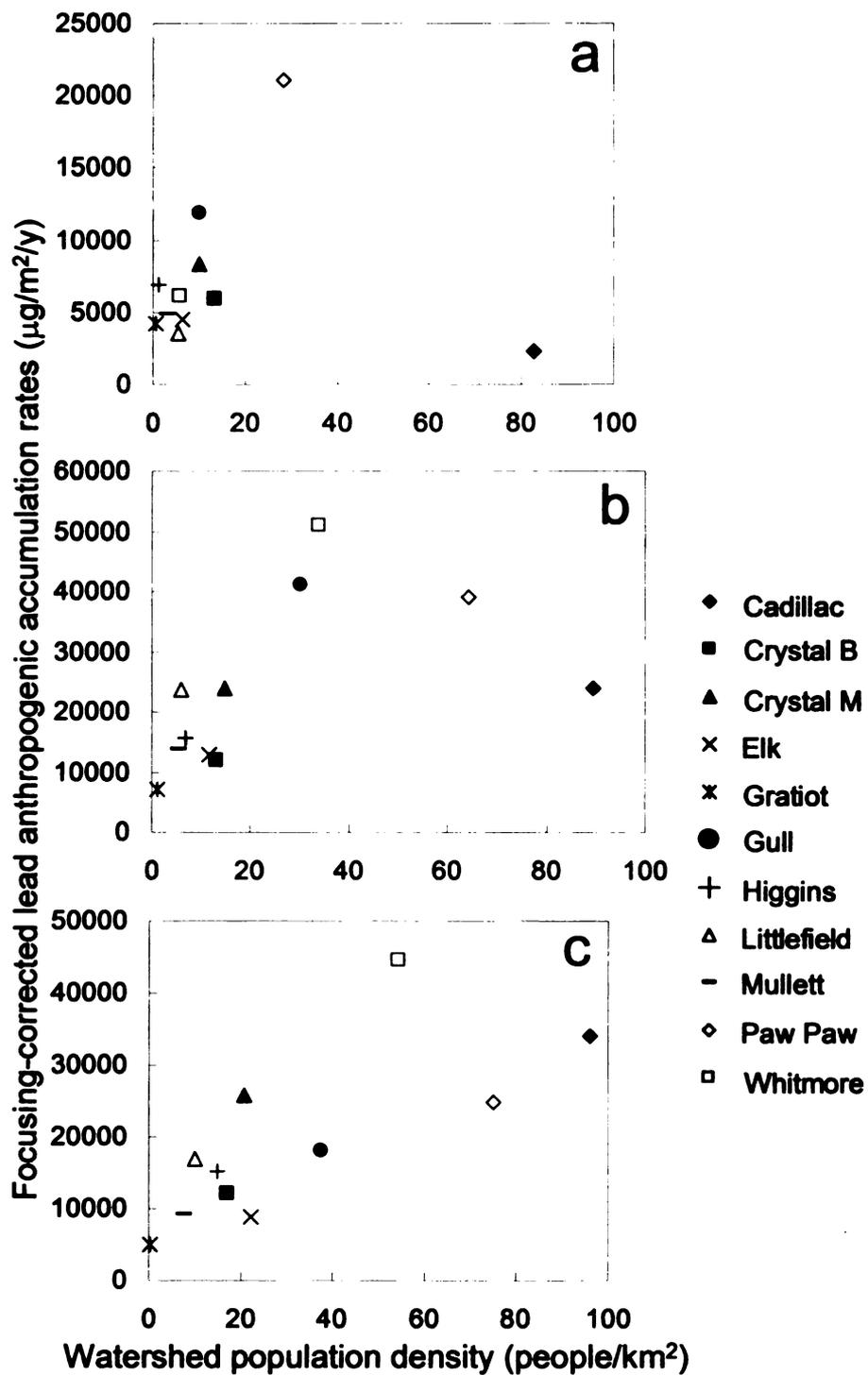
population growth are for lakes located in southern Michigan (Paw Paw, Gull, Whitmore, Cass and Crystal M Lakes). Cadillac Lake also has a high rate of population growth, but the growth occurs at a much earlier time period than the other lakes. The city of Cadillac, located within the Cadillac Lake watershed, was incorporated in 1877, and grew quickly until the 1920s, when growth slowed (Figure 9). This settlement pattern is unique among the study lakes. The settlement pattern of

Gratiot Lake watershed is also unique; population densities have decreased over time, with the highest population density in 1870. Settlement in this area was highest in the late 1800s due to the extensive copper mining, which began in the 1840s and peaked between 1890 and 1930 (Kerfoot et al., 1994).

### *Lead*

Population density data corroborate the interpretations of the spatial and temporal data. In 1930 there is little relationship between population density and lead accumulation, supporting the interpretation that lead was regionally influenced (Figure 10a). There appears to be a positive correlation between population density and lead accumulation rates, with the exception of Cadillac Lake ( $r^2 = 0.77$  with Cadillac removed), however, this relationship is an artifact of Paw Paw Lake having a high population density and high lead accumulation rate, and does not hold for the remainder of the lakes ( $r^2 = 0.22$  with Paw Paw and Cadillac removed). All but four lakes (Cadillac, Paw Paw, Gull and Crystal M) have both low lead accumulation rates and low population densities (Figure 10a), with sources for lead probably including coal burning and the use of leaded gasoline throughout the state. The high accumulation rates in Crystal M, Gull, and Paw Paw Lakes, located in southwestern Michigan, are probably being influenced by the Gary / Chicago urban and industrial area rather than the population density around the lake.

There is a positive relationship between watershed population densities and lead accumulation rates in 1970 (Figure 10b), with Cadillac and Paw Paw Lakes, and to a lesser extent Crystal B and Elk Lakes, have lower lead accumulation rates than



**Figure 10.** Average focusing-corrected lead anthropogenic accumulation rates ( $\mu\text{g}/\text{m}^2/\text{y}$ ) versus watershed population densities for (a) 1925-1935, (b) 1965-1975, (c) 1985-1995.

expected from the trend of the other lakes. However, interpretation of this relationship is complicated by the similarity between the regional population gradient and watershed population densities. If lead, as suggested above, was regionally influenced in 1970 by sources such as leaded gasoline, it should not be closely related to local watershed population densities, instead, it should be related to the regional population distribution (i.e., a watershed with low population density in a highly populated region would still have high lead accumulation rates). In the 1970s, the overall population density in Michigan was highest in the south and decreased to the north, and watershed population densities of the lakes in this study were generally consistent with that gradient, with the exception of Cadillac Lake. In other words, watershed population densities follow the same south – north gradient seen in lead and seen in the overall population distribution. Cadillac Lake, however, has a very high population density within the watershed, but is in an area of low regional population density. The lead accumulation rate in Cadillac Lake is much lower than anticipated for the watershed population density (Figure 10b), but fits into the regional gradient (Figure 7b). This implies that lead inputs to the study lakes are mostly influenced by the regional population gradient, which is consistent with lead being regionally influenced, with the probable source of atmospheric deposition of lead from the use of leaded gasoline.

In 1990 there was a positive relationship between population density and lead accumulation rates (Figure 10c). Unlike 1970, the lead accumulation rates do not seem to follow the statewide population distribution, but seem more closely linked to the watershed population density. This supports the conclusion that lead was locally

influenced in 1990, and that regional atmospheric deposition was no longer the major source for lead to the study lakes.

The presence of two separate linear trends in 1990 suggests that watershed population density is not sufficient to explain lead accumulation rates, and other factor(s) must also be important. Other sources may have been present for the lakes on the upper trend line (e.g., Whitmore, Crystal M, Higgins Lakes) that are not related to population density, or, the sources may have been similar to all lakes, but the pathway of lead to the lake is being influenced by the watershed. The characteristics (morphology, lake:watershed area ratio) of a watershed are known to influence nutrient and trace metal cycling (Dillion and Evans, 1982; Hurley et al., 1995). Elk, Gull, Cadillac and Paw Paw Lakes all have high watershed to lake ratios (Table 1), and follow a lower trajectory than the other lakes. Additionally, there are many additional factors beyond those related to population density (e.g., land use within the watershed) that were not evaluated in this study may also be influencing the loading of lead to the study lakes.

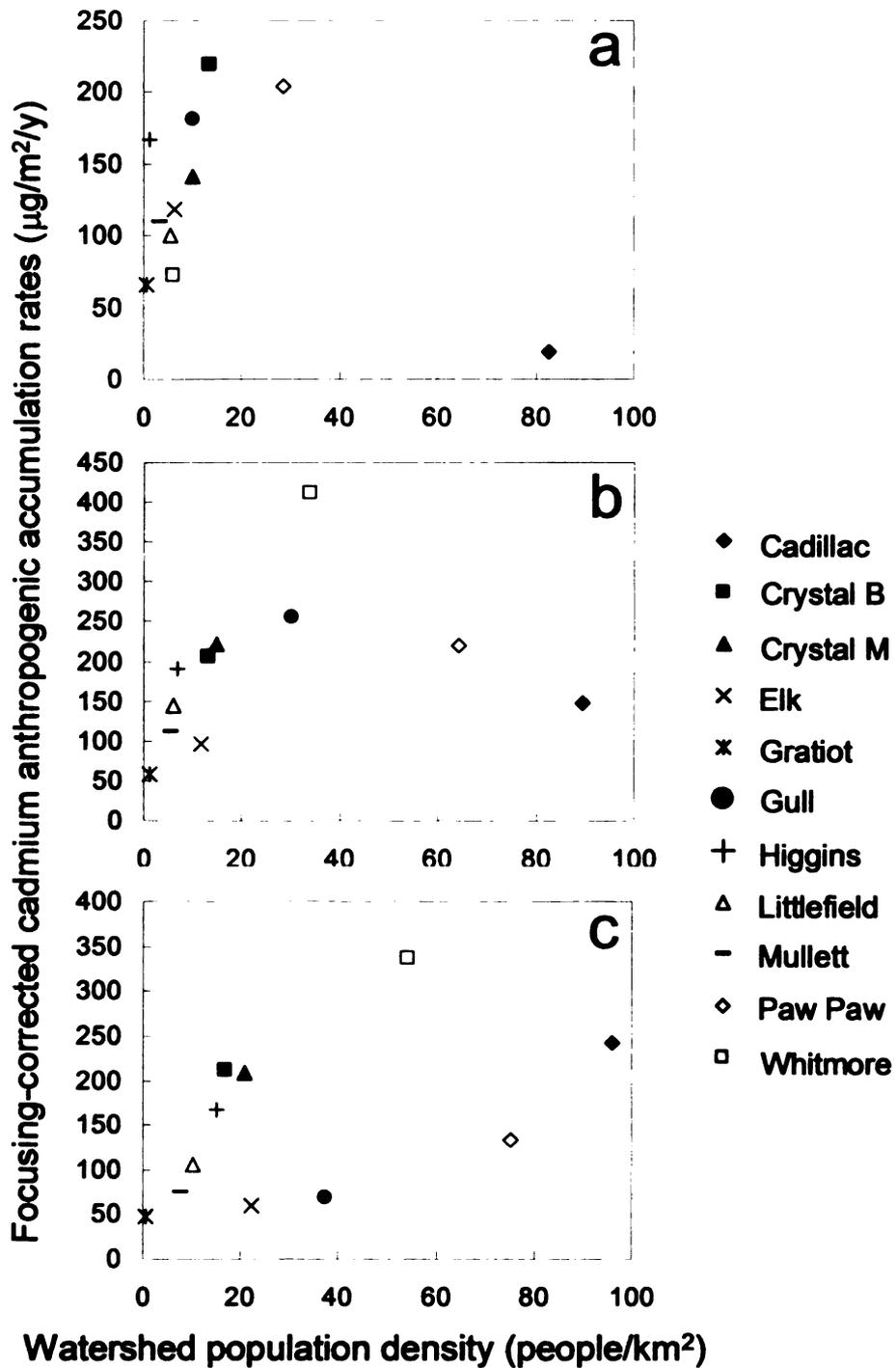
Despite the presence of two separate trends, both lines appear to cross the y-intercept (population density of zero) at an anthropogenic accumulation rate of approximately  $5000 \mu\text{g}/\text{m}^2/\text{y}$  (Figure 10c). This suggest that there is a regional lead input at that rate, and if all local influences were removed, lakes in Michigan would still have anthropogenic lead accumulation rates of at least  $5000 \mu\text{g}/\text{m}^2/\text{y}$ .

## *Cadmium*

Cadmium accumulation rates are positively correlated with population density over all three time intervals (Figure 11 a,b,c), with the exception of Cadillac Lake (1930, 1970) and Paw Paw Lake (1970). In 1990, there seems to be two separate relationships between population density and accumulation rate, with Paw Paw, Cadillac, Gull, Elk Lakes following a lower trajectory than the rest of the lakes.

The spatial and temporal patterns for cadmium deposition were more locally influenced than lead, an interpretation which is supported by the relationship between cadmium and population densities for all time intervals. In 1970, Cadillac and Paw Paw Lakes had lower accumulation rates than expected from their population densities for both cadmium and lead (Figure 11b). However, cadmium accumulation rates did not have the same spatial pattern as lead or the regional population gradient (Figure 8b). From this, it can be inferred that sources for cadmium were different than lead, and influenced locally rather than regionally. In 1990, the apparent presence of two separate relationships between population densities and cadmium accumulation rates is similar to lead. The lakes that followed the lower trajectory for lead are the same for cadmium (Figure 10c, 11c). This suggests that the input of lead and cadmium was being influenced by some characteristic of the watershed, perhaps the lake to watershed area ratio, or some factor that has not been examined.

The y-intercept of the relationship between cadmium anthropogenic accumulation rates and watershed population densities in 1990 is approximately 50  $\mu\text{g}/\text{m}^2/\text{y}$ , suggesting that at zero population density (no local influences) a lake in Michigan would still have an anthropogenic accumulation rate of cadmium of at least



**Figure 11.** Average focusing-corrected cadmium anthropogenic accumulation rates ( $\mu\text{g}/\text{m}^2/\text{y}$ ) versus watershed population densities for (a) 1925-1935, (b) 1965-1975, (c) 1985-1995.

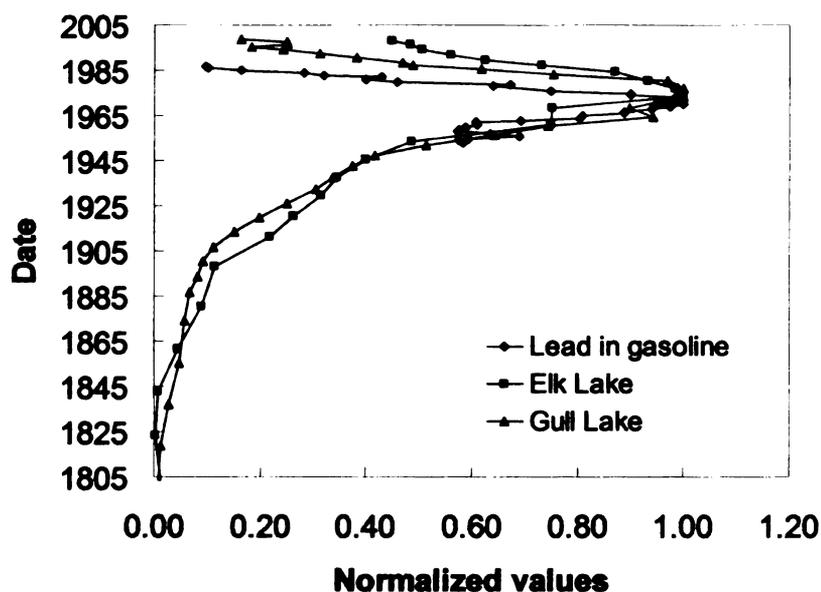
50  $\mu\text{g}/\text{m}^2/\text{y}$ . This is similar to the estimated rate of atmospheric deposition to the region (Table 3).

### **Production records**

Spatial and temporal patterns can provide insight into whether inputs of a metal are locally or regionally influenced, but cannot provide information about actual sources, except through comparison to previous work (e.g., Graney et al., 1995). Additionally, from the presence of a relationship between population densities and anthropogenic accumulation rates it may be inferred that inputs of the metal are locally influenced, and that the source is related to population density. To gain more insight into specific sources for a metal with regionally influenced inputs, we can compare industrial production records for that metal (e.g., production of cadmium from smelters) to temporal deposition patterns in lakes. National production records provide an estimation of the output over time from these industries. They do not report how much of a metal is released into the environment, but if temporal records of production are similar to depositional histories in the sediment, this may be a good indication of source. For example, the production of leaded gasoline probably releases relatively little lead to the atmosphere, but is probably highly correlated to the amount of leaded gasoline combustion. To determine if metal deposition histories were similar to production records, production records and sediment concentration profiles were normalized to their peak values and compared to each other.

Spatial and temporal patterns suggested that lead inputs were regionally influenced in 1930 and 1970, but locally influenced in 1990. The recorded use of lead

in gasoline matches the lead profiles recorded in the lake sediments very well from the 1950s to the 1970s, but decreases at a rate faster than lead in the sediment (Figure 12). This further supports the conclusion that in 1970 the lead was regionally influenced, with the use of leaded gasoline as an important source for lead, but more locally influenced in 1990. While the importance of leaded gasoline as a source of lead to the environment is well documented (e.g., Edgington and Robbins, 1976; Evans and Dillon, 1982; Eisenreich et al., 1986; Graney et al., 1995), the good correlation between the suggested source and concentration profiles in the sediment suggests that this technique may be used on cadmium, where sources are more poorly defined.

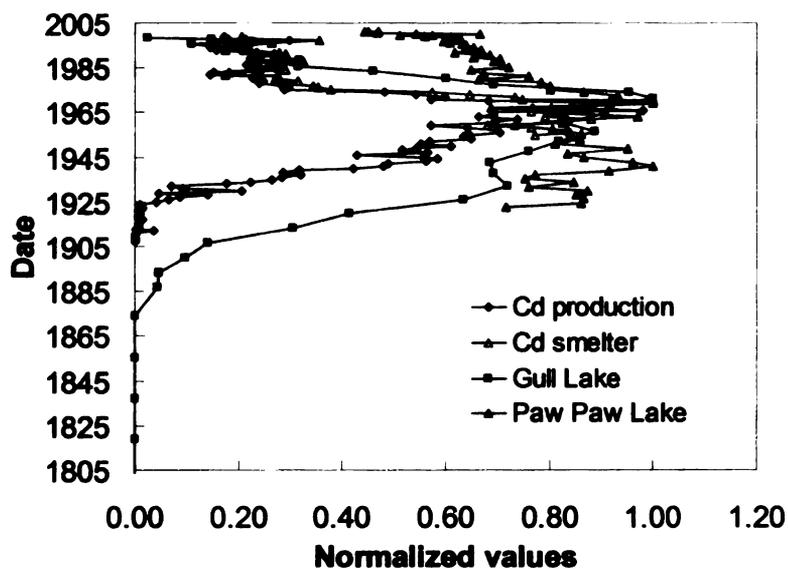


**Figure 12.** Production of leaded petroleum, and concentration profiles of Elk and Gull Lakes normalized to the peak values. Elk and Gull Lakes are plotted to represent the typical profiles seen in the Michigan inland lakes sampled in this study.

Spatial and temporal patterns indicate that cadmium is locally influenced; therefore no consistent relationship between production records and cadmium concentration profiles would be anticipated. However, it is possible that lakes in the

southwest of Michigan are influenced by industrial activities in and around Gary, Indiana and Chicago, Illinois (Souch et al., 2003). This cannot be determined from the spatial pattern of cadmium deposition, because the extent of the study area is large enough to preclude the possibility of this one source being dominant for the entire study area. Therefore, this hypothesis was investigated using production records.

Concentration profiles in Gull and Paw Paw Lakes have a similar profile to the total United States production of cadmium and smelter production of cadmium (Figure 13). No other lakes have a similar profile to any production records for cadmium. These results support the hypothesis that these two lakes, located in the southwest corner of Michigan, may have been influenced by atmospheric deposition from the industrial center of Gary, Indiana to the west, while other lakes in the state were more locally influenced. Unlike lead, the importance of the industrial production of cadmium to the region has not been previously studied.



**Figure 13.** Total production of cadmium and smelter production of cadmium in the United States, and concentration profiles of Gull and Paw Paw Lakes normalized to peak values.

## **Conclusions**

Sediment chronologies for lead and cadmium from twelve lakes throughout Michigan were compared spatially and temporally and to watershed population densities and metal production records. The broad geographic extent of this study allowed for an understanding of the relative importance of local versus regional influences on the loading of lead and cadmium to this region, as well as providing insight into possible sources for these metals.

Overall, inputs of lead to Michigan Lakes appear to be regionally influenced in 1930 and 1970. The data in this study are consistent with previous studies that suggest atmospheric deposition of lead emitted from the burning of coal (1930) and leaded gasoline (1970) controls lead loading to the environment. It is likely that local sources were also present, but were insignificant compared to atmospheric inputs. In the 1990s, inputs of lead are locally influenced, though there still appears to be a contribution from regional atmospheric deposition. Although watershed population densities are positively correlated to anthropogenic lead accumulation rates in the 1990s, they are not a good predictor of lead accumulation and other factors must also be important (e.g., watershed: lake area ratios).

Unlike lead, cadmium appears to be regionally and locally influenced over all time intervals. Again, there is a positive relationship between watershed population densities and anthropogenic cadmium accumulation rates, but there are clearly other factors influencing cadmium inputs. It is unclear what the specific sources and pathways for the cycling of cadmium are, but it appears that atmospheric deposition contributes a significant amount of total cadmium deposition in 1990.

The approach of using sediment chronologies from multiple lakes over a broad geographic extent provided information on both if a metal was locally or regionally influenced, as well as giving insight into some specific sources. Results for lead corroborate well with many other studies (Edgington and Robbins, 1976; Dillion and Evans, 1982; Evans and Dillon, 1982; Graney et al., 1995; Callender and Rice, 2000), indicating that this technique is a useful approach, and may be used on other elements. Additionally, this technique can be used to evaluate the contribution of other factors (e.g., land use) to metal loadings in lake sediments. Expanded assessment of Michigan lakes with this multi-elemental technique may eventually produce predictive models for metal loading, greatly facilitating environmental monitoring and protection.

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## CHAPTER 6 LEAD IN THE ENVIRONMENT: EVALUATING SOURCES AND PATHWAYS OVER TIME USING LAKE SEDIMENTS

### **Introduction**

Humans have significantly modified the natural cycle of contaminants such as lead, resulting in enrichment of these metals in the environment and toxicological concerns for both wildlife and humans (Nriagu, 1978; Nriagu, 1989; Eisenreich and Strachan, 1992; Catallo et al., 1995; Sanudo-Wilhelmy and Gill, 1999).

Environmental legislation, such as the Clean Air and Water Acts, reduced inputs of lead to the environment (Graney et al., 1995; Long et al., 1995; Callender and vanMetre, 1997; Callender and Rice, 2000; Simonetti et al., 2000; Mecray et al., 2001), but concentrations in the water, air and sediment remain elevated (Graney et al., 1995; Long et al., 1995; Callender and vanMetre, 1997; Mecray et al., 2001).

Humans continue to alter the environment in ever increasing ways, including population growth and urban sprawl, which may result in emerging contaminant sources. In order to continue developing strategies for the reduction of anthropogenic lead loadings to the environment, an understanding of the current sources of lead and pathways through the environment are necessary. Additionally, by understanding the history of lead inputs, it may be possible to determine if sources have remained the same over time or if new sources are emerging. One technique for understanding the history of lead inputs to a region is through the examination of sediment chronologies from multiple lakes.

Lake sediments act as collectors of contaminants both from the local watershed and regional atmospheric deposition and can provide information on current and historic rates of contaminant inputs. As a result, sediments are a valuable tool in monitoring chemical loading to the environment. While sediments can provide a history of the rate of contaminant inputs, it is possible to gain further insight by comparing loadings from multiple lakes to characteristics of the watersheds that act as a proxy for potential sources and pathways through the environment (e.g., urban land cover, soil erodibility). Ideally, anthropogenic accumulation rates in the sediment could be compared to actual rates of inputs of different sources to determine the relative importance of each source (Edgington and Robbins, 1976), but these data are not available for most lakes. Therefore, quantifiable characteristics of the watershed (e.g., population density) have been chosen to represent source(s) (Callender and Rice, 2000). In this study, the relationship between lead accumulation rates in 16 Michigan lakes to watershed characteristics, such as population density and percentage urban land cover, are explored. This comparison is done for two time periods (1970-1980 and 1990-2000) to identify potential lead sources and pathways through the environment, and if and how these relationships have changed over time.

Although there have been many studies on the relationship between watershed characteristics and nutrient concentrations in aquatic systems (Detenbeck et al., 1993; Richards et al., 1996; Soranno et al., 1996), few studies have examined the relationship between metal deposition in sediments and landscape variables (Rice, 1999; Callender and Rice, 2000). Watershed variables in this study were selected to represent physical, transport, and source characteristics for both time periods.

The physical characteristics (watershed area, lake area, watershed: lake area ratio) may give insight into the importance of atmospheric deposition. For example, a lake with a small watershed area to lake area ratio may be dominated by atmospheric deposition, whereas a lake with a large ratio may be more influenced by inputs from the watershed (Dillion and Evans, 1982).

Three characteristics (K factor, slope, pattern of sulfate deposition) were chosen to represent the pathway (transport) of metals to a lake. Metals deposited within the lake watershed from processes such as pesticides and fertilizers applications or from atmospheric deposition (Muhlbaier and Tissue, 1981; Graney et al., 1995; Rice, 1999) must be mobilized from the landscape to be deposited in the lake. Erosion might be one of those processes and the amount of metal reaching the lake via this pathway may be dependant on soil erodibility. The average slope of the watershed and K factor (a measure of soil erodibility) would represent variables that would influence the amount of metals reaching a lake by erosion within the watershed (Detenbeck et al., 1993). Steep slope and high K factors would represent high erosion potential.

Another important pathway is atmospheric transport and deposition (Winchester and Nifong, 1971; Gatz, 1975; Gatz et al., 1989; Nriagu, 1989; Callender and vanMetre, 1997; Sweet et al., 1998; Rice, 1999; Callender and Rice, 2000; Simonetti et al., 2000; Goodarzi et al., 2001; Souch et al., 2003), however there are few direct measures of the importance of this pathway for a specific lake watershed. It may be possible to use a surrogate to estimate the importance of atmospheric deposition. One might assume that a major control on the chemistry of metals in the

atmosphere is the burning of fossil fuels such as coal and oil. Considering this, sulfate, which is also released to the atmosphere from fossil fuel combustion (Nriagu, 1989; Berner and Berner, 1996) and has been monitored through the region (National Atmospheric Deposition Program (NRSP-3)/National Trends Network, 2003), may serve as a proxy for trace metals. Therefore, atmospheric deposition rates of sulfate will be used to estimate the relative distribution of atmospheric deposition of lead from the burning of coal and oil. Sulfate deposition rates will not, however, represent atmospheric deposition from the burning of leaded gasoline, which is known to be an important source of lead to the environment in the 1970s (Iskander and Keeney, 1974; Edgington and Robbins, 1976; Eisenreich et al., 1986; Graney et al., 1995; Callender and vanMetre, 1997; Benoy and Kalaff, 1999; Heyvaert et al., 2000).

The watershed characteristics that represent possible sources include Toxic Release Inventory data, population density, and land cover. Releases of toxic chemicals are required to be reported by the Emergency Planning and Community Right-to-Know Act of 1986 (EPCRA), including the location and quantity of release. These data represents point sources that may be unique to a particular lake. Watershed population density and urban land cover both represent sources related to human development, including: releases from the wear of automobile parts (Rice, 1999), automobile emissions (Callender and vanMetre, 1997; Rice, 1999), road dust (Shahin et al., 2000), wastewater, and household and yard waste (Callender and Rice, 2000). Agricultural land use represents pesticide and fertilizer usage (Muhlbaier and Tisue, 1981; Rice, 1999), and forest and wetland land cover correspond to areas that should have less anthropogenic sources.

Each of the landscape characteristics representing sources and pathways was quantified for the entire watershed, but it is conceivable that sources closer to the lake will be more important than those further away (Comeleo et al., 1996; Richards et al., 1996; Basnyat et al., 1999). Previous work on relating water quality parameters and aquatic sediments provides mixed results on the success of quantifying watershed characteristics for the total watershed versus a portion of the watershed close to the waterbody. In some cases the best predictions of water quality variables occurred using whole watershed data, and other cases the predictions were better when proximity to the waterbody was taken into account (Comeleo et al., 1996; Richards et al., 1996; Johnson et al., 1997; Basnyat et al., 1999). To study if landscape closer to the lake is more influential on metal accumulation patterns in lakes than those further away, the study variables (land cover, K factor, and slope) were characterized in a 100 m buffer around the lake (Richards et al., 1996; Johnson et al., 1997). A second approach to evaluating the importance of proximity to the lake was also used for land cover, and each land cover type was weighted by the inverse of the distance to the lake along the flow path, so that land cover close to the lake was weighted highly (Comeleo et al., 1996). Landscape characteristics within the 100 m buffer, and measures of land cover that were flow path weighted were then correlated to metal accumulation rates in the same manner as the whole watershed characteristics.

