Inland Lakes Sediment Trends: Sediment Analysis Results for Six Michigan Lakes

Yearly report: 2002-2003
Houghton Lake
Hubbard Lake
Imp Lake
Round Lake (North Manistique)
Torch Lake
Witch Lake

Project Team:
Sharon S. Yohn[1]
Matthew J. Parsons[1]
David T. Long[1]
John P. Giesy[2]
Lydia K. Scholle[1]
Lina C. Patino[1]

[1]Aqueous & Environmental Geochemical Laboratories
Department of Geological Sciences
Michigan State University
East Lansing, Michigan 48824-1115
long@msu.edu

[2]Aquatic Toxicology Laboratory
Department of Zoology
Michigan State University
East Lansing, Michigan 48824-1115
jgiesy@aol.com

Inland Lakes Sediment Trends: Sediment Analysis Results for Six Michigan Lakes

Table of Contents

Inland Lakes Sediment Trends: Sediment Analysis Results for Six Michigan Lakes

Acknowledgements

Introduction

Contaminated sediments can directly impact bottom-dwelling organisms and represent a continuing source of toxic substances in aquatic environments that may impact wildlife and humans through food or water consumption (Catallo et al., 1995). Therefore, an understanding of the trends of toxic chemical (e.g., polychlorinated biphenyls, lead) accumulation in the environment is necessary to assess the current state of Michigan's surface water quality and to identify potential future problems. A common fate of chemicals in a lake is to associate with fine-grained particulate matter and settle to the bottom (Evans and Rigler, 1983). As this deposition occurs over time, sediments in lakes become a chemical tape recorder of the temporal trends of toxic chemicals in the environment as well as of general environmental change over time (von Guten et al., 1997). Sediment trend monitoring is consistent with the framework for statewide surface water quality monitoring outlined in the January 1997 report prepared by the Michigan Department of Environmental Quality entitled, "A Strategic Environmental Quality Monitoring Program for Michigan's Surface Waters" (Strategy). A key goal of the Strategy is to measure trends in the quality of Michigan's surface waters, and one activity designed to examine these trends is the collection and analysis of high-quality sediment cores. This report details the activities and findings of the fourth year of the sediment trend component of the Strategy, and builds upon the results from the five lakes sampled in 1999 (Year 1)(Simpson *et al.*, 2000b), two lakes sampled in 2000 (Year 2) (Yohn et al., 2001), and five lakes samples in 2001 (Year 3) (Yohn et al., 2002b).

Summary

Sediment cores were collected from five lakes in 2002 to evaluate the spatial and temporal variations in lake sediment quality in Michigan, and as a continuation of the trend monitoring component of the Strategy (Simpson *et al.*, 2000b). Lakes include: Houghton (Roscommon County), Imp (Gogebic), Round or North Manistique (Luce), Torch (Antrim), and Witch (Marquette) lakes. Additionally, results from Hubbard Lake (sampled 2001, Alcona County) will also be presented. Sediment cores were collected from one site in each lake, dated with ^{210}Pb and ^{137}Cs, and analyzed for a suite of metals and organic compounds. Analysis for a suite of metals rather than just target anthropogenic metals (e.g., Pb, Cu) allows for interpretations about the sources for different chemicals. Additionally, porewater was collected from each of the lakes and analyzed for a similar suite of metals. Key findings include:

- The sediment core collected from Hubbard Lake was not taken from an area of continuous sediment deposition, and evidence of erosion was apparent in the sediment chemistry, despite the collection of the core from a water depth of 96 feet. As a result, Hubbard Lake sediment could not be dated.

- Copper concentrations in Houghton Lake are elevated due to the addition of copper sulfate to the lake.

- Sediment concentration profiles in Witch Lake appear to be greatly influenced by large inputs of terrestrial materials that are enriched in copper, possibly due to mining activities in the region.

- Houghton and Imp lakes generally have the highest surface sediment concentrations of copper, cadmium, lead and zinc compared to the six study lakes. Among all the study lakes Cadillac Lake has the highest surface sediment concentrations.

- Whitmore and PawPaw lakes generally have the highest focusing corrected anthropogenic accumulation rates, with Cadillac and Houghton lakes having the highest copper accumulation rates.

- Accumulation rates of anthropogenic elements generally increase towards the surface in Cadillac, Crystal B, Imp and Round lakes.

- Focusing corrected anthropogenic accumulation rates are relatively similar between lakes in close proximity (Houghton and Higgins lakes, and Elk and Torch lakes). This suggests that the lakes in close proximity have similar sources.

- Average focusing corrected anthropogenic inputs of cadmium, copper, lead and zinc from 1970-1980 and 1990-2000 positively correlate with watershed population density and percentage of urban land cover in the watershed. There is also a positive correlation between percentage wetland land cover and anthropogenic inputs of copper in 1990-2000, and cadmium, lead and zinc in 1970-1980.
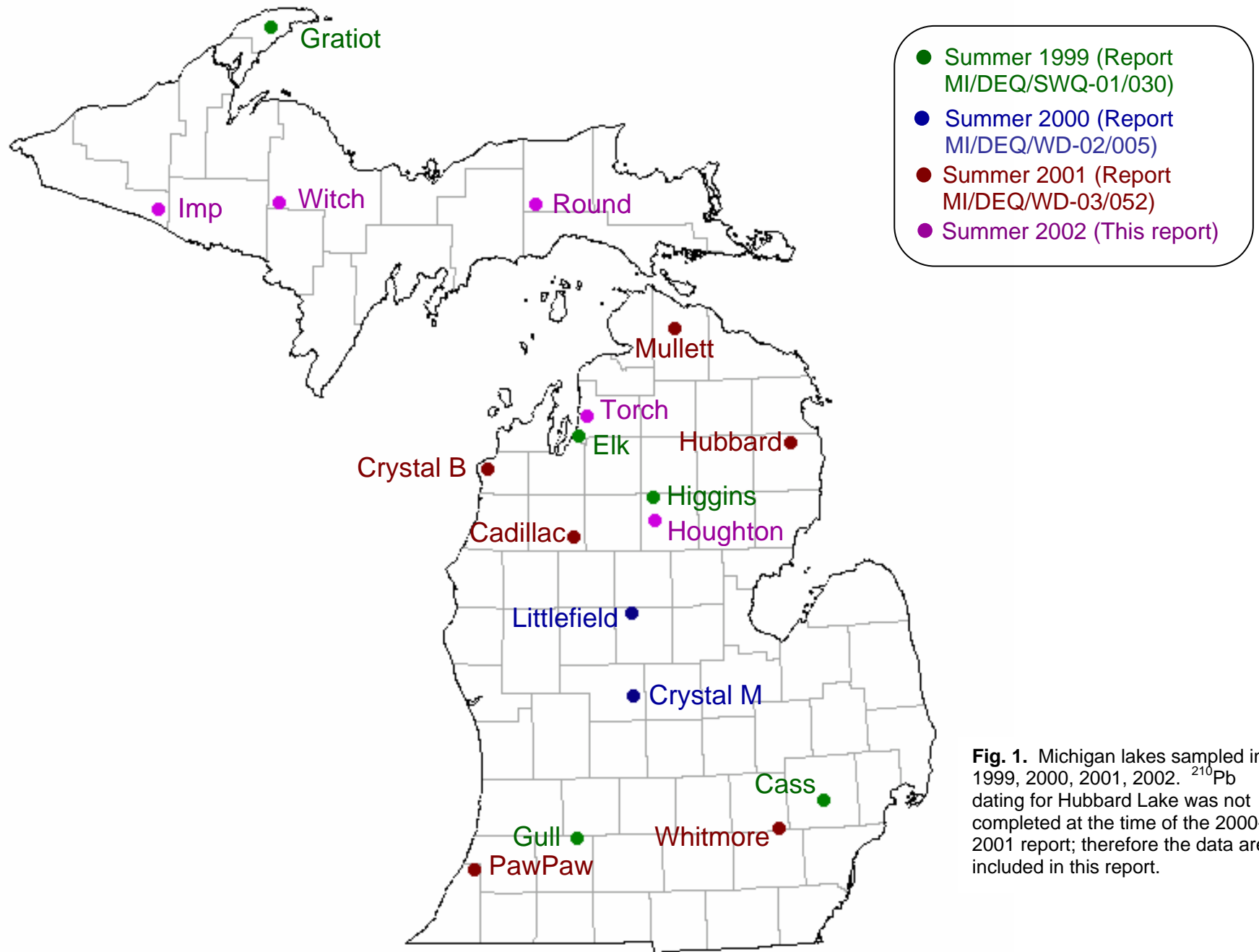
Methods

Sediment cores were collected from Houghton (Roscommon County), Imp (Gogebic), Round or North Manistique (Luce), Torch (Antrim), and Witch (Marquette) lakes in 2002 (Fig. 1, Table 1), and Hubbard Lake (Alcona) in 2001. 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. The M/V Nibi was designed to, and has successfully provided access to both major and remote inland lakes throughout Michigan. Collected sediment cores were described and examined for color, texture, and signs of zoobenthos. 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.

Table 1. Characteristics of study lakes.

Lake	Sampling year	Counties of watershed	Lake area (km²)	Sampling depth (m)	Watershed area (km²)
Cadillac	2001	Wexford, Missaukee	4.7	8.2	48
Cass	1999	Oakland	5.2	36.6	9.1
Crystal B	2001	Benzie	39.3	49.7	106
Crystal M	2000	Montcalm	2.9	16.8	12
Elk	1999	Grand Traverse, Antrim, Kalkaska	31.3	58.8	217
Gratiot	1999	Keweenaw	5.8	23.8	31
Gull	1999	Kalamazoo, Barry	8.2	33.5	61
Higgins	1999	Roscommon, Missaukee, Crawford	38.9	41.5	108
Houghton	2002	Roscommon	81.2	5.5	450
Hubbard*	2001	Alcona	37.9	29.3	
Imp	2002	Gogebic	0.3	28.0	2.1
Littlefield	2000	Isabella	0.7	21.3	17
Mullett	2001	Cheboygan, Otsego	70.3	35.7	718
Paw Paw	2001	Berrien, VanBuren	3.7	27.7	30
Round	2002	Luce	7.0	13.7	22
Torch	2002	Antrim, Kalkaska	76.0	86.0	198
Whitmore	2001	Washtenaw, Livingston	2.7	20.4	5.6
Witch	2002	Marquette	0.9	31.1	13

* A watershed was not delineated for Hubbard Lake.

^{210}Pb was measured on one sub-core from each lake to determine porosity, accumulated dry mass, sedimentation rates, sediment ages and focusing factors (Freshwater Institute in Winnipeg, Manitoba, Canada). Results from all lakes were verified using ^{137}Cs. Dating for Hubbard Lake (sampled 2001) was not completed at the time of the 2000-2001 year-end report; therefore results will be presented in this report.

Fig. 1. Michigan lakes sampled in 1999, 2000, 2001, 2002. ^{210}Pb dating for Hubbard Lake was not completed at the time of the 2000-2001 report; therefore the data are included in this report.

Legend:
- Summer 1999 (Report MI/DEQ/SWQ-01/030)
- Summer 2000 (Report MI/DEQ/WD-02/005)
- Summer 2001 (Report MI/DEQ/WD-03/052)
- Summer 2002 (This report)

Lake labels: Gratiot, Imp, Witch, Round, Mullett, Torch, Elk, Hubbard, Crystal B, Higgins, Cadillac, Houghton, Littlefield, Crystal M, Cass, Gull, Whitmore, PawPaw

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 μm polycarbonate filter. Samples were then analyzed using a Micromass Platform inductively coupled, plasma, mass spectrometer with hexapole technology (ICP-MS-HEX). Sediments were analyzed for a suite of metals and metalloids including Mg, Al, K, Ca, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, As, Sr, Mo, Cd, Ba, Pb, and U.

Another sub-core was sectioned and used for analysis of organic contaminants. There was insufficient material for analysis in the topmost sediments, so the first two sections were combined, and the third and fourth sections were combined. Polychlorinated biphenyls (PCBs), polyaromatic hydrocarbons (PAHs), organochlorine (OC) pesticides (screening only), alkylphenols, and bisphenol A (BPA) were analyzed (Khim *et al.*, 1999a, Khim *et al.*, 1999b). A portion of the sediment was dried at 100°C to determine moisture content.

The fourth sub-core was used for the collection of porewater. The sediment core was squeezed 5-6 cm, forcing water through Porex into syringes placed every 1 cm (10 samples) then 2 cm (18 samples) from the top. The collected water was filtered through an acid washed, DDW rinsed 0.40 μm polycarbonate filter and preserved with nitric acid and gold (for mercury analysis). These solutions were analyzed on the ICP-MS-HEX in a similar fashion as the digested sediments.

Porewater collection

Descriptions of the calculations for data analysis follow this section.
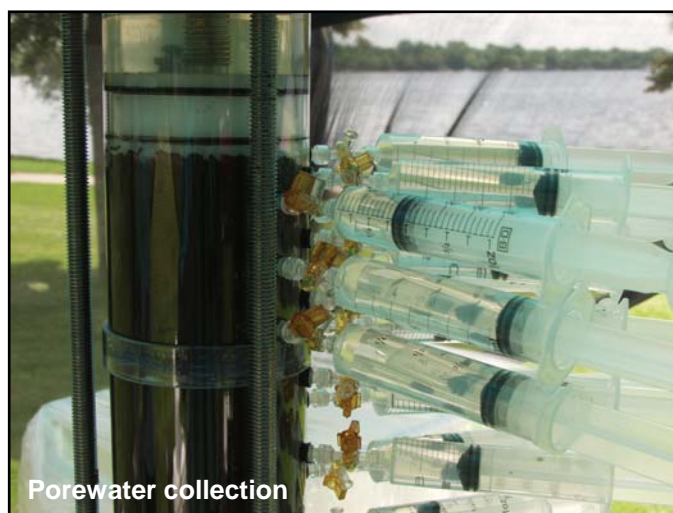
²¹⁰Pb and sedimentation rates

The radioactive isotope 210-lead (^{210}Pb) was used to date sediments from each lake. Several models exist to determine sediment ages from ^{210}Pb activities, and sediments were dated using the constant flux: constant sedimentation rate model (CF:CS) (Golden et al., 1993), segmented CF:CS (SCF:CS) (Heyvaert et al., 2000), rapid steady state mixing model (RSSM) (Robbins, 1982), and the constant rate of supply model (CRS) (Sanchez-Cabeza et al., 2000). The CF:CS model assumes a constant sedimentation rate throughout the core. The RSSM model also assumes a constant sedimentation rate, but also allows for a mixed zone. The SCF:CS model allows for more than one sedimentation rate, and accounts for the mixed zone. The CRS model determines a different sedimentation rate for each sample. Further description of each of the models may be found in the 2001-2002 year end report (Yohn et al., 2002b).

For all models, sediment deeper than the presence of excess ^{210}Pb cannot be dated. Cores from Houghton (16 samples), Imp (30) and Witch (9) lakes all had samples below the presence of excess ^{210}Pb. Therefore, dates older than this were determined for these lakes by extrapolation, using the assumption that sedimentation rates remain constant below this depth. For the RSSM, 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 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 that are reported primarily for graphing purposes.

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}Pb profile gave some insight into the most appropriate model to be used. The RSSM or CRS models are 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. Additionally, this study uses two other indicators to determine the most appropriate model to use: profiles of ^{137}Cs activity and stable lead concentration profiles. ^{137}Cs is an artificial radionuclide that was produced by atmospheric testing of nuclear weapons in the late 1950s and early 1960s. The peak level of fallout occurred in 1963, and therefore the peak activity in the sediment should occur 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 (Alfaro-De la Torre and Tessier, 2002, Callender and vanMetre, 1997). Therefore the dating method with both the most appropriate date for the ^{137}Cs peak (1963-64) and stable lead peak (early to mid-1970s) was chosen.

Overall, the lakes included in this report were more difficult to date than previous lakes. In two of the lakes (Round and Witch) the ^{137}Cs peak and the stable lead peak are in the same sample,

and in Imp Lake the ^{137}Cs peak is more recent than the stable lead peak. This suggests that one of these indicators is invalid for these lakes. Additionally, relatively large mixed zones were present in Round, Houghton and Witch lakes (Table 2). Analysis of each lake and the rationale for the choice of dating model will be described below.

Focusing factors were also determined from ^{210}Pb analysis. Focusing occurs when fine grained sediments in a lake are eroded from higher energy erosional zones near the shore of the lake, transported through transitional zones (where deposition and erosion occur episodically) and deposited in depositional zones (Downing and Rath, 1988, Hakanson, 1977). This process of focusing occurs at different extents among lakes, and must be accounted for using the focusing factor before comparing inventories and accumulation rates among lakes. A complete explanation of the focusing factor can be found in the 2001-2002 year end report (Yohn et al., 2002b).

Table 2. Select data from ^{210}Pb analysis, including the model used for dating, mixed depth, sedimentation rate (g/m^2/y), focusing factor (FF) and the age of the oldest section in the sediment core.

	Model	Approximate mixed depth (cm)	Sedimentation rate (g/m^2/y)	FF	Oldest section
Cadillac	CRS	14	117	1.7	1829[a]
Cass	CF:CS	3	3480	6[c]	1971
Crystal B	CRS	4	624	2.9	1516[a]
Crystal M	CRS	6	465	1.7	1732[a]
Elk	SCF:CS	1	337	2.1	1279[a]
Gratiot	CF:CS	5	255	2.5	1823[a]
Gull	SCF:CS	3	404	1.8	1496[a]
Higgins	CF:CS	3	232	2.0	1729[a]
Houghton	SCF:CS	8	165	1.2	1715[a]
Hubbard	NA	NA	NA	0.3	NA
Imp	CRS	3	119	1.5	1745[a]
Littlefield	Pb	NA	444	2.0[b]	1732[a]
Mullett	SCF:CS	4	801	3.6	1708[a]
Paw Paw	CF:CS	3	828	2.7[c]	1923
Round	CRS	7	317	2.3	1851
Torch	SCF:CS	0	944	2.4	1760
Whitmore	SCF:CS	6	556	2.8[c]	1887
Witch	CRS	6	269	1.7	1767[a]

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 factor based on extrapolation

Houghton Lake had a large mixing zone (8 cm), and ^{210}Pb decay that was not log-linear (Fig. 2a). This non-linearity suggests that sedimentation rates varied over time, and that the CF:CS and RSSM models are not appropriate. The CRS model placed the ^{137}Cs peak at 1948 (expected 1963), and the stable lead peak at 1962 (expected 1972). Therefore the SCF:CS model, with three sedimentation rates, was used. The ^{137}Cs peak was at 1962, and the stable lead peak at 1968 when this dating model was used.

Activity profiles of ^{210}Pb and ^{137}Cs indicate that the sediment core from Hubbard Lake was not taken in a depositional zone, and that the surface of the core may not represent current sediment deposition. The ^{137}Cs profile does not have a subsurface peak (Fig. 2a) like the other lakes, but instead has the highest activity at the sediment surface. This suggests that more recently deposited sediment may have been removed. Additionally, the stable lead concentration profile looks dissimilar to other lakes, and increases to the surface in a manner similar to ^{137}Cs. Furthermore, sand was present in the sediment core. Sediment deposited in low energy depositional zones (where no erosion occurs) typically are characterized by silts and clays, while sand is more prevalent in higher energy erosional and transitional zones (Blais and Kalff, 1995, Downing and Rath, 1988, Hakanson, 1977). Finally, Hubbard Lake has a focusing factor of only 0.28. A focusing factor greater than one is expected in a deposition zone, while a focusing factor less than one occurs in erosional zones (Golden *et al.*, 1993, Kerfoot *et al.*, 1994). Therefore, the core from Hubbard Lake does not seem to represent a continuous record of deposition, and cannot be dated. Additionally, element profiles should not be interpreted in the same manner as undisturbed cores.

Imp Lake had high ^{210}Pb activities near the sediment surface, and a three cm mixed zone (Fig. 2a). The ^{210}Pb profile is not log-linear,
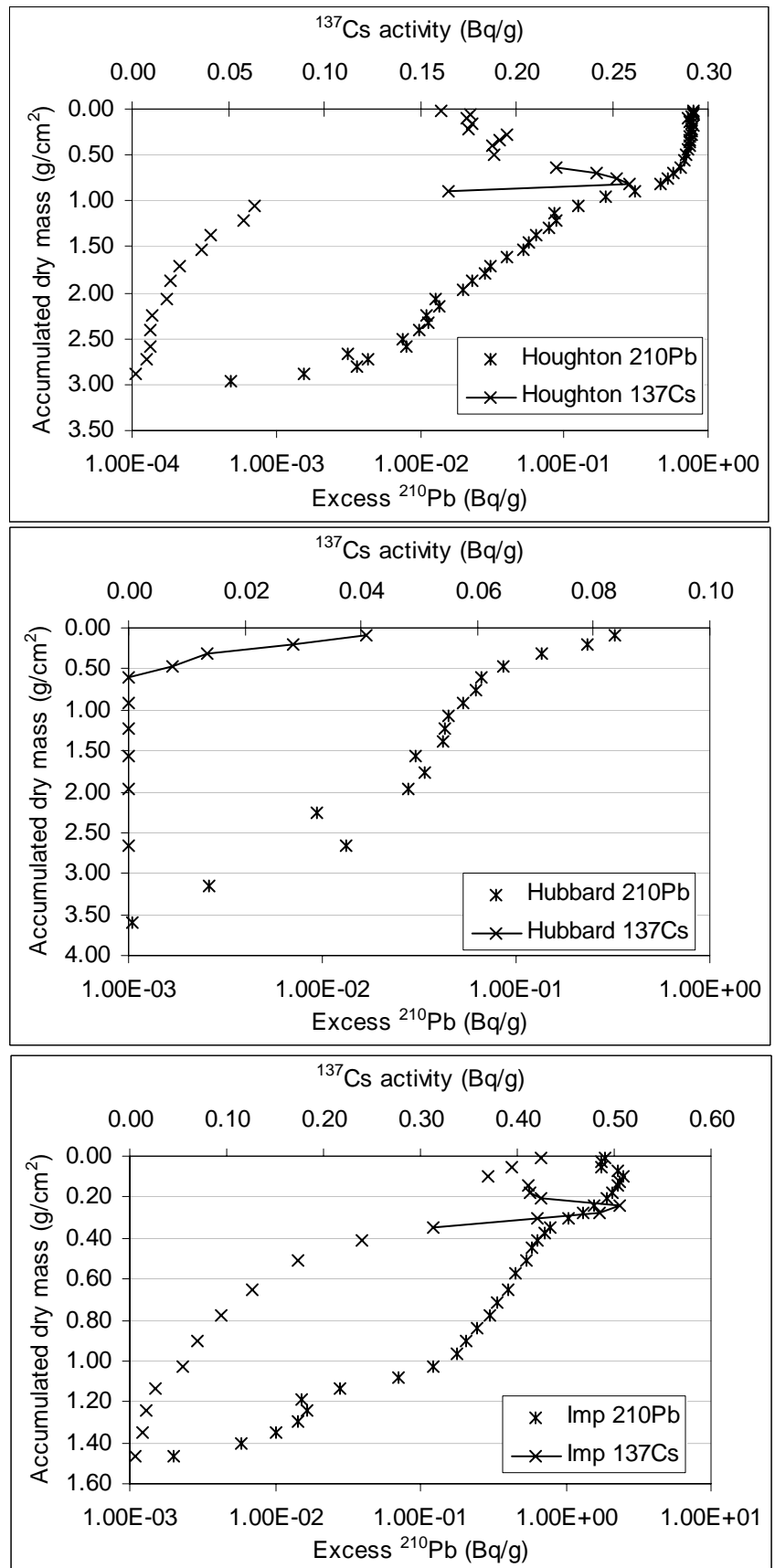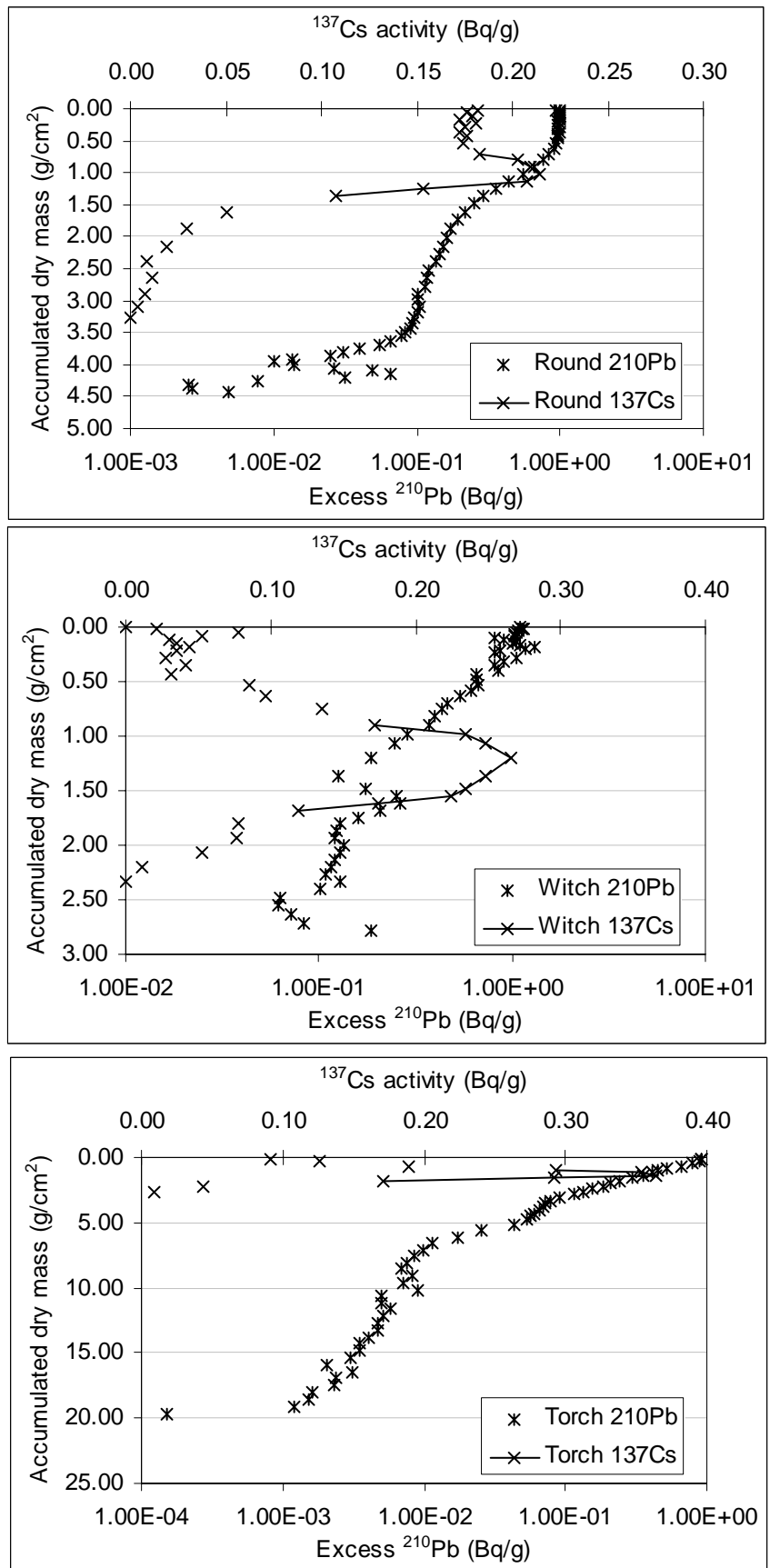

Fig. 2a. ^{137}Cs and ^{210}Pb activities (Bq/g) versus accumulated dry mass in Houghton, Hubbard and Imp Lakes. ^{137}Cs is plotted on the top scale.

suggesting changes in sedimentation rate over time. The choice of a dating model was complicated by the stable lead peak occurring below the ^{137}Cs peak in the sediment core. This suggests that one of these indicators must not be appropriate. For Imp Lake, the CF:CS, RSSM, and CRS models all placed the stable lead peak in the early 1970s, and the ^{137}Cs peak in the mid to late 1970s. Although it is unclear why, this suggests that the ^{137}Cs peak is inappropriate in this case as a dating indicator. The CRS model was chosen as the most appropriate model, placing the stable lead peak at 1974.

Round Lake had a relatively large mixing zone (6 cm), and a curvilinear ^{210}Pb profile (Fig. 2b). Stable lead and ^{137}Cs have the highest concentration in the same sample, again suggesting that one of these is not a good dating indicator. The CF:CS, RSSM, and CRS models all place this sample in the early 1970s, suggesting that stable lead may be the more appropriate indicator. The CRS model was chosen as the most appropriate, due to the apparent changes in sedimentation rate that would not be properly modeled by the CF:CS and RSSM models.

A large mixing zone (6 cm) was present in Witch Lake, and some disturbance of the ^{210}Pb profile was apparent near the surface (Fig. 2b). There is also an area of negative slope near 1.5 g/cm^2, indicating very high sedimentation rates, or some other disturbance of the lake sediment. The highest

Fig. 2b. [137]Cs and ^{210}Pb activities (Bq/g) versus accumulated dry mass in Round, Witch and Torch Lakes. [137]Cs is plotted on the top scale.

concentration of stable lead and ^{137}Cs occur in the same sample. The CF:CS, RSSM and CRS model all date this sample in the 1960s, suggesting that ^{137}Cs may be the more appropriate dating indicator. Additionally, the stable lead profile may have been dominantly influenced by processes other than atmospheric deposition, and therefore would not be expected to peak in 1972. Possible influences on this profile will be discussed further below.

