Spatial and Temporal Trends of Mercury Loadings to Michigan Inland Lakes

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Several studies of chronologies of mercury (Hg) in inland lake sediments have demonstrated that Hg accumulation decreased in recent decades. However, episodic mercury accumulation events were recorded in some of these lakes, but not investigated in detail. Recent decreases had been attributed to the reduction of regional Hg consumption and secondary removal during process waste treatment. In addition to regional sources, local sources, including watershed disturbance, might significantly contribute to Hg loading. Here, mercury chronologies of Hg loadings based on dated sediment cores are presented for 26 inland Michigan lakes. Although spatial trends of anthropogenic inventories suggest a regional pattern dominated by human activities, sub-regional to local scale sources are also found to be significant. Temporal trends show episodic Hg accumulation events superimposed on a more general, long-term trend. Episodic increases common to lakes suggest a common source or processes common to lakes. Episodic increases unique to a lake indicate a more local scale source. Similar Hg profiles from lakes that are geographically proximal provide evidence for sub-regional to regional scale sources. Local sources and pathways for mercury to inland lakes need to be more fully understood to effectively reduce Hg loading to the environment.

Introduction

Mercury (Hg) concentrations greater than historical levels, as recorded in sediment cores, have been observed in the high northern latitudes (*1–3*), New England (*4*, *5*), the Midwestern United States (*6*, *7*), Western United States (*8*, *9*), and Europe (*10*, *11*). Although regulatory controls have attempted to limit mercury emissions (*12*), the number of river miles and fresh water lakes in which Hg concentrations exceed regulatory guidelines continue to increase. The reasons for this increase have been attributed to monitoring efforts extending to water bodies that were previously untested (*13*), or increased releases from human activities and subsequent deposition in remote areas (*14*). Consumption of contaminated fish has been shown to be a principle exposure route of methylmercury to humans (*12*, *15*). As a result of elevated health risks, several midwestern states have advised consumers to reduce consumption of fish from all of the Great Lakes and all Michigan inland lakes due to potential Hg exposure (*13*).

Freshwater sediments retain mercury transported to the lake system (*16*), and, when coupled with dating techniques, sediments can record the history of mercury loadings over time. Dated sediment cores have been used to investigate the historic accumulation of Hg in sediments of the North American Great Lakes (*17*) and inland lakes (*4–7*). While analysis of Great Lakes sediment provides significant information about deposition of Hg on larger spatial scales, it is difficult to determine local watershed scale contribution to Hg loadings. Investigating inland lakes across a region allows examination of both regional and, local, including watershed scale, contribution to Hg accumulation. Earlier determinations of sediment chronologies have demonstrated that Hg loadings in some areas of the United States (U.S.) such as the Western United States (*8*, *9*), Midwestern United States (*6*, *7*), New England (*4*, *18*), the Adirondack region of New York (*5*), and Europe (*10*, *11*) have decreased in recent years. However, several of the lakes included in previous studies had recent increases in Hg accumulation.

The results reported in this paper are part of a larger study by the Michigan Department of Environmental Quality, entitled "Inland Lakes Trends Monitoring Program: Sediments", to determine trends of organic and inorganic contaminant accumulation in Michigan's inland lakes (*19*). Here the chronologies of Hg loading into lakes were determined from 26 ^{210}Pb-dated, confirmed by ^{137}Cs and stable Pb, sediment cores from inland lakes throughout Michigan. Anthropogenic mercury inventories of Hg loadings to lakes were investigated at several spatial scales and Hg accumulation rates, and examined temporally to test the hypothesis that local-scale sources of Hg significantly contribute to Hg accumulation in inland lakes. Understanding local scale sources for Hg will become increasingly important in assessing the efficacy of control measures for regional sources.

Materials and Methods

During the summers of 1999 through 2004, 26 lake sediment cores were collected aboard the U.S. Environmental Protection Agency (EPA) R/V *Mudpuppy* or Michigan Department of Environmental Quality (MDEQ) M/V *Nibi* (Figure 1). Lakes were selected to cover all regions of the state and varied in their watershed (area) and hydrological characteristics, such as whether they were headwater or seepage lakes. An MC-400 Lake/Shelf multi-corer was used to extract four simultaneous cores for ^{210}Pb-dating and analysis of Hg and other metals. The core was sectioned on shore shortly after retrieval at 0.5–1.0 cm intervals for the first 5–8 cm and 1-cm intervals for the remainder of the core; core lengths varied from 50 to 60 cm. Sectioning of the cores used for determining Hg concentrations and ^{210}Pb was conducted at the same stratigraphic resolution. More detailed descriptions of the sectioning protocols and results of ^{210}Pb are presented elsewhere (*20–23*). Specific dating related information and methodology can be found in the Supporting Information.

