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Inferring Sources for Mercury to Inland Lakes Using Sediment Chronologies of Polycyclic Aromatic Hydrocarbons

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Environmental Impact Statement

Mercury enters naturally in the environment through geogenic sources. Human activities have elevated Hg concentrations. Thus, problems of exposure to mercury in the environment continue. Mercury in fish of the Great Lakes is an example. Sediment records from some watershed for the Great Lakes region show Hg loadings to be increasing, the cause(s) of which are still unclear. There is continuing debate as to the role specific types of human processes (e.g., coal fired power plants) play in Hg loadings. Understanding these sources can better inform the development of regulatory measure to reduce environmental exposure. This work attempts to source Hg loadings in selected lakes in the Great Lakes by using diagnostic ratios of polycyclic aromatic hydrocarbons (PAHs).

Inferring Sources for Mercury to Inland Lakes Using Sediment Chronologies of Polycyclic Aromatic Hydrocarbons

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Sediment chronologies from inland lakes suggest the influence of local to sub-regional scale sources for mercury (Hg). However, apportionment of sources for Hg using sediment chronologies is difficult due to the mixing of sources and pathways. Mercury and polycyclic aromatic hydrocarbons (PAH) often share common sources and pathways into the environment. Thus, chronologies of PAHs in dated cores of sediments might be a useful tool to infer sources of Hg. Sediment cores from seven inland lakes of Michigan were collected for measurement of PAHs and Hg and dated by use of ^{210}Pb. PAH concentrations and ratios of kinetic and thermodynamic PAH compounds were used to infer sources of Hg. Ratios indicate the existence of modern combustion sources to each lake and historic combustion sources to lakes near cement kilns and an iron foundry. Coal combustion sources were identified for two lakes near urban

centers. Whereas a petroleum combustion source was identified for a lake that has a coal fired power plant along its shoreline. These results have implications for the cycling of Hg on local to regional scales.

1. Introduction

Atmospheric sources have been shown to play significant roles in the transport and deposition of mercury (Hg) into terrestrial and aquatic environments.[1] Several studies have shown that much of the anthropogenic Hg emitted to the atmosphere is a result of the combustion of coal and petroleum products. [2,3,4]. As a result of its physical properties Hg can reside in the atmosphere for up to a year and thus be transported globally.[2] For example, it is evident that Hg emitted in Asia has reached North America.[5, 6, 7, 8, 9] However, a significant portion of Hg emitted to the atmosphere can be attributed to local and regional sources.[10,3] As legislation[11] attempts to further reduce releases of Hg, further reductions will require better understanding of source(s), especially local versus regional and perhaps global. The temporal record of the environmental loadings of Hg in sediment and ice cores have been compared to record to historical national production and types of consumption records to infer anthropogenic sources for Hg[12] and event-based markers, such as major volcanic eruptions to infer natural sources.[13] This approach has limitations however in unrevealing the role of more local sources. The study of source apportionment has also been approached by use of multivariate statistical techniques to analyze data obtained from collectors of atmospheric deposition.[14, 3] Although results of these studies can give insights into local- to global-scale sources, this methodology is limited because of the lack of atmospheric collectors and the uneven distribution of collectors throughout a region, nation or the world.[15]

Sediments of inland lakes act as local (watershed) scale collectors of environmental contaminants. When cores of sediments are collected across a region, they can be used to discriminate between local and regional sources. However, since sediments incorporate material from both atmospheric and more local watershed sources differentiating source(s) can be difficult. This difficulty can be in part addressed if an independent marker, specific for one or the other of these sources is used to infer sources or apportion relative proportions for various sources. Polycyclic aromatic hydrocarbons (PAHs) have the potential to be such an independent marker for Hg. PAHs are primarily formed during the incomplete combustion of fossil fuels and vegetation.[16] Similar to Hg, PAHs can remain in the atmosphere after emission resulting in long distance transport[17, 18] and also be deposited nearer to sources.[19] Because both PAHs and Hg are particle reactive, they are scavenged out of the atmosphere and collected in sediments of lakes. Thus, comparing their loading chronologies in sediments can be used to help infer sources.[16, 20] There are a variety of activities that result in releases of PAHs into the environment. Some of the primary sources include combustion of coal and exhaust from internal combustion engines. Sources of PAHs can be natural, such as oil seeps, erosion of surficial bitumens, and forest fires, or human activities including benefaction and combustion of fossil fuels.[21, 22] Compound ratios of PAHs have been shown to be useful in the identification of types of sources.[23,24,25,26,27]

