SPATIAL AND TEMPORAL TREND OF POLYCHLORINATED BIPHENYLS IN MICHIGAN INLAND LAKES

By

Yali Wei

A THESIS

Submitted to Michigan State University
in partial fulfillment of the requirements
for the degree of

MASTER OF SCIENCE

Environmental Geosciences

2011

ABSTRACT

SPATIAL AND TEMPORAL TREND OF POLYCHLORINATED BIPHENYLS IN MICHIGAN INLAND LAKES

By

Yali Wei

Polychlorinated biphenyls (PCBs) are synthetic organic chemicals which were widely used from 1929-1979 and banned in 1979 because of health risks. PCBs are still present in the environment and questions arise as to the state of environmental recovery. Previous studies have shown that atmospheric transport is the dominant pathway for PCB loadings to the environment and that urban areas can be major sources. PCB loadings have been previously reported to be higher in the southern parts of the Great Lake region and lower in the north, possibly reflecting population density. A more detailed understanding of loading patterns is limited by the coarse spatial distribution of existing sampling sites. In this study, sediment records from 34 inland lakes in Michigan were studied to better understand the spatial distribution and changes over time. Results show there is a regional pattern, as well as a localized pattern of the PCB inventories. Higher inventories in the Lower Peninsula than in the Upper Peninsula and locations of high PCB inventories near urban areas were found. During high PCB production years, the concentration and congener cluster show clear localized patterns, but more recently, concentrations and congener distributions suggest a return to a more regional signal. This indicates that during high PCB production years, the distribution of PCBs was more controlled by local sources and in current years, it’s more dominant by regional atmospheric input.

This thesis is dedicated to

My parents

For their selfless love, infinite confidence and firm support

ACKNOWLEDGEMENTS

I would like to thank my major professor, Dr. David T. Long and co-instructor, Dr. Thomas C. Voice, for their endless inspiration and patient guidance. I feel grateful for their earnest participations in discussions that lead to completion of this thesis. They provided very important insights to my thesis research and gave help to every aspect of the thesis accomplishment. I also would like to thank my committee member, Dr. Grahame J. Larson, for his advices of the thesis. I feel grateful to everyone in Dr. Long's Aqueous Geochemistry Lab, including Amanda Robinson, Ryan Vannier, Paul Grieve, Matthew Parsons and Janelle Sommerville, since they taught me a lot during the research. I could not accomplish this research without their great assistance.

I also want to share this accomplishment with my parents, for their spiritual support and encouragements. It has never been enough to express my deepest gratitude to them.

TABLE OF CONTENTS

LIST OF FIGURES

INTRODUCTION

Spatial and temporal distribution patterns of polychlorinated biphenyls (PCBs) have been studied for decades to understand their sources, transport and fate in the environment (Eisenreich et al, 1979: 1981; Hoff et al, 1996; Hillery et al, 1997; Sun et al.,2006, 2007; Golden et al, 1993; Muir et al, 1996; Schuster et al, 2010; Gioia et al, 2011; Francu et al, 2010; Jimenez et al, 2009). Previous studies have shown that the distribution pattern of PCBs in the Great Lakes region is influenced by long-range atmospheric transport and localized atmospheric inputs. However, these studies have been limited by the coarse spatial distribution of the sampling sites (Golden et al, 1993; Sun et al. 2003). Patterns of regional versus local scale have not been studied very well, due to low data resolution. The Michigan Inland Lakes Project has collected sediment records from over 30 inland lakes in State of Michigan. The data from this project afford the opportunity to study the PCB distribution pattern at a higher resolution than in previous studies. Local and regional influences can thus be examined. The purpose of this research is to better understand the relative importance of regional versus local influences on PCB distributions in the environment and to see if this helps us to understand the recover of the environment from PCB loadings.

Polychlorinated biphenyls are a class of organic compounds with 2 to 10 chlorine atoms attached to biphenyl (Sittig et al, 1981). From 1929 to 1979, PCBs were widely used for many applications, especially as dielectric fluids in transformers and capacitors, and as coolants (Flynn et al, 1997). They are very stable and do not degrade readily (Boate et al, 2004). They persist in the environment, are capable of long-range transport (Harner, 1997; Baek et al, 2011) and have potential significant impacts on human health (Berg et al, 1998). Because of health concerns, the U.S. banned PCB manufacture and use in 1979 (Flynn et al, 1997). PCB contamination in the environment comes primarily from anthropogenic emissions. They enter the environment by leakage from supposedly closed systems, landfill sites, incinerators, agricultural lands, industrial discharges, and sewage effluent (de voogt et al, 1989; Boate et al, 2004). Total global production of PCBs is estimated to be 1.3 million tons, 97% of which were used in the northern hemisphere, between 30°N-60°N (Breivik et al, 2007). Despite the production and use of PCBs being banned in many countries decades ago, they still remain in the environment. The transport, distribution, behavior, and global fate of PCBs, is therefore of continuing concern.

Considerable research has been conducted to determine the sources and transport patterns of PCBs in the environment. Most of this work depends on passive air sampling and sediment core collection to assess current and historical deposition (Hillery et al, 1997; Sun et al.,2006, 2007; Golden et al, 1993; Muir et al, 1996; Schuster et al, 2010; Gioia et al, 2011; Francu et al, 2010; Jimenez et al, 2009). Previous research has shown that urban areas such as Chicago, Illinois and Milwaukee, Wisconsin are major sources of PCBs to the Great Lakes region and PCBs can be transferred through the atmosphere to regions far away from their sources such as the world’s oceans and poles. (Schroeder et al, 1988; Bidleman, 1988; Rapaport et al, 1988; Holsen et al, 1991; Lead et al, 1996; Fahner et al, 2003; Sun et al, 2006). Atmospheric transport is an important pathway for the transfer of PCBs from land to natural waters (Eisenreich et al. 1979, 1981; Hoff et al, 1996;

Swackhamer et al, 1988; Sweet et al, 1993; Offenberg et al. 2005). It was estimated that 55-90% of the PCBs entering Lake Superior, Huron, and Michigan and 7-13% of the PCBs entering Lakes Erie and Ontario come from atmospheric inputs (Strachan et al, 1986; 1989; Eisenreich et al, 1979, 1981; Hoff et al, 1996).

PCB distribution on a regional scale has been studied in many places (Golden et al, 1993; Haugen et al, 1999; Totten et al, 2004; Shen et al, 2009; Helm et al, 2011; You et al, 2011). The Integrated Atmospheric Deposition Network (IADN) is a long-term monitoring program that was established in 1990 to monitor persistent organic pollutants in air and precipitation in the Great Lakes region (Hoff et al., 1996; Buehler and Hites, 2002). The sampling sites were chosen to be representative of regional air near the lakes, with minimal impact from local sources. Atmospheric PCB concentrations near Lake Michigan, Erie and Ontario were found to be higher than those near Lake Superior and Huron. Another study on PCBs in Great lakes sediments (Golden et al, 1993) showed the same trend as that reported by IADN. The highest PCB concentrations were found in Lake Ontario, followed by Lake Michigan and Lake Superior. The study of PCBs in the North American atmosphere has shown that atmospheric levels of PCBs were relatively high in the south-eastern United States, at intermediate levels around the Great Lakes, and very low in the Canadian Arctic (Shen et al, 2006). Previous studies seemed to indicate that because of higher population density in the southern part of Great Lakes region, the concentration of PCBs in the Great Lakes region decrease from south to north (Golden et al, 1993; Shen et al, 2006, 2009). The same trend was found in the European atmosphere (Schuster et al, 2010). A general spatial trend for all of the studied PCB congeners show a decline in concentration from high population density (south) to low population density (north). This was explained by the higher primary source density in the UK (south), whereas in Norway (north) long range atmospheric transport of the pollutant was thought to have a considerable impact (Schuster et al, 2010).

The influence of local sources on PCB distribution near urban areas has been reported to be important. (Franz et, al, 1998, 2003; Zhang et al, 1999; Offenberg et al, 2005; Totten et al, 2004; Sun et al, 2006; Schuster et al, 2010; Harner et al, 2004). PCB concentrations were found to be more than 5-10 times higher in urban areas than in rural areas in the Great Lakes region and in the UK atmosphere. (Franz et, al, 1998, 2003; Zhang et al, 1999; Offenberg et al, 2005; Totten et al, 2004; Sun et al, 2006; Schuster et al, 2010; Harner et al, 2004). PCB emissions in the Chicago atmosphere lead to dramatically increased atmospheric concentrations and deposition to southern Lake Michigan compared to the regional signal (Offenberg et al, 2005). This indicates that near urban areas, localized, urban sources are relatively more dominant than long-range atmospheric transport.