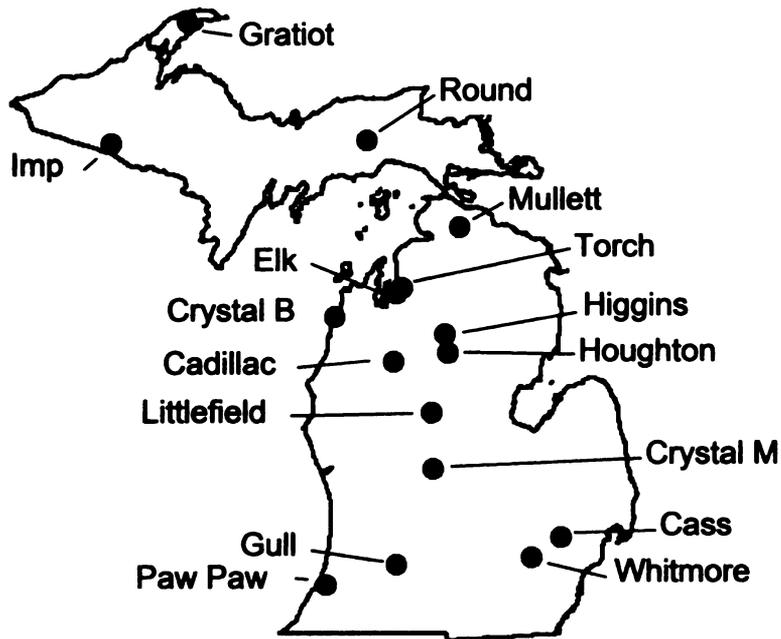
Historical sources of lead have been relatively well defined, with the dominant sources including the burning of coal and leaded gasoline (Edgington and Robbins, 1976; Eisenreich et al., 1986; Graney et al., 1995; Callender and vanMetre, 1997; Callender and Rice, 2000), but current sources are not well defined (Graney et al.,

1995) and need further investigation. The analysis of data from the 1970s and the 1990s will allow the comparison of a time period with known sources to a period when further investigation is warranted. Additionally, the impact of environmental legislation in the 1970s can be evaluated both by examining changes in the anthropogenic accumulation rates and the relative influence of the physical, transport and source characteristics between the two time periods.

### **Methods**

Four replicate sediment cores were collected from each of 16 lakes in Michigan, U.S.A. (Figure 1) from 1999-2002 using a MC-400 Lake/Shelf Multi-corer (Ocean Instruments, San Diego, CA) deployed from either the EPA Research Vessel Mudpuppy or the Michigan Department of Environmental Quality Monitoring Vessel Nibi. Cores were immediately extruded and sectioned at 0.5 cm intervals for the top 5-8 cm, and at 1 cm intervals for the remainder of the core.  $^{210}\text{Pb}$  was measured on one sub-core from each lake at the Freshwater Institute in Winnipeg, Manitoba, Canada, under the direction of Paul Wilkinson, to determine sedimentation rates, focusing factors, and sediment ages. Three different models were used to extract dates from  $^{210}\text{Pb}$  data: the constant flux, constant sedimentation model (CF:CS) (Golden et al., 1993), the segmented CF:CS model (SCF:CS) (Heyvaert et al., 2000), and the constant rate of supply model (CRS) (Oldfield and Appleby, 1984; Sanchez-Cabeza et al., 2000). The choice of model was determined based on the location of the  $^{137}\text{Cs}$  peak and the stable lead peak (Yohn et al., 2004). The focusing factor for each lake was calculated by dividing the actual  $^{210}\text{Pb}$  inventory by the expected (Golden et al.,

1993). This factor is used to account for the tendency of fine-grained materials to be transported to the deepest part of the lake (Hermanson, 1998).



**Figure 1.** Location of lakes sampled in Michigan, U.S.A.

Sediments for metals analysis were frozen for storage, freeze-dried and digested by nitric acid in a CEM-MDS-81D microwave (CEM, Matthews, NC; EPA Method 3051). Standard reference material (NIST SRM 8704 Buffalo River Sediment) and procedural blanks were processed. Three replicate digestions were performed on two samples from each lake. The concentrated-acid digests were filtered through an acid-washed, distilled-deionized water (DDW) rinsed 0.40  $\mu\text{m}$  polycarbonate filter (Nuclepore). 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, Cr, Mn, Fe, Cu, Zn, As, Sr, Mo, Cd, Ba, Pb, and U. Lead accumulation rates were determined from mass sedimentation rates and lead concentrations. Anthropogenic lead concentrations were determined from total lead concentrations with the assumption that natural lead : aluminum ratios remain constant over time, and additional lead is due to human influences (Bruland et al., 1974; Koelmans, 1998; Tuncer et al., 2001). Anthropogenic accumulation rates were calculated from these concentrations and mass sedimentation rates determined by the  $^{210}\text{Pb}$ . These accumulation rates were then divided by the focusing factor, resulting in focusing corrected anthropogenic accumulation rates. These rates were used in further comparisons among lakes and correlation calculations.

Watershed characteristic data were acquired using ArcView v. 3.2 and ArcInfo v. 8.2, and are described below.

*Lake area, watershed area, watershed: lake area ratio ( $\text{km}^2$ ):* Lake areas were taken from Michigan Department of Conservation bathymetric maps. Watersheds were delineated around each of the sixteen lakes of interest (Yohn et al., 2004) from 30 m digital elevation models (National Aeronautics and Space Administration, 2002), with the study lake not considered as part of the watershed. Cass and Whitmore Lake watersheds were defined using 90 m SRTM data because 30 m data were not available for this region of the state. If the watershed of a lake contained another lake (e.g., Mullett Lake watershed contains Burt Lake), the watershed of the second lake was removed from the watershed of the study lake.

*K factor:* The K factor is a unitless variable that is a relative measure of the susceptibility of bare cultivated soil to erosion. K factors were calculated from the

State Soil Geographic (STATSGO) database (U.S. Department of Agriculture, 1994). Area weighted averages were used to determine the average slope and K factor for each watershed.

*Slope (degrees):* Average slope of the land within the watershed was calculated in ArcInfo using the same digital elevation models that were used for determination of the watershed.

*Sulfate deposition ( $kg\ ha^{-1}\ y^{-1}$ ):* Sulfate deposition data were collected for 10 sites from Michigan, Wisconsin and Illinois from the National Acid Deposition Program database (National Atmospheric Deposition Program (NRSP-3)/National Trends Network, 2003). Data were collected from all available years from each site, but final data are from 1990-2000. Very few stations collected data from 1970-1980, making it difficult to estimate sulfate deposition values for this time period. However, the patterns of sulfate deposition appear to remain the same within the state over time, therefore the 1990-2000 data were also used to represent the spatial gradient of atmospheric deposition from 1970-1980. Inverse distance weighting was used to estimate sulfate deposition values for each watershed.

*Population (people) and population density ( $people\ km^{-2}$ ):* Census data at the census tract scale were used for population calculations. Watersheds generally only encompassed a portion of each census tract; therefore, dasymetric mapping was used to estimate population distribution. Areas that are state owned (Michigan Department of Natural Resources, 2000) or areas covered by lakes (Michigan Department of Natural Resources, 1992) were considered as non-livable areas. It was assumed that the population was evenly distributed throughout the remaining livable area within

each census tract. This assumption does not reflect the tendency of people to live near a lake, and therefore population densities are probably underestimated. Census data from 1970 and 1980 were averaged to represent the 1970s time period, and data from 1990 and 2000 were averaged to represent the 1990s time period.

*Land cover (km<sup>2</sup>, %):* Land use/cover data were collected for 1978 (Michigan Department of Natural Resources, 1999) and 1997-2001 (Michigan Department of Natural Resources, 2003). Land cover groupings were different for the two time periods, therefore the Level 1, or coarsest, land cover groupings were used so that the two time periods could be compared. Total area in the watershed and percentage land covers were calculated for each watershed, and for a 100 m buffer around the lake for each of the two time periods. 1970s data were taken from Michigan Resource Information System land cover maps; coverages derived from 1:24,000 color-infrared and black and white aerial photographs. 1990s data were taken from 1997-2001 IFMAP/GAP land cover maps; raster dataset with 30 m cell size was derived from Landsat Thematic Mapper imagery.

*Flow weighted land cover:* The flow path (m<sup>2</sup>), or distance from the lake along the path that water would flow, for each grid cell in each watershed was determined using the FLOWLENGTH command in ArcInfo. Inverted flow path was then calculated (1/flowlength). Separate grid coverages were created for each land cover, with a value of 1 for each cell that contains that land cover, and a value of 0 for all other land covers. Each of these coverages was multiplied by the inverse flow path coverage and summed. This was completed for each land cover for each time period. Additionally, the same calculations were performed using the inverse flow path squared (1/d<sup>2</sup>).

Percentages were calculated dividing the result for one land cover type by the sum for all land covers.

*Toxic Release Inventory (TRI)*: Toxic release inventory sites that released copper, cadmium, lead, or zinc for all of Michigan were identified from <http://www.epa.gov/triexplorer/>. These sites were plotted spatially, and watersheds of each of the study lakes were examined to determine if any TRI sites were present within the watershed. No TRI sites were present in any of the watersheds; therefore these data were not used.

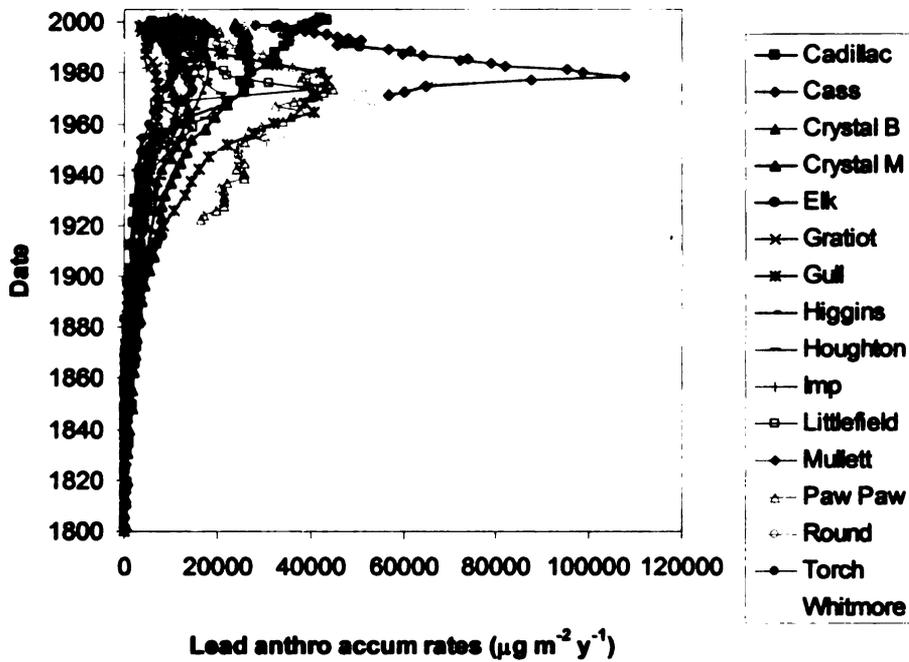
Variables were log transformed to improve the distribution, with the exception of sulfate deposition, where log transformation resulted in a skewed distribution. Data that were outliers were removed to prevent these points from becoming overly influential during correlation analysis (Yohn et al., in preparation). No data were removed from variables with high correlations with lead except slope in the 100 m buffer for Crystal B Lake.

Correlation coefficients were calculated between lead accumulation rates and watershed characteristics using SYSTAT 10. Multiple regression was used to determine the two watershed characteristics that best explained the variance in lead accumulation rates for each time period. The number of predictor variables was limited to two due to the small number of lakes sampled (Hair, 1998). All possible pairs of the ten variables with the highest correlation coefficients were modeled using multiple regression to determine which pair had the highest  $r^2$  value. Only models where both variables had a  $p < 0.05$  were considered.

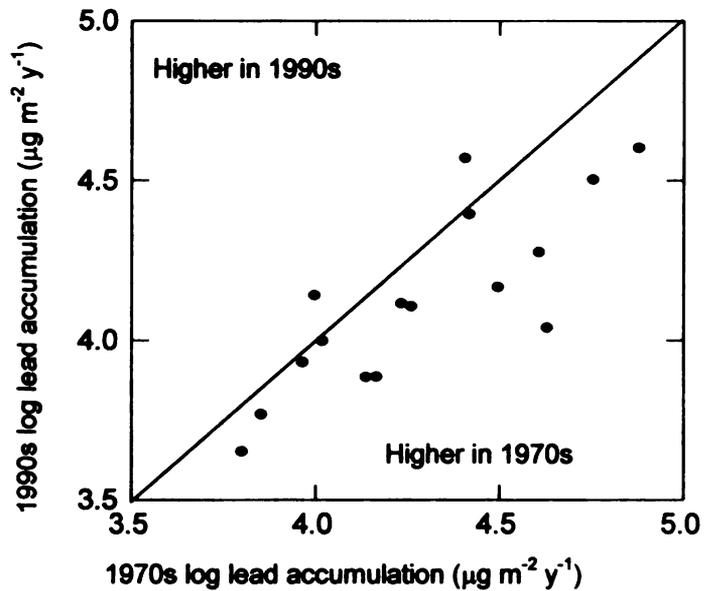
## **Results and discussion**

### **Patterns of lead deposition**

Anthropogenic accumulation rates of lead in most of the study lakes begin to increase between 1850 and 1900, continue to increase until the 1970s and decrease to the present (Figure 2). The similarity among lakes in terms of when the first significant anthropogenic inputs are detected (late 1800s) and peak accumulation rates (mid 1970s) suggests that a common source for lead existed throughout this time period in Michigan, but with varying intensity in different lakes. This is consistent with results from many studies, that suggest atmospheric deposition of lead from coal and leaded gasoline in particular were dominant sources until the 1970s (Eisenreich et al., 1986; Graney et al., 1995; Long et al., 1995; Callender and vanMetre, 1997; Callender and Rice, 2000). The overall decrease in lead accumulation rates from the 1970s to the 1990s is mainly attributed to a reduction in lead inputs to the environment from the enactment of environmental legislation of the 1970s (Clean Air Act) (Eisenreich et al., 1986; Callender and vanMetre, 1997). However, the relative decrease in accumulation rates from the 1970s until the present varies greatly among lakes (Figures 2, 3), with some lakes decreasing significantly (e.g., Gull Lake) and other lakes decreasing very little or increasing (e.g., Crystal M, Cadillac). The differing responses among lakes may indicate that while sources that were dominant in the 1970s have been reduced, other sources have emerged. These may have been present in the 1970s but masked by the dominant sources, or may represent new sources.



**Figure 2.** Anthropogenic accumulation rates of lead ( $\mu\text{g m}^{-2} \text{y}^{-1}$ ) in 16 Michigan lakes.



**Figure 3.** Log of average anthropogenic lead accumulation rates from the period 1990 – 2000 plotted versus average rates from 1970 – 1980.

### **Lead inputs - watershed characteristics relationships**

There were no significant relationships ( $p < 0.05$ ) between any of the physical characteristics (lake size, watershed size, lake:watershed ratio) and anthropogenic accumulation rates of lead in the 1970s or the 1990s (Table 1). Additionally, there were no Toxic Release Inventory (TRI) sites located in any of the study watersheds, suggesting that point source inputs from major industry should not be a source for any of the lakes.

There is a strong positive correlation between anthropogenic lead inputs and population density during both time periods, with the higher correlation in the 1990s. This is similar to other studies that have found relationships between total lead concentrations in stream sediments and population density (Callender and Rice, 2000), and between the sum of copper, mercury, lead and zinc concentrations in stream sediments and population density (Rice, 1999).

Atmospheric deposition correlates positively with sulfate deposition rates during both time periods, with a higher correlation in the 1970s. Sulfate deposition was chosen to act as a proxy atmospheric transport from sources such as the burning of coal (Graney et al., 1995; Berner and Berner, 1996), and the positive correlation may represent the importance of extensive coal burning that occurred in the Gary, Indiana, and Chicago, Illinois industrial region, as well as in the industrial region near Detroit. Coal burning also probably occurred at smaller quantities throughout the state from residential use, power production and smaller industrial sites. The lower correlation between lead accumulation rates and sulfate deposition rates in the 1990s is not surprising because the 1970s the Clean Air Act has served to reduce

contaminants released to the air, and there has been a general decline in steel production since the 1980s (Perkins et al., 2000).

**Table 1.** Correlation coefficients (r) between anthropogenic lead accumulation rates from 1970-1980 (1970s) and 1990-2000 (1990s) and watershed characteristics. Only correlations that are statistically significant ( $p < 0.05$ ) are shown.

	1970s		1990s	
	watershed	100 m buffer	watershed	100 m buffer
Watershed area		NA		NA
Lake area		NA		NA
Watershed:lake area ratio		NA		NA
Population density	0.825	NA	0.851	NA
Population (total #)	0.523	NA		NA
Sulfate deposition	0.798	NA	0.722	NA
K factor				
Slope	-0.881	-0.919	-0.755	-0.828

The K factor measure of erodibility also showed no correlation with anthropogenic lead inputs for either time period. This suggests that the pathway of erosion, at least as evaluated by the erosion tendency of the soil type, is not controlling lead deposition patterns through the state.

However, both average slope of the watershed and within a 100 m buffer of the lake have a high and negative correlation with anthropogenic lead accumulation rates. Because of the negative correlation, slope of the land clearly does not represent the transport of lead to the lakes through erosion (anticipated positive correlation). What source or process this parameter is acting as a proxy for is unclear. One possibility is that slope of the land may act as a measure of human development, because areas with steep slopes may be less likely to be urbanized. However, the watersheds of most of

the study lakes have relatively shallow slopes (< 5 degrees), which would not impede development of the land.

Because sources of lead to the environment in the 1970s have been extensively studied, we may attempt to use the results of previous work to interpret the very high correlation between lead accumulation rates and slope in the 100 m buffer. The burning of leaded gasoline is well documented to be the dominant source for lead to the environment during this time period (for example: Eisenreich et al., 1986; Graney et al., 1995; Callender and vanMetre, 1997), and temporal patterns of lead deposition in many of the study lakes match production records of leaded gasoline (Yohn et al., 2004). Additionally, measurements of atmospheric deposition in the 1970s in the region are similar to the anthropogenic accumulation rates of lead in the study lakes (Gatz, 1975; Edgington and Robbins, 1976; Cole et al., 1990; Callender and vanMetre, 1997). It is therefore conceivable that slope within the 100 m buffer is somehow acting as a proxy for the burning of gasoline, or at least the regional pattern of atmospheric deposition of lead.

There is no obvious causal relationship between the two, but slope within the 100 m buffer and the atmospheric deposition of lead from the burning of gasoline may coincidentally have a similar spatial pattern across the state. Southern Michigan has relatively little topography, and slope of the land within the watersheds are shallow. In the northern portion of the state, slopes tend to be steeper, with the steepest in the Upper Peninsula. The overall population distribution in Michigan follows a similar pattern, with the greatest population density in the south and the least in the north. This may lead to a similar distribution of automobiles releasing lead as slope within

the 100 m buffer. One might anticipate that population density should be a better predictor than slope if automobile exhaust were the source of lead, but lead emitted to the atmosphere from automobile exhaust may be deposited locally within the watershed or may move outside of the watershed. As a result, even a lake with little traffic within the watershed may have high atmospheric deposition of lead if there are many roads near the watershed. Therefore population density within a particular watershed may be less important than the overall distribution of automobiles throughout the state. Overall, it remains unclear why slope within the 100 m buffer has such a high correlation with lead accumulation rates in the 1970s, but may be due to a coincidental similar spatial distribution to population throughout the state. There is no evidence that there is a cause and effect relationship between slope and lead accumulation rates.

There is a positive correlation between percentage of urban land use and lead accumulation rates during both time periods (Table 2), but the correlation is much stronger in the 1990s. The higher correlation in the 1990s suggests that local sources, which occur within the watershed, are more important than regional atmospheric sources in the 1990s. This is supported by the higher correlation between lead and population density in the 1990s, and the lower correlation between sulfate and lead accumulation rates.

There is a negative correlation between lead accumulation rates and forest during both time periods, and rangeland in the 1970s (Table 2). Forest was the dominant land cover type for many of the watersheds, and should not act as a source of lead. There is also a negative relationship between agricultural land cover and lead

accumulation rates for both time periods, suggesting that the use of pesticides did not contribute significant amounts of lead to the study lakes.

While urban land cover consistently had the highest correlation with lead when the percentage of land cover in the entire watershed was used, other land covers correlated higher with different proximity measures. Agricultural and forest land cover had the highest correlations when flow inverted squared values were used, and rangeland and wetlands also had the highest correlations when using measures that included flow distance to the lake (Table 2). Land cover composition either in the 100 m buffer or when weighted by distance to the lake along the flow path differed greatly from the composition of the entire watershed. In general, for both time periods, urban land cover was higher in the 100 m buffer and flow weighted measures than in the entire watershed, and in many cases significantly higher. For example, in the watershed of Gull Lake in the 1970s there was 9% urban in the total watershed and 84% urban in 100 m buffer. For most lakes, urban land cover was dominant within the 100 m buffer, suggesting concentrated developments near the lake compared to the rest of the watershed. Agriculture tended to be much lower in the 100 m buffer and flow weighted measures, and forest and rangeland were generally lower.

**Table 2.** Correlation coefficients (r) between anthropogenic lead accumulation rates from 1970-1980 (1970s) and 1990-2000 (1990s) and land cover variables. Only correlations that are statistically significant ( $p < 0.05$ ) are shown.

Land cover measure	urban		agriculture		openland/range	
	1970s	1990s	1970s	1990s	1970s	1990s
Total watershed %	0.627	0.899				
Total watershed area						
100 m buffer %	0.535	0.737				
100 m buffer area				-0.588		
Flow inverted %		0.771				
Flow inverted value			-0.599	-0.642	-0.749	
Flow inv. sq. %		0.675				
Flow inv. sq. value			-0.659	-0.714	-0.668	

Land cover measure	forest		wetlands	
	1970s	1990s	1970s	1990s
Total watershed %	-0.782	-0.642	0.683	
Total watershed area				
100 m buffer %	-0.743	-0.618		
100 m buffer area	-0.681			
Flow inverted %	-0.765	-0.657	0.686	
Flow inverted value	-0.762	-0.732		
Flow inv. sq. %	-0.666	-0.575		
Flow inv. sq. value	-0.829	-0.782		

### Multivariate regression

Interpretation of correlations between watershed characteristics and lead accumulation rates is difficult, because many of the watershed characteristics are correlated to each other (e.g., population density and % urban within the watershed). Therefore, to determine the best combination of predictors of lead to the environment, it is not appropriate to choose the variables that are most highly correlated with lead, because the variables may be correlated to each other and actually act as a proxy for similar sources or processes. To avoid this problem, we used multivariate regression to select the two watershed characteristics that together best described the variation in lead accumulation rates among lakes. The number of watershed characteristics

included in the model was limited to two because of the small number of lakes sampled.

In the 1970s, the two watershed characteristics resulting in the highest multiple  $r^2$  value were the average slope within a 100 m buffer, and atmospheric deposition rates of sulfate ( $r^2 = 0.922$ ,  $p = < 0.000$ ) (Figure 4). This model is represented by the equation:

$$\text{Log (LEAD70}_{\text{faar}}) = 3.969 + 0.43 \times \text{SO4}_d - 0.823 \times \log (\text{SLOPE}_{100\text{m}})$$

Where:

$\text{LEAD70}_{\text{faar}}$  represents the average focusing corrected anthropogenic accumulation rates in the 1970s ( $\mu\text{g m}^{-2} \text{y}^{-1}$ ),

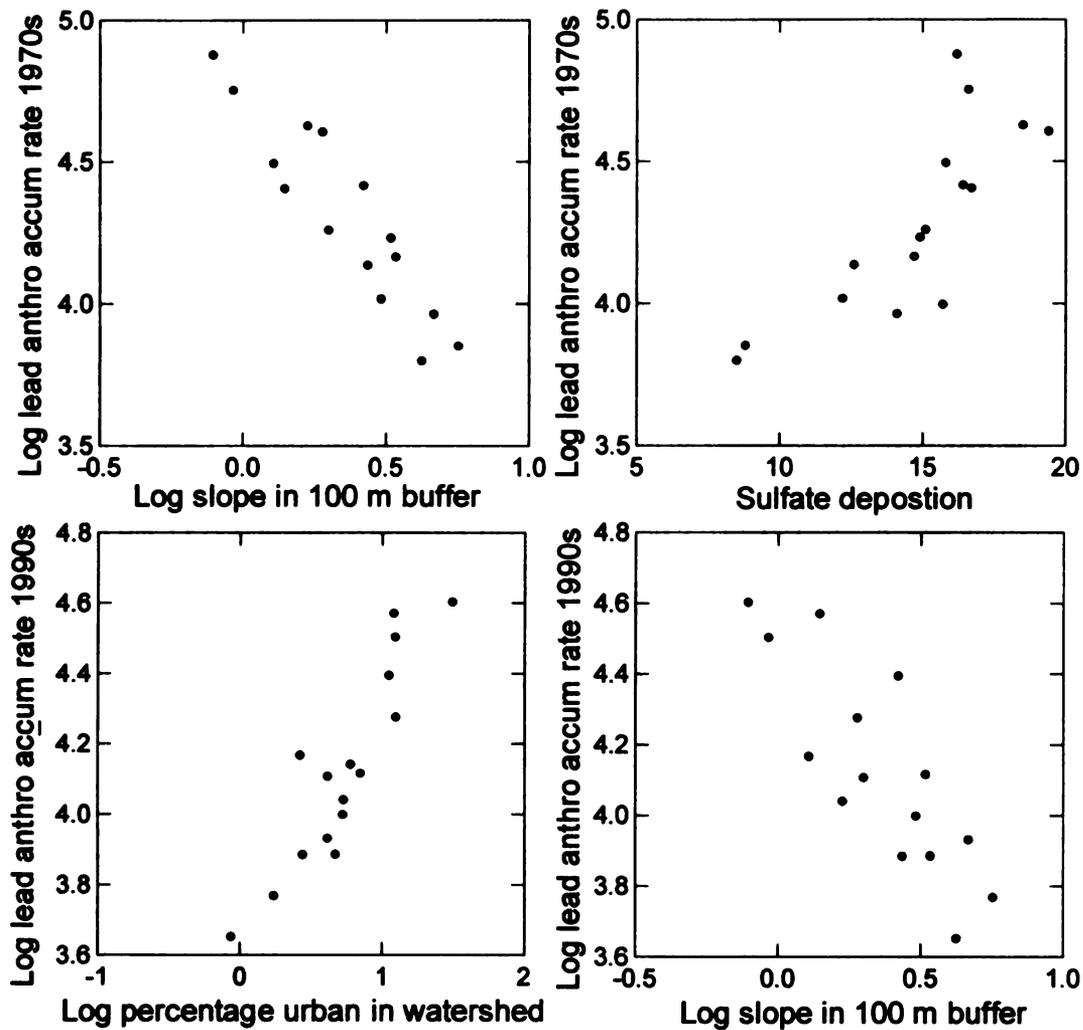
$\text{SO4}_d$  represents sulfate deposition rates in the watershed ( $\text{kg ha}^{-1} \text{y}^{-1}$ ), and

$\text{SLOPE}_{100\text{m}}$  represents the average slope of the land within a 100 m buffer of the lake (degrees).

The standardized coefficient, which is not dependant on the scale of the variable, can be used to determine the relative importance of the two variables in the model. In the 1970s, slope within the 100 m buffer is the more important variable (standardized coefficient of  $\text{SLOPE}_{100\text{m}} = -0.641$ ,  $\text{SO4}_d = 0.408$ ).

These two variables could be interpreted as representing atmospheric deposition from leaded gasoline (the dominant source, represented by slope within 100 m buffer) and coal burning (represented by  $\text{SO}_4$  deposition). While this interpretation is consistent with previous studies on the sources of lead to the environment during

this time period, the cause of the relationship between slope within the 100 m buffer and lead deposition rates is unclear and needs further investigation.



**Figure 4.** Log lead anthropogenic accumulation rates ( $\mu\text{g m}^{-2} \text{y}^{-1}$ ) for the 1970s and 1990s versus the two variables for each time period that together explains the greatest variance in lead accumulation rates.



In the 1990s, percent urban land cover in the watershed and average slope in a 100 m buffer best predicted lead accumulation rates ( $r^2 = 0.879$ ,  $p < 0.000$ ) (Figure 4):  
$$\text{Log (LEAD90}_{\text{faar}}) = 3.951 + 0.464 \times \text{log (URBAN90)} - 0.465 \times \text{log (SLOPE}_{100\text{m}})$$

Where:

LEAD90<sub>faar</sub> is the average focusing corrected anthropogenic accumulation rate in the 1990s ( $\mu\text{g m}^{-2} \text{y}^{-1}$ ),

URBAN90 is the percentage urban land cover in the watershed in the 1990s, and

SLOPE<sub>100m</sub> is the average slope within a 100 m buffer of the lake (degrees).

In the 1990s, urban land cover has a higher standardized coefficient, and this variable contributed more to the model (URBAN90 = 0.624, SLOPE<sub>100m</sub> = -0.405).

The high correlation between percentage urban land use within the watershed and lead deposition rates indicate that currently there is a source of lead that is present throughout the state that is related to urban land cover and acts at the watershed scale, such as municipal wastewater, or road dust. Slope within a 100 m buffer may continue to represent regional atmospheric deposition, similar to the 1970s, but this source is much less important in the 1990s, and has a lower standardized coefficient. The importance of slope in the 100 m buffer in the model indicates that there may be continued sources of lead to the atmosphere, including coal fly ash and smelting (Callender and Rice, 2000).

The change in the variables included in the model from the 1970s and the 1990s, and the decrease in importance of the slope in the 100 m buffer may reflect a

decrease in the importance of atmospheric deposition, and an increase in the importance of watershed scale sources, which is consistent from the conclusions made from the correlation coefficients. This is also supported by measurements of atmospheric deposition rates of lead in the region, which are similar to accumulation rates of lead in lake sediments in the 1970s (Gatz, 1975; Edgington and Robbins, 1976; Cole et al., 1990; Callender and vanMetre, 1997), but cannot account for all the lead deposited in lake sediments in the 1990s (Hoff et al., 1996; Sweet et al., 1998; Simonetti et al., 2000). The reduction of atmospheric sources is consistent with previous work showing the impacts of the Clean Air Act (Callender and vanMetre, 1997).