Several studies have measured and compared metal and PAH concentrations in the environment.[10, 28,29,30] However, although there is strong evidence that Hg and PAHs might share common sources and pathways, few studies have investigated correlations between these chemicals in terms of their environmental loadings. For example, the sum of concentrations of PAHs measured in aerosols from the North Sea was significantly correlated with those of other heavy metals.[31] More importantly for this study, Hg concentrations have been shown to be more correlated with PAHs concentrations than other trace metals (e.g., Zn, Pb)[32], which could be an indication of common source. PAH compound ratios in sediment and soil samples collected from around New Orleans, LA, USA indicated that those samples with elevated concentrations, the dominate source was from pyrolytic origins. The significant correlation between PAH and metal concentrations in both the soil and sediment samples was interpreted to indicate a common source.[33]

Influences that might affect the use of PAH compound ratios include differential degradation of individual PAHs driven by microbial processes or by differences in vapor pressure and resistance to photolytic decay[34,35, 36] Differences in the rate of degradation are greatest amongst PAHs of lesser molecular masses, such as anthracene, thus interpreting making ratios that compare PAHs of lesser molecular mass can be problematic. Corrections for differential degradation can be made when meteorological and source data are available[36] however, in most cases, as was the case during this study, such data are unavailable. To overcome this limitation most studies of PAHs in the environment use ratios of multiple PAHs compounds.[21,25]

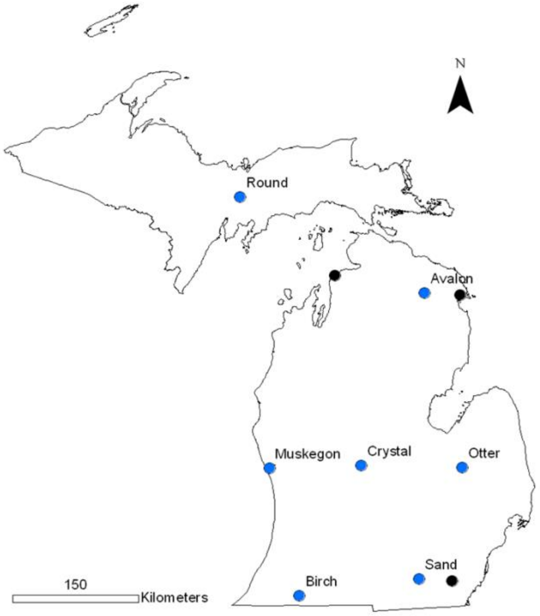

Figure 1. Location of the lakes in the State of Michigan, USA used in this study. Current cement kilns are shown. The historic cement kiln located in Cement City, MI is not shown but was located approximately 20 km due west of Sand Lake

This study used concentrations of PAHs from dated sediment cores from selected freshwater lakes in Michigan, USA to infer sources for Hg loadings to the environment (Fig. 1). The State of Michigan occupies a large footprint in the Great Lakes basin which makes it an excellent region for this sort of study. The study area covered 151,586 km^2 and extending over 7^o longitude and 6^o latitude, and included areas of more intense urban and industrial development and more remote and less developed regions.[20,37,38,39]

2.0 Materials and Methods

A detailed description of collections of cores of sediments, ^{210}Pb dating, Hg analysis and PAH analysis can be found elsewhere.[20,25] Briefly, cores were collected from selected lakes in the State of Michigan (USA) (Fig. 1) aboard the MDNRE R/V *Nibi* or US EPA R/V *Mudpuppy* from the deepest portion of the lakes.

A MC-400 Lake/Shelf Multi-corer (Ocean Instruments, San Diego, CA, USA) was used to collect the cores. The corer takes four replicate cores and is designed to collect the flocculent material at the sediment–water interface. If the cores showed any evidence of disturbance, a new set of cores was taken immediately. The cores for elemental analyses (e.g., Hg) and ^{210}Pb were sectioned immediately after collection at 0.5-cm intervals for the top 8 cm of the core, and at 1-cm intervals for the remainder of the core. The core used for measurement of organics, including PAHs was sectioned at 1 cm intervals for the entire core. Sediments used for elemental analysis were stored in acid cleaned plastic bottles and for organic analysis in combusted glass bottles on ice in the field and frozen upon return to the lab until analyses. Due to the limited quantity of sediment (i.e., 10 g dry weight) for analysis collected in each section of the core from certain lakes, sections were combined by taking equal amounts of sediment from several layers.[25]

