# SPATIAL AND TEMPORAL TRENDS OF POLYCYCLIC AROMATIC HYDROCARBON LOADINGS TO INLAND LAKES IN MICHIGAN

By

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#### ABSTRACT

## SPATIAL AND TEMPORAL TRENDS OF POLYCYCLIC AROMATIC HYDROCARBON LOADINGS TO INLAND LAKES IN MICHIGAN

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Previous work by Kannan et al. (2005) on sediment cores from inland lakes in Michigan have identified that with the use of indicator PAH compounds, major PAH sources of loading can be interpreted. In the study by Kannan et al. (2005) a major source of PAH emissions dominated the period 1940 to 1980, after the 1980s the influence of this source lessened. The underlying hypothesis in this study is that PAH loadings will be highest during the time period 1940 to 1980 (peak emission period) dominated by a common regional source. Post 1980, loadings will decrease. If the hypothesis is true, then, during peak emissions (1940-1980) a peak should be evident in PAH concentration profiles, PAH loading patterns should be highest in the south and lowest in the north, and PAH fingerprints amongst the lakes should be similar indicating a regional signal; and post 1980s PAH fingerprints amongst the lakes should be dissimilar indicating local watershed influences. The results were not consistent with the hypothesis, though some loading patterns were observed. Expected PAH fingerprints from cluster analysis were found to be dissimilar in all time periods. PAH concentrations were unexpectedly found to be increasing in some lakes in the recent, indicating a new source of PAH loadings despite environmental legislation; leading to a question as to what is the cause(s) of this unexpected increase. Specifically the hypothesis tested is that this recent increase in PAH loadings is related or attributable to the use of coal tar sealants, based on a hypothesis offered by Van Metre and Mahler (2010). The results were found to be inconsistent with this hypothesis, as sourcing methods did not indicate coal tar sealants as a viable source at this time.

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## TABLE OF CONTENTS

| LIST OF TABLES.                                     | V  |
|---|----|
| LIST OF FIGURES                                     | vi |
| CHAPTER 1: SPATIAL AND TEMPORALING LOADINGS OF PAHS | 1  |
| INTRODUCTION  | 1  |
| METHODOLOGY   | 9  |
| RESULTS   |    |
| PAH Temporal Concentration Analysis                 | 12 |
| PAH Inventory Analysis                              | 15 |
| PAH Temporal Sediment Accumulation Rate Analysis    | 20 |
| PAH Compound Cluster Analysis                       | 26 |
| DISCUSSION  |    |
| CONCLUSION  |    |
| CHAPTER 2: PAH SOURCING.                            |    |
| INTRODUCTION  | 35 |
| METHODOLOGY   | 43 |
| RESULTS AND DISCUSSION                              | 45 |
| Ratios of PAH Compounds                             | 45 |
| Factor Analysis of the PAH Compounds                |    |
| Comparison to Percent Land-use                      | 51 |
| PCA of known PAH Source fingerprints                | 53 |
| CONCLUSION  |    |
| APPENDIX  | 57 |
| BIBLIOGRAPHY  | 64 |

## LIST OF TABLES

| Table 1. PAH compounds, their corresponding abbreviations and masses and   classification as to being low or high molecular weight   |
|--|
| Table 2. PAH ratio values are shown for several different PAH ratio source methods.Also the range of values for each sources are presented. The values in red indicate whichsource range the results correspond with |
| Table 3. PAH compound tracers as formulation from A. Moteley-Massei et al. (2007)48  |
| Table 4. Factor Analysis of PAH compound concentrations for each significant timeperiod of PAH loadings  |
| Table 5. Percent Land-use Factor Analysis shows no distinct correlations regarding land-use and sources. The red values are those that were used as PAH compound tracers to estimate the sources                     |
| Table 6. PAH source fingerprint concentration ratios, based on study by Van Metre and<br>Mahler (2010)   |
| Table 7. PCA of PAH compounds and known source fingerprints  |
| Table 8. Lakes Sampled and their corresponding dates and concentrations (ng/g)   |

## LIST OF FIGURES

| Figure 1. 16 priorities PAH compounds, the asterix indicating the seven that are probable human carcinogens   |
|---|
| Figure 2. Locations of 29 inland lakes in Michigan that have been sampled, by extraction of a sediment core, for the MDEQ Inland Lakes Sediment Trend Monitoring Program  |
| Figure 3. Temporal PAH concentrations based on the peak PAH concentration during the time period 1940-1980  |
| Figure 4. Temporal PAH concentration based on a definite increasing trend to the recent; post 1970  |
| Figure 5. Graph showing PAH inventories of selected Michigan inland lakes latitudinal arranged from south to north. PAH average inventories for lakes Superior and Michigan (Eisenreich et al., 1989) are shown for comparison  |
| Figure 6. Spatial Dataset of PAH Inventories  |
| Figure 7. Spatial Dataset of PAH Inventories A) base – 1940, B) 1940-1980, and C) 1980-recent   |
| Figure 8. 1900 PAH Accumulation Rates for all lakes organized by latitude   |
| Figure 9. 1950 PAH Accumulation Rates for all lakes organized by latitude   |
| Figure 10. Recent (c. 2000) PAH Accumulation Rates for all lakes organized by latitude  |
| Figure 11. Temporal PAH accumulation rate (ng/cm2/yr), based on a definite increasing trend to the recent; after legislation was implemented, 1970  |
| Figure 12. Temporal PAH accumulation rate (ng/cm2/yr), based on a definite decreasing trend to the recent; after legislation was implemented, 1970  |
| Figure 13. Cluster analysis of compositional data for year (A) 1900, (B) 1950, and (C) recent (c.2000). Five clusters were extracted in each cluster analysis. For C there are three clusters, as shown above, that can be combined into one cluster. These three clusters show a variation trending SW to NE |
| Figure 14. Cluster analysis of log-ratio transformed data (A) 1900, (B) 1950, and (C) recent  |

| Figure 15. Modified County map of Michigan | showing population | density by color (U.S. |
|--|--------------------|------------------------|
| Census Bureau, 2000)                       |                    |                        |

## CHAPTER 1: SPATIAL AND TEMPORAL LOADINGS OF PAHS INTRODUCTION

Polycyclic aromatic hydrocarbons (PAHs) are a group of naturally occurring, chemically related compounds. PAHs consist of two or more fused aromatic rings and are products of incomplete combustion of organic materials, including fossil fuels. PAHs are released into the environment by both natural and synthetic sources, entering the terrestrial environment by atmospheric deposition, terrestrial runoff or through direct discharge from the source of contamination. Concentrations of PAHs can be found in the air, water and soil throughout the world (Neff, 1979). These organic contaminants are very stable and do not degrade easily in the environment making them ideal environmental tracers of contamination (Van Metre and Mahler, 2005). Their persistence and environmental stability has been observed to increase with increased molecular weight and angularity of the compound (Nagpal, 1993; Kanaly and Harayama, 2000).

Many PAHs have been identified as toxic, mutagenic and carcinogenic (Yang et al., 2010). It has been recognized that predominantly high molecular weight compounds (4, 5, and 6 ring PAHs) have a greater risk for carcinogenicity (Kanaly and Harayama, 2000). There are 16 commonly named PAH compounds by the United States Environmental Protection Agency (US EPA) as shown in Figure 1. These compounds are the most commonly found and have the greater risk of human exposure (ATSDR, 1995). Seven of which are considered probable human carcinogens: benzo(a)pyrene, benzo(a)anthracene, benzo(b)fluoranthene, benzo(k)fluoranthene, indeno(1,2,3-cd)pyrene, dibenzo(a,h)anthracene, and chrysene (NTP, 2005).



Figure 1. 16 priorities PAH compounds, the asterix indicating the seven that are probable human carcinogens.

Environmental legislation has been implemented specifically to reduce emission sources of such contaminants (e.g., Clean Air and Water Acts, US EPA, 2012). This study attempts to determine how the atmospheric loadings of PAHs have responded to these regulations, not only in terms of temporal changes in loading but also in terms of patterns of loadings across the region.

Lake sediments act as sinks for many contaminant chemicals (e.g. Hg, PAHs and PCBs) because of their environmental persistence and hydrophobicity (Blais and Muir, 2001). Contaminants sorb to particulates, the particulates settle out and are deposited at the bottom of the lake. Therefore lake sediments archive the historical loading record of contaminants. These sediments record both atmospheric and surrounding watershed inputs, differentiating between these two inputs remains an issue. Much of the existing research, including collected and dated sediment cores, use measured *total* PAH concentrations at different depths of the cores which can be used to construct temporal profiles of PAHs and other contaminants (Muir et al, 1996; Golden et al, 1993; Eisenreich et al., 1989).

Previous work in the Great Lakes have shown that atmospheric deposition is the major pathway for PAH loadings, particularly for the upper Great Lakes region (Simcik, 1996; Simcik, 1999). Their approach, studies the spatial patterns of PAH concentrations, accumulation rates and inventories using Great Lakes sediments. Results of this research revealed regional depositional gradients. For example, Lake Michigan was shown to have a decreasing depositional gradient from south to north, likely linked to their proximity to major urban/industrial sources in the Chicago, IL and Gary, IN area (Simcik et al., 1996). A similar study conducted by Simcik (1999) on PAH distribution in Lake Michigan revealed that PAH accumulation began in lake sediment in the period 1880-1900. PAH concentrations were also shown to peak between 1950 and 1975 and decline in recent sediment. This decrease was attributed to regulations limiting atmospheric emissions and the switch from coal to oil and natural gas as the primary fossil fuels used for heating and electricity (Simcik et al., 1999).

The peak in PAH concentrations, c.1950, was also observed in other studies of the Great Lakes (Kannan et al., 2005), the United States (Van Metre et al., 2000), and internationally (Liu et al., 2005; Liu et al., 2012; Boonyatumanond et al., 2007). A number of locations (e.g., the northern Great Lakes, Ashtabula River in Ohio, Scotland, a small rural lake in Cambria UK, and Tokyo Bay Japan) revealed a gradual decrease in PAH concentrations after c.1970 (Simcik et al., 1996; Li et al., 2001; Rose et al., 2001; Gevao et al., 1998; Yamashita et al., 2000; Schneider et al., 2001) similar to those observed in Lake Michigan (Simcik et al., 1996; Simcik et al., 1999). After the 1970s and 1980s, decreases in the amount of environmental PAH loadings have been directly attributed to the decrease in transportation related air emissions in the United States (Van Metre et al., 2000; National Air Quality, 1996), but it should be noted that there are increases in other vehicular related PAH sources (e.g. asphalt wear, tire wear, etc.) (Van Metre et al., 2000; Li et al., 2001; Bzdusek et al., 2004; Dickhut et al., 2000).

Several recent studies have shown that the lake sediment record at some locations in the Great Lakes show an increase in PAH concentrations to the present (Van Metre et al., 2000; Lima et al., 2003; Liu et al, 2012). This increase in PAH concentration in these lakes has been correlated to proximity to urban areas, and areas with increasing population density (Kannan et al., 2005; Van Metre et al., 2000). However, given that other studies show urban areas have maintained a stable concentration of PAHs (e.g. Van Metre et al., 2000), urbanization is not likely the only source for PAH loading to the environment. For example, one research group has linked PAH concentration in recent sediments to the increased application of coal tar sealant on roadways and parking lots (Mahler et al., 2003; Mahler et al, 2005; Van Metre and Mahler, 2010).

Kannan et al. (2005) identified PAH compounds in sediment cores from inland lakes across the state of Michigan. They found that during the time period 1940-1980 a common set of PAH compounds (fluoranthene, pyrene, and benzo(k)fluoranthene) occurred in all of the cores. After the 1980s these specific compounds were not common amongst the lakes and that there was an increase in the concentration of benzo(a)pyrene in the lake sediments.

Kannan et al. (2005) interpreted these results to indicate that a major source of PAH emissions dominated the period 1940 to 1980, perhaps across the region and that the PAHs (fluoranthene, pyrene, and benzo(k)fluoranthene) were characteristic of coal/coke combustion. After the 1980s the influence of this source lessened, while an increase in the concentrations of benzo(a)pyrene was found possibly due to an increasing influence of vehicular emissions.

In sum, Kannan et al. (2005) showed the possible influence of dominant PAH sources and that these sources have changed over time, as indicated by the decreased presence of common PAH compounds. Their work did not examine the relative distribution of the other PAH compounds along with indicator compounds (e.g., fluoranthene, pyrene, benzo(k)fluoranthene, and of benzo(a)pyrene), that might better reveal similarities in PAH loadings amongst the lakes or relative differences in the spatial loadings of PAHs that might help to better identify sources. Other work on PAH loadings in the Great Lakes indicate gradients in PAH deposition on a regional scale (e.g., Simcik et al., 1996; Simcik et al., 1999). Therefore, driving questions for the present study include: 1) can a regional gradient in PAH loadings in the Great Lakes be identified, 2) how have these loadings changed over time, and 3) is there more commonality in the types of PAH compounds (e.g., PAH fingerprints) amongst the lakes than just the indicator compounds (e.g., fluoranthene, pyrene, benzo(k)fluoranthene, and of

benzo(a)pyrene). Answers to these questions might help us to better understand sources (e.g., regional and local watershed or sub regional scales).