For both time periods, two watershed characteristics (slope within a 100 m buffer and sulfate deposition in the 1970s, and percentage urban land cover and slope within a 100 m buffer in the 1990s) were able to explain greater than 85% of the variance in anthropogenic lead deposition rates in the study lakes. These correlations are very high given the variety of lakes examined and error inherent in estimating both anthropogenic lead accumulation rates and watershed characteristics. Although this technique does not identify the exact sources or processes that are resulting in lead deposition in the study lakes, it successfully distinguished changes in sources over time, and identified urban areas for further study to determine the actual current sources of lead.

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## CHAPTER 7 IDENTIFYING CHANGES IN SOURCES FOR CADMIUM, COPPER AND ZINC TO INLAND LAKES OVER THREE DECADES

### **Introduction**

Sediment chronologies from lakes throughout the United States have recorded a decrease in the inputs of many metals to the environment since the 1970s and passing of the Clean Air and Water Acts (Graney et al., 1995; Long et al., 1995; Callender and vanMetre, 1997; Callender and Rice, 2000; Simonetti et al., 2000a; Mecray et al., 2001). However, despite these decreases, sediment accumulation rates and concentrations of some toxic metals remain elevated in lake sediments (Graney et al., 1995; Long et al., 1995; Callender and vanMetre, 1997; Mecray et al., 2001), suggesting that historical sources of metals are still present, or that new sources have emerged. An understanding of historical and current sources for metals to the environment through the examination of lake sediments would both lend insight into the effects of environmental legislation and potentially help further reduction of contaminant inputs to the environment.

Lake sediments act as collectors of contaminants both from the local watershed and regional atmospheric deposition and can provide information on current and historic rates of contaminant inputs. As a result, sediments are a valuable tool in evaluating chemical loading to the environment. There are many approaches to understanding sources for metals to lakes, including the thorough study of one lake (Edgington and Robbins, 1976; Kerfoot et al., 1994; Mecray et al., 2001), or the sampling of many lakes (Dillion and Evans, 1982; Catallo et al., 1995). The

advantage of sampling multiple lakes is the potential identification and reduction of sources that influence a large area rather than just one lake. Additionally, surface sediments may be used to identify current sources (Catallo et al., 1995; Callender and Rice, 2000), or sediment chronologies may be used to evaluate current and historical sources (Kerfoot et al., 1994; Long et al., 1995; Kolak et al., 1998). This study uses sediment chronologies from multiple lakes to identify changes in the sediment accumulation of cadmium, copper, and zinc in seventeen Michigan lakes over both space and time, and to evaluate the changing sources for these metals.

A three step approach will be used to help identify sources for metals to lake sediments and evaluate pathways through the environment for two time periods, 1970-1980 (1970s) and 1990 – 2000 (1990s): 1) comparison of sediment chronologies (anthropogenic accumulation rates) from multiple lakes, 2) estimation of the importance of atmospheric deposition from spatial patterns and comparison to measures of atmospheric deposition during both time periods, and 3) evaluation of potential sources by correlations with watershed characteristics.

The first step of this approach, the comparison of sediment chronologies, provides information about the increase or decrease of metal inputs to lake sediments from the 1970s to the 1990s, and therefore the effectiveness of environmental legislation. Additionally, the comparison of patterns of anthropogenic accumulation over time among lakes may indicate if sources are influenced on a regional or watershed scale. Similarities in profiles among lakes suggest that there are common sources for that metal to many lakes, and that the increase and decrease of these sources is similar throughout the state (regionally controlled). This may be due to

regional distribution of a metal (e.g., from atmospheric deposition), or from regional controls on a source (e.g., environmental legislation). If profiles among lakes are dissimilar, this suggests that either sources for this metal are different among lakes, or that sources are similar, but the strength of the source is dependant on local factors (e.g., traffic density or urban development in the watershed).

The second step, estimation of the importance of atmospheric deposition, includes both the examination of spatial patterns and comparison to measured rates of atmospheric deposition. When atmospheric deposition is the major pathway of metal inputs, the accumulation rate of metals should be dependant more on the regional distribution of sources than the sources present within a lake's watershed, and should have a regional gradient across the state. If atmospheric deposition is not significant, than accumulation rates should be influenced more by characteristics of the watershed than regional location. Rates of contaminant deposition in the lake sediments can also be compared to measured rates of atmospheric deposition in the region to further assess the importance of this pathway. The size of the lake should not influence the focusing corrected anthropogenic accumulation rates in the sediment, allowing atmospheric deposition rates to be compared to sediment accumulation rates.

Finally, potential sources for metals may be identified by correlations between anthropogenic accumulation rates and watershed characteristics. Ideally, anthropogenic accumulation rates in the sediment could be compared to actual rates of inputs of different sources to determine the relative importance of each source (Edgington and Robbins, 1976), but these data are not available for most lakes. Therefore, quantifiable characteristics of the watershed are chosen to represent

source(s) (Callender and Rice, 2000). Although these characteristics do not necessarily identify a specific source, or the exact proportion of the metal that is from that source, correlation with watershed characteristics can provide an indication of the major sources for metals to lakes in a region. This method will help identify those sources that are common to multiple lakes, and that can be represented by a watershed characteristic.

The watershed characteristics included in this study represent physical (watershed area, lake area, watershed: lake area ratio), transport (K factor of erodibility, slope, pattern of sulfate deposition), and source characteristics (total population, population density, land cover, point source data) for both time periods. The physical characteristics may give insight into the importance of atmospheric deposition; a lake with a small watershed to lake area ratio may be dominated by atmospheric deposition, whereas a lake with a large ratio may be more influenced by inputs from the watershed (Dillion and Evans, 1982).

The transport characteristics represent the pathway of metals to a lake. The presence of a source of metals in a watershed will not be recorded in the lake sediments unless those metals are transported to the lake. The average slope of the watershed and K factor (measure of erodibility) were included to represent the erodibility of soils within the watershed (Detenbeck et al., 1993). Any metal deposited on the land from sources such as pesticides or fertilizers (Muhlbaier and Tissue, 1981; Rice, 1999) must be eroded before reaching the lake, and may be dependant on soil erodibility. Sulfate deposition rates were estimated to evaluate the importance of atmospheric deposition. The atmosphere can be an important pathway

of metals to lakes (Winchester and Nifong, 1971; Gatz, 1975; Gatz et al., 1989; Nriagu, 1989; Callender and vanMetre, 1997; Sweet et al., 1998; Rice, 1999; Callender and Rice, 2000; Simonetti et al., 2000a; Goodarzi et al., 2001; Souch et al., 2003), but accurate estimations of deposition rates of metals for each watershed are difficult to determine. Sulfate deposition, however, has been monitored throughout Michigan (National Atmospheric Deposition Program (NRSP-3)/National Trends Network, 2003), and can be used to estimate the relative distribution of atmospheric deposition due to coal and oil burning. Both sulfate and trace metals are released with the burning of fossil fuels (Nriagu, 1989; Berner and Berner, 1996). Sulfate deposition rates will not, however, represent atmospheric deposition from other sources (e.g., copper from copper smelting, lead from the burning of leaded gasoline).

The source characteristics include Toxic Release Inventory data, population density, and land cover. Releases of toxic chemicals are required to be reported by the Emergency Planning and Community Right-to-Know Act of 1986 (EPCRA), including the location and quantity of release. These data represent point source inputs that may be unique to that lake. Watershed population density and urban land cover both represent sources related to human development, including: releases from the wear of automobile parts (Rice, 1999), automobile emissions (Callender and vanMetre, 1997; Rice, 1999), road dust (Shahin et al., 2000), wastewater, and household and yard waste (Callender and Rice, 2000). Agricultural land use represents pesticide and fertilizer use (Muhlbaier and Tissue, 1981; Rice, 1999). Forest and wetland land cover correspond to areas that should have few anthropogenic sources.

All of the characteristics are quantified on the watershed scale, but it is conceivable that sources that are closer to the lake will be more important than those further away (Comeleo et al., 1996; Richards et al., 1996; Basnyat et al., 1999). Previous work on water quality parameters and estuary sediments provides mixed results, with some variables predicted best with whole watershed data, and others when proximity to the waterbody was taken into account (Comeleo et al., 1996; Richards et al., 1996; Johnson et al., 1997; Basnyat et al., 1999), and conclusions are mixed among studies. To address the issue of proximity, land cover, K factor, and slope were quantified in a 100 m buffer around the lake (Richards et al., 1996; Johnson et al., 1997), and, in an alternate approach, land cover was weighted by the inverse of the distance to the lake along the flow path (Comeleo et al., 1996).

Each of these watershed characteristics was correlated separately with anthropogenic inputs of each metal during both time periods, and the individual correlation coefficients were examined. However, watershed characteristics may be correlated to each other (e.g., urban land cover and population density), and may not represent separate sources. Therefore, multiple linear regression was used to identify the two variables that best explained the variance in each metal for each time period. Each model was limited to two variables because of the relatively small sample size.

This overall approach should indicate whether watershed or regional scale processes influence metal inputs, and suggest possible sources for cadmium, copper, and zinc to Michigan lakes by correlation with watershed characteristics.

Additionally, the impact of environmental legislation in the 1970s will be shown both

by changes in the anthropogenic accumulation rates and by different relationships with watershed characteristics in the two time periods.

### **Methods**

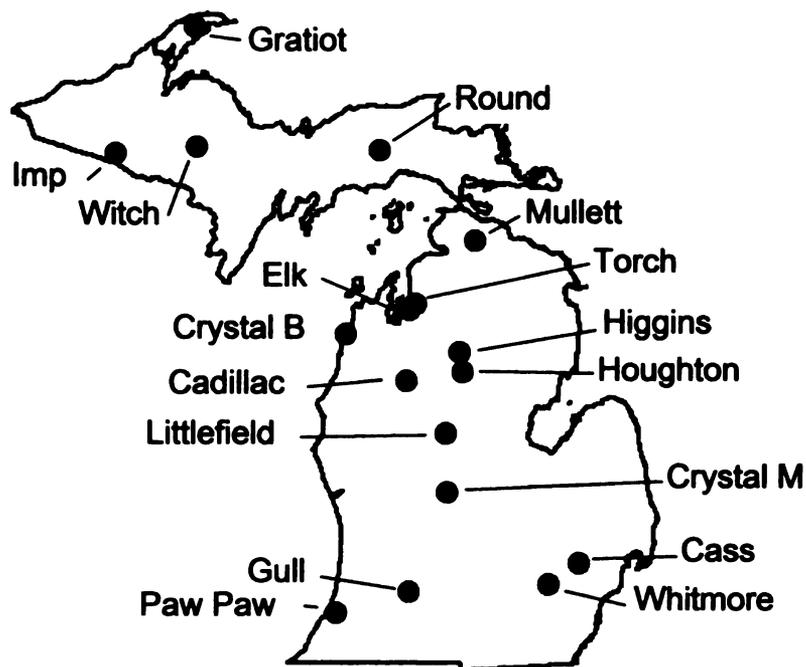
Methods are described both in the previous chapters and in the Appendix, however, a brief description of sampling and analysis techniques, and description of watershed characteristics is given below.

Sediment cores were collected from 17 lakes in Michigan (Figure 1). Lakes were selected to represent both urban and remote areas and to be distributed throughout the state. Only lakes that had a maximum depth greater than 8 m were considered (Yohn et al., 2003), and lakes with one basin were preferred to those with complicated bathymetry. Sediment cores were collected from the deepest portion of each lake using a MC-400 Lake/Shelf Multi-corer deployed from the Monitoring Vessel *Nibi*. Cores were then extruded and sectioned at 0.5 cm intervals for the top 8 cm, and at 1 cm intervals for the remainder of the core.

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

Sediments were frozen, freeze-dried and digested by nitric acid in a CEM-MDS-81D microwave (Hewitt and Reynolds, 1990). Standard reference material (NIST RM 8704 Buffalo River Sediment) and procedural blanks were processed to test for accuracy and contamination. The concentrated-acid digests were filtered through an acid-washed, e-pure (Barnstead) rinsed 0.40  $\mu\text{m}$  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, Cr, Mn, Fe, Co, Ni, Cu, Zn, As, Sr, Mo, Cd, Ba, Pb, and U.



**Figure 1.** Location of study lakes in Michigan, USA.

Calculation of anthropogenic input rates from total sediment concentrations are described in detail in Chapter 2, and are summarized below. Anthropogenic concentrations are determined from total sediment concentrations by normalizing to a terrestrial element (e.g., Al) for each depth using the equation:

$$M_S^{\text{Anthro}} = M_S^{\text{Total}} - \frac{M_{\text{BG}}}{T_{\text{BG}}} \times T_S$$

Where  $M_{\text{BG}}$  and  $T_{\text{BG}}$  are the concentrations of the anthropogenic metal of interest and the terrestrial element respectively in pre-anthropogenic sediments,  $T_S$  is the concentration of the terrestrial element in sample S,  $M_S^{\text{Total}}$  is the total concentration of the metal of interest in sample S, and  $M_S^{\text{Anthro}}$  is the anthropogenic concentration of the metal of interest in sample S.

Accumulation rates are calculated from the anthropogenic concentrations using:

$$\text{Anthropogenic accumulation rate } (\mu\text{g m}^{-2} \text{ y}^{-1}) = \text{anthro conc (mg/kg)} \times \text{mass sedimentation rate (g m}^{-2} \text{ y}^{-1})$$

The mass sedimentation rate is taken from the dating model used for that particular lake.

A focusing factor was calculated for each lake to account for the tendency of fine-grained particles to move towards the deepest portion of the lake (Golden et al., 1993; Hermanson, 1998). The focusing factor was calculated using the equation where the theoretical  $^{210}\text{Pb}$  inventory used was  $0.574 \text{ Bq/cm}^2$  (Golden et al., 1993):

$$FF = \frac{\text{actual } ^{210}\text{Pb inventory}}{\text{theoretical } ^{210}\text{Pb inventory}}$$

To account for different amounts of focusing that occurs among lakes, the anthropogenic accumulation rate is divided by the focusing factor.

In some cases constant metal: aluminum ratios were not present in the oldest portions of the core, and anthropogenic accumulation rates could not be calculated. Anthropogenic accumulation rates that could not be calculated include: cadmium: Witch Lake; copper: Imp, Littlefield, Round and Torch lakes; zinc: Imp, Littlefield, Mullett, Torch and Witch lakes.

Characteristics of the watersheds of each of the study lakes were determined using ArcView and ArcInfo, and are described below. Complete methods are described in the Appendix. Spatial data were collected from secondary sources, and were in, or were projected into the Michigan GEOREF coordinate system: oblique Mercator projection, datum NAD83, spheroid GRS 1980. Slope, K factor, and land cover were calculated both for the entire watershed and for a 100 m buffer around the study lake.

*Lake area, watershed area, watershed: lake area ratio (km<sup>2</sup>):* Lake areas were taken from Michigan Department of Conservation bathymetric maps. Watersheds were delineated around each of the seventeen lakes of interest (Yohn et al., 2004), with the study lake not considered as part of the watershed. Cass and Whitmore Lake watersheds were defined using 90 m SRTM data because 30 m data were not available for this region of the state. If the watershed of a lake contained another lake (e.g., Mullett Lake watershed contains Burt Lake), the watershed of the second lake was removed from the watershed of the study lake. Lakes are effective sediment traps (Wetzel, 2001), and outflow from a lake is likely to have very low concentrations of metals. Therefore, it is likely that the watershed of a lake within the watershed of a study lake is unlikely to significantly contribute metals to the study lake. The

watershed: lake area ratio was determined by dividing the area of the watershed by the area of the lake.

*K factor, slope corrected K factor:* K factors to estimate soil erodibility were calculated from the State Soil Geographic (STATSGO) database (U.S. Department of Agriculture, 1994). Area weighted averages were used to determine the average slope and K factor for each watershed. The K factor is standardized to a 9% slope. To create a variable that included both slope and the K factor, the K factor was multiplied by the slope divided by 9%. For slopes greater than 9%, the K factor increases when slope is included, indicating higher erosion potential. Slopes less than 9% would result in a lower K factor, and a lower erosion potential. Unfortunately, the STATSGO database defines very broad groupings of soils for large spatial areas, and may not be detailed enough for this analysis.

*Slope (degrees):* Average slope for the watershed was calculated in ArcInfo using the same digital elevation models that were used for determination of the watershed.

*Sulfate deposition ( $kg\ ha^{-1}\ y^{-1}$ ):* Sulfate deposition data were collected for 10 sites from Michigan, Wisconsin and Illinois from the National Acid Deposition Program database (National Atmospheric Deposition Program (NRSP-3)/National Trends Network, 2003). Data were collected from all available years from each site, but final data are from 1990-2000. Very few stations collected data from 1970-1980, making it difficult to estimate sulfate deposition values for this time period. However, the patterns of sulfate deposition appear to remain the same within the state over time, therefore the 1990-2000 data were also used to represent the spatial gradient of

atmospheric deposition from 1970-1980. Inverse distance weighting was used to estimate sulfate deposition values for each watershed.

*Population (people) and population density (people km<sup>-2</sup>):* Census data at the census tract scale were used for population calculations. Population data from one data set was used for population density calculations from 1870-1990, and a separate data set was used for 2000 (Michigan Center for Geographic Information, 2002). Because of this, census tracts are different for 2000, and some population densities changed significantly from 1990 to 2000 due to this. Watersheds generally only encompassed a portion of each census tract; therefore, to determine population densities within the watershed, it was essential to estimate as accurately as possible where people were living within the township. Thus, dasymetric mapping was used to estimate population distribution. Areas that are state owned (Michigan Department of Natural Resources, 2000) or areas covered by lakes (Michigan Department of Natural Resources, 1992) were considered as non-livable areas. It was assumed that the population was evenly distributed throughout the remaining livable area within each census tract. The preference of people to live near a lake (Stewart, 1994) was not accounted for, causing a possible underestimation of population densities within watersheds. Additionally, no attempt was made to account for seasonal increases in population, which may be significant around some lakes. Census data from 1970 and 1980 were averaged to represent the 1970s time period, and data from 1990 and 2000 were averaged to represent the 1990s time period. The number of people within the watershed was divided by the area of the watershed (not including the lake area) to determine the population density of the watershed (people km<sup>-2</sup>)

*Land cover (km<sup>2</sup>, %):* Land use/cover data were collected for 1978 (Michigan Department of Natural Resources, 1999) and 1997-2001 (Michigan Department of Natural Resources, 2003). Land cover groupings were different for the two time periods, therefore the Level 1, or coarsest, land cover groupings were used so that the two time periods could be compared (Table 1). The Level 1 land cover groupings were generally comparable between time periods, with the exception of the forested and wetland land covers. The 1978 dataset includes lowland forest in the forested land cover, whereas the 1997-2001 dataset includes lowland forest in the wetlands land cover, and categorizes upland forest separately. The 1997-2001 dataset was modified to include lowland forest into a new forest category (instead of upland forest), thus making the two time periods more comparable. Total area in the watershed and percentage land covers were calculated for each watershed (not including the lake), and for a 100 m buffer around the lake for each of the two time periods.

**Table 1.** Level 1 land cover groupings from two time periods. The 1997-2001 dataset was modified to correspond better to the 1978 dataset by moving the lowland forest land cover from the wetlands category to the forest category.

1978	1997-2001
Urban	Urban
Agriculture	Agriculture
Rangeland	Upland openland
Forested	Forest = upland forest + lowland forest
Water	Water
Wetland	Wetland (not including lowland forest)
Barren	Bare/sparsely vegetated

*Flow weighted land cover:* The flowpath (m<sup>2</sup>), or distance from the lake along the path that water would flow, for each grid cell in each watershed was determined using the FLOWLENGTH command in ArcInfo. Inverted flowpath was then calculated

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(1/flowlength). Separate grid coverages were created for each land cover, with a value of 1 for each cell that contains that land cover, and a value of 0 for all other land covers. Each of these coverages was multiplied by the inverse flowpath coverage and summed. This was completed for each land cover for each time period. Additionally, the same calculations were performed using the inverse flowpath squared ( $1/d^2$ ). Percentages were calculated dividing the result for one land cover type by the sum for all land covers.

*Toxic Release Inventory (TRI)*: Toxic release inventory sites that released copper, cadmium, lead, or zinc for all of Michigan were identified from <http://www.epa.gov/triexplorer/>. These sites were plotted spatially, and watersheds of each of the study lakes were examined to determine if any TRI sites were present within the watershed. No TRI sites were present in any of the watersheds; therefore these data were not used.

All watershed characteristics were examined for outliers using boxplots. All outliers were removed before correlation analysis to prevent these points from having significant influence on the correlation coefficients (Yohn et al., in preparation).

Correlation coefficients were calculated between lead accumulation rates and watershed characteristics using SYSTAT 10. Multiple regression was used to determine the two watershed characteristics that best explained the variance in lead accumulation rates for each time period. The number of predictor variables was limited to two due to the small number of lakes sampled (Hair, 1998). All possible pairs of the ten variables with the highest correlation coefficients were modeled using

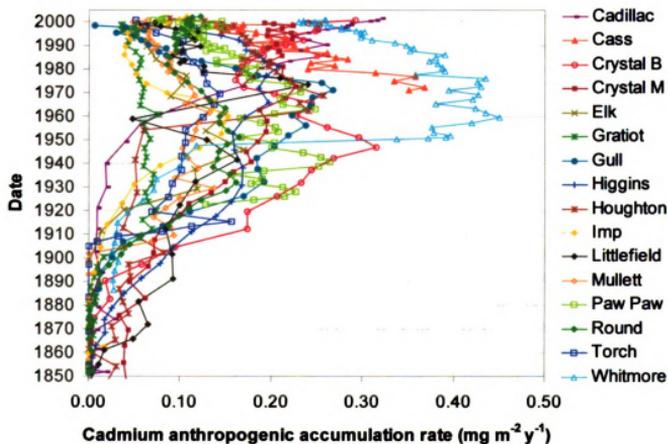
multiple regression to determine which pair had the highest  $r^2$  value. Only models where both variables had a  $p < 0.05$  were considered.

## Results

### Sediment chronologies

All three metals show a general trend of anthropogenic accumulation rates beginning to increase between 1850 and 1900, peaking in the 1970s and decreasing to the present. However, for each of the metals there are considerable differences among lakes, both in the actual values and in the patterns over time.

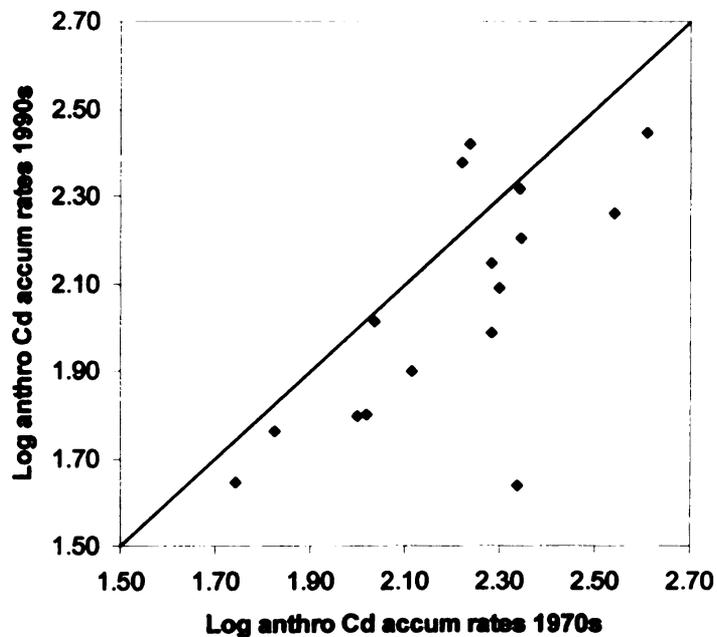
Cadmium accumulation rates generally increase from background values



**Figure 2.** Sediment anthropogenic accumulation rates ( $\text{mg m}^{-2} \text{y}^{-1}$ ) of cadmium in sixteen Michigan lakes.

within the time period of 1850-1900, but accumulation rates peak at different time periods in the study lakes (Figure 2). Some lakes (e.g., Crystal B, Paw Paw) have their highest cadmium accumulation rates in the early to mid-1900s, while other lakes (e.g., Gull, Higgins) have peak accumulation rates near the 1970s. Additionally, the overall shape of the profiles varies greatly among lakes, from broad peaks with long periods of similar accumulation rates (e.g., Gratiot, Round), to profiles with one distinct peak (e.g., Gull, Crystal B). This suggests that, over time, sources or the intensity of the sources has varied among lakes.

**Cadmium**  
anthropogenic  
accumulation rates have  
decreased in most lakes  
from the 1970s to the  
1990s (Figure 3), with two  
lakes having higher  
cadmium accumulation  
rates in the 1990s  
(Cadillac, Crystal B), and  
Gull Lake having much  
lower accumulation rates



**Figure 3.** Average cadmium sediment log anthropogenic accumulation rates ( $\mu\text{g m}^{-2} \text{y}^{-1}$ ) in the 1990s plotted versus average values for the 1970s. The line represents a 1:1 relationship, or no change between the two time periods.

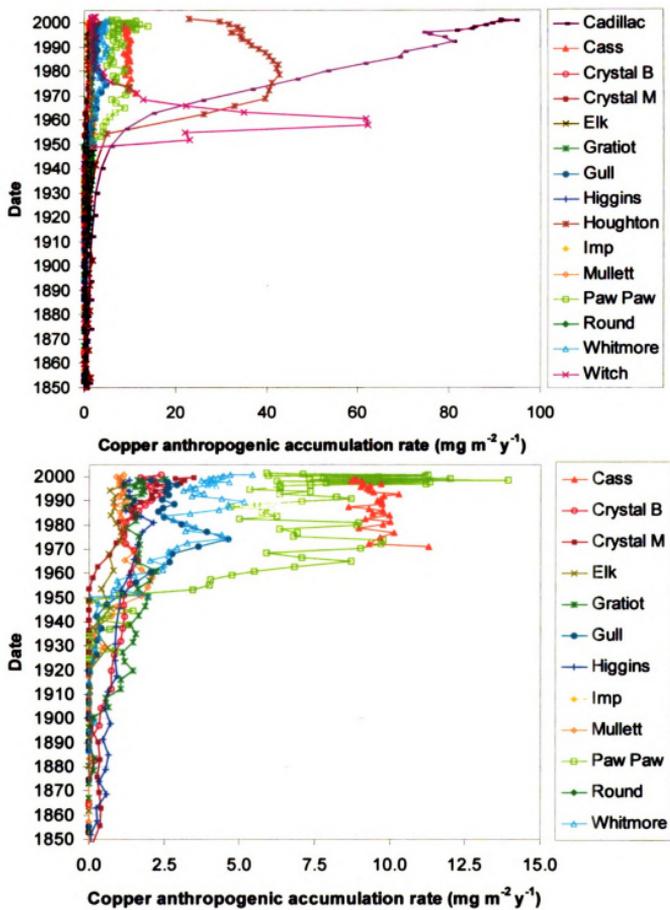
in the 1990s. The dissimilarity among lakes supports the observations made from the sediment chronologies, and suggests that either the sources for cadmium or the

intensity of the sources was dependant on local watershed characteristics for at least one of the time periods.

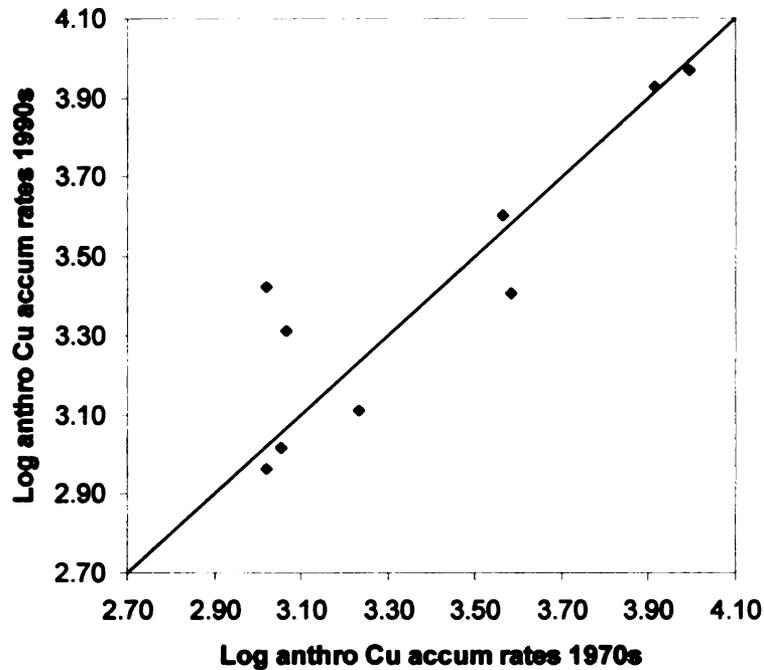
Copper profiles are the most dissimilar among lakes of the three metals (Figure 4). Three lakes clearly have much higher copper accumulation rates than the other lakes. Both Cadillac and Houghton lakes have high accumulation rates due to the use of copper sulfate (Yohn et al., 2002; Yohn et al., 2003). This is a local source that is not represented in any of the watershed characteristics, and therefore these lakes will be disregarded in further analysis of copper. Additionally, Witch Lake has a very unusual copper profile with very high copper accumulation rates. The cause of this profile is unclear, but Witch Lake is located in an area with extensive mining, and the profile is probably due to local mining activity. Gratiot Lake may also have been influenced by mining, and is located in a region with extensive copper mining. While copper accumulation rates are not exceptionally high, Gratiot Lake was consistently an outlier in preliminary correlation analysis. Because both of these lakes have a known source which is not accounted for by any of the watershed characteristics, they will also not be included in further analyses.