Sediment Focusing. Sediment focusing is the movement of fine grained materials from erosional to depositional zones of a lake basin, and can be quantified by calculating a focusing factor, which is the ratio of observed to expected ^{210}Pb inventory. The observed ^{210}Pb inventory is the product of sediment dry mass and excess ^{210}Pb summed over all core sections. The expected inventory of ^{210}Pb for this study region is 0.574 Bq/cm^2 (*24*). Accounting for sediment focusing allows

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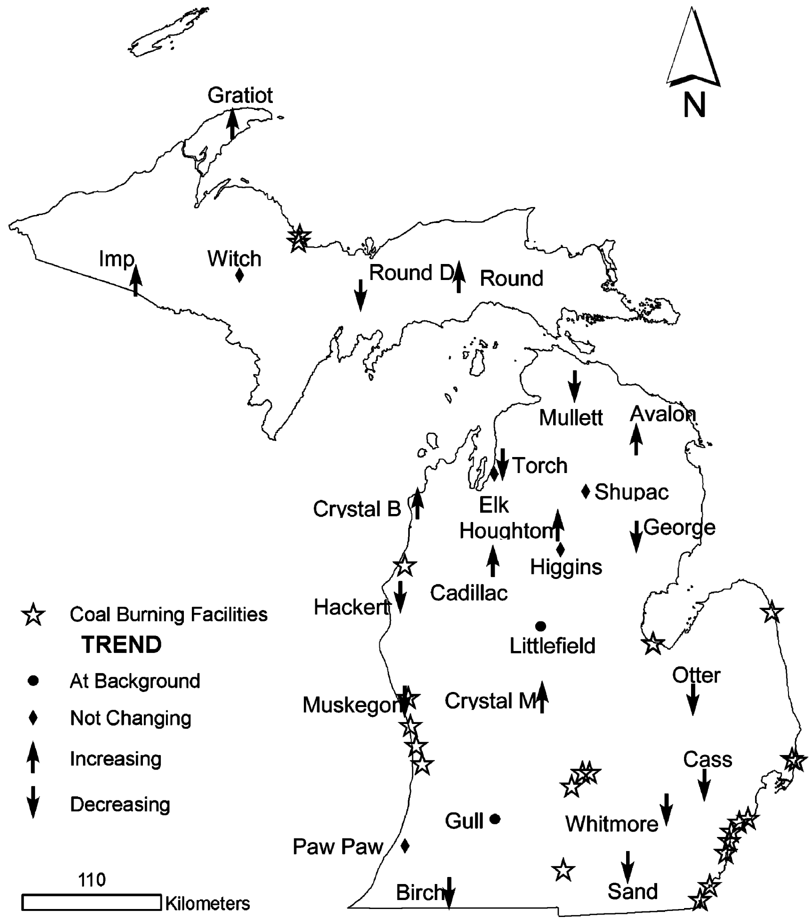

FIGURE 1. Inland lake trends monitoring program: sediments study lakes, trends of Hg loading over the past decade, and coal burning power plants. An up-arrow indicates accumulation rates had increased toward the surface, a down-arrow indicates accumulation rates had decreased. Solid triangles mean that accumulation rates were elevated but are not increasing or decreasing. Solid circles indicate that accumulation rates had returned to pre-industrial rates. Open stars represent coal burning power plants greater than 25 MW generating capacity as of 2005.

comparison of inventories and accumulation rates among lakes (*24*).