Results of several studies examining PAH loadings to surface water bodies (e.g., Simcik et al., 1996; Simcick et al., 1999; Kannan et al., 2005) allow for the formulation of the hypothesis that PAH loadings will be the highest during the 1940 to 1980 time period (peak emission period) with a common regional source dominating these PAH loadings. Post 1980, loadings will likely decrease. A lessening of dominant regional sources will be apparent and the influence of local watersheds will be seen. Following these assumptions, a regional depositional gradient of PAH loadings will be expected during the dominant loading period (1940-1980) with the highest loadings observed in the south and lower loadings in the north. Post 1980s, corresponding with the reduction of PAH emissions, a decrease in the south to north gradient of PAH loadings (e.g., concentrations and accumulation rates) is anticipated.

To test these hypotheses, spatial and temporal patterns of PAH loadings (inventories, accumulation rates, concentrations, fingerprints) are compared amongst selected inland lakes across the State of Michigan. The state of Michigan occupies a relatively large footprint in the Great Lakes region and thus results from this study can be used to help understand influences on and changes in PAHs in the Great Lakes region. In addition, the state is spatially located with lakes Michigan and Superiors. Thus the inland lakes data can be compared to these large lakes furthering insights into PAH loadings.

If the hypothesis is true, then, during peak emissions (1940-1980) 1) PAH sediment concentration profiles should peak, 2) PAH inventories and accumulation rates should be highest in the south and lowest in the north, and 3) PAH fingerprints amongst the lakes should be similar

(e.g., regional signal rather than local scale signals). Post 1980s to the recent, PAH fingerprints amongst the lakes should be dissimilar.

Cluster analysis will be used to construct PAH fingerprints. Cluster analysis is a method that can be used to observe patterns and compare contaminant loadings, it refers to a general category of algorithms designed to classify samples into groups of similar characteristics. Cluster analyses of individual PAHs have been used in several studies to delineate PAH sources (Dahle et al., 2003; Simcik et al., 1999). The most common type of cluster analysis is the hierarchical cluster analysis (HCA) which is an exploratory method that, used here, would involve calculations based on the similarity amongst the individual congener results of the sediment samples. The most common similarity metrics are based on distances calculated in multivariate space. When the distances are small, it is implied that there is greater similarity between all the present congeners representing two individual samples. Dissimilar samples will be separated by larger distances. A regional signal can be recognized by the similarity in the relative abundances (fingerprints) of individual PAH compounds among samples (i.e. lakes). PAH signals reflecting local inputs can be recognized by heterogeneity in the individual PAH concentrations in lake sediment in close proximity, both spatially and temporally. Interpretation of a regional signal assumes that the influence of well-mixed regional sources are more influential than that of local sources (e.g., greater percentage of the PAH loading), where each source has its own fingerprint composed of varying PAH compounds and their concentrations.

In this study, utilizing cluster analysis would hypothetically enable locations that have similar PAH fingerprints to be clustered together and spatial trends to be observed and compared to spatial trends of PAH inventories. Few studies have attempted to correlate trends of PAH loadings with accumulation rates, concentrations, and inventories; along with the use of cluster

analysis which enables the grouping of PAH compounds during relative time periods of importance (c.1900, c.1950, and c.2000).

## METHODOLOGY

Sediment cores have been collected from 47 individual lakes from 1999 to 2010 as part of the Michigan Department of Environmental Quality's (MDEQ) Inland Lakes Sediment Trend Monitoring Program. For this study, sediment from 29 lakes is analyzed to provide an adequate spatial dataset to observe temporal changes in the loadings of PAHs in conjunction with different land uses. The locations of the lakes sampled and used for this study are shown in Figure 2.

Sediment core extraction was conducted using an MC-400 Multi-corer modified for inland lake use, and deployed from the MDEQ M/V Nibi. The multi-corer has four sampling tubes of identical dimensions for sediment core extraction. Four replicate cores are collected from the deepest portion of each lake as determined by MDNR bathymetric maps (www.dnr.state.mi.us/spatialdatalibrary/pdf\_maps/inland\_lake\_maps) and on-board sonar. If evidence of disturbance during coring was present in the core sediment, new cores were collected. Upon retrieval of satisfactory sediment cores, sediment intended for <sup>210</sup>Pb and metals analyses were extruded and sectioned at 0.5 cm intervals for the top 8 cm, and at 1 cm intervals for the remainder of the core. The <sup>210</sup>Pb analyses were conducted by the Freshwater Institute in Winnipeg, Manitoba, Canada where porosity accumulated dry mass, sedimentation rates, sediment ages and focusing factors were determined. Dates of the cores were verified using <sup>137</sup>Cs, the temporal peak of the stable <sup>208</sup>Pb concentrations and presence/absence of excess <sup>210</sup>Pb. Samples from the second core were microwave acid digested and subsequently submitted for metals analysis to the Michigan State University Inductively-Coupled Plasma Mass Spectrometry (ICP-MS) Laboratory. The third core was submitted to the Michigan State University Aquatic Toxicology Laboratory for trace persistent organic pollutants (POPs), which included a suite of PAHs. This core was originally sectioned at 2 cm increments for the extent of the core length. However, insufficient mass of sediment required for the analysis was available at sediment core increments of 2 cm, so equal quantities of sediment were combined from 4 cm sections (2 samples) of the sediment core.



Figure 2. Locations of 29 inland lakes in Michigan that have been sampled, by extraction of a sediment core, for the MDEQ Inland Lakes Sediment Trend Monitoring Program.

Analytical methods used for the PAH analysis have been described elsewhere (Khim et al., 1999). Briefly, a total of 40 g of wet sediment was extracted for analysis. Moisture content

was determined by taking 5 g of the wet sediment and drying it overnight at 100°C. The dried sediment was Soxhlet-extracted with dichloromethane and hexane and treated with 120 g of anhydrous sodium sulfate. The extracts were passed through a Florisil column, and eluted with 10% acetone in hexane (9 mL). The extract was concentrated and injected into a gas chromatograph interfaced with a mass spectrometer for analysis of PAHs. The PAH standard consisted of 15 of the 16 priority PAH compound pollutants, excluding naphthalene, as identified by the U.S. EPA. The 15 priority PAH compounds that are used for this study include: acenaphthene, acenaphthylene, anthracene, phenanthrene, fluorine, fluoranthene, benzo(a)anthracene, chrysene, pyrene, benzo(b)fluoranthene, benzo(k)fluroanthene, dibenz(a,h)anthracene, benzo(g,h,i)perylene, and indeno(1,2,3-cd)pyrene.

## RESULTS

## PAH Temporal Concentration Analysis

Total PAH concentrations are analyzed in <sup>210</sup>Pb-dated inland lake sediment cores, temporally. Different lakes showed temporal variations in the peak PAH concentrations values, which range from the year 1934 to 1960. The peak PAH concentration year was approximated to 1950 (Figure 3). After this peak, most lakes exhibit a noticeable decrease in PAH concentration around 1970-1980. However, several of these lakes, following this decrease, show an observable trend of PAH concentration that is increasing to the present, shown in red (Figure 4).



Figure 3. Temporal PAH concentrations based on the peak PAH concentration during the time period 1940-1980.



Figure 4. Temporal PAH concentration based on a definite increasing trend to the recent; post 1970.

#### PAH Inventory Analysis

The PAH inventory is a calculation of the total mass of PAHs in the core per unit area. It is calculated as the sum of the mass of PAH in each sediment slice increment using the following equation:

$$Inv(ng/cm^{2}) = \sum_{i} [C_{sed}(ng/g) \times (1-\varphi) \times \rho(g/cm^{3}) \times d(cm)]$$

Where Inv = total PAH dry mass in a core (ng/cm<sup>2</sup>),

- C<sub>sed</sub> = sediment concentration,
- $\phi$  = porosity,
- $\rho$  = bulk density, and
- d = thickness of sediment increment.

Because the sediment cores are taken from the depositional zone or deepest portion of a lake, the sediment column is influenced not only by input from the atmosphere but also by the input of sediment, which is transported from the outside edges of the lake to the deeper portions (Golden et al., 1993). The latter is termed sediment focusing and affects the calculation of inventories and accumulation rates. The variation in the magnitude of the influence of sediment focusing among lakes precludes direct comparisons of sediment core data among lakes. In an attempt to reduce the influence of sediment focusing on the sediment record to afford comparisons amongst lakes, PAH inventories were corrected using a <sup>210</sup>Pb-determined focusing factor (FF). The FF is calculated by dividing the measured <sup>210</sup>Pb inventory by the expected <sup>210</sup>Pb inventory (0.574). This concept has been used in several studies of organochlorine inventories including those of eastern Lake Ontario sediments (Eisenreich et al., 1989) and Lake Superior sediments (Jeremiason et al., 1994). PAH inventories are divided by the FF for each lake to yield a focusing-corrected inventory. If the atmosphere was the only source for PAHs and

concentrations in the atmosphere were spatially the same, then the focusing-corrected inventories in all the lakes would be the same in a region.

The uncorrected and focusing-corrected inventories of Michigan inland lake sediment PAHs are compared to Lake Michigan and Lake Superior PAH inventories (Eisenreich et al., 1989) in Figure 5. In general, PAH inventories of the individual inland lakes correspond to the PAH inventories of the Great Lake that they are most proximal to. For example, the PAH inventories of the inland lakes in the Upper Peninsula (UP) correspond most closely with the average PAH inventory of Lake Superior. Likewise, the PAH inventories of the inland lakes in the Lower Peninsula (LP) most closely correspond to the average PAH inventory of Lake Michigan. This is clearly consistent with hypothesis that the atmosphere is the most prominent pathway for PAH loadings to the Great Lake region (Simcik, 1996; Simcik, 1999; IADN, 1997).

Examination of the changes in the inventories along strict latitudinal gradient (Fig. 5), as has been done in similar studies of other chemicals (e.g., PCBs) does not reveal a straightforward South to North gradient pattern. However, PAH inventories plotted spatially on a map of Michigan, based on subsequent ranges of their PAH inventory concentrations (Figure 6), reveals a South to North decreasing gradient of PAH inventory concentrations, trending Southwest to Northeast.



Figure 5. Graph showing PAH inventories of selected Michigan inland lakes latitudinal arranged from south to north. PAH average inventories for lakes Superior and Michigan (Eisenreich et al., 1989) are shown for comparison.

As mentioned Kannan et al., (2005) observed peak concentrations of PAHs occur during the 1940 to 1980 time period and a regional dominant source is suspected. To see if the pattern of PAH loadings changed prior to this period or following this period, the inventories were analyzed spatially at three different time periods 1) base of core-1940, 2) 1940-1980 3) and 1980-recent based on the time periods observed in Kannan et al. (2005) (Figure 7). The results of this analysis show that prior to 1940 there is no spatial trend apparent with only a few lakes revealing a higher inventory. In the period 1940 to 1980, a spatial trend is apparent, with inventories higher in the south and lower in the north. After the 1980s, the magnitude of the south to north trend decreased, with more influence by individual lakes.



Figure 6. Spatial Dataset of PAH Inventories.



Figure 7. Spatial Dataset of PAH Inventories A) base – 1940, B) 1940-1980, and C) 1980-recent.

#### PAH Temporal Sediment Accumulation Rate Analysis

The accumulation rate of PAHs is a calculation of the sedimentation rate of the sediment and the PAH concentration in the core per unit area. The accumulation rates of PAHs for each sediment slice were calculated as follows:

$$Accum(ng/cm^2/yr) = C_{sed}(ng/g) \times W(g/cm^2/yr)$$

where Accum= PAH accumulation rate  $(ng/cm^2/yr)$ ,

 $C_{sed}$  = sediment concentration,

W = mass sedimentation rate bases on  $^{210}$ Pb dating.

As with sediment PAH inventories, accumulation rates were focusing corrected (Accum/FF) to allow better comparison of accumulation rates amongst lakes and assess accumulation of PAHs from atmospheric input (Golden et al., 1993). Temporal changes in PAH accumulation rates were analyzed by observing accumulation rates during three time slices: 1900, 1950, and recent (c. 2000). These were chosen based on the results of PAH concentrations and inventories and observations of Kannan et al. (2005). The PAH accumulation rate values from the year 1900 are reflective of a time period prior to significant PAH inputs from human sources and is used as a historical reference (Figure 8) The accumulation rates during the 1950s is considered the peak in PAH emissions (Figure 9), and PAH accumulation in recently deposited sediment is used for interpretations of current PAH loadings (Figure 10).



Figure 8. 1900 PAH Accumulation Rates for all lakes organized by latitude.



Figure 9. 1950 PAH Accumulation Rates for all lakes organized by latitude.