The remainder of the lakes also have copper profiles that are somewhat dissimilar, suggesting that copper is more influenced by local factors than regional over time. Copper accumulation rates have not decreased significantly since the 1970s (Figure 5), with copper accumulation rates in most lakes remaining constant or decreasing only slightly over the last three decades.



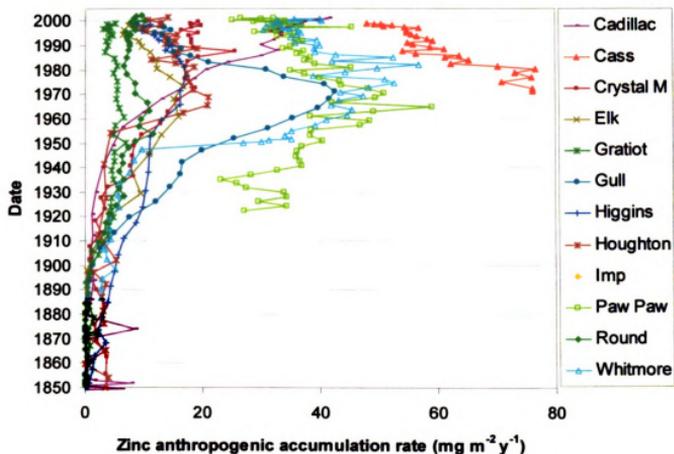


**Figure 4.** Sediment copper anthropogenic accumulation rates ( $\text{mg m}^{-2} \text{y}^{-1}$ ). Cadillac, Houghton and Witch lakes are not present on the bottom graph.

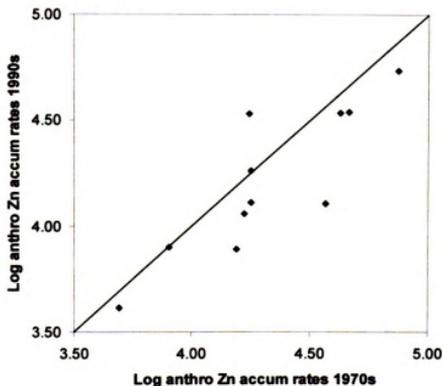


**Figure 5.** Average copper sediment log anthropogenic accumulation rates ( $\mu\text{g m}^{-2} \text{y}^{-1}$ ) in the 1990s plotted versus average values for the 1970s. The line represents a 1:1 relationship, or no change between the two time periods. Cadillac, Gratiot, Houghton and Witch lakes are not included.

Zinc anthropogenic accumulation rates begin increasing around 1900 for most lakes and many of the lakes have the highest anthropogenic accumulation rates in the 1970s (Figure 6). Additionally, most lakes have lower or the same accumulation rates in the 1990s than the 1970s (Figure 7), with the exception of Cadillac Lake. The overall similarity in the profiles of many of the lakes suggests that there may be regional sources, but local influences are also clearly important.



**Figure 6.** Sediment zinc anthropogenic accumulation rates ( $\text{mg m}^{-2} \text{y}^{-1}$ ).



**Figure 7.** Average zinc sediment log anthropogenic accumulation rates ( $\mu\text{g m}^{-2} \text{y}^{-1}$ ) in the 1990s plotted versus average values for the 1970s. The line represents a 1:1 relationship, or no change between the two time periods.

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### **Spatial patterns and atmospheric deposition**

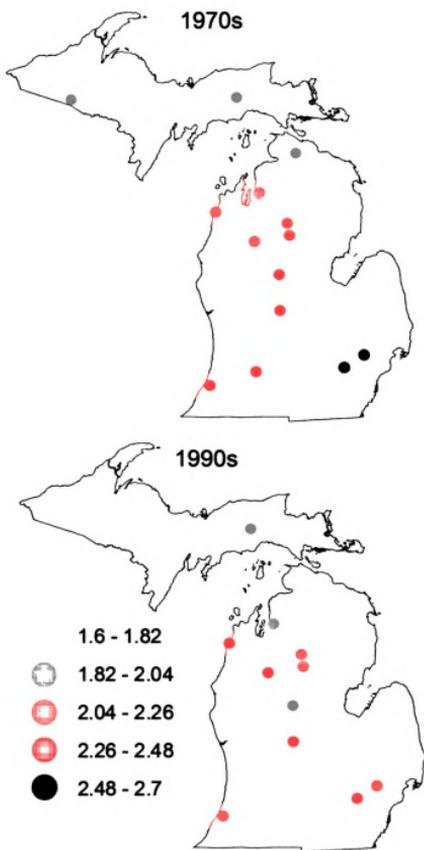
Sediment chronologies provide a history of metal inputs to the lake, and may suggest if inputs of a metal are locally or regionally influenced over time. However, looking at the spatial distribution of metals in Michigan lakes and at estimates of atmospheric deposition rates can provide some insight into the importance of atmospheric deposition during a specific time period.

There are major sources for metals to the atmosphere to the southwest of Michigan in the extensive urban and industrial areas of Chicago and Gary (Harrison and Winchest, 1971; Shahin et al., 2000; Landis et al., 2002; Souch et al., 2003), and in the southeast of Michigan where Detroit is located. Additionally, the southern part of Michigan is more developed than the northern Lower Peninsula or Upper Peninsula. As a result, if metals are released to the atmosphere from either industrial sources, or from local sources (e.g., coal burning for heat, gasoline burning) there may be a regional gradient of metal deposition across Michigan, with the highest accumulation rates in the south. If atmospheric deposition is not the pathway, then metal accumulation rates in each lake should be related to characteristics of the watershed, rather than a statewide gradient.

Cadmium does show a regional gradient in the 1970s (Figure 8), with the highest accumulation rate in southeast Michigan, and decreasing northwards. The lakes in southwest Michigan (Paw Paw and Gull) do not have significantly higher cadmium accumulation rates than those in mid-Michigan. This suggests that cadmium released to the atmosphere from the Chicago / Gary area (Cole et al., 1990) is either not reaching Michigan in significant quantities, or is well distributed throughout much

of the state. Atmospheric deposition rates in the 1970s estimated from a bog downwind of the Chicago / Gary region (Cole et al., 1990) are much higher than those measured in and around Michigan (Shahin et al., 2000; Landis et al., 2002) (Table 2), indicating that while some cadmium from this industrial area may enter Michigan, much of it is deposited closer to the original source.

Atmospheric deposition to Lake Michigan in the 1970s was measured at a deposition rate of  $0.2 \text{ mg m}^{-2} \text{ y}^{-1}$  (Eisenreich, 1980), a rate similar to or greater than many of the study lakes. This further supports the theory that atmospheric deposition was an important pathway in the 1970s. Only Cass and Whitmore lakes have accumulation rates much higher than the measured atmospheric deposition rates. These lakes may have higher rates because of additional atmospheric deposition of cadmium from the urban area of Detroit, or from sources within the watershed.



**Figure 8.** Average log cadmium anthropogenic accumulation ( $\mu\text{g m}^{-2} \text{y}^{-1}$ ) rates in sediments of Michigan lakes.

**Table 2.** Accumulation rates of cadmium, copper, and lead ( $\text{mg m}^{-2} \text{y}^{-1}$ ) during the 1970s. Rates for this study are focusing corrected anthropogenic accumulation rates.

Site	Medium	Cd ( $\text{mg m}^{-2} \text{y}^{-1}$ )	Cu ( $\text{mg m}^{-2} \text{y}^{-1}$ )	Zn ( $\text{mg m}^{-2} \text{y}^{-1}$ )
<b>This study, 1970s</b>				
Cadillac	Sediment	0.17		17
Cass	Sediment	0.35	9.9	74
Crystal B	Sediment	0.17	1.2	
Crystal M	Sediment	0.22	1.0	18
Elk	Sediment	0.11	1.0	16
Gratiot	Sediment	0.06		5.0
Gull	Sediment	0.22	3.8	37
Higgins	Sediment	0.19	1.7	17
Houghton	Sediment	0.22		18
Imp	Sediment	0.07		
Littlefield	Sediment	0.19		
Mullett	Sediment	0.10	1.1	
PawPaw	Sediment	0.20	8.2	43
Round	Sediment	0.11		8.0
Torch	Sediment	0.13		
Whitmore	Sediment	0.41	3.6	46
N. Indiana (1973-1978) <sup>a</sup>	Bog	1.9	17	189
Lake Michigan (1975-76) <sup>b</sup>	Atmospheric	0.2	2.1	19

a. (Cole et al., 1990)

b. (Eisenreich, 1980)

In the 1990s the regional gradient of cadmium accumulation rates is no longer apparent, suggesting that source(s) that are influenced on the watershed scale (Figure 8). This is supported by the measurements of atmospheric deposition (Table 3), which show atmospheric deposition rates ranging from 0.06 to 0.14  $\text{mg m}^{-2} \text{y}^{-1}$  in the region. Several of the study lakes (Cadillac, Cass, Crystal B, Crystal M, and Whitmore) have accumulation rates much higher than that anticipated from atmospheric deposition, and these lakes are probably also being influenced by local sources.

Copper accumulation rates in the 1970s are higher in the southern portion of the state and lower in the northern (Figure 9), but do not show a consistent regional gradient

because of high accumulation rates in Higgins Lake. From the atmospheric deposition rates (Table 2), it appears that this pathway may be important for many lakes, but lakes in the southern Michigan have much higher accumulation rates than those estimated from atmospheric deposition to Lake Michigan (Table 2). Additionally, Higgins Lake has a higher copper accumulation rate than Crystal M Lake, but is located much farther north, suggesting that watershed scale inputs are probably also important.

**Table 3.** Accumulation rates ( $\text{mg m}^{-2} \text{y}^{-1}$ ) of cadmium, copper, and zinc during the 1990s. Rates from this study are focusing corrected anthropogenic accumulation rates.

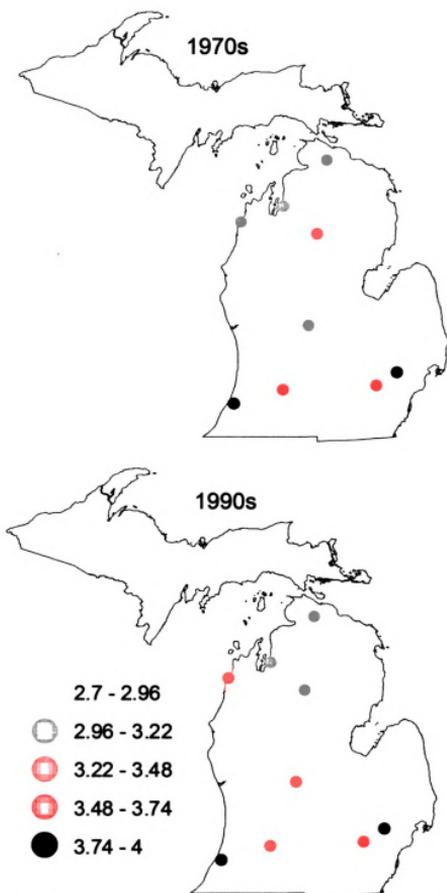
Site	Medium	Cd ( $\text{mg m}^{-2} \text{y}^{-1}$ )	Cu ( $\text{mg m}^{-2} \text{y}^{-1}$ )	Zn ( $\text{mg m}^{-2} \text{y}^{-1}$ )
<b>This study, 1990s</b>				
<b>Cadillac</b>	<b>Sediment</b>	<b>0.26</b>		<b>34</b>
<b>Cass</b>	<b>Sediment</b>	<b>0.18</b>	<b>9.3</b>	<b>54</b>
<b>Crystal B</b>	<b>Sediment</b>	<b>0.24</b>	<b>2.1</b>	
<b>Crystal M</b>	<b>Sediment</b>	<b>0.21</b>	<b>2.6</b>	<b>18</b>
<b>Elk</b>	<b>Sediment</b>	<b>0.06</b>	<b>0.92</b>	<b>7.8</b>
<b>Gratiot</b>	<b>Sediment</b>	<b>0.04</b>		<b>4.1</b>
<b>Gull</b>	<b>Sediment</b>	<b>0.04</b>	<b>2.5</b>	<b>13</b>
<b>Higgins</b>	<b>Sediment</b>	<b>0.14</b>	<b>1.3</b>	<b>12</b>
<b>Houghton</b>	<b>Sediment</b>	<b>0.16</b>		<b>13</b>
<b>Imp</b>	<b>Sediment</b>	<b>0.06</b>		
<b>Littlefield</b>	<b>Sediment</b>	<b>0.10</b>	<b>0.60</b>	
<b>Mullett</b>	<b>Sediment</b>	<b>0.06</b>	<b>1.0</b>	
<b>PawPaw</b>	<b>Sediment</b>	<b>0.12</b>	<b>8.5</b>	<b>34</b>
<b>Round</b>	<b>Sediment</b>	<b>0.10</b>		<b>7.9</b>
<b>Torch</b>	<b>Sediment</b>	<b>0.08</b>		
<b>Whitmore</b>	<b>Sediment</b>	<b>0.28</b>	<b>4.0</b>	<b>35</b>
<b>L. Tantare, Canada<sup>a</sup></b>	<b>sediment</b>	<b>0.06</b>		
<b>L. Superior, 1993-1994<sup>b</sup></b>	<b>atmospheric</b>		<b>3.1</b>	<b>8.8</b>
<b>L. Michigan, 1993-1994<sup>b</sup></b>	<b>atmospheric</b>		<b>1.9</b>	<b>6.0</b>
<b>L. Erie, 1993-1994<sup>b</sup></b>	<b>atmospheric</b>		<b>4.2</b>	<b>17</b>
<b>L. Huron<sup>c</sup></b>	<b>atmospheric</b>	<b>0.11</b>		
<b>L. Ontario<sup>c</sup></b>	<b>atmospheric</b>	<b>0.14</b>		
<b>Eastern Ontario, 1998<sup>d</sup></b>	<b>snowpack</b>	<b>0.06-0.14</b>	<b>0.52-1.3</b>	<b>47-117</b>
<b>Northeast USA, 1998<sup>d</sup></b>	<b>snowpack</b>	<b>0.025-0.06</b>	<b>0.25-0.62</b>	<b>80-199</b>

a. (Alfaro-De la Torre and Tessier, 2002)

b. (Sweet et al., 1998)

c. (Hoff et al., 1996)

d. (Simonetti et al., 2000b)

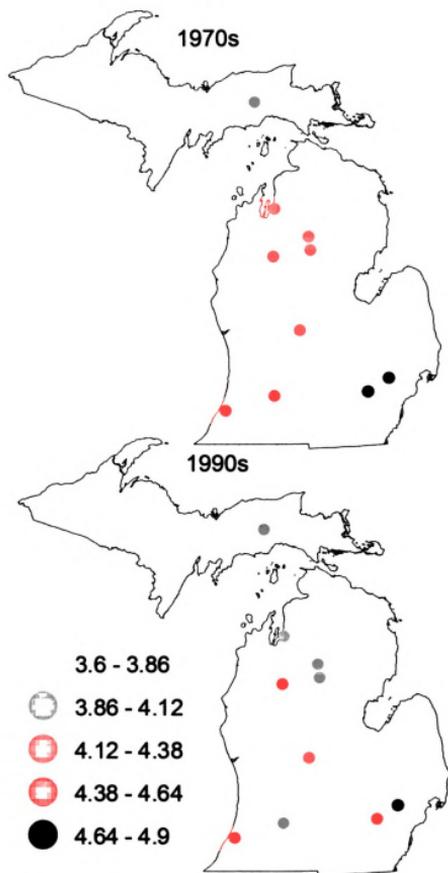


**Figure 9.** Average log copper anthropogenic accumulation ( $\mu\text{g m}^{-2} \text{y}^{-1}$ ) rates in sediments of Michigan lakes.

The importance of atmospheric deposition of copper in the 1990s is difficult to assess. There is an overall regional pattern of higher accumulation rates in the south (Figure 9), which may indicate that atmospheric deposition is important. However, estimates of atmospheric deposition from the Great Lakes region are lower than the accumulation rates in the sediments of some of the study lakes (Table 3), suggesting that local sources may also play a role.

Zinc accumulation rates in the study lakes have a consistent regional gradient in the 1970s (Figure 10) that suggests the importance of atmospheric deposition. This is corroborated by the measurement of atmospheric deposition (Table 2), which is similar to or greater than many of the study lakes. The southern lakes have much higher accumulation rates than that anticipated from atmospheric deposition in Lake Michigan, but it is unclear if this is due to local sources, or greater atmospheric deposition in these urban areas.

Similar to cadmium, the regional gradient in zinc accumulation rates that was present in the 1970s is no longer apparent in the 1990s (Figure 10), suggesting that local sources have become more significant. Measurements of atmospheric deposition from Lakes Michigan and Superior range from 8.8 – 6.0 mg m<sup>-2</sup> y<sup>-1</sup>, and are lower than many of the study lakes, supporting this conclusion (Table 3).



**Figure 10.** Average log zinc anthropogenic accumulation ( $\mu\text{g m}^{-2} \text{y}^{-1}$ ) rates in sediments of Michigan lakes.

### **Watershed characteristics**

The size of both the study lakes and their watersheds varied considerably, from 0.3 to 81 km<sup>2</sup>, and 1.7 to 1286 km<sup>2</sup> respectively. Watershed to lake area ratios vary from 1.5 (Torch Lake) to 22.1 (Littlefield Lake).

Both the K factor, a measure of erodibility, and average slope, were calculated for both the entire watershed and a 100 m buffer around the lake. Average slopes of the entire watersheds are generally shallow (<5 degrees) as well as slopes within the 100 m buffers. Slopes within the 100 m buffers were not consistently steeper or shallower than the entire watershed. The watershed for Crystal B Lake had a much higher slope in the 100 m buffer (8.7 degrees) than in the entire watershed or than any other watershed. This datum was an outlier, and slope of the 100 m buffer around Crystal Lake was not included in further analyses. The K factor for the 100 m buffer was not consistently greater or less than the average for the entire watershed.

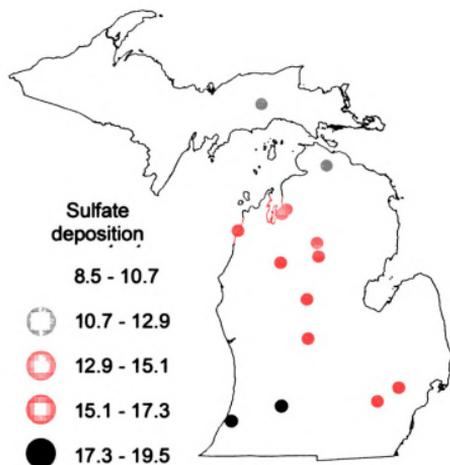
Sulfate deposition rates varied among lakes, with the lowest values in the Upper Peninsula, and highest values near the southwest corner of Michigan (Figure 11). The prevailing winds in the southern Lower Peninsula are westerly, and carry acid deposition from the Chicago, IL, and Gary, IN, industrial and urban centers (Winchester and Nifong, 1971; Perkins et al., 2000; Souch et al., 2003).

Population densities were much higher for the Cass Lake watershed than any other watershed (Appendix A). Population densities for Witch, Paw Paw, and Cadillac lake watersheds were also high. All watersheds had a higher population density in the 1990s than the 1970s, with the exception of Round and Witch lake

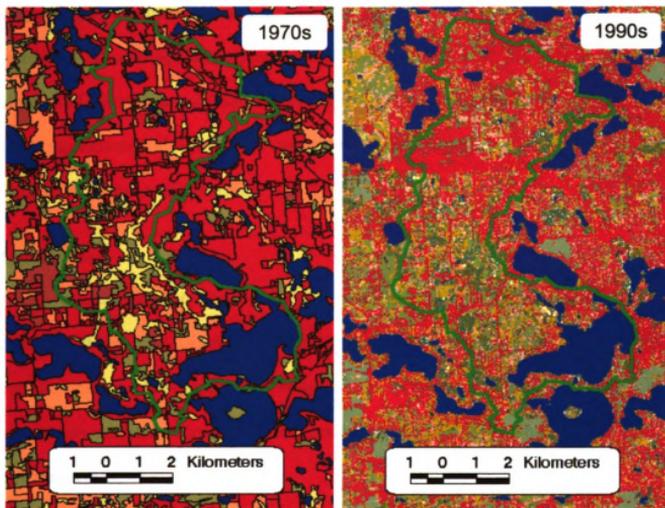
watersheds. The Upper Peninsula lakes (Gratiot, Imp, Round and Witch) have the lowest watershed population densities.

The dominant land cover in most watersheds was forest, with agriculture being dominant in a few watersheds, and urban

dominant in Cass Lake watershed. Comparison of land cover between the two time periods is difficult because of the differences in the original data. 1970s land cover maps were delineated from 1:24,000 color-infrared and black and white photos (Michigan Department of Natural Resources, 1999), whereas the 1990s land cover data are provided as a 30 m grid derived from satellite imagery (Landsat Thematic Mapper) (Michigan Department of Natural Resources, 2003). As a result, where large areas may be grouped as one land cover in the 1970s (e.g., urban in Cass Lake watershed), these areas are divided into several land covers in the 1990s (Figure 12). The percentage urban within most watersheds decreases from the 1970s to the 1990s, and this decrease in urban land cover is likely due to the increased resolution in the



**Figure 11.** Estimated rates of sulfate deposition rates ( $\text{kg ha}^{-1} \text{y}^{-1}$ ) to Michigan study lakes.



**Figure 12.** Urban land cover in the Cass Lake watershed in 1975 and 1995. Urban land cover is in red, and water is in blue. Land covers of the other colors vary between years. The watershed is outlined in green.

1990s land cover data than an actual decrease in urban land use. Because of this, comparisons between the two time periods must be evaluated carefully.

The composition of land cover within the 100 m buffer was significantly different than percentage land cover for the entire watershed. In general, for both time periods, percentage urban was higher in the 100 m buffer, in many cases significantly (e.g., 9% urban in total watershed, 84% urban in 100 m buffer for Gull Lake in the 1970s). Conversely, agriculture was much lower in the 100 m buffer. Forest and rangeland was generally somewhat lower in the 100 m buffer, and wetlands varied by watershed. For most lakes, urban land cover was dominant within the 100 m buffer,

suggesting concentrated developments near the lake compared to the rest of the watershed. Percentage land cover that was weighted by the inverse of the distance along the flow path to the lake showed a similar trend of higher urban land cover, and lower agriculture and forest. The use of inverse distance squared increased the magnitude of these differences.

### **Correlations**

Correlations between log anthropogenic accumulation rates of cadmium, copper, and zinc, and watershed characteristics were determined (Tables 4-9). These correlations do not necessarily represent a cause – effect relationship, but may give insight into possible sources for these metals, and their pathways through the environment.

There was no relationship between anthropogenic accumulation rates of cadmium, copper or zinc in the 1970s or 1990s and lake or watershed size, or watershed to lake area ratio (Tables 4,6,8). Additionally, there were no Toxic Release Inventory (TRI) sites located in any of the study watersheds, suggesting that point source inputs from major industry should not be a source for any of the lakes.

Accumulation rates of all three metals for both time periods correlated positively with population density during both time periods. This is similar to other studies that have found relationships between metal concentrations in stream sediments and population density (Rice, 1999; Callender and Rice, 2000).

Atmospheric deposition correlates positively with sulfate deposition rates during both time periods and for all metals, with generally higher correlations in the 1970s (Tables 4, 6, 8). Sulfate deposition was chosen to act as a proxy atmospheric

transport from sources such as the burning of coal (Graney et al., 1995; Berner and Berner, 1996), and the positive correlation may represent the importance of extensive coal burning that occurred in the Gary, Indiana, and Chicago, Illinois industrial region, as well as in the industrial region near Detroit. Coal burning also probably occurred at smaller quantities throughout the state from residential use, power production and smaller industrial sites. The lower correlations between cadmium and zinc accumulation rates and sulfate deposition rate in the 1990s is not surprising because in the 1970s the Clean Air Act has served to reduce contaminants released to the air, and there has been a general decline in steel production since the 1980s (Perkins et al., 2000).

There was also no relationship to the K factor measure of erodibility. This suggests that the pathway of erosion, at least as evaluated by the erosion tendency of the soil type, is not controlling copper, cadmium, or zinc deposition patterns through the state.

An unanticipated relationship was the negative correlation between metal accumulation rates and average slope of the watershed or within a 100 m buffer. Slope was chosen as a variable to represent erosion potential of the soil, with an anticipated positive relationship between metal accumulation rates and slope. Clearly slope is not representing the extent of erosion, but must instead be representing a different source or pathway. Slope may represent a measure of development in the watershed, with steeper slopes being less developed, but in general, slopes are shallow in the watersheds of the study lakes (< 5 degrees), and development should not be limited by these slopes. A similar negative relationship between slope and lead

accumulation rates exists in the 1970s, when the major source of lead to the environment was the burning of leaded gasoline (Graney et al., 1995; Callender and vanMetre, 1997). In Michigan, average slope in the watershed, or in a 100 m

**Table 4.** Pearson product moment correlations (r) between log anthropogenic cadmium accumulation rates and watershed characteristics. Only correlations where  $p < 0.05$  are shown. Data for within a 100 m buffer were only collected for K factors and slope.

	70s		90s	
	watershed	100 m buffer	watershed	100 m buffer
Watershed area		NA		NA
Lake area		NA		NA
Watershed:lake area ratio		NA		NA
Population density	0.813	NA	0.616	NA
Population (total #)	0.565	NA		NA
Sulfate deposition	0.822	NA	0.498	NA
K-factor				
K-factor, slope corrected				
Slope	-0.839	-0.836		-0.604

**Table 5.** Pearson product moment correlations (r) between log anthropogenic cadmium accumulation rates and land cover variables. Only correlations where  $p < 0.05$  are shown.

	urban		agriculture		openland/range	
	70s	90s	70s	90s	70s	90s
Total watershed %	0.720	0.725				
Total watershed area						
100 m buffer %	0.724	0.695				
100 m buffer area					-0.558	
Flow inverted %		0.714				
Flow inverted value			-0.733		-0.818	
Flow inv. sq. %		0.655				
Flow inv. sq. value			-0.691		-0.754	
	forest		wetlands			
	70s	90s	70s	90s		
Total watershed %	-0.688		0.673			
Total watershed area						
100 m buffer %	-0.764	-0.607				
100 m buffer area	-0.613					
Flow inverted %	-0.718	-0.502				
Flow inverted value	-0.672	-0.518				
Flow inv. sq. %	-0.705	-0.527				
Flow inv. sq. value	-0.784	-0.570				

**Table 6.** Pearson product moment correlations (r) between log anthropogenic copper accumulation rates and watershed characteristics. Only correlations where  $p < 0.05$  are shown. Data for within a 100 m buffer were only collected for K factors and slope.

	70s		90s	
	watershed	100 m buffer	watershed	100 m buffer
Watershed area		NA		NA
Lake area		NA		NA
Watershed:lake area ratio		NA		NA
Population density	0.855	NA	0.856	NA
Population (total #)		NA		NA
Sulfate deposition	0.668	NA	0.644	NA
K-factor				
K-factor, slope corr.				
Slope	-0.766	-0.789	-0.732	

**Table 7.** Pearson product moment correlations (r) between log anthropogenic copper accumulation rates and land cover variables. Only correlations where  $p < 0.05$  are shown.

	urban		agriculture		openland/range	
	70s	90s	70s	90s	70s	90s
Total watershed %	0.740	0.899				
Total watershed area						
100 m buffer %						
100 m buffer area			-0.713			
Flow inverted %		0.731				
Flow inverted value						
Flow inv. sq. %						
Flow inv. sq. value			-0.667			
	forest		wetlands			
	70s	90s	70s	90s		
Total watershed %						
Total watershed area						
100 m buffer %						
100 m buffer area						
Flow inverted %						
Flow inverted value						
Flow inv. sq. %						
Flow inv. sq. value						

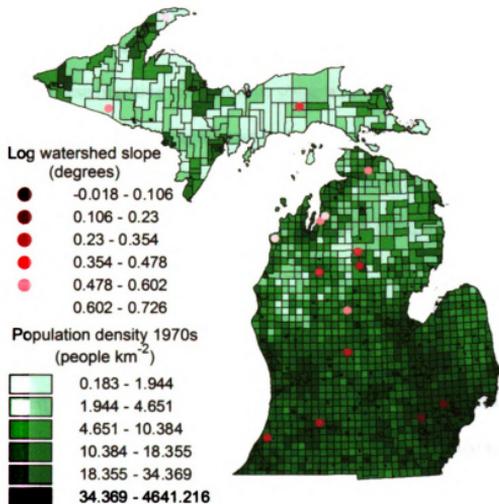
**Table 8.** Pearson product moment correlations (r) between log anthropogenic zinc accumulation rates and watershed characteristics. Only correlations where  $p < 0.05$  are shown. Data for within a 100 m buffer were only collected for K factors and slope.

	70s		90s	
	watershed	100 m buffer	watershed	100 m buffer
Watershed area		NA		NA
Lake area		NA		NA
Watershed:lake area ratio		NA		NA
Population density	0.905	NA	0.919	NA
Population (total #)	0.753	NA	0.662	NA
Sulfate deposition	0.827	NA	0.749	NA
K-factor				
K-factor, slope corr.				
Slope	-0.894	-0.847	-0.829	-0.885

**Table 9.** Pearson product moment correlations (r) between log anthropogenic zinc accumulation rates and land cover variables. Only correlations where  $p < 0.05$  are shown.

	urban		agriculture		openland/range	
	70s	90s	70s	90s	70s	90s
Total watershed %	0.874	0.918				
Total watershed area	0.621					
100 m buffer %	0.702	0.701	-0.701			
100 m buffer area			-0.871			
Flow inverted %	0.663	0.759				
Flow inverted value						
Flow inv. sq. %		0.682				
Flow inv. sq. value				-0.685		-0.677
	forest		wetlands			
	70s	90s	70s	90s		
Total watershed %	-0.778		0.734			
Total watershed area						
100 m buffer %	-0.700					
100 m buffer area						
Flow inverted %	-0.781		0.739			
Flow inverted value	-0.773	-0.810		-0.731		
Flow inv. sq. %	-0.636					
Flow inv. sq. value	-0.807	-0.833		-0.765		

buffer, generally follow a regional pattern of shallowest slopes in the south, and steepest slopes in the north. This corresponds to a pattern of greater development and higher population densities in the south and less development in the north (Figure 13). As a result, it is possible that slope is representing the regional development gradient across the state, rather than a specific source within each watershed. However, the exact meaning of this variable remains unclear.