A mixing zone was not present in Torch Lake, and several changes in sedimentation rate are apparent (Fig. 2b). Unsupported or excess ^{210}Pb values were quantifiable for almost the entire depth of the collected sediment core. This is surprising, because excess ^{210}Pb is only present in sediment deposited from the present to ~150-200 years ago, and cores collected in lakes similar to Torch (e.g., Elk and Gull) contained much older sediment (e.g., 600-800 years old) (Yohn et al., 2002b). Interpretation of the ^{210}Pb profile is also difficult because all dating methods (CF:CS, CRS, RSSM and SCF:CS) place the stable lead and ^{137}Cs peaks at dates that are too recent. Dates were also calculated using the stable lead peak (assigned to 1972) or the ^{137}Cs peak (assigned to 1963). These two methods resulted in stable lead profiles that were more similar to other lakes, however, much of the sediment core was assigned dates older than 1800, where excess ^{210}Pb should not be present. Additionally, these methods did not account for changing sedimentation rates within the lake that were apparent from the ^{210}Pb profile. The most appropriate dating model was determined to be the SCF:CS model with five sedimentation rates. This model still places the stable lead and ^{137}Cs peaks too young (1983 and 1969 respectively), but appears to be the best estimation of the sediment dates. The difficulty in dating Torch Lake was unforeseen, as both Elk and Gull lakes did not have similar problems. It is unclear why none of the models placed the stable lead and ^{137}Cs peaks at the correct dates.

Organics

Surface concentrations of organic contaminants are generally highest in Houghton Lake and lower in Witch Lake (Table 2). All lakes, except Hubbard, contain polychlorinated biphenyls (PCBs) and pesticides and all lakes contain polyaromatic hydrocarbons (PAHs).

Total wet weight PAH concentrations are similar to Lower Peninsula lakes sampled previously, Figure 3. PAH concentrations in Hubbard Lake were lowest.
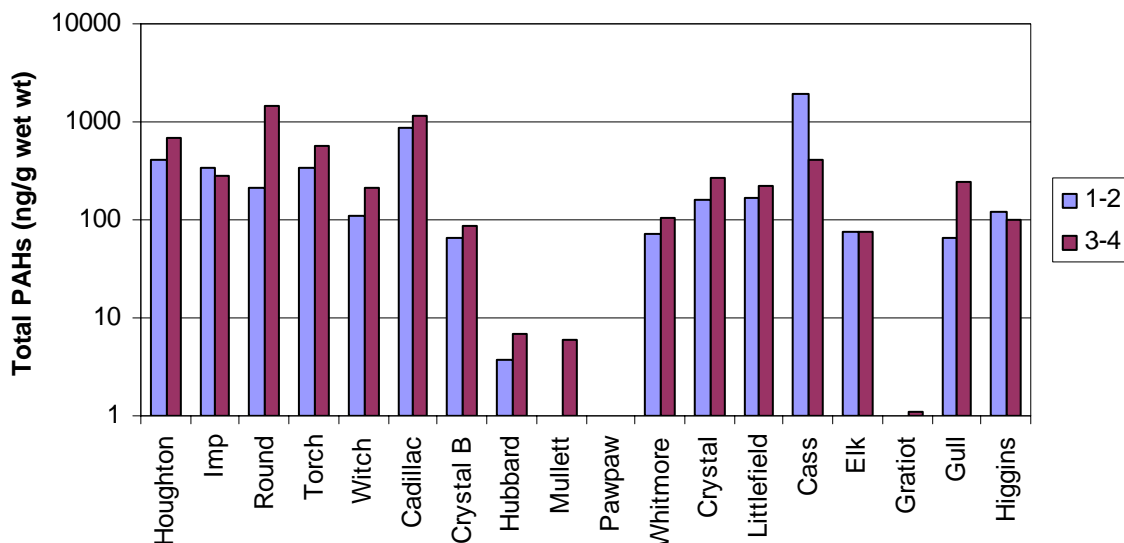
Fig. 3. Concentrations (ng/g wet wt) of total PAHs from the sediments for samples 1-2 (0-2 cm), and samples 3-4 (2-4 cm) for 18 Michigan Lakes. Concentrations are plotted on a log scale
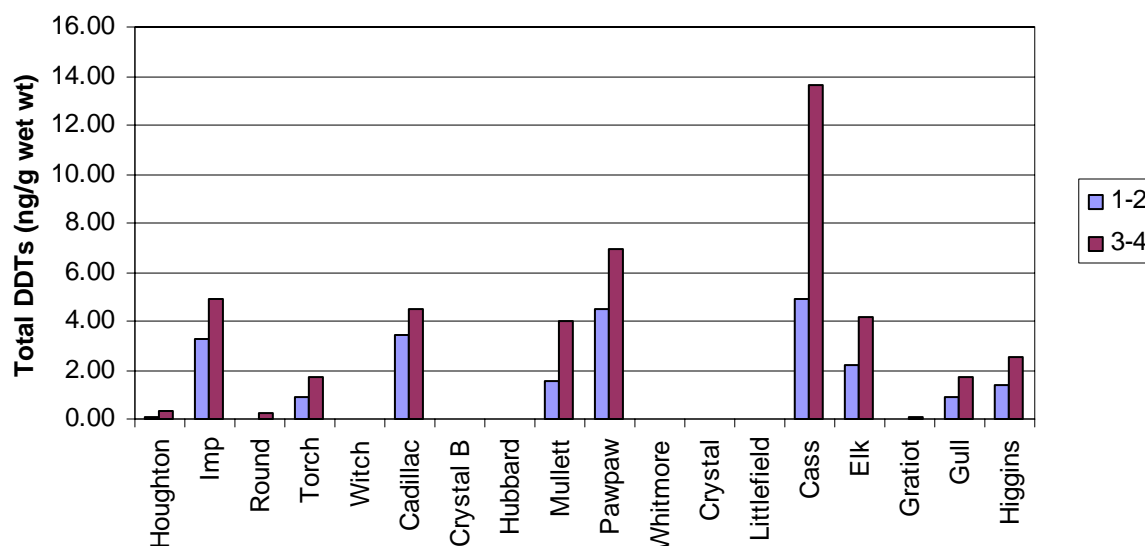
Fig. 4. Concentrations (ng/g wet wt) of total DDTs from the sediments for samples 1-2 (0-2 cm) and samples 3-4 (2-4 cm) for 18 Michigan Lakes

Total DDTs remain highest in Cass Lake, with Imp, Cadillac, Mullet, Paw Paw and Elk Lakes having lower values (Fig. 4.). The remaining lakes have little to no DDTs present. The concentration of DDTs will be influenced both by the current inputs of DDTs to the lake and by historic inputs. Historically, DDTs were used extensively, but use has decreased significantly over the last three decades. Samples from different lakes are from different ages, dependant on the sedimentation rate. Therefore, Elk Lake, with a low sedimentation rate, represents older sediments, and might be expected to have higher concentrations of DDTs (Simpson *et al.*, 2000a). All lakes have lower values of DDT's at the surface than in the sample below the surface, indicating that inputs of DDTs to these lakes are declining, as would be expected from the ban of DDT in the United States.

Table 2. Concentrations (ng/g dry wt) of various organic compounds for six Michigan Lakes

	Houghton 1	Houghton 2	Imp 1	Imp 2	Round 1	Round 2	Torch 1	Torch 2	Witch 1	Witch 2	Hubbard 1	Hubbard 2
cm depth[1]	0-2	2-4	0-2	2-4	0-2	2-4	0-2	2-4	0-2	2-4	0-2	2-4
Age[2]	2001	2000	2002	2001	2002	2002	2001	1998	2002	2002	NA	NA
Total polychlorinated biphenyls (PCBs)	4.62	43.13	6.89	8.13	2.95	1.55	2.14	43.13	1.57	0.88	<1	<1
Total polyaromatic hydrocarbons (PAHs)	3101.4	5478.6	485.7	416.5	337.6	2146.2	656.7	1114.8	178.4	318.6	13.7	17.5
Naphthalene	38.7	194.0	37.5	18.0	19.6	20.7	19.8	76.7	7.4	118.0	<10	<10
Acenaphthylene	<6.3	39.1	1.9	1.6	1.4	1.7	4.9	5.4	<6.3	<6.3	<10	<10
Acenaphthene	<6.3	18.3	4.1	<6.3	2.0	3.0	4.0	15.9	<6.3	<6.3	<10	<10
Fluorene	75.2	156.8	7.5	7.5	2.4	2.1	5.2	7.0	1.7	1.5	<10	<10
Phenanthrene	344.4	732.4	42.2	44.8	25.9	23.3	78.3	122.6	16.1	12.0	<10	<10
Anthracene	15.9	51.1	<6.3	<6.3	2.5	2.2	<6.3	3.6	<6.3	<6.3	<10	<10
Fluoranthene	730.6	735.2	42.0	42.5	51.2	105.3	132.1	169.0	24.2	20.6	<10	<10
Pyrene	516.5	1657.3	27.7	27.7	38.2	1598.2	104.8	138.6	15.5	14.9	<10	<10
Benzo-A-anthracene	236.2	135.4	8.5	8.5	10.3	8.5	28.1	39.3	5.0	4.6	<10	<10
Chrysene	484.8	485.7	34.9	34.2	31.5	30.1	91.6	125.1	19.6	17.8	<10	<10
Benzo-B-fluoranthene	519.0	717.4	57.8	55.7	67.5	58.1	117.6	150.2	12.5	12.9	<10	<10
Benzo-K-fluoranthene	97.4	206.0	13.9	16.1	13.7	11.8	30.4	46.1	38.7	26.3	10.0	10.5
Benzo-A-pyrene	<6.3	34.1	83.8	<6.3	12.2	232.1	<6.3	<6.3	<6.3	<6.3	3.7	7.0
Indeno-1,2,3-CD-pyrene	42.6	44.4	60.3	48.3	13.0	10.3	26.0	145.8	37.7	33.4	<10	<10
Dibenz-a,h-anthracene	<6.3	219.6	5.7	46.6	46.3	38.9	13.8	69.6	<6.3	56.4	<10	<10
Benzo-G,H,I-perylene	<6.3	51.8	57.8	65.0	<6.3	<6.3	<6.3	<6.3	<6.3	<6.3	<10	<10
Total Pesticides	111.7	97.4	61.4	84.5	191.1	321.3	17.0	126.8	24.2	13.5	<10	<10

1. The first two slices were combined (cm 0-2), and the third and fourth slices (3-4 cm), due to insuffcient sample mass for analysis.
2. Since samples were combined[1] each analysis covers a range of years. The median age is presented for each of the combined samples.

Inorganic chemical sediment chronologies

There are multiple ways to examine and interpret sediment chronologies, and the most appropriate approach is dependant on objectives of the study. In this report, total concentration profiles will be presented, followed by surface concentrations, and focusing corrected anthropogenic accumulation rates. The concentration profile for each of the elements analyzed were compared within each lake, and grouped by similar profiles to determine the major influences on that element (Yohn et al., 2002b). Surface concentrations of arsenic, cadmium, copper, lead and zinc were compared among lakes and to sediment quality guidelines (MacDonald et al., 2000) to determine potential toxicity. Finally, focusing corrected anthropogenic accumulation rates were calculated and compared among all lakes. These rates provide the best possible estimate of the rate of input of a metal to the lake sediments due to humans. These profiles were also compared among lakes of close proximity to the 2002-2003 study lakes (Higgins and Houghton, and Torch and Elk lakes). The comparison of nearby lakes provides some insight to whether sources are unique to a lake, or present throughout the area.

Total concentration profiles

Introduction

Many different sources and processes influence the patterns of metal deposition in a sediment core, making it a challenge to interpret the historical records. The multi-element approach, which includes the analysis of more elements than just those of anthropogenic concern, helps provide insight into the history of the lake and assists in the interpretation of anthropogenic inputs. The first step to understanding multi-element data is grouping the elements that are influenced by similar sources and processes. Elements that have similar profiles in the sediment were grouped for each lake using cluster analysis (Table 4) (Yohn et al., 2002b). Four classes of elements were examined: terrestrial, calcium carbonate, diagenetic, and anthropogenic.

The first class includes the terrestrial elements, which are those that are influenced by the amount of allocthonous (material from outside the lake) non-organic material entering the lake. Changes in the input of terrestrial materials may be caused by increased erosion by natural (e.g., forest fires) or human (e.g., land use changes) processes (Davis, 1976). Elements that may be primarily influenced by these processes include aluminum, titanium and sometimes iron, potassium, cobalt, nickel, magnesium, sodium, scandium, and the rare earth elements (Boyle *et al.*, 1999, Bruland *et al.*, 1974, Johnson and Nicholls, 1988, Kemp and Thomas, 1976, Kerfoot and Robbins, 1999, Qu *et al.*, 2001, Sanei *et al.*, 2001).

Table 4. 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), Whitmore (Whit), Houghton (Hou), Hubbard (Hub) Imp, Round (Rou), Torch (Tor), and Witch (Wit). OR indicates that outliers were removed.

	Grat	Elk	Elk OR	Gull	Hig	Lit	Cr M	Cad	Cr B	Mul	Paw	Whit	Hou	Hub	Imp	Rou	Tor	Wit
Mg	T	T	T	C	T	C, T				T				T			T	T
Al	T	T	T	T	T	T	T	T	T	T	T	T	T	T	T	T	T	T
K	D	T	T	T	T	T	T		T	--	--	--	T				T	
Ca	T	C	C	C	C	C	C	C	C	C	C	C	C	C		C	C	
Ti	T	T	T	T		T		T		T	T	T	T	T		T		T
V	T	T	T	T			T	T	T	T	T	T	T	T		T	T	
Cr	T			T			T		T	T	A	T	T	T	T	T	T	T
Mn	D	D		D1	D2	D2	D1	D		D								D
Fe	A	D	T	D1		D1		D	T	D			D1		A	T	T	
Cu	A	A	A	A	A	T		A	A	A	A	A2	A	T	A		A	
Zn	A	A	A	A	A		A	A	A	A	A	A1	A		A	A	A	A
As	A	D	A	A,D2	D1	D1	D1	D		D	D2		D1		A			
Sr	T	--	--	--	C	C	C	C	C	C	C	C	C	C	T	C	C	
Mo		D		D2	D1	D1	D2				D2	D	D2			D		
Cd	A	A	A		A	A	A	A	A	A	A	A1	A	A	A	A	A	
Ba	D	D	T	C	D2	D2		C	C	D		T	T					D
Pb	A	A	A	A	A	A	A	A	A	A	A	A1	A	A	A	A	A	A
U	T	T	T	D2	D1	D1	D2	T				D	D2			D		

The second class includes calcium and strontium, which may be influenced by deposition of calcium carbonate. Soils, glacial material, and bedrock in most of the Great Lakes contain abundant limestone ($CaCO_3$). Thus, lakes become enriched in dissolved Ca and HCO_3 that can precipitate in the lake as a consequence of evaporation or photosynthesis (photosynthesis consumes CO_2, which raises the pH of the water). This portion of the sediment tends to have low concentrations of most metals and therefore acts as a diluting phase (Auer et al., 1996). The presence of carbonates may increase the concentration of calcium and strontium, and sometimes magnesium and barium (Auer *et al.*, 1996, Sanei *et al.*, 2001).

A third class includes those elements influenced by diagenesis. Early diagenesis is the alteration of sediment after deposition, and will obscure the depositional record. In the top few centimeters of sediment, there are major geochemical changes that occur. Organic matter is decomposed, which uses the oxygen in the sediment, and changes the sediment from an oxidizing to a reducing environment. This will change the mobility of many metals, and metals may mobilize from the sediment into the porewater (remobilization). For example, those metals that are associated with organic matter in the sediment can be released to the porewater as decomposition progresses. Those metals associated with iron and manganese oxyhydroxides would be released to the porewater when these oxyhydroxides dissolve because of the reducing conditions. Once in the porewater, metals may move from areas of high concentration to lower concentrations

through diffusive flux and/or be readsorbed to other sediments phases (Brown *et al.*, 2000, Cooper and Morse, 1998, Douglas and Adeney, 2000, Harrington *et al.*, 1998, McKee *et al.*, 1989, Urban *et al.*, 1990). In particular, arsenic is strongly adsorbed to iron oxyhydroxides, and profiles in the sediment may not reflect the historical record of arsenic deposition. For arsenic, which is influenced by both diagenesis and anthropogenic inputs, it is essential to be able to differentiate patterns caused by diagenesis from those caused by changes in anthropogenic inputs (Harrington et al., 1998). Another complication is that elements respond to changing redox conditions in different manners. While iron oxyhydroxides mobilize in reducing conditions, uranium and molybdenum remobilize in oxidizing environments (Brown et al., 2000). Therefore, it may be possible to have more than one group of diagenetic elements.

The final class is the anthropogenic elements. These elements have accumulated in lake sediments due to human actions, and may enter lakes from atmospheric deposition, or from inputs within the watershed. Humans may influence any element, but the geochemical cycles of arsenic, cadmium, copper, chromium, mercury, lead, and zinc have been modified by humans on the global scale (Bruland *et al.*, 1974, Evans and Dillon, 1982, Iskander and Keeney, 1974, Spiethoff and Hemond, 1996). Since the sources of each metal may be different (e.g., copper from copper smelting emissions, or lead from leaded gasoline), anthropogenic elements may follow similar trends or the trends may vary among elements, depending on the dominant sources and processes. Therefore, while elements in the terrestrial class should have very similar profiles, profiles of anthropogenic elements may vary. The profiles of the anthropogenically-influenced elements listed above were examined closely and compared to profiles of terrestrial elements to determine for each lake if deposition of that element was influenced by human activities. Although terrestrial elements are also influenced by human activities, we will consider the anthropogenic elements as those elements with sources due to humans in addition to increased erosion.

Houghton Lake

Terrestrial elements in Houghton Lake include aluminum, potassium, titanium, vanadium, chromium, and barium (Table 4). The concentrations of these elements remain relatively constant over time (Fig. 5), suggesting there were no large increases in terrestrial inputs (e.g., erosion due to logging) to Houghton Lake.

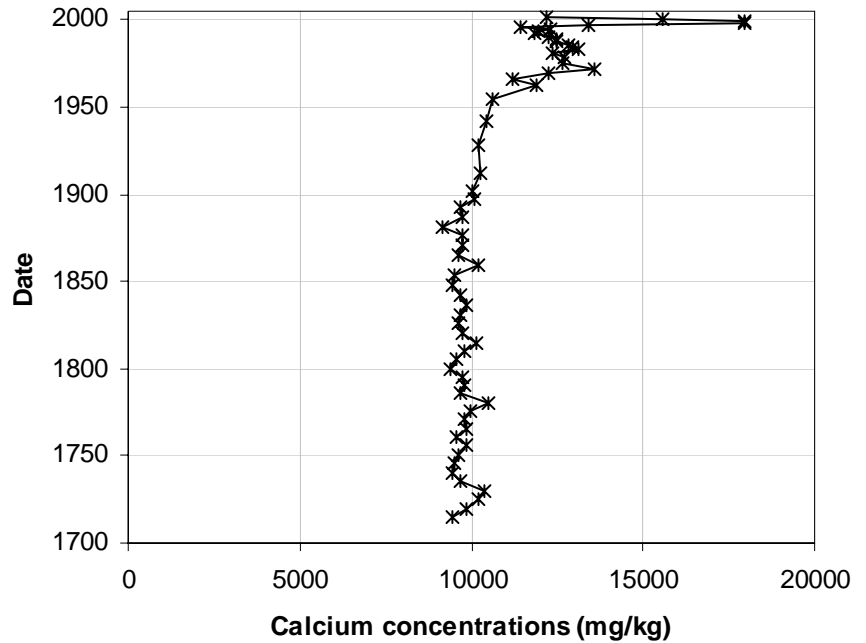Calcium and strontium are influenced by carbonate
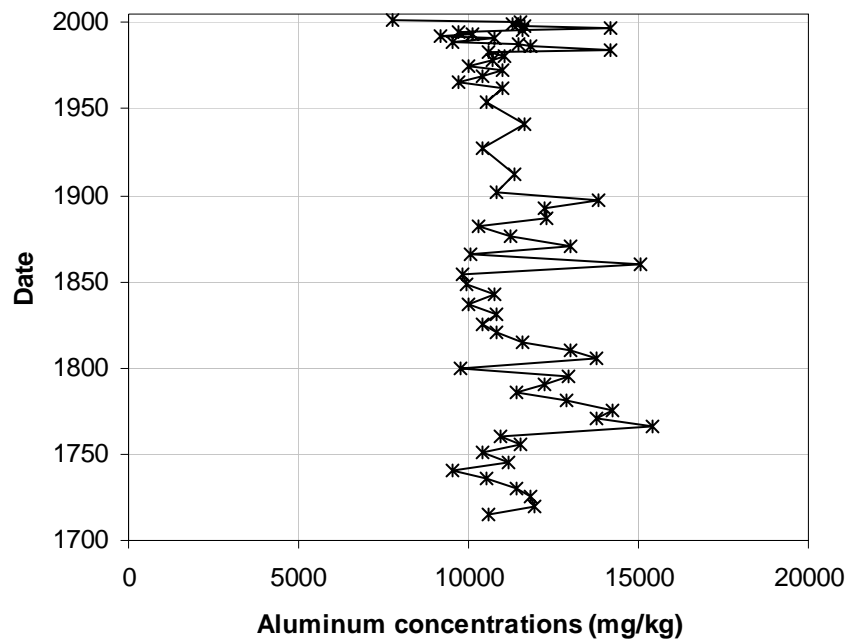
Fig. 5. Sediment concentration of aluminum (mg/kg) in Houghton Lake.

deposition in Houghton Lake (Table 4). Calcium and strontium concentrations do not vary greatly within much of the sediment core, however, there are higher concentrations in sediment deposited in the 1960s and 70s, and significantly higher concentrations in the late 1990s (Fig. 6). This may be due to increased productivity in the lake, where increased photosynthesis results in higher dissolved CO_2 concentration, and therefore more carbonate precipitation.

Arsenic in Houghton Lake sediment has a similar profile to iron (Fig. 7). This suggests that the arsenic profile is probably influenced more by diagenetic processes than anthropogenic inputs. It is possible that human inputs are partially responsible for the increased concentration in sediment deposited in the 1960s, however, it is not possible to determine the extent of human inputs due to the likelihood of remobilization in the sediment.

Concentration profiles of cadmium, copper, lead and zinc in Houghton Lake all show an increase in concentration from the late 1800s (Fig. 8). Cadmium, lead and zinc all have peak concentrations in sediment deposited near 1970, while copper peaks in the early 1980s. While cadmium, lead,

Fig. 6. Sediment concentrations of calcium in Houghton Lake.
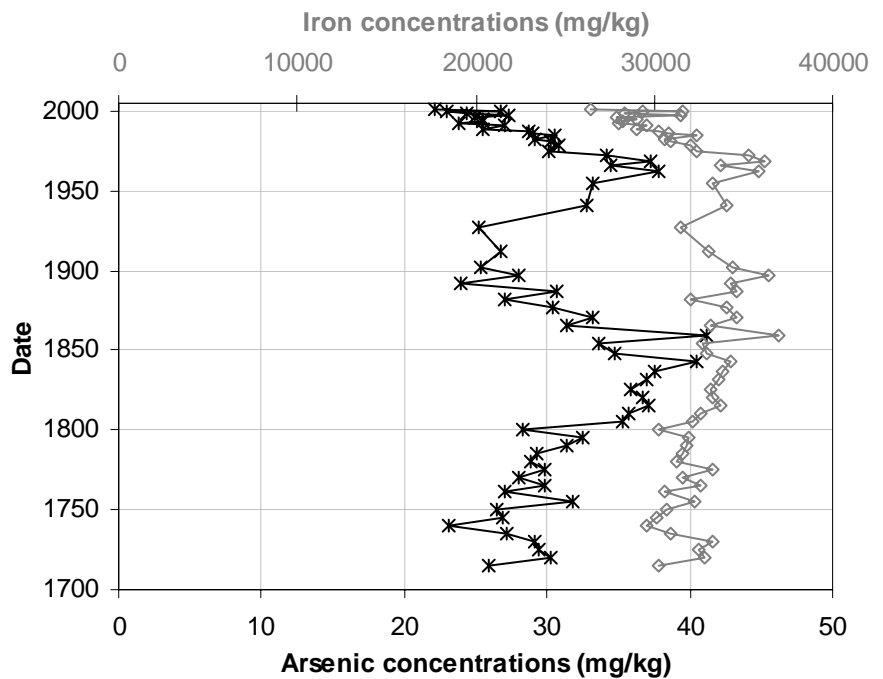
Fig. 7. Arsenic (black) and iron (grey) concentrations (mg/kg) in Houghton Lake.

and zinc concentrations are similar to other study lakes throughout the state (Yohn et al., 2002b), copper concentrations are much higher. The high copper concentrations in Houghton Lake are

likely due to the addition of copper sulfate to the lake to reduce the occurrence of swimmer's itch (schistosome cercarial dermatitis). The concentration of copper in Houghton Lake is much higher than most lakes, but lower than Cadillac Lake, which was also treated with copper sulfate (Yohn et al., 2002b).
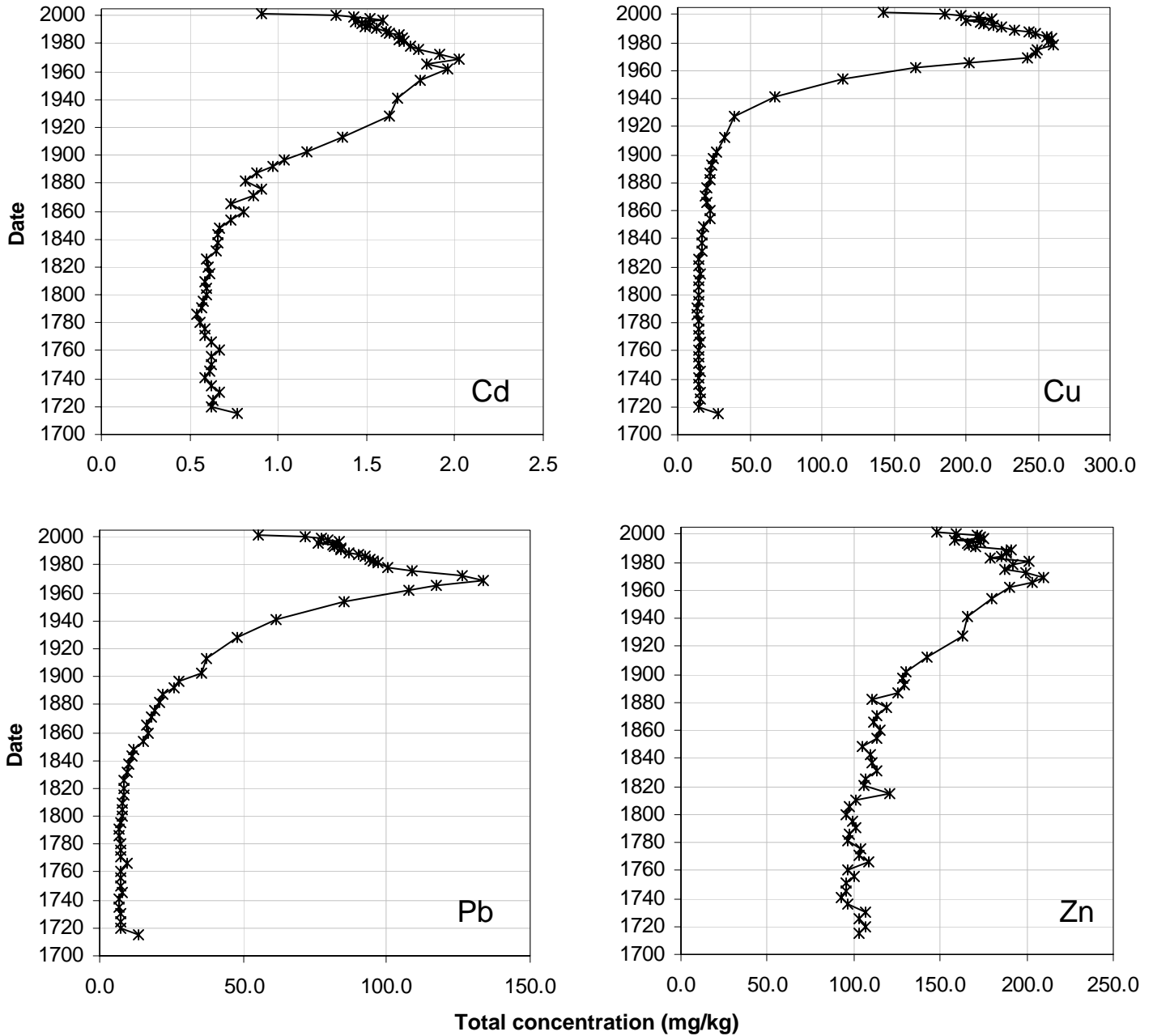

Fig. 8. Concentration profiles (mg/kg) of cadmium (Cd), copper (Cu), lead (Pb), and zinc (Zn) in Houghton Lake.
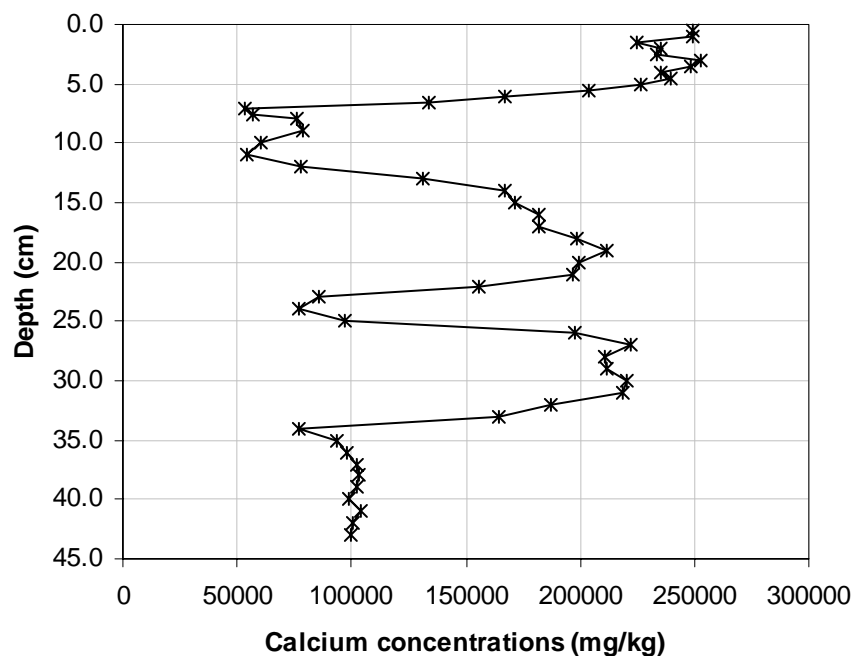
Hubbard Lake

Concentration profiles in Hubbard Lake are dissimilar to the other Michigan study lakes, and seemed to be dominantly controlled by the sediment type. The sediment core from Hubbard Lake contained sand throughout much of the core, and the sediment chemistry is influenced by this in much the same manner as Crystal Lake (Benzie County) (Yohn et al., 2002b). The surfaces of clays are reactive, and tend to have metals associated with them. Sands are less reactive, and therefore sand is depleted in all elements, including aluminum. The terrestrial elements include magnesium, aluminum, titanium, vanadium, chromium, and possibly copper (Table 4). These elements all have much higher concentrations at depths greater than 35 cm (Fig. 9), where the sediment is dominantly clay. Above 35 cm, where there is significant sand in the sediment, the concentration of the terrestrial elements is much lower.
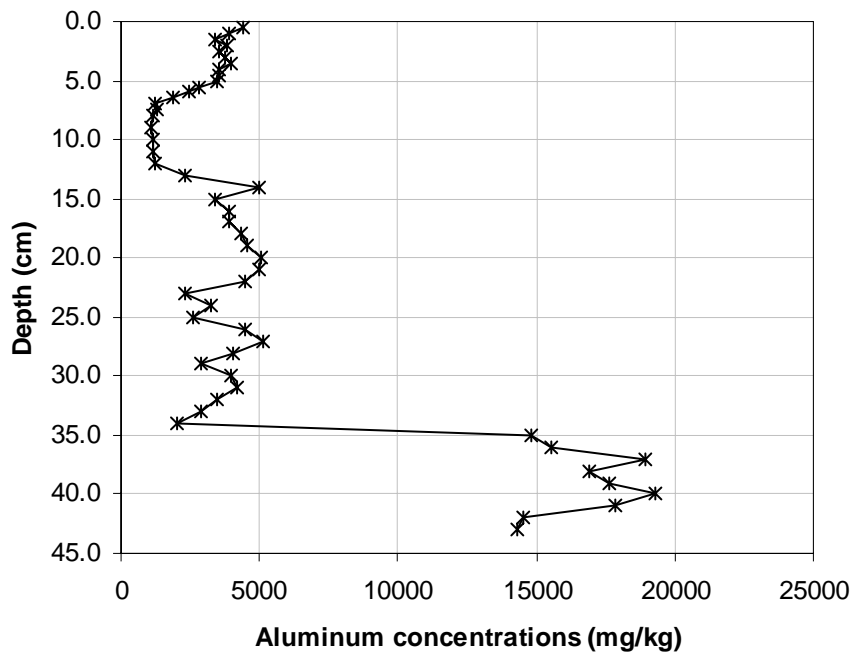
Fig. 9. Sediment aluminum concentrations (mg/kg) over depth in Hubbard Lake.

