MI/DEQ/WB-06/090

Inland Lakes Sediment Trends: Mercury Sediment Analysis Results for 27 Michigan Lakes

1999: Cass, Elk, Gratiot, Gull, Higgins
2000: Crystal (Montcalm County), Littlefield
2001: Cadillac, Crystal (Benzie County), Hubbard, Mullet, Paw Paw, Whitmore
2002: Imp, Houghton, Round, Torch, Witch
2003: Avalon, Birch, Muskegon, Sand, Shupac
2004: George, Hackert, Round (Delta County), Otter

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Sediment Mercury Analysis for 27 Michigan Lakes
Report # MI/DEQ/WB-06/090

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Executive Summary

Sediment cores were collected from 27 lakes starting in 1999 and continuing through 2004. Cores were collected from one site in each lake and sediment ages determined by ^{210}Pb and ^{137}Cs. The analyses of a suite of inorganic, excluding mercury, and organic chemicals have been reported elsewhere (Simpson *et al.*, 2000, Yohn *et al.*, 2001, Yohn *et al.*, 2002b). Key findings for mercury include:

- Recent sediment mercury concentrations in all of the study lakes, except Gull and Littlefield lakes, remain elevated above background values.
- In general, sediment mercury concentrations begin to increase above background levels in the mid 1800s and peak in the 1950s to late 1970s.
    - Houghton Lake sediments have the highest observed peak mercury concentrations.
- Mercury accumulation rates have increased since the late 1800s, with the highest accumulation rates generally found in the mid 1960s-1980s.
    - A regional pattern of mercury accumulation can be related to a "background" anthropogenic atmospheric input.
    - Several of Michigan's inland lakes still have anthropogenic mercury accumulation rates that are increasing to the surface suggesting, increased loading to these lakes. This differs from regional atmospheric mercury deposition measurements.
- Mercury accumulation in the lakes is also characterized by episodic short term enhanced accumulation events. The timing of some episodic accumulations are common among lakes apparently related to historical events such as WWII manufacturing and the California gold rush.
    - Spatial analyses of these common events indicate that at times a regional atmospheric source was responsible for the anthropogenic loadings (e.g., California gold rush) and that at other times similar processes with in individual watersheds were seemingly responsible (e.g., WWII).
- The cause(s) for the episodic accumulations at other times is(are) not well understood, but are most likely related to processes within individual watersheds.
- The importance of processes occurring within an individual watershed on mercury accumulations is supported by the spatial trends of decadal average focusing corrected anthropogenic accumulation rates and focusing corrected anthropogenic inventories.

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, understanding 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". A key goal of the monitoring program 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 sediment mercury analysis for 27 inland lakes in Michigan.

Background

Mercury contamination and its subsequent methylation and bioaccumulation in aquatic food-webs has resulted in elevated levels of mercury in fish and thus statewide fish consumption advisories for the Great Lakes region, including inland lakes throughout the state of Michigan (Keeler *et al.*, 1994, Watras *et al.*, 1994). Fish consumption has been shown to be a primary exposure pathway of mercury, and its more toxic form, methylmercury, to humans (Hightower and Moore, 2003). Toxicity issues related to methylmercury contaminated fish consumption were highlighted in the 1950's and 1960's with deaths in Minamata Bay and Niigata, Japan (Tsubaki and Irukayama, 1977). Although reported emissions of mercury have declined in the past decade (Engstrom and Swain, 1997, EPA, 2002), the amount of river miles and lake acreage under fish consumption advisories have continued to increase (EPA, 2003). The cause is two-fold: 1) the geochemical cycle of mercury which allows it to be transported long distances creating a contaminated water body in an otherwise pristine setting (Tseng *et al.*, 2004), and 2) increased monitoring of previously untested water bodies (EPA, 2003).

Mercury has become a global concern because it is ubiquitous in the environment, and characterized by long (>one year) atmospheric residence time (Fitzgerald, 1989). For example, Arctic region lakes (Hermanson, 1998) and Antarctic ice cores (Vandal *et al.*, 1993) are contaminated with mercury although they are far from anthropogenic sources. Anthropogenic sources for mercury include coal fired utilities, smelting activities, medical and municipal waste incineration, agricultural and paint fungicides, gold and silver mining activities, chlor-alkali facilities, and municipal waste streams (Jasinski, 1994); due to environmental legislation, the use of mercury in many of these anthropogenic activities has declined in the last 30 years. Current U.S. consumption of

mercury includes manometers, thermometers, electronic switches and lamps, batteries, and dental amalgams.

Although U.S. consumption of mercury has declined in the last three decades (Brooks, 2003), sediment mercury accumulation rates do not reflect a concomitant decline in mercury accumulation (Engstrom and Swain, 1997, Engstrom *et al.*, 1994, Lorey and Driscoll, 1999a, Swain *et al.*, 1992). Recent work has demonstrated that mercury may enter the environment as high loadings over a short period (e.g., years) (Schuster *et al.*, 2002). Such episodic loadings have been documented in lake sediment cores but the cause for these loadings is not well understood (Engstrom and Swain, 1997, Swain *et al.*, 1992). Thus, although atmospheric deposition from global or regional sources is a principle pathway for mercury contamination of inland lakes (Fitzgerald, 1989, Fitzgerald *et al.*, 1998, Mason *et al.*, 1994a, Watras *et al.*, 2000), it may be possible that watershed scale sources, via runoff or local atmospheric deposition, may contribute to these episodic accumulation events.

Natural Sources

Major geologic sources of mercury are contained in a geologic belt associated with plate tectonic boundaries including areas of geothermal activity, volcanic belts and precious and base metal deposits (Gustin, 2003, Nriagu, 1979). Most geologic deposits are in the form of cinnabar, a mercuric sulfide, but others include elemental mercury, tetrahedrite ($Cu_{12}Sb_4S_{13}$), sphalerite (Zn[Fe]S), wurtzite (ZnS) and other sulfides and sulfosalts including lead, gold and silver (Faust and Aly, 1981).

According to the USGS (USGS, 2003), the largest mercury mines are in Spain, Italy, Slovenia, Peru, China, the former U.S.S.R., Algeria, Mexico, and Turkey. The largest mine in the United States, Nevada's McDermitt Mine, closed in 1992 (Brooks, 2003). In 2003, no primary production of mercury occurred in the United States. Imports from Germany (19 metric tons) and Peru (19 metric tons) comprised the bulk of mercury consumed in the U.S in addition to secondary production (that mercury recovered from electrical devices, thermometers, and fluorescent light bulbs). The majority of current production occurs in four countries: China; Kyrgyzstan; Algeria; and Spain (Brooks, 2003).

Consumption

Mercury is used in a variety of industrial applications due to its physical and chemical properties. Elemental mercury is a dense (13.5 g/mL), silver white liquid (melting point –38.89^{o}C; boiling point 357.25^{o}C) at ambient temperatures, a rather conductive metal, and has a uniform coefficient of expansion over its liquid range (Andren and Nriagu, 1979). The uniform expansion coefficient is important for its use in barometers, manometers, thermometers and thermostats. Because of its color, mercuric sulfide has historically been used as a pigment in paints and cosmetics (Jasinski, 1994). Mercury has also been utilized as a catalyst for the simultaneous production of caustic soda and chlorine in chloro-alkaline plants (Jasinski, 1994). Pulp and paper manufacture, agriculture, and paint and golf course management have utilized mercurial organics as a fungicide. Mercury's ability to amalgamate with precious metals such as gold and silver has led to its use in precious metal reclamation and dental fillings (Jasinski, 1994).

Mercury dynamics in lakes

Mercury from various pathways (i.e. atmospheric deposition) can enter the lake ecosystem where the fate (i.e. uptake by biota) of the metal is determined by the water geochemistry, species deposited (i.e. Hg(0) or Hg(II)), and species conversion (i.e. reduction of Hg(II) to Hg(0)) (Stumm and Morgan, 1981). According to Hudson *et al.* (1992), species of mercury important in freshwater are methylmercury, dissolved gaseous mercury (DGM) primarily present as Hg(0), and the "reactive" and "non-reactive" species of Hg(II). Only methylmercury and elemental mercury are analytically defined (Hudson *et al.*, 1992). Whereas the reactive (that which is reducible by $SnCl_2$ (Morel *et al.*, 1998)) and non-reactive (probably corresponding to strong organic complexes or the uncharacterized species produced through the combustion of coal (Hudson *et al.*, 1992)) Hg(II) species are operationally defined.

Sediments act as sinks for mercury in the lake ecosystem and are thought to be primarily HgS. HgS acts as a control on the Hg(II) concentration in anoxic waters (Morel *et al.*, 1998). Metacinnabar and cinnabar, both mercury sulfide minerals, are known to have low solubility products but their solubility increases in the presence of high sulfide concentrations (Morel *et al.*, 1998, Wang and Driscoll, 1995). Polysulfide complexes can also increase the solubility of cinnabar and metacinnabar (Paquett and Helz, 1997). Adsorption on organic material or iron oxides particles may contribute to sedimentary material (Triffreau *et al.*, 1995). The cycling of dissolved organic mercury complexes are poorly understood (Mason *et al.*, 1994b, Morel *et al.*, 1998, Tseng *et al.*, 2004) but recent work has shown that thiols, sulfur containing groups, are important and bind strongly to both CH_3Hg and Hg(II) (Alderighi *et al.*, 2003).

Transport of mercury from soils

Leaching of metals from soils can transport metals, such as mercury, to deeper soil horizons, groundwater, or surface waters (Lodenius, 1992). Soil organic matter is the principal carrier of mercury to aquatic ecosystems (Lodenius, 1992, Lodenius *et al.*, 1987) and field studies have found that the organic horizon contains higher concentrations of mercury and methylmercury (Lee *et al.*, 1995, Lindqvist *et al.*, 1991, Schwesig *et al.*, 1999). As mentioned above, soils differ in their ability to retain mercury based upon the soil matrix. Highly organic soils tend to retain mercury over a wide soil pH range, whereas clays and oxide minerals will lose mercury to the soil solution below a soil pH of 7 (Andersson, 1979). The influence of chloride ions may be of more significance than hydrogen ions as they have been shown to significantly reduce the sorption of mercury (Lodenius, 1992).

Field studies have demonstrated the ability of both inorganic mercury complexes and methylmercury to become mobile during runoff events. Schwesig and Matzner (2000) found export of $Hg_{(tot)}$ and methylmercury occurred in a conifer forest with soils derived from deeply weathered granite and a deciduous forest with a five centimeter deep organic horizon. Allen and Heyes (1997) found 10% of total and 20% of methylmercury contained in precipitation was exported from low order North Carolina (USA) watersheds after rain events. Snowmelt has also been indicated as a major transport mechanism for export, from watershed to aquatic systems, of both total and methylmercury (Schwesig and Matzner, 2001, Schwesig and Matzner, 2000).

Methods

Sediments were collected from 27 inland lakes of Michigan between 1999 and 2004(Figure 1, Table 1. Sediment trends sample lakes: 1999-2004.). 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 or Environmental Protection Agency (EPA) Research Vessel Mudpuppy. The M/V Nibi was designed to provide access to both major and remote inland lakes throughout Michigan. Collected sediment cores were described and examined for color, texture, and signs of

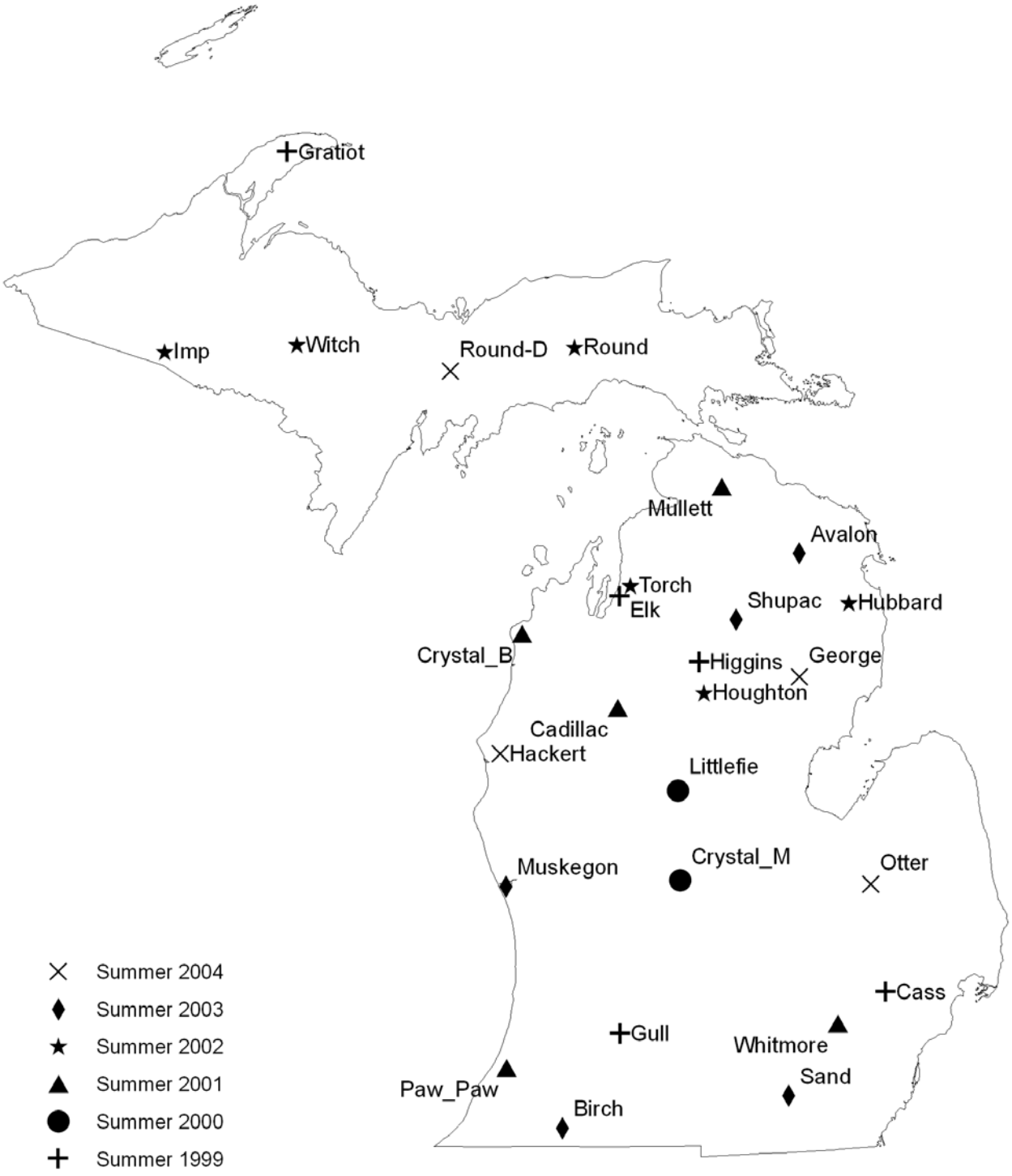
Table 1. Sediment trends sample lakes: 1999-2004.