Sediment samples for Hg analysis were stored frozen until being freeze-dried prior to microwave-assisted HNO_3 digestion using EPA Method 3051. Quantification of Hg was performed by use of an Ohio Lumex Hg Analyzer according to EPA Method 7473. Procedural blanks were analyzed with each digestion batch. Concentrations of Hg in procedural blanks were consistently lower than the quantification limit (MDL) of the analytical method (HgMDL = 0.69 ng/mg). Calibration verification was performed using NIST SRM 1633b or SRM 1515 and a separate NIST SRM was performed every 10 samples. ^{210}Pb was measured (Freshwater Institute in Winnipeg, Manitoba, Canada) to determine porosity, accumulated dry mass, sedimentation rates, sediment ages and focusing factors. Results from analyses of ^{210} Pb were verified in selected lakes using ^{137}Cs and ^{206}Pb (stable Pb). The US EPA's 16 priority PAHs were identified and quantified by use of gas chromatography-mass spectrometry. Sediments for organics analysis were Soxhlet extracted then treated with activated copper. Extracts were passed through 10 g of activated Florisil (60-100 mesh; Sigma, St. Louis, MO) and the fraction eluted with 100 mL of 20% dichloromethane in hexane and then concentrated. Total concentrations of PAHs calculated by the sum of 15 PAHs. Recoveries of PAHs in spiked blanks and spiked matrix ranged from 75.8±4.9% to 114.3±8.2% and from

Table 1. PAH compounds measured and abbreviations.

Mass	**Compound**	**Abbreviation**
152	Acenaphthylene	Ayl
154	Acenaphthene	Aen
166	Fluorene	F
178	Phenanthrene	Ph
	Anthracence	An
202	Pyrene	Py
	Fluoranthene	Fl
228	Chrysene	Ch
	Benz[*a*]anthracene	BaA
252	Benzo[*b*]fluoranthene	BF
	Benzo[*j*]fluoranthene	BF
	Benzo[*k*]fluoranthene	BF
276	Benzo[*ghi*]perylene	BghiP
	Indeno[1,2,3-*cd*]pyrene	IP
278	Dibenz[a,h]anthracene	DhA

60.8±1.1% to 120.9±9.1%, respectively. Recoveries of surrogate standards added to all samples were 109.3±9.8% for PCB-30, 104.8±10.9% for PCB-65 and 78.2±22.4% for PCB-204, respectively. Detection limits of individual PAHs were 0.01-0.02 ng/g sediment, wet mass. Results of PAHs are reported here as ng/g dry weight. Total concentrations of PAHs (ΣPAH) is defined here as the sum of all 15 US EPA priority PAHs (Table 1).

Since the core used for quantification of PAHs was not sectioned at the same intervals as cores in which ^{210}Pb was used to establish dates of sedimentation for the organic core were estimated by calculating the local polynomial regression of depth versus age using the *loess* command in the statistical package R.[40] Concentrations of Hg were then estimated by interpolation using the estimated dates from the regression analysis. Depending on the conditions of the lake, one of three models were used to date the sediments, the constant flux, constant sedimentation rate model (CF:CS) and a modification of this method, the segmented SCF:CS, and the constant rate of supply model (CRS).[39] Deeper sediment that lacked of excess ^{210}Pb could not be dated by this technique. Both cores had samples below the presence of excess ^{210}Pb and dates for these sediments were estimated by extrapolation, using the assumption that sedimentation rates remain constant below this depth. For the SCF:CS and CF:CS models, the sedimentation rate in the lower portion of the core was used to extrapolate dates. For the CRS model, the average sedimentation rate in the last five samples was used.[38]

3.0 Results and Discussion

3.1 Patterns of PAH and Hg.

Lakes chosen for this study (Fig. 1) have a moderately high correlation (Pearson's r > 0.7, Table 2) between ΣPAH (ng/g) and Hg (mg/kg). This might be an indication of a common source for these contaminants. The pattern of peak and surficial ΣPAH loosely follows the South to North industrialization and population trend, a pattern which was also found for peak lead (Pb) concentrations for this region.[39] The years of the peak concentrations of ΣPAH vary more than those for Hg. The variation in the peak concentration years has been previously reported for sediments from inland lakes in Michigan.[25] Greater concentrations in surficial and peak ΣPAH concentrations in two lakes, Muskegon and Otter, suggest a more local than regional source, which was also observed for Pb[39] (Table 2). Concentrations of peak and surficial ΣPAHs were greatest in Otter and least in Avalon Lake. The year of the peak concentration of ΣPAH occurred earliest in Avalon, 1915, and Round lakes, 1929, whereas peak concentration was observed in the surficial sediments of Crystal Lake. The timing of peak ΣPAHs in Avalon and Round were not consistent with the peak in atmospheric deposition described by others[19, 21, 41, 43]; peaks in ΣPAH near the turn of the last century have been attributed to burning of wood, including forest fires and home heating.[41] Crystal Lake showed a peak concentration in the middle of the last century which was consistent with an anthropogenic combustion source, but had greater concentrations in the surficial sediment which may be evidence of newer sources.