Lake sediments record the historical PCB concentration from both atmospheric inputs and surrounding watershed inputs. Previous studies have collected and dated sediment cores and measured PCB concentrations at different depths of the cores to construct temporal profiles of PCBs (Eisenreich et al, 1989; Golden et al, 1993; Muir et al, 1996). PCB temporal profiles from previous studies reflect the production and usage history of PCBs (Eisenreich et al, 1989; Oliver et al, 1989; Rapaport et al, 1988; Golden et al, 1993; Hu et al 2010; Helm et al, 2011). PCBs appear in the record around 1930 in the Great Lakes region, at the time they were first produced, and remain at very high levels between

1960 and 1980. The production peak year was around 1970, followed by a decrease after 1980 when the US government banned them. (Eisenreich et al, 1989; Oliver et al, 1989; Rapaport et al, 1988; Golden et al, 1993; Hu et al 2010; Helm et al, 2011). The concentration differences through time among different lakes can be studied by temporal profiles. Around 1970, total PCBs concentration in Lake Superior sediment peaks at 15ng/g while in Lake Ontario it peaks at 800ng/g. Around 1990, the concentrations decreased to about 7 and 200ng/g respectively (Golden et al, 1994). PCB temporal profiles aid in the understanding of how long-range atmospheric transport and localized atmospheric inputs influence PCB distributions.

PCB congener profiles can help to identify the source of PCB mixtures. There are 209 distinct PCB compounds with 2 to 10 chlorine atoms on a biphenyl molecule, each of these PCB compounds is called a PCB congener. PCBs were produced commercially under the trade name Aroclors in the U.S. The product name reflects the percent of chlorine (by weight) of the mixture (e.g., Aroclor 1242 is 42% chlorine by weight). PCB congener compositions vary in the environment. This is potentially due to: the composition of the emissions, which may be quite variable on a local scale (Wania et al, 2004); global fractionation, which results in changes in the composition of persistent organic pollutant mixtures with latitude (Wania et al, 1993;Waldow et al, 2010); PCB dechlorination, where more highly chlorinated congeners dechlorinate to lower chlorinated congener through time (Magar et al, 2005).

Multivariate data analysis is one method that is being used to aid in the identification of sources and to examine differences and similarities of the PCBs at various locations. The most commonly used are principal component analysis (PCA) and cluster analysis (Cacela et al, 2002; Howel, 2007; Zhang et al, 2010; Carro et al, 2002; Ikonomou et al, 2002; Motelay-Massei et al, 2004; Jiang et al, 2011; Lee et al, 2004). Principal component analysis creates combinations of the original variables that explain decreasing amounts of the total variation in the data with the first combination having the maximum variance. On the other hand, cluster analysis is an exploratory method that attempts to group similar samples based on some set for variables such as chemical compositions. (Krzanowski, 1988).

Principal component analysis and cluster analysis have been used to examine the differences and similarities of PCBs at various locations. (Cacela et al, 2002; Howel, 2007; Carro et al, 2002; Ikonomou et al, 2002; Motelay-Massei et al, 2004; Lee et al, 2004). PCA and hierarchical cluster analysis indicated that PCB congener profiles in outer Green Bay are more similar to the congener profiles of inner Green Bay than that of Lake Michigan; (Cacela et al, 2002). PCA-cluster analysis of PCB levels across Europe show that there were considerable differences in the pollution profiles of 71 samples surveyed and there was a significant difference between typical profiles from rural and urban areas (Howel, 2007). These studies indicate that geographically related locations have similar congener patterns.

Based on previous studies on atmospheric long-range transport, localized atmospheric inputs, historical profiles and congener profiles of PCBs, questions arise as to what is the recovery state of PCBs in the Great Lakes region. How did they distribute spatially and how did PCB loadings in different areas change historically.

According to what has been learned from previous studies, the hypothesis that drives this study is that during the time (1970s) of high PCB production the influence of population centers on loadings will cause a localized spatial pattern in PCB distribution and that in recent times (2000), PCB loadings reflect more of a regional signal.

To test the hypothesis, sediment cores from 34 inland lakes were collected and dated. Temporal concentrations of all detectable congeners were measured. Total PCB concentrations, total PCB inventories, and accumulation rates were calculated. Congener cluster analysis of high PCB emission year and recent year were compared. If the hypothesis is true: 1) total PCB inventories in Michigan inland lakes would show a south to north decreasing pattern due to larger population and more industries in the south, and would show a relatively higher PCB concentrations in the urban/industry area, 2) temporal PCB concentration profiles would show significant differences during high PCB production years among different lakes, with higher concentration near urban areas and lower concentration in the remote areas but the difference among lakes would become smaller in recent years, and 3) PCB congeners cluster would show a south to north pattern in high PCB production year, but in recent years, the south to north congener pattern would disappear due to decreasing and mixing of PCBs in the atmosphere.

MATERIAL AND METHODS

Sampling method

Sediment cores were collected from the deepest portion of 34 Michigan inland lakes from 2002 to 2008 using an MC-400 Lake/Shelf Multi-corer deployed from the monitoring vessel Nibi. Cores 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. ^{210}Pb was measured on one sub-core from each lake to determine porosity, accumulated dry mass, sedimentation rates, sediment ages and focusing factors (Freshwater Institute in Winnipeg, Manitoba, Canada). Dating models were verified using ^{137}Cs, stable Pb peak and presence of excess ^{210}Pb. Another sub-core was sectioned and used for analysis of polychlorinated biphenyls. Unlike the ^{210}Pb sub-core, it was sectioned at 1 cm increments for the entire core length. There was insufficient material for analysis in the topmost sediments, so the first two sections were combined, and the third and fourth sections were combined.

Analytical methods for PCBs have been previously described (Khim et al, 1999). 20 g sediment (wet) was homogenized with 120 g of anhydrous sodium sulfate and extracted with dichloromethane and hexane (3:1, 400 mL) in a Soxhlet apparatus for 16 h. Sulfur was removed, if necessary, by treating the extracts with activated copper. Extracts were then concentrated to 1 mL. The sample cleanup was done using an SPE cartridge packed with Florisil (Waters, Sep-Pak Florisil 6 mL). The cartridge was eluted with 10% acetone in hexane (9 mL). The eluent was concentrated to 1 mL and placed in GC vial for analysis of PCBs. $^{13}C_{12}$ Di through Deca polychlorinated biphenyls were added as internal standards. PCBs were quantified using bracketed calibration generated by averaging two calibration curves that were run before and after each set of ten samples to better adjust to changes in instruments during analytical runs.

Data analysis

The radioactive isotope ^{210}Pb was used to date sediments from each lake. Several models exist to determine sediment ages from ^{210}Pb activities, and sediments were dated using the constant flux: constant sedimentation rate model (CF:CS) (Golden et al., 1993), segmented CF:CS (SCF:CS) (Heyvaert et al., 2000), rapid steady state mixing model (RSSM) (Robbins, 1982), and the constant rate of supply model (CRS) (Sanchez-Cabeza et al.,2000).

For all models, only sediment layers containing excess-^{210}Pb could be dated. The ages of sediment slices not containing excess-^{210}Pb were estimated by extrapolation using the assumption that sedimentation rates remain constant below the existence of excess ^{210}Pb.

Sedimentation rates in each lake were determined using all models possible for that lake, and then the models were evaluated to ascertain which was the most appropriate for determining sediment ages. Profiles of ^{137}Cs activity and stable lead concentration profiles were used as indicators to determine the most appropriate model (Robbins, 1978, 1982).

Focusing factors were also determined from ^{210}Pb analysis. Sediment focusing occurs when fine-grained sediments in a lake are eroded from higher energy erosional zones near the shore of the lake, transported through transitional zones (where deposition and erosion occur episodically) and deposited in depositional zones (Downing and Rath, 1988; Hakanson, 1977). This process of focusing occurs to different extents among lakes, and must be accounted for by using the focusing factor before comparing inventories and accumulation rates among lakes. Focusing factors (FF) were estimated at each site from the ratio of unsupported ^{210}Pb inventory measured in the core to the ^{210}Pb inventory expected from atmospheric deposition (Golden et al., 1993; Muir et al., 1996).

RESULT AND DISCUSSION

Temporal concentration profile

In the Upper Peninsula, PCB concentrations in the lakes range from 0 to 28ng/g dry wt except Lake Imp and Lake Gratiot (Fig.1A). There is no clear historical trend found in these lakes. Lake Imp and Lake Gratiot have relatively higher PCBs concentrations than other lakes, the concentrations reach 42 to 63 ng/g dry wt. These sediment concentrations are assumed to be representative of uncontaminated ecosystems dominated by atmospheric deposition.

Figure 1: PCB concentration profiles. For interpretation of the references to color in this and all other figures, the reader is referred to the electronic version of this thesis.