Lake	Sampling year	Counties of watershed	Lake area (km^2)	Sampling depth (m)	Watershed area (km^2)
Avalon	2003	Montmorency	1.5	21.3	2
Birch	2003	Cass	1.2	29.6	2.2
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
George	2004	Ogemaw	0.7	26.2	5.1
Gratiot	1999	Keweenaw	5.8	23.8	31
Gull	1999	Kalamazoo, Barry	8.2	33.5	61
Hackert	2004	Mason	0.5	15.5	1.5
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	1354
Muskegon	2003	Muskegon, Newaygo	16.8	14.5	53
Otter	2004	Lapeer, Tuscola, Genesee	0.3	36.9	3.4
Paw Paw	2001	Berrien, VanBuren	3.7	27.7	30
Round	2002	Luce	7.0	13.7	22
Round D	2004	Delta, Alger	1.8	16.0	2.0
Sand	2003	Lenawee	1.8	17.3	24.5
Shupac	2003	Crawford	0.4	30.4	2.2
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

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.

^{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.

Figure 1. Sediment trends sample lakes: 1999-2004.



Sediments were frozen and freeze dried prior to analysis. Sediment mercury concentration was determined using a Lumex Zeeman Corrected-Thermal Decomposition-Atomic Absorption Spectrophotometer (ZC-TD-AAS). Analysis protocol followed EPA Method 7473 including blanks and standard reference materials checked every ten samples. The limit of detection for this method is 0.001 mg/kg.

Total Concentration Profiles

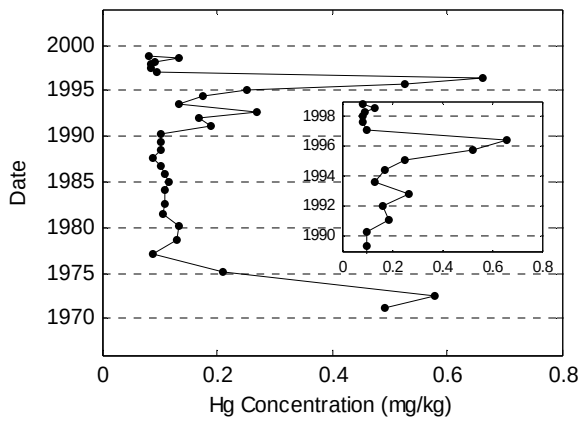


Figure 2. Cass Lake sediment mercury concentration

Cass Lake

Cass Lake has a high rate of sedimentation (Simpson *et al.*, 2000) consequently mercury does not reach background values within the length of the sediment core (Figure 2). Sediment mercury concentration peaks in three distinct periods 1970s, early 1990s, and late 1990s. Excluding episodic events, mercury concentrations decrease from the late 1980s to the present. Figure insets in this and all remaining concentration profiles represent 10 years of sediment record prior to the sampling year

Elk Lake

Sediment mercury concentrations (Figure 3) in Elk Lake begin to rise in the early 1800s peak in the mid-1950s then decline and appear to reach a new equilibrium concentration extending from the 1970s to the present. Three episodic increases in concentration are apparent in Elk Lake during the 1920s, mid 1950s and mid-1990s.

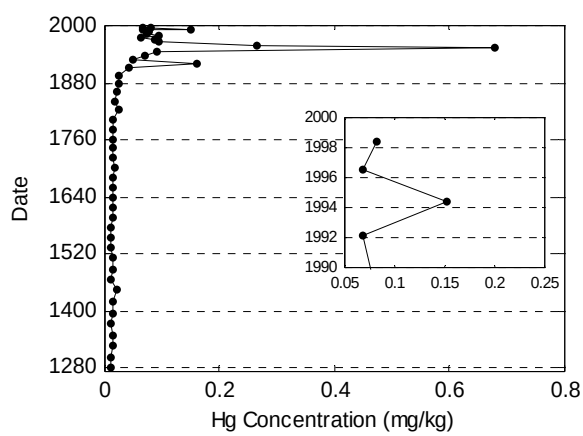


Figure 3. Elk Lake sediment mercury concentration.

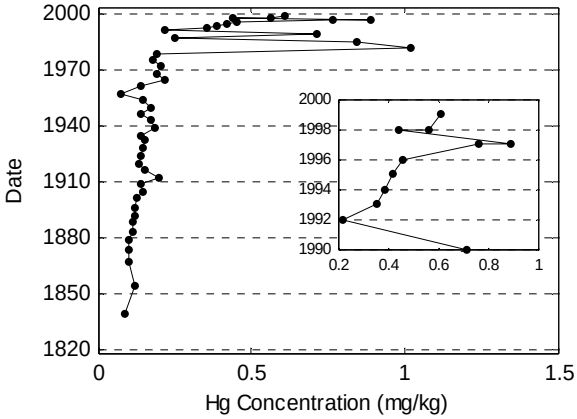


Figure 4. Gratiot Lake sediment mercury concentration.

Gratiot Lake

Sediment mercury concentrations in Gratiot Lake (Figure 4) increase from the early 1800s to the present with a clear change in trajectory of increase occurring in the late 1980s. Although ^{210}Pb dating places the deepest portion of the core in the early 1800s mercury concentrations do not appear to reach a steady state background value. Gratiot Lake also experiences episodic increases in concentration during the mid 1980s and late 1990s.

Gull Lake

Gull Lake sediment mercury concentrations (Figure 5) show episodic concentration peaks in the early 1700s, late 1800s, early 1940s, early 1970s and early 1990s. More generally, concentration increases begin in the late 1880s and peaks during the mid 1970s then decreases to the present.

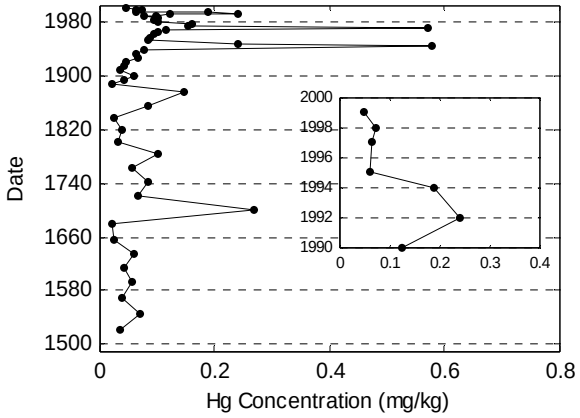


Figure 5. Gull Lake sediment mercury concentration.

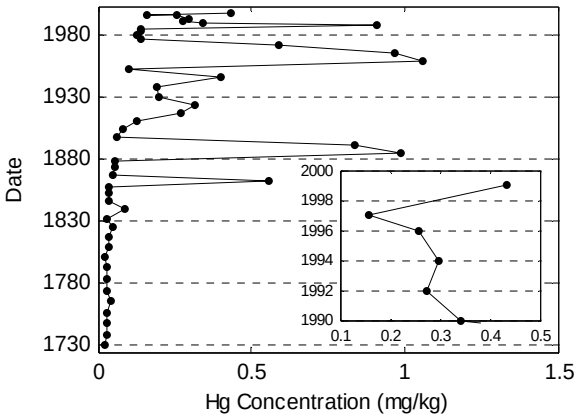


Figure 6. Higgins Lake sediment mercury concentration.

Higgins Lake

Higgins Lake mercury concentrations (Figure 6) begin to increase in the mid 1800s and remain elevated above background level. However it is unclear if the concentrations are increasing or decreasing to the surface. Higgins Lake has experienced multiple episodic events including: 1863, late 1880s, 1920s, 1940s, 1960-1970, and the late 1980s.

Crystal Lake (Mecosta County)

Crystal M Lake mercury concentrations (Figure 7) rise above background values around the mid to late 1700s including several episodic events. Notably, mercury concentrations have increased in the 1860s, 1940s, and mid 1990s. Mercury concentrations are increasing to the surface, suggesting an active source to the lake.

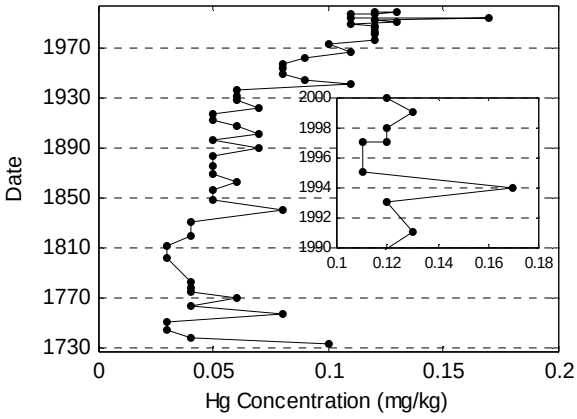


Figure 7. Crystal (Mecosta County) Lake sediment mercury concentration.

Littlefield Lake

Littlefield Lake sediment mercury concentrations (Figure 8) appear to be elevated above background values throughout the entire core. Episodic increases in concentration occur in the 1880s, 1950s and 1970s. Care should be taken in interpreting this data due to evidence that suggests Littlefield Lake was mined for marl (Yohn *et al.*, 2001)

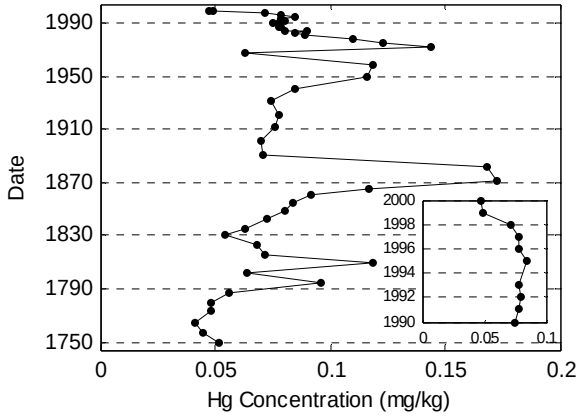


Figure 8. Littlefield Lake sediment mercury concentration.

Lake Cadillac

Lake Cadillac sediment mercury concentrations (Figure 9) increase above background values in the mid to late 1800s peaking in the 1980s. Mercury concentrations then start to decline, rising again starting in the mid 1990s. This suggests that a new source of mercury exists for Lake Cadillac.

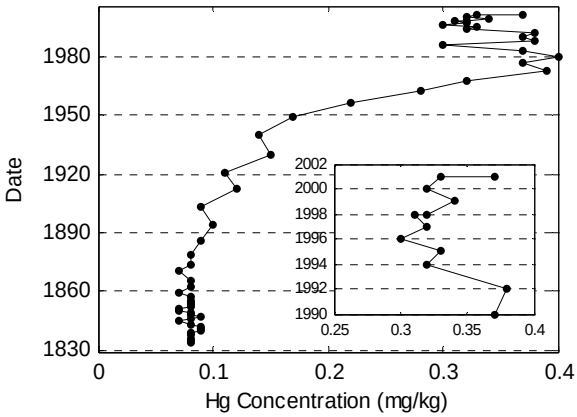


Figure 9. Lake Cadillac mercury sediment mercury concentration.

Crystal Lake (Benzie County)

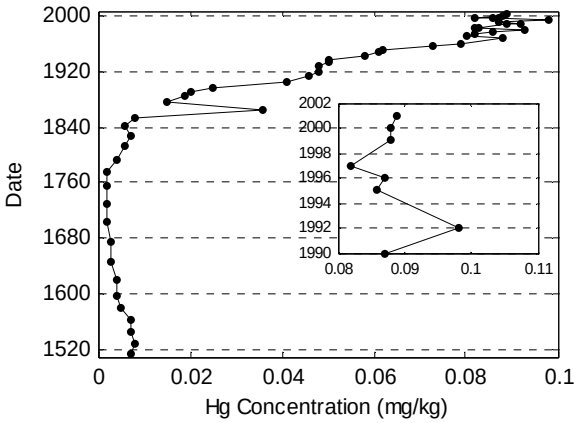


Figure 10. Crystal (Benzie) Lake sediment mercury concentration.

Sediment mercury concentrations in Crystal B Lake (Figure 10) decline to background from the 1500s to the mid 1700s then rise gradually to the mid 1800s and then experience a sharp change in concentration increase. This suggests that the predominant source for mercury changed between the mid 1800s and post 1900. Generally, mercury concentrations are elevated above background concentrations and are increasing towards the surface.

Mullett Lake

Mullett Lake sediment mercury concentrations (Figure 11) increase above background levels around the mid 1700s peaking in the 1970s and decline to the present. Episodic increases in concentration are observed in the 1870s, 1920s, 1940s, and early 1990s.

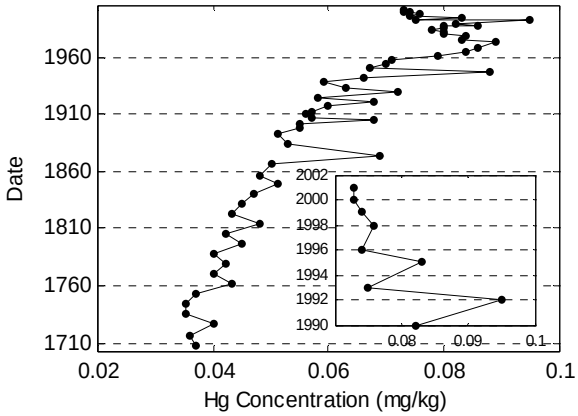


Figure 11. Mullett Lake sediment mercury concentration.

Paw Paw Lake

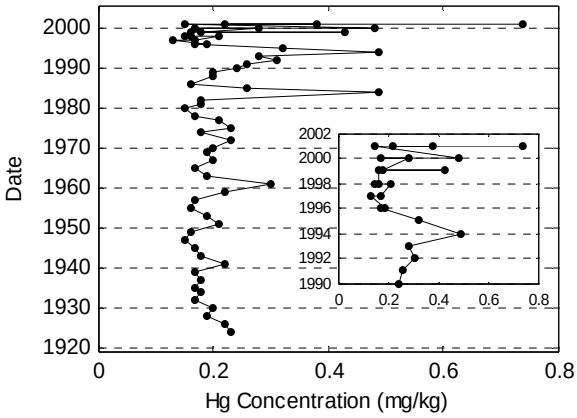


Figure 12. Paw Paw Lake sediment mercury concentration.

Sediment mercury concentrations in Paw Paw Lake (Figure 12) do not reach background values and appear to stay relative constant over the entire core length. Episodic increases in concentration occur in several time periods including: early 1960s, 1980s, and 1990s. Currently sediment mercury concentrations are increasing to the surface.

Whitmore Lake

Sediment mercury concentrations in Whitmore Lake (Figure 13) generally rise in concentration from the late 1800s peaking in early 1980s followed by a short, ~20 year, decline. Sediment mercury concentrations then rise sharply in the late 1990s to the present. Episodic increases are evident in the early 1950s and late 1970s and 2000. Mercury concentrations do not appear to reach background values.

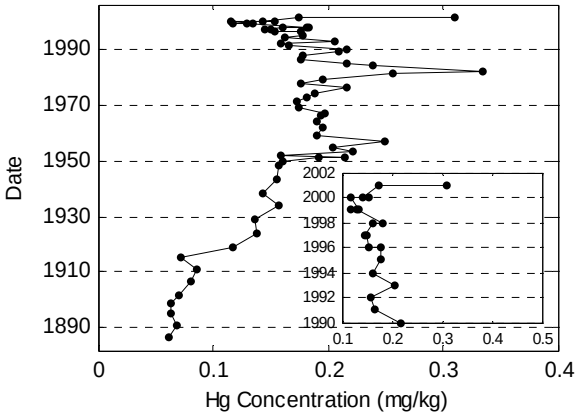


Figure 13. Whitmore Lake sediment mercury concentration.