The carbonate elements (calcium and strontium) are also influenced by the changing sediment type (Fig. 10). The depths with the low concentrations of carbonate elements, 7-11 cm and near 25 cm, are visibly the sandiest areas within the core. It is likely that the sediment at these depths represent rapid deposition of the coarse sandy material, with little time for calcium carbonate precipitation. Below 35 cm, calcium concentrations are also low, suggesting less calcium carbonate deposition during this time period.

Fig. 10. Sediment calcium concentrations (mg/kg) over depth in Hubbard Lake.

Cadmium and lead both have higher concentrations in the surface sediments than elsewhere in the core, and are likely influenced by human inputs (Fig. 11). Profiles of copper and zinc are less clear, but it is likely that these elements have human sources as well (Fig. 11). The stable lead profile is dissimilar to other study lakes, and supports the conclusion made from the ^{210}Pb profile that portions of the sediment were eroded.
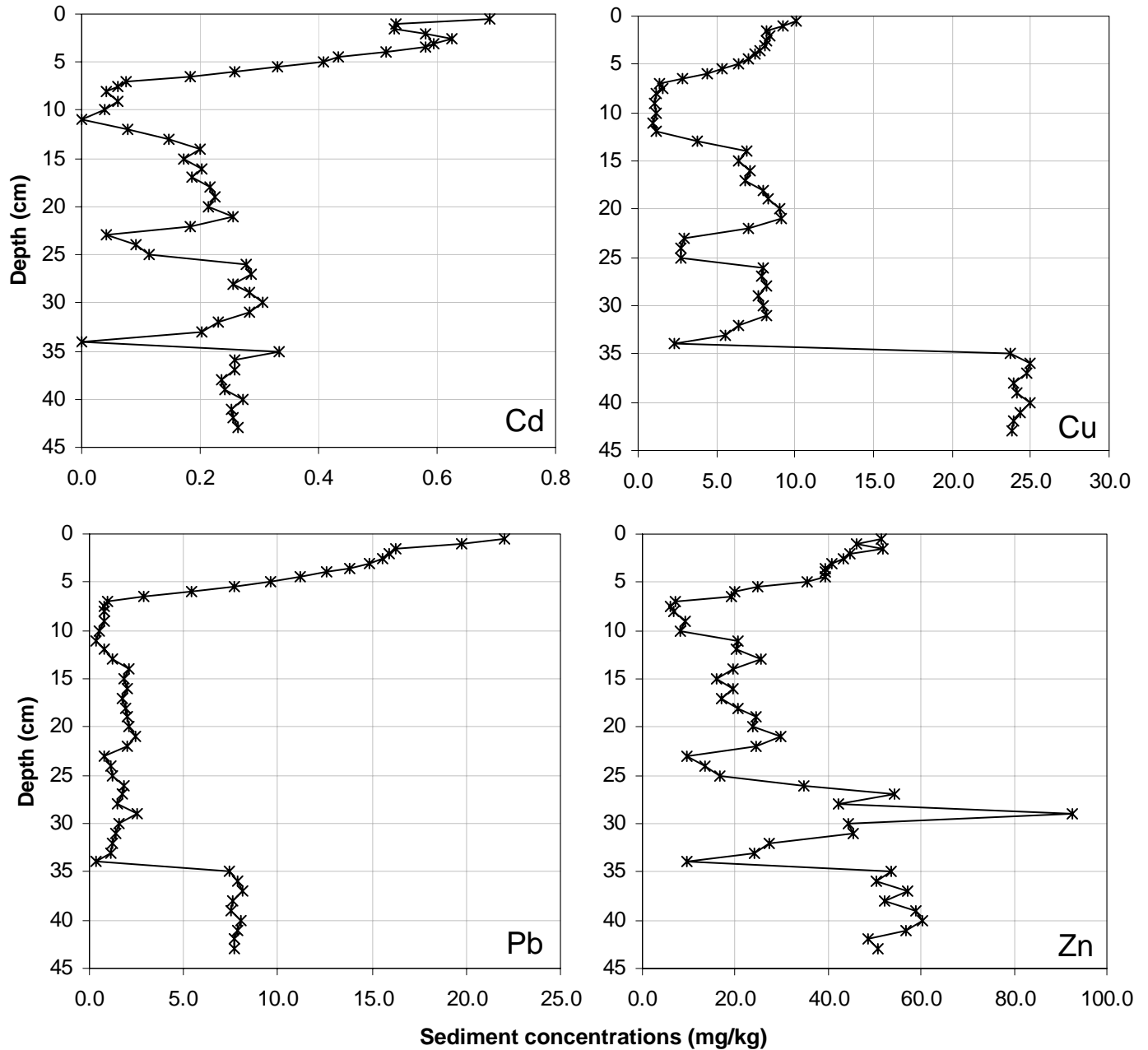
Fig. 11. Sediment concentration profiles of cadmium (Cd), copper (Cu), lead (Pb) and zinc (Zn) in Hubbard Lake.

Imp Lake

Unlike Hubbard Lake, there are no significant changes in concentration of the terrestrial elements in the sediment core collected from Imp Lake (Fig. 12). Elements that are clearly influenced by terrestrial inputs include aluminum, chromium and strontium (Table 4). However, magnesium, potassium, titanium and calcium also have somewhat similar profiles, with little change in concentration in the sediment core. Carbonate deposition is likely not an important processes in Imp Lake, which is located in the western portion of the Upper Peninsula. This portion of Michigan is on the Canadian Shield, which is poor in limestone (Door and Eschman, 1970).
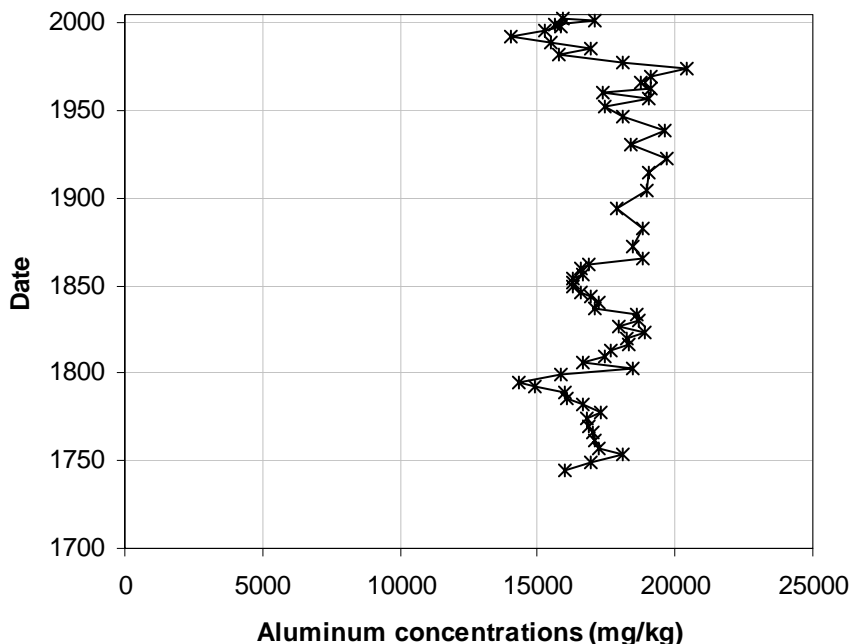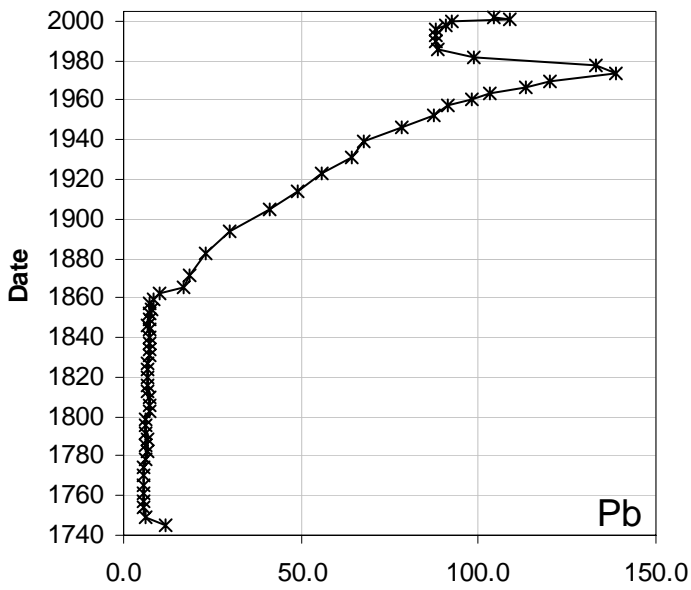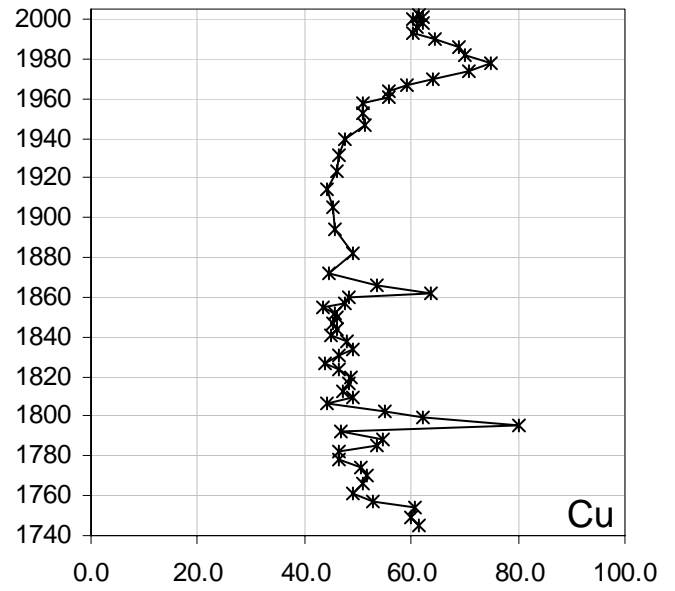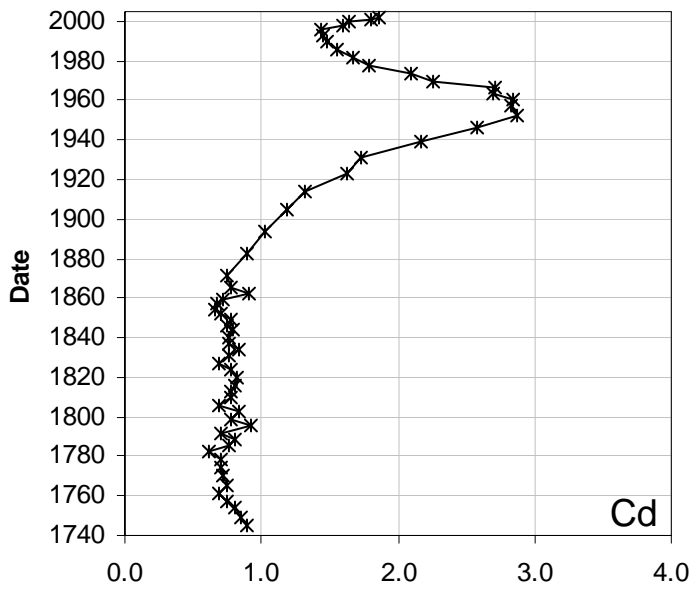

Fig. 12. Sediment aluminum concentration profile for Imp Lake.

The sediment concentration profiles of cadmium, copper, lead, zinc and iron suggest that these elements have human sources to Imp Lake (Fig. 13). All of these elements have the highest concentrations in sediment deposited in the 1960s or 1970s. Concentrations of cadmium, lead, zinc and iron decreased from peak values, but have increased concentrations in sediment deposited from the late 1990s to the present. This suggests the existence of newly emerging sources of these metals to Imp Lake. This result is surprising, as the watershed has very little development.

The concentration of copper in sediment older than 1800 is higher than all other study lakes during this time period, with the exception of Gratiot Lake. The high concentration of copper in the older sediment of Imp and Gratiot lakes is due to copper rich bedrock in this area of the Upper Peninsula (Door and Eschman, 1970). The concentration profile of iron also appears to be influenced by human inputs. Gratiot Lake, also in the Upper Peninsula, is the only other study lake that shows clear anthropogenic influences on iron. Both these lakes are within areas of Michigan that have experienced both copper and iron mining, potentially resulting in the higher iron concentrations in sediment deposited in the 1960s and 70s.
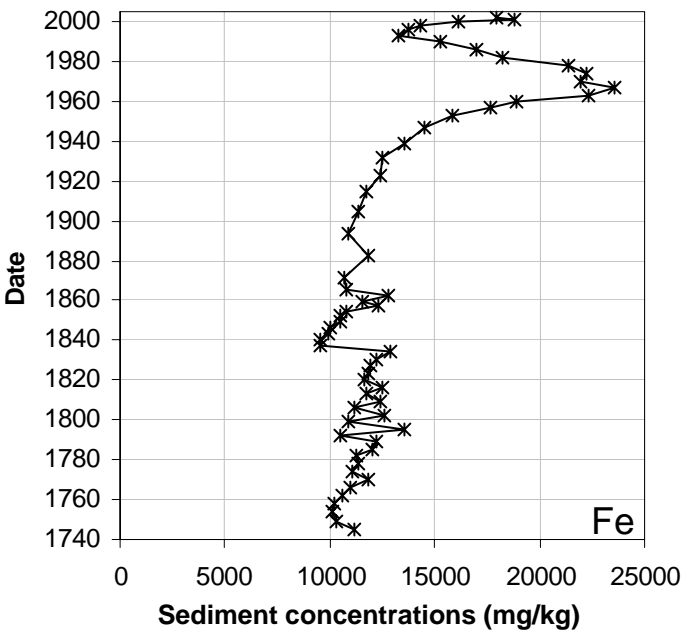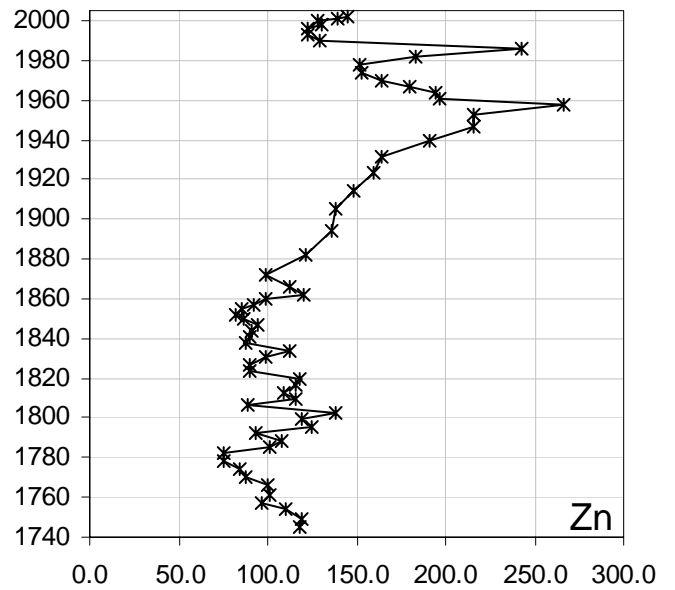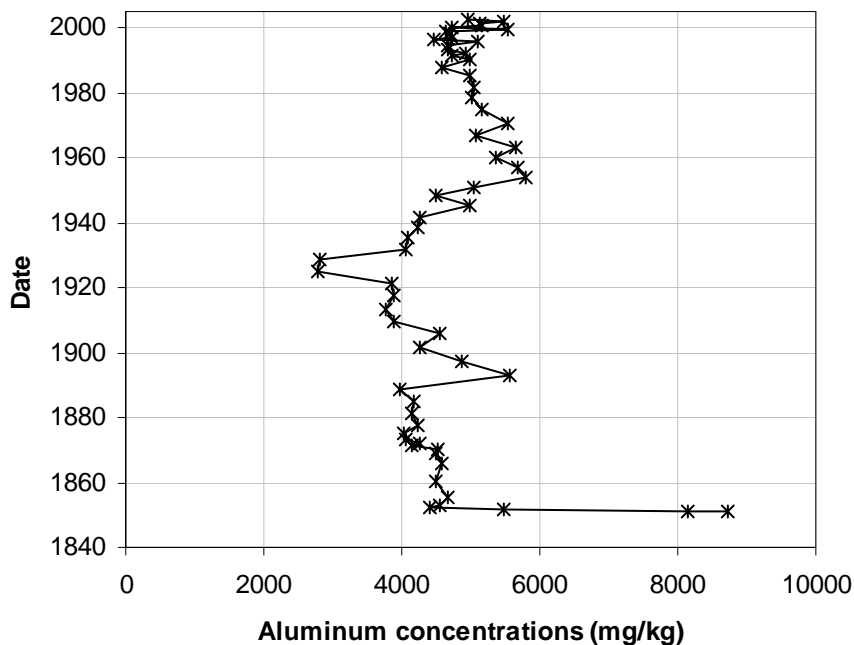
Fig. 13. Sediment concentration (mg/kg) profiles of cadmium (Cd), copper (Cu), lead (Pb) zinc (Zn) and iron (Fe) in Imp Lake.

Round Lake (N. Manistique)
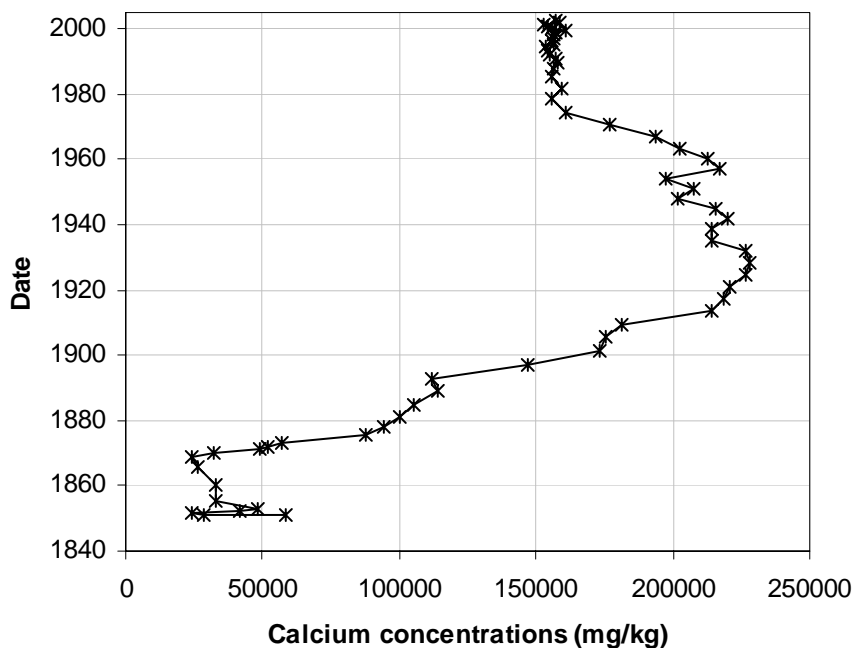

Fig. 14. Sediment aluminum concentrations (mg/kg) in Round Lake.

Fig. 15. Sediment calcium concentrations (mg/kg) in Round Lake.

Elements influenced by terrestrial inputs in Round Lake include aluminum, titanium, vanadium, chromium, and iron (Table 4). These elements have the lowest concentrations in sediment deposited in the 1930s, and much higher concentrations near the bottom of the collected sediment core (mid-1800s) (Fig. 14). The sediment collected from Round Lake only represents deposition after 1851, and European settlement began before that time. Therefore, it is possible that the high concentrations in sediment deposited in the 1850s represent the influence of mining, logging, or some other human disturbance of the watershed.

Calcium and strontium are influenced by calcium carbonate deposition in Round Lake (Table 4). Concentrations in the sediment of these elements increase until the mid-1900s, decrease, and remain constant for the last two decades (Fig. 15). Neither calcium nor strontium shows the large increase in concentration at the bottom of the core that is present in the terrestrial elements, but nor do these elements show a large decrease from dilution.

Inputs of cadmium, lead, and zinc to Round Lake appear to be influenced by humans (Fig. 16), with increasing concentrations in sediment deposited from the late 1800s to the 1970s, and decreasing concentrations to the present. Copper concentrations in the 1970s are only slightly greater than concentrations in the late 1800s, indicating either that human inputs of copper in the 1900s were relatively low, or there were already anthropogenic inputs of copper in the late 1800s. Sampling of additional lakes in this region may clarify this. However, total concentrations of copper are not exceptionally high compared to the other study lakes (Yohn et al., 2002b).
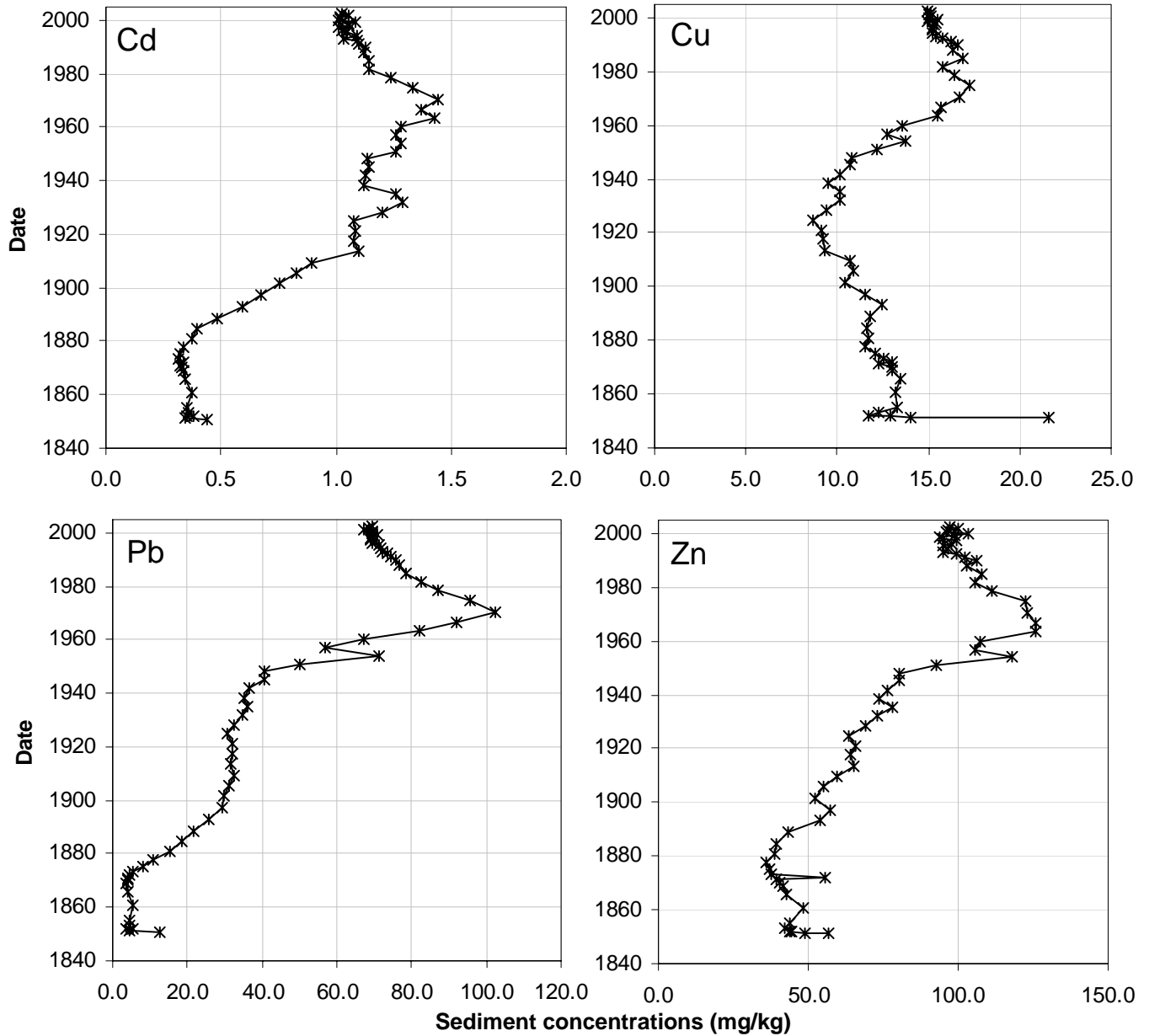
Fig. 16. Sediment concentration (mg/kg) profiles of cadmium (Cd), copper (Cu), lead (Pb) and zinc (Zn) in Round Lake.
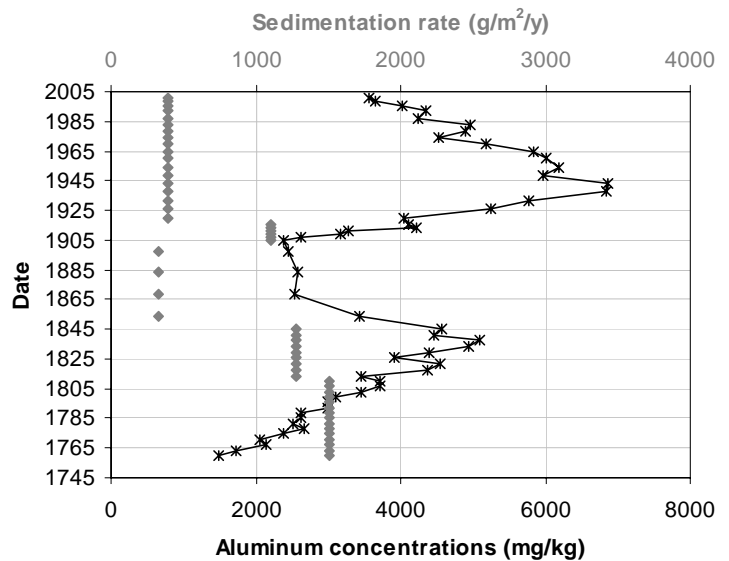
Torch Lake

The terrestrial elements in Torch Lake include magnesium, aluminum, potassium, vanadium, chromium and iron (Table 4). Sediment concentrations of these elements increase from the bottom of the core (late 1700s) until sediment deposited in the mid-1800s, decrease, and increase again until the 1930s (Fig. 17). The 1930s peak occurs at a similar time period to the large increase in aluminum concentrations in Elk Lake (Simpson *et al.*, 2000b), and may be a result of logging in the region. Sedimentation rates in Torch Lake were high during the entire increase or the beginning of the increases in aluminum concentrations (Fig. 17), suggesting an increased input of terrestrial materials due to erosion from the watershed. However, it is unclear why Torch Lake has two increases in terrestrial elements, when this pattern is not seen in nearby Elk Lake.
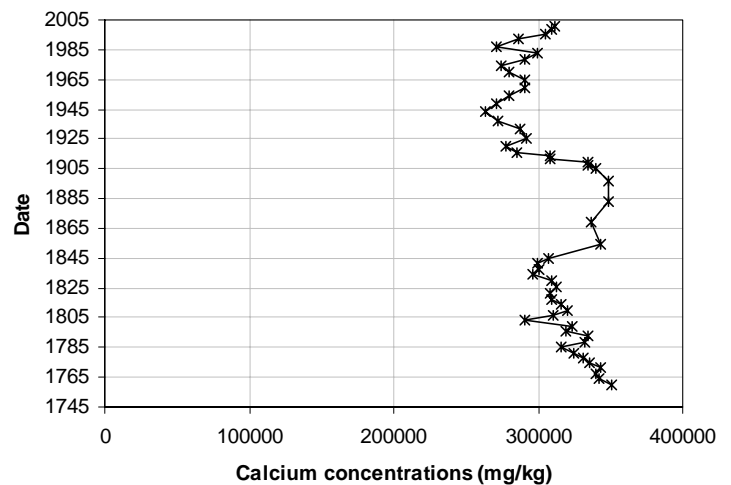
Concentrations of calcium and strontium increase in late 1800s to 1900, during the time period when aluminum concentrations were lower (Fig. 18), and concentrations of calcium generally follow the opposite trend as the terrestrial elements.