A. Lakes in the Upper Peninsula

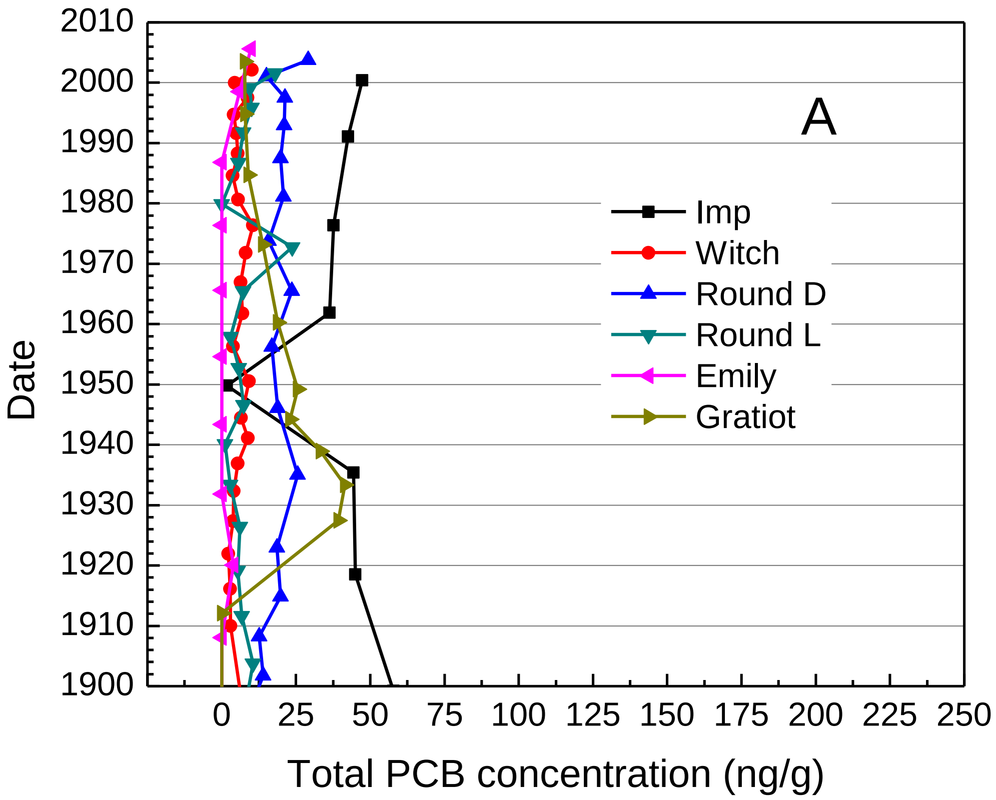
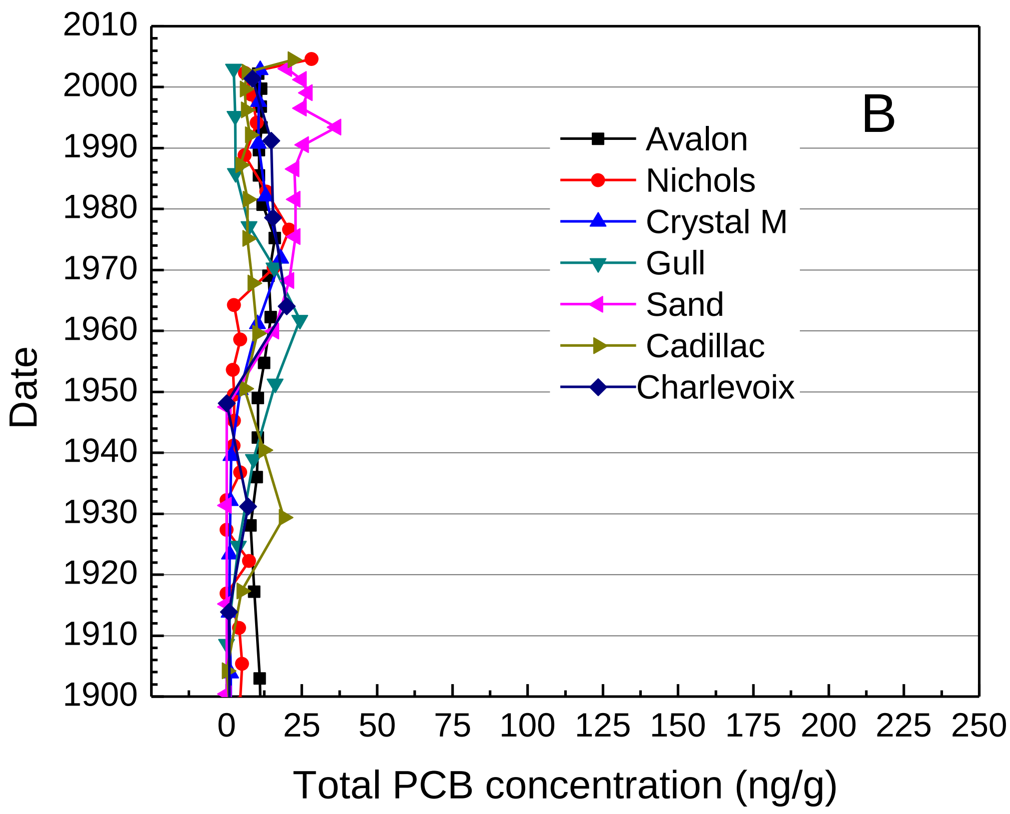


Figure 1 continued

B. Lakes in the Lower Peninsula that have low PCB concentrations



C.Lakes in the Lower Peninsula with high PCB concentrations and clear historical trend

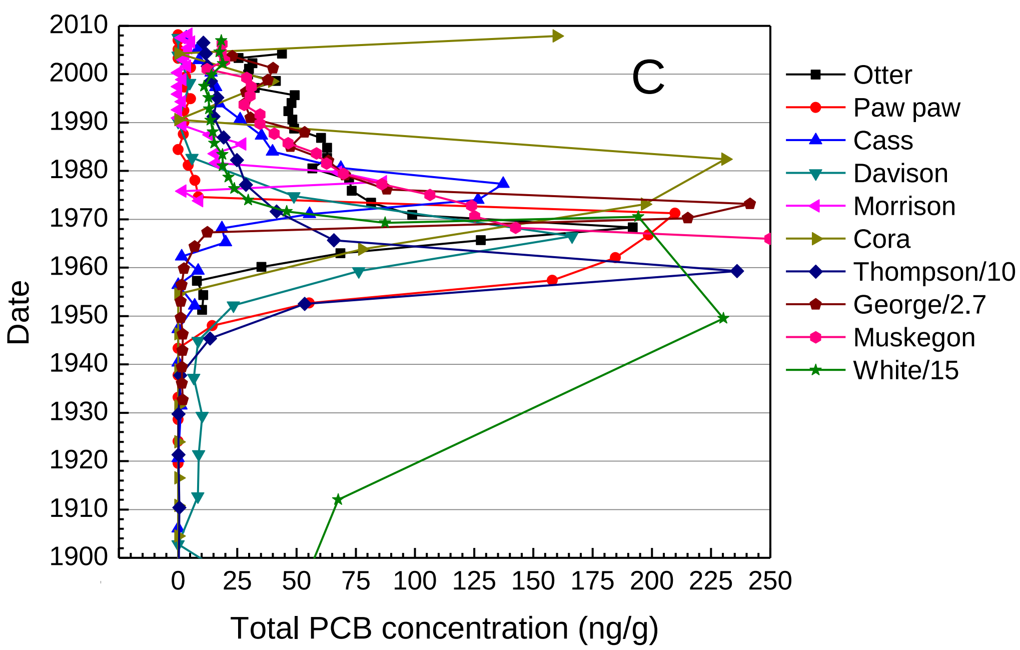
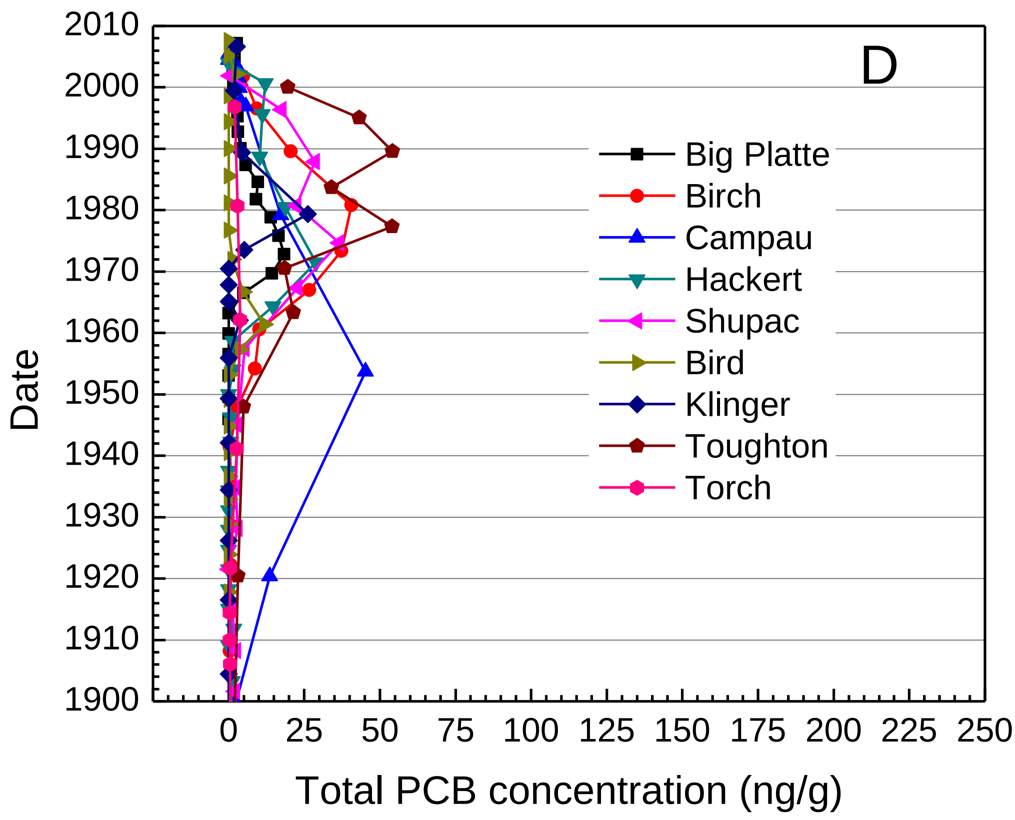