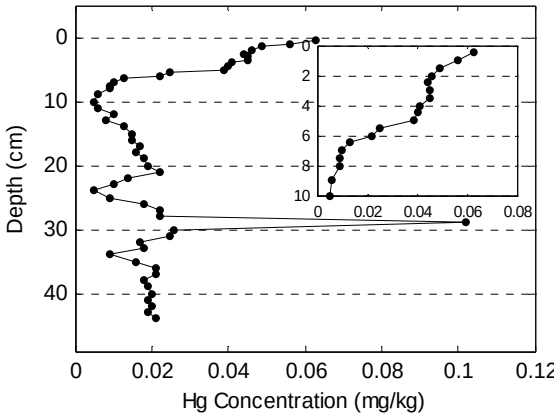


Figure 14. Hubbard Lake sediment mercury concentration.

Hubbard Lake

Care should be taken in interpreting results from Hubbard Lake. Detailed in Yohn et al (2002), it is suspected that the Hubbard Lake (Figure 14) core was collected from an erosional zone. Notably, sediment mercury concentrations appear to be elevated and are increasing towards the surface. This can be important for bottom dwelling organisms.

Houghton Lake

Houghton Lake (Figure 15) sediment mercury concentrations generally increase above background levels during the first half of the nineteenth century peaking in the late 1940s, excluding episodic events, and remain relatively constant until the present. Houghton Lake has also experienced several episodes of increased concentration especially in the lower portion of the core relating to the mid 1700s. Other episodes include the 1860s and mid 1990s. The concentrations of mercury observed in Houghton Lake are the highest in this study.

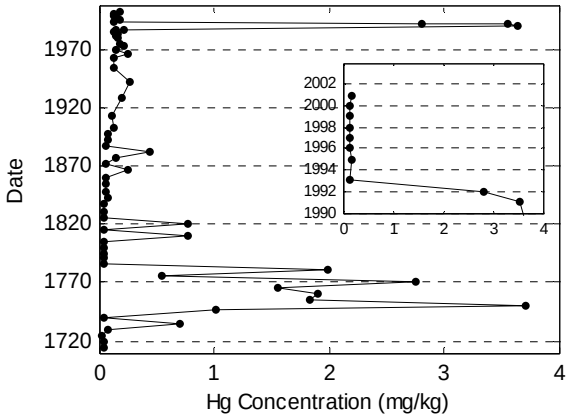


Figure 15. Houghton Lake sediment mercury concentration.

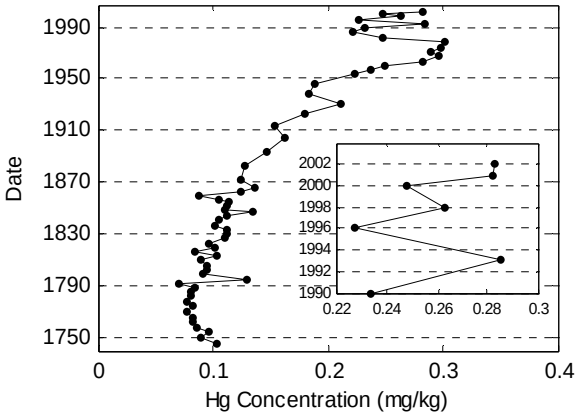


Figure 16. Imp Lake sediment mercury concentration.

Imp Lake

Sediment mercury concentrations in Imp Lake (Figure 16) begin to increase above background values starting in the late 1700s peaking in the mid 1970s then decline to the mid 1980s. Episodic increases in concentration are observed in the early 1860s and 1990s. Mercury concentrations are increasing to the surface in Imp Lake.

Round Lake

Round Lake sediment mercury concentrations (Figure 17) do not appear to reach background values. Generally, mercury concentrations rise after the 1940s peaking in the mid 1990s and decline sharply until the late 1990s only to rise again. Episodic increases in concentration are observed in the late 1800s, late 1930s and late 1990s.

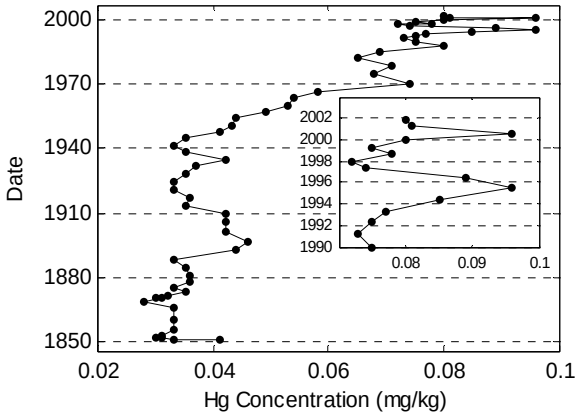


Figure 17. Round Lake sediment mercury concentration.

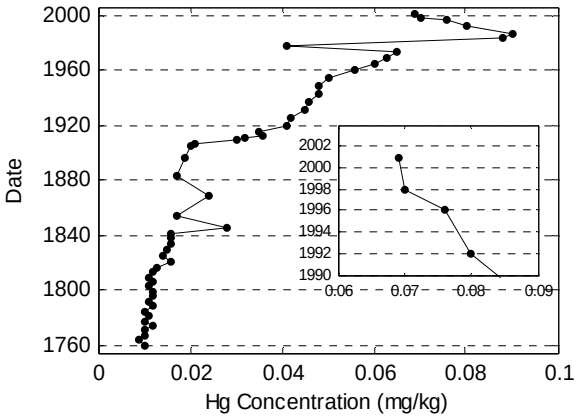


Figure 18. Torch Lake sediment mercury concentration.

Torch Lake

Sediment mercury concentrations in Torch Lake (Figure 18) gently rise above background values starting in the late 1700s until the late 1800s. The rate of increase changes sharply after the early 1900s. Mercury concentrations peak in the late 1980s and decline to the present.

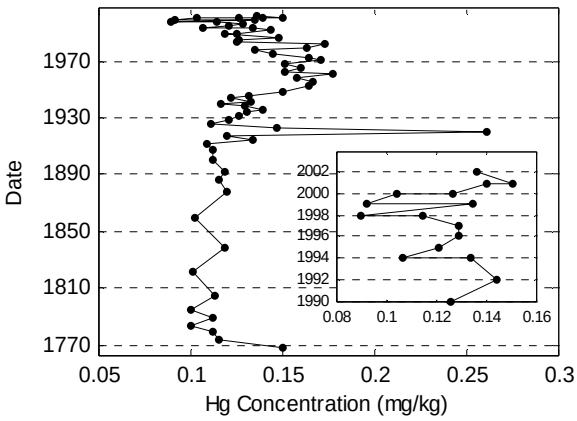


Figure 19. Witch Lake sediment mercury concentration.

Witch Lake

It is unclear whether background mercury concentrations are achieved in Witch Lake sediments (Figure 19). In general, concentrations rise slightly from the late 1700s to the early 1900s. Then a sharp increase in the rate of concentration change is observed after 1930. Excluding the episode in 1920, mercury concentrations peak in the late 1950s followed by a decrease until the late 1990s. Mercury concentrations then increase to the surface.

Avalon Lake

Sediment mercury concentrations generally rise from the late 1700s peaking in the early 1970s in Avalon Lake (Figure 20). Since the early 1970s mercury concentrations have remained relatively constant. An episodic increase in concentration is observed in the 1920s. It is unclear whether background concentrations are achieved in the Avalon Lake core.

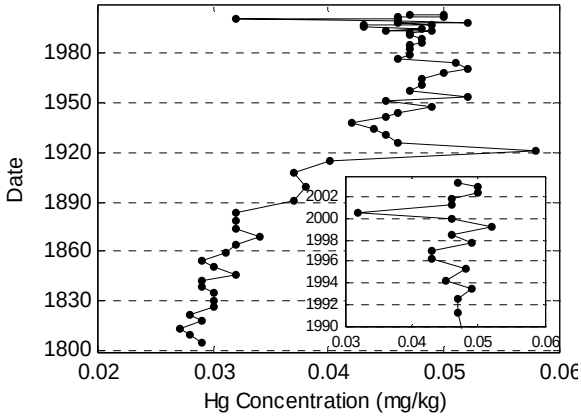


Figure 20. Avalon Lake sediment mercury concentration.

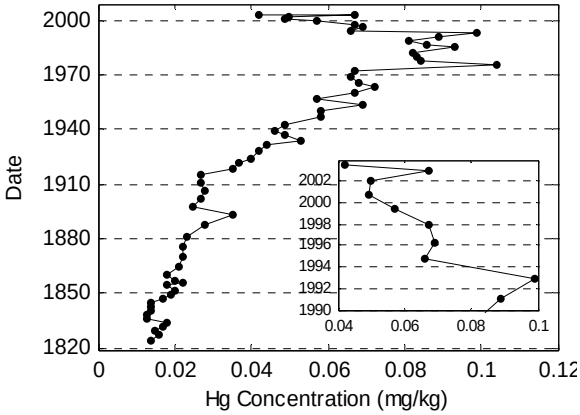


Figure 21. Birch Lake sediment mercury concentration.

Birch Lake

Birch Lake sediment mercury concentrations (Figure 21) gently rise above background values during the mid 1800s. The rate of concentration increase changes sharply after the early 1900s leading to a peak in concentration (excluding episodic events) in the late 1970s. Mercury concentrations then decline to the present. Episodic increases in concentration are observed in the late 1890s, the mid 1970s and early 1990s.

Muskegon Lake

Muskegon Lake sediment mercury concentrations (Figure 22) do not reach background values, however they appear to peak in the late 1950s. This is followed by a curvilinear decrease to the present. Due to the high concentration of mercury in Muskegon Lake it is difficult to determine if episodic increases in mercury concentration occur. Possible evidence of episodic increases are found in the late 1960s and early 1990s.

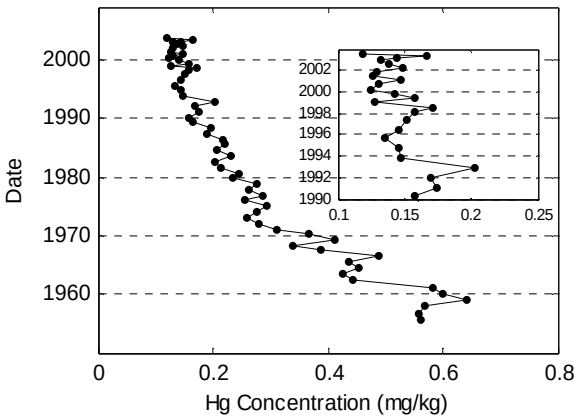


Figure 22. Muskegon Lake sediment mercury concentration.

Sand Lake

Sediment mercury concentrations in Sand Lake (Figure 23) rise above background concentrations in the late 1800s. Peak concentrations (excluding episodic increases) occurred during the early to mid 1990s and appear to be declining to the present. A disturbance in the core is evident at 1880-1900. This disturbance is also evident in other anthropogenic elements such as lead (Parsons *et al.*, 2004). Episodic increases of mercury are observed in the early 1990s and 2000s.

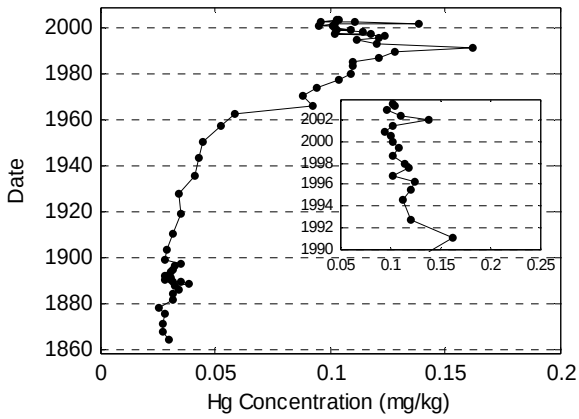


Figure 23. Sand Lake sediment mercury concentration.

Shupac Lake

Shupac Lake sediment mercury concentrations (Figure 24) rise above background values after the mid 1800s peaking in the early 1980s. Concentrations then decline followed by two sharp episodic increases in the 1990s. Episodic increases are also evident in the early 1930s and mid 1950s.

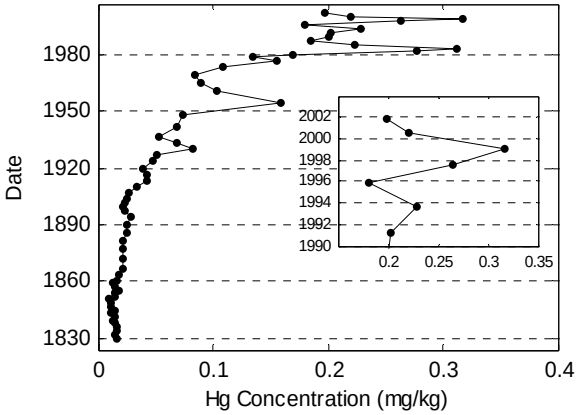


Figure 24. Shupac Lake sediment mercury concentration.

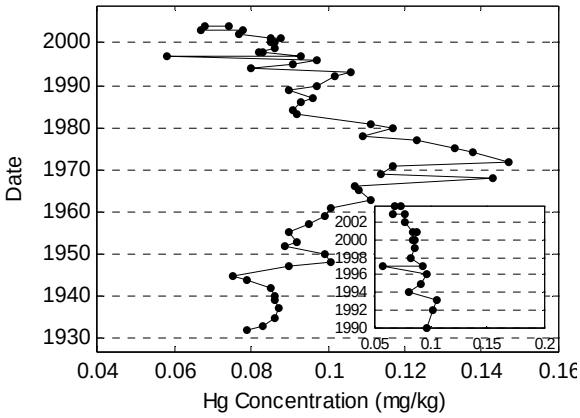


Figure 25. George Lake sediment mercury concentration.

George Lake

Sediment mercury concentrations in George Lake do not reach background values (Figure 25). In general, concentrations rise from the early 1900s peaking in the early 1970s and decline to the present. Episodic increases in concentration are evident during the late 1940s and late 1960s.

Hackert Lake

Preindustrial Hackert Lake sediment mercury concentrations (Figure 26) are not at background levels indicating there may have been some disturbance leading to increased mercury loading to Hackert Lake. It does appear that background concentrations are achieved in the early 1930s followed by an increase in sediment concentration peaking in the late 1980s. Mercury concentrations then decrease to the present.

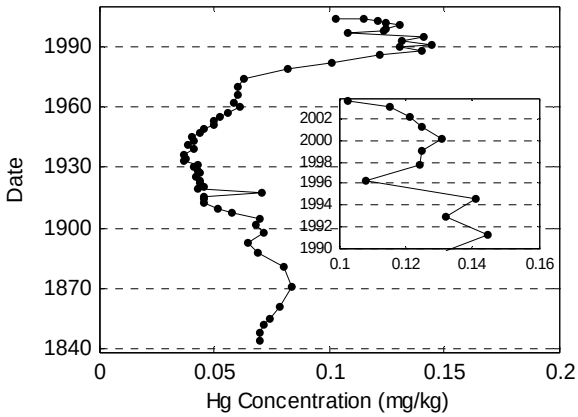


Figure 26. Hackert Lake sediment mercury concetration.