Calculations. Anthropogenic Hg concentration was calculated by subtracting the long-term geochemical background Hg concentration from the total concentration. The background concentration was defined as that average concentration from the deepest core section to the point where concentrations began to increase that could be associated with human activities, primarily after colonization of the area by Europeans. This point was determined graphically by determining where the concentration increased significantly. Anthropogenic inventories, the mass of chemical in a sediment core due to human inputs, were calculated as the product of anthropogenic Hg concentration and sediment dry mass for each individual core section. Results for each core section were then summed over the entire core to determine the inventory. The anthropogenic accumulation rate was calculated as the product of the sedimentation rate and the anthropogenic Hg concentration. Inventories and accumulation rates were corrected for sediment focusing.

Sedimentation rates in lakes vary considerably, and when sedimentation rates are great bottom sections of the sediment core will not contain background concentrations of Hg. Therefore, it was necessary to estimate the focusing-corrected background accumulation rate (FCBGAR). These estimates were based on results of a backward stepwise multivariate regression model taking into account physical variables and surficial soil properties of the watershed. This model assumes that soil properties have not significantly changed since the pre-industrial period and soil properties that control the mobility of Hg do not vary among watersheds. Physical variables entered into the model included lake area, watershed area, and watershed/lake area ratio (WS:LA). Soil properties were determined via dasymetric mapping of STATSGO (*25*) soil characteristics using ArcInfo (*26*) and included the following: cation-exchange capacity, % organic matter, % clay, carbonate as $CaCO_3$, kfact and kffact, which is a slope adjusted kfact value. Parameters for variables to enter the model included tolerance greater than 0.6 and probability to enter/leave less than 0.15. The final model (n = 14, adjusted $r^2 = 0.66$) is presented in eq 1; variables were significant at $p < 0.05$ (one-tail t-statistic), tolerances were greater than 0.75, and residuals were randomly distributed.

$$\mathrm{FCBGAR} = 5.016 + 0.225\ \%\mathrm{ORG} + 0.015\mathrm{WA} - 0.091\mathrm{LA} \quad (1)$$

where % ORG is the percent organic matter in soil, WA is the watershed area, and LA is the area of the lake. The average (±SD) modeled FCBGAR was 7.9 (3.7) μg Hg/m^2/yr, whereas the average of the observed FCBGAR was 6.0 (3.5) μg Hg/m^2/yr. The intercept, which would represent the FCBGAR in the hypothetical absence of the variables above, was reasonably close to the median FCBGAR of the observed values, 5.8 μg Hg/m^2/yr. Thus, the predicted FCBGAR values were used to approximate anthropogenic accumulation rates for lakes in which geochemical background sediment Hg concentrations could not be determined. Background estimations were not used to calculate anthropogenic inventories due to the temporal variation of mercury accumulation; however, these estimates would not change the accumulation rate profile.

Previous models have used WA and LA to predict Hg accumulation, and organic matter has been demonstrated to play a significant role in the cycling of mercury in the watershed (*5*, *7*). Although the positive relationship between WA and FCBGAR was expected, the negative relationship between LA and FCBGAR was not anticipated. Removal of LA from the model consistently resulted in poorer estimates (lower adjusted r^2) of FCBGAR. Greater inputs of Hg would be expected for large lakes and thus background values would reflect this relationship. We suspect that the LA variable may in part explain differences in sedimentation rates observed in the larger lakes. Observed background Hg concentrations and sedimentation rates, both of which would result in a low FCBGAR, were both least for larger lakes. Organic matter is important in the biogeochemical cycling of Hg in soils (*27*, *28*). Greater concentrations of organic matter in soils effectively retain Hg and other metals. More effective retention in soils might lead to greater concentrations during runoff events resulting in the transport of Hg from the watershed (*29*).

Quantification of Mercury. Total Hg concentrations were determined in lyphophilized sediment by use of a Lumex thermal decomposition atomic absorption spectrometer in accordance with EPA Method 7473 (*30*). Calibration of the instrument and in-run validation were performed using standard reference material (SRM) 1515 Apple Leaves or SRM1633b Coal Fly Ash; detection limits were 0.69 ng Hg/g, dw and 0.58 ng Hg/g, dw, respectively. In-run SRM validation measurements were consistently within the range specified.