Figure 1 continued

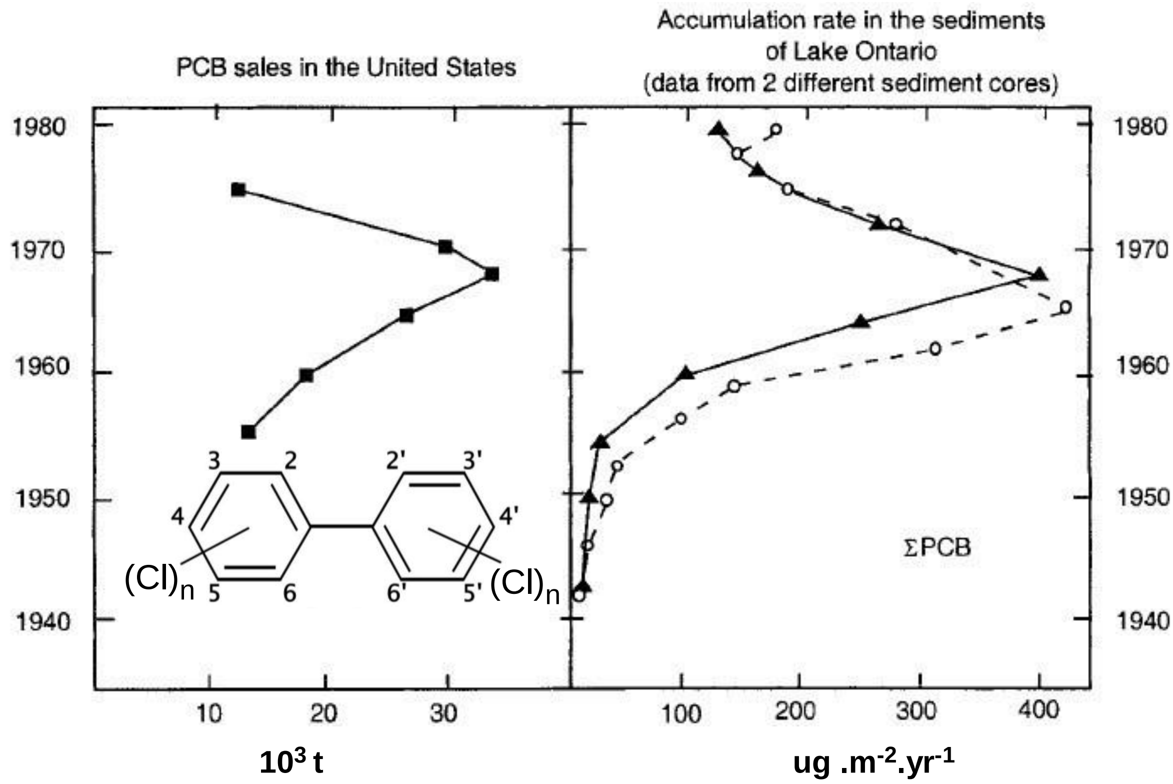
D.Lakes in the Lower Peninsula with less PCB concentrations and clear historical trend



In the Lower Peninsula, the temporal profiles vary significantly from lake to lake. The PCB concentrations of the lakes shown in Figure1B remain at low values ranging from 0 to 36ng/g. In Figure 1C, the PCB concentrations of the lakes dramatically change through time. Clear historical changes in concentrations are shown in these lakes. With the exception of White Lake and Lake Cora, PCB deposition onset occurs after 1940 and peaks between 1960 and 1980. Peak concentrations range from 87ng/g (Morrison) to 3500 ng/g (White). PCB concentrations in Lake George, Lake Thompson, and White Lake are much higher than other lakes. In order to plot all the concentrations in the same scale, the concentrations of each of the three lakes were divided by a constant: 2.7, 10 and 15 for Lake George, Lake Thompson and White Lake respectively, After 1980, PCB concentrations have all decreased to a low value, less than 50ng/g except these same three lakes. The lakes in Figure 1D from the Lower Peninsula shows the same historical change as the lakes in Figure 1C, onset and peak years are also clear. But the concentrations are much lower than the lakes in Figure 1C, varying from 0-60ng/g.

The lakes in Figure 1B are also thought to be representative of uncontaminated ecosystems dominated by atmospheric deposition as mentioned for the lakes in the Upper Peninsula. The lakes in Figure 1C are highly influenced by localized urban PCB sources. The PCB concentration profiles of these lakes reflect the production and usage history (Fig.2). PCBs began to be produced at 1929 and being banned by the U.S government at 1979, production peak was around 1970. The lakes in Figure 1D are less influenced by local sources than the lakes in Figure 1C but also follow the production history. These results correspond well with previous reports (Eisenreich et al, 1989; Rapaport et al, 1988; Golden et al, 1993; Hu et al 2010). The low PCB concentrations in Lake Superior which is close to the Upper Peninsula reflect atmospheric inputs and the higher concentrations in Lake Michigan and Ontario reflect regional and localized atmospheric deposition (Golden et al., 1993)

Figure 2: Historical records of the sales/production volumes of PCBs and the similarity of these time-varying trends to the accumulation rates of these chemicals in the sediments of Lake Ontario (from Eisenreich et al., 1989)



Accumulation rate and concentration in 1970 and 2000

PCB accumulation rates and concentrations in the year of high PCB emission (1970) and a current year (2000) were compared.

Accumulation rate of PCBs in the sediment cores were calculated as follows:

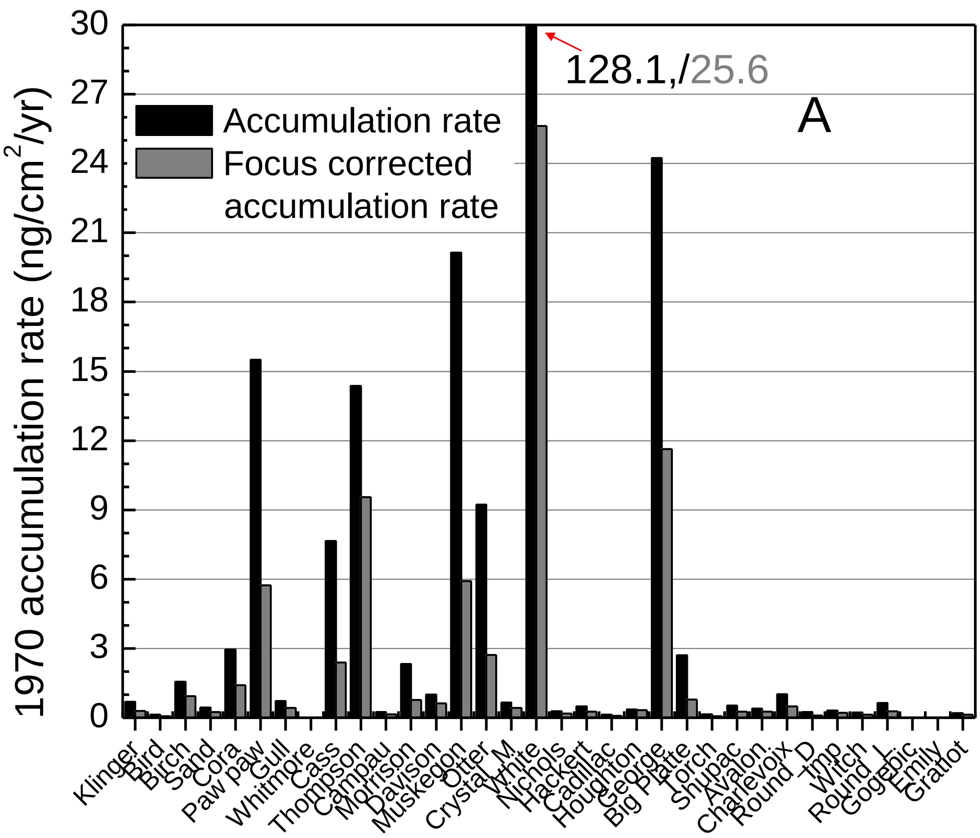
$$Accum(ng / cm^2 / yr) = C_{sed}(ng / g) \times W(g / cm^2 / yr) \qquad \text{Eq. 1}$$

Where Accum = PCB accumulation rate (ng/cm^2/yr), Csed= concentration of PCB in surficial sediment (ng/g dry wt), and W= mass sedimentation rate (ng/cm^2/yr) based on ^{210}Pb dating. Focusing-corrected sediment accumulation rates, calculated as Accum/FF, reflect the accumulation rate from atmospheric input (Golden et al, 1993).