Figure 10. Recent (c. 2000) PAH Accumulation Rates for all lakes organized by latitude.

In 1900 low PAH accumulation rates are observed overall with the exception of Lakes Campau and Muskegon, the cause for the high inventories in these lakes is unclear. In 1950, elevated accumulation rates are observed relative to the older sediment. It is noted that lakes exhibiting the elevated accumulation rates are located in close proximity. In recent sediment, significant differences in accumulation rates amongst lakes become evident. Lakes showing increased accumulation rates include Klinger, Cora, Cass, Davidson, Crystal M, White, Cadillac, Charlevoix, Round, Morrison, Avalon and Hackett (Figure 11). While lakes that exhibit a decrease in recent accumulation rates include Emily, Otter, Big Platte, Whitmore, and Campau (Figure 12).



Figure 11. Temporal PAH accumulation rate (ng/cm2/yr), based on a definite increasing trend to the recent; after legislation was implemented, 1970.



Figure 12. Temporal PAH accumulation rate (ng/cm2/yr), based on a definite decreasing trend to the recent; after legislation was implemented, 1970.

## PAH Compound Cluster Analysis

The relative distribution of the individual PAH concentrations in a given sediment sample or suite of samples can be used to develop a PAH "fingerprint". Research by others (De Raat et al., 1991; Harrison et al., 1996; Duval et al., 1981) has shown that a PAH fingerprint can be used to determine a source by comparison to the compound profiles of common source types. Thus, lake sediment that have similar PAH compound compositions will most likely have a similar source, and, ideally, the PAH compositions can then be tied to a particular source.

One method utilized for fingerprinting of the PAH profiles is cluster analysis (Simcik et al., 1998; Dahle et al., 2003). Cluster analysis offers the ability to form groups based upon the similarities in the distribution of the individual PAH compounds, allowing trends to be observed. Cluster analysis was performed on the PAH compound data for this study using JMP 5.0 for Windows (SAS Institute, 2013). There were inconsistencies in the benzo(a)pyrene results, the compound was not measured for each lake, preventing this compound from utilization in the cluster analysis. Also, it should be noted that benzo(b)fluoranthene and benzo(k)fluoranthene were summed together and characterized as benzo(bk)fluoranthene, due to the difficulties of gas chromatograph separation of the two isomers (Bzdusek et al.,2004). Also, values that were below the detection limit for the compounds were assigned a value of zero (Kannon and Perrotta, 2008).

Two methods were used in the cluster analyses:, a ratio approach and a log-ratio approach. With each approach, the three time periods used for PAH accumulation rates (restate them), were examined. For each time period three, four, five and six clusters were extracted for examination. The five cluster extraction provides the most definitive patterns for regional interpretations and therefore only the results of the five cluster extraction are presented.

The ratio approach uses the proportion of the PAH concentration to the sum of all the PAH compound concentrations. By using this method, the data may be referred to as "compositional data" based on the fact that the proportion of the compounds in the sample sum to 1 or 100% (Howel, 2007). The results of the ratio plots are shown in Figure 13. The colors used do not represent any one source uniformly and cannot be used as a comparison from one

cluster analysis to the next; they are only used to show trends or correlations that are present in the data, reflecting similar fingerprints.

In 1900 (Figure 13A), there is no pattern apparent in the PAH clusters. In 1950 (Figure 13B), there is also no apparent pattern despite the significant increase in concentrations in sediment dated to this period. In recent sediment (Figure 13C), a clear pattern of PAH loadings becomes evident, as shown in Figure 6, there are three primary clusters with variance from the south to the north. The most northern clusters are the combination of three clusters. The three clusters show a trend from south west to the north, the reasoning for this is unclear at this time.

Compositional data have known complications with correlation coefficients in standard multivariate techniques (Pearson, 1897), there is a possibility of error with interpretation of the summary statistics with the compositional data. Log-ratio transformation of the compositional data prior to cluster analysis has been suggested and proven to be useful by some, since compositional data relates to relative rather than absolute magnitudes of the compound (Aitchisons, 1986; Howel, 2007). This methodology was also applied by Howel (2007) to study the relative proportions of polychlorinated biphenyls (PCBs) in ambient air samples. Log-ratios were calculated by dividing the compositional data of the PAH compounds for each lake by the geometric mean of all 15 PAH compounds of that lake. The log-ratios were calculated using the following equation:

$$Log \ ratio = log(\frac{p_{ij}}{g(p_j)})$$

Where  $p_{ij}$  = proportion of PAH compound i in lake j,

 $g(p_{j)} = (p_{1j}p_{2j}...,p_{dj})^{1/(\# \text{ of compounds})}$ , and d = number of compounds (Howel, 2007). The cluster analysis of the log-ratio transformed data showed similar patterns as those from the compositional data. In 1900 (Figure 14A), a mixture of the clusters are found and interpreted to form one cluster, indicating a state-wide regional pattern. In 1950 (Figure 14B), a regional trend is interpreted with small-watershed-scale effects seen. In recent sediments (Figure 14C), a gradient is observed from three main clusters with differences from the south to the north. The most northern cluster being comprised of two clusters with variance from the south west to the north east. It is unclear as to why there are two clusters comprising the most northern cluster.



Figure 13. Cluster analysis of compositional data for year (A) 1900, (B) 1950, and (C) recent (c.2000). Five clusters were extracted in each cluster analysis. For C there are three clusters, as shown above, that can be combined into one cluster. These three clusters show a variation trending SW to NE.


Figure 14. Cluster analysis of log-ratio transformed data (A) 1900, (B) 1950, and (C) recent.

## DISCUSSION

Analysis of the temporal total concentrations of PAHs in sediment collected from 29 inland lakes in Michigan shows definitive peaks in most of the lakes in sediment dated between 1934 and 1960. Similar to other studies, the year associated with peak PAH concentrations for each lake was close to 1950. A significant decrease in PAH concentrations was observed around 1970, illustrating the response in environmental PAH distribution likely related to legislatively-induced emission reductions. Recently, following the decrease, an increase in PAH concentrations are observed in several of the lakes studied, the reason for which is unknown at this time.

Examining the relationship between sediment PAH concentrations and sediment PAH accumulation rates during the peak year (1950), it is evident that a portion of the lakes in close proximity to one another have all increased in PAH concentrations relative to their sediment concentrations in 1900. The lakes included in this phenomenon are: Cora, Gull, Whitmore, Thompson, Cass, Morrison, Campau, Davidson, Otter, and Muskegon, all of which are located in the southern half of Michigan. These lakes not only show an overall increase but show an elevated accumulation rate compared to the other inland lakes studied. Based on accumulation rate trends above, it can be acknowledged that c.1950; accumulation rates are higher in the south than that of the north. Accumulation rates were examined in recent sediments to correlate trends between accumulation rates and concentrations, and determine if they are coupled. When comparing the lakes with increasing concentrations and those of increasing accumulation rates in the recent, it is apparent that most of the lakes that show an increase in PAH concentrations (Fig 4) are also increasing in PAH accumulation rates (Fig 11). Lakes that are both increasing in

concentration and accumulation rate in the recent include: Cora, Cass, Davidson, Round, Morrison, Hackert, Klinger, Charlevoix and Crystal M.

The cluster analyses for both the compositional data and log-ratio transformed data in both 1900 and 1950 show no pattern of PAH loadings. The clusters show a well-mixed pattern throughout the region, that at is thought to indicate a regional signal but it cannot be proven at this time. An evident trend was observed in the recent cluster analysis for both data treatments, trending from the southeast to the northwest. This result is consistent with the hypothesis in that the PAH fingerprints are found to be dissimilar in the recent sediments, transformation to several different sources based on local influences.

A similar south to north gradient is observed in the spatial plot of PAH inventories. Overall the PAH concentration inventories have been greatest in the south and least in the north. If compared to a population density map of Michigan (Fig. 15) it can be observed that a decreasing gradient evident from south to north can be correlated with the spatial inventory plot. The areas of high inventory correlate with areas of high population density which would be expected. Furthermore, the spatial inventory plots show that from 1900 to 1940 the inventories are homogeneous with some outliers, in 1950 it is evident that the inventories are highest in the south and lowest in the north, as hypothesized, and that in recent years there is decrease to more localized influences.



Figure 15. Modified County map of Michigan showing population density by color (U.S. Census Bureau, 2000).

# CONCLUSION

Sediment records from 29 inland lakes in the State of Michigan were studied to better understand PAH spatial and temporal patterns. The hypothesis driving this study is that PAH loadings will be the highest during the 1940 to 1980 time period (peak emission period) with a common regional source dominating these PAH loadings, a lessening of this dominant source will be apparent, after the 1980s, enabling local watershed influences to be seen. To test this hypothesis spatial and temporal patterns of PAH loadings (inventories, accumulation rates, concentrations, fingerprints) were compared amongst selected inland lakes across the State of Michigan.

Results indicate that some expected loading patterns were observed. During the time of high PAH emissions, a peak in PAH concentration was apparent c.1950, a south to north decreasing gradient was observed in PAH inventories. PAH fingerprints analyzed by cluster analysis were found to be dissimilar, not showing the regional signal that was expected. During the time period from 1970-80, there is an evident decrease in PAH concentrations, leading to the conclusion that environmental legislation had an impact on PAH loadings to the environment. In recent years, the influence of high population areas on loadings causes a spatial gradient in PAH distribution. The intensity of peak loadings of PAHs resulted in a more regional signal. Reduced emissions as a result of legislation, is revealing a spatial regional gradient with local watershed sources being observed. This is also observed by the differences in PAH fingerprints indicating several different sources throughout the region. Localized sources are becoming more apparent than long range atmospheric transport of PAHs through the region.

#### **CHAPTER 2: PAH SOURCING**

### **INTRODUCTION**

In chapter one, it was revealed that some of the inland lakes in Michigan show increasing PAH concentrations in recent sediments. This correlates along with several other recent studies that have shown that the lake sediment record at some locations in the Great Lakes have also shown a recent increase in PAH concentrations.(Van Metre et al., 2000; Lima et al., 2003; Liu et al, 2012). The increase in these lakes has been correlated to proximity to urban areas, and areas with increasing population density (Kannan et al., 2005; Van Metre et al., 2000). However, given that other studies show urban areas have not increased in concentration of PAHs (e.g. Van Metre et al., 2000), urbanization is not likely the only cause for increased PAH loading to the environment. For example, one research group links PAH concentrations in recent sediments to the increased application of coal tar sealant on roadways and parking lots (Mahler et al., 2003; Mahler et al., 2005; Van Metre et al., 2005; Van Metre et al., 2005; Van Metre and Mahler, 2010). The purpose of the present research is to explore the cause(s) of this recent increase in PAH loadings in inland lakes throughout Michigan. Specifically the hypothesis tested is that this recent increase in PAH loadings is related or attributes to the use of coal tar sealants.

PAHs are organic contaminants of which there is over 100 different compounds, 16 of which that pose the greatest human and environmental risk (U.S. Department of Health and Human Services, 1995). The PAH compounds can be divided into two groups: low molecular weight (LMW) compounds and high molecular weight (HMW) compounds. The LMW compounds are composed of two to three benzene rings, while the HMW compounds are composed of four to seven (Neff, 1979). PAH compounds and their molecular weight category, low or high (Table 1).

| PAH Compound          | Abbrev. | Mass | Mol. Wgt. |
|-----------------------|---------|------|-----------|
| Acenaphthene          | Aen     | 154  | LMW       |
| Acenaphthylene        | Ayl     | 152  | LMW       |
| Anthracene            | Anthr   | 178  | LMW       |
| Phenanthrene          | Phen    | 178  | LMW       |
| Fluorene              | Flu     | 166  | LMW       |
| Fluoranthene          | Fth     | 202  | HMW       |
| Benzo(a)anthracene    | BaA     | 228  | HMW       |
| Chrysene              | Chry    | 228  | HMW       |
| Pyrene                | Pyr     | 202  | HMW       |
| Benzo(b)fluoranthene  | BbF     | 252  | HMW       |
| Benzo(k)fluoranthene  | BF      | 252  | HMW       |
| Dibenzo(ah)anthracene | DahA    | 278  | HMW       |
| Benzo(ghi)perylene    | BghiP   | 276  | HMW       |
| Indeno(123cd)pyrene   | IcdP    | 276  | HMW       |
| Benzo(a)pyrene        | BaP     | 252  | HMW       |

Table 1. PAH compounds, their corresponding abbreviations and masses and classification as to being low or high molecular weight.

As the molecular weight increases in these compounds, resistance to changes in the reduction and oxidation conditions in the environment increases and aqueous solubility's decrease, rendering them more persistent in the environment. The physical, chemical, and biological characteristics and behavioral distributions of PAHs vary with different PAH compounds (Neff, 1979; U.S. Department of Health and Human Services, 1995).