Fig. 17. Sediment aluminum concentrations (mg/kg) and total sedimentation rate (g/m^2/y) over time in Torch Lake. Sedimentation rates were determined using the SCF:CS model.

Fig. 18. Sediment calcium concentrations (mg/kg) in Torch Lake.

Cadmium, copper, lead, and zinc sediment concentrations are all highest in sediment deposited in the late 1900s, with copper, lead and zinc concentrations peaking in 1983, and cadmium concentrations peaking in 1969 (Fig. 19). The cadmium sediment concentration profile appears to be influenced little by the changes in terrestrial inputs, and has a relatively constant background concentration. Copper does appear to be influenced by terrestrial inputs, with high concentrations occurring at the same times as aluminum (1838, 1943). However, copper concentrations continue to increase after 1943, when aluminum concentrations decrease, probably due to human sources of copper to Torch Lake. Zinc sediment concentrations also increase at a different time period than the terrestrial elements, and appear to be influenced by human inputs.

Unlike most lakes, lead concentrations do not reach a constant background value in the sediment sampled (Fig. 19). Lead concentrations increase slowly from sediment deposited in the mid-

1700s to 1838 in a similar pattern as the terrestrial elements. Lead concentrations may also be influenced in sediment deposited in the early 1900s by terrestrial inputs, but concentrations of lead continue to increase to the 1980s as terrestrial inputs decrease. For many lakes, the dominant source of lead in the 1930-1980s was atmospheric deposition of lead released to the environment through the burning of leaded gasoline (Graney *et al.*, 1995, Yohn *et al.*, 2002b), with the largest release to the environment occurring in 1972 (United States. Bureau of Mines.). Most of the study lakes have peak lead concentrations near this time; however, in Torch Lake the peak lead concentration occurs in sediment deposited in 1983. It is unclear if this is due to additional sources of lead to Torch Lake, or difficulty with dating the sediment.
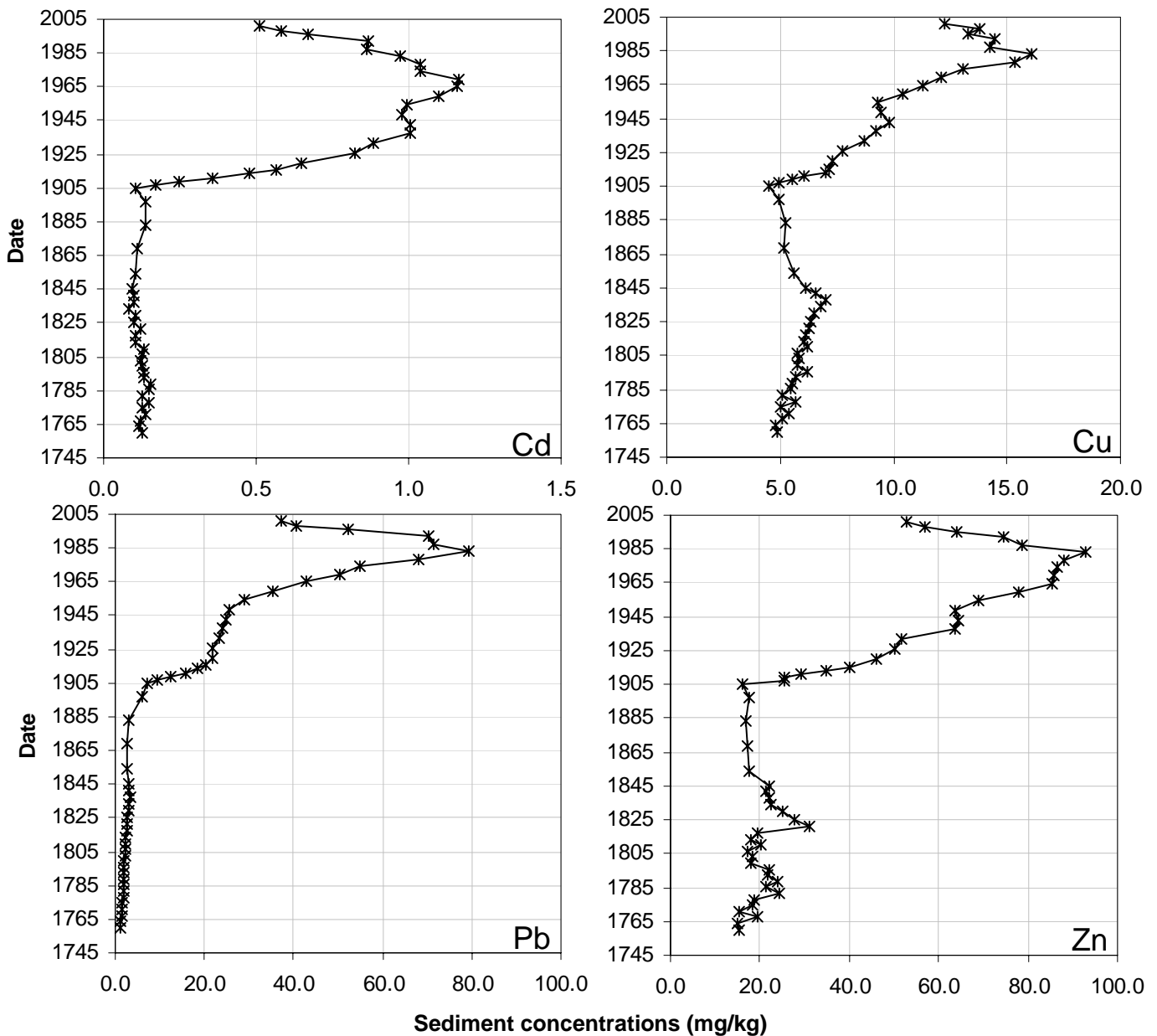

Fig. 19. Sediment concentration (mg/kg) profiles of cadmium (Cd), copper (Cu), lead (Pb) and zinc (Zn) in Torch Lake.

Witch Lake

Sediment concentration profiles in Witch Lake are dominated by two major events (late 1800s and early 1960s), leading to increased concentrations in most elements. The terrestrial elements, magnesium, aluminum, titanium, and chromium (Table 4), have large increases in concentration in the sediment deposited during those time periods (Fig. 20). These elements have similar maximum concentration for both peaks, while another suite of elements (nickel, cobalt, vanadium, uranium and copper) have higher concentrations in the 1960s peak (Fig. 21). Peak copper concentrations in Witch Lake are significantly higher than all of the study lakes, with the exception of Houghton and Cadillac lakes. The cause of these increases in concentration is probably related to mining in the area. Witch Lake is located near Republic, where a large mining operation was present, which may have resulted in the increased concentration of terrestrial elements in Witch Lake.
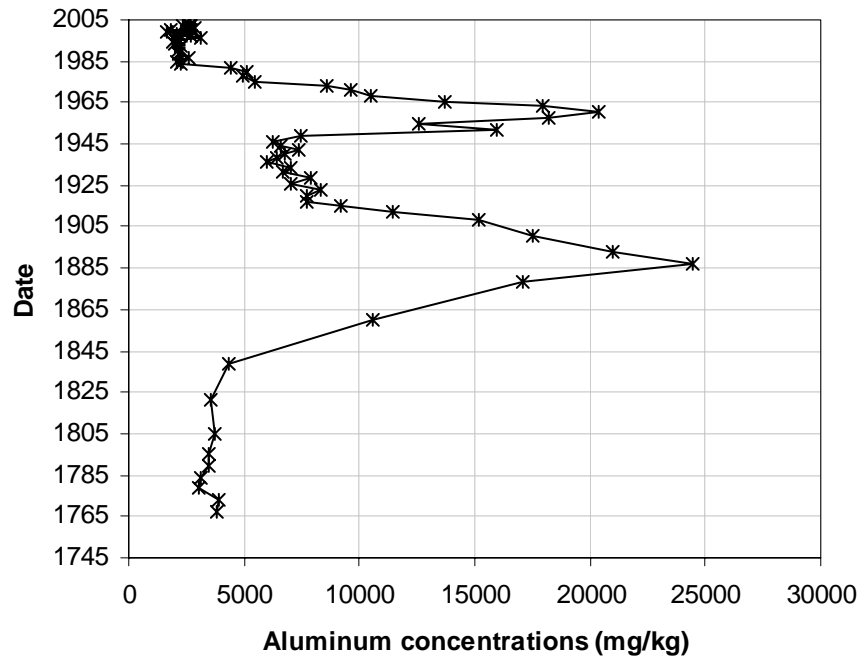
Fig. 20. Sediment aluminum concentrations (mg/kg) in Witch Lake.
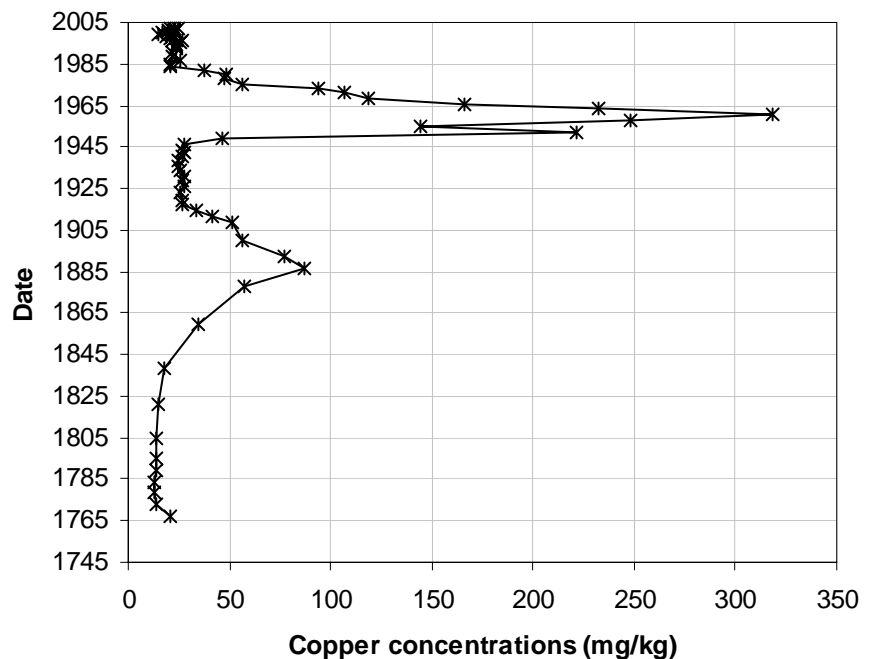
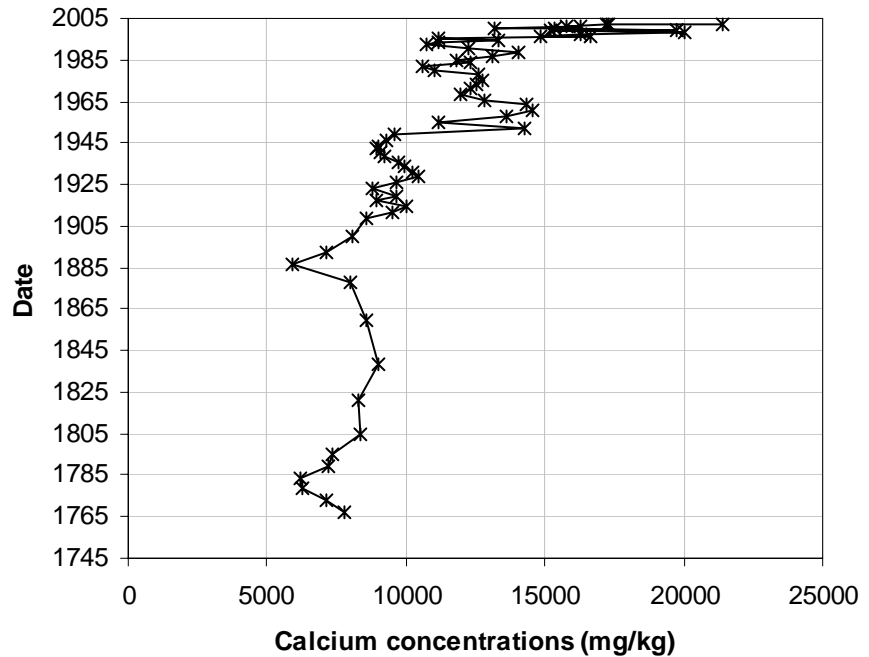**Fig. 21.** Sediment copper concentrations (mg/kg) in Witch Lake.

Calcium has a concentration profile that is dissimilar from the terrestrial elements described above, and seems to be influenced very little by the two events (Fig. 22). Calcium has slightly lower concentrations during the late 1800s event, and slightly increased concentrations

in the 1960s, but does not show an increase in concentration on a magnitude of the terrestrial elements.

Arsenic in Witch Lake has a similar profile to iron; however, it is unclear what processes are influencing this pattern (Fig. 23). Typically, if iron and arsenic have similar sediment concentration profiles, this indicates that both of these elements are influenced by diagenesis, or remobilization in the sediment. However, concentrations of iron and arsenic are high in sediment deposited in the 1960s to the 1980s, the time period where human influences are frequently apparent (Yohn et al., 2002b). Additionally, manganese and barium sediment concentration profiles do appear to have been influenced by diagenesis, with the profiles having high concentrations near the surface water interface. This suggests that the higher concentrations of arsenic and iron in sediment deposited in the 1960s-80s may be due to human inputs; however, it is possible that other processes or sources are influencing these elements.

Fig. 22. Sediment calcium concentrations (mg/kg) in Witch Lake.

Fig. 23. Arsenic (black) and iron (grey) concentrations (mg/kg) in Witch Lake.

The large changes in terrestrial inputs complicate distinguishing direct human inputs. While it is apparent that humans greatly influenced inputs to Witch Lake in the late 1800s and 1960s, it is more difficult to distinguish direct anthropogenic inputs. Cadmium concentrations are low in the late 1800s and 1960s, suggesting that cadmium was diluted by the input of terrestrial materials
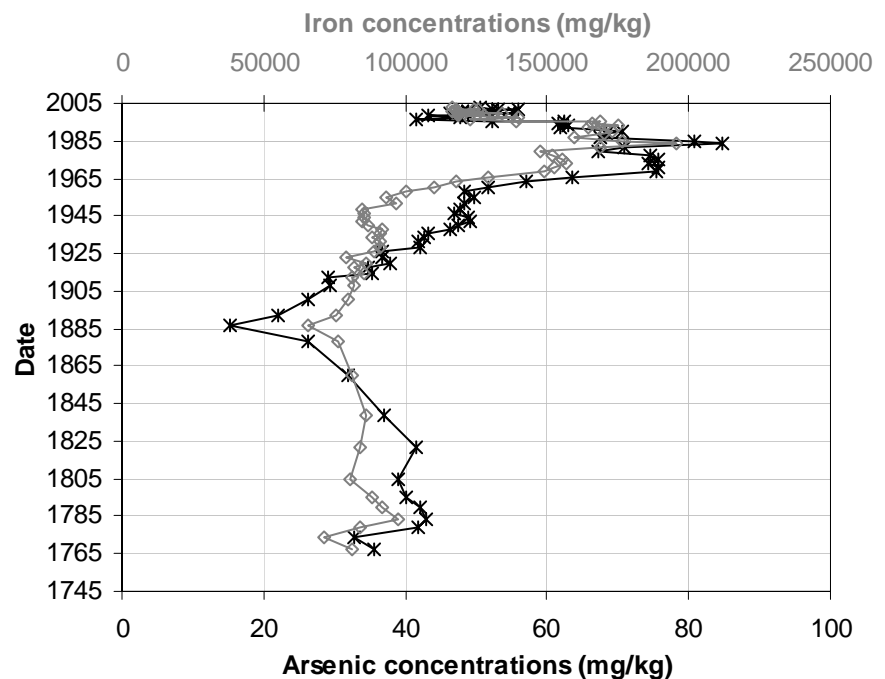
(Fig. 24). However, it is not possible to quantify human inputs of cadmium, due to the large influence of terrestrial inputs on the sediment profile. Lead concentrations are highest in 1961, which may be related to the terrestrial inputs, but there is a second, smaller peak in 1971, which suggests that the burning of leaded fuel was also a source of lead to Witch Lake (Fig. 24). Zinc concentrations are highest in the sediment at the sediment-water interface, and are also high in 1966 (Fig. 24).
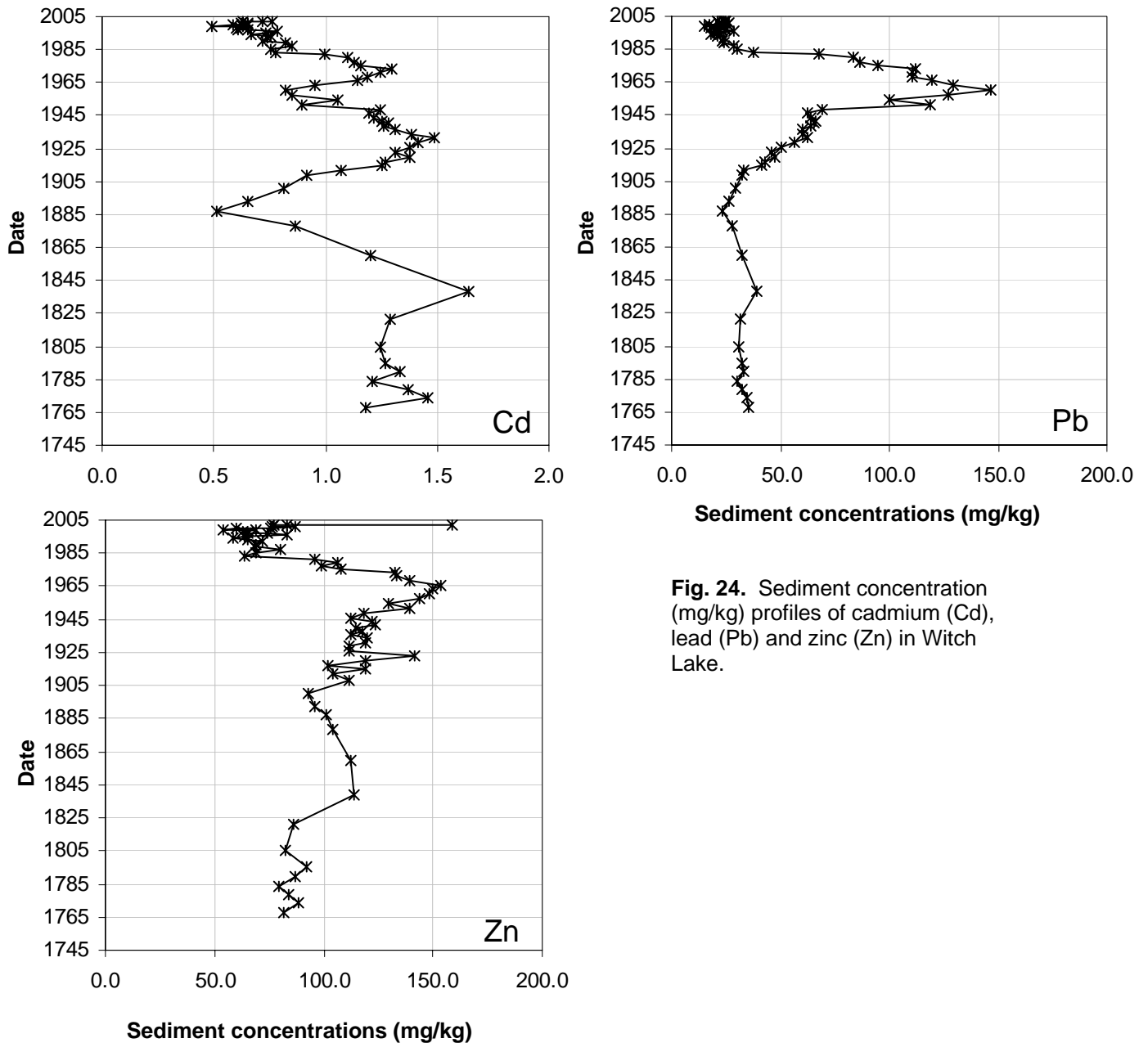
Fig. 24. Sediment concentration (mg/kg) profiles of cadmium (Cd), lead (Pb) and zinc (Zn) in Witch Lake.

Surface concentrations

While high concentrations of some contaminants may exist in sediments deposited in the 1960s and 70s, the concentrations in the surface sediments are of more concern to the health of aquatic organisms. We have averaged the top three samples, 1.5 cm, to represent the surface samples. Three samples were averaged to reduce the possible effects of one anomalous sample. These concentrations were compared among lakes, and compared to sediment quality guidelines (Table 5) (MacDonald et al., 2000). MacDonald et al. (2000) define a threshold effect concentration (TEC) and a probable effect concentration (PEC). The TEC is the concentration below which harmful effects on sediment dwelling organisms are unlikely to be observed, while the PEC is the concentration above which harmful effects are likely to be observed. Surface concentrations of arsenic, cadmium, copper, lead and zinc will be examined. Only 2002-2003 study lakes will be discussed, but data from all study lakes are presented for comparison. Discussion of previous lakes can be found in the 2001-2002 year end report (Yohn et al., 2002b). The concentrations reported are total concentrations, and represent both the human influenced and natural component. Results from Hubbard Lake should not be compared to the other lakes, as the top 1.5 cm may represent a very different time period.
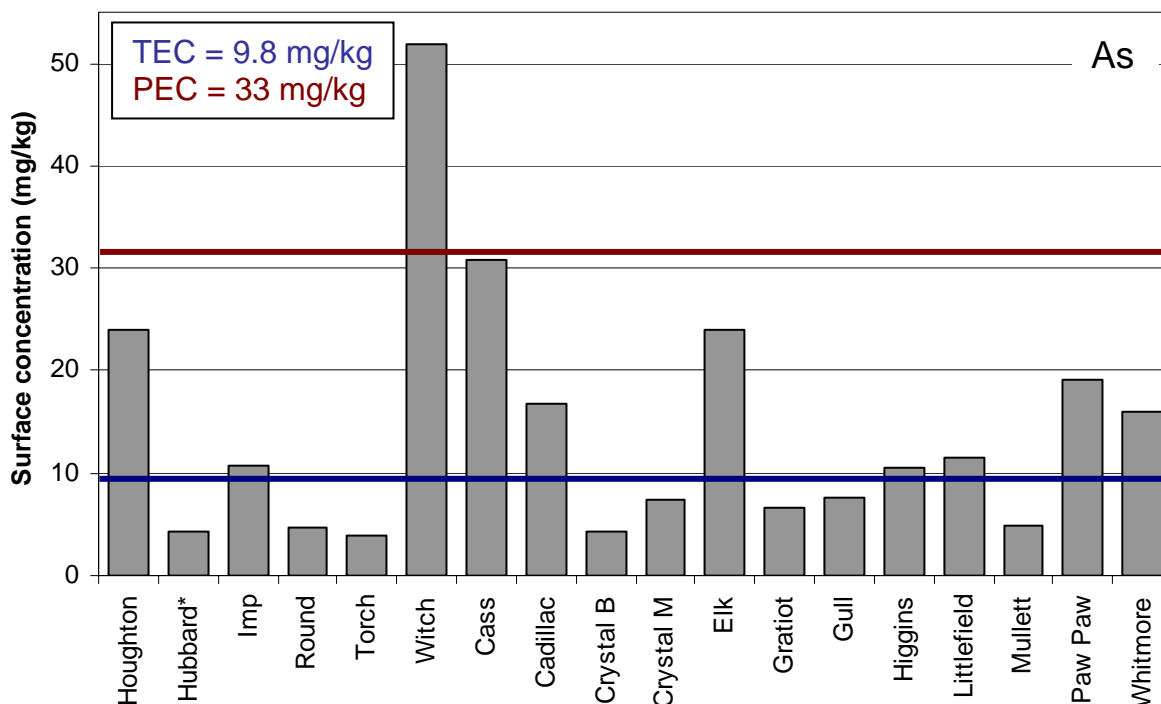
Table 5. Surface (1.5 cm) concentrations (mg/kg) of five elements for eighteen lakes in Michigan, threshold effect concentrations (TEC) and probable effect concentrations (PEC) (MacDonald et al., 2000). Italics indicates values greater than TEC, bold indicates concentrations greater than PEC. The 2002-2003 study lakes are listed first, previous study lakes are listed for reference.

	As	Cd	Cu	Pb	Zn
Houghton	*23.9*	*1.2*	**175.1**	*67.9*	*159.6*
Hubbard*	4.4	0.6	9.1	19.3	49.8
Imp	*10.7*	*1.8*	*61.3*	*102.0*	*137.4*
Round	4.7	*1.0*	15.1	*68.4*	98.0
Torch	3.9	0.6	13.1	43.3	57.9
Witch	**51.9**	0.7	22.7	23.4	106.3
Cass	*30.8*	0.3	15.4	*53.7*	85.4
Cadillac	*16.8*	*2.2*	**404.2**	**185.4**	*265.7*
Crystal B	4.4	*1.1*	18.0	*56.1*	106.7
Crystal M	7.3	0.9	21.9	*78.9*	106.5
Elk	*23.9*	0.3	8.8	29.9	38.4
Gratiot	6.6	0.8	*61.0*	*39.5*	82.4
Gull	7.6	0.1	11.6	32.4	52.4
Higgins	*10.5*	*1.2*	21.1	*109.1*	*122.1*
Littlefield	*11.5*	0.5	12.2	30.1	49.0
Mullett	4.9	0.4	12.7	26.6	57.9
Paw Paw	*19.2*	0.6	*43.8*	*49.7*	*151.8*
Whitmore	*16.1*	*1.5*	*49.7*	**143.9**	*229.0*
TEC	9.8	1.0	31.6	35.8	121
PEC	33	5.0	111	128	459

*Data suggest that the surface sediments of Hubbard Lake have been eroded, therefore the top 1.5 cm will represent a different time period than other lakes.