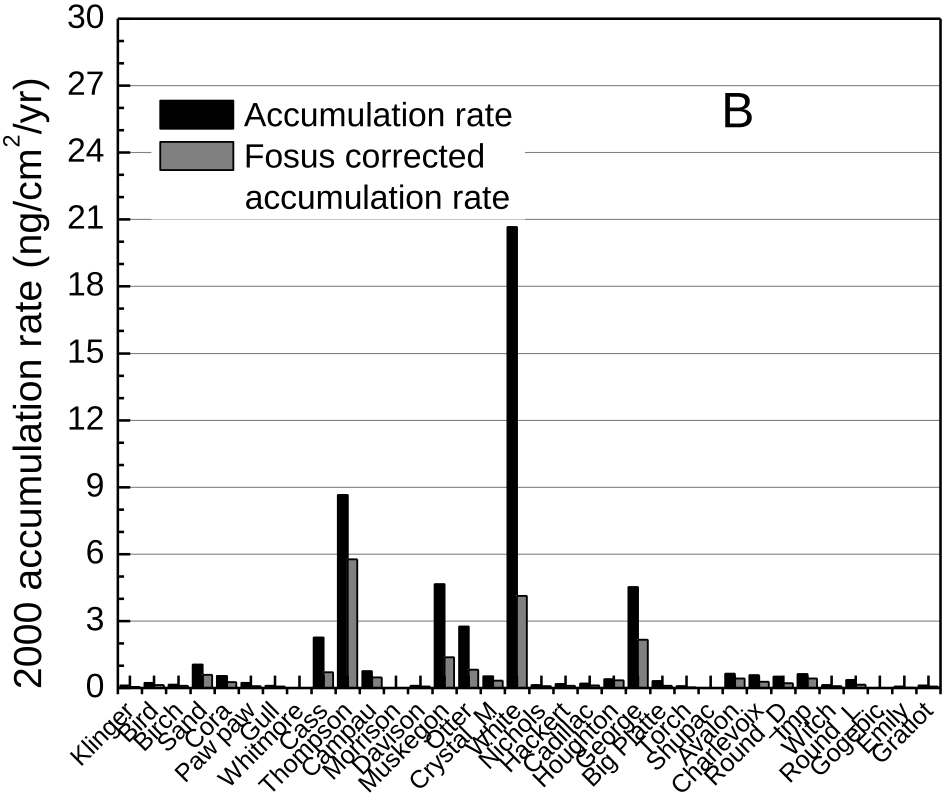
Figure 3A and 3B show that the focusing corrected accumulation rates in 1970 vary from 0-25 (ng/cm^2/yr) and in 2000 vary from 0-6 (ng/cm^2/yr). Figures 1C and D and Figures 3C and D show that in the production peak year (around 1970) total PCB concentrations among lakes vary significantly, from 0 to 3000ng/g. However, in recent years (e.g. 2000), with decreasing of total PCB concentrations, the difference among lakes becomes smaller (0-200 ng/g) as predicted. The above results indicate that the atmospheric input in 2000 is much less than 1970. In production peak year, PCB loading patterns were more influenced by local sources while in recent years, it is more influenced by regional atmospheric deposition, which is consistent with the hypothesis.

Figure 3: PCB accumulation rate and concentration in year 1970 and 2000

A. PCB accumulation rates in 1970



B. PCB accumulation rates in 2000



C. PCB accumulation rates in 2000

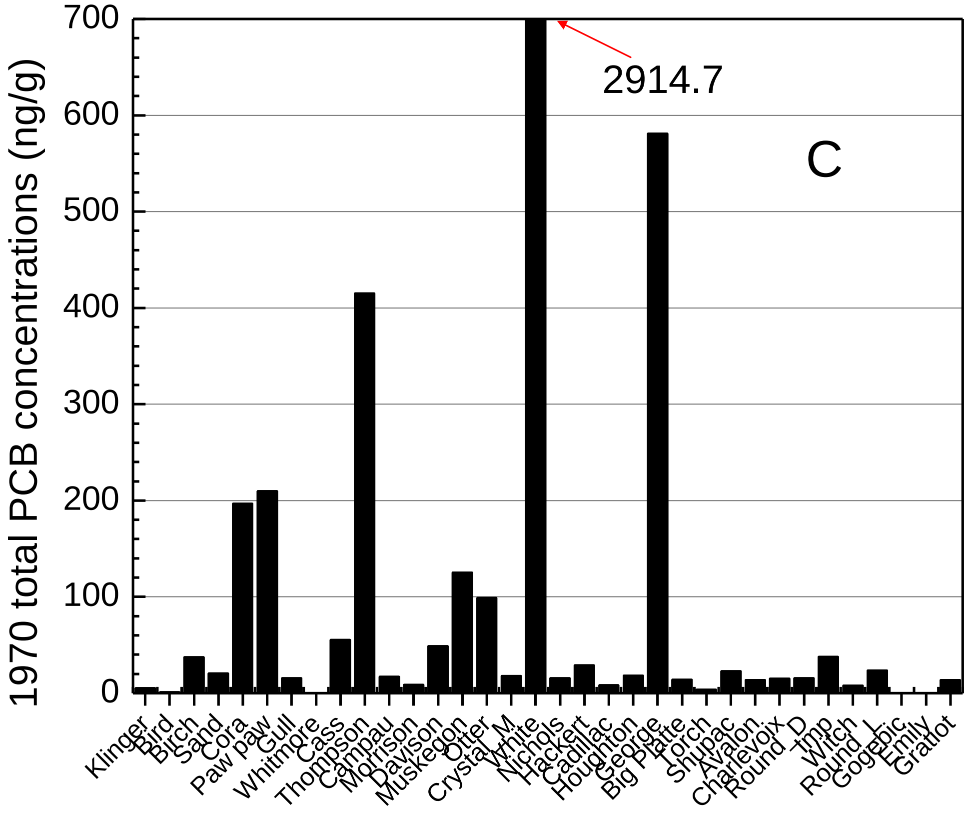
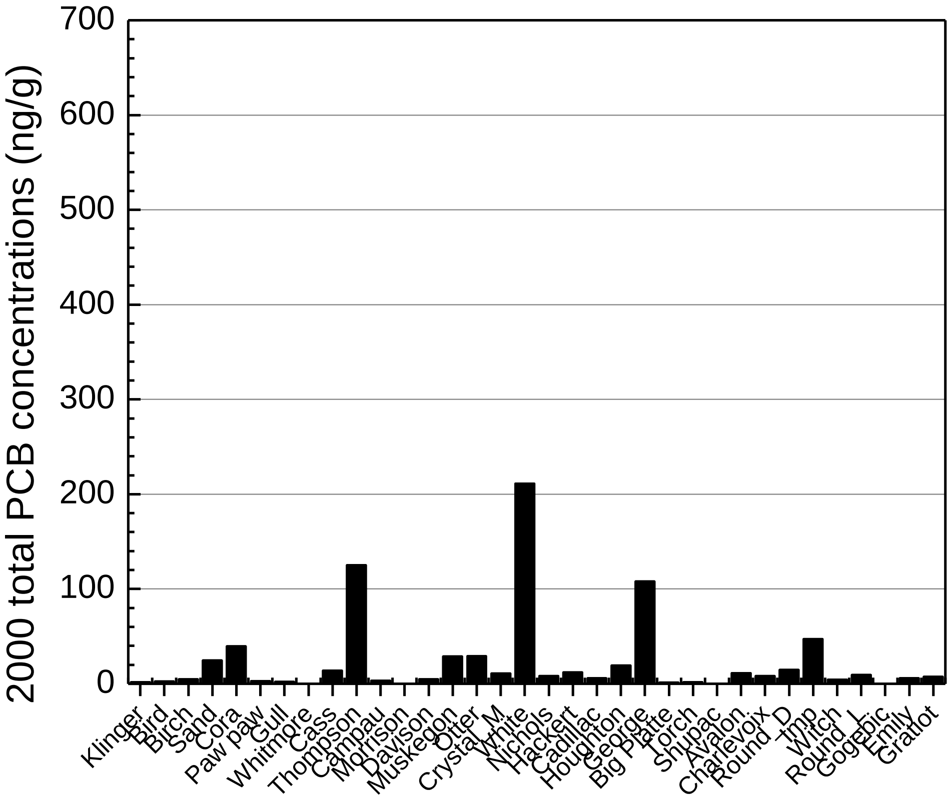


Figure 3 continued

D. PCB concentrations in 1970



Inventories

Inventories of PCBs in sediment cores were calculated as:

$$Inv(ng/cm^2) = \sum_i \; [C_{sed}(ng/g) \times (1-\varphi) \times \rho(g/cm^3) \times d(cm)] \quad \text{Eq.2}$$

Where Inv= total PCB dry mass in a core (ng/cm^2), C_{sed} = sediment concentration, ϕ = porosity, ρ = bulk density, d = thickness of sediment increment. Focusing of fine sediment from non-depositional zones to depositional zones causes the sediment inventories to be site-specific (Golden et al, 1993). Focusing-corrected inventories were calculated as Inv/FF to yield PCB burdens which may reflect basin or lake-wide inventories, where FF=focusing factor. Therefore, the focusing corrected inventory represents the PCB loading from atmospheric deposition. This concept was used in studies of organochlorine inventories in eastern Lake Ontario sediments (Eisenreich et al, 1989) and Lake Superior sediments (Jeremiason et al, 1993).