Results and Discussion

Anthropogenic Inventories. Anthropogenic inventories are an accounting of the long-term loading of a contaminant to a lake. Analysis of the spatial patterns of inventories among lakes can reveal patterns of source in a region. For the purposes of this discussion a region has been defined as the entire state of Michigan whereas sub-regions are smaller areas within the region, such as southeast Michigan. A regional pattern of deposition is indicated if inventories decrease along some gradient, such as population density or industrial development. The source for the pattern of deposition may be common to all lakes, a common source, or similar watershed processes occurring at different rates, a source common to all lakes. For example, Pb inventories in these study lakes decrease from the South to the North, implying a regional source (*31*). Lead from the use of leaded gasoline is the most commonly accepted cause for this trend; greater lead inventories in the southern, more populated and industrialized portion of the state trend toward lesser inventories in the northern, less populated, portions of the state. A regional source may also be present if inventories are similar among lakes within a sub-region. Focusing-corrected copper inventories were found to be similar among depositional basins of Lake Michigan (*32*). This suggests a regional source for copper entering Lake Michigan.

Recent measurements of atmospheric deposition of Hg for the Great Lakes region have demonstrated a south-to-north gradient (*33*). If this general south to north trend has been persistent over time then inventories plotted along this spatial gradient should follow a similar pattern, evidence of a regional source. Results of focusing-corrected anthropogenic Hg inventories for 18 Michigan lakes (Figure 2) were plotted along a south to north gradient to investigate the possibility of a regional source. Mercury inventories varied among lakes, ranging from 0.3 μg Hg/cm^2 in Round Lake to 1.6 μg Hg/cm^2 in Houghton Lake (Figure 2). Anthropogenic Hg inventories were found to vary slightly in Lakes Michigan

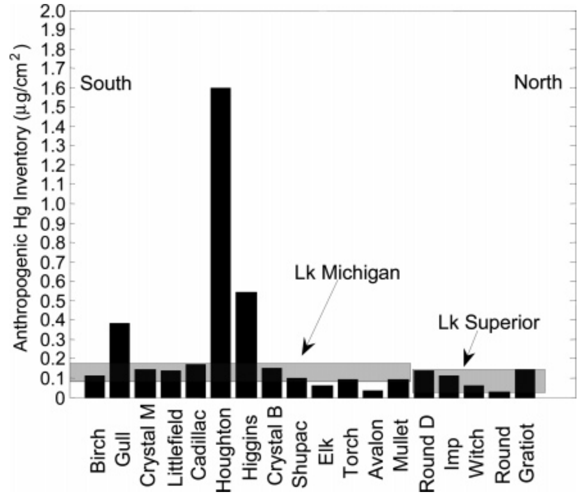

FIGURE 2. Focusing-corrected anthropogenic Hg inventories from 18 inland Michigan lakes. Inventories are plotted along a south to north gradient. The boxes represent the range of anthropogenic inventories for Lake Michigan and Lake Superior (*17*).

(0.08−0.17 μg Hg/cm^2) and Superior (0.02−0.15 μg Hg/cm^2), with anthropogenic inventories decreasing from the south to the north (*17*). If the range of inventories determined in the Great Lakes represents a regional estimate of Hg loading for this region (both the Upper and Lower Peninsulas of Michigan), then deviations from these patterns suggest the influence of sub-regional to local scale sources. Most anthropogenic inventories from inland lakes are consistent with a regional source; however, notable exceptions include, Higgins, Houghton, and Gull lakes.

The relative importance of local sources can be determined by comparing the anthropogenic inventories of lakes from the same geographic region because these lakes would be expected to have similar loadings due to long-range atmospheric loading so that differences could be attributed to more local sources. Lakes Higgins and Houghton, in the central Lower Peninsula, and Elk and Torch lakes, in the NW Lower Peninsula, are examples of geographically proximal lakes. Anthropogenic inventories differ among these pairs of lakes indicating that local, likely watershed-scale, sources were contributing to Hg loadings. Crystal M and Littlefield lakes lie within the central portion of the state and have similar anthropogenic inventories. Inventories for these lakes are within the range of those from Lake Michigan suggesting that Hg loading in this area is most likely due to regional sources of Hg. The differences among the Upper Peninsula lakes, Gratiot, Imp, Round D, and Round, imply that local sources contribute significantly to Hg loadings; however, these lakes are within the range of anthropogenic inventories found in Lake Superior. Portions of the Upper Peninsula are more mineralized than other areas of the state and have undergone intense mining, which may have led to increased export of Hg from the watershed (*34*, *35*).