Surface arsenic sediment concentrations in Witch Lake are the highest of the study lakes, and much greater than PEC, the level above which harmful effects on sediment dwelling organisms are likely to be observed (Fig. 25). The sediment chemistry of Witch Lake is unique among the study lakes, with very high concentrations of elements such as iron, manganese, barium and arsenic. The high concentrations of arsenic may be due to human inputs, but may also be a result of the natural lake chemistry. Imp and Houghton lakes have sediment surface concentrations greater than the TEC.
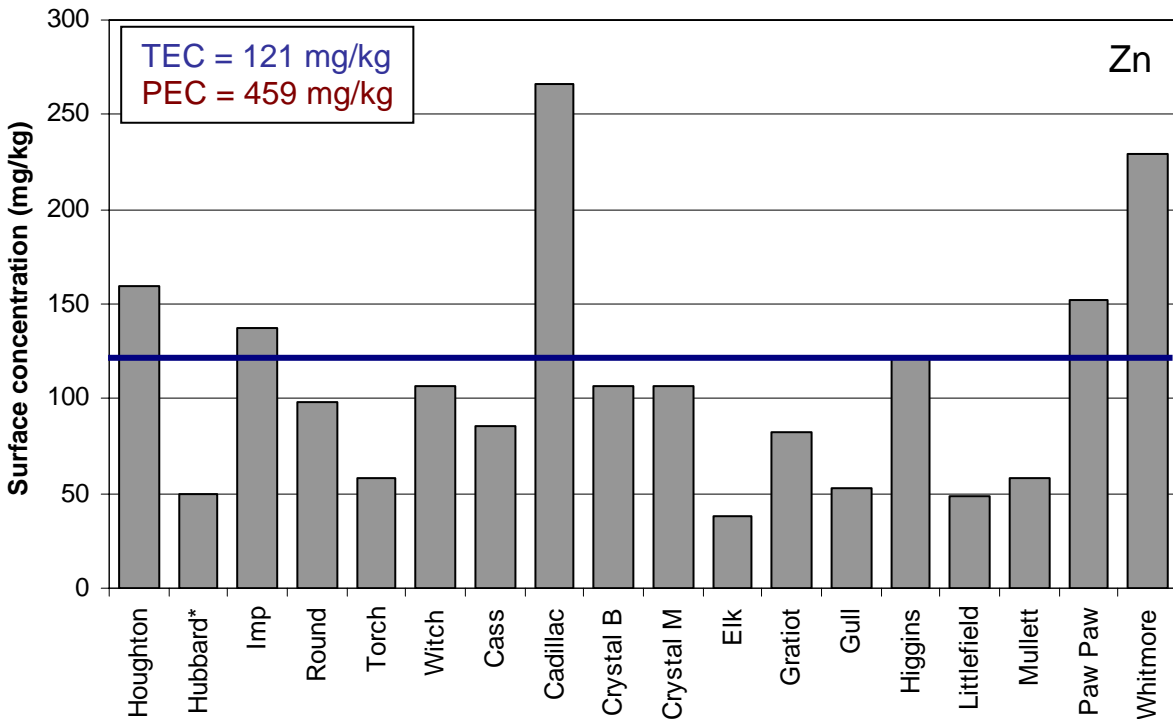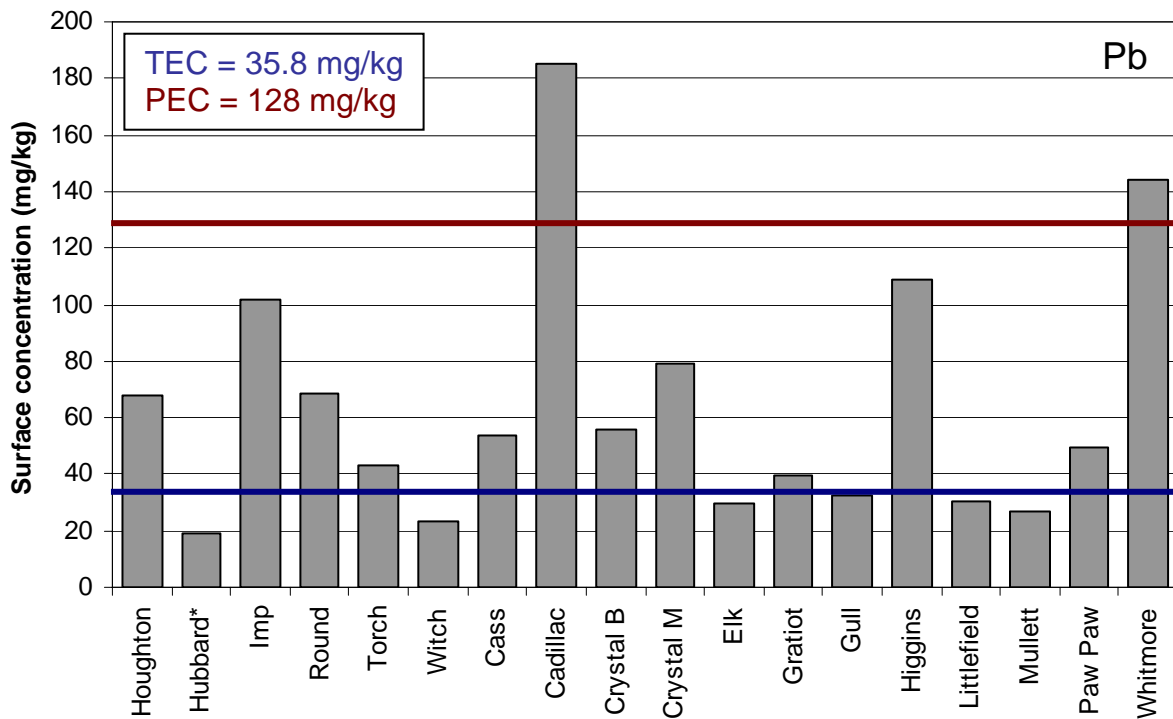

Fig. 25. Surface (1.5 cm) concentrations (mg/kg dry wt) for arsenic (As), in eighteen Michigan lakes. The lower blue line indicates the TEC, the upper red line indicates the PEC. *Data suggest that the surface sediments of Hubbard Lake have been eroded, therefore the top 1.5 cm will represent a different time period than other lakes.

Houghton, Imp and Round lakes had surface sediment concentrations greater than the TEC for cadmium (Fig. 26). None of the study lakes had concentrations near the PEC. Copper sediment concentrations in Houghton Lake were much higher than the PEC, though lower than Cadillac Lake (Fig. 26). Both of these lakes were treated with copper sulfate to control swimmer's itch. Sediment concentrations of copper in Imp Lake are greater than the TEC, and similar to those of Gratiot Lake, which is located in a geologically similar area. Almost all lakes are greater than the TEC for lead, including Houghton, Imp, Round and Torch lakes (Fig. 27). Houghton and Imp lakes have sediment surface concentrations of zinc greater then the TEC, but no lake has values greater than the PEC (Fig. 27).

Houghton and Imp lakes have the highest surface sediment concentrations, and exceed the TEC or PEC value for all five elements. Torch and Hubbard lakes have the lowest concentration of the 2002-2003 study lakes.
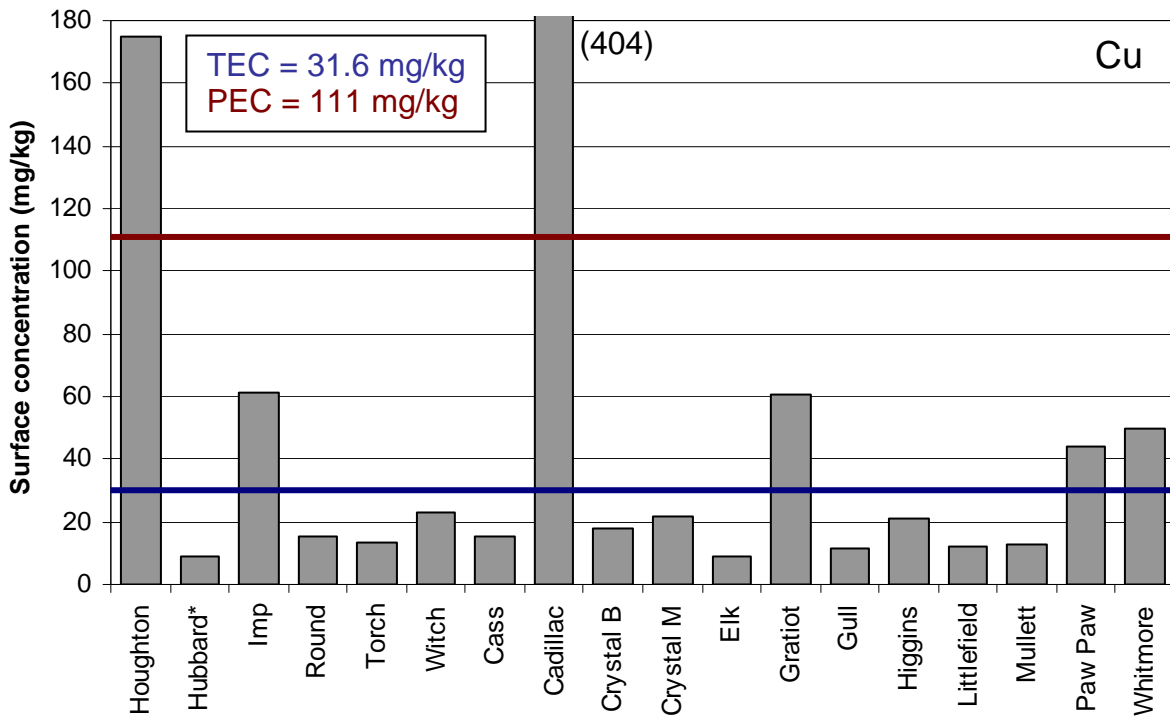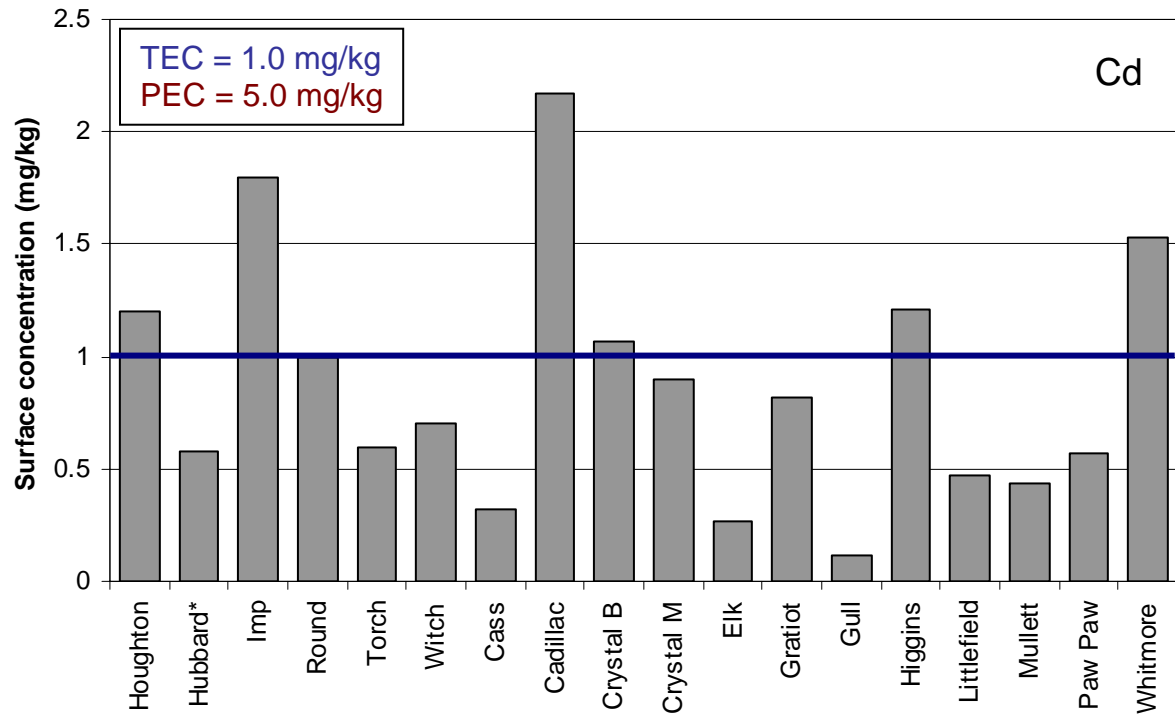
Fig. 26. Surface (1.5 cm) concentrations (mg/kg dry wt) for cadmium (Cd) and copper (Cu) in eighteen Michigan lakes. The lower blue line indicates the TEC, the upper red line indicates the PEC. The PEC is not shown for cadmium. *Data suggest that the surface sediments of Hubbard Lake have been eroded, therefore the top 1.5 cm will represent a different time period than other lakes.

Fig. 27. Surface (1.5 cm) concentrations (mg/kg dry wt) for lead (Pb) and zinc (Zn) in eighteen Michigan lakes. The lower blue line indicates the TEC, the upper red line indicates the PEC. The PEC is not shown for zinc. *Data suggest that the surface sediments of Hubbard Lake have been eroded, therefore the top 1.5 cm will represent a different time period than other lakes.

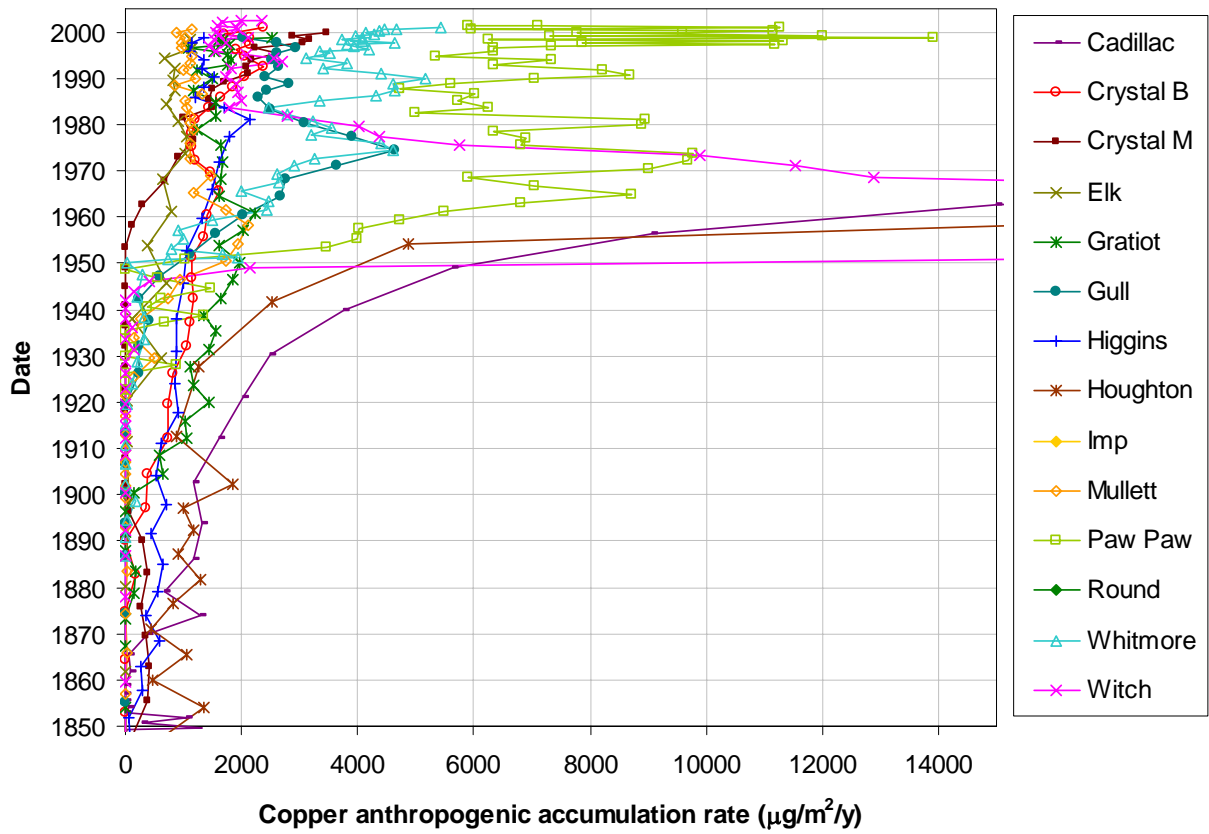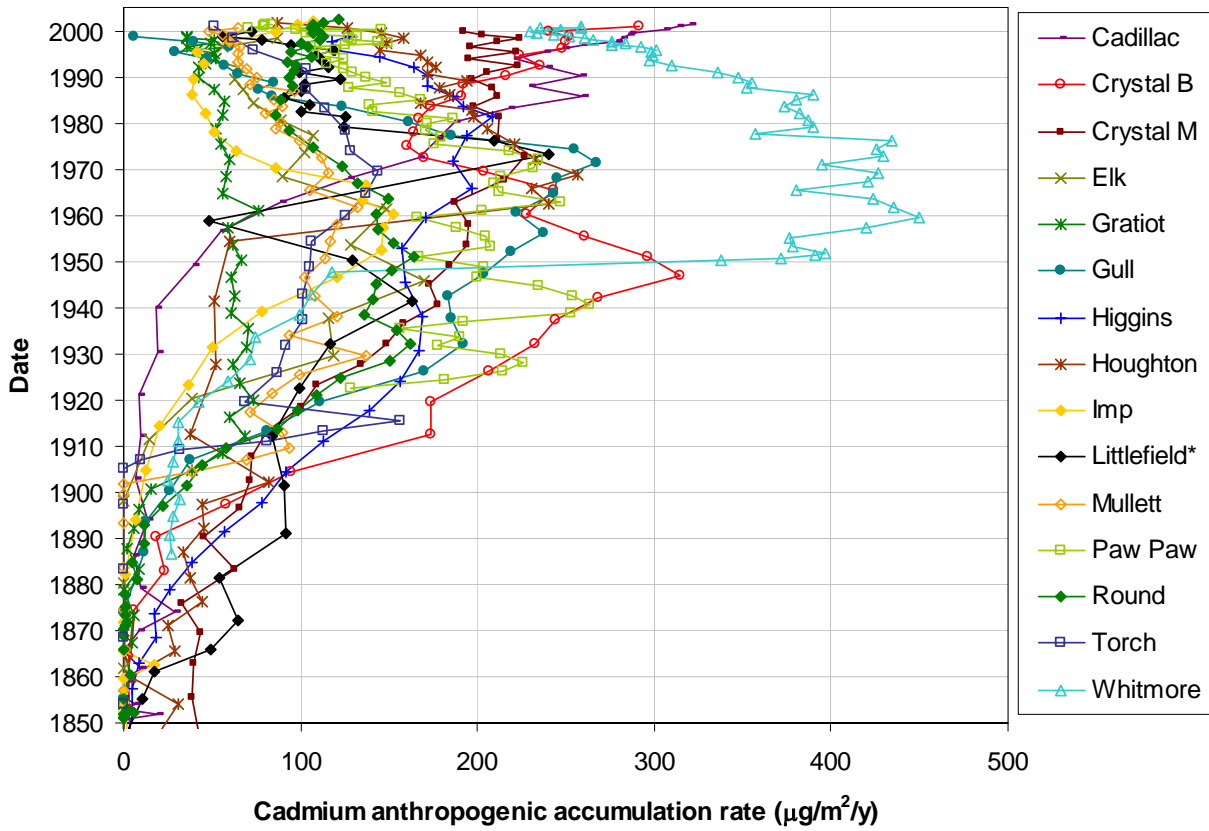## Focusing corrected anthropogenic accumulation rates

Concentrations of metals in the sediment have important implications on bottom-dwelling organisms; however, they do not provide insight into how much of the element is present due to human actions. For example, Gratiot Lake has high copper concentrations even in deep sediments because the lake is located in an area that is naturally rich in copper. Therefore, in addition to the interpretation of the total concentration profiles, focusing corrected anthropogenic accumulation rates were calculated and compared among lakes. These calculations take into account the natural inputs of elements of interest as well as the process of sediment focusing, and provide the best estimate of the actual rate of input of that element to the lake due to human actions. The calculations are described further in the 2001-2002 year end report (Yohn et al., 2002b).

The 2002-2003 study lakes do not have high anthropogenic accumulation rates compared to the other study lakes, with the exception of copper in Witch and Houghton lakes (Fig. 28). Whitmore and Paw Paw lakes have high accumulation rates among all the study lakes. The Upper Peninsula lakes (Gratiot, Imp, Round and Witch lakes) typically have low to medium accumulation rates when compared to the other study lakes. Cadillac, Houghton and Witch lakes have much higher copper accumulation rates than the other study lakes, due to the addition of copper sulfate in Cadillac and Houghton lakes, and probably due to mining influences in Witch Lake.

Accumulation rates in Torch Lake have an unusual pattern with high values in 1915, and then a sudden decrease to 1920 (Fig. 28). This pattern is due to a much higher total sedimentation rate from 1905-1915 (Fig. 17). While it is likely that sedimentation rates were higher during this time period, part of the weakness of using the SCF:CS model to determine sedimentation rates is that the model produces sudden changes in sedimentation rate that in reality probably occur gradually. The result of this is accumulation rate profiles with sudden changes, which only estimate actual rates of input. However, although it is unlikely the change in accumulation rates was as rapid as shown in the Torch Lake profile, it is likely that there was an increase in anthropogenic accumulation rates in the early 1900s, followed by a decrease, and another increase to the 1980s.

Overall, most lakes have the highest anthropogenic accumulation rates in the 1970s, with rates decreasing to the present. However, some lakes, such as Crystal B, Cadillac, Imp and Round lakes have anthropogenic accumulation rates that increase to the present. These lakes may be appropriate for continued monitoring.

Some of the 2002-2003 study lakes are located in close proximity to previously sampled lakes, and these lakes will be compared to determine if human inputs are similar for adjacent lakes (Houghton and Higgins, and Torch and Elk lakes).

Fig. 28a. Cadmium and copper focusing corrected anthropogenic accumulation rates (μg/m²/y) for study lakes in Michigan. Copper accumulation rates for Cadillac, Houghton and Witch Lakes are greater than the scale used.
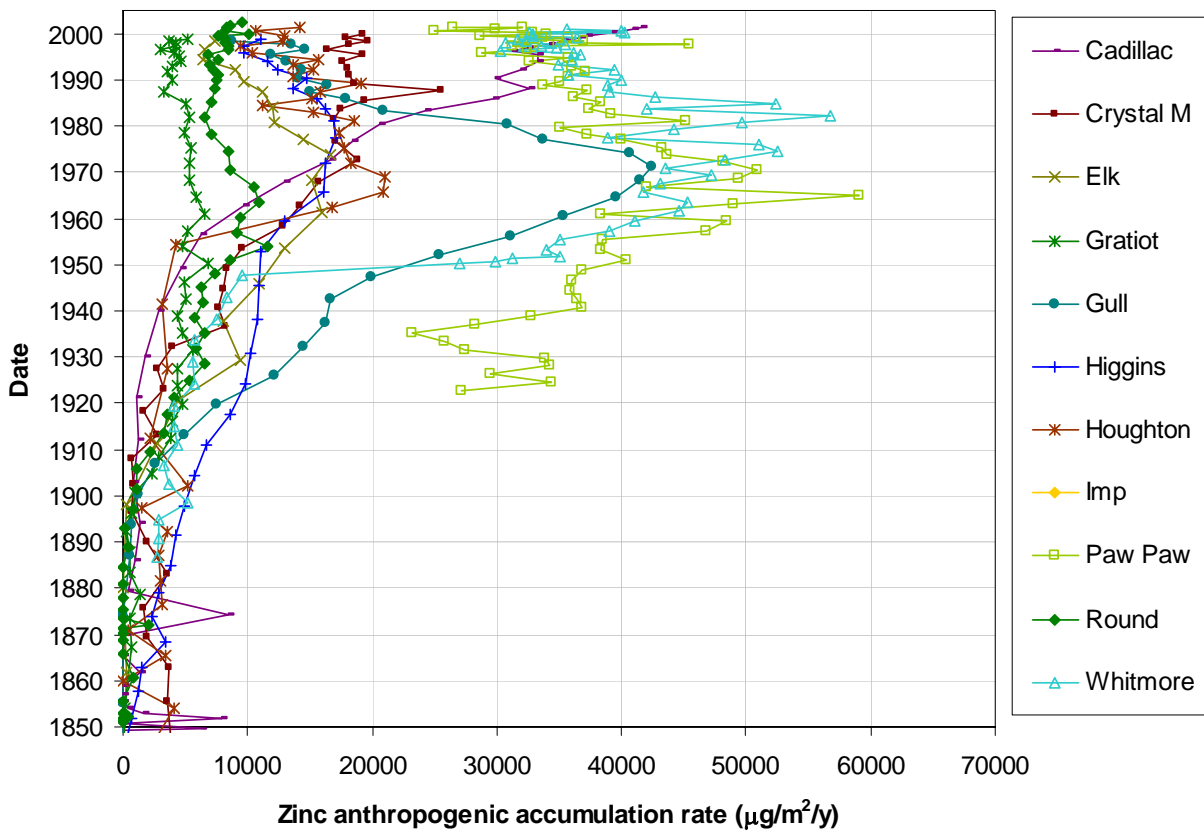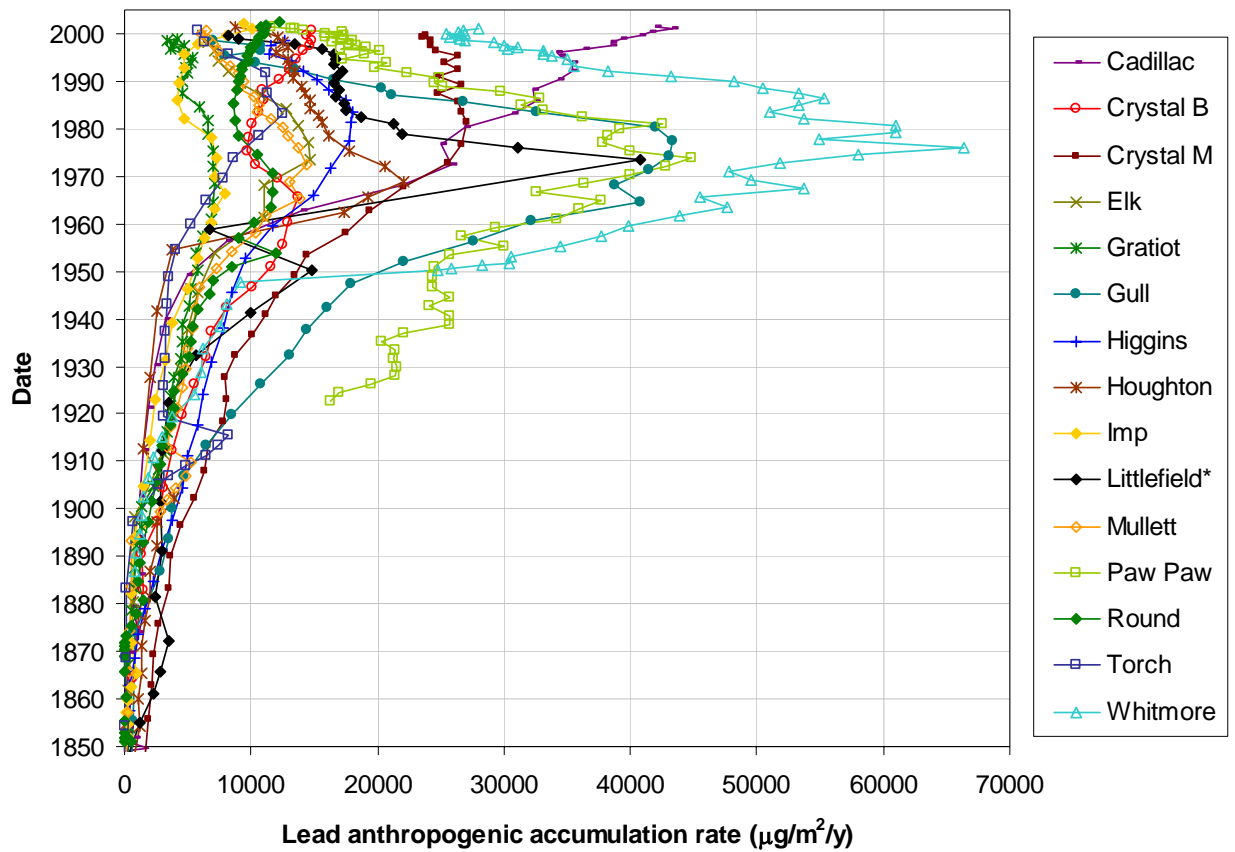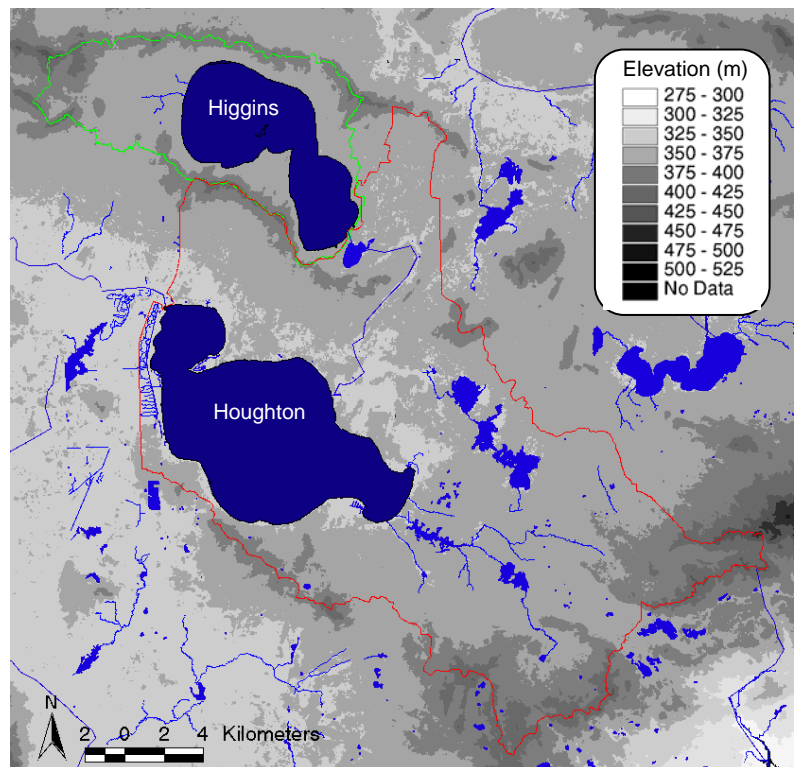
Fig. 28b. Lead and zinc focusing corrected anthropogenic accumulation rates ($\mu g/m^2/y$) for study lakes in Michigan.
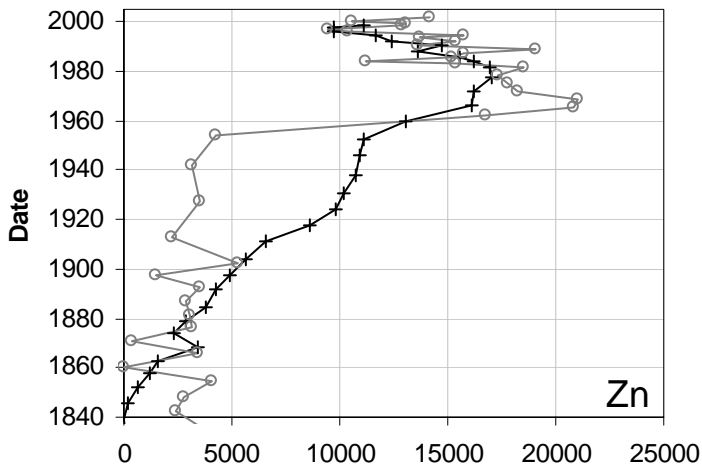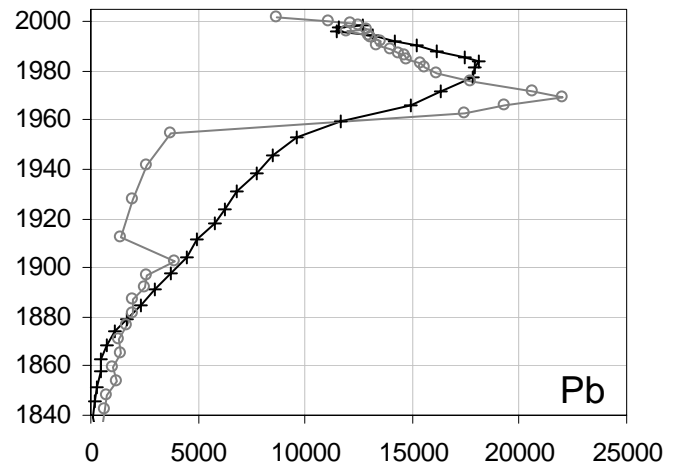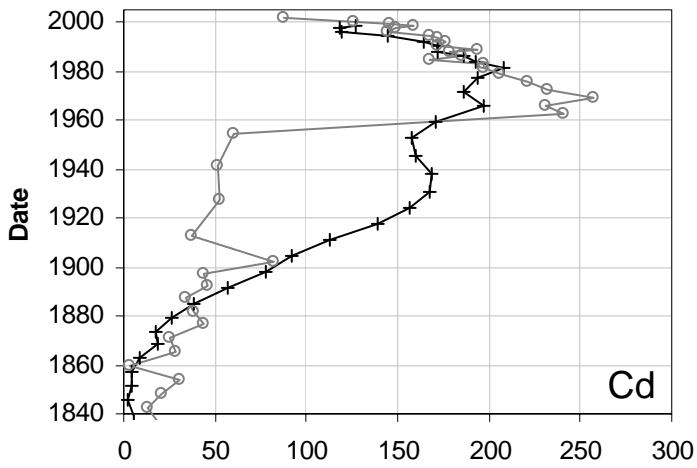
Houghton and Higgins Lakes

Houghton and Higgins lakes are hydrologically connected, with the Cut River flowing from Higgins Lake into Houghton Lake (Fig. 29). Houghton Lake is larger and significantly shallower than Higgins Lake (Table 1).