Figure 4: PCB inventories of studied Michigan Inland Lakes

A. PCB inventories from south to north, the data of Lake Michigan and Lake Superior were from Golden et al, 1993.

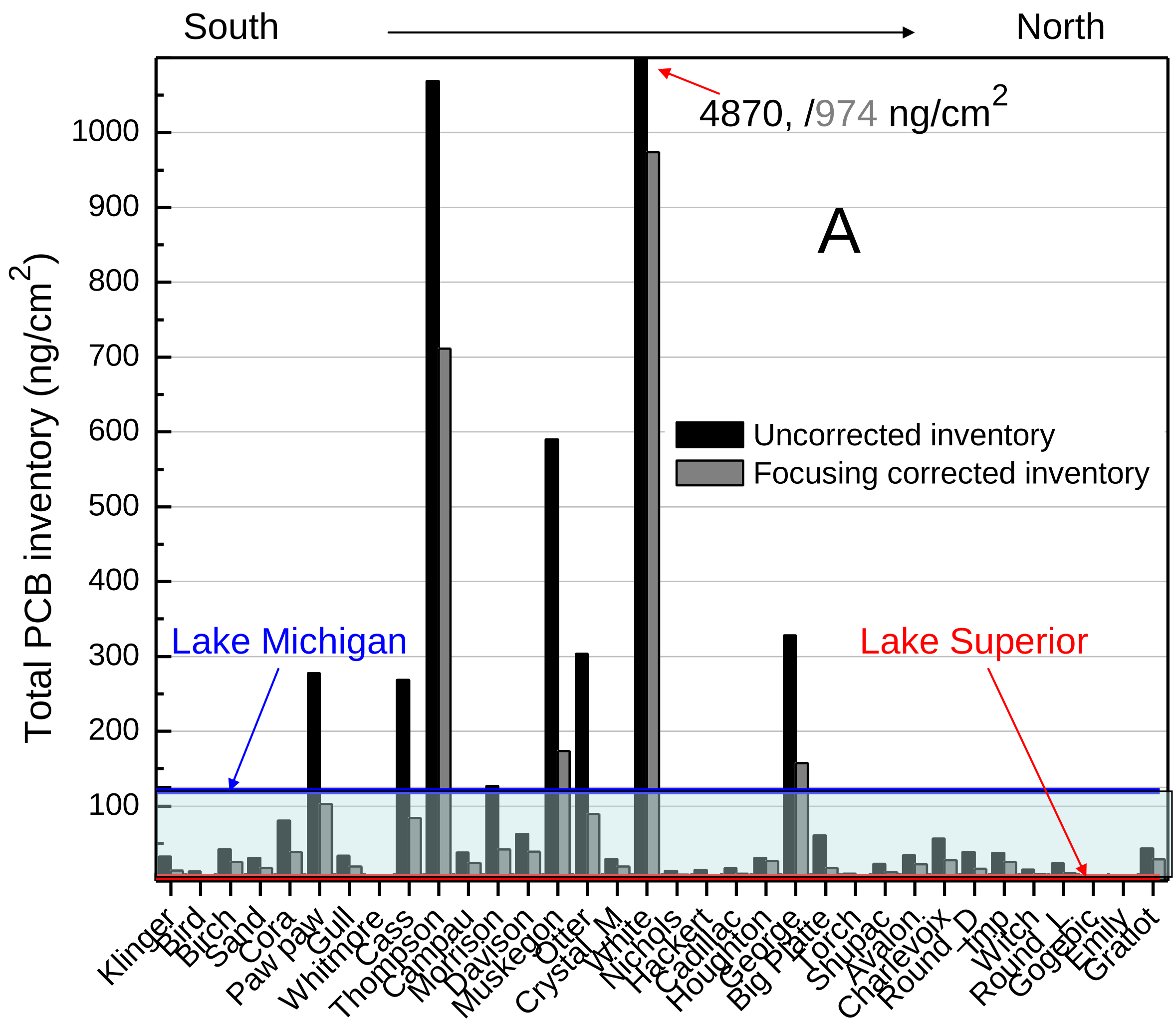


Figure 4 continued

B. spatial pattern of PCB inventories

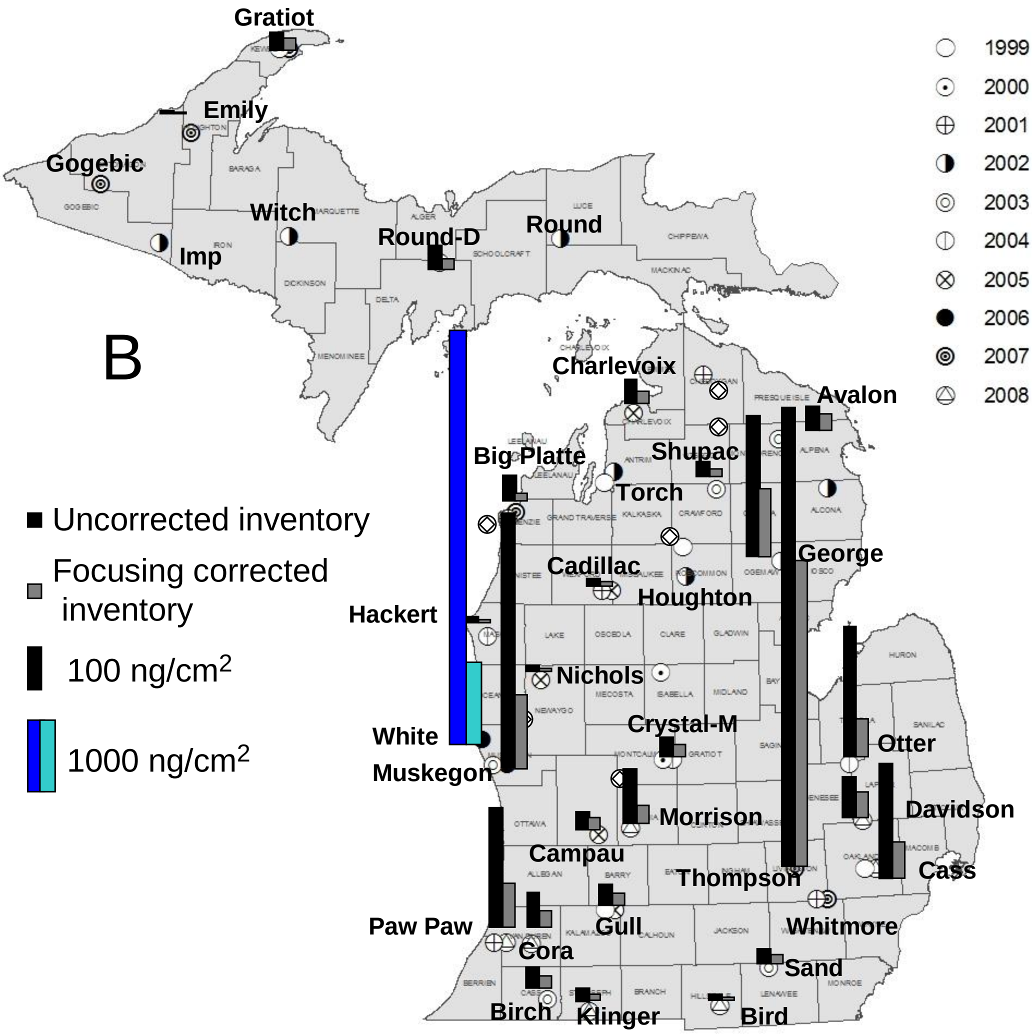


Figure 4 shows the calculated PCB inventories in Michigan inland lake sediments. Lake George, Otter, Muskegon, and Morrison only date back to 1932, 1948, 1964 and 1973, respectively, thus the real inventories of those four lakes are higher than those shown in figure 4. This should not affect our interpretation because the inventories of those four lakes are already higher than most other lakes. It is shown in figure 4 that PCB inventories of sediment cores in the Lower Peninsula are higher than that in the Upper Peninsula. There is no apparent south to north decreasing gradient as predicted. The total PCB inventories of most lakes lie between the average PCB inventories of Lake Superior (4 ng/cm^2) and Lake Michigan (125 ng/cm^2) reported by Golden et al, (1993). These values reflect the regional PCB background, indicating that the regional atmospheric loadings are similar across Michigan. Some lakes (e.g. White, Thompson, Muskegon) have high inventories (1000, 700, 200 ng/cm^2) reflecting localized atmospheric deposition due to the population and industry in the urban area. The inventory profiles show that near urban areas, PCBs arise from highly localized, urban sources and long- range transport is relatively unimportant. However, in rural areas, PCBs are more influenced by long-range atmospheric transport.

Congener pattern

To examine differences and similarities of the PCB congeners measured at various locations, cluster analysis was performed on the PCB congener data using JMP 5.0 for Windows. Twenty PCB congeners were measured and analyzed in this study. The values that are below the detection limit were assigned the half detectable value for that particular congener before analysis.