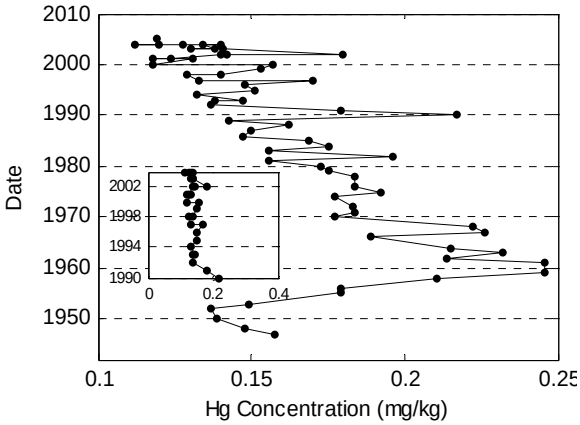


Figure 27. Otter Lake sediment mercury concentration.

Otter Lake

Otter Lake sediment mercury concentrations (Figure 27) appear to peak in the early 1960s and decline to the present. Episodic increases in mercury concentration are evident in the late 1980s, late 1990s, and early 2000s. Due to the high rate of sedimentation in Otter Lake background concentrations of mercury are not observed.

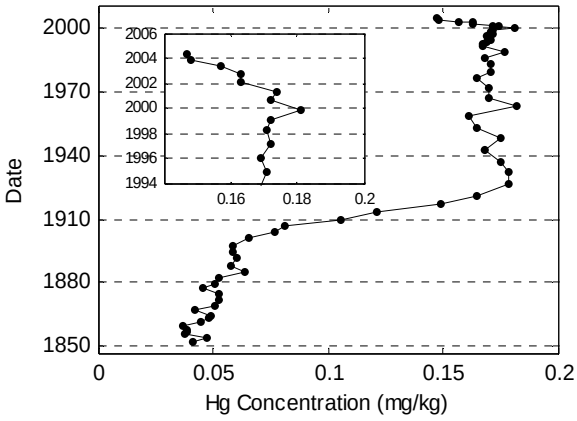


Figure 28. Round (Delta County) Lake sediment mercury concentration.

Round Lake (Delta County)

Sediment mercury in Round (Delta) Lake (Figure 28) concentrations rise from the lowest portion of the core, with a change in trajectory (rate of concentration increase) occurring in the late 1800s, suggesting a change in source, until the early 1930s. After 1930 mercury concentrations stay relatively unchanged until the early 1990s, where they rise slightly and then decrease until the present.

Focusing Corrected Anthropogenic Accumulation Rates

Total concentrations of metals in sediments provide insight into exposure and possible ecosystem and human health issues. However, concentration profiles do not necessarily provide insights into the process(es) of metal accumulation in lakes and are difficult to compare among lakes. Therefore, in addition to the interpretation of the total concentration profiles, focusing corrected anthropogenic accumulation rates were calculated and compared among lakes. These calculations subtract the background or natural inputs of mercury and take into account the process of sediment focusing, and thus provide the best estimate of the actual rate of input of that element to the lake due to human actions. These rates can be compared among lakes. For example, if the major input of anthropogenic mercury to a set of closely spaced lakes is from the atmosphere, one would expect these calculated accumulation rates to be the same. On the other hand if rates are different, then more local or individual watershed scales influences for mercury accumulations might need to be explored. These rate calculations are described further in the 2001-2002 year end report (Yohn *et al.*, 2002b). Hubbard Lake was not included in this analysis.

Sample Year 1999 (Cass, Elk, Gratiot, Gull, and Higgins lakes)

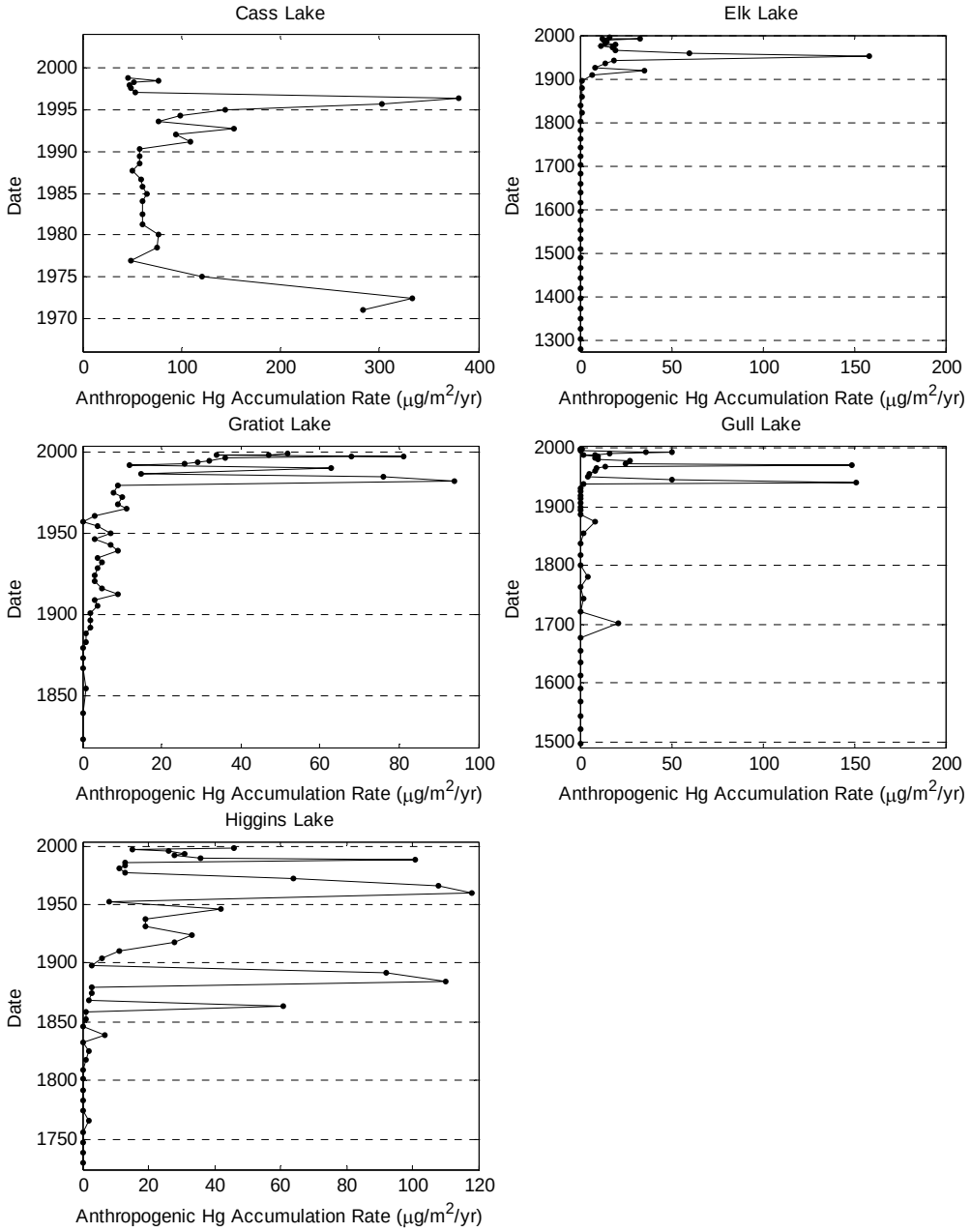


Figure 29. ^{210}Pb-Dated focusing corrected anthropogenic accumulation rate for 1999 study lakes. Cass Lake focusing corrected accumulation rate was estimated.

Some inland lakes sampled during this study experience high sedimentation rates due to their geologic setting and influence from human activities. Due to the high sedimentation rate and relative short length of the sampling cores background concentrations of mercury could not be reached. Therefore, background accumulation rates were estimated for these lakes using a step-wise multivariate linear regression model. Focusing corrected background mercury accumulation rates, from lakes that provided adequate estimations, were regressed against STATSGO (USDA) soil properties of the surficial soils in the watershed to estimate focusing corrected pre-industrial accumulation rates (FCPIACC). Variables from the STATSGO database entered into the model include: percent organic matter, cation exchange capacity, percent clay, K-factor, slope corrected K-factor, watershed area, lake area, and watershed:lake area ratio. Only percent organic carbon (%Org), lake area (LA), and watershed area (WA) entered into the final FCPIAAC model with high tolerance (>0.800) and at $p<0.150$ two-tailed t-test significance.

$$FCPIACC = 5.490 + 0.243\%Org - 0.082LA + 0.004WA$$

$$Adjusted\ R^2 : 0.526$$

The results for the 1999 study lakes (Figure 29) indicate that focusing corrected anthropogenic accumulation rates vary among lakes and that there are numerous episodic events when accumulation rates increased for a relatively short time period. Maximum accumulation rates, including those contained in episodic events, range from 379 $\mu g/m^2/yr$ in Cass Lake to 94 $\mu g/m^2/yr$ in Gratiot Lake. Current accumulation rates, based on the top sample, are greatest in Gratiot Lake (52 $\mu g/m^2/yr$) followed by Higgins Lake (46 $\mu g/m^2/yr$), Cass Lake (45 $\mu g/m^2/yr$) , Elk Lake (16 $\mu g/m^2/yr$) and Gull Lake (0 $\mu g/m^2/yr$). The background focusing corrected accumulation rate for Cass Lake was estimated using a multivariate regression model.

Anthropogenic mercury generally begins to accumulate in 1999 study lakes during the later half of the nineteenth century, concurrent with industrialization. Gull and Elk lakes have the latest onset of mercury accumulation, 1920s and 1890s respectively. Gratiot Lake records onset of anthropogenic loading during the early 1880s whereas Higgins Lake shows the earliest onset, 1850s.

Current loading trends, estimated in this study as the ten years prior to sampling, indicate that <u>only</u> Gull Lake may be returning to “background” values. Loadings to Elk Lake are elevated above background but have been relatively constant over the last two decades. Accumulation rates in Gratiot Lake are increasing to the present and have experienced a source or loading rate change in the early 1990s (identified as the change in trajectory of the accumulation rate profile). Cass Lake anthropogenic accumulation rates are decreasing to the present. It is unclear from the data whether current loadings are increasing or decreasing in Higgins Lake.

Time to peak accumulation rates, identified here as the inflection of the accumulation rate profile from increasing to decreasing, also varies among lakes. Gull Lake and Elk Lake peak in the early 1970s and early 1950s respectively (excluding the

episodic events). The data are unclear as to whether peak mercury accumulation rates are observed in Gratiot, Cass, and Higgins lakes.

Sample Year 2000 (Crystal (Montcalm County) and Littlefield lakes)

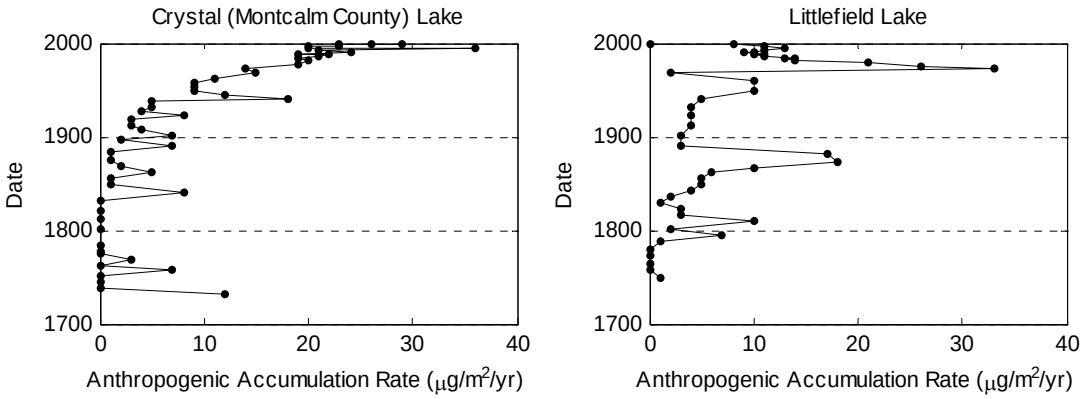


Figure 30. ^{210}Pb-Dated focusing corrected anthropogenic accumulation rate for 2000 study lakes.

Results from the 2000 (Figure 30) lakes are similar to those observed in the 1999 sampling year. Episodic accumulation events are present in both Crystal and Littlefield lakes. Maximum focusing corrected anthropogenic accumulation rates vary from 33-36 $\mu g/m^2/yr$. Current accumulation rates suggest that Littlefield Lake may have recovered from anthropogenic activity. Crystal Lake's current accumulation rates (26 $\mu g/m^2/yr$) are near those of historical peak values, indicating little to no recovery. A change in trajectory during the 1940s in Crystal Lake indicates a source change or loading rate increase to the lake. Peak mercury loading to Littlefield Lake occurred in the 1970s.

Crystal and Littlefield lakes are both located within the central portion of the state of Michigan (Fig. 1) and should hypothetically be affected by the same regional source of mercury, both currently and historically. However, Littlefield Lake, prior to the 1800s, shows the earliest anthropogenic mercury onset of all 26 study lakes. Crystal Lake begins to accumulate anthropogenic mercury in the early mid 1800s, similar to the 1999 study lakes. The variability in the anthropogenic mercury profiles may suggest presence of local anthropogenic sources of mercury to Littlefield Lake

Sampling Year 2001 (Cadillac, Crystal (Benzie County), Mullett, Paw Paw, and Whitmore lakes)

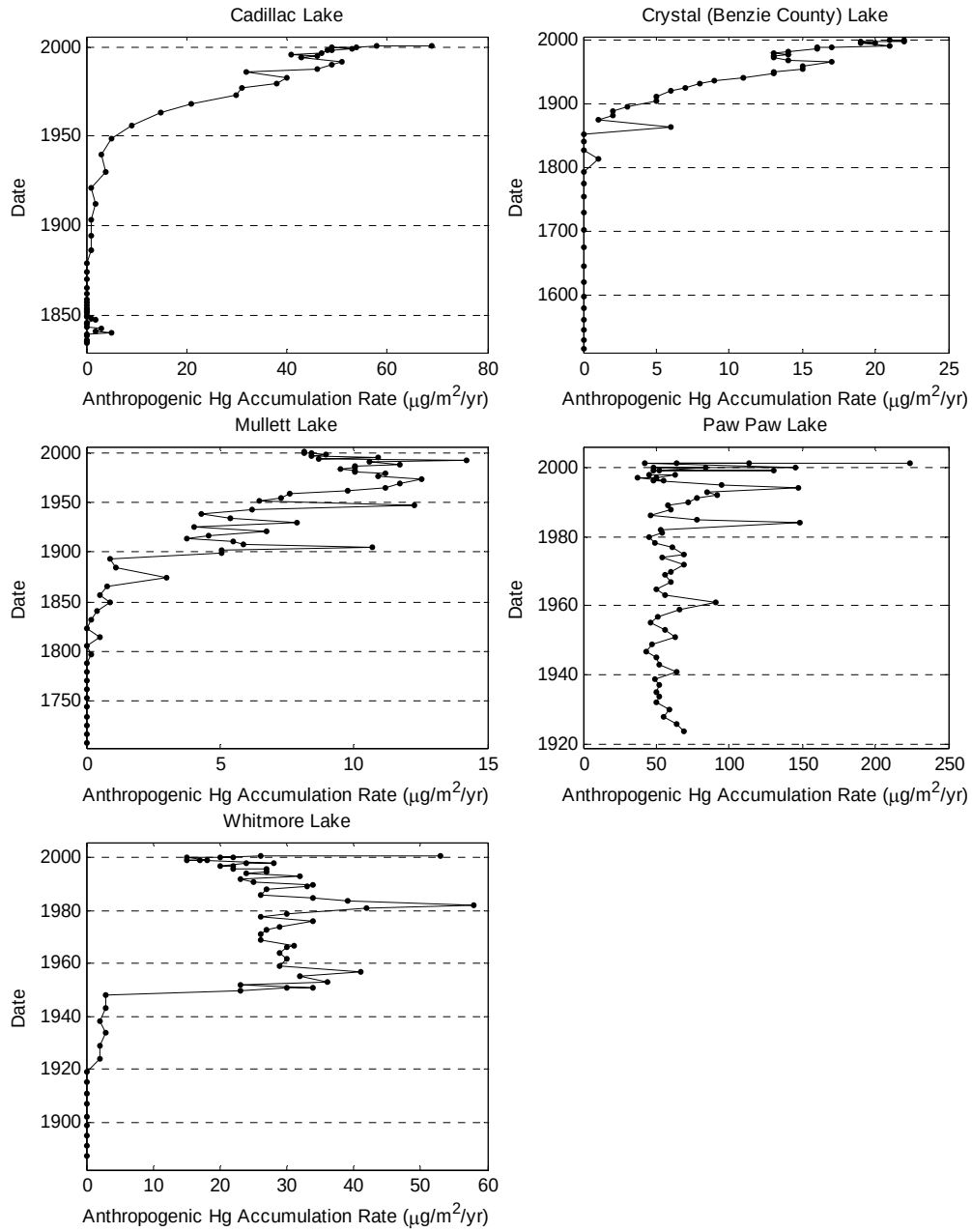


Figure 31. ^{210}Pb-Dated focusing corrected anthropogenic accumulation rate for 2001 study lakes. Paw Paw and Whitmore lakes focusing corrected background accumulation rates were estimated.