The focusing corrected anthropogenic accumulation rates of cadmium, lead and zinc are very similar between the two lakes, despite the differences in bathymetry (Fig. 30). However, there is some discrepancy in the dating of the two sediment cores. For example, cadmium accumulation profiles have a very similar shape, except the accumulation rate for Higgins Lake peaks in 1981, and peak in Houghton Lake in 1969. Additionally, accumulation rates in Houghton Lake are much lower than Higgins lakes in the early 1900s. Both of these differences are probably the result of interpretation of the ^{210}Pb data. The CF:CS model, with one sedimentation rate, was used for Higgins Lake. The segmented CF:CS

Fig. 29. Map showing the surface elevation (m), location of Higgins and Houghton Lakes, and watersheds of Higgins (green) and Houghton (red) lakes. The area shown is dominantly in Roscommon County, MI, with small portions of Higgins Lake watershed in Missaukee, Kalkaska and Crawford Counties.

model was used for Houghton Lake, which resulted in three different sedimentation rates. The early 1900s had a low sedimentation rate, and therefore lower anthropogenic accumulation rates. As described above, the SCF:CS model probably results in more extreme and rapid changes than occur in reality. Despite these dating issues, the similarity among the lakes is clear, and suggests that there are few sources of cadmium, lead, and zinc that are not common to both lakes. Copper accumulation rates are much higher in Houghton Lake, due to the addition of copper sulfate to the lake. Copper sulfate was not added to Higgins Lake.

Fig. 30. Focusing corrected anthropogenic accumulation rates for cadmium, lead, and zinc in Higgins (black) and Houghton (grey) lakes.

**Focusing corrected anthropogenic accumulation rates (µg/m²/y)**

Torch and Elk Lakes

Torch and Elk lakes are also hydrologically connected, with Torch Lake flowing into Clam Lake, which flows into Elk Lake. Both Torch and Elk lakes are calcium carbonate rich, and deep narrow lakes (Fig. 31).

Similar to Houghton and Higgins lakes, Torch and Elk lakes have very similar values and profiles of anthropogenic accumulation rates, but show some discrepancies in the dating of the core (Fig. 32). The peak accumulation rate of both cadmium and zinc occurs at a more recent date in Torch Lake sediments than Elk, but the shape of the profiles are relatively similar, with the exception of the early 1900s. The rapidly increasing, and then decreasing accumulation rates in Torch Lake in the early 1900s are due to a high sedimentation rate for that time period.

It was not possible to calculate zinc anthropogenic accumulation rates for Torch Lake, because no constant concentration or constant zinc to aluminum ratio was reached.

Anthropogenic accumulation rates for copper in both Elk and Torch lakes increase to the late 1970s or early 1980s and do not decrease significantly to the present (Fig. 32). In Elk Lake, the two samples closest to the sediment water interface have the highest anthropogenic accumulation rates. However, it appears from the trend in Torch Lake (sampled four years later), that copper accumulation rates decreased from the time Elk Lake was sampled.
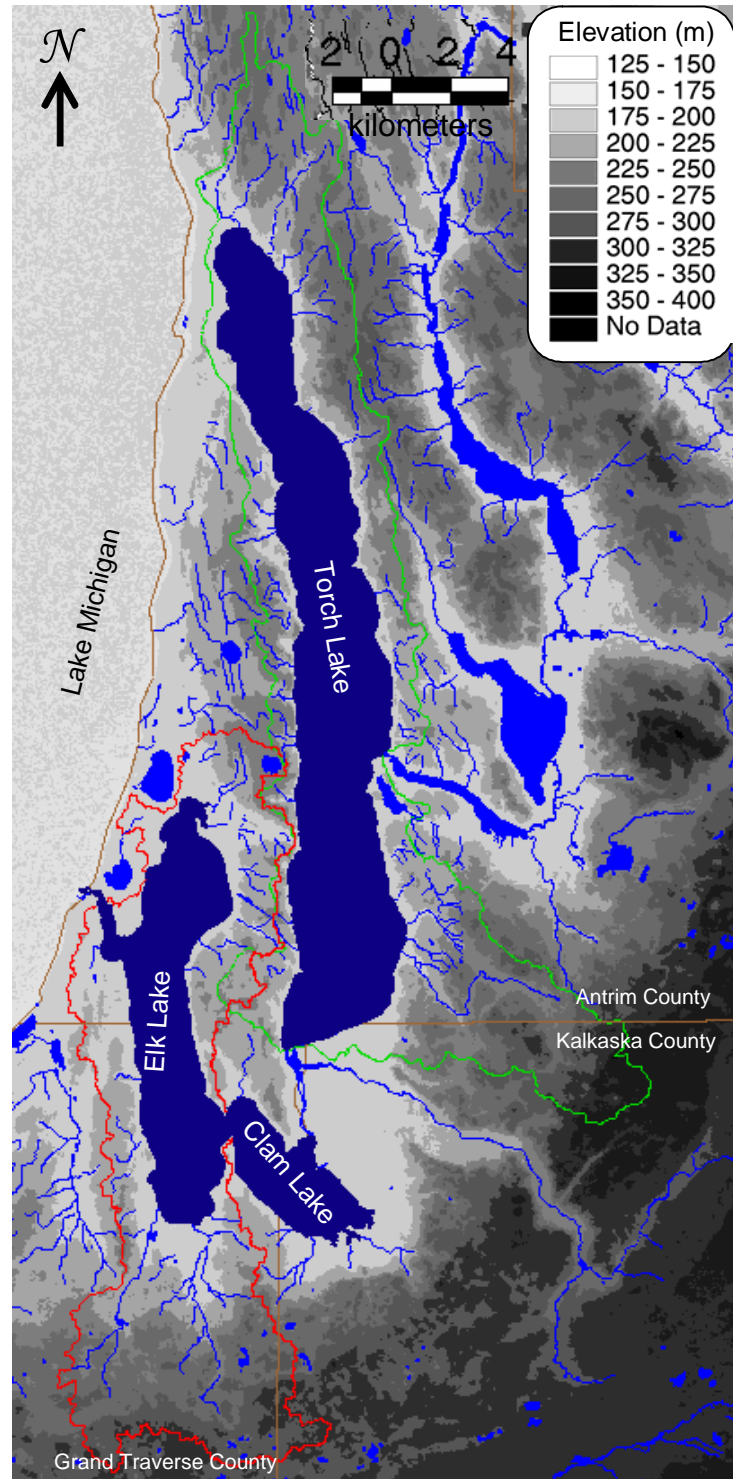
Fig. 31. Map showing the surface elevation (m), location of Torch and Elk Lakes, and watersheds of Torch (green) and Elk (red) lakes. County lines are shown in brown.

The similarity between the anthropogenic accumulation rates of the two lakes suggests that, similar to Houghton and Higgins lakes, most human sources of lead, cadmium and copper are common to the two lakes.
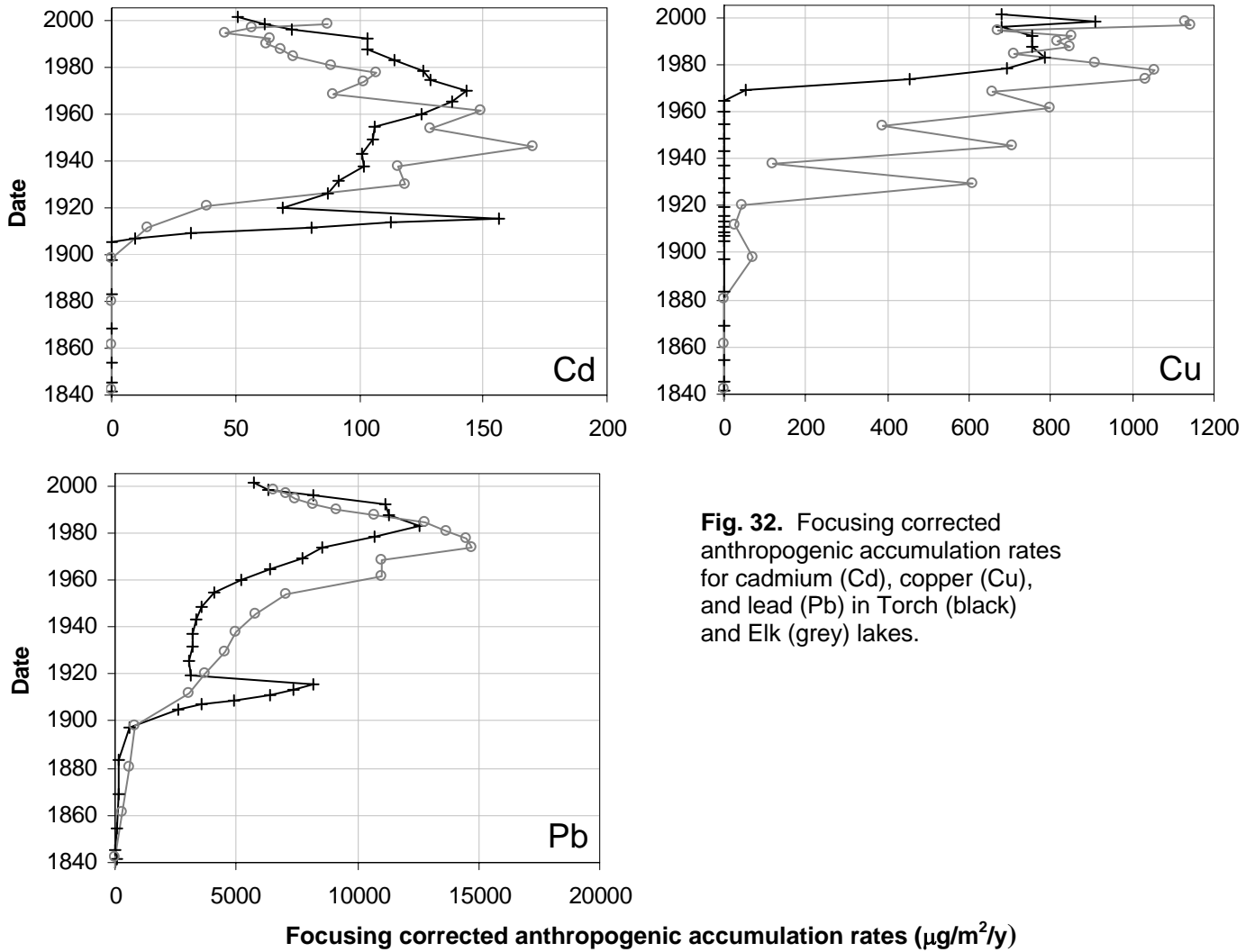
Fig. 32. Focusing corrected anthropogenic accumulation rates for cadmium (Cd), copper (Cu), and lead (Pb) in Torch (black) and Elk (grey) lakes.

Porewater

Introduction

Lake sediments represent a complicated mixture of various materials or substrates such as iron and manganese oxides (amorphous and mineral), carbonate minerals (e.g., $CaCO_3$), clays, sulfide minerals (e.g., FeS), organic matter and relatively refractory minerals such as feldspars. These substrates (except for those that are refractory) are environmentally reactive. This means that metals can be sequestered (via sorption and precipitation reactions) by or released from these substrates due to the changes (diagenesis) that occur in sediments related to physical (e.g., bioturbation), microbiological (e.g., sulfate reduction), and chemical (e.g., CO_2 exchange) processes (Frey and Deevey, 1999). If metals are released (re mobilized) from any of these substrates, they can be resequestered by another substrate or their concentration increased in the water phase (pore water) of the sediment. Elevated chemical concentrations in pore water can increase the potential for exposure of benthic organisms to contaminants. As discussed earlier, remobilization can alter sediment concentration profiles.

Similar to vertical sediment concentrations profiles, vertical chemical concentration profiles in sediment pore water (or pore water profiles) can give insights into processes occurring in the sediment. Pore water profiles are particularly useful in helping to discern processes altering metal mobility, improve interpretation of sediment concentration profiles, and assess potential for exposure. The potential flux of released chemical from the sediment to the overlying lake water can be estimated from the pore water concentration gradients (McKee *et al.*, 1989).

A significant influence (both direct and indirect) on metal mobility is the reduction-oxidation (redox) state of the sediment environment. Typically the sediments near the sediment water interface contain oxygen (oxic environments), but deeper in the sediment oxygen is depleted (anoxic environments) by both abiotic and microbial processes. Depending on the availability of labile carbon, and terminal electron acceptors (e.g., sulfate), different microbial reactions will take place. With increasing depth in the sediments the sequence of the reactions typically include (but are not limited to), nitrate reduction, iron and manganese reduction, sulfate reduction, and methanogenesis. This sequence is often complete in the top 20 centimeters of the sediments.

Abiotic and microbial processes will influence the oxidation state of metals (e.g., Fe^{2+}, Fe^{3+}) and the availability of ligands (e.g., sulfide, bicarbonate). Changes in oxidation state and ligand (i.e., solutes that can form complexes with dissolved metals) concentrations alter the solubility of metals. Two of the most profoundly affected metals are iron and manganese. In oxic environments, dissolved iron and manganese precipitate as oxy-hydroxides to the sediment column. In deeper anoxic sediments, these oxides dissolve and iron and manganese exist in their reduced forms. In the presence of dissolved sulfide or high dissolved concentrations of silica or carbonate, iron and manganese will precipitate. Generally, iron and manganese are ubiquitous compared to these ligands in lake sediments allowing dissolved concentrations of these metals to become elevated in the pore waters.

Because of the higher concentrations of iron and manganese at depth and lower concentrations near the sediment water interface, these metals diffuse upward. Upon entry into the oxic

sediments, the iron and manganese again precipitate as oxy-hydroxides. Other redox sensitive metals (e.g., those metals that have variable valence states in the environment) such as molybdenum can follow a unique oxidation-reduction cycle in the sediment or participate directly (through co-precipitation) with the iron-manganese cycle (e.g., arsenic).

The mobility of redox insensitive metals (e.g., lead) can be indirectly influenced by the cycle of redox sensitive metals, such as the reactive surfaces of iron and manganese oxy-hydroxides. Metals can be strongly sorbed to these oxides. When these oxides dissolve, any sorbed metal will be released to the pore water, where they can diffuse upward or be sequestered to another substrate. Mobility of redox sensitive and insensitive metals may also be enhanced through the formation of complexes with dissolved organic carbon (Stumm and Morgan, 1981) which can concentrate in the pore water during the decay of organic matter. Metals released during the decay of organic matter will be another source for metals in the pore water.

In sum, sediments in lakes can be very biogeochemically dynamic, and because of their ubiquitous concentration, vertical total concentration profiles of iron and manganese can be used as a measure of these processes. Comparing pore water metal concentration to redox condition suggested by iron and manganese pore water metal concentration profiles provide insight into influences on metal behavior.

Results

Houghton Lake - Pore water iron concentrations, Fig. 33, are greater than 10,000 ng/mL at 45.5 cm depth decreasing to the sediment surface to less than 100 ng/mL. Three major concentration slopes appear (20 – 35 cm, 5 to 15 cm, and 0 to 5 cm) and no steady state concentration of iron at depth is readily apparent. The manganese pore water profile, Figure 34, declines from an apparent steady state concentration of 2,500 ng/mL at 35 cm depth, decreasing towards the sediment water interface to less than 100 ng/mL. Both profiles indicate an upward flux of dissolved iron and manganese. Samples obtained just above the sediment water interface (top water), are indicated as a zero depth in Figures 33 and 34. Top water manganese concentrations of 86 ng/mL are lower than the first pore water sample allowing manganese to diffuse across the sediment water interface. Iron top water concentrations are higher than the first pore water sample.
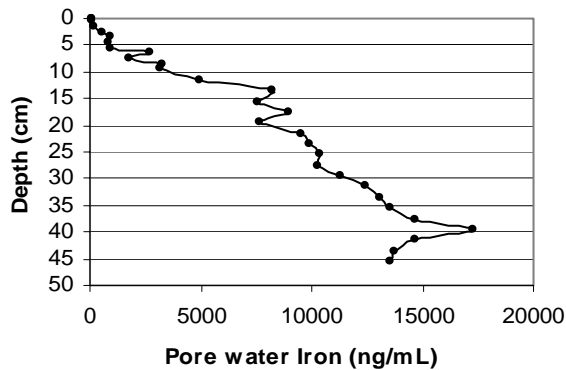
Fig. 33. Pore water iron concentration in Houghton
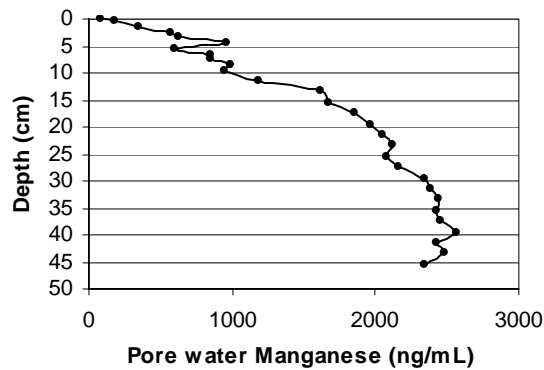
Fig. 34. Pore water manganese concentration in

The sediment concentration profiles of iron, manganese, and arsenic, Figure 35, show a peak in iron and arsenic concentrations at about 1 cm and in manganese near the sediment water interface. These peak concentrations are most likely due to the precipitation of the upward diffusing iron and manganese as oxyhydroxides. The offset locations of the iron and manganese peaks are the result of differences in the redox chemistry of these two elements (Azcue *et al.*, 1994). Reduced iron is less stable in oxic environments than manganese, or put in another way reduced manganese needs higher concentrations of dissolved oxygen before it is oxidized and precipitates as the oxyhydroxide.
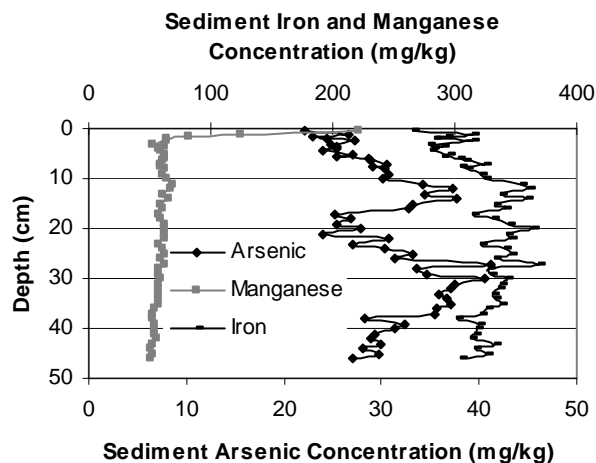
Fig. 35. Sediment arsenic, iron, and manganese concentrations in Houghton Lake

The pore water profile for arsenic, Figure 36, is similar to those of iron and manganese in that concentrations are higher at depth and decrease to the sediment water interface.
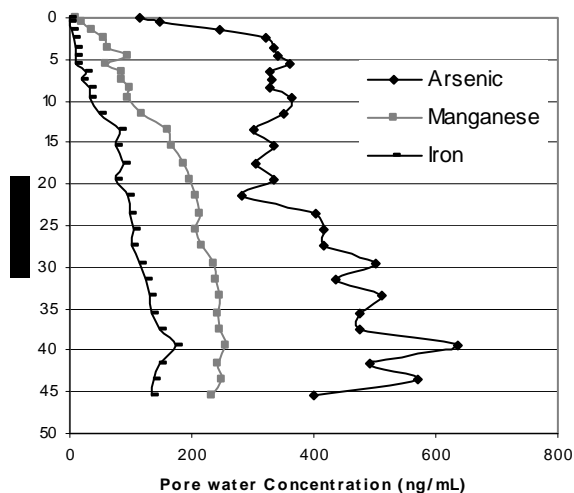
Fig. 36. Pore water arsenic, iron, and manganese concentrations (ng/mL) in Houghton Lake

Since the arsenic concentration is not zero at the sediment water interface, there is potential for some it to enter the overlying lake water. Near the sediment water interface decreases in pore water arsenic, Fig 36, concentrations correspond well to sharp increases of sediment arsenic concentrations, Fig 8, inferring that arsenic may be scavenged from the pore water.

Figures 37 and 38 compare iron and arsenic and manganese and arsenic pore water concentrations, respectively.
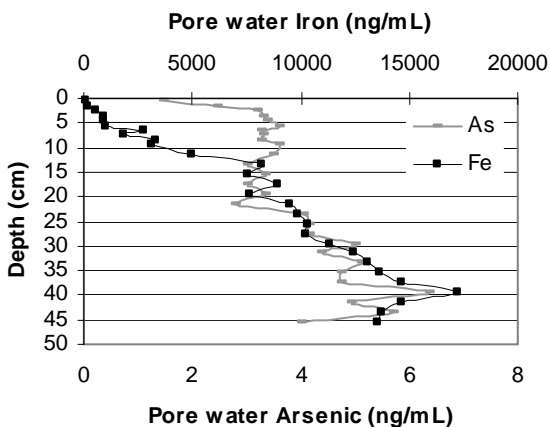
Fig. 37. Pore water iron and arsenic concentrations in Houghton Lake
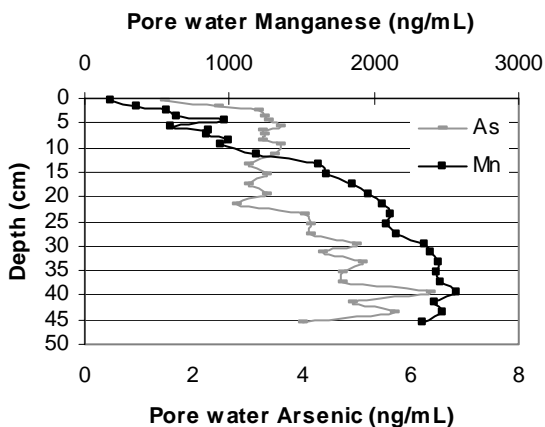
Fig. 38. Porewater manganese and arsenic in Houghton Lake

In the section of the core deeper than 25 cm, the trajectories of the arsenic and iron profiles match. Their trajectories change from 15 to 5 cm although they differ from one another; arsenic concentrations are relatively constant while that of iron decreases. Their trajectories change again from 5 to 0 cm and both show decreasing concentrations. Overall, pore water

concentrations of arsenic trend with iron consistent with other studies of freshwater sediment pore water (Azcue *et al.*, 1994, Fabian *et al.*, 2003, Widerlund and Ingri, 1995).

One might conclude then that reducing conditions deeper in the sediment provide conditions for the dissolution of iron and manganese minerals causing the enrichment of dissolved iron and manganese. Arsenic minerals might also be dissolving, but more likely its enrichment in pore water is due to the arsenic released from the dissolution of the iron (and manganese) minerals. Near the sediment-water interface, arsenic is being scavenged from solution by co-precipitation or sorption reactions evidenced by the sharp increases in sediment arsenic concentrations, Figure 36. The scavenging is not complete, however, and some arsenic could enter the overlying lake water. The cause of the relatively constant concentrations of arsenic in the pore water between 5 cm and 15 cm is not known at this time.

Diffusion across the sediment water interface can result in exposure of aquatic biota to toxic metals/metalloids such as arsenic. The extent for exposure can be estimated by calculating the potential diffusive flux using Fick's First Law where the diffusive flux, (F_d) is:

$$F_d = -\phi \cdot D \cdot \frac{d\,[\,As\,]}{dx}.$$

Where:

ϕ = average porosity of the sediment over dx

D_B = bulk sediment diffusion coefficient (cm^2/yr)

$\dfrac{d[As]}{dx}$ = measured pore water concentration gradient (ng/cm^3)/cm

Average porosity, ϕ, was calculated as the average porosity of the top five centimeters, 0.98. The bulk sediment diffusion coefficient (D_B) was calculated as $D_B = \phi^2 \cdot D_s$. The diffusion coefficient (D_s) of the arsenate ion at infinite dilution corrected to 7°C was obtained from Azcue and Nriagu (1994) (Azcue *et al.*, 1994) as 4.8 x 10^{-6} cm^2/s. The pore water concentration gradient, 0.85 ng/cm^3/cm, was determined by linear regression of the arsenic concentration in the water directly overlying the sediment and the first three pore water samples. The following assumptions were made 1) D_B is constant over the sediment depth of interest 2) arsenic is in the form of the free ion and valence state does not influence diffusion properties (Azcue *et al.*, 1994) and bioturbation effects are negligible (Azcue *et al.*, 1994, McKee *et al.*, 1989).

The vertical diffusive flux of arsenic from the sediments to the overlying water column for Houghton Lake is 120 ng/cm^2/yr, representing conditions within the sampling core observed on this sampling date. If the top water concentration of arsenic, 1.16 ng/mL, represents the water column directly above the sediment water interface extending to 7.6 cm above the sediment surface the diffusive flux of arsenic accounts for 3.7% of the arsenic top water concentration if the diffusive flux occurred over a 24 hour period. Assuming that the diffusion of arsenic occurs across the sediment water interface in 30% of the sediment surface area, estimated as 30% of the lake surface area, correlating to the deepest portions of the lake where dissolved oxygen levels would likely be lowest. In addition, the lake represents a closed system with no arsenic inputs other than the sediment-derived contribution and the flux does not vary with time. The diffusive flux of arsenic from the sediment over the span of one year would account for a whole-lake

sediment-derived arsenic contribution of 0.117 ng/mL, assuming an average lake depth of 10 feet and a total lake volume of 2.5 x 10^{11} liters. If the top water sample, 1.16 ng/mL, were to represent arsenic concentrations for the entire lake it would require approximately 10 years of arsenic diffusion across the sediment water interface to achieve the concentration of arsenic in the lake.

The ultimate fate of arsenic diffusing from the lake sediment can include: resedimentation to the sediment column, continued diffusion to the water column, and uptake by aquatic biota. In a sediment column consisting of a permanently oxidized surface layer, Widerlund and Ingri (1995) (Widerlund and Ingri, 1995) found that nearly all of the arsenic diffusing from the sediment column was returned to the sediment. Whereas in a sediment column characterized by permanently reduced sediments, Fabian et al (2003) (Fabian *et al.*, 2003) found that 22% of arsenic deposited during sedimentation was remobilized to the water column. Benthic communities including zooplankton and fish species could also be affected by the diffusive flux of arsenic. Chen and Folt (2000) (Chen and Folt, 2000) observed that different trophic levels of zooplankton show increased arsenic concentration due to elevated levels of arsenic in the sediment, compared to more pristine lakes, and also found fish species that feeding on the zooplankton demonstrated higher arsenic levels.

A final comment is that the pore water conditions observed and processes inferred for Houghton Lake are specifically for this particular sampling date. Unlike the sediment concentration profiles that are more invariant over time, pore water profiles can be more dynamic as environmental conditions in the lake change (e.g., amount of dissolved oxygen in bottom waters) and thus one must be careful not to assume these conditions observed reflect the most common condition of the lake sediments.

Comparison of human inputs to watershed characteristics

Focusing corrected anthropogenic accumulation rates were compared to watershed characteristics for two time periods, 1970-1980 (1975) and 1990-2000 (1995). This comparison was performed to help determine possible influences on metal inputs to inland lakes throughout Michigan. The watershed characteristics examined include: population density, %land cover, atmospheric deposition of sulfate, erodibility of the watershed, lake size, watershed size, and watershed:lake area ratio. None of these watershed characteristics portray one particular source, but rather represent a variety of sources and processes that may influence metal inputs to a lake. The sources and processes that each watershed characteristic represents are described below.

Population density within the watershed represents many different human sources, including: releases from wear of automobile parts (Rice, 1999), car emissions (Callender and vanMetre, 1997, Rice, 1999), zinc from road dust and vehicle exhaust (Shahin et al., 2000), wastewater (Callender and Rice, 2000), and household and yard waste (Callender and Rice, 2000). Metals from these sources may enter the lake through direct overland flow from the watershed to the lake, from stream or sewer input, or from local atmospheric input and deposition (e.g., vehicle exhaust). Previous studies have found some correlation between the sum of copper, lead, mercury, and zinc concentrations in stream sediments and population density (Rice, 1999), and that population density strongly correlates to traffic density and is a predictor of Pb and Zn concentrations in the environment derived from anthropogenic activities (Callender and Rice, 2000).