PAHs are released into the environment by incomplete combustion of fossil fuels and other organic substances. They originate from both natural and synthetic (anthropogenic) sources. Natural combustion sources include forest fires and volcanic eruptions (U.S. Department of Health and Human Services, 1995). However, anthropogenic sources represent the predominant environmental input of PAHs. The major sources are residential heating (e.g. burning of wood in homes), power plants and industrial activities, vehicle emissions, coal tar pitch, refuse and open burning (Bzdusek and Christensen, 2004; Li et al., 2003; U.S. Department of Health and Human Services, 1995).

Formation of PAHs occurs by three broad processes: pyrogenic, petrogenic and phytogenic. Pyrogenic processes include high temperature pyrolysis of fossil fuels or other organic materials usually through rapid and combustive reactions. Petrogenic processes are characterized as low to moderate temperature changes in the compound to form fossil fuels, most likely petroleum. Phytogenic processes are the direct biosynthesis of PAHs by microbes and plants (Neff, 1979). The ratios of LMW PAHs to HMW PAHs have been used to estimate the type of process responsible for the occurrence of PAHs in the environment (e.g. petrogenic vs. pyrogenic) present; where a large proportion of HMW PAHs is typically of pyrogenic origin and a large proportion of LMW PAHs is typically of petrogenic origin (Hwang et al., 2006), as can be determined by LMW/HMW ratios. Researchers have used PAH ratio methods to determine the main processes that have been contributing to PAH emissions (Daisey et al., 1979; Smith and Harrison, 1996; Cschwed and Hites, 1981; Rogge et al., 1993; Levendis et al, 1996; Masclet et al., 1987; Westerholm et al., 1991; Khalili et al, 1995; Simcik et al., 1999; and A. Motelay-Massei et al., 2007). The ratios are calculated based on PAHs with the same molecular weight, e.g. FTH/PYR, BaP/BghiP, Phen/Anthr, and BaA/Chry (Simcik et al., 1999). It is considered best to not use more than two ratios to identify potential sources because if more are used it can lead to contradictory interpretations between the ratios (A. Motelay-Massei et al., 2007). This observation is potentially a fatal aspect of using ratios to sourcing PAHs.

A primary pathway for PAH entry to the environment atmosphere release (Simcik, 1996; Simcik, 1999; U.S. Department of Health and Human Services, 1995). In the air, PAHs

predominantly sorb to particulate matter, though LMW-PAH compounds can be found in the gaseous phase. While in the atmosphere, PAHs are subject to degradation (photo-oxidation and chemical oxidation). LMW-PAH compounds are more susceptible to degradation while in the atmosphere (U.S. Department of Health and Human Services, 1995). Atmospheric residence time is dependent on the size of the particulate matter with which the PAH compound sorbs to and climate conditions subject to different areas. PAH compounds sorbed to smaller sized particulates are more likely to have a longer residence time, and travel longer distances, than those sorbed to larger diameter particulates (Neff, 1979).

Release of PAHs into surface or ground water can also occur by terrestrial runoff or through direct discharge from the source, such as industrial plants, wastewater treatment facilities, and waste storage tanks (U.S. Department of Health and Human Services, 1995). The hydrophobic properties of PAHs and their ability to sorb to particulates and sediments within the watershed, allow them to accumulate and persist in the environment (Kannan et al, 2005; Kim et al., 2008). These sediments then settle to the bottom of lakes and rivers, creating a historical record of PAH deposition and concentration fluxes (Kannan et al., 2005), which likely persist for a long periods of time in anoxic sediments (Neff, 1979).

In the terrestrial environment, PAHs predominantly sorb to organic matter (OM). They are subject to many degradation processes including, but not limited to, microbial degradation and chemical oxidation (Rojo-Nieto et al., 2012). There are many soil and sediment characteristics and factors in the environment that can alter the biodegradation of PAHs. Factors that may affect the rate of biodegradation include pH, temperature, oxygen and nutrient availability, microbial population, and substrate type (Rojo-Nieto et al., 2012; Zhang et al., 2005).

Oxygen availability is often the limiting factor degradation of hydrocarbons. Under aerobic conditions algae, bacteria, and fungi breakdown and metabolize PAHs; bacteria having the ability to use PAHs as a source of carbon and energy. Microbial degradation can occur naturally under anaerobic conditions, but the biodegradation rate is much slower than under aerobic conditions (Rojo-Nieto et al., 2012). Recent studies, such as those by Meckenstock et al. (2004), suggest that microbial degradation occurs under anaerobic conditions where the microorganisms utilize nitrate and sulfate as terminal electron acceptors to aid in the degradation of PAHs.

Degradation and transport of PAHs has been shown to be functions of soil characteristics in a watershed. PAH biodegradation has been shown to increase in the following sequence: silty loam (New Mexico) < sandy loam (Ohio) < sandy clay loam (Columbia) (Hwang and Cutright, 2003). A study by Amellal et. al (2001) found that PAHs were more concentrated in finer grain sized substrate (e.g. clay and fine silt) and less concentrated in larger and coarser grain sizes (e.g. sand). It is important to note that the degradation of PAHs can produce more mutagenic and carcinogenic daughter PAH compounds (Baek et al, 1991), yet it is difficult to follow the degradation processes of PAHs. When determining PAH sources, the assumption that there is no change in the PAH compound or ratio, from source to receptor, is followed.

Source characterization methods (i.e., source-receptor modeling) can be used to determine PAH sources, regarding PAH compounds. Source-receptor modeling is a technique that assumes that there is no change in the PAH ratio from source to receptor. This technique is used to quantify contributions of different sources to a receptor, for example the receptor being aquatic sediments most likely from the deepest point of a lake (Van Metre and Mahler, 2010). These sediments can be used as a historical record of deposition and are easily proportioned and

analyzed for organic materials and other parameters (e.g. trace metals) temporally. By sampling several sites, one may obtain a spatial dataset to determine correlations and trends (Van Metre and Mahler, 2010).

There are two principle types of source-receptor modeling: multivariate analysis (principal component analysis [PCA] and multiple linear regressions) and mass balance modeling (Li et al., 2003; Van Metre and Mahler, 2010). Multivariate analysis looks at multiple variables at once to determine source profiles; while mass balance modeling has known PAH source profiles in which sources are determined by fractional contributions (Van Metre and Mahler, 2010). These techniques, along with molecular ratio analysis (Kim et al., 2008; Yunker et al., 2002), have been used. Temporal plots of PAH concentrations have been used to reconstruct historical trends in several areas, including previous studies on PAHs in Michigan inland lakes (Kannan et al., 2005).

It has been observed that concentrations in both air (Hafner et al., 2005) and surface water have a direct correlation between increased human populations/human activity (e.g., industrialization) and PAH concentrations (Yunker et al., 2002, Neff, 1979), with those areas that are distant from intense human activities being the least contaminated (Neff, 1979). A shift in the source of PAH's has been observed in several lakes throughout the United States over the last 40 years, along with this observation is a correlation of an increase in PAHs with the increase of urbanization (Van Metre et al., 2000).

Land use characterization methods can be implemented to observe correlations between increasing PAH trends and changes in land use. A study by Zheng et al. (2011) on the correlation of land use with PAH concentration in streambed sediment indicates that industrialresidential and urban-residential streams contain significantly higher concentrations of PAHs

than agricultural streams, with industrial-residential streams having the highest concentrations. Strong correlations are seen in urban-residential streams between PAH concentrations and population and vehicle density (Zheng et al., 2011). ArcGIS is a program that can be used to collect data including: watershed geographies, population densities, major land uses, etc. These data can then be analyzed against change in PAH concentrations. PCA can be used to differentiate collected sediments to different land uses (Zheng et al., 2011), and correlations then can be made to PAH concentrations within those sediments.

Until recently, research to identify and understand PAH sources has not considered the role of coal tar sealant as a source of PAHs in explaining the recent increase in PAH concentrations that is observed in lake sediments . Coal tar sealants have been suggested to be a predominant source of PAHs since 1960 (Van Metre and Mahler, 2010). Coal tar is a known carcinogen and has about 50 percent of PAHs by weight. Coal tar is used to create a coal tar based sealant, or sealcoat, and is applied to driveways and parking lots around the United States (predominantly the central and eastern regions) to protect the underlying asphalt and enhance appearance (Mahler et al., 2005; Mahler et al., 2003, Van Metre and Mahler, 2010), and reapplied every two to three years due to rapid breakdown of the surface (Scoggins, 2009). This raises a question as to the fate of previously applied material and its breakdown products in the environment

One of the first attempts to identify the presence of coal tar sealants in the environment was first conducted in Austin, Texas. Runoff from coal tar sealed parking lots have revealed higher concentrations of PAHs than runoff from other surfaces, indicating that the PAHs are potentially entering into the environment through breakdown of the coal tar sealant and transport through runoff (Mahler et al., 2003; Mahler et al., 2005).

Using source receptor mass balance modeling (CMB8.2), Van Metre and Mahler (2010) suggest that coal tar sealant is a potential PAH source. This analysis indicated that coal tar sealcoat is the largest PAH source to 40 lakes analyzed throughout the United States, with vehicle emissions being second. This result is consistent with observed trends of high environmental concentrations of PAHs in areas of high areas of sealant application. The eastern and central United States, where coal tar sealcoats are applied predominantly, have higher PAH environment concentrations at higher rates (Van Metre and Mahler, 2010).

Previous studies have indicated that this increase in PAH concentrations in recent the recent sediment record has also been observed in several inland lakes in Michigan, as demonstrated in Chapter One. This leads to the question as to why are some lakes increasing in concentration recently, despite the prior decrease. Also, can these sources be identified and if so, what are they spatially and temporally?

As previously stated, the hypothesis driving this research is that this recent increase in PAH loadings is related or attributable to the use of coal tar sealants. To test this hypothesis this study attempts to identify sources for PAHs and possible changes in these sources during five significant time periods are chosen for analysis 1) 1900 as a background, 2) 1950 during peak PAH loadings, 3) 1970 representative of environmental legislation, 4) 1990 post environmental legislation, and 5) 2000 representing recent loadings. The time periods were chosen based in part from the work discussed in Chapter One and the research done by Kannan et al (2005). To help identify these courses, for each of these time slices in the lakes the PAH compounds will be analyzed using ratios, factor analysis (R-Mode), comparisons to land use , and cluster analysis (fingerprinting).

# METHODOLOGY

Sediment cores have been collected from 47 individual lakes from 1999 to 2010 as part of the Michigan Department of Environmental Quality's (MDEQ) Inland Lakes Sediment Trend Monitoring Program. For this study, sediment from 29 lakes is analyzed to provide an adequate spatial dataset to observe temporal changes in the loadings of PAHs in conjunction with different land uses.

Sediment core extraction was conducted using an MC-400 Multi-corer modified for inland lake use, and deployed from the MDEQ M/V Nibi. The multi-corer has four sampling tubes of identical dimensions for sediment core extraction. Four replicate cores are collected from the deepest portion of each lake as determined by MDNR bathymetric maps (www.dnr.state.mi.us/spatialdatalibrary/pdf\_maps/inland\_lake\_maps) and on-board sonar. If evidence of disturbance during coring was present in the core sediment, new cores were collected. Upon retrieval of satisfactory sediment cores, sediment intended for <sup>210</sup>Pb and metals analyses were extruded and sectioned at 0.5 cm intervals for the top 8 cm, and at 1 cm intervals for the remainder of the core. The <sup>210</sup>Pb analyses were conducted by the Freshwater Institute in Winnipeg, Manitoba, Canada where porosity accumulated dry mass, sedimentation rates, sediment ages and focusing factors were determined. Dates of the cores were verified using <sup>137</sup>Cs, the temporal peak of the stable <sup>208</sup>Pb concentrations and presence/absence of excess <sup>210</sup>Pb. Samples from the second core were microwave acid digested and subsequently submitted for metals analysis to the Michigan State University Inductively-Coupled Plasma Mass Spectrometry (ICP-MS) Laboratory. The third core was submitted to the Michigan State University Aquatic Toxicology Laboratory for trace persistent organic pollutants (POPs), which included a suite of PAHs. This core was originally sectioned at 2 cm increments for the extent of the core length. However, insufficient mass of sediment required for the analysis was available at sediment core increments of 2 cm, so equal quantities of sediment were combined from 4 cm sections (2 samples) of the sediment core.

Analytical methods used for the PAH analysis have been described elsewhere (Khim et al., 1999). Briefly, a total of 40 g of wet sediment was extracted for analysis. Moisture content was determined by taking 5 g of the wet sediment and drying it overnight at 100°C. The dried sediment was Soxhlet-extracted with dichloromethane and hexane and treated with 120 g of anhydrous sodium sulfate. The extracts were passed through a Florisil column, and eluted with 10% acetone in hexane (9 mL). The extract was concentrated and injected into a gas chromatograph interfaced with a mass spectrometer for analysis of PAHs. The PAH standard consisted of 15 of the 16 priority PAH compound pollutants, excluding naphthalene, as identified by the U.S. EPA. The 15 priority PAH compounds that are used for this study include: acenaphthene, acenaphthylene, anthracene, phenanthrene, fluorine, fluoranthene, benzo(a)anthracene, chrysene, pyrene, benzo(b)fluoranthene, benzo(k)fluroanthene, dibenz(a,h)anthracene, benzo(g,h,i)perylene, and indeno(1,2,3-cd)pyrene.