Maximum focusing corrected anthropogenic accumulation rates for the 2001 sampling year (Figure 31) range from 14 μg/m2/yr (Mullett Lake) to 224 μg/m2/yr (Paw Paw Lake). Frequent episodic accumulation events are recorded in Whitmore, Paw Paw and Mullett lakes, but less so in Crystal and Cadillac lakes. Current accumulation rates were highest in Paw Paw Lake (224 μg/m2/yr) followed by Cadillac (69 μg/m2/yr), Whitmore (53 μg/m2/yr), Crystal (22 μg/m2/yr) and Mullett (8.1 μg/m2/yr). Background focusing corrected accumulation rates were estimated for Paw Paw and Whitmore Lakes. Whitmore Lake showed the latest anthropogenic mercury onset (early 1900s) while Mullett, Cadillac, and Crystal were similar to previous sampling years (mid to late 1800s). Both Lake Cadillac and Mullett Lake experience a trajectory change after the 1930s. Whitmore Lake experiences a unique step change in anthropogenic mercury loading to the lake during the 1950s due to a rapid increase in the sedimentation rate. Both lead and zinc experience a similar step change increase during this period (Yohn *et al.*, 2002b) suggesting that the sources and pathway for lead, zinc, and mercury in the 1950s may have been similar.

Regional atmospheric deposition measurements suggest that mercury deposition has decreased in recent years (NADP, 2003). Paw Paw, Crystal, Whitmore and Cadillac lakes show current loading trends that increase to the surface in contrast to regional atmospheric deposition trends. These results suggest undefined sources of mercury contributing to the lakes at an increasing rate and are likely sub-regional to local in scale. Anthropogenic mercury loading in Mullett Lake peaked in the early 1970s (13 $\mu g/m^2/yr$); recent accumulation rates indicate recovery. Anthropogenic accumulation rates in Whitmore Lake decrease from the peak in the mid 1950s to the late 1990s; since 2000 this trend has reversed.

Sampling Year 2002 (Houghton, Imp, Round, Torch, and Witch lakes)

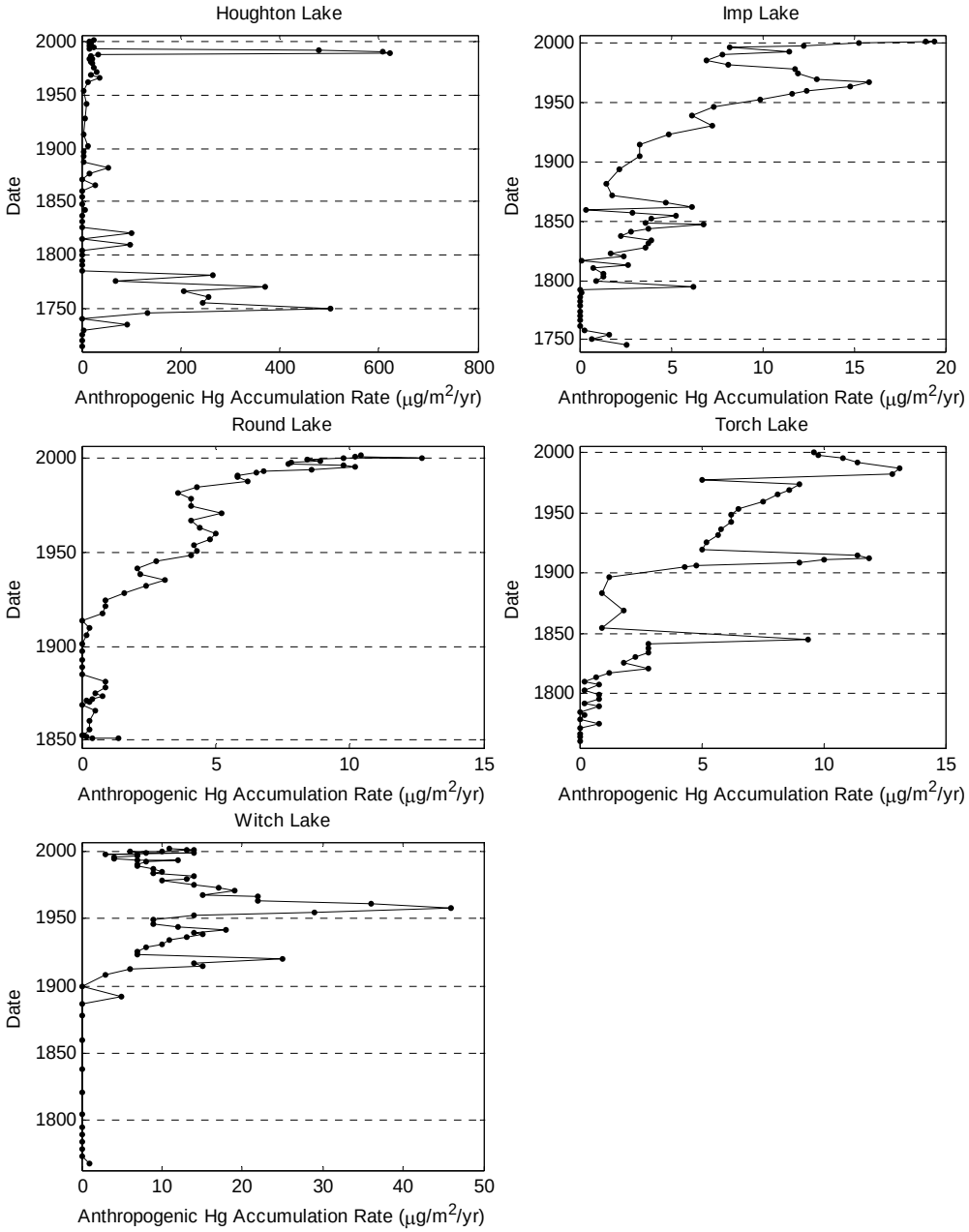


Figure 32. ^{210}Pb-Dated focusing corrected anthropogenic accumulation rate for 2002 study lakes. Witch and Round lakes focusing corrected background accumulation rates were estimated.

Excluding Houghton Lake, anthropogenic accumulation rates found in the 2002 study lakes are similar to those found in previous years. Maximum focusing corrected anthropogenic accumulation rates observed in Houghton Lake are the highest of all 26 study lakes, 623 $\mu g/m^2/yr$ in the late 1980s (Figure 32). Accumulation rates in Cass Lake are the next highest at 379 $\mu g/m^2/yr$. Maximum anthropogenic accumulation rates, excluding episodic events, range from 46 $\mu g/m^2/yr$ in Witch Lake to 11 $\mu g/m^2/yr$ in Round Lake. Houghton Lake currently has the highest anthropogenic accumulation rate at 25 $\mu g/m^2/yr$ followed by Imp Lake (19 $\mu g/m^2/yr$), Witch Lake (11 $\mu g/m^2/yr$), Round Lake (10 $\mu g/m^2/yr$), and Torch (9.6 $\mu g/m^2/yr$). Witch and Round lakes background focusing corrected accumulation rates were estimated.

Houghton Lake's profile records a high loading of mercury during the eighteenth century that is not recorded in any other study lake. The absence of such loadings in Higgins Lake (Figure 30) indicates a source for mercury that is unique to Houghton Lake and its watershed. Forest fires have been shown to be sources for mercury to aquatic systems, however no record of early forest fire activity in the watershed exists (Stearns, 1997, Yohn *et al.*, 2003) and there is no reported population in the watershed until the late 1800s (Roscommon, 2003). Excluding the considerable loadings in the 1700s and late 1980s, Houghton Lake loading rates are similar to other study lakes.

Witch, Round, and Houghton (excluding the events in Houghton Lake during the early 1700s) lakes all begin to show evidence of anthropogenic mercury accumulation during the late 1800s or early 1900s. Anthropogenic mercury accumulation in Imp and Torch lakes begins much earlier, late 1780s and early 1810s, respectively.

Years for peak mercury accumulation rates for the 2002 study lakes were similar to those of the previous study years. Peak rates, excluding episodic events, occur in Houghton Lake during the early 1970s; the recovery status of Houghton Lake is unclear. Loadings in Witch Lake peak in the late 1950s whereas Torch Lake peaks more recently, late 1990s. Since the late 1990s Witch Lake accumulation rates have increased but remain below historic peak levels. Imp Lake mercury accumulation rates reach a peak during the late 1960s and decreased until the mid 1980s; since 1986 Imp Lake accumulation rate have increased and have reached a maximum loading rate in recent years. Since the 1980s anthropogenic accumulation rates in Round Lake have increased. The similarity of the onset of recent increasing trends and their close proximity suggest that Imp and Round lakes share a common source of mercury.

Sampling Year 2003 (Avalon, Birch, Muskegon, Sand, and Shupac lakes)

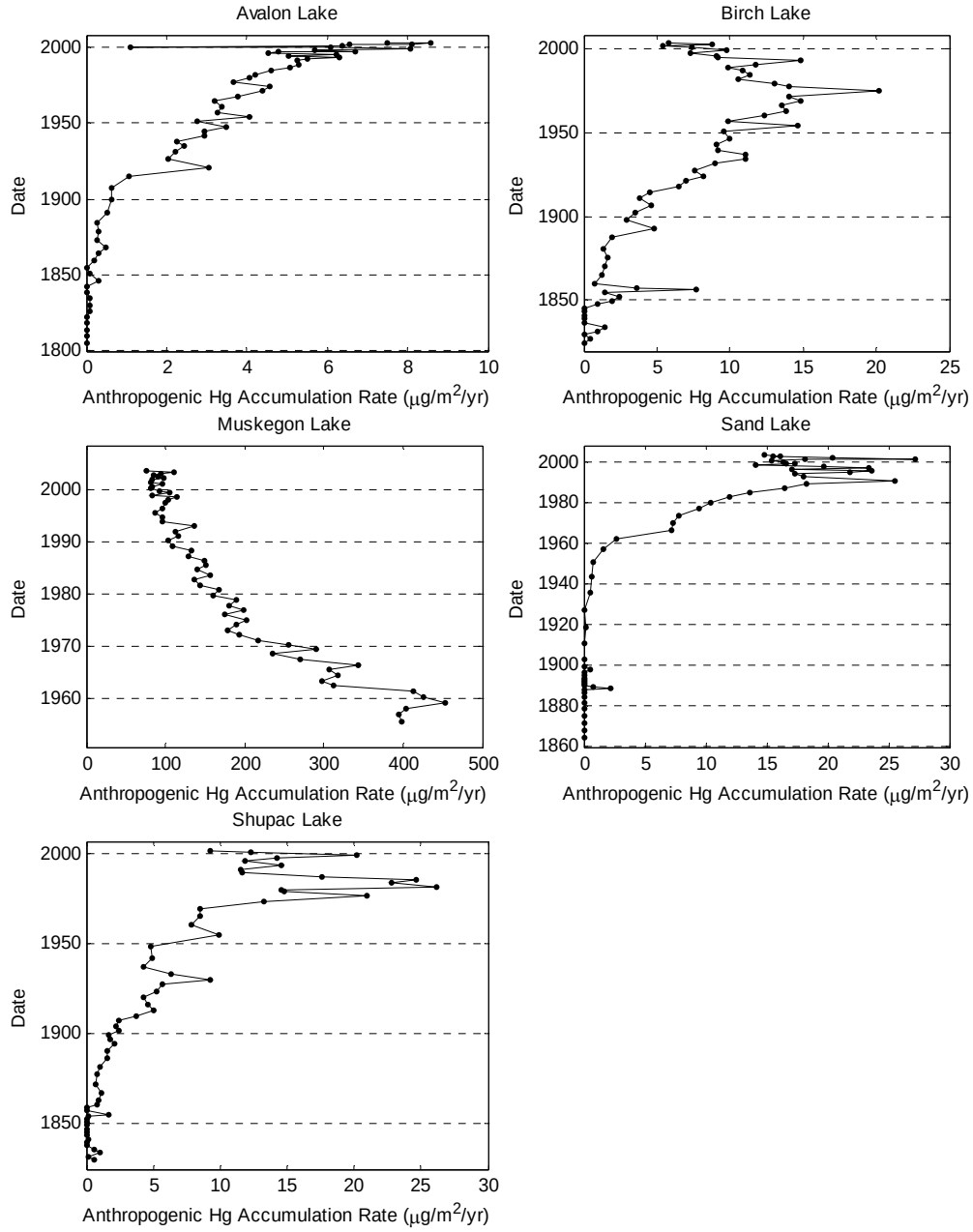


Figure 33. ^{210}Pb-Dated focusing corrected anthropogenic Hg accumulation rate for 2003 study lakes. Muskegon Lake's focusing corrected background accumulation rate was estimated.

Results for the 2003 study lakes are shown in Figure 33. Muskegon Lake had high (460 $\mu g/m^2/yr$) anthropogenic accumulation rates during the late 1950s. Excluding Muskegon Lake accumulation rates vary from 27 $\mu g/m^2/yr$ in Shupac Lake to 8.6 $\mu g/m^2/yr$ in Avalon Lake. Current accumulation rates are highest in Muskegon Lake (82 $\mu g/m^2/yr$) followed by Sand Lake (14.8 $\mu g/m^2/yr$), Shupac Lake (9.3 $\mu g/m^2/yr$), Avalon Lake (7.5 $\mu g/m^2/yr$), and Birch Lake (5.8 $\mu g/m^2/yr$). Loadings of mercury to Muskegon Lake are currently very high; only Paw Paw Lake demonstrated a higher anthropogenic accumulation rate in the surface sample. The background accumulation rate for Muskegon and Sand lakes were estimated.