**Figure 13.** Average slope (log degrees) of study lake watersheds and population density (people km<sup>-2</sup>) distribution in Michigan. Population density is categorized so that there are equal areas of each grouping, resulting in categories of unequal interval.

Percentage urban land cover within the watershed has a consistently positive correlation with accumulation rates of all three metals in both time periods (Tables 5,

7, 9). In almost all cases, the total percentage urban within the watershed has a higher correlation with metal accumulation rates than any of the landcover measures that are based on proximity to the lake (100 m buffer, flow path weighted). This suggests that the overall urbanization of the watershed is more critical than where the development is located. Additionally, correlations with urban land cover are generally higher in the 1990s, further suggesting the importance of local sources during this time period.

Correlations between agricultural or openland / range and metal accumulation rates were negative if significant, and generally lower than correlations with urban land cover. These negative relationships suggest that the use of pesticides or fertilizers did not contribute significant cadmium, copper or zinc to Michigan lakes. Correlations with forest land cover were also negative. Copper accumulation rates correlated poorly with land cover in general, with the exception of urban in the 1990s (Table 7).

### **Multivariate regression**

Interpretation of correlations between watershed characteristics and lead accumulation rates is difficult, because many of the watershed characteristics are correlated to each other (e.g., population density and % urban within the watershed). Therefore, to determine the best combination of predictors of cadmium, copper, and zinc to the environment, it is not appropriate to choose the variables that are most highly correlated with these metals, because the variables may be correlated to each other and actually act as a proxy for similar sources or processes. To avoid this problem, we used multivariate regression to select the two watershed characteristics

that together best described the variation in each of these metals accumulation rates among lakes. The number of watershed characteristics included in the model was limited to two because of the small number of lakes sampled. Only models where both variables contributed significantly ( $p < 0.05$ ) were considered, and in some cases no two watershed characteristics explained significantly greater variance than one variable.

### *Cadmium*

The two best predictors of anthropogenic cadmium accumulation rates in the 1970s are average slope of the watershed and sulfate deposition ( $r^2 = 0.85$ ,  $n = 16$ , Figure 14):

$$\text{Log (CD70}_{\text{faar}}) = -0.607 \times \text{log (SLOPE)} + 0.039 \times (\text{SO4}_{\text{d}}) + 1.873$$

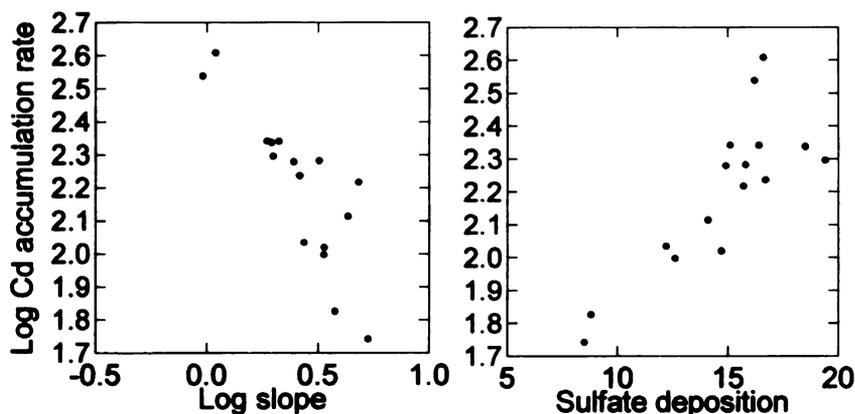
Where:

CD70<sub>faar</sub> represents focusing corrected cadmium anthropogenic accumulation rates in the 1970s ( $\mu\text{g m}^{-2} \text{y}^{-1}$ ),

SLOPE represents average slope in the watershed (degrees), and

SO4<sub>d</sub> is the estimated rate of sulfate deposition in the watershed ( $\text{kg ha}^{-1} \text{y}^{-1}$ ).

The standardized coefficients, which account for the differences in scale among variables, indicate the relative importance of each variable to the model. For cadmium in the 1970s, the two variables are of similar importance (standardized coefficient of SLOPE = -0.545, SO4<sub>d</sub> = 0.505).



**Figure 14.** Average log anthropogenic accumulation rates ( $\text{mg m}^{-2} \text{y}^{-1}$ ) of cadmium in sediments deposited in the 1970s plotted versus log average slope of the watersheds (degrees) and sulfate deposition rates ( $\text{kg ha}^{-1} \text{y}^{-1}$ ).

The importance of sulfate deposition and slope suggest that atmospheric deposition was an important source of cadmium during the 1970s. This is in agreement with the conclusions made from the spatial pattern of cadmium accumulation rates and estimates of atmospheric deposition of cadmium. Cadmium is released to the atmosphere from the combustion of fossil fuels (e.g., coal, oil) (Harrison and Winchest, 1971; Mecray et al., 2001), and atmospheric deposition was found to be a significant component of cadmium inputs to southern Lake Michigan (Muhlbaier and Tissue, 1981). All of these results suggest that the atmosphere was a dominant pathway of cadmium to Michigan lakes during the 1970s.

In the 1990s, the best predictor of cadmium accumulation rates in the sediments of the study lakes was percentage urban land cover within the watershed ( $r^2 = 0.53$ ,  $n = 16$ , Figure 15):

$$\text{Log (CD90}_{\text{faar}}) = 0.523 \times \text{log (URBAN90)} + 1.665$$

Where:

CD90<sub>faar</sub> represents focusing corrected anthropogenic cadmium accumulation rates in the 1990s ( $\mu\text{g m}^{-2} \text{y}^{-1}$ ), and

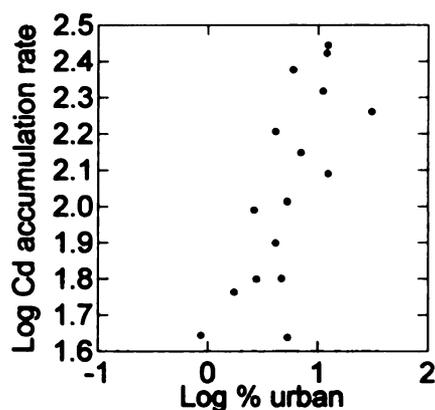
URBAN90 represents percentage urban land cover within the watershed.

Only 53% of the variance of cadmium can be explained by watershed

characteristics in the 1990s, as opposed to the 85% explained in the 1970s. This may be explained by the increasing importance of local inputs that are not well described by the watershed characteristics examined in this study.

This conclusion is supported by the lack of a regional gradient of accumulation rates, and from comparison to measures of atmospheric deposition. The exact sources for cadmium are unclear, but appear to be related to urban land

cover, and may include sources such as releases from wear of automobile parts, wastewater, or household waste such as batteries (Rice, 1999; Callender and Rice, 2000). It is probable that there is also some continued atmospheric deposition of cadmium, but local sources are more significant for some Michigan lakes.



**Figure 15.** Average log anthropogenic accumulation rates ( $\text{mg m}^{-2} \text{y}^{-1}$ ) of cadmium in sediments deposited in the 1990s plotted versus log percent urban landcover of the watersheds.

## *Copper*

Watershed population density and slope corrected K factor are the two variables that best predict the anthropogenic accumulation rates of copper in the 1970s ( $r^2 = 0.84$ ,  $n = 9$ , Figure 16):

$$\text{Log (CU70}_{\text{faar}}) = 0.489 \times \text{log (POPDENS70)} - 0.947 \times \text{log (KFACT}_s) + 1.776$$

Where:

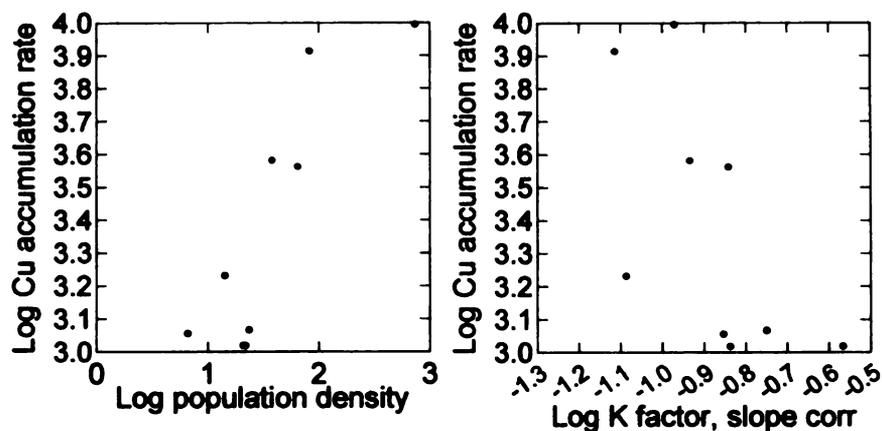
CU70<sub>faar</sub> is focusing corrected anthropogenic copper accumulation rates in the 1970s ( $\mu\text{g m}^{-2} \text{y}^{-1}$ ),

POPDENS70 is population density in the 1970s ( $\text{people km}^{-2}$ ), and

KFACT<sub>s</sub> is the average K factor in the watershed corrected for slope.

POPDENS70 has a higher standardized correlation coefficient than KFACT<sub>s</sub> (0.732, -0.409).

These two variables suggest that copper inputs were controlled at the watershed scale rather than at the regional scale, which is supported by the lack of regional pattern in anthropogenic accumulation rates. The relationship with the K factor suggests that erosion may be an important pathway of copper to Michigan lakes; however, this relationship is not strong (Figure 16), and this variable is less important to the predictive model than population density. Due to regional influence of mining in northern Michigan, and the usage of copper sulfate in two southern lakes, only nine lakes were included in the analyses, and results must be interpreted with care.



**Figure 16.** Average log anthropogenic accumulation rates ( $\text{mg m}^{-2} \text{y}^{-1}$ ) of copper in sediments deposited in the 1970s plotted versus log population density (people  $\text{km}^{-2}$ ), and log slope corrected k-factor.

Similar to cadmium, the best predictor of copper accumulation rates in the 1990s is urban land cover ( $r^2 = 0.81$ ,  $n = 10$ , Figure 17):

$$\text{Log (CU90}_{\text{faar}}) = 1.094 \times \text{log (URBAN90)} + 2.410$$

Where:

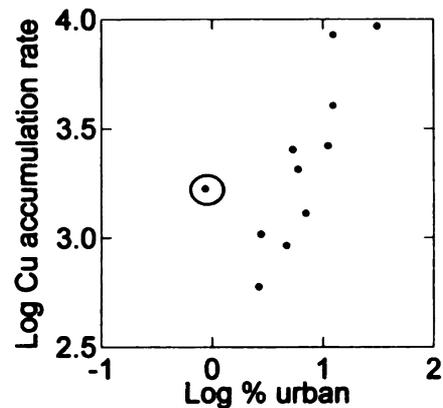
CU90<sub>faar</sub> is focusing corrected anthropogenic accumulation rates of copper in the 1990s ( $\mu\text{g m}^{-2} \text{y}^{-1}$ ), and

URBAN90 is percentage urban land cover in the watershed.

These results suggest that watershed scale sources remain influential during the 1990s with sources related to urban land cover. Possible sources may include wear from household plumbing and automobiles, and household waste (Rice, 1999; Callender and Rice, 2000; Mecray et al., 2001).

In addition to identifying possible source of copper, examination of the relationships between copper accumulation rates and watershed characteristics provided evidence that Gratiot Lake was influenced by copper mining in the region. Although this lake is located in a region with extensive copper mining, no mining

occurred within the watershed of Gratiot Lake, and copper accumulation rates were not higher than most other lakes (Figure 4). Therefore, although it was likely that smelting and other sources in the region influenced the lake, there was little direct evidence until copper accumulation rates were correlated with watershed characteristics. Gratiot Lake consistently had higher copper accumulation rates than anticipated from the watershed



**Figure 17.** Average log anthropogenic accumulation rates ( $\text{mg m}^{-2} \text{y}^{-1}$ ) of copper in sediments deposited in the 1990s plotted versus log percent urban landcover of the watersheds. Gratiot Lake is circled, and was not included in regression analysis.

characteristic (e.g., Figure 17). This lends strong support to the conclusion that there was a source for copper that influenced Gratiot Lake and not other lakes in the state. This also suggests that this approach will be useful in identifying lakes with unique sources within their watersheds.

### *Zinc*

The best predictor of zinc accumulation rates in Michigan lakes in the 1970s is population density ( $r^2 = 0.92$ ,  $n = 10$ , Figure 18) if Cadillac Lake is removed:

$$\text{Log (ZN70}_{\text{faar}}) = 0.466 \times \text{log (POPDENS70)} + 3.678$$

Where:

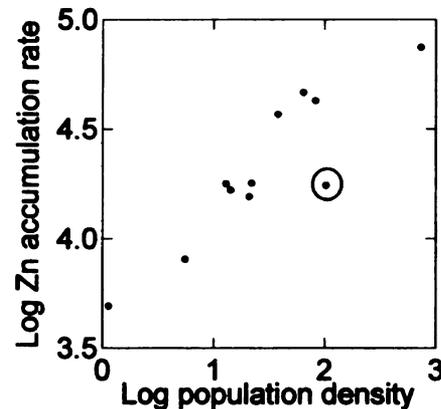
$\text{ZN70}_{\text{faar}}$  is focusing corrected anthropogenic accumulation rates of zinc in the 1970s ( $\mu\text{g m}^{-2} \text{y}^{-1}$ ), and

$\text{POPDENS70}$  is population density in the watershed in the 1970s ( $\text{people km}^{-2}$ )

Cadillac Lake is an outlier in this relationship, and the inclusion of this one lake reduces the  $r^2$  to 0.82. The cause of this is unclear, but Cadillac Lake is one of two lakes (Cadillac and Cass) with a city located in the watershed. Only some of the City of Cadillac is located within the watershed, and it is possible that sewage and stormwater is directed outside of the watershed. This could result in the lower than anticipated zinc accumulation rates for the population density of the watershed.

Zinc is known to have both regional atmospheric sources [fossil fuel combustion (Callender and Rice, 2000), iron and steel industry (Winchester and Nifong, 1971)] and

watershed scale sources [corrosion of metal products containing zinc (Callender and Rice, 2000), wear from automobile tires (Callender and Rice, 2000)]. The strong positive correlation between population density and zinc anthropogenic accumulation rates in the 1970s suggests that watershed scale influences are significant during this



**Figure 18.** Average log anthropogenic accumulation rates ( $\text{mg m}^{-2} \text{y}^{-1}$ ) of zinc in sediments deposited in the 1970s plotted versus log population density ( $\text{people km}^{-2}$ ). The circled data point represents Cadillac Lake.

time period. Atmospheric sources are probably still present, as suggested by the measurement of atmospheric deposition of zinc, but local sources related to population density seem to be more significant.

Percentage urban land cover in the watershed and slope in a 100 m buffer are the best predictors of zinc accumulation rates in the 1990s ( $r^2 = 0.909$ ,  $n = 11$ , Figure 19):

$$\text{Log (ZN90}_{\text{faar}}) = 0.506 \times \text{log (URBAN90)} - 0.649 \times (\text{SLOPE}_{100\text{m}}) + 3.980$$

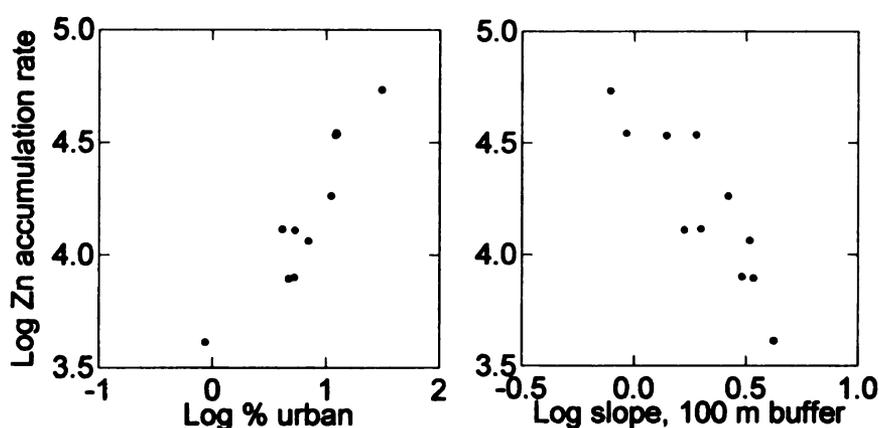
Where:

$\text{ZN90}_{\text{faar}}$  is focusing corrected anthropogenic accumulation rates of zinc in the 1990s ( $\mu\text{g m}^{-2} \text{y}^{-1}$ ),

URBAN90 is percentage urban land cover in the 1990s, and

$\text{SLOPE}_{100\text{m}}$  is average slope (degrees) in a 100 m buffer around the lake.

URBAN90 is weighted more highly in the model (standardized coefficient URBAN90 = 0.581,  $\text{SLOPE}_{100\text{m}} = -0.445$ ).



**Figure 19.** Average log anthropogenic accumulation rates ( $\text{mg m}^{-2} \text{y}^{-1}$ ) of zinc in sediments deposited in the 1990s plotted versus log percentage urban in the watershed, and log slope within a 100 m buffer of the lake (degrees).

This model may reflect the continued importance of watershed scale sources of zinc, including wear of tires and corrosion of metal products, as well as some contribution from atmospheric deposition.

### **Summary and Conclusions**

Anthropogenic accumulation rates of both zinc and cadmium have decreased from the 1970s to the 1990s in the majority of Michigan lakes sampled. This suggests that the combination of reduced industrial activity (e.g., reduction of steel production, Perkins et al., 2000) and increased environmental legislation has effectively reduced inputs of cadmium and zinc to Michigan lakes.

Sources of cadmium appear to have shifted from dominantly atmospheric in the 1970s to watershed scale sources dominating in the 1990s, though atmospheric sources are probably still present. Atmospheric sources may include burning of fossil fuels, while watershed scale sources may include tire wear and other sources related to urban land cover.

Zinc has both watershed scale and regional sources as well, with the burning of fossil fuels releasing zinc to the atmosphere, and tire wear and metal corrosion potentially releasing zinc within the watershed. Zinc anthropogenic accumulation rates correlate with watershed scale characteristics during both time periods, population density in the 1970s, and percentage urban land cover in the 1990s, but it is unclear whether sources have remained the same over time or if new sources have appeared. Zinc also correlates with slope in a 100 m buffer in the 1990s, which may suggest that atmospheric deposition is also an important pathway during this time period.

Copper anthropogenic accumulation rates have not decreased in many lakes from the 1970s to the 1990s, suggesting that sources of copper to the environment have not been reduced. Copper may be released to the atmosphere from the burning of coal and fossil fuels, or from wear of disk pads on automobiles, wear of copper pipes, and other urban related sources. Anthropogenic accumulation rates of copper correlate with watershed scale characteristics during both time periods, suggesting that, even if atmospheric deposition contributes to copper accumulation in lake sediments, local sources are important as well.

For all metals, percentage urban land cover within the entire watershed is one of the best predictor of rates metal accumulation rates in the 1990s. This indicates that urban land cover is one of the dominant sources of these metals to Michigan lakes, and that the location of the urban land cover within the watershed does not matter. The exact sources of metals from the urban land cover cannot be determined by this study, and future work should focus on sources and pathways of metals to the lake from urban land cover. These sources could potentially then be reduced, resulting in sediment quality improvement and decreased loading of these trace metals to the environment.

The approach of examining anthropogenic accumulation rates of metals in lake sediments over space and time, and correlating these patterns to watershed characteristics has successfully provided insight into effects of environmental legislation, and the changing sources of metals over time. It is also useful in identifying lakes with unique sources, such as the influence of mining on Gratiot Lake. Additionally, this approach has identified the area to examine for current sources of

**these metals to urban land cover. This knowledge could help to further reduce anthropogenic inputs of cadmium, copper and zinc to the environment.**

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## CHAPTER 8 SUMMARY AND RECOMMENDATIONS

### Summary

The working hypothesis of this research is: sources and pathways controlling anthropogenic accumulation rates of metals sediments have changed over time, and these changes should be reflected both in the spatial patterns of metal accumulation rates in lake sediments and the changing correlations between metal accumulation rates and characteristics of the lake watersheds. This was investigated through a three step approach: 1) identification of groups of elements that are influenced by the same sources and processes, and selection of elements that are representative of each group to assist in calculating anthropogenic accumulation rates, 2) determination of correlations between different watershed characteristics (e.g., percentage urban land cover) and calculated anthropogenic accumulation rates of each of the elements determined to have direct anthropogenic inputs for each of the two time periods (1970-1980, 1990-2000), 3) examination of temporal changes in correlations with different watershed characteristics.

Four groupings of elements, terrestrial, diagenetic, carbonate and anthropogenic, were present in the majority of lakes and were differentiated using cluster analysis. The two groupings that were the most useful in quantifying anthropogenic accumulation rates were the diagenetic and terrestrial groups. The elements representative of the diagenetic group (iron, manganese, and molybdenum), were used to help determine if elements with known anthropogenic sources (e.g., arsenic) were also influenced by diagenesis. The elements representing terrestrial

inputs (aluminum and titanium), were used to differentiate natural inputs, inputs due to increased erosion, and direct human inputs for cadmium, copper, lead and zinc. The effects of logging and other land cover changes were clearly seen in the temporal patterns of the terrestrial elements in some lakes (e.g., Elk and Gull lakes).

To evaluate the relationships between watershed characteristics and anthropogenic accumulation rates of lead, copper, cadmium, and zinc, multiple variables representing different sources and pathways to the lake with a two variable linear regression model were used. The six most effective variables for predicting anthropogenic accumulation rates of the four metals include sulfate deposition, slope corrected K factor, percentage urban land cover, population density, average slope within the watershed, and average slope in a 100 m buffer around the lake.

Sulfate deposition was chosen as a watershed characteristic to represent the pathway of atmospheric deposition, and may represent metals released from the burning of coal and other fossil fuels from both the urban and industrial area of Chicago, Illinois and Gary, Indiana, and smaller sources throughout Michigan. The slope corrected K factor should represent the pathway of erosion, and transport of metals deposited on land to the lake. Percentage urban land cover in the watershed and watershed population densities may represent similar sources, including: releases from wear of automobile parts (Rice, 1999), car emissions (Callender and vanMetre, 1997; Rice, 1999; Shahin et al., 2000), road dust (Shahin et al., 2000), wastewater and household and yard waste (Callender and Rice, 2000). The significance of average slope of the watershed and slope within a 100 m buffer are less clear, because the negative relationship between metal accumulation rates and slope clearly shows that

slope is not representing the pathway of erosion. There is no apparent causal relationship between slope and metal anthropogenic accumulation rates, but watershed slopes do tend to follow a similar pattern to the overall population density and urban development in the state, with shallower slopes and greater development in the south-east. As a result, slope may be representing local atmospheric deposition that is not confined to the watershed, but influenced by the overall population distribution in the area. The meaning of this variable, however, needs to be further investigated for clarification.

Correlations between anthropogenic accumulation rates of lead, copper, cadmium, zinc and watershed characteristics were surprisingly high; multiple  $r^2$  values using one or two watershed characteristics as predictor variables were greater than 0.8 for all cases except cadmium in the 1990s ( $r^2 = 0.53$ ). The watershed characteristics that were included in the multiple regression models for each of the elements include:

**Cadmium 1970s: average slope of the watershed, sulfate deposition rates**

$$(r^2 = 0.85)$$

**1990s: percentage urban land cover in watershed ( $r^2 = 0.53$ )**

**Copper 1970s: watershed population density, slope corrected K factor**

$$(r^2 = 0.84)$$

**1990s: percentage urban land cover in watershed, slope in 100 m buffer around lake ( $r^2 = 0.81$ )**

**Lead 1970s: sulfate deposition rates, slope in 100 m buffer around lake**

$$(r^2 = 0.92)$$

1990s: percentage urban land cover, slope in 100 m buffer

$$(r^2 = 0.92)$$

Zinc 1970s: watershed population density ( $r^2 = 0.92$ )

1990s: percentage urban land cover, slope in 100 m buffer

$$(r^2 = 0.91)$$

There are changes over time in anthropogenic accumulation rates, spatial patterns and correlations with watershed characteristics. Anthropogenic accumulation rates of cadmium, lead, and zinc decrease in the majority of lakes from the 1970s to the 1990s, indicating that inputs of these metals to the environment have been reduced, probably due to environmental legislation. Copper anthropogenic accumulation rates have not consistently decreased since the 1970s, suggesting that historic sources have not decreased or that new sources have emerged.

Both spatial patterns and multivariate regression models for lead and cadmium suggest that there has been a shift from atmospheric deposition in the 1970s to more local sources in the 1990s that are related to urban land cover. The major atmospheric sources that were present in the 1970s, such as the burning of leaded gasoline in automobiles or burning of coal for major industries, were reduced by environmental legislation such as the Clean Air Act. As a result, anthropogenic accumulation rates are lower in the 1990s and the dominant sources are different than the 1970s. Copper and zinc do not show this same change over time; with population density the best predictor in the 1970s and urban land cover in the 1990s, suggesting that local sources were important during both time periods. Atmospheric transport and deposition is

probably present during both time periods, but appears to be less important than local sources. Percentage urban land cover within the watershed is the best predictor of anthropogenic accumulation rates of all four metals in the 1990s, suggesting that sources within the watershed contribute more significantly than atmospheric deposition. Future work may identify specific sources of these metals and reduce their inputs to the environment.

This research both corroborates previous work and provides new insight into the changing sources and pathways of trace metals in the environment. Lead in the environment has been extensively studied, and this work is in agreement with previous studies concluding that atmospheric transport of lead from the burning of leaded gasoline and coal burning were important sources in the 1970s, and that the Clean Air Act significantly reduce lead inputs to the environment (Callender and vanMetre, 1997; Edgington and Robbins, 1976; Eisenreich et al., 1986; Evans and Dillon, 1982; Graney et al., 1995; Nriagu, 1978). However, current sources of lead are not well defined. This work has identified a definitive correlation between urban land cover and anthropogenic accumulation rates of lead in the 1990s, indicating that current sources are present that need to be identified and reduced.

Cadmium, copper, and zinc in the environment have not been as intensively studied as lead, and trends over time have not been thoroughly explored. The regional decrease of cadmium and zinc inputs to the environment after the 1970s corroborates previous work (Alfaro-De la Torre and Tessier, 2002; Mecray et al., 2001), but shows that these decreases are present over a broader region than their studies. The relatively constant accumulation rates of copper over the last three decades were unexpected,

and are in contrast with previous work on the Great Lakes (Kolak et al., 1998). This study shows that environmental legislation has been less effective for copper, and methods for reducing copper loading to the environment must be reevaluated.

The impact of urban land cover has been determined previously, but this is the first research to show strong correlations between several metals and urban land cover over a broad geographic scale. Additionally, little work has been done on historic regional sources of cadmium, copper, and zinc. Much of the previous work done on these elements included the sampling of only one lake, making it difficult to determine if the results represented only that specific watershed or what was occurring in the regional environment. The relatively large number of lakes sampled in this work allows generalized conclusions to be made about the change in sources from regional to atmospheric for cadmium, and the continuing importance of local sources in both the 1970s and 1990s for copper and zinc.

The approach of sampling spatially and correlating a current environmental parameter with watershed characteristics is becoming common for stream, rivers, estuaries, and lakes (Detenbeck et al., 1993; Gergel et al., 2002; Griffith, 2002; Hunsaker and Levine, 1995; Jones et al., 2001; Paul et al., 2002; Rice, 1999; Soranno et al., 1996), but this study has taken this approach one step further by combining historical and regional aspects, and is the first such study to use sediment chronologies for such a large number of lakes. The high correlations found between metal accumulation rates and watershed characteristics show that this approach can successfully provide new insight into the history of metal loading to a region, and the sources and pathways of those metals through the environment.

## **Recommendations**

This work has many practical applications, both with the current results and as guidance for future work. Outlined below are suggestions for future work, and a discussion of the benefits and possible applications of this study.

1. Correlate level 3 urban land cover with metal accumulation rates to obtain more information about possible sources that are associated with urban land cover. The 1990s land cover data can be sub-divided into low intensity urban ( $\geq 10\%$  cover with manmade structures) and high intensity urban ( $\geq 25\%$  covered with manmade structures), which can be further divided into “airport”, “road/parking lot”, and “other high intensity urban”. It is possible that one of these subcategories, such as road/parking lot, may correlate as well, or better than total percentage urban in the watershed. This would result in a clearer idea of possible sources of cadmium, copper, lead and zinc to the environment.
2. Investigate actual urban sources. This work has identified urban land cover as representing significant sources of trace metals to the environment in the 1990s, but to identify the actual sources further work is needed. A more detailed study with measurements of releases of metals from potential sources could provide the information necessary to reduce trace metals inputs to the environment.
3. Determine the significance of the slope and slope within a 100 m buffer variables. The meaning of these variables remains unclear, and yet these two watershed characteristics correlate very highly with metal

anthropogenic accumulation rates. Other variables that might represent regional population distribution (e.g., population density in a 10 km buffer around the lake) could be quantified, and correlated with both metal accumulation rates and slope. Additionally, lakes that have relatively steep slopes and are located in southern Michigan could be identified and sampled to help determine if a causal relationship exists. If there is no causal relationship, and slope represents a regional gradient that is present only in Michigan, another variable should be identified before this model can be applied to other regions.