#### **RESULTS AND DISCUSSION**

### Ratios of PAH Compounds

PAH ratios are used to characterize different PAH sources within each of the five time slices (1900, 1950, 1970, 1990, and 2000). The ratios of low molecular weight PAHs to high molecular weight PAHs are used to determine the PAH origin (petrogenic vs. pyrogenic), with an inferred pyrogenic (combustive) origin as having a value less than one (REF). The ratio FTH to PYR can also be used to discriminate between petrogenic vs. pyrogenic origins of PAH loadings, a value greater than one indicating pyrogenic origin and a value less than one indicating petrogenic origin (REF). Three other ratios are utilized 1) Bap/BghiP, 2) Phen/Anthr, and 3) BaA/Chry. For the ratio Bap/BghiP if the value is found between the range of 0.3 - 0.78 it can be correlated to vehicles, 0.3 - 0.4 to gasoline exhaust, 0.9 - 6.6 to coal, 0.46 - 0.81 to diesel, 5.1 to coke oven, 0.14 - 0.6 to incinerators, greater than 2 to oil burning power plants and 0.65 - 1.7 to petroleum refineries. For the Phen/Anthr ratio if the value is found to be 2.7 then it can be correlated to vehicles, 8 to street dust, within the range of 3.4 - 8 to gasoline exhaust, 3 to coal or firewood fire, 7.6 - 8.8 to diesel, and 0.79 to coke oven. The ratio of BaA/Chyr can be correlated to vehicles if the value is found to be 0.63, if it is within the range of 0.28 - 1.2 it can be correlated to gasoline exhaust, 0.93 to firewood fire, 1 - 1.2 to coal, 0.17 - 0.36 to diesel and 0.7 to coke oven. The potential sources and correlating ranges can be observed in Table 2 below the results. This table shows the ratio values within each time slice. The ratio LMW/HMW for all time slices yielded a value less than one, within the range for combustion. The FTH/PYR value for all time slices yielded a value greater than one, within the range for petrogenic origin. The BaP/BghiP ratio yielded an average value around 0.7, within the range for vehicles, diesel and petroleum refineries. The Phen/Anthr ratio yielded an average value around 7, most similar

to gasoline exhaust. The BaA/Chry ratio yielded an average value around 0.4, also within the range for gasoline exhaust. Over time is appears that the source of PAHs has not changed. For each time period the source is combustive in nature, petrogenic and related to vehicular emissions, including gas and diesel.

|                                       | LMW/HMW | <u>FTH/PYR</u> | <u>BaP/BghiP</u>              | Phen/Anthr             | r <u>BaA/Chry</u>       |
|---------------------------------------|---------|----------------|-------------------------------|------------------------|-------------------------|
| 1900 Average                          | 0.32    | 1.34           | 0.7                           | 10.41                  | 0.38                    |
| 1950 Average                          | 0.13    | 1.9            | 0.64                          | 7.63                   | 0.39                    |
| 1970 Average                          | 0.11    | 1.21           | 0.72                          | 7.2                    | 0.39                    |
| 1990 Average                          | 0.11    | 1.17           | 0.79                          | 7.15                   | 0.4                     |
| 2000 Average                          | 0.11    | 1.19           | 0.65                          | 6.24                   | 0.42                    |
| vehicles                              |         |                | 0.3-0.78 <sup>a,b</sup>       | 2.7 <sup>b</sup>       | 0.63 <sup>b</sup>       |
| street dust <sup>c</sup>              |         |                |                               | 8                      |                         |
| gasoline exhaust                      |         |                | 0.3-0.4 <sup>d</sup>          | 3.4-8 <sup>d</sup>     | 0.28-1.2 <sup>c,d</sup> |
| firewood fire <sup>c</sup>            |         |                |                               | 3                      | 0.93                    |
| coal                                  |         |                | 0.9 <b>-</b> 6.6 <sup>a</sup> | 3 <sup>c,e</sup>       | 1-1.2 <sup>c,f</sup>    |
| diesel <sup>d,g</sup>                 |         |                | 0.46-0.81                     | 7.6-8.8                | 0.17-0.36               |
| coke oven <sup>h</sup>                |         |                | 5.1                           | 0.79                   | 0.7                     |
| incinerators <sup>a</sup>             |         |                | 0.14-0.6                      | <sup>a</sup> Daisey e  | t al., 1979             |
| oil burning power plants <sup>a</sup> |         |                | >2                            | <sup>b</sup> Smith ar  | nd Harrison, 1996       |
| petroleum refineries <sup>a</sup>     |         |                | 0.65-1.7                      | <sup>c</sup> Gschwe    | nd and Hites, 1981      |
| combustion                            | < 1     |                |                               | <sup>a</sup> Kogge e   | t al., 1993             |
| pyrogenic                             |         | >1             |                               | <sup>c</sup> Levendi   | s et al., 1996          |
| petrogenic                            |         | < 1            |                               | <sup>2</sup> Wasterb   | alm at al 1001          |
| 1 0                                   |         |                |                               | <sup>b</sup> Khalili 4 | onn et al., 1991        |
|                                       |         |                |                               | Simeik a               | nai, 1995<br>tal 1000   |
|                                       |         |                |                               | Simcik e               | et al, 1999             |

Table 2. PAH ratio values are shown for several different PAH ratio source methods. Also the range of values for each sources are presented. The values in red indicate which source range the results correspond with.

# Factor Analysis of the PAH Compounds

Sources for each data slice can also be inferred using factor analysis. Factor analysis attempts to group together related variables, in this case the PAH compounds. These calculations were done using JMP 5.0 based on correlations. For each data slice (1900, 1950, 1970, 1990, and 2000) each PAH compound for each lake is run through a factor analysis and correlated to one another based on similar compound signatures. The correlations are run through a factor rotation providing factors that are created based on similar compound signatures. PCA is chosen to represent the total variability of the PAH data using a minimum number of factors, with the smallest covariance. The first factor accounts for the greatest variability with each subsequence factor having less variability than the previous. By evaluation of the factor analysis an estimate of the source can be made. The sources that characterize a particular factor are interpreted from the type of compounds that are loaded on the factor. Moteley-Masseri et al., (2007) provide a template for inferred sources as a function of PAH correlations (Table 3).

| Diesel               | Vehicle            | Coal Combustion     |
|----------------------|--------------------|---------------------|
| Bb/kF*               | BghiP              | Flu                 |
| BghiP                | IcdP               |                     |
| IcdP                 | Phen               |                     |
| Chry                 | Bb/kF              |                     |
|                      |                    |                     |
| Petroleum Industries | <u>Natural Gas</u> | Industrial Emission |
| Anthr                | BaA                | Fth                 |
| DahA                 | Chry               | Pyr                 |
|                      |                    |                     |

Table 3. PAH compound tracers as formulation from A. Moteley-Massei et al. (2007).

Each time slice has multiple factors. The factors that are analyzed are those that have an eigenvalue that is greater than one. The factors are correlated by similar compound signatures, and analyzed only utilizing the positive values. The PAH compound tracers as shown in Table 3, are used as representation of potential sources within each factor. The sources are estimated given the assumption that each source can only be used once, excluding vehicles. Vehicles have several different indicator compounds that also can be used for gasoline exhaust, diesel, etc.; they cannot be differentiated within this group. The interpreted results of the factor analysis can be observed in Table 4. Each time slice is shown with their estimated sources and % variance (relative dominance).

It can be observed in Table 4, that the relative dominance of the PAH sources changed over time. The first two factors, as estimated from each time period of importance will be discussed. Factor 1, shows a change from vehicular emissions in 1900 to vehicle/coal combustion in 1950 to coal combustion in the most recent period. Factor 2, indicates that the main PAH source in 1900 was natural gas, then shifted to industrial emissions in the 1950, 1970 time period and then to vehicular emissions in the most recent period. These results show the decline of industrial emission post 1970s, correlating with the increase in environmental legislation. Based on these source estimates of this study, it is perceived that vehicular loadings and coal combustion are the greatest sources for PAH loadings in the region overall. This correlates with previous results, both being combustive in nature and related to vehicular emission.

|                           |  |   | petroleum   |   |   |             |
|---------------------------|--|---|---|---|---|-------------|
| 1900                      | vehicle*   | natural gas   | industries  | vehicle   |   |             |
| %                         | 27.24429   | 19.83008  | 15.0585733  | 13.29035  |   |             |
|                           | coal   | industrial  |   |   |   |             |
|                           | combustion/  | emissions/vehicl  |   | petroleum   |   |             |
| 1950                      | vehicle  | e   | natural gas   | industries  | vehicle*  |             |
| %                         | 28.9822536   | 24.19901  | 12.0354876  | 11.4155245  | 9.701865  |             |
|                           | coal   | industrial  |   | petroleum   |   |             |
| 1070                      | agentice   |   | *********   | in duration   | real de la  |             |
| 19/0                      | combustion   | emissions   | venicie   | industries  | venicie   | natural gas |
| 1970                      | 30.4421635   | 20.45405  | 12.07216  | 10.2658892  | 9.880015  | 8.396539    |
| 1970                      | 30.4421635<br>coal   | 20.45405  | 12.07216<br>industrial  | 10.2658892<br>petroleum   | 9.880015  | 8.396539    |
| 1970                      | 30.4421635<br>coal<br>combustion                                   | 20.45405<br>vehicle *                                     | 12.07216<br>industrial<br>emissions                                     | 10.2658892<br>petroleum<br>industries   | 9.880015<br>vehicle   | 8.396539    |
| 1970<br>1990<br>%         | 30.4421635<br>coal<br>combustion<br>31.94468                       | 20.45405<br>vehicle *<br>17.51376                         | 12.07216<br>industrial<br>emissions<br>11.65517                         | 10.2658892<br>petroleum<br>industries<br>11.12044                                     | 9.880015<br>vehicle<br>8.744858                                       | 8.396539    |
| 1970<br>1990<br>%         | 30.4421635<br>coal<br>combustion<br>31.94468<br>coal               | 20.45405<br>vehicle *<br>17.51376                         | 12.07216<br>industrial<br>emissions<br>11.65517                         | 10.2658892<br>petroleum<br>industries<br>11.12044<br>vehicle/industri                 | vehicle<br>9.880015<br>vehicle<br>8.744858<br>petroleum               | 8.396539    |
| 1970<br>1990<br>%<br>2000 | 30.4421635<br>coal<br>combustion<br>31.94468<br>coal<br>combustion | emissions<br>20.45405<br>vehicle *<br>17.51376<br>vehicle | venicle*<br>12.07216<br>industrial<br>emissions<br>11.65517<br>vehicle* | 10.2658892<br>petroleum<br>industries<br>11.12044<br>vehicle/industri<br>al emissions | vehicle<br>9.880015<br>vehicle<br>8.744858<br>petroleum<br>industries | 8.396539    |

Table 4. Factor Analysis of PAH compound concentrations for each significant time period of PAH loadings.

### Comparison to Percent Land-use

Factor analysis is again used to determine if there is any correlation of the PAH compounds with land use. The analysis was performed for two time slices 1970 and 1990. These time slices were chosen because land-use data are only available for these two dates. The land-use data are incorporated into the factor analysis with the PAH compound abundances to determine if potential sources could be correlated to specific types of land-use. The correlations are run through a factor rotation providing factors that are created based on similar compound signatures. This method is used to represent the total variability, using a minimum number of factors, with the smallest covariance. The first factor accounts for the greatest variability with each subsequence factor having less variability than the previous. The factors with eigenvalues greater than one and with positive values are chosen for evaluation. By evaluation of the factor analysis an estimate of the source can be made.