Onset of anthropogenic mercury in 2003 study lakes is similar to previous study lakes, but a notable exception would be Sand Lake. Mercury accumulation in Sand Lake did not begin until the early 1900s, similar to Whitmore Lake (Figure 31). Whitmore and Sand Lake are similar in their proximity to the large urban center, Detroit. These observations may be an artifact of difficulties in ^{210}Pb dating due to core disturbances (Parsons *et al.*, 2004, Yohn *et al.*, 2002b). Avalon, Birch and Shupac lakes show first signs of anthropogenic mercury during the middle of the 1800s. It was not possible to determine the onset of anthropogenic mercury in Muskegon Lake.

Peak values of anthropogenic mercury accumulation vary among the 2003 study lakes. Birch Lake showed the earliest peak in the early 1970s. Shupac followed in the early 1980s whereas Sand Lake appears to peak in the early 1990s. Peak accumulation rates could not be determined for Muskegon Lake. Avalon Lake anthropogenic mercury accumulation rates do not peak historically and are increasing towards the surface, indicating an active source of mercury to the lake. Recent trends in Birch, Muskegon and Sand lakes suggest recovery; the status of Shupac Lake's recovery is unclear. However, because mercury accumulation rates in Muskegon Lake are so large, patterns of mercury accumulation as observed in others lakes, are not observed here.

Sampling Year 2004 (George, Hackert, Otter, and Round (Delta County) lakes)

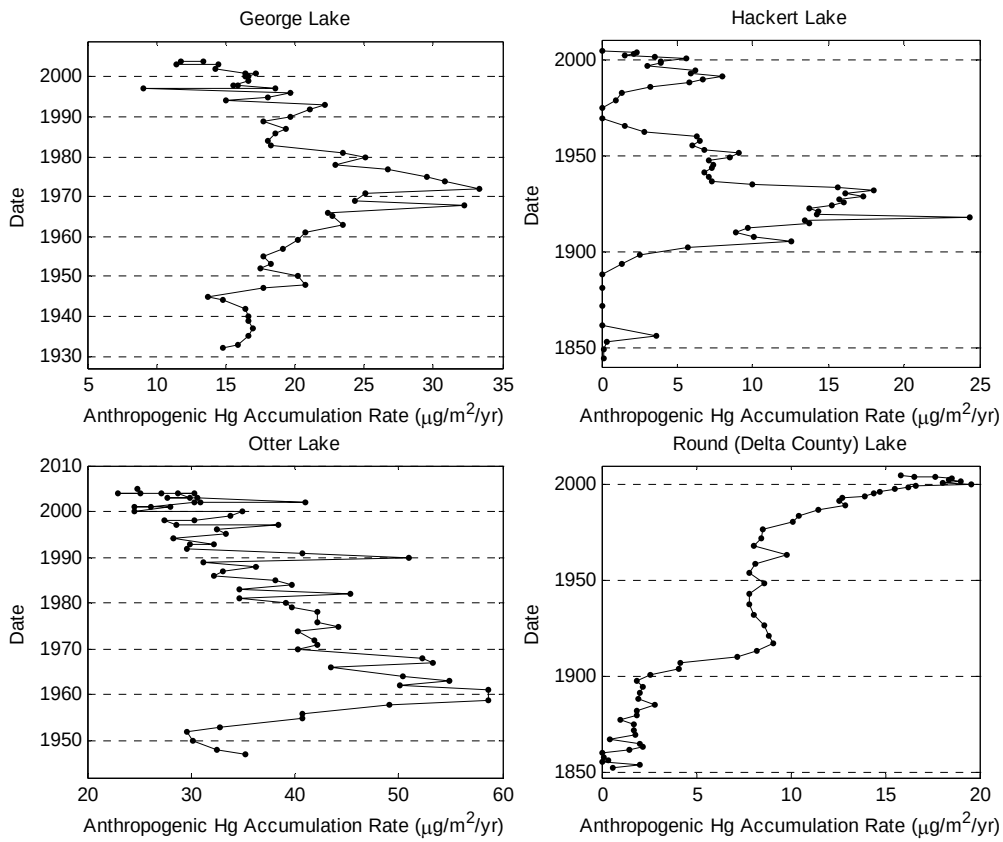


Figure 34. ^{210}Pb-Dated focusing corrected anthropogenic accumulation rate for 2004 study lakes. Otter, George, and Hackert lakes focusing corrected background accumulation rates were estimated.

Maximum focusing corrected anthropogenic accumulation rates for the sampling year 2004 (Figure 34) range from 59 μg/m^2/yr in Otter Lake and 24 μg/m^2/yr in Hackert Lake, similar to previous study lakes. Anthropogenic mercury accumulation rates in the top sediment fraction are highest in Otter Lake (25 μg/m^2/yr) followed by Round Lake (16 μg/m^2/yr), George Lake (13 μg/m^2/yr), and Hackert Lake (2.3 μg/m^2/yr). Background focusing corrected accumulation rates were estimated using a multivariate regression model for George, Otter and Hackert lakes.

Peak anthropogenic mercury loading period varies among lakes in 2004. Round Lake shows the latest peak, 2000 (20 μg/m^2/yr), whereas Hackert Lake shows the earliest, early 1930s (18 μg/m^2/yr). George and Otter lakes peak in the early 1970s (33 μg/m^2/yr) and early 1960s (59 μg/m^2/yr) respectively. Onset of anthropogenic mercury in the 2004 lakes is typical of Michigan's inland lakes, occurring during the mid to late 19th century.

Several notable characteristics are evident in the 2004 lakes. Round Lake experiences an abrupt change in slope occurring during the mid 1970s. Hackert Lake has undergone a brief period of recovery during the early 1970s followed by increase during the late 1980s; more recently the lake has shown signs of recovery. None of the 2004 study lakes show recent trends that increase to the surface, although recent episodic events are apparent in George, Otter, and Hackert lakes.

Spatial Trends

Due to its geochemical cycle, elemental mercury can remain in the atmosphere for up to a year (Fitzgerald *et al.*, 1998). The result is that mercury deposition can occur at great distances from its anthropogenic and natural sources, raising new concerns. For example, mercury deposition in the U.S. as a result of long range transport from Southeast Asia has become of growing research interest (Seigneur *et al.*, 2004). However, in addition to long range transport, local sources (i.e., those at the watershed scale) may also be contributing to deposition of mercury. Therefore, to better understand the sources, pathways, and fate of mercury in Michigan's inland lakes, more knowledge on the relative influences of global, regional and watershed scale sources for mercury is needed. In this report we use spatial investigations of mercury inventories and accumulation rates to examine regional vs. local sources of contaminants to inland lakes.

Anthropogenic inventories are the long term accounting of contaminant loadings in a system (e.g., lake). In other words they reflect the total mass of chemicals in the system due to additions from human activities. Spatial comparisons of inventories among lakes can be used to reveal dominant source areas. For example, comparing anthropogenic inventories along a south to north transect in Michigan, may show trends that indicate mercury sources from the highly industrial areas of Gary, Indiana and Detroit, Michigan. If Gary and Detroit are acting as regional source areas, inventories should be higher in the southern half of the Lower Peninsula and decrease farther away from the source area; similar to what is found for lead in Michigan's inland lakes (Yohn, 2003). Similarly, the trends may identify other source areas of mercury to inland lakes.

Anthropogenic accumulation rates investigated on a spatial scale can also lend insight into regional source areas. Anthropogenic accumulation rates, if influenced by a regional source, should decrease with increasing distance away from the source area or demonstrate similar rates among lakes if influenced by a regional source. Anthropogenic accumulation rates that are similar among lakes suggest that 1) a regional source is present to all lakes or 2) watershed processes are occurring at similar rates. A regional source was identified for lead to Michigan's inland lakes due to leaded gasoline (Yohn *et al.*, 2002a). Although we have found our ^{210}Pb age dating of the sediments to be of high quality, comparing the accumulation rates among lakes for a specific year is not appropriate. Sediment cores are sectioned at equal 0.5 or 1.0 cm intervals for each lake in the study. However, due to the variability of sedimentation rates among lakes the range of sediment ages contained in a particular section may also vary. In this report we compare anthropogenic accumulation rates averaged over a ten year period to address this problem. We use the term "average decadal anthropogenic accumulation rates" (adaar) to describe these rates.

Focusing corrected anthropogenic inventories

Focusing corrected anthropogenic mercury inventories for Michigan's inland lakes are highly variable, ranging from 0.04 μg/cm^2 in Avalon Lake to 1.60 μg/cm^2 in Houghton Lake (Figure 35); lakes that did not reach background concentrations of mercury were not included in this comparison. In general, inventories are higher in the southern Lower Peninsula and lower in the Upper Peninsula. Spatial trends do not indicate that highly industrialized regions are acting as a source area for anthropogenic

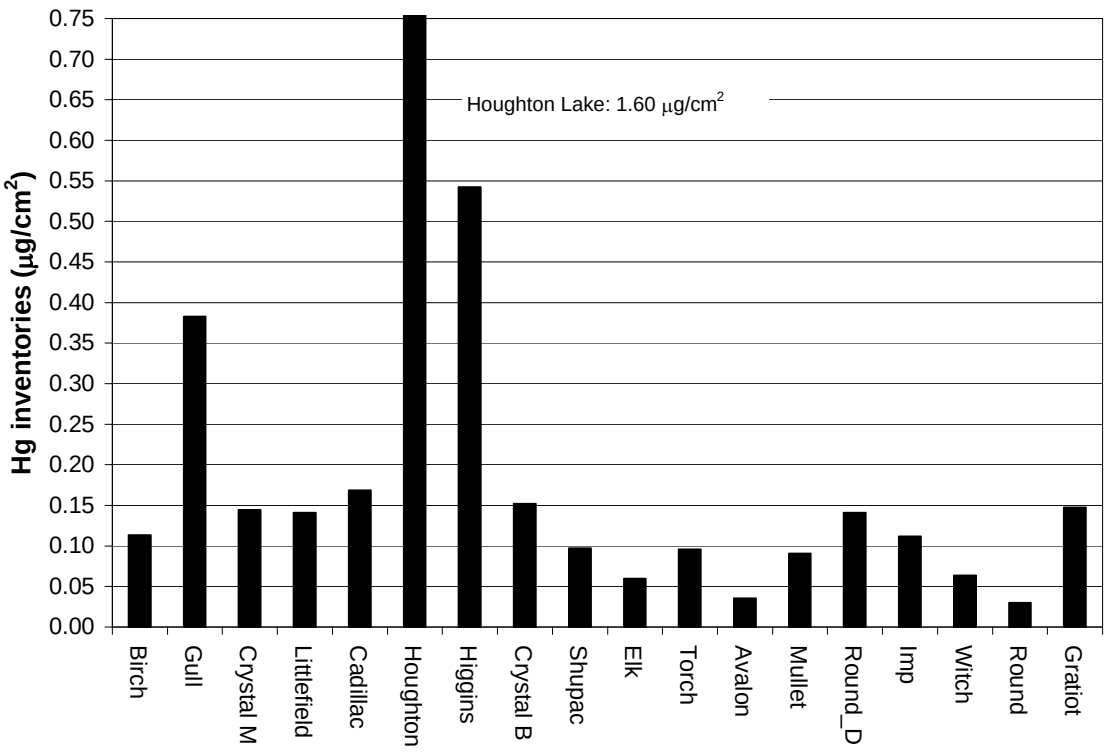


Figure 35. Focusing corrected anthropogenic mercury inventories for 1999-2004 study lakes. Lakes are plotted from South (Birch Lake) to North (Gratiot Lake).

mercury although background values in Metro Detroit area lakes were not reached and thus anthropogenic inventories could not be calculated; more lakes and deeper cores in this region would assist the analysis of this potential source area. The variability in these inventories among lakes suggests that local sources play a significant role in mercury accumulation in Michigan's inland lakes.

Focusing corrected anthropogenic accumulation rates

Figure 36 summarizes the spatial trends of mercury adaar for the lakes sampled from 1999 to 2004 . For the decade reported, the years represent five years preceding and five years post the reported period. For example, the decade 1990 represents the average anthropogenic accumulation rate for the years 1985-1995. As noted above several lakes did not reach background concentrations of mercury and their focusing corrected

anthropogenic accumulation rates were estimated using a multivariate regression model described above. Hubbard Lake was removed from the analysis due to difficulties in ^{210}Pb dating (see Yohn et al., 2003).

Key observations of adaar analysis include:

1870: A regional source appears to be present in this period consistent with limited industrialization in Michigan; Houghton and Littlefield lakes are slightly elevated above the remaining lakes.

1880-1890: The majority of study lakes are responding to a regional signal although Houghton, Littlefield and Higgins lakes are higher than other lakes in the study area suggesting a sub-regional source.

1900: All lakes are responding similarly, suggesting the source of mercury present to Houghton, Littlefield, and Higgins lakes during the 1880s and 1890s was relatively short; this may have been a result of logging in the area.

1910: Higgins and Hackert lakes are higher than other study lakes, but in general lakes respond to a regional source.

1920: Adaar of several lakes are high and no spatial pattern is apparent.

1930: Lakes that were high in the 1920s are not necessarily high in the 1930s (e.g., Elk Lake) suggesting reduction of a source unique to the lake during the 1920s.

1940: Mercury is loading to lakes in sub-regions of Michigan at similar rates. Sub-regional areas include 1) Higgins, Houghton, and George lakes, 2) Paw Paw and Gull lakes, 3) Crystal (Benzie) and Elk lakes.

1950: Whitmore and Otter lakes are reflecting the importance of the Detroit area and support a hypothesis of sub-regional sources of mercury to Michigan's lakes. Paw Paw, Gull, and Birch lakes adaar are also elevated.

1960-1990: Variation in the response of lakes to mercury loadings over this forty-year period, the absence of a spatial pattern, and the observation that mercury loadings have not decreased in recent decades suggest the significance of watershed scale sources of mercury. In general lakes near industrial and population centers (e.g., Cass, Muskegon, Paw Paw) are higher than those in more rural settings (e.g., Upper Peninsula Lakes). Sub-regions of interest include Southeast and Southwest Michigan as well as Roscommon (Higgins and Houghton).

The variability in response to mercury loading over time and space and the lack of a strong regional signal contrast with what was found for lead in these study lakes (Simpson *et al.*, 2000, Yohn *et al.*, 2001, Yohn *et al.*, 2003) where a regional source was identified. This implies, compared to lead, that local watershed scale sources play a more significant role in the loading of mercury to Michigan's inland. Response of lakes to population and industrial areas is consistent with current atmospheric measurements made by Lynam and Keeler (2005) assuming that higher atmospheric concentrations of mercury results in increased mercury deposition.