Temporal Trends. In general, anthropogenic accumulation began in the late 1800s and reached nominal peak values during the 1950s to 1980s depending on the lake (Figures 3−7). Episodic events have been superimposed on this general trend. These events may be unique to a lake or may be common among many lakes in a sub-region. Episodic increases common among lakes indicate that they resulted from increased accumulation and not postdepositional mobilization or spatial variability within the sediments. Episodic increases that are common among lakes may be due to a common source or watershed processes that are common to all lakes. Profiles are grouped by sub-region to highlight accumulation rate patterns. Profiles for all of the

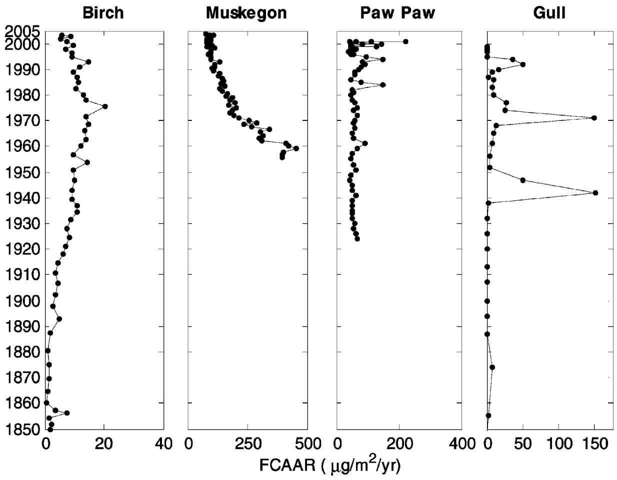

FIGURE 3. ^{210}Pb dated focusing-corrected anthropogenic accumulation rates for four southwestern Michigan lakes; dates older than 1850 were truncated to highlight more recent loading. Note the change in scale of the *x*-axis.

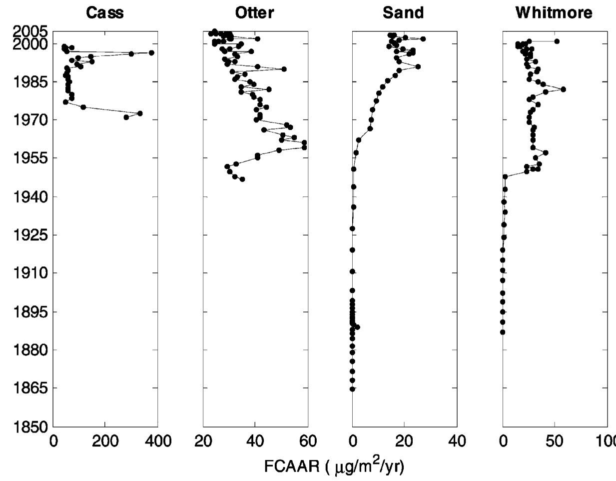

FIGURE 4. ^{210}Pb dated focusing-corrected anthropogenic accumulation rates for 4 southeastern Michigan lakes. Note the change in scale of the *x*-axis.

other lakes that were studied can be found in the Supporting Information.

Anthropogenic Hg profiles from lakes in southwestern Michigan reflect the proximity to industrialized areas and also include several episodic accumulation events (Figure 3). The proximity of this sub-region to the Chicago, IL/Gary, IN area suggests that these lakes should reflect the impact of Hg from this highly industrialized region. It has been suggested previously that the Chicago/Gary area is a source of Hg to southern Lake Michigan (*36*, *37*) and it has been proposed that the Chicago/Gary industrial complex was a major source for lead, cadmium, and zinc to these study lakes (*38*). The similarity, excluding episodic accumulation events, of the loading profiles observed for Gull and Birch lakes implies a source of Hg common to both lakes was present until the early 1990s, although the onset of the anthropogenic Hg accumulation occurred earlier in Birch Lake. The recent recovery of Gull Lake to a rate of anthropogenic loading that is near zero is notable, since this was observed in only 2 of the 26 study lakes studied (see Littlefield Lake, Figure S1 in Supporting Information). Accumulation rates in Birch and Muskegon lakes decreased toward the surface whereas the rates in Lake Paw Paw have increased. The uniqueness of the accumulation rates observed near the surface of the core from Lake Paw Paw and the unique episodic events (ca 1960 and 1984) suggests a local source. Paw Paw Lake was dated with a linear dating model using a single sedimentation rate (see Table S1 in the Supporting Information). Meaning, in Paw Paw Lake, episodic events were due to increased Hg concentration on the sediment and not increased sediment delivery. Episodic events that were common among all southwestern lakes include a peak in the early 1990s and early to mid 1970s. Great anthropogenic Hg accumulation rates in Paw Paw and Muskegon lakes suggest that local-scale sources are significant contributors of Hg to these lakes.