Table 2. ΣPAHs (ng/g dry wt) and Hg (mg/kg dry wt) concentrations in the surficial sediments and their peak concentrations and year of the peak. The first column shows the Pearson's correlation coefficient between Hg and ΣPAH. Lakes are arranged from a north to south gradient (Fig. 1).

Lake	r	ΣPAHs (surficial)	ΣPAHs (peak)	ΣPAH Peak Year	Hg (surficial)	Hg (peak)	Hg Peak Year
Round	0.92	1888	1977	1929	0.17	0.18	1929
Avalon	0.75	949	1612	1915	0.050	0.052	1971
Muskegon	0.70	2844	4663	1978	0.16	0.37	1973
Crystal	0.90	1707	1707	2006	0.082	0.084	1990
Otter	0.76	3323	8046	1958	0.12	0.25	1960
Birch	0.86	1224	2093	1957	0.068	0.095	1977
Sand	0.92	1849	2932	1982	0.095	0.12	1988

The year of peak concentrations of ΣPAH corresponded to the year of peak concentration of Hg in Round Lake. Muskegon, Otter and Sand lakes had peak ΣPAH years similar to that of Hg; whereas, in Avalon, Birch and Crystal lakes, peak concentrations of ΣPAH and Hg did not occur in the same year. Concentrations of Hg in surficial sediments were least in Avalon and greatest in Round and there was a positive correlation between concentrations of Hg and ΣPAHs in surficial sediments. Lakes with greatest PAH and Hg concentrations tend to be located near urban centers of the State; Muskegon near the City of Muskegon, Otter near the City of Flint, and Sand near the City of Detroit. The exception being Round, located in the Michigan's Upper Peninsula, which could be described as a remote lake lacking significant urban development other than sparse shoreline housing.

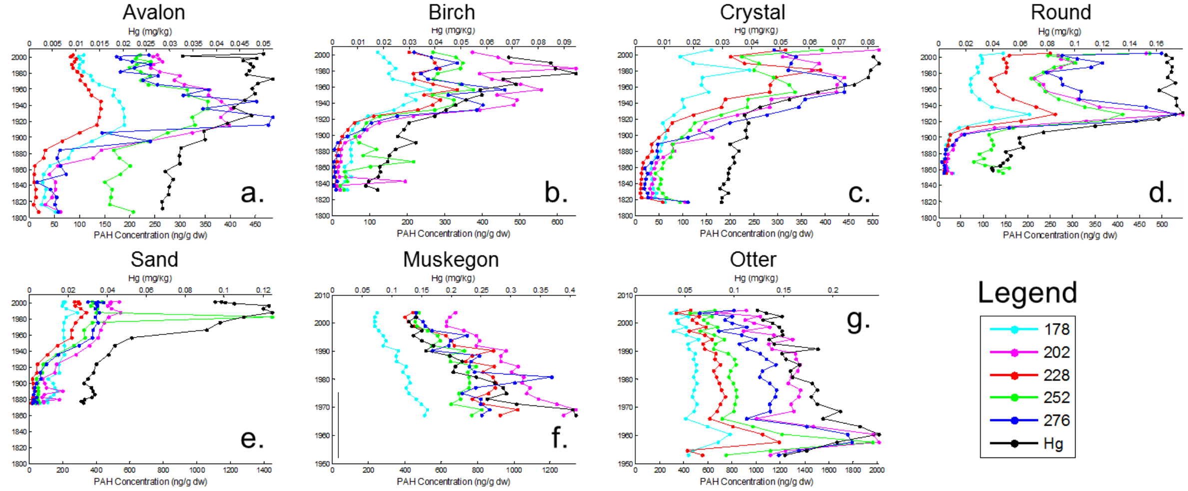

Figure 2. Concentration profiles of Hg and PAH isomer groups for lakes a. Avalon, b. Birch c. Crystal, d. Round, e. Sand, f. Muskegon, and g. Otter Lake.