The results are shown in Table 5, no distinct correlations are found. Water correlates with a high value of dibenz(ah)anthracene in both the 1970 and 1990 data, which is unknown as to why this correlation is found. The highest loading is interpreted to be coal combustion which is unrelated to any land use; this might be consistent with a regional signal. A correlation between vehicles and forest is seen, but it is not clear why. The urban land-use shows a relationship to vehicles also, this correlation seems logical but it is a lower loading, given it is in a higher factor. Based on these results it can be interpreted that land-use is not a key determinant of specific PAH sources. It is clear that the significant PAH sources include coal combustion and vehicles, as seen using previous methods.

|             | 1970   |         |          |          |          | 1990   |          |          |         |          |         |         |
|-------------|--------|---------|----------|----------|----------|--------|----------|----------|---------|----------|---------|---------|
| Factors     | 1      | 2       | 3        | 4        | 5        | 1      | 2        | 3        | 4       | 5        | 6       | 7       |
| Agriculture |        |         |          |          |          |        |          |          |         |          |         |         |
| Forest      |        | Forest  |          |          |          |        | Forest   |          |         |          |         |         |
| Urban       |        |         |          |          | Urban    |        |          |          |         |          |         | Urban   |
| Wetland     |        |         |          |          |          |        |          |          | Wetland |          |         |         |
| Water       |        |         |          | Water    |          |        |          | Water    |         |          |         | Water   |
| Ayl         | 0.927  |         |          |          |          | 0.907  |          |          |         |          |         |         |
| Aen         | 0.922  |         |          |          |          | 0.797  |          |          |         |          |         |         |
| Flu         | 0.837  |         |          |          |          | 0.880  |          |          |         |          |         |         |
| Phen        | 0.282  |         | 0.287    |          |          | 0.730  |          | 0.496    |         |          |         |         |
| Anthr       | 0.937  |         |          |          |          | 0.920  |          |          |         |          |         |         |
| Fth         |        |         | 0.940    |          |          |        | 0.269    |          |         | 0.730    |         |         |
| Pyr         |        |         | 0.921    |          |          |        |          |          | 0.528   | 0.307    |         |         |
| BaA         | 0.362  |         |          |          |          | 0.331  |          |          | 0.249   |          |         |         |
| Chry        |        |         |          | 0.233    | 0.560    |        |          |          |         |          |         |         |
| BbkF        |        |         |          |          | 0.925    |        | 0.568    |          |         |          |         |         |
| IcdP        |        | 0.480   | 0.623    |          | 0.406    |        |          |          |         | 0.125    | 0.906   |         |
| DahA        |        |         |          | 0.940    |          |        |          | 0.760    |         |          |         | 0.291   |
| BghiP       |        | 0.237   |          |          |          |        |          |          |         | 0.350    |         | 0.571   |
|             | coal   |         | industry | petro    |          | coal   |          | petro    | natural | industry |         |         |
| Est. Source | comb   | vehicle | emiss.   | industry | vehicle* | comb   | vehicle* | industry | gas     | emiss.   | vehicle | vehicle |
| Variance    | 20.512 | 14.532  | 13.667   | 10.247   | 8.589    | 22.028 | 16.262   | 9.225    | 8.79    | 10.142   | 7.078   | 8.666   |

Table 5. Percent Land-use Factor Analysis shows no distinct correlations regarding land-use and sources. The red values are those that were used as PAH compound tracers to estimate the sources.

#### PCA of known PAH source fingerprints

PCA is used using JMP 5.0. All sources are identified using the approach of Van Metre and Mahler (2010), PAH compound source fingerprints for a number of PAH sources have been determined (Table 6). Source fingerprints are composed of relative ratios of PAH compounds that create the fingerprints, which can be used as an indicator for a specific PAH source. The 1990 land-use data are used to determine three lakes that could be used as representation of an agricultural, rural and urban landscape. The lakes that are used are Gull to represent the agricultural landscape, Nichols to represent the urban landscape and Crystal M to represent the rural landscape. These lakes along with their corresponding PAH compound values for each time slice were correlated to the known source fingerprints using PCA. This method, compares each source fingerprint and the signatures of the lakes to one other, and is based on correlations. Each one is compared to one another and determined how similar they are on a range from 0 to 1, 1 being the most identical. The values over 0.5 are only analyzed in this study, and those over 0.75 are seen as those of importance. The results are shown in Table 7. No significant changes in sources overtime are observed. Coal tar sealants, based on the results, are observed to be a predominant factor as far back as 1900. This does not seem likely as these materials were commercially used at before the 1950s. This observation calls into question the results for recent time slices that also show coal tar sealants as a major source contribution. Traffic tunnel air is also seen as a major source contribution, but note that this area has very few of these.

| ID                      | TPAH-C | PhA-C | An-C | FlA-C | <u>Py-C</u> | BaA-C | Chy-C | BbkF-C | BaP-C | IP-C | BgP-C |
|-------------------------|--------|-------|------|-------|-------------|-------|-------|--------|-------|------|-------|
| Power plant             | 0.98   | 0.15  | 0.02 | 0.17  | 0.15        | 0.11  | 0.21  | 0.06   | 0.04  | 0.03 | 0.04  |
| Residential heating     | 1.00   | 0.35  | 0.07 | 0.23  | 0.09        | 0.05  | 0.07  | 0.08   | 0.04  | 0.02 | 0.02  |
| Coke oven               | 0.91   | 0.08  | 0.02 | 0.08  | 0.08        | 0.12  | 0.12  | 0.20   | 0.10  | 0.04 | 0.07  |
| Coal average            | 0.95   | 0.17  | 0.03 | 0.15  | 0.12        | 0.09  | 0.13  | 0.12   | 0.06  | 0.03 | 0.04  |
| Diesel vehicle          | 0.95   | 0.24  | 0.04 | 0.26  | 0.17        | 0.03  | 0.09  | 0.05   | 0.03  | 0.03 | 0.03  |
| Gasoline vehicle        | 0.98   | 0.03  | 0.01 | 0.15  | 0.26        | 0.07  | 0.10  | 0.12   | 0.06  | 0.03 | 0.14  |
| Traffic tunnel          | 0.91   | 0.10  | 0.02 | 0.10  | 0.12        | 0.06  | 0.10  | 0.13   | 0.07  | 0.09 | 0.11  |
| Vehicle-related average | 0.95   | 0.17  | 0.03 | 0.17  | 0.17        | 0.05  | 0.10  | 0.09   | 0.05  | 0.06 | 0.07  |
| Used motor oil 1        | 0.77   | 0.09  | 0.09 | 0.08  | 0.08        | 0.08  | 0.08  | 0.07   | 0.08  | 0.06 | 0.06  |
| Used motor oil 2        | 1.00   | 0.29  | 0.10 | 0.13  | 0.21        | 0.06  | 0.05  | 0.04   | 0.05  | 0.03 | 0.04  |
| Tire particles          | 1.00   | 0.05  | 0.01 | 0.15  | 0.42        | 0.02  | 0.09  | 0.04   | 0.03  | 0.02 | 0.17  |
| Asphalt                 | 1.00   | 0.22  | 0.04 | 0.10  | 0.14        | 0.03  | 0.09  | 0.12   | 0.08  | 0.05 | 0.12  |
| NIST diesel particles   | 1.00   | 0.37  | 0.00 | 0.27  | 0.25        | 0.00  | 0.11  | 0.00   | 0.00  | 0.00 | 0.00  |
| Fuel-oil combustion     | 0.68   | 0.12  | 0.04 | 0.14  | 0.13        | 0.01  | 0.01  | 0.04   | 0.04  | 0.11 | 0.05  |
| Pine-wood particles     | 1.00   | 0.05  | 0.02 | 0.31  | 0.19        | 0.10  | 0.09  | 0.11   | 0.06  | 0.04 | 0.03  |
| NIST coal tar           | 0.79   | 0.22  | 0.05 | 0.16  | 0.12        | 0.05  | 0.03  | 0.05   | 0.05  | 0.03 | 0.02  |
| SC scrape Milwaukee     | 0.97   | 0.20  | 0.02 | 0.21  | 0.15        | 0.06  | 0.08  | 0.15   | 0.06  | 0.03 | 0.03  |
| SC-dust                 | 0.98   | 0.09  | 0.01 | 0.21  | 0.16        | 0.06  | 0.10  | 0.16   | 0.07  | 0.06 | 0.06  |
| SC-Austin               | 0.99   | 0.02  | 0.00 | 0.18  | 0.15        | 0.08  | 0.13  | 0.21   | 0.08  | 0.08 | 0.08  |

Table 6. PAH source fingerprint concentration ratios, based on study by Van Metre and Mahler (2010).

|                                 |   |         | 1900        |         | 1950       |       |         | 1970        |         | 1990  |            |         | 2000             |
|---------------------------------|---|---------|-------------|---------|------------|-------|---------|-------------|---------|-------|------------|---------|------------------|
| source category coal combustion | source<br>power plant emission<br>residential heating | Ag<br>* | Rural Urban | Ag<br>* | Rural<br>* | Urban | Ag<br>* | Rural Urban | Ag<br>* | Rural | Urban<br>* | Ag<br>X | Rural Urban<br>* |
|                                 | emissions   |         |             |         |            |       |         |             |         |       |            | *       |                  |
|                                 | coke oven emission                                    | *       | *           | *       | *          | *     | *       | *           | *       |       | *          | *       | *                |
|                                 | coal average  | *       | *           | x       | *          | *     | x       | *           | x       |       | *          | X       | *                |
| vehicle related                 | diesel vehicle emission                               | *       |             | *       | *          |       | *       |             | *       |       |            | *       |                  |
|                                 | gasoline vehicle emission                             | *       |             | X       | *          | *     | x       | * *         | X       |       | *          | X       | *                |
|                                 | traffic tunnel air                                    | X       | *           | x       | X          | X     | x       | X X         | X       | *     | X          | X       | х                |
|                                 | traffic average                                       | *       |             | x       | *          | *     | x       | * *         | X       |       | *          | X       | *                |
|                                 | used motor oil 1                                      |         |             |         |            |       |         |             |         |       |            | *       |                  |
|                                 | use motor oil 2                                       |         |             |         |            |       | *       |             | *       |       |            | *       |                  |
|                                 | tire particles  |         |             | *       |            |       | *       |             | X       |       | *          | *       |                  |
|                                 | asphalt   | *       | *           | *       | *          | *     | *       | * *         | *       |       | *          | Х       | *                |
|                                 | NIST diesel particles                                 |         |             | *       |            |       | *       |             | *       |       |            | *       |                  |
| fuel oil<br>combustion          | fuel oil combustion                                   |         |             |         |            |       |         |             |         |       |            |         | *                |
| wood burning<br>CTB sealcoat    | pine wood soot partices                               | *       |             | X       | *          | *     | x       | *           | x       |       | *          | X       | *                |
| realted                         | NIST coal tar   |         |             |         |            |       |         |             |         |       |            |         |                  |
|                                 | SC scrape Milwaukee                                   | *       | *           | x       | *          | *     | x       | * *         | x       |       | *          | X       | *                |
|                                 | SC-dust   | X       | *           | x       | X          | *     | x       | * *         | X       |       | x          | X       | X                |
|                                 | SC-Austin   | X       | *           | x       | X          | *     | x       | * <b>X</b>  | X       | *     | X          | х       | X                |
|                                 |   |         |             |         |            |       |         |             |         |       |            |         |                  |

\* 0.5-0.75 X 0.75 - 1.00

Table 7. PCA of PAH compounds and known source fingerprints.

## CONCLUSION

Results of the analysis of the compound concentrations of PAHs in sediment collected from 29 inland lakes are not consistent with the hypothesis. Coal tar sealants are not shown to be a predominate player in recent PAH loadings.

The PAH ratios suggest the PAH loading sources be that of combustive nature and related majorly to vehicular loadings into the environment. The estimated sources are determined based on the values calculated by the ratios, and then within which range of values for a specific source the found values most correlate with.

The factor analyses for all of the significant time slices show a high correlation to coal combustion and vehicles. The sources are estimated in this method using the PAH tracers. The tracers are used to indicate a specific source. If the tracer is found within the factor, the factor is correlated with the source that the tracer correlates with. This method does not prove to be a definitive way of determining the PAH loading source. Nor can land-uses be correlated to particular sources using factor analysis.

PCA used in a mass balance approach to determine if known source fingerprints can be used on PAH compound data for inland lakes does not provide any distinct correlations or observable changes in sources over time. Previous works have suggested that coal tar sealants are significant source in the recent. This data does not support this finding. Coal tar sealants, based on their source fingerprint, are suggested as the predominant input as far back as 1900, and this is inconsistent with the evidence on the production and use of these materials.