All congener concentration values were expressed as the proportion of total PCB mass (by wt), where total PCB mass is defined as the sum of congeners. This is termed percentage standardization, which was used by Stern et al. (1997). These data are often described as "compositional data" as they have the feature that the proportions of pollutants in a sample sum to 1. Since compositional data have been known problems with correlation coefficients and standard multivariate techniques (Pearson, 1897) which leads to problems with the interpretation of simple summary statistics, log-ratio transformation of the compositional data was also used as proposed by some (Aitchison, 1986; Howel, 2007). The log-ratios are calculated by dividing the compositional data of each PCB congener in each lake by the geometric mean of the twenty PCB congeners of that lake. Log-ratio=

$\log(p_{ij}/g(p_j))$. Where p_{ij} = the proportion of PCB congener i in Lake j, $g(p_j) = (p_{1j}p_{2j} \ . \ . \ . \ ,p_{dj})^{1/20}$ (Howel, 2007). The congener compositional data and log ratio transformed data of two particular time horizons: 1970 (high PCB emission) and 2000 (current year) were studied by cluster analysis. Three, four, five and six clusters were studied for both data sets and similar patterns were found. The four cluster analysis show the pattern clearer than the others, only this is presented. The analysis indicates which lakes are similar in the relative abundance or fingerprint of the congeners. Examining these relationships helps to identify common sources.