Concentrations of benzofluoranthenes were greatest in the late 1800s and early 1900s in Avalon, Birch, Crystal and Round lakes (Figs. 2a, b, c, d). This is in contrast to what has been found for the Fraser River Basin[22] where the mass 178 and 202 PAHs were greatest. This might suggest a petrogenic origin for the mass 252 PAHs to these lakes.[44] In Sand Lake (Fig. 2e) mass 178 and 202 were greater than the other PAHs which is consistent with the burning of grass, hardwood and softwoods[45, 46, 47] Masses 228 and 276 were for the most part the least prevalent PAH prior to 1900 in all lakes which, a reflection of the lack of petroleum combustion in the region at the time.[21]

After the turn of the last century to the present the masses 202, 252 and 276 PAHs were dominant in most lakes. In Avalon, Round and Sand lakes all three of these mass groups were elevated to near equal concentrations after their respective peaks (Avalon and Round) or after 1940 (Sand). Mass 202 was greater after the ΣPAH peak in Avalon and after 1920 in Sand Lake; whereas, mass 276 was greatest among PAH mass groups after ca. 1920 in Round Lake. Birch was similar to Avalon and Sand lakes, but mass 202 was clearly the major constituent after the peak in ΣPAH around ca. 1960. During the mid-century ΣPAH peak, 1950-1970, the masses 202 and 276 were dominant in Crystal Lake. The mass 202 PAHs were the major constituent in Muskegon and Otter throughout the entire core (Figs. 2f & 2g, respectively). Profiles of PAHs from the Strait of Georgia also showed mass 202 to be the major constituent[21] and is associated with sources from urbanized or industrialized areas.[44, 48] These sources include the burning of gasoline, diesel and coal, which have also been shown to be important sources for masses 202, 252, and to a lesser extent 228 and 276.[49. 50, 51]

The significant correlation between concentrations of ΣPAH and Hg in these lakes implies a common source for both contaminants. However, there are several instances of coincident increases and decreases that can be either unique or shared among the PAH mass groups. In Avalon Lake the slight increase in concentrations among all mass groups during the mid-1990s might be related to the coincident increase in concentrations of Hg during the same period. Curiously, Hg does not peak until more recent times, ca. 1970, in Avalon while those of the PAH mass groups peaked much earlier, ca. 1920, and have since declined. The Huron

Portland Cement Company started near the town of Alpena (located about 20 miles to the east of Avalon Lake) around the turn of the 19th century and by 1910 was the largest cement plant in the world.[52] Cement kilns have long been recognized as contributors of Hg to the environment[53], that combined with the increased demand for cement due to the construction of the first concrete roads in Michigan[54] could be a likely reason for the earlier than expected peak of PAHs in Avalon Lake. In Birch Lake the peak of Hg in ca. 1980 followed by decreases until the present is mimicked by most PAH mass groups. The trajectory of increase in Hg after 1920 in Crystal Lake closely resembles that of PAH mass groups 202 and 276 than the other groups. This would be consistent with an urbanization of the watershed and the combustion of grasses for the clearing of agricultural land.[45,46,47] Whereas the increase in Hg between 1830 and 1890 more closely resembles the increases in masses 252 and 202. Profiles of Hg from Muskegon and Otter lakes (Figs. 2f & 2g, respectively) resembles all of the PAH masses suggesting a common influence for all mass groups and Hg. In Round Lake the profiles of Hg and the PAH masses were quite similar from 1860 until the 1920s when Hg becomes nearly constant.

3.2 Ratios of PAH Compounds.

The ratio of PAH compounds are used to identify sources. However, their use as a diagnostic tool to differentiate sources can be confounded by differences in volatility, water solubility, and adsorption.[35] These attributes can cause differential environmental transport and thus alter ratios. To deal with this phenomenon researchers generally limit studies to PAHs with multiple compounds with interpretive support using multiple ratios.[21, 22, 33 ,] The compound ratios compare the least stable, or kinetic, isomer to the more stable, thermodynamic, isomer. When combustion sources are predominant the least stable isomer is enhanced[5] thus, the PAH mass groups with the greatest range in stabilities between the compounds that have more potential to differentiate between petroleum and combustion sources.[22] The PAH molecular masses with the greatest range of stability, in order of most potential for discrimination to least, are 276, 202, 252 and 178.[22] Examples of specific compound ratios include the following. A ratio of anthracene to phenanthrene plus anthracene (An/178) less than 0.1 indicates a dominance of petroleum, e.g., naturally occurring oil seeps or unburned gasoline, while ratios greater than 0.10 indicates combustion processes.[22] Fluoranthene to fluoranthene plus pyrene (Fl/Fl + Py) less than 0.40 indicates petroleum, a value between 0.40 and 0.50 reflects liquid fossil fuels and ratios greater than 0.50 are characteristic of grass, wood or coal combustion. Ratios of Benzo[a]anthracene to benzo[a]anthracene plus chrysene (BaA/228) tend to be less than 0.20 for petroleum sources, between 0.20 and 0.35 can indicate petroleum or combustion sources, and greater than 0.35 for combustion sources. Values of the indeno[1,2,3-cd]pyrene to indeno[1,2,3-cd]pyrene plus benzo[ghi]perylene (IP/IP + Bghi) ratio less than 0.20 are likely representative of petroleum whereas those values greater than 0.5 imply grass, wood and coal combustion, while those values in between 0.20 and 0.50 are characteristic of liquid fossil fuel combustion.