4. Install atmospheric deposition traps near lake shorelines to compare actual rates of atmospheric deposition to deposition rates in the lake sediment.
5. Identify a quantifiable factor to represent the intensity of recreation use of the lake. Many Michigan lakes have extensive recreational usage which may act as a source of trace metals, but is not accounted for by any of the watershed characteristics in this study.
6. Test the multivariate regression models with additional Michigan lakes for model validation. As part of the Michigan Department of Environmental Quality's Sediment Trend Monitoring Program, Michigan lakes will continue to be sampled and these lakes can be used for model validation.
7. Test the multivariate regression models in other regions. The approach for developing these statistical models should have widespread applicability in any region with sufficient lakes or reservoirs. However, it is unclear if the variables that correlate highly will remain the same in the different region,

particularly the slope variable. Using this approach in a different region will allow a comparison of the importance of different watershed characteristics over a broader spatial area.

Overall, this work has benefits at many different scales. Locally, contaminant sediment concentrations and accumulation rates of trace metals are of great interest to those living around a lake. The sediment chronologies collected also provide detailed histories of contaminant inputs, and if metals accumulation rates are increasing or decreasing. Regionally, information on metal accumulation rates and concentrations across the state help identify those lakes with high levels of contamination. Additionally, the multivariate regression models that were determined can be used to help identify sources that are present in most Michigan lakes, as well as identify lakes with unique sources (e.g., copper in Gratiot Lake). The importance of urban land cover in the 1990s was identified which will allow for further investigation and possible reduction of sources of trace metals. It is now also possible to assess whether a lake is likely to have high accumulation rates of trace metals based on the characteristics of the watershed. This will help identify those lakes that are most appropriate to sample in the future.

Scientifically, this approach to identifying potential sources and evaluating changes over time was successful, and may be applied to other regions. This provides an important method for evaluating not only current sources and pathways, but also comparing these results to historical data. Although the approach of correlating watershed characteristics to current water quality variables has been extensively investigated, the success of using lake sediment chronologies may result in a better

**understanding in of the changing importance of different sources and pathways of  
contaminants in the environment.**

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## APPENDICIES

**APPENDIX A**

**SEDIMENT CHEMICAL AND WATERSHED CHARACTERISTICS DATA**

## APPENDIX A. SEDIMENT CHEMICAL AND WATERSHED CHARACTERISTICS DATA

Sediment concentration,  $^{210}\text{Pb}$  activities and dates, and core descriptions can be found in Michigan Department of Environmental Quality reports including:

### Cass, Gratiot, Gull, Elk and Higgins lakes:

Simpson, S.J., Long, D.T., Geisey, J.P. and Fett, J.D., 2000. Inland lakes sediment trends: sediment analysis results for five Michigan Lakes (MI/DEQ/SWQ-01/030), Department of Environmental Quality, East Lansing, MI.  
[http://www.michigan.gov/deq/0,1607,7-135-3313\\_3686\\_3728-32365--,00.html](http://www.michigan.gov/deq/0,1607,7-135-3313_3686_3728-32365--,00.html)

### Crystal M and Littlefield lakes:

Yohn, S.S., Long, D.T., Giesy, J.P., Fett, J.D. and Kannan, K., 2001. Inland lakes sediment trends: sediment analysis results for two Michigan Lakes. MI/DEQ/WD-02/115, Department of Environmental Quality, East Lansing.

### Cadillac, Crystal B, Mullet, Paw Paw and Whitmore lakes:

Yohn, S.S., Long, D.T., Giesy, J.P., Scholle, L.K., Patino, L.C., Fett, J.D. and Kannan, K., 2002. Inland lakes sediment trends: sediment analysis results for five Michigan Lakes. MI/DEQ/WD-03/052, Department of Environmental Quality, East Lansing.

### Houghton, Hubbard, Imp, Round, Torch, Witch lakes:

Yohn, S.S., Parsons, M.J., Long, D.T., Giesy, J.P., Scholle, L.K. and Patino, L.C., 2003. Inland lakes sediment trends: sediment analysis results for six Michigan Lakes, Michigan Department of Environmental Quality, East Lansing, MI.

**Table 1.** Focusing corrected anthropogenic inventories ( $\mu\text{g}/\text{cm}^2$ ) of cadmium, copper, lead and zinc in fifteen Michigan lakes. Inventories could not be calculated for Cass and Witch lakes.

Lake	Cadmium	Copper	Lead	Zinc
Cadillac	1.0	246	140	121
Crystal B		14	98	
Crystal M	2.0	6	169	111
Elk	0.9	7	74	103
Gratiot	0.6	15	51	48
Gull	1.5	14	208	193
Higgins	1.8	14	112	132
Houghton	1.4	173	92	116
Imp	0.7		51	
Littlefield*	1.2		108	
Mullett	1.0	8.5	81	
Paw Paw**			227	
Round	1.2		78	69
Torch	1.2		61	

\* Focusing factor (2.0) was estimated from lakes sampled in 1999-2000.

\*\* Background concentrations were estimated from Higgins Lake.

**Table 2.** Focusing corrected anthropogenic accumulation rates ( $\mu\text{g}/\text{m}^2/\text{y}$ ) of cadmium, copper, lead and zinc averaged from 1970 – 1980.

Lake	Copper	Cadmium	Lead	Zinc
Cadillac	41546	172	25447	17481
Cass	9876	345	75462	74481
Crystal B	1165	165	9921	
Crystal M	1043	219	26113	17908
Elk	1044	105	14604	15531
Gratiot	1471	55	6299	4913
Gull	3810	217	42479	36941
Higgins	1702	190	17068	16653
Houghton	41448	219	18172	17788
Imp	285	67	7098	2196
Littlefield		191	31246	
Mullett	1136	99	13686	
Paw Paw	8198	197	40381	42589
Round		108	10402	8041
Torch		130	9196	
Whitmore	3647	405	56650	46397

**Table 3.** Focusing corrected anthropogenic accumulation rates ( $\mu\text{g}/\text{m}^2/\text{y}$ ) of cadmium, copper, lead and zinc averaged from 1990 – 2000.

Lake	Copper	Cadmium	Lead	Zinc
Cadillac	82245	264	37193	34077
Cass	9299	182	40067	54103
Crystal B	2058	238	13837	
Crystal M	2637	208	24814	18275
Elk	922	63	7685	7824
Gratiot	1678	44	4484	4102
Gull	2537	43	10969	12875
Higgins	1296	141	13049	11547
Houghton	34166	161	12787	13025
Imp	651	58	5862	2210
Littlefield	598	98	14692	
Mullett	1038	63	7670	
Paw Paw	8491	123	18881	34324
Round		103	9961	7945
Torch		79	8535	
Whitmore	4023	278	31858	34897

**Table 4.** Watershed characteristics that do not vary over time.

Watershed parameter	Watershed area	Lake area	Watershed: lake ratio	SO <sub>4</sub>	K-factor	K-factor slope corr.	Slope
Lake/Units	km <sup>2</sup>	km <sup>2</sup>		kg/ha/y			degrees
Cadillac	42.8	4.7	9.2	16.7	0.15	0.14	2.62
Cass	41.9	5.2	8.1	16.2	0.22	0.11	0.96
Crystal B	66.2	39.3	1.7	15.7	0.16	0.18	4.82
Crystal M	9.2	2.9	3.2	16.4	0.25	0.15	2.11
Elk	98.1	31.3	3.1	14.7	0.19	0.27	3.38
Gratiot	21.1	5.8	3.6	8.5	0.16	0.12	5.32
Gull	53.4	8.2	6.5	18.5	0.26	0.12	1.96
Higgins	67.2	38.9	1.7	14.9	0.12	0.08	2.46
Houghton	380.3	81.2	4.7	15.1	0.13	0.06	1.87
Imp	1.7	0.3	5.0	8.8	0.31	0.20	3.77
Littlefield	16.4	0.7	22.1	15.8	0.21	0.09	3.20
Mullett	1285.8	70.3	18.3	12.6	0.16	0.14	3.36
Paw Paw	25.9	3.7	6.9	19.4	0.28	0.08	1.99
Round	15.5	7.0	2.2	12.2	0.18	0.12	2.74
Torch	115.7	76.0	1.5	14.1	0.19	0.29	4.31
Whitmore	9.1	2.7	3.3	16.6	0.23	0.14	1.10
Witch	11.1	0.9	13.0	9.3	0.29	0.16	2.90

**Table 4 (cont'd)**

Watershed parameter	k-factor, 100 m	k-factor, slope, 100 m	Slope, 100 m
Lake/Units	degrees		
Cadillac	0.14	0.07	1.398
Cass	0.28	0.09	0.785
Crystal B	0.17	0.17	8.741
Crystal M	0.32	0.16	2.636
Elk	0.18	0.28	3.419
Gratiot	0.16	0.09	4.213
Gull	0.26	0.12	1.681
Higgins	0.13	0.10	3.29
Houghton	0.13	0.06	1.991
Imp	0.31	0.20	5.661
Littlefield	0.26	0.01	1.28
Mullett	0.15	0.07	2.727
Paw Paw	0.33	0.09	1.896
Round	0.19	0.10	3.04
Torch	0.19	0.29	4.643
Whitmore	0.20	0.18	0.924
Witch	0.29	0.16	3.136

**Table 5.** Watershed characteristics for the 1970s (1970-1980). “Ag” indicates agriculture, “100 m” indicates within 100 m buffer of the lake, “fiv” indicates flow inverted value, “fip” indicates flow inverted percent, “fisv” indicates flow inverted squared value, “fisp” indicates flow inverted squared percent.

Watershed parameter	Population density	Population	% urban	% ag	% range	% forest	% wetland
Lake/Units	people/km	people	%	%	%	%	%
Cadillac	102.6	4394.7	19.7	40.7	10.2	24.4	4.1
Cass	736.6	30580.5	60.5	2.4	13.9	8.6	12.2
Crystal B	23.5	1572.0	12.4	12.9	21.2	51.9	1.2
Crystal M	21.9	201.9	11.1	58.2	5.0	16.9	8.2
Elk	20.9	2084.7	6.3	28.0	19.8	41.0	3.9
Gratiot	1.1	24.1	0.8	0.0	0.0	98.1	0.6
Gull	37.9	1998.9	9.7	59.0	7.9	14.1	5.8
Higgins	14.2	981.8	15.0	0.5	3.5	77.4	3.4
Houghton	12.9	4776.6	7.1	1.6	5.3	74.5	9.8
Imp	1.4	2.4	7.3	0.0	0.0	86.7	4.9
Littlefield	8.0	131.5	1.8	9.3	13.8	69.7	4.2
Mullett	6.6	8474.7	3.0	7.4	15.2	70.8	2.9
Paw Paw	82.5	2127.0	17.3	30.1	13.2	35.0	2.1
Round	5.5	84.9	4.8	13.8	11.4	68.5	1.0
Torch	16.1	1961.6	7.3	23.5	21.9	44.8	1.9
Whitmore	64.3	558.1	22.1	23.5	20.5	23.7	8.7
Witch	4.8	53.3	1.8	2.9	6.7	80.6	6.5

Table 5 (cont'd).

Watershed parameter	Urban	Ag	Range	Forest	Wetland	%Forest 100 m	%Ag 100 m
Lake/Units	km <sup>2</sup>	%	%				
Cadillac	8.45	17.41	4.35	10.43	1.76	3.06	0.00
Cass	25.34	1.02	5.83	3.59	5.11	2.68	0.00
Crystal B	8.20	8.55	14.06	34.34	0.80	26.34	0.47
Crystal M	1.02	5.38	0.46	1.56	0.76	0.56	12.84
Elk	6.20	27.43	19.46	40.22	3.85	20.92	7.88
Gratiot	0.18	0.00	0.00	20.67	0.13	79.07	0.00
Gull	5.18	31.51	4.22	7.55	3.09	4.86	0.07
Higgins	10.07	0.33	2.33	52.01	2.31	12.24	0.00
Houghton	27.04	6.16	20.09	283.39	37.41	4.19	0.38
Imp	0.12	0.00	0.00	1.48	0.08	60.99	0.00
Littlefield	0.30	1.53	2.26	11.42	0.69	43.16	0.00
Mullett	38.45	94.59	195.22	910.66	36.78	38.83	0.43
Paw Paw	4.50	7.81	3.42	9.08	0.54	1.90	0.64
Round	0.74	2.14	1.77	10.63	0.15	43.66	0.00
Torch	8.48	27.20	25.39	51.88	2.21	24.02	0.15
Whitmore	2.00	2.13	1.86	2.15	0.79	3.00	0.27
Witch	0.20	0.33	0.74	8.94	0.72	75.67	0.00
Watershed parameter	%range 100 m	%urban 100 m	%wetland 100 m	Forest 100 m	Ag 100 m	Range 100 m	Urban 100 m
Lake/Units	%	%	%	km <sup>2</sup>	km <sup>2</sup>	km <sup>2</sup>	km <sup>2</sup>
Cadillac	1.36	86.67	1.95	0.03	0.00	0.01	0.92
Cass	1.58	63.80	8.65	0.04	0.00	0.02	0.94
Crystal B	0.64	68.18	1.43	0.96	0.02	0.02	2.49
Crystal M	0.00	76.74	1.37	0.00	0.09	0.00	0.53
Elk	9.40	49.83	5.83	1.01	0.38	0.46	2.41
Gratiot	0.00	10.52	2.25	0.87	0.00	0.00	0.12
Gull	3.42	84.25	0.00	0.10	0.00	0.07	1.72
Higgins	0.40	82.48	0.00	0.42	0.00	0.01	2.81
Houghton	1.24	86.39	4.14	0.25	0.02	0.07	5.09
Imp	0.00	35.62	0.00	0.17	0.00	0.00	0.10
Littlefield	1.60	25.52	9.10	0.34	0.00	0.01	0.20
Mullett	5.22	38.65	12.30	2.83	0.03	0.38	2.81
Paw Paw	2.70	82.42	4.67	0.03	0.01	0.04	1.24
Round	10.28	37.67	0.60	0.49	0.00	0.12	0.42
Torch	10.99	62.34	0.83	1.61	0.01	0.74	4.18
Whitmore	7.88	83.19	2.91	0.02	0.00	0.06	0.64
Witch	8.72	10.53	0.00	0.38	0.00	0.04	0.05

Table 5 (cont'd).

Watershed parameter	Wetland 100 m	Urban fiv	Ag fiv	Range fiv	Forest fiv	Wetland fiv	Urban fip
Lake/Units	km <sup>2</sup>						%
Cadillac	0.02	22.26	5.10	1.96	4.43	1.87	62.5
Cass	0.13	2.58	0.05	0.47	0.32	0.56	64.9
Crystal B	0.05	49.57	5.17	7.75	48.86	0.76	44.2
Crystal M	0.01	10.16	5.43	0.31	1.36	0.52	57.2
Elk	0.28	44.84	21.34	24.68	33.02	7.83	34.0
Gratiot	0.02	2.35	0.00	0.00	154.75	2.18	1.5
Gull	0.00	29.11	12.56	4.23	8.58	2.18	51.4
Higgins	0.00	61.95	0.32	1.78	43.67	1.35	56.8
Houghton	0.24	88.42	2.25	5.87	65.66	16.04	49.6
Imp	0.00	1.93	0.00	0.00	5.95	0.24	23.8
Littlefield	0.07	1.66	0.59	1.41	14.65	2.00	8.2
Mullett	0.90	56.92	12.69	29.00	127.08	13.34	23.8
Paw Paw	0.07	20.69	4.23	2.32	5.31	1.66	60.5
Round	0.01	6.61	2.59	4.64	18.39	0.18	20.4
Torch	0.06	73.13	16.11	39.43	76.63	3.07	35.1
Whitmore	0.02	1.04	0.18	0.36	0.34	0.16	50.3
Witch	0.00	1.18	0.21	1.34	14.09	0.42	6.9
Watershed parameter	Ag fip	Range fip	Forest fip	Wetland fip	Urban fiv	Ag fiv	Range fiv
Lake/Units	%	%	%	%			
Cadillac	14.3	5.5	12.4	5.3	0.316	0.003	0.009
Cass	1.1	11.8	8.1	14.1	0.014	0.000	0.001
Crystal B	4.6	6.9	43.6	0.7	1.096	0.011	0.012
Crystal M	30.6	1.7	7.7	2.9	0.217	0.019	0.000
Elk	16.2	18.7	25.1	5.9	0.996	0.057	0.192
Gratiot	0.0	0.0	97.2	1.4	0.065	0.000	0.000
Gull	22.2	7.5	15.1	3.8	0.542	0.008	0.017
Higgins	0.3	1.6	40.0	1.2	1.199	0.000	0.003
Houghton	1.3	3.3	36.8	9.0	1.588	0.010	0.023
Imp	0.0	0.0	73.3	2.9	0.049	0.000	0.000
Littlefield	2.9	7.0	72.1	9.8	0.027	0.000	0.001
Mullett	5.3	12.1	53.2	5.6	1.169	0.022	0.124
Paw Paw	12.4	6.8	15.5	4.9	0.341	0.005	0.005
Round	8.0	14.3	56.7	0.6	0.159	0.004	0.047
Torch	7.7	18.9	36.8	1.5	1.583	0.023	0.303
Whitmore	8.5	17.2	16.3	7.6	0.009	0.000	0.002
Witch	1.2	7.8	81.7	2.4	0.023	0.000	0.013

Table 5 (cont'd).

Watershed parameter	Forest fisv	Wetland fisv	Urban fisp	Ag fisp	Range fisp	Forest fisp	Wetland fisp
Lake/Units			%	%	%	%	%
Cadillac	0.015	0.007	90.5	0.7	2.6	4.2	1.9
Cass	0.001	0.002	74.7	0.1	7.6	6.4	11.2
Crystal B	0.308	0.002	76.7	0.8	0.8	21.6	0.2
Crystal M	0.003	0.005	89.2	7.6	0.1	1.1	1.9
Elk	0.317	0.120	59.2	3.4	11.4	18.8	7.2
Gratiot	2.786	0.053	2.2	0.0	0.0	96.0	1.8
Gull	0.038	0.003	89.2	1.4	2.7	6.2	0.5
Higgins	0.192	0.002	85.9	0.0	0.2	13.7	0.1
Houghton	0.124	0.123	85.0	0.5	1.2	6.6	6.6
Imp	0.071	0.001	40.8	0.0	0.0	58.6	0.6
Littlefield	0.103	0.040	16.0	0.1	0.7	59.8	23.4
Mullett	0.553	0.134	58.4	1.1	6.2	27.6	6.7
Paw Paw	0.014	0.028	86.5	1.4	1.4	3.6	7.2
Round	0.145	0.000	44.6	1.1	13.3	40.9	0.1
Torch	0.688	0.024	60.4	0.9	11.6	26.2	0.9
Whitmore	0.001	0.000	73.4	1.9	15.1	7.0	2.7
Witch	0.175	0.000	11.0	0.1	6.2	82.5	0.1

**Table 6.** Watershed characteristics for the 1990s (1990-2000). “Ag” indicates agriculture, “up” indicates upland/openland, “100 m” indicates within 100 m buffer of the lake, “fiv” indicates flow inverted value, “fip” indicates flow inverted percent, “fisv” indicates flow inverted squared value, “fisp” indicates flow inverted squared percent.

Watershed parameter	Population density	Population	% urban	% ag	% up	% forest	% wetland
Lake/Units	people/km	people	%	%	%	%	%
Cadillac	120.3	5154.5	12.0	33.5	18.7	30.9	2.0
Cass	832.2	34550.5	31.0	0.5	19.1	38.1	10.2
Crystal B	29.8	1989.0	6.0	10.8	22.3	58.9	0.9
Crystal M	29.5	271.3	11.1	49.4	2.8	21.1	13.5
Elk	36.0	3588.9	4.7	24.7	17.7	49.6	1.8
Gratiot	1.6	34.8	0.9	0.0	6.2	89.0	3.5
Gull	45.8	2416.5	5.3	57.7	6.3	22.2	5.8
Higgins	35.3	2434.6	7.0	0.1	15.3	72.9	3.7
Houghton	23.5	8660.2	4.1	0.8	15.3	62.2	15.7
Imp	1.7	2.9	1.7	0.0	0.5	94.9	0.7
Littlefield	11.6	189.0	2.6	5.1	13.1	73.6	4.2
Mullett	9.8	12600.1	2.8	7.5	17.6	68.0	3.1
Paw Paw	101.7	2621.0	12.4	33.6	14.1	31.9	6.6
Round	4.8	74.1	5.3	8.3	9.3	67.2	9.1
Torch	22.1	2682.8	4.1	18.1	19.3	55.3	1.6
Whitmore	144.8	1256.4	12.3	17.0	16.0	41.8	11.7
Witch	3.1	34.6	4.0	0.0	4.9	86.7	2.1

Table 6 (cont'd).

Watershed parameter	Urban	Ag	Up	Forest	Wetland	%Forest 100 m	%Ag 100 m
Lake/Units	km <sup>2</sup>	%	%				
Cadillac	5.2	14.3	8.0	13.2	0.9	25.4	0.8
Cass	13.0	0.2	8.0	15.9	4.3	48.7	0.0
Crystal B	3.9	7.2	14.8	39.0	0.6	45.4	1.9
Crystal M	1.0	4.6	0.3	1.9	1.2	10.7	7.9
Elk	4.6	24.3	17.3	48.7	1.8	48.8	7.5
Gratiot	0.2	0.0	1.3	18.8	0.7	68.9	0.0
Gull	2.8	30.8	3.4	11.8	3.1	46.1	0.7
Higgins	4.7	0.1	10.3	49.0	2.5	47.8	0.2
Houghton	15.7	3.2	58.1	236.6	59.6	21.1	0.0
Imp	0.0	0.0	0.0	1.6	0.0	79.7	0.0
Littlefield	0.4	0.8	2.1	12.1	0.7	29.7	1.3
Mullett	35.5	95.9	226.8	874.1	40.4	44.3	0.6
Paw Paw	3.2	8.7	3.7	8.3	1.7	25.2	3.9
Round	0.8	1.3	1.4	10.5	1.4	45.7	2.7
Torch	4.8	21.0	22.4	64.0	1.8	50.1	3.5
Whitmore	1.1	1.5	1.5	3.8	1.1	29.1	0.2
Witch	0.4	0.0	0.5	9.6	0.2	74.7	0.0
Watershed parameter	%up 100 m	%urban 100 m	%wetland 100 m	Forest 100 m	Ag 100 m	Up 100 m	Urban 100 m
Lake/Units	%	%	%	km <sup>2</sup>	km <sup>2</sup>	km <sup>2</sup>	km <sup>2</sup>
Cadillac	6.1	47.3	5.6	0.27	0.01	0.06	0.51
Cass	13.3	16.0	19.3	0.73	0.00	0.20	0.24
Crystal B	11.3	24.5	4.3	1.53	0.06	0.38	0.82
Crystal M	4.9	63.1	2.4	0.07	0.05	0.03	0.43
Elk	11.1	9.7	8.5	1.98	0.30	0.45	0.39
Gratiot	7.3	3.3	14.5	0.71	0.00	0.08	0.03
Gull	13.0	21.6	9.9	0.94	0.01	0.27	0.44
Higgins	11.7	17.4	6.3	1.59	0.01	0.39	0.58
Houghton	9.1	46.2	9.8	1.03	0.00	0.44	2.24
Imp	1.0	7.3	1.3	0.23	0.00	0.00	0.02
Littlefield	9.1	15.4	20.1	0.23	0.01	0.07	0.12
Mullett	9.0	16.8	14.0	2.32	0.03	0.47	0.88
Paw Paw	8.2	42.3	20.0	0.38	0.06	0.12	0.64
Round	12.1	4.6	24.4	0.47	0.03	0.12	0.05
Torch	14.2	9.0	6.2	3.29	0.23	0.93	0.59
Whitmore	13.2	41.7	8.0	0.22	0.00	0.10	0.31
Witch	5.5	8.5	2.7	0.38	0.00	0.03	0.04

Table 6 (cont'd).

Watershed parameter	Wetland 100 m	Urban fiv	Ag fiv	Up fiv	Forest fiv	Wetland fiv	Urban fip
Lake/Units	km <sup>2</sup>						%
Cadillac	0.06	12.97	4.31	4.76	10.31	1.61	38.18
Cass	0.29	0.77	0.01	0.88	1.95	0.46	18.89
Crystal B	0.14	19.92	4.02	13.56	68.18	3.08	18.31
Crystal M	0.02	8.06	4.86	0.69	2.63	1.05	46.61
Elk	0.34	11.57	23.79	20.74	66.27	6.97	8.94
Gratiot	0.15	1.17	0.00	5.49	139.68	11.42	0.74
Gull	0.20	8.14	12.71	7.68	22.64	4.47	14.63
Higgins	0.21	16.75	0.26	12.95	69.27	4.91	16.09
Houghton	0.48	50.77	1.63	21.93	72.27	27.87	29.10
Imp	0.00	0.29	0.00	0.03	7.46	0.03	3.68
Littlefield	0.16	1.15	0.52	2.51	12.19	3.09	5.92
Mullett	0.74	23.80	13.25	33.77	145.51	16.51	10.22
Paw Paw	0.30	11.24	5.84	3.60	10.57	3.84	32.04
Round	0.25	1.34	1.88	2.94	19.95	5.46	4.26
Torch	0.41	17.45	17.63	34.87	117.49	7.49	8.95
Whitmore	0.06	0.45	0.10	0.37	0.97	0.19	21.43
Witch	0.01	1.33	0.00	1.01	14.39	0.41	7.78
Watershed parameter	Ag fip	Up fip	Forest fip	Wetland fip	Urban fiv	Ag fiv	Up fiv
Lake/Units	%	%	%	%			
Cadillac	12.69	14.02	30.35	4.75	0.163	0.004	0.028
Cass	0.14	21.55	48.06	11.37	0.003	0.000	0.004
Crystal B	3.70	12.47	62.69	2.83	0.432	0.020	0.149
Crystal M	28.13	3.98	15.21	6.06	0.168	0.016	0.012
Elk	18.39	16.03	51.24	5.39	0.164	0.150	0.207
Gratiot	0.00	3.48	88.54	7.24	0.020	0.000	0.066
Gull	22.85	13.81	40.69	8.03	0.109	0.015	0.125
Higgins	0.25	12.44	66.52	4.71	0.237	0.004	0.147
Houghton	0.93	12.57	41.42	15.98	0.841	0.001	0.191
Imp	0.00	0.41	95.55	0.36	0.005	0.000	0.000
Littlefield	2.68	12.92	62.62	15.87	0.015	0.002	0.017
Mullett	5.69	14.50	62.49	7.09	0.348	0.019	0.217
Paw Paw	16.64	10.25	30.13	10.94	0.170	0.021	0.036
Round	5.94	9.30	63.19	17.31	0.008	0.009	0.034
Torch	9.04	17.89	60.27	3.84	0.246	0.092	0.365
Whitmore	4.93	17.86	46.69	9.09	0.003	0.000	0.002
Witch	0.00	5.91	83.90	2.41	0.021	0.000	0.013

Table 6 (cont'd).

Watershed parameter	Forest fiv	Wetland fiv	Urban fisp	Ag fisp	Up fisp	Forest fisp	Wetland fisp
Lake/Units			%	%	%	%	%
Cadillac	0.100	0.018	52.119	1.223	8.829	31.943	5.885
Cass	0.011	0.002	13.226	0.006	22.061	55.093	9.614
Crystal B	0.627	0.082	32.977	1.539	11.375	47.824	6.285
Crystal M	0.027	0.007	72.863	6.965	5.319	11.647	3.206
Elk	0.918	0.159	10.290	9.364	12.978	57.410	9.957
Gratiot	2.493	0.290	0.714	0.000	2.315	86.864	10.108
Gull	0.236	0.082	19.237	2.597	22.105	41.643	14.418
Higgins	0.756	0.104	18.961	0.350	11.805	60.544	8.340
Houghton	0.470	0.261	47.663	0.078	10.835	26.614	14.810
Imp	0.109	0.000	4.473	0.000	0.131	95.329	0.066
Littlefield	0.060	0.049	10.480	1.168	11.934	41.966	34.452
Mullett	1.067	0.212	18.683	1.027	11.634	57.289	11.367
Paw Paw	0.114	0.074	41.055	4.973	8.780	27.366	17.826
Round	0.174	0.112	2.269	2.546	10.190	51.676	33.319
Torch	1.320	0.165	11.226	4.185	16.683	60.357	7.550
Whitmore	0.006	0.001	29.160	0.497	17.923	47.804	4.616
Witch	0.163	0.008	10.278	0.000	6.422	79.279	4.021

## **APPENDIX B**

### **METHODS FOR ACQUISITION OF WATERSHED CHARACTERISTIC DATA**

## APPENDIX B. METHODS FOR ACQUISITION OF WATERSHED CHARACTERISTICS DATA

The following methods were used in the acquisition of the watershed characteristics data used in Chapters 4, 5, and 6. ArcView v. 3.2, and ArcInfo v. 8.2 run on a UNIX platform were used for all geographic information systems work.