Land use and land cover within a watershed have the potential to significantly influence metal inputs to a lake (Paul et al., 2002). Metals such as cadmium, chromium, copper, lead, mercury, nickel and zinc have been found to occur at higher levels in urban areas than rural areas in stream sediments (Rice, 1999), reservoir sediments (Callender and vanMetre, 1997), and soils (Parker et al., 1978). Agricultural land use may also contribute not only increased nutrient inputs to the environment, but also increased metal inputs such as arsenic, copper, mercury, lead, selenium and zinc from pesticides and fertilizers (Rice, 1999).

The importance of atmospheric deposition of metals to freshwater systems has been well documented (e.g., Callender and vanMetre, 1997, Gatz, 1975, Gatz et al., 1989, Sweet et al., 1998, Winchester and Nifong, 1971). However, while some studies have been done in the Great Lakes region, accurate metal deposition rates throughout Michigan are not well defined. It is likely that there is a spatial gradient of atmospheric deposition in Michigan, with the highest rates occurring near and downwind of major urban and industrial centers, such as Chicago, IL, Gary, IN, and Detroit, MI. Because sufficient data for metal deposition were not available, sulfate deposition data were used instead. Sulfate is released into the atmosphere as a result of the burning of fossil fuels, and deposition of sulfate is monitored as part of the National Atmospheric Deposition Program (NADP) (National Atmospheric Deposition Program (NRSP-3)/National Trends Network, 2003). The burning of fossil fuels is a source of metals to the environment (Goodarzi et al., 2001, Rice, 1999, Simonetti et al., 2000, Souch et al., 2003, Winchester and Nifong, 1971), and sulfate deposition may represent deposition of metals from this source. Sulfate deposition will not represent deposition of specific metals from sources such

as copper smelters. Wet deposition of sulfate has previously been found to correlate with lead and cadmium deposition (Gatz et al., 1989).

Many of the above described inputs of metals to lakes rely on erosion of soils containing contaminants and subsequent transport to the lake. Sources relating to land cover, such as application of pesticides and fertilizer to agricultural land, are not input directly to the lake, but to the land, and must be transported to the lake to act as a source. Additionally, atmospheric deposition occurs not only directly to the lake, but also to soils within the watershed, which may then be transported to the lake (Callender and vanMetre, 1997, Sanudo-Wilhelmy and Gill, 1999). Because of this, it may be necessary to represent not only possible sources of metals within the lake, but also the pathways in which those metals reach the lake. Therefore, the susceptibility of each watershed to erosion was calculated using the average K factor and slope of soils within the watershed. The K factor is the "relative index of susceptibility of bare, uncultivated soil to particle detachment and transport by rainfall,"(United States Division of Soil Survey, 1993). This value is standardized to a slope of 9%. Because slope does influence erosion, the K factor was adjusted to include the influence of slope.

Several characteristics of the lake and watershed were also included into the data analysis, including lake size, watershed size, and watershed:lake area ratio. The lake size should not influence the focusing corrected anthropogenic accumulation rates, but this variable was included to test this hypothesis. The size of the watershed and watershed:lake area ratio may provide information about transport of contaminants.

Methods
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 (National Aeronautics and Space Administration, 2002) with 30 m grid cells and ≤ 16 m absolute vertical height accuracy.

Watersheds were delineated around each of the eighteen lakes of interest (Yohn, 2003) using Arc/INFO. In further analyses, the lake is not considered 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.

Census data at the census tract scale were used for population density 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 1975 time period, and data from 1990 and 2000 were averaged to represent the 1995 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^2)

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 6). 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. Percentage land covers were calculated for each watershed (not including the lake) for each of the two time periods.

Table 6. 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

Sulfate deposition data (kg/ha/y) 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.

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.

All of these watershed characteristics were then compared to focusing corrected anthropogenic accumulation rates. Witch Lake was not included in the analyses because of difficulties in calculating anthropogenic inputs, and the influence of local mining activities. A high correlation between accumulation rates of a metal (e.g., cadmium) and a watershed characteristic (e.g., percent agricultural land use within the watershed) suggests that the characteristic is somehow related to a source or process influencing that metal. This may provide insight into the important sources and processes influencing metal inputs to inland lakes throughout Michigan.

Results

Population densities were much higher for the Cass Lake watershed than any other watershed. Population densities for Witch, Paw Paw, and Cadillac Lake watersheds were also high. The much higher population density in 1995 than 1975 in Whitmore Lake watershed is probably partly due to differences in census tracts between the two time periods. The Upper Peninsula lakes (Gratiot, Imp, Round and Witch) have the lowest watershed population densities.
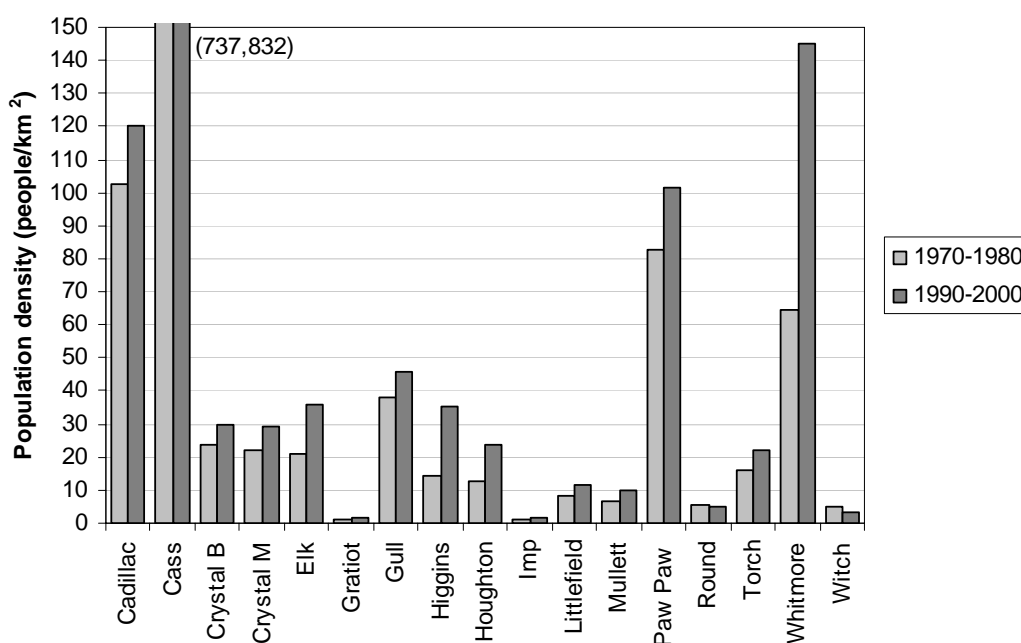

Fig. 39. Population densities (people/km^2) for the watersheds of the 17 Michigan study lakes.

The proportion of land uses within each watershed varied greatly among lakes and over time (Fig. 66, 67). There are also significant changes in land cover seen over time. Unfortunately, changes over time may reflect differences in the datasets more than actual land cover changes. The resolution of the 1975 dataset is much coarser than that of the 1995 dataset (Fig. 67). As a result, where large areas may be grouped as one land cover in 1975 (e.g., urban in Cass Lake watershed), these areas are divided into several land covers in 1995 (Fig. 67). Because of this, it will be difficult to compare land cover data over time.

None of the watersheds had a significant percentage of the land use as water or barren barely/sparsely vegetated, therefore, these land covers were not included in further analysis (Fig. 68). The watershed around Cass Lake has the highest percentage of urban land cover, while Gull, Paw Paw, Cadillac, and Crystal M watersheds have the highest proportions of agricultural land cover. Many lakes have high percentages of forested land cover within their watersheds, including all of the Upper Peninsula lakes.
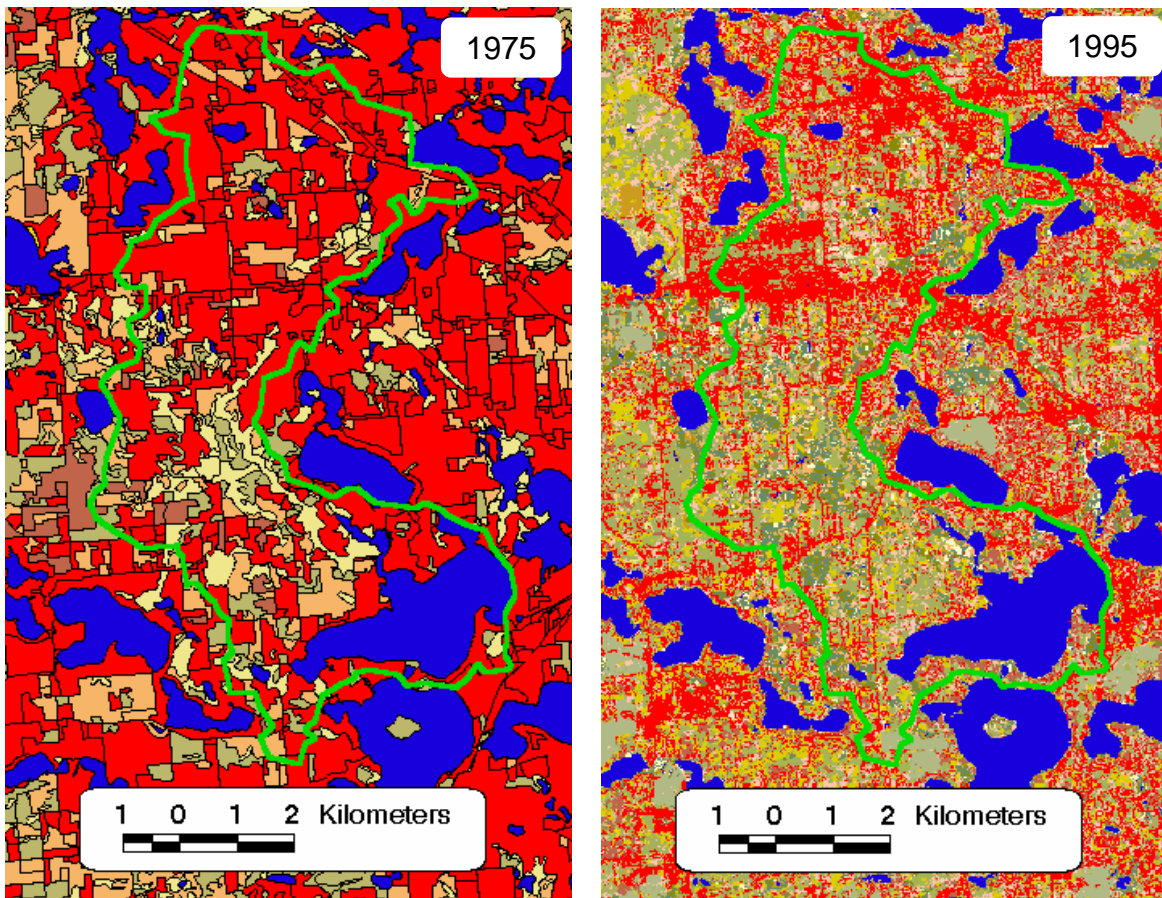

Fig. 40. Urban land cover in the Cass Lake watershed in 1975 and 1995. Urban land cover is in red, and water is in blue. Land covers of the other colors vary between years. The watershed is outlined in green.
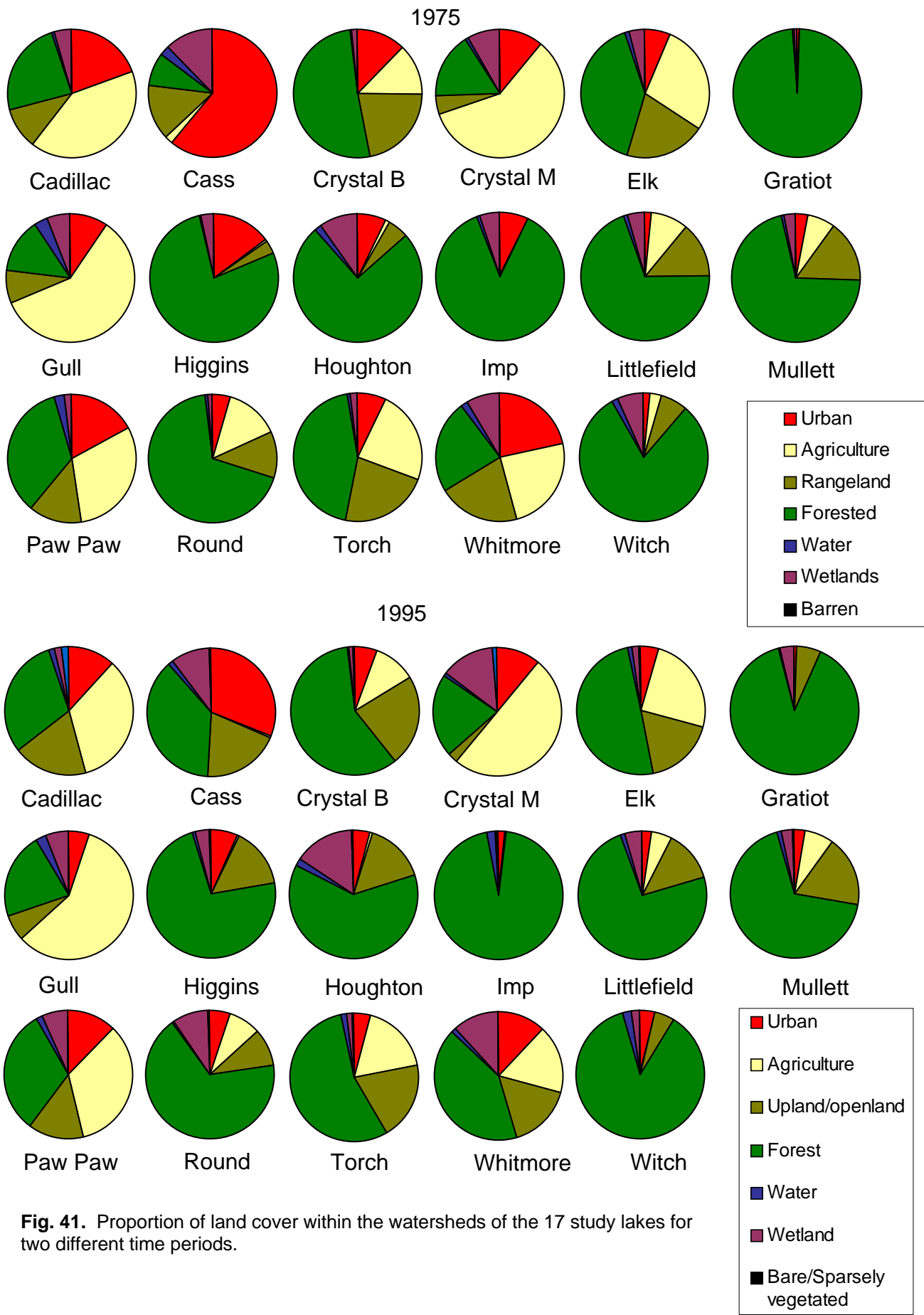
Fig. 41. Proportion of land cover within the watersheds of the 17 study lakes for two different time periods.

Sulfate deposition values varied among lakes, with the lowest values in the Upper Peninsula, and highest values near the southwest corner of Michigan (e.g., Gull and Paw Paw lakes) (Fig. 69). 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 (Perkins *et al.*, 2000, Souch *et al.*, 2003, Winchester and Nifong, 1971).
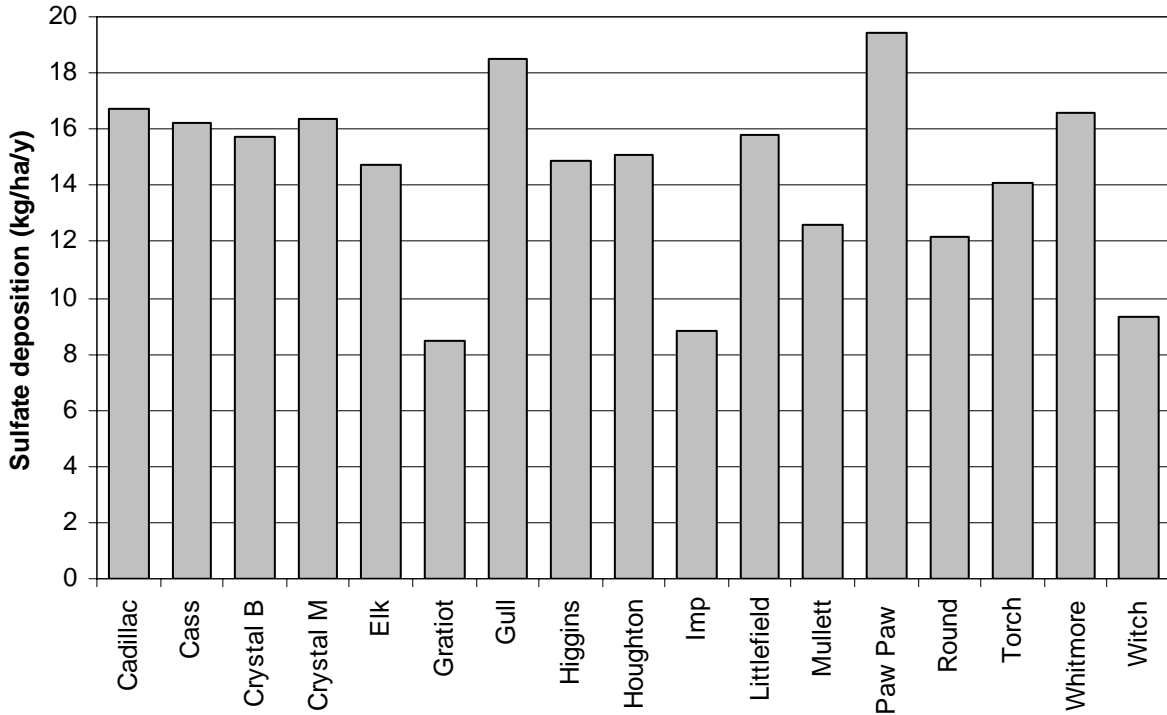
Fig. 42. Average estimated rates of sulfate deposition (kg/ha/y) for the watersheds of the study lakes from 1990-2000.

K factors were highest in Imp, Paw Paw and Whitmore Lake watersheds, and low in Higgins and Houghton lakes (Fig. 70). Accounting for slope changed the K factor significantly, with Elk, Torch and Imp lakes having the highest slope corrected K factors (Fig. 70).
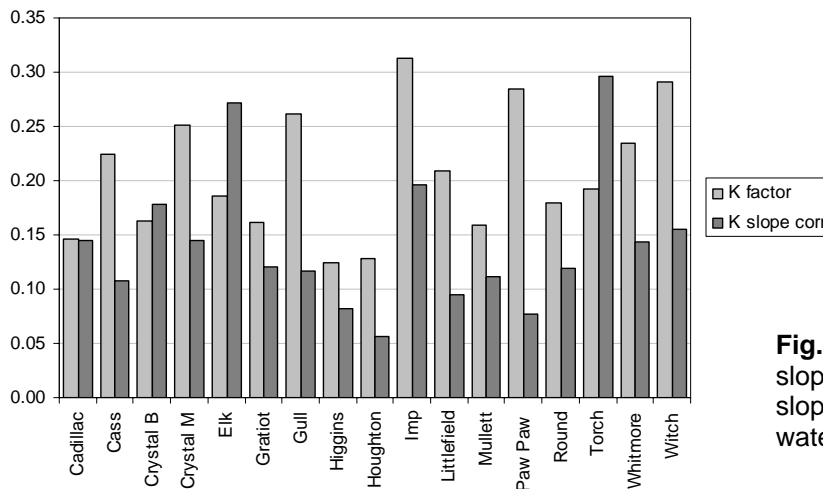
Fig. 43. K factors (light grey) and slope corrected k factors (k factor * slope/9) (dark grey) for the watersheds of the study lakes.

Each of the watershed characteristics described above was plotted versus each the anthropogenic input rates for each of the metals, and a correlation coefficient was determined. Additionally, correlation among the different elements was examined. Most variables were unevenly distributed, with many low values and few high values. To improve the distribution, all variables, including landscape characteristics and metals, were log transformed. Copper data for Cadillac and Houghton lakes were removed for the calculation of r values, because the source of copper to these lakes was unique and local (addition of copper sulfate). Copper data for Witch and Gratiot lakes was also removed, because the source of copper to these lakes is probably related to local mining activities. Copper was also removed for Littlefield Lake because log accumulation rates were much lower than all other lakes.

There are relatively high positive correlations among copper, cadmium, lead, and zinc during both time periods (Table 7). Correlations between lead and zinc, and cadmium and zinc have particularly high values.

Lake size, watershed size, watershed : lake area and erodibility measures do not correlate with metal inputs, except lake area and slope corrected k factor correlate negatively with copper in 1995.

Sulfate deposition is correlated with all metals in the 1970s, but less so in the 1990s (Table 7, Fig. 71). This supports previous conclusions that atmospheric deposition was a more important source in the 1970s, while more localized sources are influential in the 1990s (Yohn, 2003, Yohn *et al.*, 2002a). Lead and zinc may still have important atmospheric sources in the 1990s.

Table 7. Pearson's correlations (*r* value) between focusing corrected anthropogenic accumulation rates and watershed characteristics. Values greater than 0.6 are shown. All variables and metals have been log transformed. Bold indicates the highest correlation for each metals, italics the second highest correlation.

	1970-1980				1990-2000			
	Cd	Cu	Pb	Zn	Cd	Cu	Pb	Zn
Watershed area								
Lake area		-0.607						
Watershed:lake								
SO4	**0.835**	0.657	0.778	0.821			0.728	0.751
K factor								
K factor, slope corr		-0.628						
Pop dens	*0.813*	**0.855**	**0.825**	**0.905**	*0.616*	*0.856*	*0.851*	**0.919**
% urban	0.720	*0.740*	0.627	*0.874*	**0.725**	**0.899**	**0.899**	0.918
% ag								
% range, openland				0.637				
% forest	-0.688		*-0.782*	-0.778			-0.642	
% wetlands	0.673		0.683	0.734				
Cu		0.604	0.802	0.802			0.652	0.860
Cd			0.880	0.882			0.843	0.739
Pb				0.980				0.950
Zn								
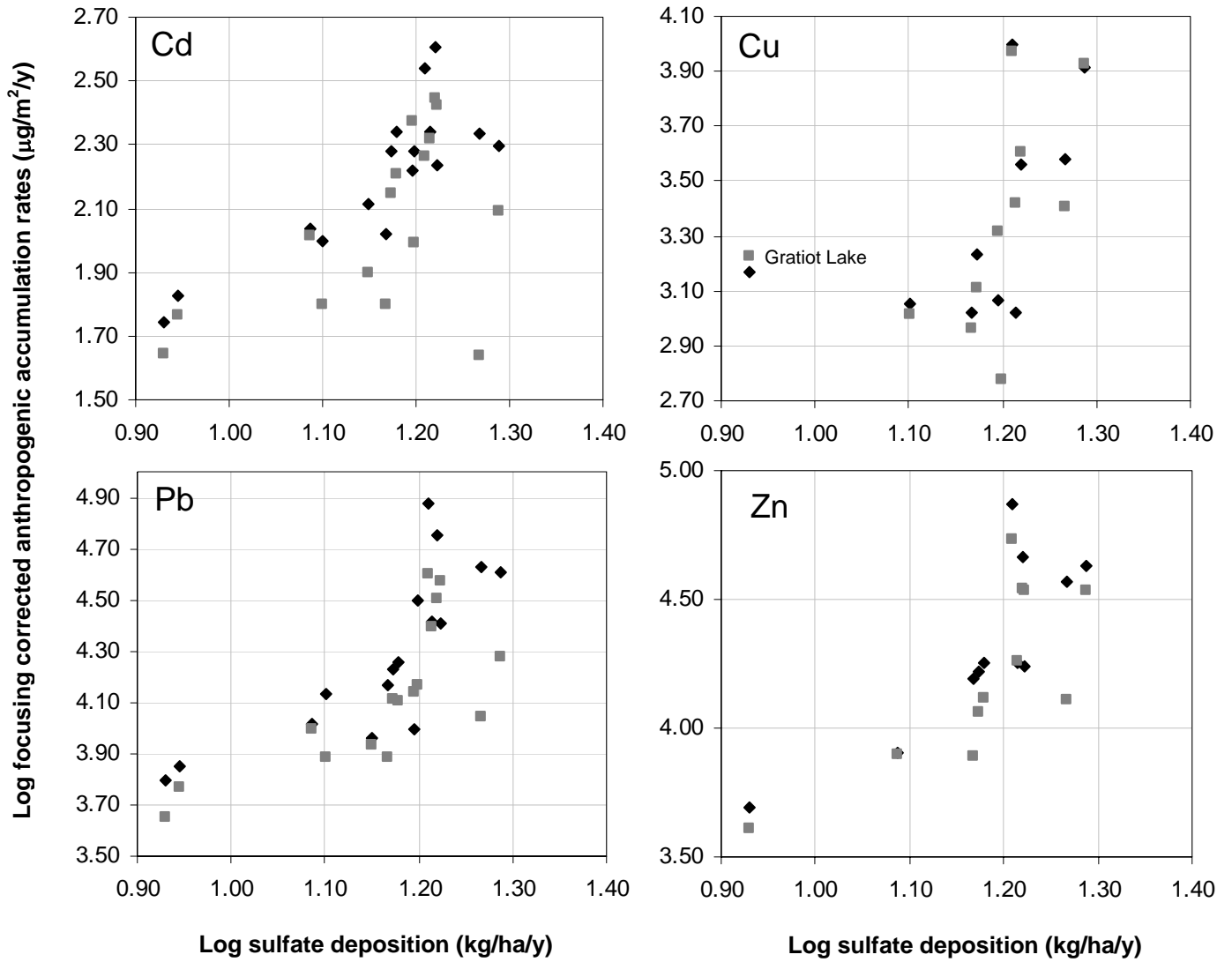
Fig. 44. Log focusing corrected anthropogenic rates of cadmium (Cd), copper (Cu), lead (Pb), and zinc (Zn) from 1970-1980 (black) and 1990-2000 (grey) versus average log sulfate deposition (kg/ha/y).