Prior to ca. 1930 Avalon, Birch and Sand lakes showed a predominance of petroleum sources (Figs. 3a, b, c); whereas, Crystal and Round (Figs. 3d, and 3e, respectively) lakes

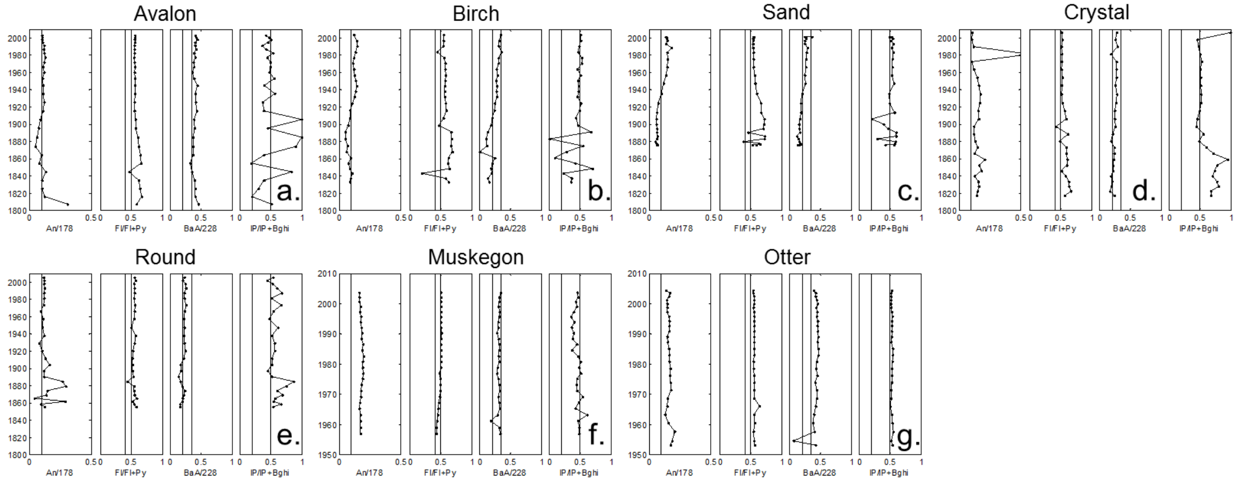

Figure 3. Selected PAH compound ratios for lakes a. Avalon, b. Birch, c. Sand, d. Crystal, e. Round, f, Muskegon, and g Otter.

showed influence from combustion sources as indicated by the An/178 ratio. Muskegon and Otter (Figs. 3f and 3g, respectively) lakes show evidence of only combustion sources, likely due to the short time period covered by the sediment cores and industrial sources within proximity of these lakes. The Fl/Fl+Py ratio reveals grass/wood/coal combustion for nearly all sediment slices in all lakes except for Muskegon where petroleum combustion was found to be important prior to the early 1980s while afterwards a predominant source could not be identified. In Birch, Crystal, Round and Sand lakes the ratio of BaA/228 is lower at the base of the sediment cores, indicative of petroleum sources, then increases towards petroleum combustion ratios between 1880 and 1900 except for Sand Lake where the transition was later, ca. 1930. Conversely in Avalon Lake, the BaA/228 ratio suggests combustion sources throughout much of the core. In Otter Lake a combustion source was identified for the entire core; whereas a mixture of petroleum and combustion sources was found for Muskegon Lake. The sources indicated by the ratio of IP/IP+Bghi were mixed between grass/wood/coal combustion and petroleum combustion. In Crystal, Round and Sand lakes the older portions of the core are characterized by grass/wood/coal combustion sources. Round and Sand showed grass/wood/coal combustion important recently in contrast to Crystal which like Muskegon Lake was dominated by PAHs from combustion of petroleum. Avalon and Birch lakes IP/IP+Bghi ratios varied between petroleum and grass/wood/coal combustion source. Conversely, Otter Lake seems dominated by grass/wood/coal combustion.

In Avalon Lake ratios of Fl/Fl+Py and IP/IP+Bghi in sediments do not indicate the same source for PAHs. The Fl/Fl+Py ratio can be interpreted as being from a combustion source which is consistent with the PAH profile plots that revealed the cement plant in Alpena as the most likely source for both Hg and PAHs. The conflict then is likely a result of sources mixing.