### **Delineating watersheds using Shuttle Radar Topography Mission (SRTM) digital elevation data**

1. Determine what county the lake is in.
  - a. Download the lake coverage from the Michigan DNR spatial data library, and open it in ArcView to get a good sense of where the lake is.
2. Download SRTM DEM data from USGS enhanced download site:  
<http://seamless.usgs.gov/viewer.htm>
  - a. Make sure the 30 m DEM is checked on the right – this is the data you want. Some areas (near Detroit) don't have 30 m DEMs. Then use 60 m DEM instead, but note the different resolution.
  - b. Zoom into the area around the lake
  - c. Select area to download – here try to guess the size of the watershed – if too small an area is downloaded it will have to be done again, but the larger the area the longer everything takes.
  - d. Download only the 30 m DEM file, extract in winzip. FTP to unix machines.
3. Rename all files and folders in lowercase. Renaming can be in WS-FTP, or before FTPing to Unix machines.
4. If the file names have 8 numbers, rename the first 3 numbers to “dat” so that the results is, for example, dat52369. Leave the last 5 numbers as they were. (I have no idea why this is necessary – but when it was all numbers it didn't seem to work).
5. Build the statistics file with buildsta command in GRID:  
GRID: buildsta dat28789
6. Project the data in GRID with the project command - use cubic convolution:  
Usage: (\*) PROJECT (<grid>, {projection\_file}, {NEAREST | BILINEAR | CUBIC}, {out\_cellsize}, {x\_register, y\_register})

\*To get to the GRID module type **grid** at the Arc> prompt.

Grid: mul\_elev = project(dat28397,#,cubic)

\*\*\*\*\*

\* The INPUT projection has been defined. \*

\*\*\*\*\*

Use OUTPUT to define the output projection and END  
to finish.

Project: output  
Project: projection oblique\_mercator  
Project: datum nar\_c  
Project: units meters  
Project: spheroid grs1980  
Project: parameters  
Projection type < 1 | 2 >: 2  
Scale factor at the projection's center [ 1.00000 ]: 0.99960  
Longitude of the projection's center (DMS) [ 0 0 0.000 ]: -86 0  
0.000  
Latitude of the projection's center (DMS) [ 0 0 0.000 ]: 45 18  
33.000  
Azimuth at the projection's center [ 0.00000 ]: 337.25556  
False easting (meters) [ 0.00000 ]: 2546731.49600  
False northing (meters) [ 0.00000 ]: -4354009.8160  
Project: end

7. At this point I usually open this coverage in ArcView with a file for the lakes of that county (Available at DNR spatial data library) to make sure that I projected right. If there is a typo, the DEM will not appear on top of the lake in ArcView.
8. In Arcview, look at the DEM and check for missing data (will appear as black grid cells). IF data are missing, you MUST put data into these spots – or else the water will flow into the missing data. See separate file to determine how to do this.
9. Go back to Arc Info. Fill the sinks: Usage: FILL <in\_grid> <out\_grid> {SINK | PEAK} {z\_limit} {out\_dir\_grid}  
GRID: fill mul\_elev mul\_elevf sink
10. Compute flowdirection in GRID:  
Usage: (I) FLOWDIRECTION (<surface\_grid>, {o\_drop\_grid}, {NORMAL | FORCE})  
mul\_fdir = flowdirection(mul\_elevf)
11. Compute flowaccumulation (only to help determine point of highest accumulation to delineate watershed from)  
Usage: (F) FLOWACCUMULATION (<dir\_grid>, {weight\_grid})  
GRID: mul\_facc = flowaccumulation(mul\_fdir)
12. Open Arcview and find point with highest flow accumulation within the lake. You will have to change the scale – I usually use standard deviation, in units of ¼ deviation.

13. Create shapefile with points to delineate watershed:
  - a. view>new theme
    - i. feature type: point
    - ii. mulout.shp
  - b. Click on point button, then pick points with high flow accum around lake. Arc will delineate the areas that flow into these points. May be one or many for a lake. Always try one first.
  - c. theme>stop editing
14. Arc info – goto lake/mullett/ directory.  
 shapearc mulout mulout  
 Shapearc changes it from a shp to a coverage. shapearc shp-file coverage
15. Go into Grid (type “grid”)
16. mulshed = watershed(mul\_fdir,selectpoint(mul\_fdir,mulout,inside))  
 selectpoint says to select all the grid points inside of mulout for the grid coverage mul\_fdir. Watershed says use the flow direction grid stating at the point given and delineate the area that flows into the points given.
17. Open this grid up in arcview to determine if the area covers what appears to be the whole watershed. If not, reopen shapefile and edit it. Go into arc and kill mulout all and kill mulshed all. Then repeat steps 5-7. IF the watershed touches the edge of the DEM or comes very near it, go back to step one and download a larger area.
18. IF more than one point was used to delineate the watershed, change to one grid:
  - create a text file reclass.txt with the text: 1 500 : 3 where 3 is an arbitrary #.
  - GRID> mulshedg = reclass(mulshed,reclass.txt)
19. Change to poly  
 ARC> gridpoly mulshedg mulshedv
20. IF one or several points will not define the watershed, use a polygon.  
 Shapefile > new theme > polygon  
 Draw a polygon around lake, save and close.  
 In arcview, transform it to a grid Theme>convert to grid  
 Then skip to watershed delineation step.  
 mulched = watershed(mul\_fdir,muloutg)  
 If necessary, add onto the polygon using the append new polygon button.

**NOTES:**

Projections – we project everything into Michigan Georef. You can tell what projection a file is in by (1) Opening it in Arcview and opening up something else you know is in MI Georef and seeing if they line up, and (2) in Arc, type describe coveragename, and it will give you info on the projection. The datum that we type in

to switch the SRTM data to Michigan Georef is not real datum, but a code for ArcInfo that allows it to switch between those two particular datums. The actual Michigan Georef datum is NAD83 (see the help menu for more info about this)

I often check the watershed against the previously delineated file – for small lakes they usually don't have a watershed delineated just for that lake, but some of the edges should match up. There is a UP and LP file already on the UNIX machines.

IF there is another lake in the watershed, I remove the watershed of that lake from the overall watershed. [rationale: lakes act as sediment traps, most metals are on sediments. Therefore, the land upstream from a lake within the watershed of interest will not contribute to the sediment of the lake of interest. This will be significant for some lakes (e.g., Mullett, Torch) some of this will be a judgment call.]. To do this: delineate the watershed of the secondary lake in the same way. Merge the watersheds of the primary and secondary lakes (the secondary watershed should be within the primary) – both will have to be coverages or shape files to do this, it can be done in ArcView. Then select the portion of the merged watershed that is just the primary watershed with the secondary removed, and convert to shapefile (again, arcview). Then change this to a coverage (shapearc command in Arcinfo).

### **Creation of a watershed with sample lake removed (watershed\_nl)**

For many of the analyses, it is desirable to have a coverage or shape file of the watershed without the lake present. For example, soils data in the watershed, land cover not including the lake, slope of the watershed – all of these characteristics of the watershed should not include the actual lake.

This watershed\_nl file will also need to be used to clip grids for flow weighted land cover and average slope calculations. The grid clip command does not work well if the clip shape (in this case, the watershed\_nl file) is too complex. Therefore, it is necessary to try clipping a grid after the watershed\_nl file is created to determine if this file will work. If not, sometimes the shape of the lake has to be simplified (see Cass Lake). Grid clip is most likely not to work when the watershed\_nl file is made of more than one polygon (e.g., if there are 2 places where the lake touches the watershed).

1. Lake must touch the watershed edge so that the lake is not an “island polygon”.
  - a. If the lake does NOT touch the edge of the watershed, edit the shape file of the lake and add a polygon to create a small channel from the edge of the lake to the boundary of the watershed. It is preferable to do this where the lake is closest to the watershed boundary, and/or where there is a river outflow from the lake to the watershed boundary. Typically, the lake should touch or be very close to the watershed boundary.
2. In Arcview: Open shp file for the lakes in that county.
3. Select the sampled lake, and create a new shape file. (e.g., cass\_lake.shp)
4. Union this with the watershed polygon. (Using geoprocessing wizard)
5. Select the watershed without the lake, and make this a new shapefile. (Theme>convert to shapefile)
6. In arcinfo Shapearc this to get a coverage of the watershed without the lake.
  - a. ARC: shapearc *shapefile coveragename*
7. Clean the new coverage

- a. ARC: clean *coveragename*
8. Check to see if gridclip will work
  - a. Go to arcinfo, grid module
  - b. Grid: gridclip *gridtobeclipped outgrid cover clipcoverage*
  - c. For example – to clip the IFMAP landcover grid for Cadillac Lake:  
Grid: gridclip ifmap\lp cadillac\cad\_ifmap cover cadillac\cadshed\_nl
  - d. \*NOTE that the grid module does NOT like the path ..\ to go back up a directory, therefore you MUST be in the lowest common directory of the files that you want to use.
  - e. Open the clipped grid in Arcview and see if the landcover file was clipped properly. If it did not work, there will active grid cells either in the lake or outside the watershed, and often no active grid cells within a part of the watershed.
  - f. If the grid was clipped correctly, continue using this watershed\_nl file, if it was not clipped correctly, modify this file or the lake file until the gridclip will work. Then use this new watershed\_nl file for all appropriate analysis. Although modifications to make the gridclip work add some inaccuracy to the file, it is necessary to be consistent through all data acquisition.

**NOTES:**

- There will be some error in method because the DNR lake files will not be identical to where the lakes are located on the DEMs or land cover files.

**Filling in no data cells**

Grid: outgrid = con (isnull (ingrid1), 0, ingrid1)

The above expression says that if (CON) the cell value on ingrid1 equals NODATA (ISNULL), then assign 0 to it (true\_expression = 0); if it does not (it is a valid value), then get the input value back (false\_expression = ingrid1). To perform the reverse and set cells with specific valid values to NODATA (to mask out cells), use the SETNULL function.

However, we don't want to set nodata cells to 0, we want to set them to a reasonable elevation. So, pick a value slightly lower than those around the missing data point (so that it will get filled). Usually the missing data is in the lake anyway, so the exact elevation is unimportant.

Grid: crb\_elev2 = con (isnull (crb\_elev),169,crb\_elev)

### **Determining watershed population density 1990-1870**

This method determines the population density in the watershed with the assumption that if the land is state owned or underwater people will not be living there. Township census data are used. To determine the “livable” area in each township census area, the area of each census polygon that is completely or partially in the watershed is determined, then the area of each census polygon within the watershed is determined. Then the area owned and the area in lakes within each census polygon is determined, then the area within each census polygon within the watershed is determined. This allows the calculation of what % of the livable land in a census polygon is in the watershed. The assumption is that if 5% of the livable land of a census polygon is in the watershed, then 5% of the people live in the watershed.

The calculations are as follows.

For EACH census area:

Total livable area = total area – lake area – owned area

Total livable in watershed (in that census area) = total watershed – lake in watershed – owned in watershed

% livable of census area that is in watershed = livable in watershed / total livable

For each census area: people in watershed = total people in census area \* % livable of census area in watershed.

Sum this for all of the census areas, then divide by the size of the watershed to get population density (people/km<sup>2</sup>). It seems best to use the size of the watershed without the sampled lake to determine population density, since this is the land size of the watershed. Whether or on the sampled lake is included in the watershed area will make a significant difference for lakes with small watersheds.

1. Determine lake area within all of the township census areas
  - a. Copy or download lake shape files to the correct lake directory.
  - b. In arcview open mi\_pop4 and lake.shp
  - c. Anaysis>Tabulate areas:
    - i. Row theme: lake.shp
    - ii. Row field: Lake\_type
    - iii. Column theme: poly (from mi\_pop4)
    - iv. Column field: poly#
    - v. Save resulting table as tab delimited text.
2. Determine lake area within the watershed
  - a. Union watershed and mi\_pop4
    - i. In arcview: Arctools>command tools> analysis>overlay> union, mi\_pop4 and watershed
  - b. Open new union coverage in arcview, open the polygon, not the region
  - c. Tabulate area:
    - i. Row theme: lake.shp
    - ii. Row field: Lake\_type
    - iii. Column theme: lakeunion
    - iv. Column field: lakeunion#
    - v. Save resulting table as tab delimited text.
  - d. Manually relate which union polygon is in which original mi\_pop4 polygon by using arcview and seeing which polygon numbers correspond. Write this down.
3. Determining area owned in mi\_pop4
  - a. Download or copy state ownership files for each county, open in Arcview
  - b. Theme>Query: surf\_cn >= 1 or fee\_cnt >= 1, new set
  - c. Theme> convert to shapefile
  - d. Analysis> tabulate area:
    - i. Row theme: lakeown.shp
    - ii. Row field: county
    - iii. Column theme: poly
    - iv. Column field: poly#
    - v. Save resulting table as tab delimited text.
4. Determine area owned in watershed
  - a. Open lakeunion
  - b. Analysis> tabulate area:
    - i. Row theme: lakeown.shp
    - ii. Row field: county
    - iii. Column theme: lakeunion
    - iv. Column field: lakeunion#
    - v. Save resulting table as tab delimited text.

5. Determine area of each mi\_pop4 that is in the watershed
  - a. Analysis> tabulate area:
    - i. Row theme: lakeunion.shp
    - ii. Row field: lakeunion#
    - iii. Column theme: watershed
    - iv. Column field: watershed\_id
    - v. Save resulting table as tab delimited text.
6. Excel calculations: areas calculated are the areas that are owned, and the areas that are lake, and therefore the remaining area must be calculated.
  - a. FTP all .txt files to disk, open in Excel
  - b. Copy files into calculation file (See area calculations with ownership.xls), transpose data when copying so that the poly number is a column.
  - c. From the watershed area, copy the lakeunion#. These are the polygons from union in the watershed.
  - d. Go to arcview and determine what the poly# are for the union#. These polygons are the only ones of importance, and other poly#s can be ignored.
  - e. If there are multiple union polygons in one mi\_pop4 polygon, make only one row and add all lake and union data for that one mim\_pop4 polygon.
  - f. Total area can be collected from the population data, matching the correct poly# (NOT union#!)
  - g. Lake area and owned area: match poly#, include lake and island area (most islands are small, we assume no one lives on them)
  - h. Total livable area = total area – lake area – owned area
  - i. Watershed area, lake area in watershed and owned in watershed: match union#
  - j. Total livable in watershed = total watershed – lake in watershed – owned in wshed
  - k. % livable in watershed = livable in watershed / total livable

## Population densities for 2000

This method is the same concept as the historical population densities, except that everything must be recalculated because the census bocks are different.

1. Downloaded Tigerline census tract data from DNR spatial data library  
<http://www.mcgi.state.mi.us/mgdl/?action=thm>
2. Determined which census tracts were included in each watershed  
Collected total population information for each of these census tracts from the American Factfinder on the US Census website:  
[http://factfinder.census.gov/servlet/CTGeoSearchByListServlet?ds\\_name=DEC\\_2000\\_SF4\\_U&lang=en&ts=79955755602](http://factfinder.census.gov/servlet/CTGeoSearchByListServlet?ds_name=DEC_2000_SF4_U&lang=en&ts=79955755602)
3. Since census tracts had changed, the dasymetric mapping and all other parts of the population density calculations have to be redone.
4. First tract00\_miv2a.shp was transformed into a polygon coverage using shapearc  
tract00\_miva tract00 polygon (this can be found on UNIX machine)
5. Determine lake area within all of the township census areas
  - a. Copy or download lake shape files to the correct lake directory.
  - b. In arcview open tract00 (open entire coverage, not polygon) and lake.shp
  - c. Analysis>Tabulate areas:
    - i. Row theme: lake.shp
    - ii. Row field: Lake\_type
    - iii. Column theme: polygon
    - iv. Column field: tract\_lbl (these are the actual census tract numbers)
    - v. Save resulting table as tab delimited text (county lake)
6. Determine lake area within the watershed
  - a. Union watershed and tract00
    - i. In arcINFO: Type Arctools. Then command tools>  
analysis>overlay> union, tract00 (..\tract00) and watershed
  - b. Open new union coverage in arcview, open the polygon, not the region
  - c. Tabulate area:
    - i. Row theme: lake.shp
    - ii. Row field: Lake\_type
    - iii. Column theme: lakeunion
    - iv. Column field: lakeunion#
    - v. Save resulting table as tab delimited text (county lakeshed).
  - d. For all polygons within the watershed (and ONLY within the watershed), manually determine in Arcview which cadunion# number(s) are in each census tract.
7. Determining area owned in tract00 if necessary. This is completed for year 1-4 lakes.
  - a. Download or copy state ownership files for each county, open in Arcview
  - b. Theme>Query: surf\_cn >= 1 or fee\_cnt >= 1, new set
  - c. Theme> convert to shapefile
  - d. Analysis> tabulate area:

- i. Row theme: lakeown.shp
  - ii. Row field: county
  - iii. Column theme: polygon
  - iv. Column field: tract\_lbl
  - v. Save resulting table as tab delimited text (county own).
- 8. Determine area owned in watershed
  - a. Open lakeunion
  - b. Analysis> tabulate area:
    - i. Row theme: lakeown.shp
    - ii. Row field: county
    - iii. Column theme: lakeunion
    - iv. Column field: lakeunion#
    - v. Save resulting table as tab delimited text (county ownshd).
- 9. Determine area of each mi\_pop4 that is in the watershed
  - a. Analysis> tabulate area:
    - i. Row theme: polygon
    - ii. Row field: tract\_lbl
    - iii. Column theme: watershed
    - iv. Column field: watershed\_id
    - v. Save resulting table as tab delimited text.
- 10. Determine the total area of the census tracts
  - a. Using the select tool, select the census tracts included in the watershed
  - b. Go to the table and move highlighted records to the top.
  - c. Export these records as tab delimited text (tract areas).
- 11. Excel calculations: areas calculated are the areas that are owned, and the areas that are lake, and therefore the remaining area must be calculated.
  - a. FTP all .txt files to disk, open in Excel
  - b. Copy files into calculation file (See area calculations with ownership.xls), transpose data when copying so that the poly number is a column.
  - c. Paste tract area, lake area, owned area, and watershed area into the appropriate columns for the proper census tracts. For lake areas, use lake + island when there is island area (assume that there are no islands big enough for people to be living on)
  - d. Fill in the appropriate lakeunion#(s) for each of the census tracts (this relationship was determined manually in step 6d). Using these numbers, paste the appropriate lakeshed, and ownshd data into the columns.
  - e. Total livable area = total area – lake area – owned area
  - f. Watershed area, lake area in watershed and owned in watershed: match union#
  - g. Total livable in watershed = total watershed – lake in watershed – owned in wshed
  - h. % livable in watershed = livable in watershed / total livable

### **Area of land cover in total watershed**

The area or percentage land cover in the watershed can be calculated two ways – with or without the study lake. Whether or not the lake is included will significantly influence the percentage land cover, as the lake will cover very different proportions of the watershed. If the lake is included, then all percentage land covers will be significantly influenced by the lake to watershed: area ratio. Because of this, all calculations for the Yohn dissertation were completed using the watershed without the lake. The instructions below will be for this method, but the percentages for the entire watershed may be determined by using the entire watershed coverage instead of the watershed no lake coverage.

Data are acquired at the most detailed level (Level 3 or 4) and then the coarser land cover categories are calculated from these data (Level 1). Because the classifications are different for the two time periods, the Level 1 data is the most appropriate for comparisons, but the acquisition of Level 3 data allows for more detailed analyses if desired.

1. Open necessary land cover file(s) and watershed without lake file (watershed\_nl)
  - a. For IFMAP files, open lower or upper peninsula
  - b. For 1978 MIRIS files, open lands cover for all counties necessary for that watershed.
2. IF the watershed is in more than one watershed, it is easier if the county land cover files are merged before analysis
  - a. Use the merge command in geoprocessing wizard in ArcView.
3. Using analysis>tabulate area in ArcView, determine the Level 3 label area of land cover.
  - a. For the 1978 landcover area, use 30 m for the resolution – this is the same resolution of the DEM.
4. Import as tab-delimited text into Excel.

5. Using the codes listed below, determine the level 1 land cover for each time period.
6. Sum the total area for each watershed, and calculate percentage Level 1 land cover for each watershed.
  - a. The total area for each watershed should be very close to the area of the watershed\_nl coverage. If it is not similar, there is some error.

**NOTES:**

- For the UP IFMAP landcover the classification is numbers and not text descriptions. See table below to match land cover codes with descriptions.
- IFMAP classification system places lowland forest as wetlands, while the MIRIS classification places lowland forest as forests. To make the two datasets more consistent, lowland forests and upland forests in the IFMAP coverage were combined to create a “forest” category.

**Table 1. MIRIS land cover data codes.**

Level 3	Level 2	Level 1	
Multi-Family-Medium to High Rise	Residential	Urban	
Multi-Family-Low Rise			
Single Family, Duplex			
Mobile Home Park			
Commercial, Services, and Institutional (Level 2)	Commercial, Services, Institutional		
Central Business District			
Shopping Center, Mall			
Neighborhood Business Institutional			
Industrial (Level 2)	Industrial		
Industrial Park			
Transportation, Communication, and Utilities (L2)	Transportation, communications utilities		
Air Transportation			
Water Transportation			
Road Transportation			
Utilities, Waste Disposal	Extractive		
Open Pit Wells			
Outdoor Recreation	Open Land and other		
Cemeteries			
Cropland, Rotation, and Permanent Pasture	Cropland, Rotation, and Permanent Pasture	Agriculture	
Orchards, Vineyards, and Ornamental			
Confined feeding			
Permanent Pasture			
Other Agricultural Land			
Herbaceous Rangeland	Herbaceous Rangeland	Nonforested	
Shrub Rangeland			
Pine or Oak Opening (Savanna)			
Northern Hardwood	Deciduous	Forested	
Central Hardwood			
Aspen, Birch			
Lowland Hardwood			
Pine	Coniferous		
Other Upland Conifer			
Lowland Conifer			
Christmas Tree Plantation			
Streams and Waterways	Streams and Waterways		Water
Lakes			
Reservoirs			

Table 1 (con't)

Wooded Wetland	Forested wetlands	Wetlands
Shrub/Scrub Wetland		
Aquatic Bed Wetland	Nonforested wetlands	
Emergent Wetland		
Flats		
Beaches and Riverbanks	Beaches and Riverbanks	Barren
Sand Other than Beaches	Sand Other than Beaches	

Table 2. 2001 IFMAP land cover data codes.

Value	Level 4 or 3	Level 2	Level 1
0	Background		
1	Low Intensity Urban	Low Intensity Urban	Urban
2	High Intensity Urban	High intensity urban	
3	Airports		
4	Roads / Paved		
5	Non-vegetated Farmland	Herbaceous agriculture	Agriculture
6	Row Crops		
7	Forage Crops / Non-tilled herbac		
9	Orchards / Vineyards / Nursery	Non-herbaceous agriculture	
10	Herbaceous Openland	No level 2	Upland openland
12	Upland Shrub / Low-density trees		
13	Parks / Golf Courses		
14	Northern Hardwood Association		
15	Oak Association	Upland deciduous forest	Upland forest
16	Aspen Association		
17	Other Upland Deciduous		
18	Mixed Upland Deciduous		
19	Pines		
20	Other Upland Conifers		
21	Mixed Upland Conifers		
22	Upland Mixed Forest	Upland mixed forest	
23	Water	Water	Water
24	<i>Lowland Deciduous Forest</i>	<i>Lowland forest</i>	Wetland
25	<i>Lowland Coniferous Forest</i>		
26	<i>Lowland Mixed Forest</i>		
27	Floating Aquatic	Nonforested wetlands	
28	Lowland Shrub		
29	Emergent Wetland		
30	Mixed Non-Forest Wetland		
31	Sand / Soil	No level 2	Bare/Sparsely vegetated
32	Exposed Rock		
35	Other Bare / Sparsely Vegetated		

\* Upland and lowland forests (italics) were reclassified into a "forest" group. Lowland forests were NOT included in wetlands.

## Flow path weighted land cover

Flow path weighted land cover is a measure of the amount of land cover within the watershed, but is weighted by the inverse distance to the lake along the flow path.

Data were calculated using the inverse distance, and the inverse distance squared.

Additionally, both data using the actual value calculated and the percentage (of values for all land cover types) were calculated. The use of percentage compensates for the size of the watershed.

The flow path weighted value for each land cover was determined by:

1. Clip flow direction grid, calculate flow length
2. Clip land cover grid
3. Assign all of one land use to 1, rest to 0
4. Calculate 1/ flow length
5. Multiply 1/flow length by land cover # (0 or 1)
6. Sum
7. Do this for all desired land uses (level 1, excluding water and barren)

The detailed method follows.

### 2001 IFMAP data method

1. Create a flow length grid:
  - g. Clip the SRTM flowdirection grid with watershed without lake file  
Grid: `gridclip cad_fdir cadshed_fdir cover cadshed_ni`
    - i. Must do this from a common directory- it will not take ..\
  - h. Calculate flowlength:  
Grid: `cad_flow = flowlength(cadshed_fdir,#,downstream)`
2. Create a land cover grid for land cover of choice (IFMAP) (ag, for, urban, wet, up)
  - i. Clip the IFMAP grid in a similar fashion to the flowdirection grid  
Grid: `gridclip ifmap\lp cadillac\cad_ifmap cover cadillac\cadshed_ni`
  - j. Open this in arcview and assign all cells with the appropriate landcover a "1", and the rest a "0".
    - i. Analysis>map query
    - ii. For urban: `cad_ifmap >= 1 and cad_ifmap <= 4` (see below for correct code numbers)
    - iii. Convert this to a grid:
      1. Theme>convert to grid, save as abbreviate of land cover type, urb, ag, for, up, wet

3. Take the inverse and inverse squared of the flowlength grid (so cells closest to the lake have the highest values)
  - k. Grid:  $fli = 1 / cad\_flow$
  - l. Grid:  $fli2 = 1 / \text{sqr}(cad\_flow)$
4. Multiply the inverted flowlength grid and the selected landcover grid. Do this for each land cover, and for flow inverted and flow inverted squared.
  - m. Grid:  $urb\_fli = urb * cad\_fli$
  - n. Grid:  $urb\_fli2 = urb * fli2$
5. Sum the resultant grid for the final flow weighted land cover, and then show the results. Total and total2 can be any words that aren't commands.
  - a. In GRID:
 

```
Grid: docell
:: total += urb_fli
:: total2 += urb_fli2
:: end
Running... 100%
Grid: show total
12.97288418311
Grid: show total2
0.3155395542706
* The scalars (total and total2) are not preserved in the ArcInfo memory –
it is critical to type the “show” commands right after the docell.
```
6. Numbers produced from show will have to be cut and paste into Excel (x-win, copy to clipboard)

IFMAP codes

Urban: 1-4

Agriculture: 5,6,7,9

Upland openland: 10,12,13

FOREST (this will include lowland forest which they define as wetland but I define as forest):14-22,24-26

Water: 23

Wetland: 27-30

Barren: 31,32,35

Method for 1978 landcover.

1. Open 1978 landcover file that has been clipped with the watershed no lake.
2. Convert to grid:
  - a. Theme>convert to grid
  - b. Save this in the 78lu file
  - c. Output grid extent: same as landcover shapefile
  - d. Cell size: 30 m.
  - e. Field area for cells: label 1
  - f. Join feature attributes to grid? No.

3. Query this grid to create a new grid file for each landcover type
  - a. Analysis>map query
  - b. S\_value = land cover of interest...
  - c. Convert the map query coverage to a grid file, save as the name of the land cover in the 78lc folder
4. Using data manager in arc view, copy the inverted flow (fli) and inverted flow squared (fli2) to the 78 land cover folder.
5. Follow directions from above (directions 5-7)

### **Soil erodibility – k factor**

K factor is standardized to a 9 % slope, therefore K should be greater of slope >9% and less if slope <9%. Determine both k-factor and clope corrected k-factor (k-factor \* slope/9).

Rock fragments reduce erodibility (rain hits rocks instead of erodible soil). K-factor includes rock fragments, Kf-factor removes them. If there is a difference, the Kf-factor will be greater than the k-factor. Often they are the same. Collect data on both to find difference. K factor is probably more appropriate than Kf-factor.

Map units are the area on the map. These map units are broken down into components. The % of each component within the map unit is in the comp table under compct. Components are broken down into depth layers – I am only interested in the surface layer. So, each component has a sequence number (seqnum) that is listed in both the layer and comp databases. Use the surface layer for each comp. Then calc a weighted average of the k-factor for each map unit. Then determine the weighted average k-value of the watershed from the relative areas of the map units in the watershed.

To use slopes from the STATGO database:

- 1) Calculate area of MUID within each watershed without lake.
  - a. The statsgo coverage was converted to grid to speed the area tabulation.
  - b. Tabulate areas: lakeshedv, lakeshedv#, statsgo\_grd, MUID. Export as tab delimited.
- 2) In excel: For all MUIDs of interest, go to *layer*, and for each sequence number get the k-factor values for the top layer.
- 3) Then, using the sequence number to correlate, go to *comp* and find the %comp of each sequence number. Use this to do a weighted average of the k-factor values. This will give the average k-factor for each MUID. Do the same for slope, using the average of the min and max slope.
- 4) Multiply k-factor \* slope/9
- 5) The do a weighted average with all the MUIDs in the watershed, using the % of the watershed that is covered by each MUID. EXCLUDE the area of water from the total area within the watershed, since there will be no erodibility for this.

When kfact or kfact were missing for some MUID layers, that values was estimated from the average of the other layers. These are noted in RED on the page of k-fact calculations

#### **Determining slope of the watershed**

1. Clip the filled elevation file with the watershed\_no lake vector file.
2. Calculate slope:
  - a. Grid:  $\text{cad\_slope} = \text{slope}(\text{shed\_elevf}, \text{degree})$
3. Then describe this in the grid module and use the result from the mean value.
  - a. Grid: describe cad\_slope

#### **Creating buffers around lake:**

1. Open lake file – polygon or shp file
2. Units MUST be set for in ArcView to create buffers (must do this every time you reopen ArcView)
  - a. Go to View> properties
  - b. Set map units and distance units as meters
3. IF the lake file includes more than one polygon, use geoprocessing wizard to dissolve it. Find a parameter (e.g., ID) that is common to all polygons and use that to dissolve. If there is not a common parameter, edit the table and make the ID the same for all polygons. There is no need to append any of the data.
4. Go to Theme> create buffer
  - a. Choose The Features of a theme, and choose the lake file, next

- b. Choose At a specified distance (100 m, or 10000 m), and make sure distance units are meters, next
- c. Choose outside polygon, and choose to save it in a new theme (buffm for 100m temporary and buffkm for 10 km).
- 5. For buffm: This will create a shape file that includes the lake and the extra 100m. The goal is to get a shape file only 100 m wide.
  - a. Use Geoprocessing wizard (View>geoprocessing wizard) and union buffm and lake files. Save as buffunion
  - b. Select the outer ring, and save as shape file buffm\_nl. This should be just the outer ring.
- 6. For buffkm: do a similar thing if the entire watershed is not included in the 10 km boundary – that is, create the buffer no lake shape file. This is necessary for the soils data.
- 7. \* Most watersheds are <10 km, and using this buffer is probably unnecessary.