Southeastern Michigan is a highly populated and industrialized area of the state. This area also has the highest number of coal-fired utilities in the State; although all of these facilities lie to the east of the study lakes (Figure 1). Winds are generally westerly or southerly in this region. Mercury accumulation rates are greater in lakes from this sub-region which may be a consequence of greater atmospheric deposition in this region compared to less urban regions of Michigan (*39*). Mercury in the cores from Whitmore, Cass, and Otter lakes exhibit large anthropogenic accumulation rates with peak rates that were among the greatest measured for all of the lakes studied (Figure 4). Lakes Otter and Whitmore, which are situated in the northern part of this sub-region, exhibit rapid increases in anthropogenic Hg accumulation during the later part of the 1940s into the early 1950s. This implies a common source or a source that is common to both lakes of Hg loading to both lakes during that period. Furthermore, several of the episodic increases in Hg loading occurred simultaneously among these lakes, suggesting a source of Hg loading common to both lakes. Episodic events in the early and mid 1990s are common among all of the southeastern lakes. During the early 2000s, episodic events occurred in Sand and Otter Lakes. When accumulation profiles in these lakes were compared to those observed in the surficial portion of the core from Whitmore Lake it was possible that Whitmore Lake was currently experiencing a spike in Hg accumulation. If Whitmore Lake were revisited, the most recent sediments should show a decline in accumulation rate. Dating-model error, measurement error. and field methodologies all contribute to possible errors in sediment core chronologies. However, the observation that so many episodic events "line up" among lakes suggests that the events are real. Similar to Paw Paw and Muskegon lakes, the accumulation rates in Cass Lake were anomalously great; these rates suggest a unique source or a sub-regional source in close proximity to the lake. Recently, decreases in Hg loading have been observed among all of the lakes in the southeastern sub-region (Figure 1), generally from maximal loading rates, in anthropogenic Hg accumulation. Sediment cores from lakes in urban areas of Minneapolis, MN have demonstrated that loading rates of Hg have decreased in recent years (*6*). The hypothesis stated for the decreased Hg loading to urban Minneapolis lakes is that limited growth in already built-up areas has slowed the potential for new sources of Hg to the lakes. This also adequately explains the recent declines observed for southeastern Michigan (suburban Detroit and Flint) lakes in our study; although the reasons for episodic increases are unclear at this time.

Rates of anthropogenic Hg loading to five Upper Peninsula (UP) lakes, Gratiot, Imp, Round D, Round, and Witch, appear to be sub-regional in nature (Figure 5). Other than the episodic accumulation events, this conclusion is further supported by the similarity of profiles in the eastern portion of the UP (Round D and Round) compared to those in the western UP (Imp and Witch). Both Round D and Round lakes appear to have reached a steady state accumulation rate shortly after reaching maxima in the early 1900s and 1950s respectively. Then, during the late 1970s, Hg accumulation