Flouranthene can be enriched in particulate transported long distances[31] resulting in the higher Fl/Fl+Py ratios observed in Avalon Lake while the more local source of IP would be from the combustion of petroleum products, possibly the power generating station located due west of the lake (Fig. 16) which combusts natural gas or local vehicle traffic. . Although both natural gas combustion and cement production are sources of Hg it is likely that cement production would be more dominant in this case since the IP/IP+Bghi ratio hovers between petroleum and biomass combustion and the Fl/Fl+Py clearly indicates biomass combustion. The cause for the decoupling of the Hg profile from that of the PAH profile is unclear. Decreases in PAH could be a result of decreased demand for cement coupled with new sources of limestone or coal fly ash used in the production that had a higher Hg content resulting in further increases of Hg between 1920 and 1980.

The cause of concurrent peaks of Hg and PAHs in the sediments of Birch Lake in the 1990s could not be clearly identified using indicator ratios or profile plots. However, similar to Avalon Lake, PAH ratios do not indicate the same source. The ratio of Fl/Fl+Py indicates a combustion source while that of IP/IP+Bghi varies between petroleum product sources and biomass combustion. The mixture of sources is confirmed by the BaA/228 ratios which transition from petroleum deep in the core towards combustion and petroleum sources coincident with the stabilization of the Fl/Fl+Py and IP/IP+Bghi ratios. Since Birch Lake is located in a highly agricultural landscape it is likely that the combustion source identified by the increased Fl is from the increased combustion of coal from the greater Chicago, IL/Gary, IN area. The State Line Power Plant along the Indiana/Illinois border, to the southwest of Birch Lake, was built in the 1920s[56] concurrent with the transition of the An/178 ratio from petroleum to combustion and a change in the rate of Hg increase. During the peak of PAHs in the late 1980s into the 1990s mass group 202 and 252 are dominant consistent with results found for areas downwind of industrialized and urbanized areas.[21]

In Crystal Lake between 1820 and 1880 the Fl/Fl+Py and IP/IP+Bghi ratios indicate biomass combustion, consistent with the burning and clearing of forest that occurred in this region.[38] After about 1930, both of these indicator ratios become stabilized near the ratio discriminating between petroleum and biomass combustion. This is likely the result of sources mixing since Crystal Lake is within close proximity of several natural gas consumers and immediately east of several coal fired power plants (Fig. 4).

Muskegon Lake is located within a large metropolitan area and has a coal fired power plant, along with other industrial activities, on its shoreline. It might be assumed that PAH compound ratios would be dominated by a coal signal. However, the Fl/Fl+Py and IP/IP+Bghi ratios both indicated petroleum combustion as the dominant source rather than coal. Ratios indicating petroleum combustion could be due to a vehicular source which would be likely for this urbanized region; vehicle emissions were found to contribute just under 10% of PAH load to southern Lake Michigan[24] but, it is unlikely that a vehicular source could result in the concentrations of Hg in the lake sediments.[20] Therefore, a potential source

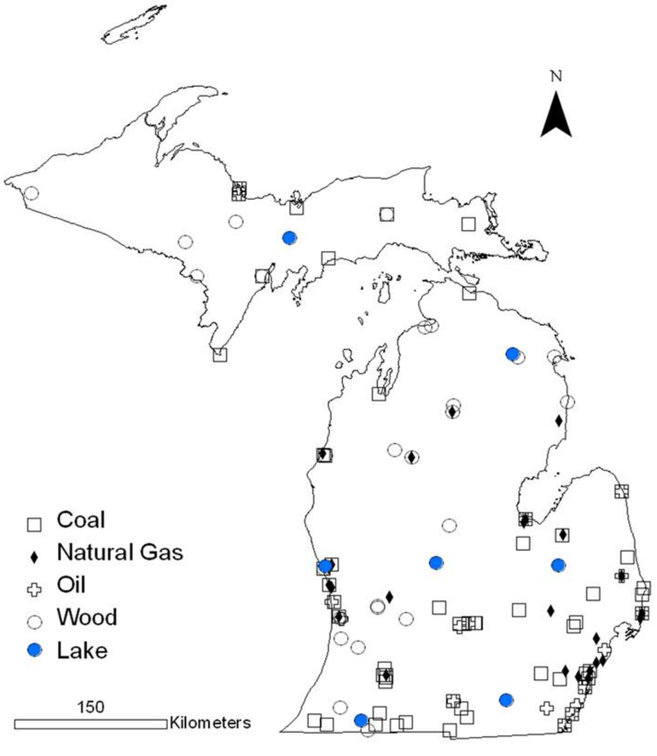

Figure 4. Industrial and utility energy emitters according to the 2002 Mercury Emissions Inventory for the State of Michigan.

could be the natural gas and fuel oil electricity generating stations located in southeast Wisconsin, about 90 miles west and west-southwest of Muskegon Lake, for example the Milwaukee County Power Plant has burned natural gas or #2 fuel oil for electricity generation since 1970.[57]

The compound ratios from Otter Lake reveal a dominant source for PAHs from biomass combustion. Mercury and PAHs concentrations are highly correlated suggesting a common source for these contaminants; the proximity of Otter Lake to the coal fired power plants (Fig. 16) combined with compound ratio data could indicate a common source, the combustion of coal for power production.