Anthropogenic inputs of metals had the most number of correlations and highest correlation values with population density and percentage of urban land cover in the watershed (Table 7) (Fig. 72, 73). For lead, copper, and zinc, correlations are higher in 1995 than 1975 for both urban land cover and population density. Population densities in both 1995 and 1975 are positively correlated to the % urban land cover in the watershed (1975: 0.845, 1995: 0.918) (Fig. 74). It is likely that these two variables represent similar sources, such as release of metals from wear of automobile parts (Rice, 1999), car emissions (Callender and vanMetre, 1997, Rice, 1999, Shahin *et al.*, 2000), wastewater (Callender and Rice, 2000), and household and yard waste (Callender and Rice, 2000).
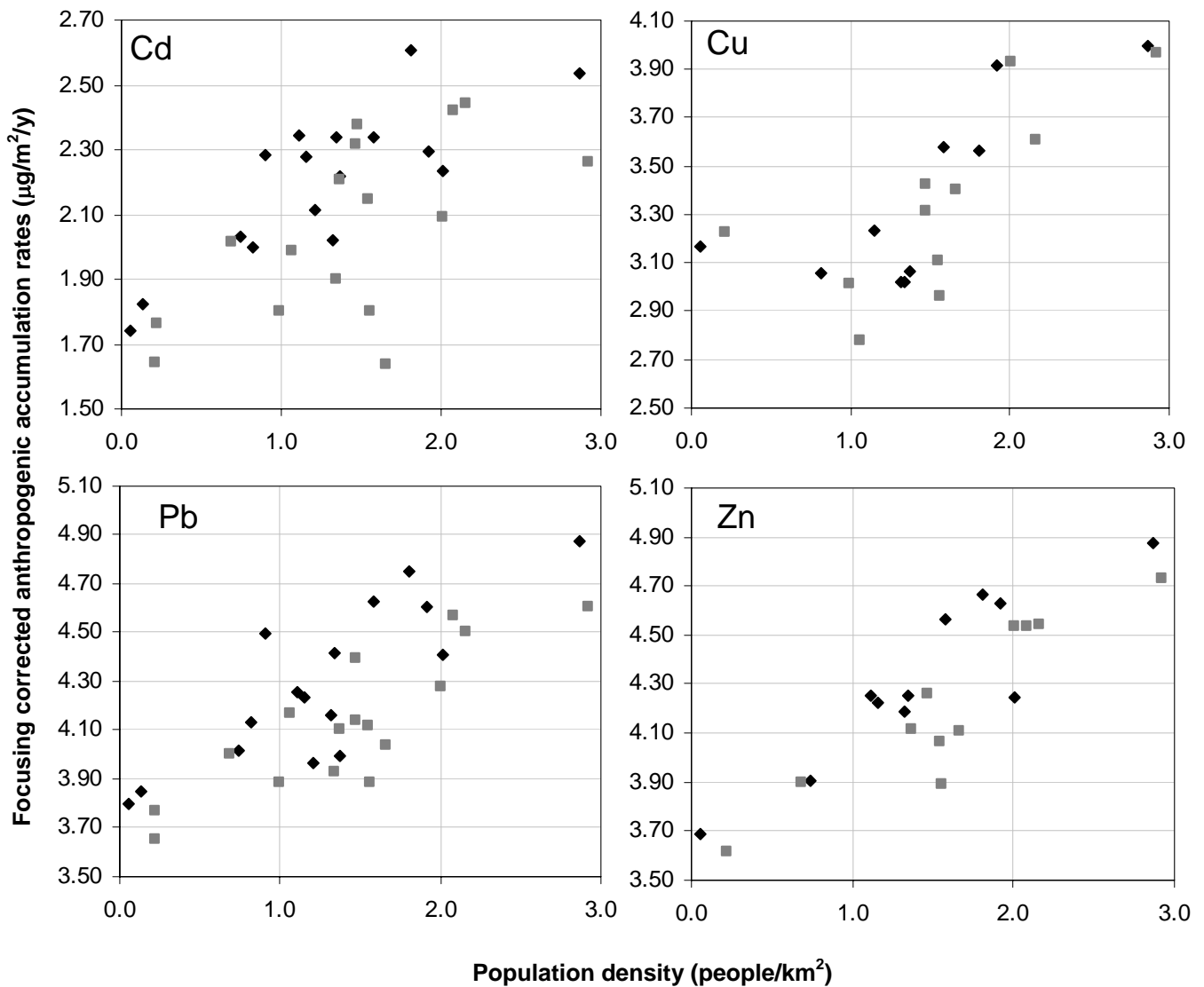
Fig. 45. Log focusing corrected anthropogenic accumulation rates of cadmium (Cd), copper (Cu), lead (Pb) and zinc (Zn) (μg/m^2/y) versus log watershed population densities (people/km^2).
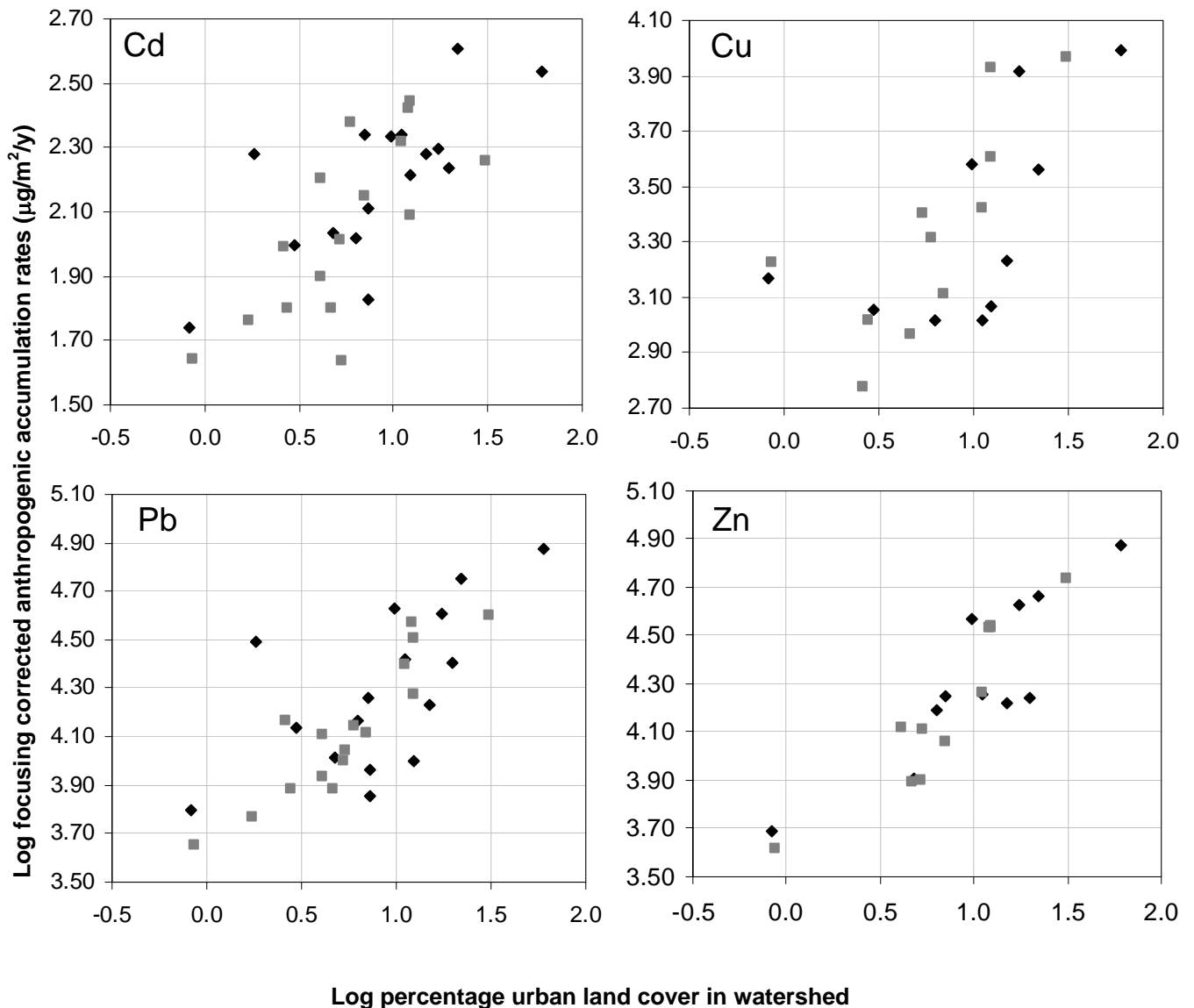
Fig. 46. Log focusing corrected anthropogenic accumulation rates of cadmium (Cd), copper (Cu), lead (Pb) and zinc (Zn) (μg/m^2/y) versus log percentage of urban land cover within the watersheds.

Percent forest is negatively correlated with cadmium, lead and zinc in the 1970s, and lead in the 1990s. This is a result of % forest being negatively correlated with both population density and % urban.

There is also a positive correlation between the percentage of wetlands and accumulation rates of cadmium, lead and zinc from 1970-1980 (Table 7, Fig. 40). This result is surprising, as typically wetlands act as sediment traps, and should reduce the input of metals (Paul et al., 2002). Additionally, the percentage of wetlands within the watershed does not correlate highly or moderately with any other variable. The reason for this positive correlation is unclear.
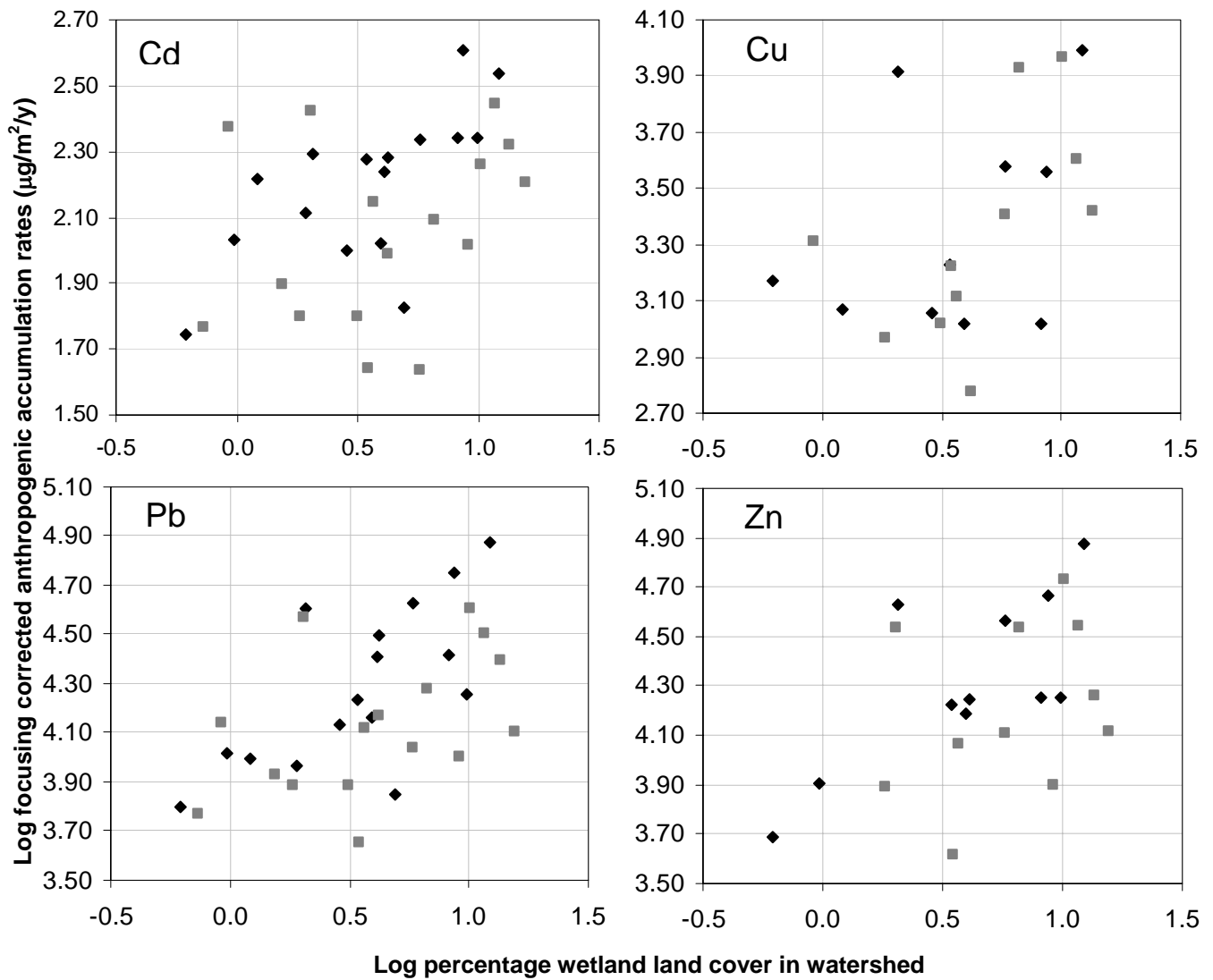
Fig. 47. Log focusing corrected anthropogenic accumulation rates of cadmium (Cd), copper (Cu), lead (Pb) and zinc (Zn) (μg/m^2/y) versus log percentage of wetland land cover within the watersheds.

Overall, it is apparent that the presence of humans within the watershed of a lake, represented either by percentage of urban land cover or population density within the watershed, results in greater inputs of copper, cadmium, lead and zinc to the lake. Additionally, atmospheric deposition, as represented by sulfate deposition, also appears to be an important source of metals in the 1970s. The physical characteristics of the watershed (e.g., erodibility) do not have a dominant role in determining rates of metal inputs.

Recommendations of a lake monitoring strategy

Designing a monitoring strategy should include the determination of two different things: (1) which lakes to monitor, and (2) how often to sample those lakes.

Several factors should be considered when determining which lakes to monitor. One important consideration is the quality of the core. The sediment core from Littlefield Lake has a disturbed record, and cannot be dated. If this lake were resampled, ^{210}Pb dating could not be used to determine the depth of new deposition. It would be possible to match element profiles to differentiate the depth of new deposition, however, unless there are particular contaminant concerns, resampling this lake is not recommended. Additionally, the sediment core collected from Hubbard Lake did not represent undisturbed deposition. This lake could be resampled, but should only be analyzed and ^{210}Pb dated if the core visually does not contain any sand or appear disturbed in any way.

An overall monitoring strategy should include:
1. Lakes of concern: lakes with increasing levels of contaminants to the surface, or concentrations of contaminants higher than most other Michigan lakes
2. Background lakes: lakes with low concentrations of contaminants with few point sources in the watershed. These lakes would provide background data on atmospheric deposition and provide a comparison for the lakes of concern. Ideally, these lakes would be spatially dispersed throughout Michigan.

It is not appropriate to make final recommendations on which lakes to monitor until all the preliminary sampling is completed; however, some of the lakes may be classified as lakes of concern or background lakes. Classifying a lake as "of concern" is not an evaluation of the toxicity of the sediments, but rather a comparison to other Michigan lakes in this study.

The lakes that have been most affected by anthropogenic activities are classified as lakes of concern. Cass Lake has clearly been influenced by human activities, and has relatively high concentrations of anthropogenic elements near the surface. Concentrations of anthropogenic elements are also higher than most lakes in Whitmore, Paw Paw and Cadillac lakes. Additionally, Cadillac, Crystal B, Round and Imp lakes have anthropogenic accumulation rates that increase to the present. Crystal B, Imp and Round lakes are particularly interesting, because they do not have high rates of metal inputs, and the cause of the increasing anthropogenic inputs is not clear.

Elk Lake has consistently low concentrations of contaminants. Gratiot, Mullett, Imp and Round lakes also have low anthropogenic accumulation rates. These lakes appear to be the "cleanest" of the lakes sampled. Imp Lake would be particularly useful to sample, as it has little development in the watershed, generally low accumulation rates, but rates are increasing in the past decade.

After all the preliminary lakes are sampled, it will be possible to determine the lakes with the greatest issues of concern. It will also be possible to identify background lakes, which will serve as monitors of contaminants entering lakes with few known point sources.

The second thing to determine is the frequency of sampling a lake. The intent of monitoring is to be able to detect change from when the last sample was taken. Change can be in the concentration of a chemical or a change in the trend of the environmental loading of a chemical. In the first case only the very surface sediment sample would need to be taken. But given the complexities of lake dynamics (e.g., bioturbation) a single sample would not be informative. What is more important is to determine the change in the trend of the chemical inputs. However, one surface sample will not reveal a trend. One might consider a minimum of four samples that reflect new sediment input from the last sampling as necessary to define a trend.

Our current sampling protocol involves taking 0.5 cm samples from the top sediments. Therefore, the accumulation of 2.0 cm of new sediment would be needed to obtain the four samples. The time to deposit 2.0 cm of sediment can be determined from the sedimentation rate (Table 8).

Table 8. Minimum number of years needed to deposit approximately 2 cm of new sediment for seventeen inland lakes in Michigan. * Littlefield estimated

Cadillac	Cass	Crystal B	Crystal M	Elk	Gratiot
2 y	1 y	4 y	3 y	10 y	2 y
Gull	Higgins	Houghton	Imp	Littlefield*	Mullett
4 y	6 y	4 y	6 y	5 y	3 y
Paw Paw	Round	Torch	Whitmore	Witch	
1 y	3 y	13 y	1 y	2 y	

In addition to the issues described above, other factors to consider when determining a monitoring plan could include the usage of the lake for recreation (e.g., Houghton Lake), and spatial distribution of the monitoring lakes.

A possible suite of lakes to sample could include: Gratiot, Imp, and Round lakes in the Upper Peninsula. Gratiot Lake would represent a "clean" lake, while Imp and Round lakes represent relatively undeveloped lakes, but also have increasing human inputs entering the lake. In the Lower Peninsula, PawPaw, Whitmore and/or Cass, and Cadillac lakes could be monitored as lakes of concern, while Elk Lake could be sampled as a more pristine lake. Crystal B Lake would be useful to monitor, as anthropogenic inputs are also increasing in this lake. Crystal M Lake could be sampled to represent the middle portion of the state. However, final determination of the monitoring lakes should be made after sampling of the preliminary lakes is completed.

References

Alfaro-De la Torre, M.C., Tessier, A., 2002. Cadmium deposition and mobility in the sediments of an acidic oligotrophic lake. Geochimica et Cosmochimica Acta 66, 3549-3562.

Auer, M.T., Johnson, N.A., Penn, M.R., Effler, S.W., 1996. Pollutant sources, depositional environment, and the surficial sediments of Onondaga Lake, New York. Journal of Environmental Quality 25, 46-55.

Azcue, J.M., Nriagu, J.O., Schiff, S., 1994. Role of Sediment Porewater in the Cycling of Arsenic in a Mine-Polluted Lake. Environment International 20, 517-527.

Blais, J.M., Kalff, J., 1995. The influence of lake morphometry on sediment focusing. Limnology and Oceanography 40, 582-588.

Boyle, J.F., Rose, N.L., Bennion, H., Yang, H., Appleby, P.G., 1999. Environmental impacts in the Jianghan Plain: evidence from lake sediments. Water, Air, and Soil Pollution 112, 21-40.

Brown, E.T., Callonnec, L.L., German, C.R., 2000. Geochemical cycling of redox-sensitive metals in sediments from Lake Malawi: A diagnostic paleotracer for episodic changes in mixing depth. Geochimica et Cosmochimica Acta 64, 3515-3523.

Bruland, K.W., Bertine, K., Koide, M., Goldberg, E.D., 1974. History of metal pollution in Southern California costal zone. Environmental Science and Technology 8, 425-432.

Callender, E., Rice, K.C., 2000. The urban environmental gradient: Anthropogenic influences on the spatial and temporal distributions of lead and zinc in the environment. Environmental Science and Technology 24, 232-238.

Callender, E., vanMetre, P.C., 1997. Reservoir sediment cores show US lead declines. Environmental Science and Technology 31, A424-A428.

Catallo, W.J., Schlenker, M., Gambrell, R.P., Shane, B.S., 1995. Toxic chemicals and trace metals from urban and rural Louisiana lakes: recent historical profiles and toxicological significance. Environmental Science and Technology 29, 1439-1446.

Chen, C.Y., Folt, C.L., 2000. Bioaccumulation and diminution of arsenic and lead in a freshwater food web. Environmental Science & Technology 34, 3878-3884.

Cooper, D.C., Morse, J.W., 1998. Biogeochemical controls on trace metal cycling in anoxic marine sediments. Environmental Science and Technology 32, 327-330.

Davis, B.M., 1976. Erosional rates and land use history in southern Michigan. Environmental Conservation 3, 139-148.

Door, J.A., Eschman, D.F., 1970. Geology of Michigan. University of Michigan Press, Ann Arbor.

Douglas, G.B., Adeney, J.A., 2000. Diagenetic cycling of trace elements in the bottom sediments of the Swan River Estuary, Western Australia. Applied Geochemistry 15, 551-566.

Downing, J.A., Rath, L.C., 1988. Spatial patchiness in the lacustrine sedimentary environment. Limnology and Oceanography 33, 447-458.

Evans, R.D., Dillon, P.J., 1982. Historical changes in anthropogenic lead fallout in southern Ontario, Canada. Hydrobiologia 91, 131-137.

Evans, R.D., Rigler, F.H., 1983. A test of lead-210 dating for the measurement of whole lake soft sediment accumulation. Canadian Journal of Fisheries and Aquatic Sciences 40, 506-515.

Fabian, D., Zhou, Z., Wehrli, B., Friedl, G., 2003. Diagenetic cycling of arsenic in the sediments of eutrophic Baldeggersee, Switzerland. Applied Geochemistry 18, 1497-1506.

Frey, D.G., Deevey, E.S., 1999. Metals and models: Digenetic modelling in freshwater lacustrine sediments. Journal of Paleolimnology 44, 227-251.

Gatz, D.F., 1975. Pollutant Aerosol Deposition into Southern Lake-Michigan. Water Air and Soil Pollution 5, 239-251.

Gatz, D.F., Bowersox, V.C., Su, J., 1989. Lead and Cadmium Loadings to the Great-Lakes from Precipitation. Journal of Great Lakes Research 15, 246-264.

Golden, K.A., Wong, C.S., Jeremiason, J.D., Eisenreich, S.J., Sanders, M.G., Hallgren, J., Swackhammer, D.L., Engstrom, D.R., Long, D.T., 1993. Accumulation and preliminary inventory of organochlorines in Great Lakes sediments. Water Science Technology 28, 19-31.

Goodarzi, F., Sanei, H., Duncan, W.F., 2001. Monitoring the distribution and deposition of trace elements associated with a zinc-lead smelter in the Trail area, British Columbia, Canada. Journal of Environmental Monitoring 3, 515-525.

Graney, J.R., Halliday, A.N., Keeler, G.J., Nriagu, J.O., Robbins, J.A., Norton, S.A., 1995. Isotopic record of lead pollution in lake sediments from the northeastern United States. Geochimica et Cosmochimica Acta 59, 1715-1728.

Hakanson, L., 1977. The influence of wind, fetch, and water depth on the distribution of sediments in Lake Vanern, Sweden. Canadian Journal of Earth Science 14, 397-412.

Harrington, J.M., Laforce, M.J., Rember, W.C., Fendorf, S.E., Rosenzweig, R.F., 1998. Phase associations and mobilization of iron and trace elements in Coeur d'Alene Lake, Idaho. Environmental Science and Technology 650-656.

Hewitt, A.D., Reynolds, C.M., 1990. Dissolution of metals from soils and sediments with a microwave-nitric acid digestion technique. Atomic Spectroscopy 11, 1425-1436.

Heyvaert, A.C., Reuter, J.E., Slotton, D.G., Goldman, C.R., 2000. Paleolimnological reconstruction of historical atmospheric lead and mercury deposition at Lake Tahoe, California-Nevada. Environmental Science and Technology 34, 3588-3597.

Iskander, I.K., Keeney, D.R., 1974. Concentration of heavy metals in sediment cores from selected Wisconsin Lakes. Environmental Science and Technology 8, 165-170.

Johnson, M.G., Nicholls, K.H., 1988. Temporal and spatial trends in metal loads to sediments of Lake Simcoe, Ontario. Water, Air and Soil Pollution 39, 337-354.

Kemp, A.L.W., Thomas, R.L., 1976. Cultural impacts on the geochemistry of the sediments of Lakes Ontario, Erie and Huron. Water, Air and Soil Pollution 5, 469-490.

Kerfoot, W.C., Lauster, G., Robbins, J.A., 1994. Paleolimnological study of copper mining around Lake Superior: Artificial varves from Protage Lake provide a high resolution record. Limnology and Oceanography 39, 649-669.

Kerfoot, W.C., Robbins, J.A., 1999. Nearshore regions of Lake Superior: Multi-element signatures of mining discharges and a test of Pb-210 deposition under conditions of variable sediment mass flux. Journal of Great Lakes Research 25, 697-720.

Khim, J., Kannan, K., Villeneuve, D., Koh, C., Giesy, J., 1999a. Characterization and distribution of trace organic contaminants in sediment from Masan Bay, Korea: 1. Instrumental analysis. Environmental Science and Technology 33, 4199-4205.

Khim, J., Villeneuve, D., Kannan, K., Lee, K., Snyder, S., Koh, C., Giesy, J., 1999b. Alkylphenols, polycyclic aromatic hydrocarbons (PAHs), and organochlorines in sediment from Lake Shihwa, Korea: Instrumental and bioanalytical characterization. Environ Toxicol Chem 8, 2424-2432.

MacDonald, D.D., Ingersoll, C.G., Berger, T.A., 2000. Development and evaluation of consensus-based sediment quality guidelines for freshwater ecosystems. Archives of Environmental Contamination and Toxicology 39, 20-31.

McKee, J.D., Wilson, T.P., Long, D.T., Owen, R.M., 1989. Pore water profiles and early diagenesis of Mn, Cu and Pb in sediments from large lakes. Journal of Great Lakes Research 15, 68-83.

Michigan Center for Geographic Information, 2002. Statewide Layer: Michigan geographic framework. In: Michigan Center for Geographic Information, Lansing, MI.

Michigan Department of Natural Resources, 1999. 1978 Land cover / use. In: MDNR, Lansing, MI.

Michigan Department of Natural Resources, 2003. IFMAP/GAP land cover. In: MDNR Forest, Mineral, and Fire Management Division, Lansing, MI.

Michigan Department of Natural Resources, 1992. MIRIS base data. In: MDNR, Lansing, MI.

Michigan Department of Natural Resources, 2000. State ownership. In: MDNR, Lansing, MI.

National Aeronautics and Space Administration, 2002. Shuttle Radar Topography Mission (SRTM) Spatial Dataset. In: U.S. Geological Survey, Sioux Falls, SD.

National Atmospheric Deposition Program (NRSP-3)/National Trends Network, 2003. NADP Program Office, Illinois State Water Survey, 2204 Griffith Drive, Champaign, IL 61820.

Oldfield, F., Appleby, P.G., 1984. Empirical testing of 210Pb-dating models for lake sediments. In: Haworth, E.Y., Lund, J.W.G. (Eds.), Lake Sediments and Environmental History. University of Minnesota Press, Minneapolis, pp. 93-124.

Parker, G.R., McFee, W.W., Kelly, J.M., 1978. Metal Distribution in Forested Ecosystems in Urban and Rural Northwestern Indiana. Journal of Environmental Quality 7, 337-342.

Paul, J.F., Comeleo, R.L., Copeland, J., 2002. Landscape metrics and estuarine sediment contamination in the mid-Atlantic and southern New England regions. Journal of Environmental Quality 31, 836-845.

Perkins, S.M., Filippelli, G.M., Souch, C.J., 2000. Airborne trace metal contamination of wetland sediments at Indiana Dunes National Lakeshore. Water Air and Soil Pollution 122, 231-260.

Qu, W.C., Dickman, M., Wang, S.M., 2001. Multivariate analysis of heavy metal and nutrient concentrations in sediments of Taihu Lake, China. Hydrobiologia 450, 83-89.

Rice, K.C., 1999. Trace-element concentrations in streambed sediment across the conterminous United States. Environmental Science and Technology 33, 2499-2504.

Robbins, J.A., 1982. Stratigraphic and dynamic effects of sediment reworking by Great Lakes zoobenthos. Hydrobiologia 92, 611-622.

Sanchez-Cabeza, J.A., Ani-Ragolta, I., Masque, P., 2000. Some considerations of the Pb-210 constant rate of supply (CRS) dating model. Limnology and Oceanography 45, 990-995.

Sanei, H., Goodarzi, F., Van der Flier-Keller, E., 2001. Historical variation of elements with respect to different geochemical fractions in recent sediments from Pigeon Lake, Alberta, Canada? Journal of Environmental Monitoring 3, 27-36.

Sanudo-Wilhelmy, S.A., Gill, G.A., 1999. Impact of the Clean Water Act on the levels of toxic metals in Urban Estuaries: the Hudson River estuary revisited. Environmental Science and Technology 33, 3477-3481.

Shahin, U., Yi, S.M., Paode, R.D., Holsen, T.M., 2000. Long-term elemental dry deposition fluxes measured around Lake Michigan with an automated dry deposition sampler. Environmental Science & Technology 34, 1887-1892.

Simonetti, A., Gariepy, C., Carignan, J., 2000. Pb and Sr isotopic compositions of snowpack from Quebec, Canada: Inferences on the sources and deposition budgets of atmospheric heavy metals. Geochimica Et Cosmochimica Acta 64, 5-20.

Simpson, S.J., Long, D.T., Geisey, J.P., Fett, J.D., 2000a. Inland lakes sediment trends: sediment analysis results for five Michigan Lakes. In: MI/DEQ/SWQ-01/030. Department of Environmental Quality, East Lansing, MI, pp. 17.

Simpson, S.J., Long, D.T., Geisey, J.P., Fett, J.D., 2000b. Inland lakes sediment trends: sediment analysis results for five Michigan Lakes (MI/DEQ/SWQ-01/030). In: MI/DEQ/SWQ-01/030. Department of Environmental Quality, East Lansing, MI, pp. 17.

Souch, C.J., Filippelli, G.M., Dollar, N., Perkins, S., Mastalerz, M., 2003. Accumulation rates of airborne heavy metals in wetlands. Physical Geography 23, 21-43.

Spiethoff, H.M., Hemond, H.F., 1996. History of toxic metal discharge to surface waters of the Aberjona Watershed. Environmental Science and Technology 30, 121-128.

Stewart, S.I., 1994. The seasonal home location decision process: toward a dynamic model. In: Park and Recreation Resources. Michigan State University, East Lansing, MI, pp. 156.

Stumm, W., Morgan, J.J., 1981. Aquatic chemistry : an introduction emphasizing chemical equilibria in natural waters. Wiley, New York.

Sweet, C.W., Weiss, A., Vermette, S.J., 1998. Atmospheric deposition of trace metals at three sites near the Great Lakes. Water Air and Soil Pollution 103, 423-439.

U.S. Department of Agriculture, 1994. State Soil Geographic (STATSGO) database for Michigan. In: U.S. Department of Agriculture, Natural Resources Conservation Service, Fort Worth, Texas.

United States Division of Soil Survey, 1993. Soil survey manual. U.S. Dept. of Agriculture : For sale by the Supt. of Docs. U.S. G.P.O., Washington, DC.

United States. Bureau of Mines., Minerals yearbook. The Bureau : Supt. of Docs. U.S. G.P.O. [distributor, Washington.

Urban, N.R., Gorham, E., Underwood, J.K., Martin, F.B., Ogden, J.G., 1990. Geochemical processes controlling concentrations of Al, Fe, and Mn in Nova Scotia lakes. Limnology and Oceanography 35, 1516-1534.

von Guten, H.R., Sturm, M., Moser, R.N., 1997. 200-year record of metals in lake sediments and natural background concentrations. Environmental Science and Technology 31, 2193-2197.

Walling, D.E., Qingping, H., 1992. Interpretation of caesium-137 profiles in lacustrine and other sediments: the role of catchment-derived inputs. Hydrobiologia 235, 219-230.

Wetzel, R.G., 2001. Limnology : lake and river ecosystems. Academic, San Diego, Calif. London.

Widerlund, A., Ingri, J., 1995. Early Diagenesis of Arsenic in Sediments of the Kalix-River Estuary, Northern Sweden. Chemical Geology 125, 185-196.

Winchester, J.W., Nifong, G.D., 1971. Water pollution in Lake Michigan by trace elements from pollution aerosol fallout. Water, Air, and Soil Pollution 1, 50-64.

Yohn, S.S., 2003. Regional versus local influences on lead and cadmium loading in the Great Lakes region. Applied Geochemistry In press.

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

Yohn, S.S., Long, D.T., Giesy, J.P., Fett, J.D., Kannan, K., 2001. Inland lakes sediment trends: sediment analysis results for two Michigan Lakes. In: Department of Environmental Quality, East Lansing, pp. 49.

Yohn, S.S., Long, D.T., Giesy, J.P., Scholle, L.K., Patino, L.C., Fett, J.D., Kannan, K., 2002b. Inland lakes sediment trends: sediment analysis results for five Michigan Lakes. In: Department of Environmental Quality, East Lansing, pp. 64.