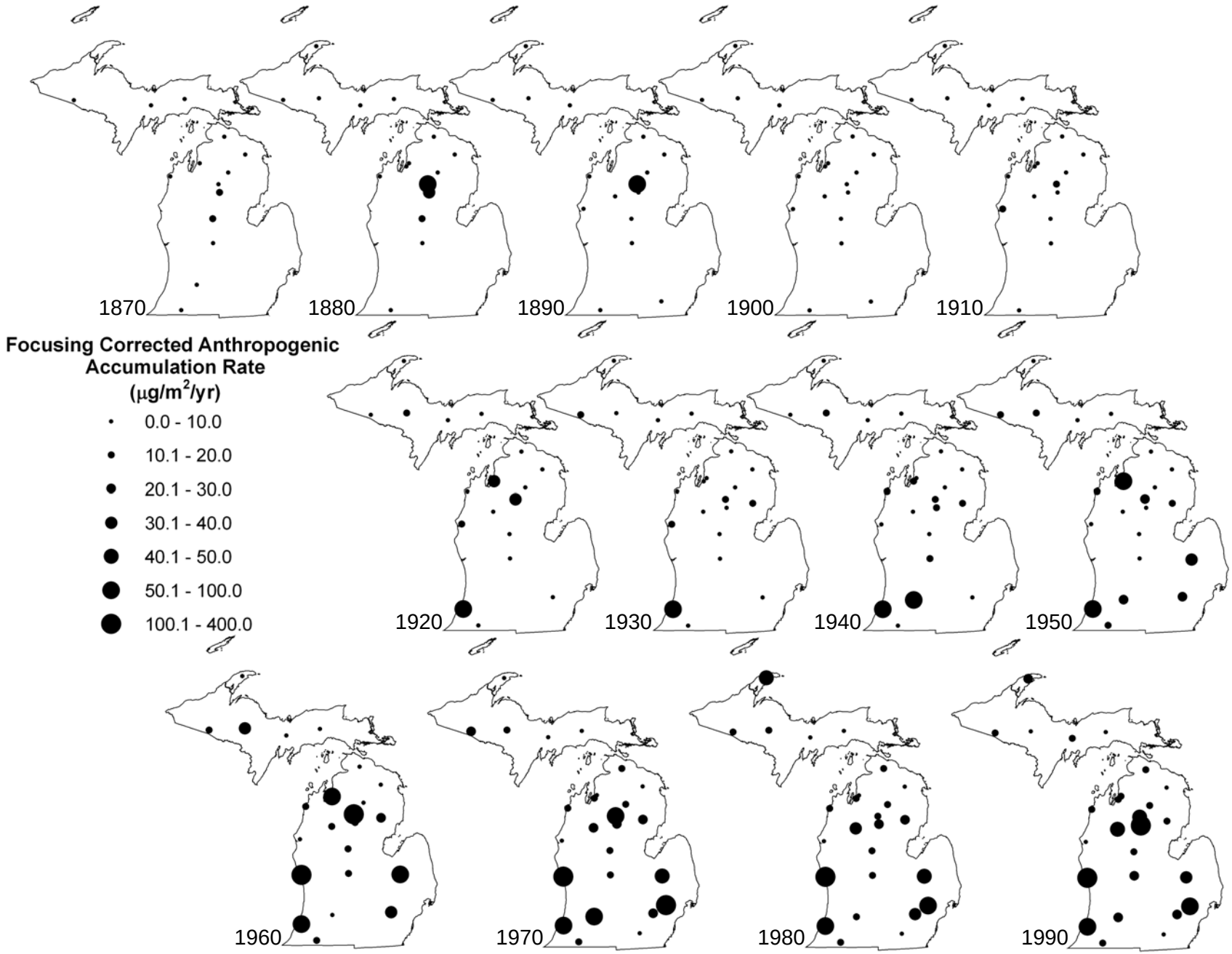


Figure 36. Decadal average focusing corrected anthropogenic mercury accumulation rates in Michigan's inland lakes.

Historic indicators of common influence

Episodic mercury accumulation events recorded in the sediment profiles are often common among lakes, indicating either a regional source or similar processes occurring in many watersheds. These historical indicators of common influences (sources and or activities), in addition to the stable lead profile and ^{137}Cs, are useful to confirm the ages of sediments established using ^{210}Pb dating. However, they may also be used to evaluate the effect of sources of mercury loading to inland lakes of Michigan. Shuster et al. (2002) observed episodic mercury accumulation events in an ice core from a Wyoming glacier and correlated them to both natural processes (e.g., volcanic eruptions) and anthropogenic activities (e.g., California Gold Rush). Sediment cores from lakes in the Midwest, Upstate New York, and New England have also recorded episodic events but their origin was not interpreted (Engstrom and Swain, 1997, Kamman and Engstrom, 2002, Lorey and Driscoll, 1999b).

This analysis compares three episodic events observed in the Wyoming ice core to the sediment record found in Michigan's inland lakes: California Gold Rush (CGR), World War II (WWII), and the 1970s industrialization. These periods reflect important historical mercury consumption periods:

1. Shuster observed a peak deposition rate of 4.84 $\mu g/m^2/yr$, between the years 1850 and 1864, coinciding with the CGR. It is commonly thought that mercury in Michigan and the Midwest did not significantly accumulate in the environment until the late 1800s. If the CGR is the only anthropogenic source of mercury to Michigan lakes a super-regional signal of deposition should be evident in the sediment record (e.g., lakes should respond equally).

2. Industrial activity during the World War II war effort, approximately 1940 until 1945, was known to involve the use of mercury to assemble munitions and batteries ((Jasinski, 1994)). However, anthropogenic loading rates in individual watersheds may differ due to differences in mercury consumption and thus the sediment record should reflect the variability in these activities. Maximum deposition rates observed in Wyoming glacial ice was less than 5 $\mu g/m^2/yr$ (Schuster *et al.*, 2002).

3. Peak consumption of mercury in the United States occurred during the late 1960s (Engstrom and Swain, 1997). However, several Midwestern lake sediment cores and those presented above have recorded maximum mercury loading more recently. Shuster et al. (2002) recorded the maximum deposition rate, 20 $\mu g/m^2/yr$, of mercury in Wyoming glacial ice in 1984 and attributed it to an industrial maximum.

Figure 37 shows the results of these episodic accumulation events for three of the time periods observed in the Shuster et al. (2002) glacial ice core: California gold rush (1850-1878), World War II (1938-1946) and the 1970s industrialization. All lakes,

except Hubbard, were considered for this analysis. Lakes that did not contain sediments of adequate age were labeled as missing peaks (grey triangles), those lakes exhibiting anthropogenic activity but no episodic event were identified as masked peaks (grey squares). Masking of peaks may occur as a result of activities that may lead to a dilution of mercury such as high export of watershed soils. Some lakes did not show anthropogenic activity during the time period in question and are identified (black diamond).

Five of the 26 study lakes have anthropogenic activity but do not display a peak during the CGR, identified as masked, and seven lakes do not contain sediment of adequate age. Lake Cadillac does not show anthropogenic activity during the period. Although the number of lakes not exhibiting peaks during this time period is troubling, preliminary results indicate that a regional source was present and that in general the magnitudes observed in Michigan's inland lakes agree with those observed by Shuster et al. (2002) (indicated by grey circles). This suggests that the pathway of mercury to these lakes was long range atmospheric transport since mercury and gold mining primarily occurred in Western states (Schuster *et al.*, 2002). Anthropogenic accumulation rates in Imp, Higgins, Houghton and Birch lakes exceed those found in the work of Shuster et al. (2002) (indicated by black circles) implying pre-industrial watershed scale sources of mercury.

During the manufacturing activities of WWII, loading rates in Shupac and Witch lakes are similar to those observed by Shuster et al. (2002). Eleven of the study lakes are masked by unidentified processes. Cass, Otter, and Muskegon lakes do not have sediment of adequate age to record WWII activity. Accumulation rates in the remaining lakes appear to reflect watershed scale or possibly sub-regional scale sources of mercury. The spatial variability of lake response suggests that local watershed scale sources of mercury are significantly contributing to anthropogenic mercury loadings during WWII in addition to long range atmospheric transport.

All lakes record anthropogenic activity during the 1980s. Several lakes have watershed activity that masks the industrial maximum peak recorded by Shuster et al. (2002). Eight of the lakes in this study record episodic mercury accumulation in excess of that observed in Wyoming glacial ice; eight others record events in agreement with Shusters' observations. The variability in the spatial extent of those lakes that record episodic events in excess of those recorded by Shuster et al. (2002) suggests a local source of mercury to these lakes. However, it is evident from this analysis that a super-regional source of mercury was also contributing to mercury loadings.

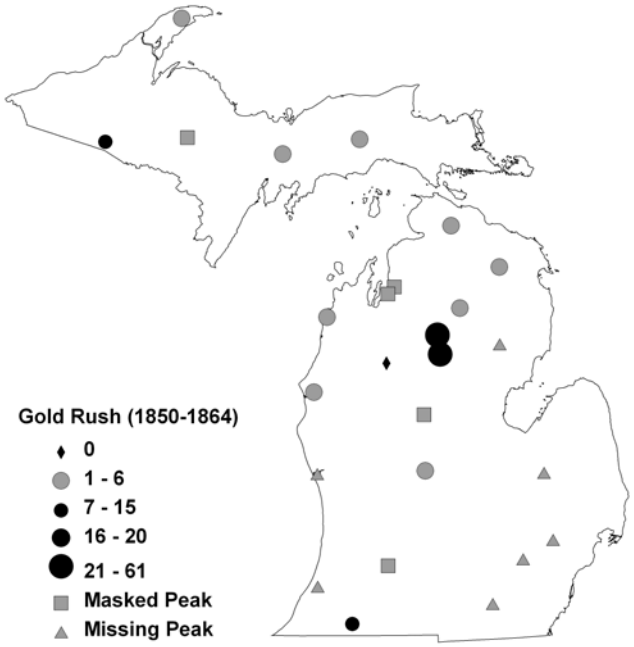
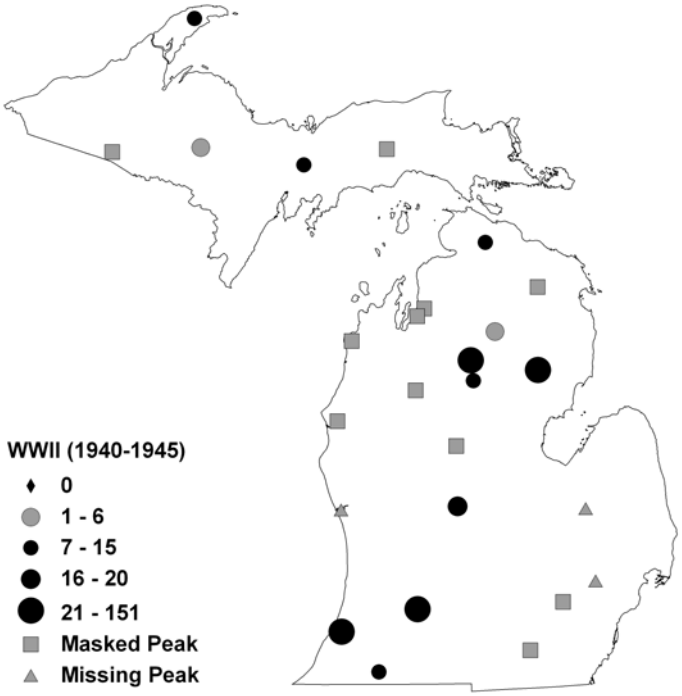
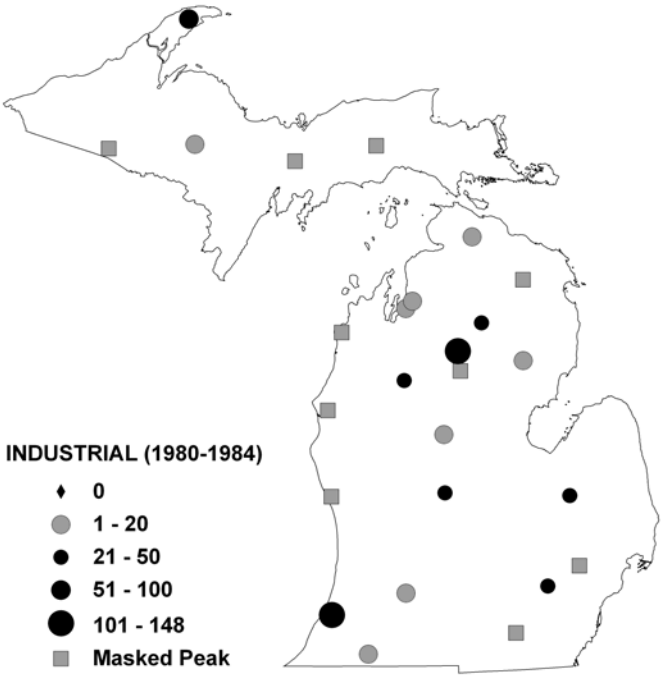


Figure 37. Episodic focusing corrected anthropogenic mercury accumulation events recorded in sediments of Michigan's inland lakes during the California gold rush[a], WWII[b], and the 1970s[c]. Gray circular markers indicate those lakes that agree with observations of Shuster *et al.* (2002). Focusing corrected accumulation rates are measured in μg/m^2/yr.





Current Trends

One of the objectives of the Inland Lakes Sediment Trends program is to determine current trends of contaminant loadings to Michigan's inland lakes. Current trends can highlight areas that require further investigation to identify sources of contaminants. Previous work has indicated that mercury deposition rates are generally decreasing (e.g., Swain et al., 1992; Lorey and Driscoll, 1999; Landis and Keeler, 2002 ; and Engstrom and Swain, 1997). Results from the Mercury Deposition Network (MDN) over five years of record (1997 to 2002) for the Upper Midwest (Figure 38) indicate mercury deposition rates increased from 1997 to 2000 but have since decreased. If regional atmospheric deposition, as recorded by MDN, can be considered a proxy for mercury accumulation in Michigan lakes then sediment accumulation rate profiles should show a recent decrease in mercury loading.

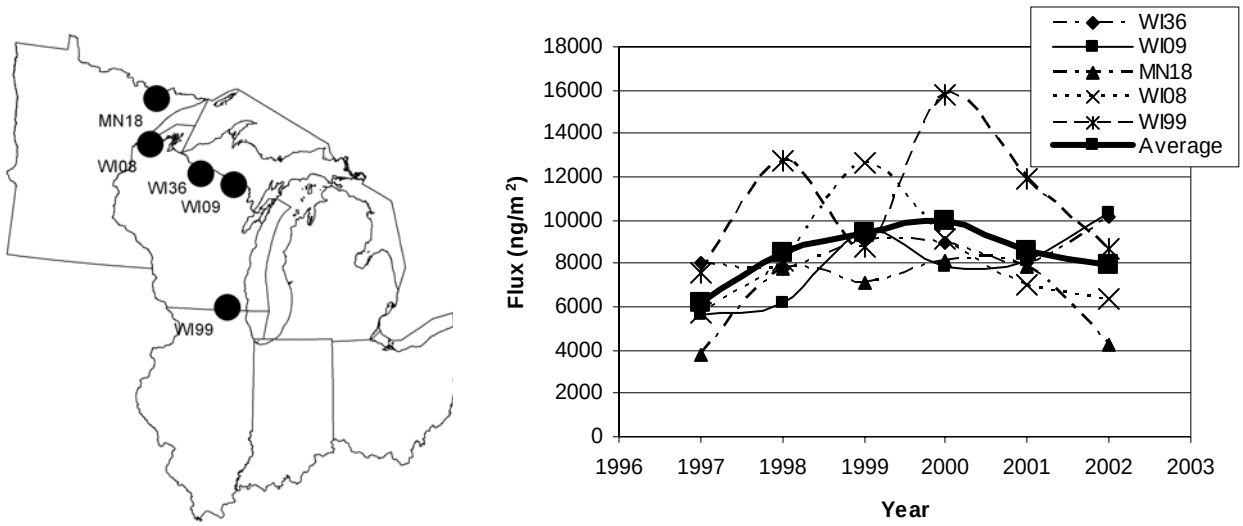


Figure 38. Mercury Deposition Network yearly sums and overall average for five Upper Midwest sites.