In Round Lake, ratios of Fl/Fl+Py and IP/IP+Bghi indicate a biomass combustion source throughout much of the core. Combustion sources in this area would likely be limited to the burning of grasses and forests prior to 1900. Round Lake, located in the middle of Michigan's Upper Peninsula, is not currently in close proximity to any industrial sources (Fig. 4). A major industrial activity in Upper Peninsula is mining; however, most historic mining related activities have been located to the northwest on the Keewenaw Peninsula. The town of Fayette, approximately 80 km south of the lake, would have been the closest industrial source. Located on the shores of Little Bay De Noc between 1867 and 1891, Fayette was a major iron ore smelter and used local timber to fuel the process.[58] The peak of Hg and PAHs occurred during the late 1920s into the 1930s, similar to Avalon Lake. And much like Avalon the higher mass PAHs were predominant during the peak. This would be consistent with a biomass combustion source[21] during the industrial period of the town and until recent times. PAH compound ratios tend to show biomass combustion after about 1900, which may be an indication of the mining related activities occurring in Michigan's Upper Peninsula at the turn of the last century or the clearing of forests for agriculture or timber. The Hg profile was similar to those of the PAHs until the peak and then became decoupled. The decoupling occurs at the time of decline in the mining industry, due to the economic factors and maturity of the mines in the region. Compound ratios after the peak ca. 1920 are consistent with the combustion of biomass (e.g., coal) a likely source for Hg to Round Lake.

Sand Lake is located near the metropolitan area of Detroit, Michigan, the most populated area of the State. Prior to 1900 Fl/Fl + Py and IP/IP + Bghi ratios in the sediment indicate biomass combustion, consistent with biomass burning during intense clear cutting of forests. Mercury also shows an increase prior to 1900 which is likely due to erosion of forest cleared watersheds.[38] After 1900, Hg and PAH start to increase which is most likely due to installation of the cement kiln in Cement City due west of Sand Lake (Fig. 1). The kiln was shut down in the early 1960s.[54] After ca. 1940, the ratios of Fl/Fl + Py and IP/IP + Bghi were consistent with a biomass combustion source. The predominance of the mass group 202 after 1920 suggests burning of vegetation; although it is usually accompanied by the mass group 178.[45,46,47] The presence of the mass group 202 may be related to the use of marl at the Cement City cement manufacturer, which would contain remnants of grasses and softwoods washed in from the marl source watershed. The slope of Hg and PAH concentration profiles are similar between 1900 and 1950. After 1950, concentrations of both contaminants continue to increase; however, Hg does so at a much greater rate. This might be due to the decommissioning of the cement kiln and commissioning of 2 major coal-fired power plants to the east of Sand Lake in the City of Detroit. The coincident peak and decline of Hg and PAH in the 1980s and 1990s implies a common source or influence and would be consistent with the implementation of abatement technologies required by the Clean Air Act.

4.0 Conclusions

Sediment chronologies of contaminants are related to activities within the watershed and atmospheric sources that could be located within or outside of the watershed. This makes the identification of sources challenging since the concentration recorded in the sediment profile contains potential information from all sources. Production/consumption records compared to sediment Hg chronologies have been successfully used by others to assign the source for Hg to lakes.[12,,58] This work compliments those studies and helps to confirm sources identified using production/consumption methods. An advantage to the approach in this study versus production/consumption record is the identification of historic sources of Hg which may have not been identified using for example the cement kiln influence to Avalon and Sand lakes, and mining related activity to Round Lake. Modern coal combustion sources were found to be significant for lakes in the southern portion of the State and in some cases could be correlated to plant start-ups (i.e., Birch Lake). A coal combustion source could not be identified for Muskegon Lake, which has a coal-fired power plant on its shoreline suggesting that the Hg emitted from this source might not be deposited on an extremely local scale, i.e., miles. This approach has demonstrated that sources for PAHs, both historic and modern, to inland lakes throughout the State of Michigan vary by locale, implying more local to sub-regional scale sources for these contaminants. Assuming that PAHs and Hg share common sources and pathways, and that the compound ratios of PAHs can be used as proxies for Hg sources, then local to regional scale sources of Hg can be identified which has important implications for legislation seeking to limit the release of Hg to the environment

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