APPENDIX

| En      | <u>iily</u> | Gra     | <u>tiot</u> | Gogebic |       | Ro      | <u>und</u> | <u>Charlevoix</u> |         |
|---------|-------------|---------|-------------|---------|-------|---------|------------|-------------------|---------|
| Date    | Conc        | Date    | Conc        | Date    | Conc  | Date    | Conc       | Date              | Conc    |
| 2006.25 | 208.45      | 2004.33 | 164.29      | 2002.99 | 0.00  | 2003.89 | 1887.69    | 2002.49           | 2615.89 |
| 1999.65 | 363.04      | 1996.17 | 159.73      | 2000.63 | 0.00  | 2001.33 | 1085.34    | 1992.42           | 847.76  |
| 1987.60 | 600.42      | 1986.04 | 305.15      | 1997.66 | 21.56 | 1998.16 | 1133.73    | 1980.87           | 849.27  |
| 1977.80 | 846.78      | 1974.88 | 367.06      | 1994.27 | 16.14 | 1993.70 | 1246.44    | 1966.28           | 1082.76 |
| 1969.25 | 1048.58     | 1963.13 | 279.86      | 1991.15 | 24.36 | 1989.03 | 1130.80    | 1951.97           | 1056.11 |
| 1958.30 | 1755.35     | 1950.59 | 485.74      | 1987.04 | 15.98 | 1983.10 | 977.40     | 1934.38           | 892.00  |
| 1946.20 | 3103.54     | 1945.38 | 483.60      | 1982.39 | 0.00  | 1976.11 | 898.21     | 1917.90           | 166.15  |
| 1932.40 | 2288.46     | 1940.28 | 221.97      | 1977.16 | 0.00  | 1967.48 | 951.04     | 1902.07           | 0.00    |
| 1922.90 | 3497.14     | 1934.89 | 0.00        | 1971.27 | 0.00  | 1958.43 | 1019.05    | 1884.65           | 0.00    |
| 1911.90 | 4349.75     | 1928.95 | 0.00        | 1964.34 | 0.00  | 1947.95 | 1170.59    | 1867.03           | 0.00    |
| 1900.10 | 2997.57     | 1917.95 | 0.00        | 1957.28 | 0.00  | 1937.39 | 1509.96    | 1857.00           | 0.00    |
| 1880.25 | 2279.47     | 1891.82 | 0.00        | 1951.19 | 0.00  | 1926.27 | 1977.37    | 1841.06           | 0.00    |
| 1865.70 | 528.52      | 1861.00 | 0.00        | 1944.58 | 0.00  | 1916.90 | 1460.12    | 1822.61           | 0.00    |
| 1859.30 | 176.25      | 1824.69 | 0.00        | 1938.26 | 0.00  | 1909.92 | 571.84     | 1803.94           | 0.00    |
| 1856.95 | 101.03      | 1789.75 | 0.00        | 1930.79 | 0.00  | 1903.95 | 282.24     | 1784.52           | 0.00    |
| 1853.79 | 49.85       | 1773.81 | 0.00        | 1920.60 | 0.00  | 1897.64 | 255.65     | 1764.98           | 0.00    |
| 1849.86 | 49.82       | 1756.11 | 0.00        | 1907.50 | 0.00  | 1891.34 | 233.69     | 1745.46           | 0.00    |
| 1845.93 | 38.71       | 1740.81 | 0.00        | 1890.69 | 0.00  | 1884.98 | 201.05     | 1724.82           | 0.00    |
| 1842.12 | 0.00        | 1728.91 | 0.00        | 1878.37 | 0.00  | 1879.88 | 155.86     | 1703.82           | 0.00    |
| 1838.13 | 50.07       | 1717.97 | 0.00        | 1868.33 | 0.00  | 1874.78 | 165.61     | 1682.52           | 0.00    |
| 1834.31 | 42.99       | 1707.77 | 0.00        | 1859.07 | 0.00  | 1869.48 | 129.49     |                   |         |
| 1830.44 | 59.22       |         |             | 1850.54 | 0.00  | 1864.71 | 161.48     |                   |         |
| 1826.50 | 92.39       |         |             | 1842.27 | 0.00  | 1861.47 | 220.41     |                   |         |
| 1822.25 | 46.39       |         |             | 1834.26 | 0.00  | 1858.06 | 199.41     |                   |         |
| 1818.02 | 48.74       |         |             | 1825.93 | 0.00  | 1855.72 | 245.90     |                   |         |
| 1813.70 | 53.30       |         |             | 1817.75 | 0.00  |         |            |                   |         |
| 1809.31 | 66.67       |         |             |         |       |         |            |                   |         |
| 1804.52 | 69.42       |         |             |         |       |         |            |                   |         |

Table 8. Lakes Sampled and their corresponding dates and concentrations (ng/g).

| Ava     | lon     | <u>Big P</u> | latte  | Geo     | orge    | Shu     | pac     | Hackert |         |
|---------|---------|--------------|--------|---------|---------|---------|---------|---------|---------|
| Date    | Conc    | Date         | Conc   | Date    | Conc    | Date    | Conc    | Date    | Conc    |
| 2002.99 | 949.23  | 2007.17      | 87.65  | 2003.95 | 1331.83 | 2002.69 | 1352.56 | 2004.25 | 5284.98 |
| 2000.63 | 854.17  | 2005.36      | 86.04  | 2001.38 | 1358.64 | 1997.54 | 1108.81 | 2001.23 | 2640.00 |
| 1997.66 | 887.27  | 2003.19      | 93.25  | 1998.98 | 1312.65 | 1989.19 | 1078.66 | 1996.29 | 1995.59 |
| 1994.27 | 953.34  | 2000.79      | 83.74  | 1996.60 | 1273.85 | 1981.81 | 1292.83 | 1989.67 | 1665.21 |
| 1991.15 | 925.87  | 1998.63      | 94.19  | 1994.34 | 1092.02 | 1976.47 | 1214.20 | 1982.34 | 2040.97 |
| 1987.04 | 876.58  | 1996.01      | 90.99  | 1991.52 | 1236.84 | 1969.70 | 1359.58 | 1974.44 | 2074.30 |
| 1982.39 | 909.82  | 1993.29      | 89.17  | 1988.71 | 1469.58 | 1960.73 | 1904.12 | 1965.57 | 2722.00 |
| 1977.16 | 1071.30 | 1990.50      | 96.56  | 1985.84 | 1346.90 | 1948.20 | 1750.46 | 1959.62 | 2494.61 |
| 1971.27 | 1013.52 | 1987.71      | 125.75 | 1982.88 | 1555.76 | 1937.06 | 2216.20 | 1955.22 | 2299.29 |
| 1964.34 | 1106.30 | 1984.84      | 131.33 | 1979.89 | 1508.95 | 1930.25 | 1918.84 | 1951.09 | 2200.80 |
| 1957.28 | 1386.22 | 1982.05      | 125.19 | 1976.90 | 1251.75 | 1923.51 | 1825.94 | 1947.23 | 1873.51 |
| 1951.19 | 1343.25 | 1979.23      | 140.41 | 1973.95 | 1478.25 | 1916.44 | 1320.87 | 1943.19 | 1623.53 |
| 1944.58 | 1590.36 | 1976.37      | 200.94 | 1970.92 | 1717.62 | 1909.93 | 837.07  | 1939.02 | 1614.73 |
| 1938.26 | 1514.94 | 1973.41      | 302.87 | 1967.98 | 1239.17 | 1904.30 | 727.23  | 1934.77 | 1786.23 |
| 1930.79 | 1605.83 | 1970.30      | 389.17 | 1964.68 | 1509.90 | 1899.58 | 542.00  | 1931.68 | 1830.33 |
| 1920.60 | 1612.36 | 1967.29      | 387.02 | 1961.13 | 1319.07 | 1894.08 | 289.96  | 1928.60 | 1943.18 |
| 1907.50 | 1087.40 | 1964.31      | 474.96 | 1957.01 | 1396.20 | 1886.15 | 211.35  | 1925.49 | 1767.90 |
| 1890.69 | 977.06  | 1961.33      | 568.06 | 1953.38 | 1512.97 | 1877.07 | 152.34  | 1922.49 | 1556.22 |
| 1878.37 | 555.34  | 1958.10      | 604.85 | 1950.13 | 1559.22 | 1866.73 | 151.30  | 1919.22 | 1836.49 |
| 1868.33 | 528.58  | 1954.62      | 640.70 | 1946.87 | 1303.77 | 1860.84 | 166.04  | 1915.93 | 1413.60 |
| 1859.07 | 421.10  | 1951.01      | 557.83 | 1943.52 | 942.74  | 1857.06 | 229.44  | 1912.32 | 1717.47 |
| 1850.54 | 383.28  | 1947.23      | 592.89 | 1940.46 | 1673.22 | 1854.00 | 111.89  | 1907.57 | 1670.58 |
| 1842.27 | 294.06  |              |        | 1937.24 | 1492.19 | 1850.76 | 135.52  | 1901.89 | 1728.54 |
| 1834.26 | 345.99  |              |        | 1933.26 | 1603.20 | 1847.00 | 134.73  | 1893.22 | 1175.75 |
| 1825.93 | 340.10  |              |        |         |         | 1843.31 | 162.78  | 1881.12 | 628.76  |
| 1817.75 | 310.51  |              |        |         |         | 1839.76 | 133.21  | 1861.44 | 554.27  |
| 1809.15 | 437.71  |              |        |         |         |         |         | 1852.59 | 664.16  |

| Cac     | lillac   | Wh      | <u>nite</u> | Nicl    | hols    | Mus     | kegon    | egon <u>Campau</u> |          |
|---------|----------|---------|-------------|---------|---------|---------|----------|--------------------|----------|
| Date    | Conc     | Date    | Conc        | Date    | Conc    | Date    | Conc     | Date               | Conc     |
| 2005.02 | 3883.75  | 2006.25 | 2698.96     | 2005.03 | 497.77  | 2006.07 | 7774.51  | 2005.39            | 4137.76  |
| 2002.68 | 2627.43  | 2004.84 | 1434.39     | 2002.44 | 483.08  | 2004.76 | 12662.98 | 2004.59            | 8368.70  |
| 1999.72 | 2327.70  | 2002.78 | 1432.16     | 1999.28 | 665.09  | 2003.16 | 8065.70  | 2003.25            | 10979.43 |
| 1996.36 | 2516.74  | 2000.35 | 1497.17     | 1994.79 | 825.35  | 2001.47 | 6525.76  | 2001.74            | 11754.60 |
| 1993.13 | 2409.18  | 1998.28 | 1871.32     | 1990.69 | 1007.15 | 1999.91 | 12048.88 | 2000.32            | 12702.38 |
| 1988.81 | 2490.17  | 1996.10 | 2421.21     | 1984.77 | 1156.40 | 1998.08 | 12312.40 | 1998.60            | 16212.27 |
| 1983.79 | 2370.70  | 1993.77 | 1809.52     | 1977.77 | 1269.27 | 1996.18 | 7560.98  | 1997.14            | 18230.47 |
| 1977.80 | 2280.84  | 1991.36 | 1771.65     | 1971.93 | 1061.24 | 1994.20 | 7857.27  | 1984.42            | 24723.13 |
| 1970.02 | 2445.47  | 1988.84 | 1706.30     | 1965.72 | 892.71  | 1992.25 | 12117.71 | 1960.83            | 45321.16 |
| 1960.94 | 3085.08  | 1986.39 | 1722.72     | 1960.41 | 958.03  | 1990.31 | 11841.93 | 1929.12            | 24349.50 |
| 1951.82 | 2601.63  | 1983.96 | 1835.35     | 1955.29 | 1066.27 | 1988.29 | 11725.72 | 1900.95            | 25553.39 |
| 1942.76 | 13442.09 | 1981.48 | 1780.05     | 1950.65 | 1026.10 | 1986.19 | 11353.18 | 1896.86            | 15875.87 |
| 1933.37 | 15839.48 | 1979.02 | 1596.88     | 1946.16 | 1274.10 | 1984.12 | 12630.31 | 1892.81            | 9053.35  |
| 1921.60 | 15219.68 | 1976.70 | 1520.05     | 1942.05 | 1376.41 | 1981.94 | 8200.58  | 1888.91            | 6061.83  |
| 1906.79 | 7692.78  | 1974.45 | 1545.36     | 1937.83 | 2095.11 | 1979.71 | 12079.79 | 1885.15            | 1233.91  |
| 1893.38 | 2898.55  | 1972.05 | 1262.58     | 1933.58 | 2779.71 | 1977.55 | 13157.90 | 1881.30            | 944.67   |
| 1883.17 | 2389.31  | 1969.69 | 1159.61     | 1928.54 | 2040.50 | 1975.39 | 13465.41 | 1877.53            | 813.12   |
| 1875.65 | 1871.14  | 1957.63 | 944.77      | 1923.32 | 1706.34 | 1973.24 | 13907.79 | 1873.96            | 720.23   |
| 1869.87 | 2004.32  | 1935.52 | 700.90      | 1918.29 | 1774.55 | 1971.13 | 13477.90 | 1870.28            | 723.50   |
| 1866.59 | 526.73   | 1900.47 | 150.81      | 1912.82 | 1251.37 | 1968.87 | 12399.82 | 1866.30            | 499.79   |
| 1864.91 | 279.14   | 1846.76 | 163.79      | 1906.95 | 758.42  | 1966.73 | 13718.18 | 1862.21            | 507.29   |
| 1863.94 | 272.75   | 1807.10 | 515.32      | 1899.69 | 249.56  |         |          | 1858.15            | 498.63   |
| 1863.23 | 175.66   |         |             | 1891.56 | 190.07  |         |          | 1854.20            | 435.55   |
| 1857.49 | 182.11   |         |             |         |         |         |          |                    |          |
| 1849.71 | 172.90   |         |             |         |         |         |          |                    |          |
| 1842.07 | 192.68   |         |             |         |         |         |          |                    |          |