Figure 39 shows the results of current anthropogenic mercury accumulation rates spatially; determined as the linear trend for 10 years prior to the sampling year (episodic events, if present, were excluded). Anthropogenic accumulation rates increasing towards the surface indicate that a current source of mercury exists for the lake that cannot be explained by regional atmospheric deposition measurements. Results indicate anthropogenic accumulation rates of mercury are increasing in 9 of the 26 study lakes. Lakes that are increasing do not display a spatial pattern, suggesting the source of mercury to these lakes is not regional. Notably four of the five Upper Peninsula lakes are increasing towards the surface; this is not expected as most of these lakes are in relatively pristine environments. Only two lakes, Gull and Littlefield, are currently at background (i.e., zero anthropogenic mercury accumulation). Interestingly, mercury accumulation is decreasing in lakes found near industrial centers (e.g., Cass, Otter, Paw Paw, Muskegon, Sand, and Whitmore). These lakes generally have high accumulation rates compared to lakes in the Northern portion of the state suggesting local or sub-regional scale sources. Anthropogenic accumulation rates in Elk, Houghton, and Shupac

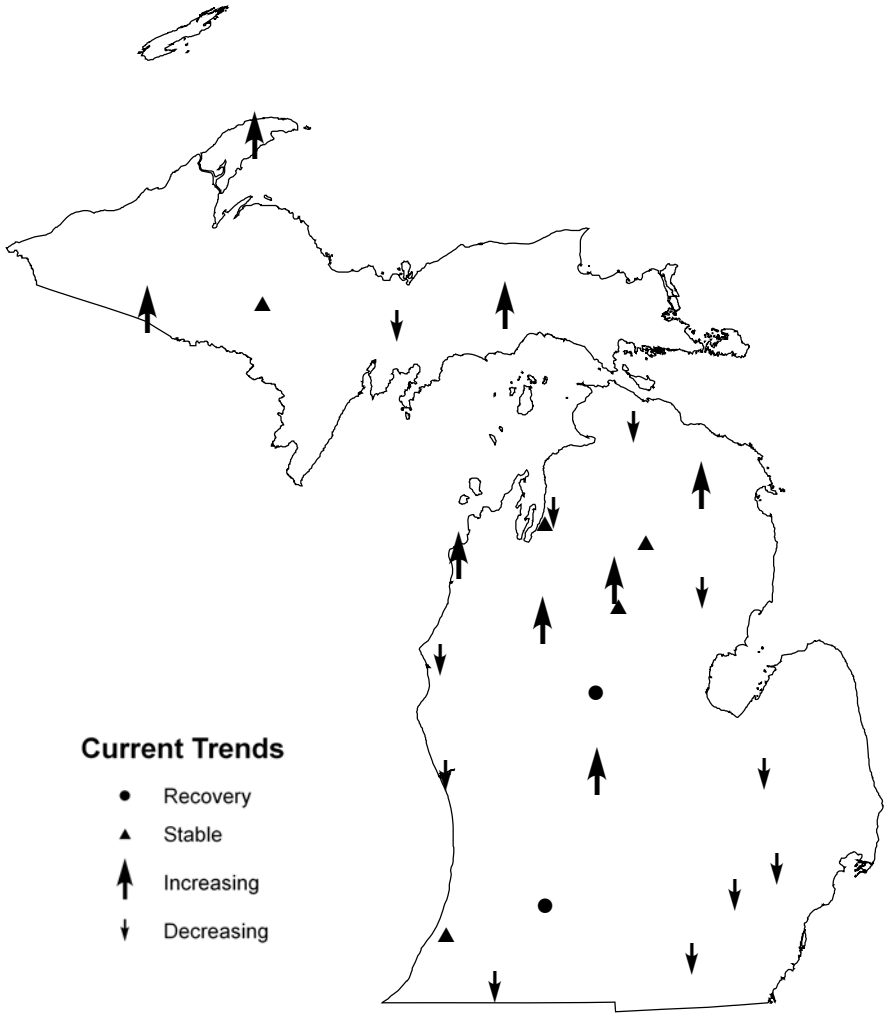


Figure 39. Current trends of anthropogenic mercury loadings to Michigan's inland lakes.

lakes are stable but still elevated above background. Although reported as stable Shupac Lake has undergone several episodic events in the last ten years; thus, stable may not accurately describe current trends.

All of the preceding analyses demonstrate that loadings of mercury to Michigan's inland lakes vary in both space and time. These results suggest that local or sub-regional scale sources are significant contributors of mercury. This does not suggest that regional or super-regional sources are insignificant only that local sources should not be over-looked in future mercury research efforts.

References

Alderighi, L., Gans, P., Midollini, S., Vacca, A., 2003. Co-ordination chemistry of the methylmercury(II) ion in aqueous solution: a thermodynamic investigation. Inorganica Chimica Acta 356, 8-18.

Andersson, A., 1979. Mercury in soils. In: Nriagu, J. (Ed.), The biogeochemistry of Hg in the environment. Elsevier, Amsterdam, pp. 79-106.

Andren, A.W., Nriagu, J., 1979. The global cycle of mercury. In: Nriagu, J. (Ed.), The biogeochemistry of mercury in the environment. Elsevier, New York.

Brooks, W.E., 2003. Minerals Yearbook - Mercury. In: Minerals Yearbook. United States Geological Survey, Reston.

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.

Engstrom, D.R., Swain, E.B., 1997. Recent declines in atmospheric mercury deposition in the upper Midwest. Environmental Science & Technology 31, 960-967.

Engstrom, D.R., Swain, E.B., Henning, T.A., Brigham, M.E., Brezonik, P.L., 1994. Atmospheric Mercury Deposition to Lakes and Watersheds - a Quantitative Reconstruction from Multiple Sediment Cores. Environmental Chemistry of Lakes and Reservoirs 237, 33-66.

EPA, 2003. National Listing of Fish Advisories. In: Bigler, J. (Ed.), Office of Science and Technology, Washington.

EPA, 2002. Toxic Release Inventory. In: Environmental Protection Agency.

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.

Faust, S., Aly, O., 1981. Chemistry of Natural Waters. Ann Arbor Science Publishers, Inc., Ann Arbor.

Fitzgerald, W.F., 1989. Atmospheric and oceanic cycling of mercury. Academic Press, New York.

Fitzgerald, W.F., Engstrom, D.R., Mason, R.P., Nater, E.A., 1998. The case for atmospheric mercury contamination in remote areas. Environmental Science & Technology 32, 1-7.

Gustin, M.S., 2003. Are mercury emissions from geologic sources significant? A status report. Science of the Total Environment 304, 153-167.

Hermanson, M.H., 1998. Anthropogenic mercury deposition to arctic lake sediments. Water Air and Soil Pollution 101, 309-321.

Hightower, J., Moore, D., 2003. Mercury Levels in High-End Consumers of Fish. Environmental Health Perspectives 111, 604-608.

Hudson, R.J.M., Gherini, S.A., Watras, C.J., Porcella, D.B., 1992. Modeling the Biogeochemcial Cycle of Mercury in Lakes: The Mercury Cycling Model (MCM) and Its Application to the MTL Study Lakes. In: Watras, C.J., Huckabee, J.W. (Eds.), Mercury Pollution: Integration and Synthesis. Lewis Publishers, Ann Arbor.

Jasinski, S.M., 1994. The Materials Flow of Mercury in the United States. In: US Department of the Interior: Bureau of Mines, pp. 28.

Kamman, N.C., Engstrom, D.R., 2002. Historical and present fluxes of mercury to Vermont and New Hampshire lakes inferred from Pb-210 dated sediment cores. Atmospheric Environment 36, 1599-1609.

Keeler, G.J., Hoyer, M.E., Lamborg, C.H., 1994. Measurements of Atmospheric Mercury in the Great Lakes Basin. In: Watras, C.J., Huckabee, J.W. (Eds.), Mercury Pollution: Integration and Synthesis. Lewis Publishers, Ann Arbor, pp. 727.

Landis, M.S., Keeler, G.J., 2002. Atmospheric mercury deposition to Lake Michigan during the Lake Michigan Mass Balance Study. Environmental Science & Technology 36, 4518-4524.
Lee, Y.H., Bishop, K., Hultberg, H., Pettersson, C., Iverfeldt, A., Allard, B., 1995. Output of Methylmercury from a Catchment in Northern Sweden. Water Air and Soil Pollution 80, 477-481.
Lindqvist, O., Johansson, K., Aastrup, M., Andersson, A., Bringmark, L., Hovsenius, G., Hakanson, L., Iverfeldt, A., Meili, M., Timm, B., 1991. Mercury in the Swedish Environment - Recent Research on Causes, Consequences and Corrective Methods. Water Air and Soil Pollution 55, R11-&.
Lodenius, M., 1992. Mercury in Terrestrial Ecosystems: A Review. In: Watras, C.J., Huckabee, J.W. (Eds.), Mercury Pollution: Integration and Synthesis. Lewis Publishers, Ann Arbor.
Lodenius, M., Seppanen, A., Autio, S., 1987. Sorption of Mercury in Soils with Different Humus Content. Bulletin of Environmental Contamination and Toxicology 39, 593-600.
Lorey, P., Driscoll, C.T., 1999a. Historical trends in mercury deposition in Adirondack Lakes. Environmental Science and Technology 33, 718-722.
Lorey, P., Driscoll, C.T., 1999b. Historical trends of mercury deposition in Adirondack lakes. Environmental Science & Technology 33, 718-722.
Lynam, M.M., Keeler, G.J., 2005. Automated speciated mercury measurements in Michigan. Environmental Science & Technology 39, 9253-9262.
Mason, R.P., Fitzgerald, W.F., Morel, F.M., 1994a. The biogeochemical cycling of elemental mercury: anthropogenic influences. Geochimica at Cosmochimica Acta 58, 3191-3198.
Mason, R.P., Fitzgerald, W.F., Morel, F.M.M., 1994b. The Biogeochemical Cycling of Elemental Mercury - Anthropogenic Influences. Geochimica Et Cosmochimica Acta 58, 3191-3198.
Morel, F.M.M., Kraepiel, A.M.L., Amyot, M., 1998. The chemical cycle and bioaccumulation of mercury. Annual Review of Ecology and Systematics 29, 543-566.
NADP, N.A.D.P.N.-N.T.N., 2003. In: NADP Program Office, Illinois State Water Survey, 2204 Griffith Drive, Champaign, IL.
Nriagu, J., 1979. Production and uses of mercury. In: Nriagu, J. (Ed.), The biogeochemistry of mercury in the environment. Elsevier, New York.
Paquett, K.E., Helz, G.R., 1997. Inorganic speciation of mercury in sulfidic waters: the importance of zero-valent sulfur. Environmental Science & Technology 31, 2148-2153.
Parsons, M.J., Yohn, S.S., Long, D.T., Giesy, J.P., Bradley, P.W., 2004. Inland Lakes Sediment Trends: Sediment Analysis Results for Five Michigan Lakes. In: Michigan Department of Environmental Quality.
Roscommon, C.o., 2003. Roscommon County. In.
Schuster, P.F., Krabbenhoft, D.P., Naftz, D.L., Cecil, L.D., Olson, M.L., Dewild, J.F., Susong, D.D., Green, J.R., Abbott, M.L., 2002. Atmospheric mercury deposition during the last 270 years: A glacial ice core record of natural and anthropogenic sources. Environmental Science & Technology 36, 2303-2310.
Schwesig, D., Ilgen, G., Matzner, E., 1999. Mercury and methylmercury in upland and wetland acid forest soils of a watershed in NE-Bavaria, Germany. Water Air and Soil Pollution 113, 141-154.
Schwesig, D., Matzner, E., 2001. Dynamics of mercury and methylmercury in forest floor and runoff of a forested watershed in Central Europe. Biogeochemistry 53, 181-200.
Schwesig, D., Matzner, E., 2000. Pools and fluxes of mercury and methylmercury in two forested catchments in Germany. Science of the Total Environment 260, 213-223.
Seigneur, C., Vijayaraghavan, K., Lohman, K., Karamchandani, P., Scott, C., 2004. Global source attribution for mercury deposition in the United States. Environmental Science & Technology 38, 555-569.

Simpson, S.J., Long, D.T., Geisey, J.P., Fett, J.D., 2000. 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.

Stearns, F.W., 1997. History of the Lake States Forests: Natural and human impacts. In: Vasievich, M.J., Webster, H.H. (Eds.), Lake States Regional Forest Resources Assessment: Technical Papers. Department of Agriculture, North Central Forest Experiment Station, St. Paul, MN, pp. 8-29.

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

Swain, E.B., Engstrom, D.R., Brigham, M.E., Henning, T.A., Brezonik, P.L., 1992. increasing rates of atmospheric mercury deposition in Midcontinental North America. Science 257, 784-787.

Triffreau, C., Lutzenkirchen, J., Behra, P., 1995. Modeling the adsorption of mercury(II) on (hydr)oxides: I. Amorphous Iron Oxide and a-quartz. Journal of Colloidal Interference Science 172, 82-93.

Tseng, C.M., Lamborg, C., Fitzgerald, W.F., Engstrom, D.R., 2004. Cycling of dissolved elemental mercury in Arctic Alaskan lakes. Geochimica Et Cosmochimica Acta 68, 1173-1184.

Tsubaki, T., Irukayama, K., 1977. Minamata Disease: Methylmercuy Poisoning in Minamata and Niigata, Japan. Elsevier, New York.

USDA, N.R.C.S., Soil Survey Staff, State Soil Geographic (STATSGO) Database for Michigan. In: United States Department of Agriculture.

USGS, 2003. Geologic Studies of Mercury by the U.S. Geological Survey. In: Gray, J. (Ed.), USGS, Reston, VA, pp. 41.

Vandal, G.M., Fitzgerald, W.F., Boutron, C.F., Candelone, J.P., 1993. Variations in Mercury Deposition to Antarctica over the Past 34,000 Years. Nature 362, 621-623.

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.

Wang, W., Driscoll, C.T., 1995. Patterns of Total Mercury Concentrations in Onondaga Lake, New-York. Environmental Science & Technology 29, 2261-2266.

Watras, C.J., Bloom, N.S., Hudson, J.M., Gherini, S., Munson, R., Claas, S.A., Marrison, K.A., Hurely, J., Wiener, J.G., Fitzgerald, W.F., Mason, R., Vandal, G., Powell, D., Rada, R., Rislov, L., Winfrey, M., Elder, J., Krabbenhoft, D., Andren, A.W., Babiarz, C., Porcella, D.B., Huckabee, J.W., 1994. Sources and fates of mercury and methylmercury in Wisconsin lakes. In: Watras, C.J., Huckabee, J.W. (Eds.), Mercury Pollution: Intergration and Synthesis. CRC Press, Ann Arbor, pp. 153-179.

Watras, C.J., Morrison, K.A., Hudson, R.J., Frost, T.M., Kratz, T.K., 2000. Decreasing mercury in northern Wisconsin: temporal trends in bulk precipitation and a precipitation-dominated lake. Environmental Science and Technology 34, 4051-4057.

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.

Yohn, S.S., Long, D.T., Giesy, J.P., Scholle, L.K., Patino, L.C., Parsons, M., Kannan, K., 2003. Inland Lakes Sediment Trends: sediment analysis results for six Michigan Lakes. In: Michigan Department of Environmental Quality, East Lansing, pp. 66.