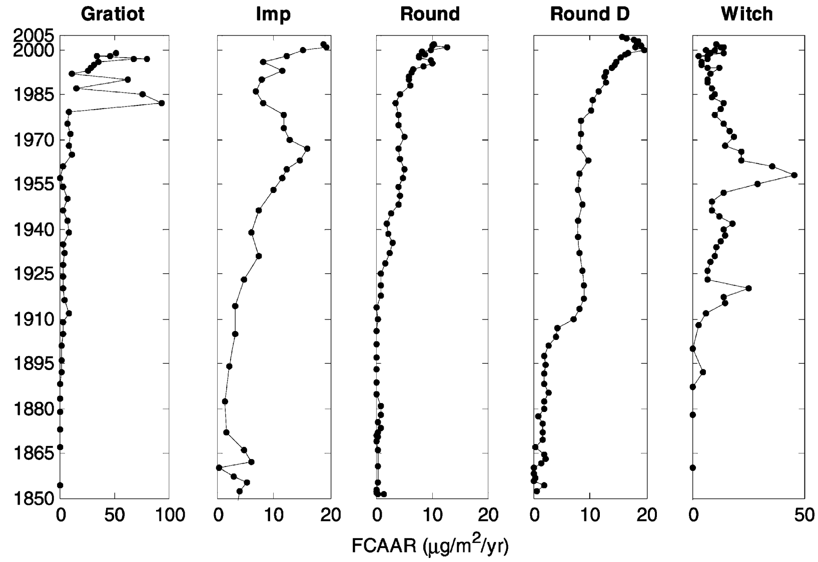

FIGURE 5. ^{210}**Pb dated focusing-corrected anthropogenic accumulation rates for five Upper Peninsula of Michigan lakes; dates older than 1850 were truncated to highlight more recent loading. Note the change in scale of the *x*-axis.**

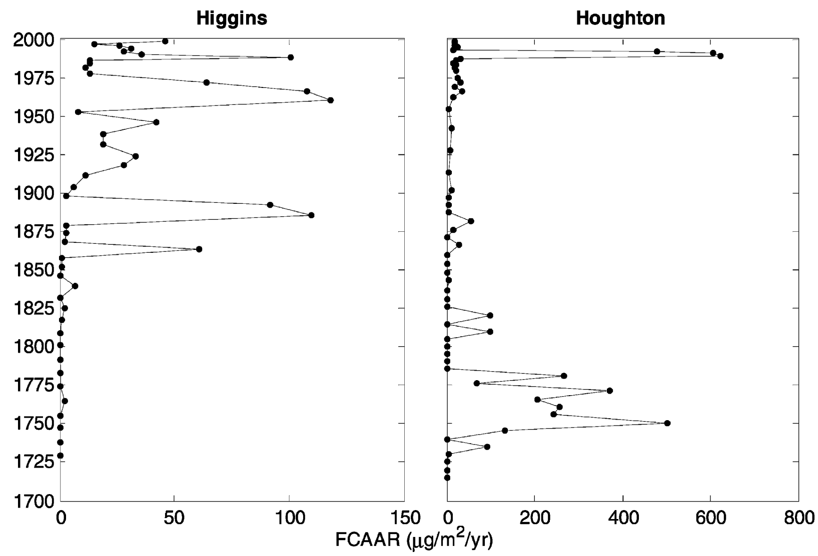

FIGURE 6. ^{210}**Pb dated focusing-corrected anthropogenic Hg accumulation rates for two north-central Michigan lakes. Note the change in scale of the *x*-axis.**

rates in both lakes increased and followed similar trajectories. Witch and Imp lakes both reached maximal Hg accumulation rates in the 1960s followed by a steady decline until the 1990s. After 1990, both Imp and Witch lakes exhibited greater accumulation rates until 2000, followed by a more recent decrease. Except for a unique accumulation rate profile in more recent times, certain episodic increases in Hg accumulation during the 1910s, 1940s, and 1980s in Gratiot Lake were common to other western UP lakes, suggesting that Gratiot Lake would be included in this sub-region. The episodic events after 1975 in Gratiot were superimposed on a generally increasing trend. The extent of these events suggests that the source was local, most likely watershed, in scale.

Anthropogenic Hg accumulation rate profiles from Lakes Higgins and Houghton in the north-central portion of the Lower Peninsula of Michigan exhibit simultaneous occurrence of episodic increases (Figure 6). A notable deviation was observed during the mid to late 18th century in Houghton Lake. Reasons for not observing this phenomenon in other Michigan lakes that contain sediment of adequate age to record the disturbance are not yet clear, but may be due to the unique geography of the Houghton Lake area. Higgins Lake lies 14 km due north of Houghton Lake, and their watersheds share a common boundary. Houghton Lake lies at or near the headwaters of three major river systems, two of which flow into Lake Michigan (Muskegon and Manistee rivers) and one flows into Lake Huron (Au Sable River). Native Americans commonly used rivers as efficient transportation corridors from West to East (*40*) and the advantage of efficient travel may have led to early settlement. Native American tribes during this period were known to travel inland over 100 km from the Lake Michigan shoreline (*40*). Other metals, such as, aluminum (Al), zinc, and cadmium, do show an accumulation rate increase during this period suggesting a terrestrial input (*23*). The disturbance that led to the increase of these metals is unclear, but may be due to the early trading and land-clearing activities in the region.