1833.79 112.78

| Cry     | <u>vstal</u> | Mor     | <u>rison</u> | Thor    | npson    | <u>G</u> | ull     | <u>ll</u> <u>Otter</u> |         |  |
|---------|--------------|---------|--------------|---------|----------|----------|---------|------------------------|---------|--|
| Date    | Conc         | Date    | Conc         | Date    | Conc     | Date     | Conc    | Date                   | Conc    |  |
| 2002.99 | 1707.46      | 2008.25 | 1089.73      | 2006.71 | 2204.66  | 2003.86  | 1830.63 | 2004.43                | 3323.00 |  |
| 2000.63 | 1190.44      | 2007.66 | 1396.49      | 2004.53 | 3298.23  | 1996.49  | 1263.29 | 2003.53                | 2427.47 |  |
| 1997.66 | 1353.05      | 2006.70 | 1185.17      | 2001.76 | 2876.68  | 1986.85  | 1273.32 | 2002.35                | 3688.23 |  |
| 1994.27 | 1604.75      | 2005.57 | 1112.64      | 1998.89 | 2238.91  | 1978.18  | 1225.24 | 2001.13                | 3193.56 |  |
| 1991.15 | 1623.72      | 2004.53 | 1167.42      | 1996.45 | 2440.80  | 1971.59  | 1357.12 | 1999.91                | 3401.60 |  |
| 1987.04 | 1646.42      | 2003.29 | 1017.18      | 1992.91 | 2337.37  | 1964.17  | 1759.49 | 1998.46                | 3908.44 |  |
| 1982.39 | 1672.89      | 2002.01 | 1134.79      | 1988.88 | 3012.43  | 1954.83  | 2363.28 | 1997.21                | 3023.61 |  |
| 1977.16 | 1190.36      | 2000.67 | 986.24       | 1984.25 | 3054.71  | 1942.71  | 2350.60 | 1995.90                | 3870.23 |  |
| 1971.27 | 1171.14      | 1999.28 | 852.84       | 1978.78 | 3213.79  | 1929.06  | 2110.14 | 1994.38                | 4433.82 |  |
| 1964.34 | 897.03       | 1997.82 | 973.11       | 1973.18 | 3024.40  | 1912.22  | 1374.14 | 1992.59                | 3825.99 |  |
| 1957.28 | 620.52       | 1996.33 | 958.13       | 1966.76 | 3155.83  | 1894.05  | 832.67  | 1991.03                | 3937.49 |  |
| 1951.19 | 563.15       | 1994.73 | 722.99       | 1961.34 | 5038.60  | 1875.47  | 266.81  | 1989.34                | 4530.26 |  |
| 1944.58 | 501.66       | 1993.09 | 664.77       | 1953.87 | 11474.82 | 1863.85  | 49.48   | 1987.49                | 4592.66 |  |
| 1938.26 | 310.88       | 1991.33 | 639.66       | 1945.36 | 9396.07  | 1859.32  | 0.00    | 1985.44                | 4806.06 |  |
| 1930.79 | 313.90       | 1989.70 | 564.01       | 1938.23 | 4626.94  | 1856.02  | 0.00    | 1983.38                | 4555.73 |  |
| 1920.60 | 268.60       | 1988.00 | 570.96       | 1932.26 | 4075.05  | 1849.92  | 0.00    | 1981.23                | 4468.80 |  |
| 1907.50 | 202.67       | 1986.09 | 649.20       | 1925.07 | 3310.20  | 1832.05  | 0.00    | 1978.81                | 4642.93 |  |
| 1890.69 | 180.35       | 1984.12 | 621.92       | 1915.02 | 2752.83  | 1815.16  | 0.00    | 1976.34                | 4804.44 |  |
| 1878.37 | 148.59       | 1982.10 | 811.70       | 1899.26 | 3135.38  | 1798.10  | 0.00    | 1973.71                | 4803.89 |  |
| 1868.33 | 177.73       | 1980.21 | 958.44       | 1878.78 | 1714.32  | 1780.00  | 0.00    | 1970.97                | 4690.56 |  |
| 1859.07 | 170.68       | 1978.34 | 942.89       | 1855.73 | 1464.66  | 1762.02  | 0.00    | 1968.30                | 4626.50 |  |
| 1850.54 | 159.76       | 1976.41 | 916.45       | 1836.20 | 524.99   | 1742.92  | 0.00    | 1965.70                | 3879.10 |  |
| 1842.27 | 197.40       | 1974.29 | 916.90       | 1816.57 | 0.00     | 1723.41  | 0.00    | 1963.03                | 5589.97 |  |
| 1834.26 | 198.21       |         |              | 1794.98 | 0.00     | 1703.67  | 14.71   | 1960.52                | 7185.06 |  |
| 1825.93 | 452.64       |         |              | 1771.11 | 0.00     | 1683.75  | 15.92   | 1957.82                | 8046.09 |  |
|         |              |         |              |         |          | 1664.27  | 14.12   | 1955.00                | 4869.24 |  |
|         |              |         |              |         |          |          |         | 1951.81                | 4278.33 |  |

| Davi    | dson    | Whit    | tmore    | Cass    |         | Bi      | rd_     | Sand    |         |
|---------|---------|---------|----------|---------|---------|---------|---------|---------|---------|
| Date    | Conc    | Date    | Conc     | Date    | Conc    | Date    | Conc    | Date    | Conc    |
| 2007.92 | 8094.46 | 2006.79 | 4131.76  | 2007.92 | 5886.64 | 2007.88 | 868.64  | 2003.16 | 1849.47 |
| 2004.63 | 5412.95 | 2003.77 | 4886.27  | 2005.58 | 3266.20 | 2005.56 | 849.58  | 2001.42 | 1886.32 |
| 1999.17 | 3778.74 | 1999.41 | 4540.06  | 2003.17 | 2713.71 | 2002.53 | 1118.47 | 1999.28 | 1887.72 |
| 1991.07 | 2777.81 | 1994.40 | 4810.03  | 2000.65 | 3319.67 | 1999.08 | 1683.38 | 1996.81 | 1872.21 |
| 1984.57 | 2918.68 | 1990.14 | 5088.10  | 1998.03 | 3189.93 | 1995.57 | 1005.59 | 1994.38 | 1793.38 |
| 1976.89 | 2588.22 | 1987.60 | 4211.19  | 1994.87 | 3371.96 | 1991.17 | 780.19  | 1990.96 | 1909.40 |
| 1968.41 | 3539.02 | 1984.87 | 4487.18  | 1991.36 | 3392.96 | 1986.37 | 574.24  | 1987.16 | 2099.05 |
| 1960.98 | 2492.87 | 1981.92 | 4226.14  | 1988.14 | 3145.35 | 1982.04 | 534.16  | 1982.86 | 2932.30 |
| 1954.13 | 3130.57 | 1978.60 | 4358.76  | 1984.95 | 2857.50 | 1977.92 | 535.38  | 1977.17 | 1805.51 |
| 1946.68 | 5131.03 | 1974.69 | 3909.55  | 1981.57 | 3345.09 | 1973.46 | 535.11  | 1970.24 | 1666.79 |
| 1939.10 | 4746.43 | 1970.89 | 3864.28  | 1977.99 | 3518.02 | 1967.91 | 327.30  | 1962.07 | 1653.26 |
| 1931.45 | 3546.92 | 1966.77 | 4669.49  | 1974.71 | 2967.94 | 1962.59 | 253.31  | 1950.78 | 1363.82 |
| 1923.48 | 4212.59 | 1962.47 | 4809.21  | 1971.61 | 2479.38 | 1958.18 | 271.66  | 1935.91 | 1012.18 |
| 1915.18 | 4549.88 | 1957.85 | 4921.84  | 1969.01 | 3163.94 | 1954.27 | 414.74  | 1918.87 | 645.96  |
| 1905.45 | 3489.21 | 1952.82 | 6660.58  | 1965.99 | 4819.26 | 1950.04 | 594.43  | 1903.20 | 600.15  |
| 1894.10 | 2805.89 | 1948.07 | 11404.62 | 1963.17 | 6213.30 | 1946.12 | 762.30  | 1897.63 | 380.01  |
| 1878.95 | 2112.19 | 1943.13 | 12811.04 | 1960.22 | 5845.44 | 1941.31 | 874.64  | 1894.91 | 431.30  |
|         |         | 1935.90 | 7021.96  | 1956.76 | 4373.48 | 1937.48 | 801.41  | 1892.75 | 448.79  |
|         |         | 1928.27 | 5672.44  | 1953.08 | 3713.22 | 1934.07 | 1018.15 | 1891.33 | 575.66  |
|         |         | 1920.80 | 4475.86  | 1948.29 | 2288.13 | 1929.93 | 616.49  | 1890.44 | 422.75  |
|         |         | 1913.69 | 3004.50  | 1942.05 | 1408.96 | 1925.00 | 562.81  | 1889.62 | 394.10  |
|         |         | 1906.50 | 1973.72  | 1934.30 | 486.14  | 1919.54 | 764.51  | 1887.83 | 463.35  |
|         |         | 1899.34 | 910.37   | 1923.87 | 159.28  |         |         | 1884.33 | 362.25  |
|         |         | 1892.64 | 745.22   |         |         |         |         | 1878.67 | 405.22  |
|         |         | 1885.54 | 444.11   |         |         |         |         | 1871.62 | 254.71  |
|         |         | 1878.56 | 1010.02  |         |         |         |         | 1864.70 | 178.71  |
|         |         |         |          |         |         |         |         |         |         |

| PawPaw  |         | Cora    |          | Klinger |         | Birch   |         |
|---------|---------|---------|----------|---------|---------|---------|---------|
| Date    | Conc    | Date    | Conc     | Date    | Conc    | Date    | Conc    |
| 2008.29 | 1112.00 | 2008.10 | 41296.55 | 2006.45 | 1595.01 | 2002.95 | 1224.37 |
| 2007.17 | 1799.35 | 2004.93 | 16984.70 | 1996.84 | 1107.95 | 1997.98 | 1500.12 |
| 2005.40 | 1541.02 | 1999.26 | 23370.39 | 1983.90 | 628.31  | 1991.05 | 1655.44 |
| 2003.57 | 1532.30 | 1991.65 | 32462.98 | 1967.05 | 603.33  | 1982.30 | 1794.91 |
| 2001.86 | 1717.58 | 1984.44 | 36107.35 | 1953.73 | 549.22  | 1975.36 | 1328.75 |
| 1999.95 | 1777.16 | 1975.60 | 24353.67 | 1943.81 | 558.20  | 1968.80 | 1388.94 |
| 1997.91 | 1711.21 | 1965.99 | 21487.50 | 1935.31 | 781.43  | 1962.90 | 1753.53 |
| 1995.51 | 1728.17 | 1956.80 | 19742.11 | 1931.49 | 718.06  | 1956.94 | 2093.25 |
| 1993.05 | 1408.82 | 1948.22 | 15740.17 | 1927.17 | 691.22  | 1950.56 | 1523.64 |
| 1990.60 | 1389.60 | 1940.87 | 16605.76 | 1920.17 | 767.26  | 1942.82 | 1764.31 |
| 1988.18 | 1201.41 | 1933.23 | 12449.81 | 1913.01 | 782.14  | 1936.80 | 1714.40 |
| 1985.31 | 1264.74 | 1925.84 | 6118.39  | 1905.44 | 716.44  | 1931.32 | 1513.68 |
| 1981.98 | 985.73  | 1918.54 | 5613.44  | 1897.60 | 703.94  | 1924.26 | 742.89  |
| 1978.81 | 915.45  | 1912.19 | 4007.94  | 1889.94 | 643.82  | 1917.96 | 464.92  |
| 1975.50 | 832.27  | 1906.13 | 3258.20  | 1882.23 | 233.02  | 1910.65 | 365.21  |
| 1971.99 | 848.47  | 1899.82 | 2293.64  | 1874.79 | 44.13   | 1902.39 | 257.88  |
| 1967.73 | 768.90  | 1893.02 | 610.46   | 1867.60 | 21.14   | 1893.01 | 206.34  |
| 1963.24 | 806.17  | 1885.70 | 2023.20  | 1859.90 | 18.64   | 1880.74 | 228.28  |
| 1958.60 | 975.63  | 1878.66 | 1347.62  | 1852.57 | 14.33   | 1869.84 | 211.97  |
| 1954.02 | 1086.76 | 1872.25 | 479.42   |         |         | 1860.10 | 327.99  |
| 1949.29 | 1470.22 |         |          |         |         | 1855.95 | 173.64  |
| 1943.91 | 1819.17 |         |          |         |         | 1851.90 | 119.55  |
| 1938.77 | 1451.81 |         |          |         |         | 1847.45 | 147.93  |
| 1934.19 | 1763.88 |         |          |         |         | 1842.97 | 313.27  |
| 1929.78 | 1388.29 |         |          |         |         | 1838.56 | 72.68   |
| 1925.27 | 1267.84 |         |          |         |         | 1833.82 | 137.15  |
| 1920.70 | 1546.68 |         |          |         |         |         |         |

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