#### **To calculate land cover in buffer**

- 1. Open the watershed\_nl clipped ifmap file for that lake (MUST use this and not the total ifmap coverage in case the buffer goes outside of the watershed)
- 2. Open the buffer
- 3. Analysis, tabulate area with lake\_ifmap value, and buffm and ID.
  - a. It will be better to use buffm and buffkm rather than buffm\_nl because the lake is already missing. Using buffm will make sure everything near shore will be included, and hopefully reduce error.

#### **To calculate k factor in buffer**

- 1. First calculate areas of MUID in each of the buffers, using the no lake buffers.
  - a. Tabulate area: Statsgo\_grd, S\_value; buffm\_nl, ID
- 2. Put these areas into the already prepared sheet to calculate k values – this will be the same as calculating it for the entire watershed, only with different areas.
- 3. This does create some error – if the 100m buffer is outside the watershed, it will still be included. However, I think this error will be minor in most cases. If it is not, then will have to gridclip the statsgo\_grd with the lakeshed\_nl file, and then tabulate area.

### **To calculate average slope in buffer**

1. To calculate the average slope in the buffer area, it is necessary to clip the lake\_slope file (slope calculated on lake\_fdir clipped with watershed\_nl) with the buffer file.
  - a. Shape arc the buffm file: shapearc buffm buffm
  - b. Clean buffm
  - c. Grid: gridclip lake\_slope lake\_slopem cover buffm
  - d. Describe lake\_slopem

The average value is the average slope for that portion of the watershed

### **Plotting lat/long coordinates in ArcView in Michigan Georef projection**

This method can be used not only to plot locations of data points, but can also be used to associate data with those points. This method was used in plotting lake sampling locations (and inputting metal inputs and watershed characteristics with these points), Toxic Release Inventory, and sulfate deposition.

1. Make table in Excel with latitude, longitude (lat/long MUST be in decimal degrees), and any other variables of interest. Make sure that all column headers have no spaces or odd characters. There may be a header character limit. Save table as delimited text.
2. Arcview:
  - Add table, DELIMITED TEXT  
table.txt
  - Open a view
    - View>add event theme
    - X field longitude
    - Y field latitude
3. Theme> convert to shapefile *filename*
4. Got to Arc and use shapearc *shapefile coverage*
5. Define projection of coverage – tell Arc that this coverage is in geographic projection.
  - Arc: projectdefine cover *coverage*
  - Define Projection
  - Project: projection geographic
  - Project: units dd
  - Project: datum wgs84
  - Project: spheroid wgs84
  - Project: parameters

6. Now project into MI georef using the same info as for the SRTM data, except do not do this in grid, do it in arc.

Arc: project cover *coverage projected\_coverage*

\*\*\*\*\*

\* The INPUT projection has been defined. \*

\*\*\*\*\*

Use OUTPUT to define the output projection and END to finish.

Project: output

Project: projection oblique\_mercator

Project: datum nar\_c

Project: units meters

Project: spheroid grs1980

Project: parameters

Projection type < 1 | 2 >: 2

Scale factor at the projection's center [ 1.00000 ]: 0.99960

Longitude of the projection's center (DMS) [ 0 0 0.000 ]: -86 0 0.000

Latitude of the projection's center (DMS) [ 0 0 0.000 ]: 45 18 33.000

Azimuth at the projection's center [ 0.00000 ]: 337.25556

False easting (meters) [ 0.00000 ]: 2546731.49600

False northing (meters) [ 0.00000 ]: -4354009.8160

Project: end

### Toxic Release Inventory

The EPA Toxic Release Inventory (TRI) can be used to determine if there are point sources of metals within the watershed. Data were acquired from the EPA TRI

Explorer, plotted in ArcView, and each watershed was checked visually to see if there were any TRI sites within it.

To acquire TRI data:

1. Go to TRI explorer: <http://www.epa.gov/triexplorer/>
2. Choose Facilities, Michigan, Metal and metal category compounds.
3. Some sites will not have Lat/long listed – for those sites within the counties of interest click on the location to get more information, and take lat/long from this.

### **Sulfate deposition**

Data were collected from the National Atmospheric Deposition Program (NADP <http://nadp.sws.uiuc.edu/>) for sites within Michigan and from sites in adjacent states that were near the MI border. Data from all time periods were collected, but there were only enough sites available for interpolation from 1990-2000 (and more recent).

Latitude / longitude and average sulfate deposition (kg/ha/y) for 1990-2000 were input into ArcView (see Plotting lat/long coordinates in ArcView in Michigan Georef projection). Used inverse distance weighting in ArcView (power of 2), and used information tool to determine approximate value for each watershed.

## APPENDIX C

### INDUCTIVELY COUPLED MASS SPECTROMETER ANALYTICAL METHODS

## APPENDIX C. INDUCTIVELY COUPLED MASS SPECTROMETER ANALYTICAL METHODS

### ICP-MS

#### Making standards and other preparatory lab work

##### Introduction

A typical suite of elements that are analyzed in water and digested sediments (sample preparation details given in another document) include:  $^{24,25}\text{Mg}$ ,  $^{27}\text{Al}$ ,  $^{29}\text{Si}$ ,  $^{31}\text{P}$ ,  $^{39}\text{K}$ ,  $^{44}\text{Ca}$ ,  $^{47}\text{Ti}$ ,  $^{51}\text{V}$ ,  $^{52}\text{Cr}$ ,  $^{54}\text{Fe}$ ,  $^{55}\text{Mn}$ ,  $^{59}\text{Co}$ ,  $^{60}\text{Ni}$ ,  $^{63}\text{Cu}$ ,  $^{66}\text{Zn}$ ,  $^{75}\text{As}$ ,  $^{88}\text{Sr}$ ,  $^{95}\text{Mo}$ ,  $^{114}\text{Cd}$ ,  $^{120}\text{Sn}$ ,  $^{138}\text{Ba}$ ,  $^{208}\text{Pb}$ , and  $^{238}\text{U}$ . These include some of the common, important environmental elements and the first row transition metals. Metals may be added or removed, depending on the project. However, the more elements that are analyzed, the higher the detection limits will be; there is a compromise between number of elements and time spent by the quadrupole in the settings for each isotope. Ca and Fe may be analyzed on the AA, or diluted and run on the ICP-MS. Lithium and boron will have very high detection limits due to contamination by samples analyzed using laser ablation. Phosphorous has high background concentrations, and the lowest concentration in the standard curve should not be less than 200 ppb.

Elements present in high concentrations (100s ppm), like calcium, have severe effects on the response of the instrument, causing matrix effects, especially in digested sediment samples. The calcium may increase the background concentration for some elements (e.g.  $^{80}\text{Se}$ ,  $^{88}\text{Sr}$ ), or suppress the signal for other elements. Because of this, if Ca concentrations are above 10 ppm, a concentration similar to that of the samples should be added to the standards to provide a similar matrix. High concentrations of sodium will also cause significant matrix effects. Because of potential matrix effects,

and to determine which elements might be of interest, a full mass scan should be performed on representative samples before a new experiment is carried out. Then concentrations of Ca should be determined by using a higher dilution or using the AA. These concentrations can be used to matrix match the standards. Standards have only been matrix matched with calcium successfully, attempts to matrix match with iron failed – it was better to run the samples with no matrix match than with iron.

In order to analyze for mercury, use a mercury analyzer and not the ICP-MS.

The standards made for the ICP-MS must be multi-elemental (if carrying out multi-element analysis), however, not all the elements should cover the same concentration ranges (e.g. arsenic concentrations may be in the low ppb, while iron may be in the ppm range). Therefore elements are grouped according to their concentration ranges, with each group representing a different standard curve. For example:

**Table 1.** Final concentrations of standards in ppb.

	Blank	STD 1	STD 2	STD 3	STD 4	STD 5	STD 6	STD 7
V, Cr, Co, Mo, Cd, U, Sn, Se	0	0.03	0.05	0.07	0.1	0.2	0.5	1
Ti, Ni, Cu, As, Pb, Sr, Sc, Rb, Ba	0	0.1	0.2	0.5	1	5	10	25
K, Na, Zn, Mn	0	10	20	30	40	60	80	100
P, Si	0	25	50	100	300	500	750	1000
	STD 8	STD 9	STD 10					
V, Cr, Co, Mo, Cd, U, Sn, Se	5	10	25					
Ti, Ni, Cu, As, Pb, Sr, Sc, Rb, Ba	50	100	200					
K, Na, Zn, Mn	150	200	500					
P, Si	1500	2000	3000					

Concentrations of ICP-MS standards (ppb to low ppm range) are much lower than the purchased original standards (1,000 ppm). Because of this it is not possible to dilute from the original standards to the ICP-MS standards. Therefore *solutions* are made, and these solutions are used to make the *standards*. A *solution* is a lower concentration solution of all the elements in one group (e.g. a 1 ppm solution of V, Cr, Co, Mo, Cd, U, Sn and Se). This solution is then diluted to different extends to make the different standards.

To obtain the greatest accuracy, the concentration range of the standards will differ for each type of sample, and therefore will likely be different for each project. The standards given in this method are merely examples of standards for the Inland Lakes project.

To choose concentration ranges for the standards it is best to first do a preliminary analysis of some samples. By looking at the minimum and maximum concentration for each of the elements, elements should be grouped into several ranges of concentration (e.g. one group may be 0.2 to 10 ppb, while another may be 10 to 500 ppb – see above for example groupings). Things to consider: (1) The smaller the range of concentrations the more accurate the curve is (a curve from 0.2-10 ppb will be much better for analyzing a 2 ppb solution than a curve from 0.2-100 ppb) - however – the more concentration groups of elements, the more work it is to make the standards. (2) 0.03 ppb is reaching near detection limits and/or the concentrations in the blank – this varies for each element and the clean methods used – but as a general guide, low concentrations should not go below 0.03 ppb unless discussed with the lab manager: (3) The upper limit of the mass spectrometer is reached by saturating the

detector, which occurs as low as 1000 ppb for some elements, and as high as >15 ppm in other element. Check notes on specific elements for a better idea, but keep standards below the saturation levels of the elements.

Five standards plus a blank is the minimum number of standards that should be used. Currently, 7 to 10 standards are typical. More points allow for greater flexibility in the range of concentration in the metal without losing accuracy, and therefore it is often worth the extra work in preparing the standards. There should be more points near the low concentration end of the curve than the high (see example above). For more examples of standard curves, see the lab manager or the Inland Lakes lab book.

From each of these concentration groupings at least one *solution* is made. This solution contains all the elements in the group and is needed because the purchased standards are too high to dilute directly to the ppb range. The dilutions are typically done in 100 mL volumetric flasks, and the volume that can be accurately pipetted limits the size of the dilution. The solution should be transferred to a Nalgene bottle soon after it is prepared to avoid contamination from the volumetric flask. As a general rule, volumes  $\sim < 50 \mu\text{L}$  begin to be less accurate, and we cannot pipette  $< 10 \mu\text{L}$ . Also, the larger pipettors ( $> 1 \text{ mL}$ ) often leave significant volume in the pipette tip and should not be used to make ICP-MS standards. Because of these constraints, it is sometimes necessary to use two solutions for one group of elements (e.g. 1 ppm and 100 ppb), either because the low concentration is too low to reach in two dilutions (e.g. 0.05 ppb), or the range of concentrations is too great (e.g. 1-500 ppb).

Nitric acid is added to each standard to both prevent precipitation and to create a similar matrix to the sample. Nitric acid will enhance the ionization of different elements, therefore the concentration of nitric acid in the standards should be as close as possible to the concentration in the sample. All solutions should be prepared in 2% HNO<sub>3</sub>.

Samples in the ICP-MS vial include 1 mL of internal standard and 1 mL of sample. The internal standard is used to account for drift in the instrument, and for different instrument response to different matrixes. In other words, if one sample was run multiple times, the area (actual area beneath the peak) may change over time. In order to correct for this, we run an element as an internal standard at a constant concentration in every sample. The theory is that the element acting as the internal standard will behave in the instrument in exactly the same manner as the elements of interest, and can be used to correct for any drift or effects of matrix. The *response* is calculated for each element for each sample as the area of the element for that sample divided by the area of the internal standard for the sample. The response (rather than the area) is used to calculate the standard curves and concentrations. Unfortunately, elements behave differently in the instrument, and it is impossible to have internal standards that behave exactly the same as the elements of interest, making it desirable to minimize the drift and matrix effects in the instrument. Traditionally, indium (<sup>115</sup>In) and bismuth (<sup>209</sup>Bi) have been used as internal standards (In for low masses, Bi for <sup>208</sup>Pb and <sup>238</sup>U). Currently, beryllium (isotope 9), scandium (45), germanium (74), and yttrium (89) are also being used. For further discussion on internal standards, see below.

Digested sediments are run at a dilution of 1:10 (not including the internal standard dilution) so that most elements do not saturate the detector (e.g. 1 mL internal standard + 900 uL 2% nitric acid + 100 uL sample). Additionally, the matrix effects may be too significant for concentrated digested sediment samples. Water samples can often be run without dilution.

Three rinses of 2% nitric acid are run before and after each set of standards. For some elements, the high standard may contaminate the next sample if the sample has a low concentration. Rinses are used to eliminate this possibility. It is a good idea to check for samples that have high concentrations of some elements to make sure that the next sample is not contaminated.

The ICP-MS should be conditioned to the type of sample before the run (e.g. digested sediments have a very different matrix than the solutions used to tune the machine). 1-4 vials should be prepared with 3 times the normal volume of a sample (including internal standard) to use as the conditioning solution (e.g., 3 mL internal std, 3 mL sample). If the instrument has just been cleaned and the samples have a heavy matrix (e.g., digested sediments), it is advisable to use more than one conditioning solution.

Concentrations are determined by the standards run before and after each group of ~ 30 samples. Therefore the run should be organized as follows: standards, 2 rinses, SRM 1643d, 2 rinse, ~30 samples, 3 rinses, another set of standards, 3 rinses, ~30 samples, 3 rinses, standards. Typically runs have up to ~60 samples, though longer runs can be done.

## Procedure

All ICP-MS work should be scheduled with the lab manager (currently Lina Patino patinol@msu.edu, 432-3100 ext 138).

This is an example method from digested sediments – actual concentrations should be varied dependant on the type of sample.

\*Be sure to check pipettors before use!!

\*Use only Ultrapure nitric acid and Nanopure water from the ICP-MS lab

\*All ICP-MS vials should be hot acid washed

\* All solutions are made in 2% nitric acid.

1. Prepare solutions for standards:

- a. Add 2% nitric acid and appropriate volumes of 1,000 ppm standards to 100 mL volumetric flasks. For example:

**Table 2.** Dilutions to create solutions for ICP-MS standards

	Conc ppb	volume	to 100 mL
Solution A	500	50 uL	of 1000 ppm std
Solution A2	10	2 mL	of A
Solution B	10 ppm	1 mL	of 1000 ppm std
Solution B2	100	1 mL	of B
Solution C	10 ppm	1 mL	of 1000 ppm std
Solution D	100 ppm	10 mL	of 1000 ppm std

2. Prepare standards from solutions:

- a. Add 2% nitric acid, appropriate matrix match, and appropriate amounts of each solution to the standards, and fill to the line with the 2% HNO<sub>3</sub>. A blank should be prepared with 2% HNO<sub>3</sub> and matrix match. Matrix match currently only includes Ca, but may be needed with high concentrations of Na. Calcium should be added to the standards in concentrations similar to what is found in the samples.

**Table 3.** Volume of solution added in uL to create ICP-MS standards.

	Conc ppb	STD 1	STD 2	STD 3	STD 4	STD 5	STD 6	STD 7
Solution A	500						100	200
Solution A2	10	300	500	700	1000	2000		
Solution B	10000						100	250
Solution B2	100	100	200	500	1000	5000		
Solution C	10000	100	200	300	400	600	800	1000
Solution D	100000	25	50	100	300	500	750	1000
	STD 8	STD 9	STD 10					
Solution A	1000	2000	5000					
Solution A2								
Solution B	500	1000	2000					
Solution B2								
Solution C	1500	2000	5000					
Solution D	1500	2000	3000					

**Table 4.** Final concentrations of ICP-MS standards.

	Blank	STD 1	STD 2	STD 3	STD 4	STD 5	STD 6	STD 7
V, Cr, Co, Mo, Cd, U, Sn, Se	0	0.03	0.05	0.07	0.1	0.2	0.5	1
Ti, Ni, Cu, As, Pb, Sr, Sc, Rb, Ba	0	0.1	0.2	0.5	1	5	10	25
K, Na, Zn, Mn	0	10	20	30	40	60	80	100
P, Si	0	25	50	100	300	500	750	1000
	STD 8	STD 9	STD 10					
V, Cr, Co, Mo, Cd, U, Sn, Se	5	10	25					
Ti, Ni, Cu, As, Pb, Sr, Sc, Rb, Ba	50	100	200					
K, Na, Zn, Mn	150	200	500					
P, Si	1500	2000	3000					

3. Standards may be stored in acid washed Nalgene bottles, and should be refrigerated to prevent evaporation. Do NOT store ANY solution in volumetric flasks or any glass container.
4. Prepare internal standard (20 ppb In, Bi, Sc, Y; 100 ppb Ge; 1000 ppb Be in 2% nitric acid): (there is a 1 L bottle of this in the hood. Make more when necessary. ALWAYS use the same batch for a run, internal standard concentrations should be exactly the same in all solutions for a run.)
  - a. Dilute 1000  $\mu$ L of 1,000 ppm standard In, Bi, Sc, Y to 100 mL in a volumetric flask with 2% HNO<sub>3</sub> to make a 10 ppm solution.

- b. In a 1 L volumetric add:
  - i. 28 mL Optima HNO<sub>3</sub>
  - ii. 2 mL of 10 ppm In, Bi, Y, Sc solution
  - iii. 100 uL of 1,000 ppm Ge
  - iv. 1000 uL of 1,000 ppm Be
5. All ICP-MS vials should be taped with less than one full rotation at the very top of the vial (if there is excess tape it is harder to get the vials into the auto sampler).
6. Pipette samples:
  - a. For standards: pipette 1 mL of internal standard and 1 mL of standard
  - b. For samples: pipette 1 mL of internal standard and a total of 1 mL of straight or diluted sample (e.g. 100 μL sample + 900 μL water for a 1:10 dilution).
  - c. For rinses: pipette 2 mL of 2% HNO<sub>3</sub>.
  - d. For SRMs: pipette 1 mL internal standard and 1 mL of aqueous SRM (1643d). Liquid SRMs should be run even if digested SRMs are run. The SRMs are used for quality control. The digested SRMs do not represent total digestions and it is harder to compared obtained values with known concentrations.
7. Prepare a conditioning solution:
  - a. To an ICP-MS vial add 3 mL of internal standard and 3 mL of appropriately diluted sample (if samples are not diluted, add 3 mL of sample: if a 1:10 dilution is used, add 30 μL of sample and 2700 μL of water)
8. Organize samples in the test tube holder:
  - a. one set of blank and standards
  - b. 2 rinses
  - c. SRM
  - d. 2 rinses
  - e. ~ 30 sample
  - f. 3 rinses
  - g. blank and standards...etc.
  - h. Conditioning solution may be set aside on the rack
9. List down a column in Excel the labels of all the samples (including standards) in order. This is cut and pasted into the ICP-MS software to provide the labels on the data that is returned. This file should be e-mailed to the lab manager or given to her on a Zip disk. Also send or give the lab manager a chart of the standards used.
10. When the data are returned, there may be columns for area, response, concentration and flags. The area is the actual counts by the mass spec, the response is the area normalized to the internal standard, and the concentration is in ppb. The flags apply only to the standards. Each standard curve is examined, and if any points are anomalous, they are not considered in the calculation of the concentrations. Standards that are not used are flagged.
11. Check for samples that saturated the detector (therefore concentrations are not valid):
  - a. Select the entire "area" column in Excel and format for scientific notation.
  - b. Any sample with an area  $\times 10^8$  has saturated the detector and the concentration is not valid.

12. Graph the internal standard areas (indium area as y, arbitrary sample number as x). Internal standard should remain relatively constant throughout the run. If it does not, notify the lab manager. Rinses will have much lower concentrations because they have no internal standard, these samples can be ignored.
13. Carefully look through the data for any unusual points. Rerun ALL anomalous samples – especially Cu, Ni, Al, Fe, these elements are in the lab and the instrument.

### ICP notes

This section includes notes and observations from analysis of digested sediment solutions.

This instrument seems to have significant matrix issues, and line splitting is frequently a problem, especially for the low masses. In order to combat this, I have tried adding additional internal standards, matrix matching, and conditioning for longer. Thoughts on these attempts are below:

#### Internal standards:

The current suite of internal standards that we run is:

20 ppb  $^{115}\text{In}$ ,  $^{209}\text{Bi}$ ,  $^{89}\text{Y}$ ,  $^{45}\text{Sc}$

100 ppb  $^{74}\text{Ge}$

1000 ppb  $^9\text{Be}$

I have found that frequently, especially for majors and the low masses, that other internal standards than In and Bi are necessary to correct for line splitting. However, the success is not complete. Some elements, especially  $^{39}\text{K}$ ,  $^{31}\text{P}$  and  $^{29}\text{Si}$ , are not satisfactorily fixed by any of the internal standards. Unfortunately, it seems that very little is consistent, and each element for each run needs to be evaluated to see which internal standard is best.

My method involves:

- Running an SRM, and if possible, the same sample at the beginning and end of the run.
- I quantify first with In and Bi (Bi seems to work really well, so I don't mess with Pb and U), and remove points like normal. Any lines that are split so that all points are <15% deviation I do not try to improve.

- Next I look at the other internal standards and see the shift in that internal standard over the run. First I check to see if it looks like that element is in the samples (much higher areas in the samples than the standards). Next I try to choose the next best internal standard to try. For example, if I have a lot of line splitting, and Ge looks similar to In, I would not try Ge next because it probably won't improve things. I would try an internal standard that had changed more over the run than In.

- Then I quantify with what I guess is the next best internal standard. IF the standard line appears to be better or similar to In, then I remove necessary points etc., to create a good line. IF the line appears worse than In (more splitting), I just ignore it and move on.

- I continue this process, quantifying with each of the internal standards, and only fixing up those lines that appear to be less split than with any of the other internal standards (this is just to save time...).

- After all the data are in Excel, I look at each element and determine which internal standard is the best to use. In general, I try to use as few different internal standards as possible (i.e., if  $^{89}\text{Y}$  is just slightly better than  $^{115}\text{In}$  for one element only, I would choose consistency and use  $^{115}\text{In}$ ).  $^{115}\text{In}$  and  $^{74}\text{Ge}$  are the most consistently useful, but sometimes other elements are necessary for the low masses. See discussion below on the specific elements. The way I judge which element is "best" is by looking at (1) the SRM – if the values of the elements are way off, then I become concerned.

Unfortunately, the SRM has a different matrix than the samples... Note that the SRM 1643d has Bi and Be in it, so can't be used to evaluate these. (2) Line splitting and % error in standards. I try to reduce the error in the standards and have as low a % as possible. (3) Drift – if I ran a sample at the beginning and end of the run, I look to see how much the concentration changed. This can be pretty significant sometimes. (4) Consistency among internal standards. Occasionally, one internal standard will give really different sample concentrations, maybe due to the presence of the internal standard in the standard (e.g., Sc and Y in UP lakes), or due to I have no idea. But, if one internal standard gives really different results, I don't trust it.

- Typically, I take the columns of sample name, % deviation, flags and concentrations and put results from all of the internal standards on one sheet and compare them. If  $^{115}\text{In}$  looked good originally (no line splitting) I won't bother with any of this. Or, if an internal standard didn't seem to improve any of the line splitting I will not ever bring it into Excel.

$^9\text{Be}$ : Seems to be more affected by matrix than  $^{115}\text{In}$ . Occasionally proves to be useful, but doesn't consistently fix the low masses.

$^{45}\text{Sc}$ : Has been useful in getting the standard lines to not split, but we seem to have Sc in our samples. Areas will suddenly jump to 200% with samples – not a good sign...

1870-1871

1872-1873

1874-1875

1876-1877

1878-1879

1880-1881

1882-1883

1884-1885

1886-1887

1888-1889

1890-1891

<sup>74</sup>Ge: Often provides an improvement over <sup>115</sup>In for the lower masses, but not great for the lowest masses (e.g., Al, Mg, etc).

<sup>89</sup>Y: Seems to be more affected by matrix than <sup>115</sup>In. This sometimes can be advantageous in bringing the split lines together. May be Y in Upper Peninsula Lakes.

<sup>115</sup>In: I still trust this one the most, but it really isn't working with the low masses these days. Works great for <sup>114</sup>Cd...

<sup>209</sup>Bi: Can get very high % deviations during the run, but seems to do a good job w/ Pb and U (though still some line splitting with U). I have not tried to replace Bi, and always use it for these masses (above method does not apply). Could try thallium.

### **Conditioning**

Recently, due to the large amount of line splitting, I have increased the amount of conditioning that we do. I have conditioned with up to 6 x 6mL of conditioning solution, but it is hard to tell how much it helps, since we still have line splitting. The instrument clearly runs better the second day of a similar matrix, so it seems that hours of conditioning are what the instrument really needs. Unfortunately, the tune tends to drift as the instrument cleans itself, and I'm not sure that it is worth running the tune until the drift stops, as this may just make the actual run drift more as the instrument gets dirty again. I still recommend at least 4 conditioning solutions (6mL ea) when the instrument is clean. This could be tested... And I don't rinse for a long time between the conditioning and actual run.

### **Matrix matching**

Matrix matching with Ca still seems necessary. If you want data for Sr, it is necessary to run a blank without Ca. Do NOT include this blank in the line, run it as an analyte, we will use the data later in Excel to calculate corrected Sr conc.

Ca is the only element I so far have had success matrix matching with. I tried matrix matching Witch Lake with Fe (60 ppm), but that lead to poor results in elements such as <sup>114</sup>Cd. Samples I reran at the beginning and end of the core had drifted considerably. I reran the lake with no matrix match, and it ran fine, so Fe should not be used to matrix match. Na might be necessary to match with, but I've never had enough Na to find out.

It seems that the instrument is not intensely sensitive to exact amount of Ca, just that there is some. I have run lakes with a large variation of Ca concentrations and just used a value in the middle and gotten good results. I just look at the entire core and visually estimate an average Ca value, and pick a nice round number. I recommend matrix matching >10 ppm Ca, but this is a guess, not experimentally proven.

## Other

Overall, the amount of line splitting that has been occurring recently has resulted in a lot of lost data. My last thought to try is to let background go >400 so that baking will not be necessary so often. There seems to be the worst splitting after baking or after cones / torch has been cleaned. This should perhaps be experimented with. Additionally, running several days in a row will probably help things, especially if done without baking.

### ICP-MS element notes

<sup>7</sup>Li: Interference from laser, high background

<sup>11</sup>B: interference from laser, high background

<sup>24</sup>Mg: Saturates 5000 ppb, not at 2000

<sup>25</sup>Mg: Corresponds well with <sup>24</sup>Mg, does not saturate at 5000 ppb

<sup>27</sup>Al: Saturates at 5000 ppb, not 2000. Good curve to 15 ppb (6-13-02 LS)

<sup>29</sup>Si: Tend to get split lines, ok after ~200 ppb. Try <sup>28</sup>Si.

<sup>31</sup>P: Tend to get split lines, ok > 200 ppb. Have run 30 ppm without saturating on old instrument. High ionization energy.

<sup>39</sup>K: Saturates near 1 ppm. Splits easily.

<sup>44</sup>Ca: Does not saturate at 15 ppm, use instead of <sup>40</sup>Ca

<sup>45</sup>Sc: Low end poor, only good > 10 ppb

<sup>47</sup>Ti: OK > 10 ppb, but does not run well at all at low end. Much line splitting.

<sup>51</sup>V: good to 0.05 ppb

<sup>52</sup>Cr: good

<sup>54</sup>Fe: does not saturate at 5000 ppb. Low end ok, ~0.1 ppb.

<sup>55</sup>Mn: Saturates detector near 1 ppm

<sup>59</sup>Co: fine, but does not always run well at low end. Splitting issues.

<sup>60</sup>Ni: good >0.2 ppb. Ni in cones, watch for odd high pts.

<sup>63</sup>Cu: watch blanks and spikes, Cu in instrument

<sup>66</sup>Zn: runs fine, watch for contamination from latex gloves.

<sup>70</sup>Ge: consistently non-linear on old instrument

<sup>74</sup>Ge: fine, but conc diff from <sup>70</sup>Ge

<sup>75</sup>As: good

<sup>78</sup>Se: OK, also try <sup>80</sup>Se (interference by <sup>40</sup>Ar, watch background)

<sup>85</sup>Rb: great

<sup>88</sup>Sr: fine curve, but Ca matrix match also adds Sr. Need to correct for this or Sr conc will be artificially low.

<sup>95</sup>Mo: fine

<sup>114</sup>Cd: fine

<sup>115</sup>In: internal std

<sup>120</sup>Sn: very good lines

<sup>138</sup>Ba: very good lines

<sup>208</sup>Pb: good

<sup>209</sup>Bi: internal std

<sup>238</sup>U: great

For more ICP info:

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