Prior to 1930, the Hg accumulation rate profiles of 4 northwestern Michigan lakes, Elk, Torch, Crystal B, and Mullett, were similar (Figure 7), which suggests a regional to sub-regional source of Hg. After the 1930s, Lakes Mullett and Torch appear to have been influenced by a more sub-regional source, whereas Elk and Crystal lakes show the effects

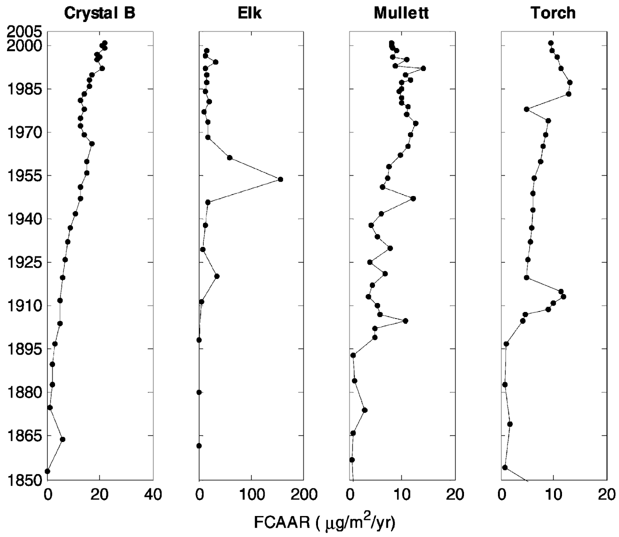

FIGURE 7. ^{210}Pb dated focusing-corrected anthropogenic accumulation rates for four northwestern Michigan lakes; dates older than 1850 were truncated to highlight more recent loading. Note the change in scale of the *x*-axis.

of more local sources. Loading rates of Al to Elk Lake decreased during the mid-20th century episodic Hg increase. These two observations, taken together, suggest that the source was a point source or local atmospheric deposition rather than terrestrial (*41*). Mercury accumulation rates in Crystal B Lake were found to be increasing toward the sediment water interface, which is unique for this sub-region, suggesting a local source.

While it is clear that some episodic accumulation events are due to local-scale sources it is unclear at this time the reasons for these events. Possible sources being considered include waste incinerators (*42*), fuel combustion (*43*), dental office waste (*44*), forest fire (*45*), clear-cutting of forest (*46*), pulp and paper mills (*47*), and cement manufacturing (*48*).

Recent Trends. Hg concentration profiles in sediments from several lakes have recorded recent increases in Hg loading (*5*−*7*, *18*). Over the past decade in Michigan, 8 of the 26 lake profiles showed anthropogenic Hg accumulation rates that increased toward the surface, 11 showed trends that indicate anthropogenic loading had declined, 5 showed elevated accumulation rates but no clear increasing or decreasing trend, and 2 had anthropogenic accumulation rates at background levels (Figure 1). Considering the lakes experiencing increased loading, the lack of a spatial trend suggests that the source was not regional in scale. Those lakes in which FCAAR was increasing are not located in areas of the state that have a high density of coal-fired power plants (Figure 1), further evidence of the importance of local-scale sources of Hg to these lakes. In addition, these results are inconsistent with a decrease in Hg emissions (*6*). Possible local sources include: mobilization from watershed soils, industry, and agriculture. The increase observed in sediment cores from Adirondack lakes have been attributed to a decrease in the retention of Hg by watershed soils (*5*). Some researchers have attributed the increase recorded in western Minnesota lakes to Hg-laden soils delivered from agricultural fields (*6*). At this time it is unclear as to why we observe increased accumulation rates in more recent periods but one or all of the above may have contributed.

Acknowledgments

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Supporting Information Available

Dating methodology, ^{210}Pb data, and profiles of FCAAR for other lakes in this study (Figures S1 and S2 and Table S1). This material is available free of charge via the Internet at http://pubs.acs.org.

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