Figure 5: PCB congeners cluster patterns

A. Cluster analysis of compositional data-1970

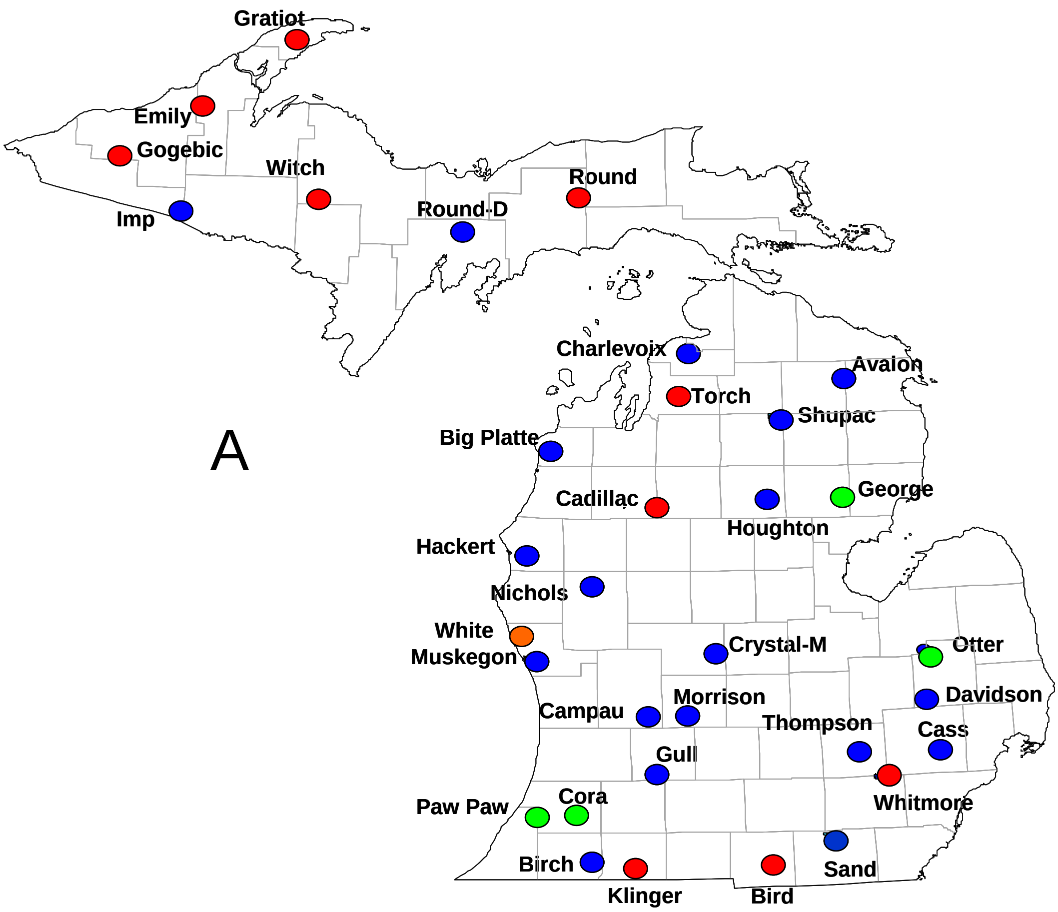


Figure 5 continued

B. Cluster analysis of compositional data-2000

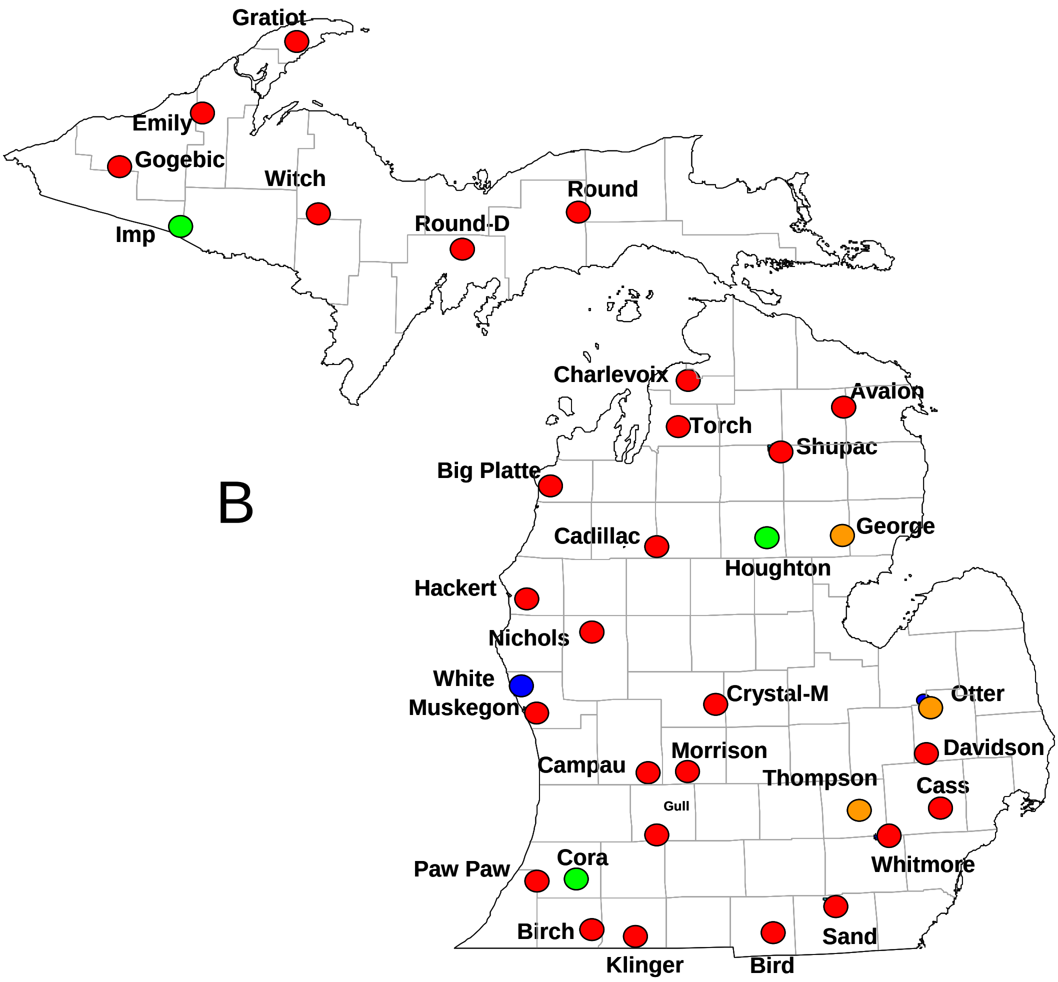


Figure 5 continued

C. Cluster analysis of log ratio transformed data-1970

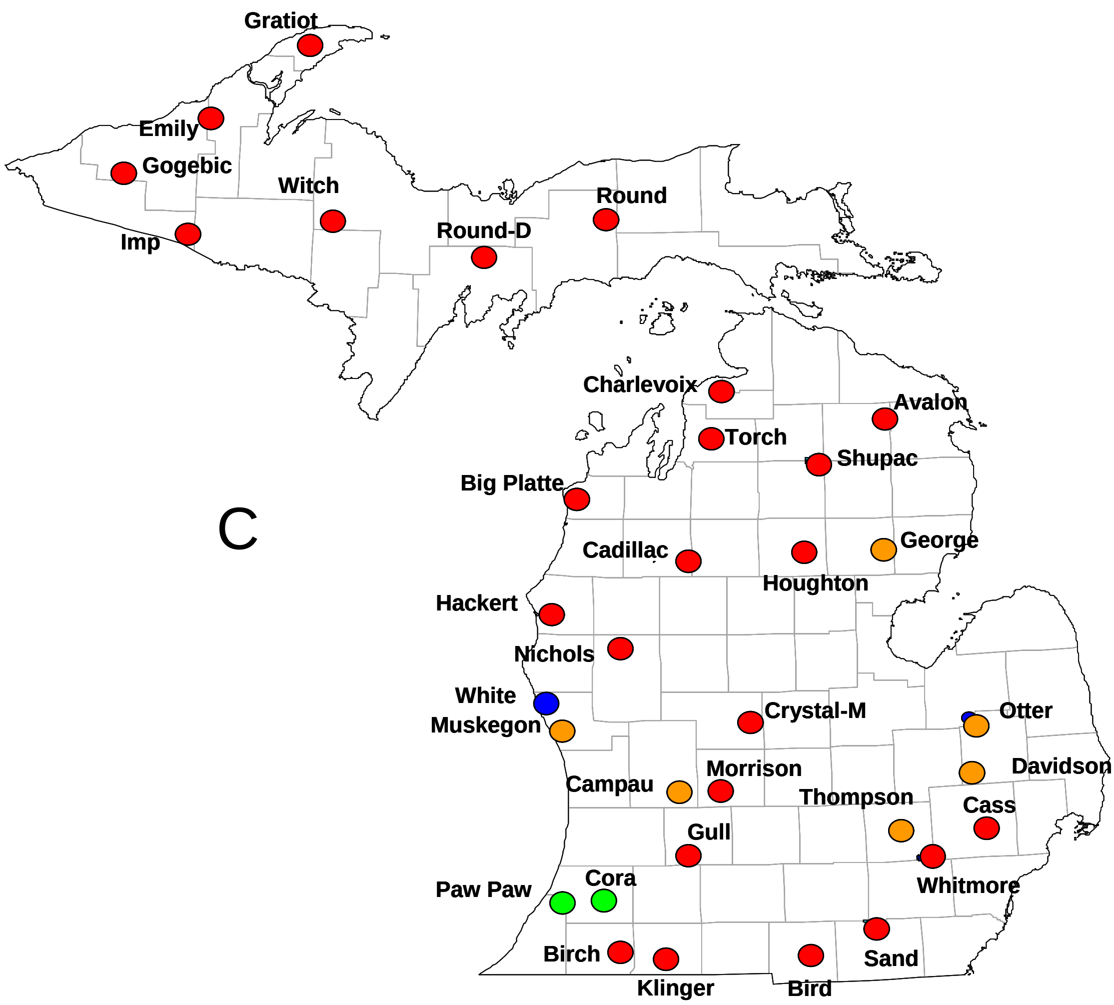
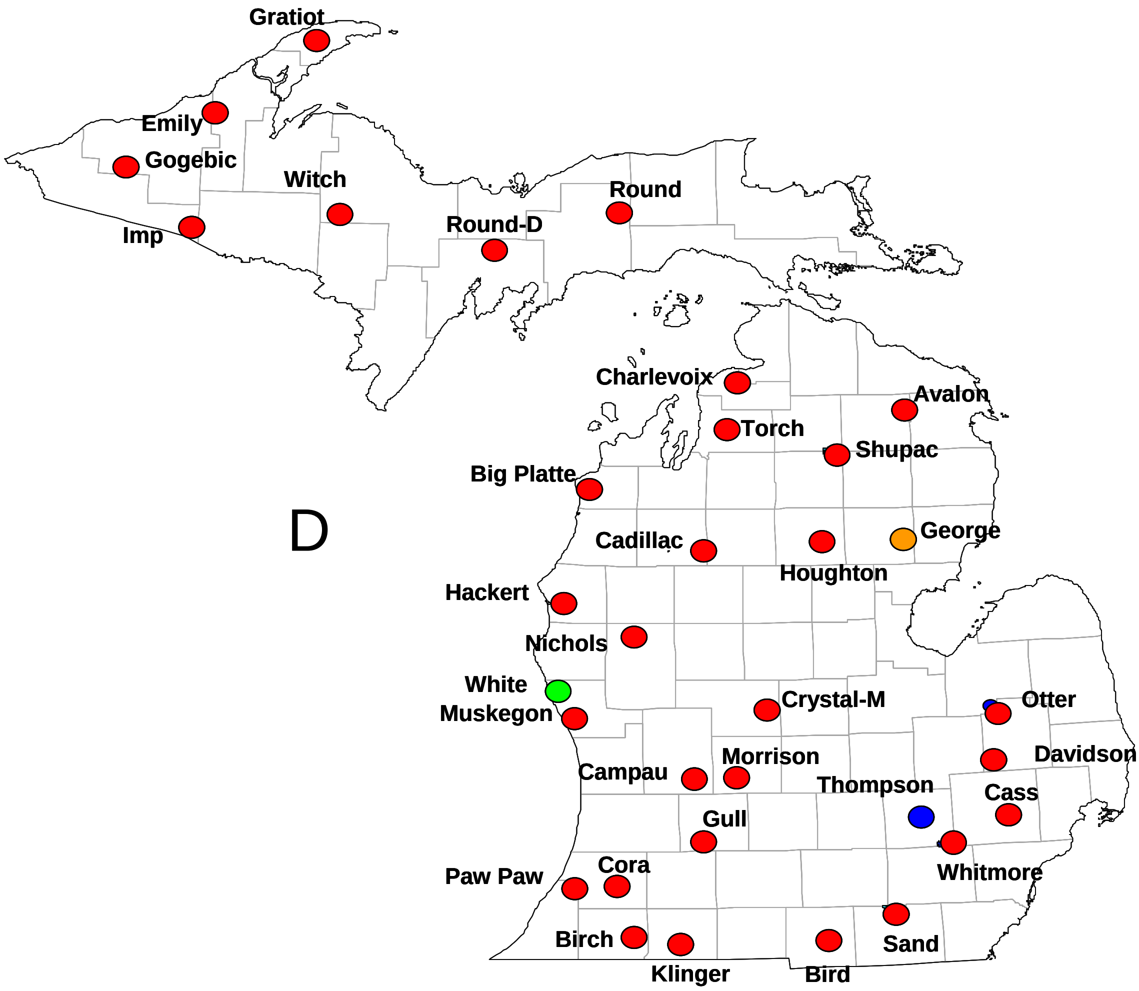


Figure 5 continued

D. Cluster analysis of log ratio transformed data- 2000



The results of the cluster analysis are shown in figure 5 where similar colors reflect similar fingerprints. In 1970, the congener cluster pattern of compositional data shows two major clusters (Fig.5A). The Upper Peninsula is dominated by one cluster and the Lower Peninsula is dominated by another cluster. In 2000, one major cluster dominates (Fig.5B) from south to north. It indicates that in 1970, the sources of PCBs in the south and the north regions are apparently different. But in 2000, PCBs in the atmosphere are well mixed and represent a regional pattern.

The cluster analysis of the log ratio transformed data (Fig. 5C, Fig.5D) showed similar patterns. In 1970, Lake White, Muskegon, Thompson and six other lakes stand out (Fig. 5C), and those lakes happened to have higher PCB concentrations and inventories (Fig.1C, Fig.4). The congener pattern together with the concentration and inventory profiles (Fig.1C, Fig.4) indicate PCBs in those lakes arise from highly localized, urban or industrial sources. However, in 2000, localized congener pattern disappear (Fig. 5D) which is similar with the compositional data, the pattern is dominated with one cluster. The PCBs in the atmosphere are more mixed than in 1970 and localized atmospheric deposition is no longer the controlling factor of PCB distributions in Michigan. The spatial and temporal congener cluster pattern again indicates during high PCB production years, the distribution of PCBs was more controlled by local sources and in current years, it’s more dominant by regional atmospheric input.

CONCLUSIONS

Sediment records from over 30 inland lakes in the State of Michigan were studied to better understand PCB spatial and temporal patterns. The hypothesis driving this study is that during the time of high PCB production (e.g., 1970) the influence of population centers on loadings will cause a spatial gradient in PCB loadings and that in recent times (e.g., 2000), PCB loadings reflect more of a regional signal. To test this hypothesis, total PCB inventories and temporal concentrations of all the lakes were studied. The accumulation rates and congener cluster analysis of high PCB production years and recent times were compared, specifically in 1970 and 2000. The concentration profiles of most lakes reflect PCB production and usage history, onset after 1940, peak during 1960-1980, and decrease after 1980. During high PCB production years, the total concentrations and accumulation rates among the lakes were significantly different. Lakes near urban areas have higher PCB concentrations and accumulation rates than lakes in remote areas. In recent years, those differences appear to be smaller. PCB inventories show a regional pattern and a localized pattern, with higher inventories in the Lower Peninsula than in the Upper Peninsula and with higher inventories in urban areas than in rural areas. PCB congener cluster analysis for the year 1970 shows a clear localized pattern, while in 2000 the localized pattern disappeared and congener compositions are similar across the State of Michigan.

The above results indicate that during the time of high PCB production, the influence of population centers on loadings caused a spatial gradient in PCB distribution and that in recent years; PCB loadings reflect more of a regional signal. Near the population centers, localized, urban sources are relatively more dominant than long-range atmospheric transport, and in remote areas, long-range atmospheric transport is the primary source of PCB loading to the lake regions.

REFERENCES

REFERENCES

Aitchison, J., 1986. The Statistical Analysis of Compositional Data.Chapman and Hall, London.

Baek, S. Y; Choi, S. D; Chang, Y. S. Three-Year Atmospheric Monitoring of Organochlorine Pesticides and Polychlorinated Biphenyls in Polar Regions and the South Pacific. *Environ. Sci. Technol.* 2011, 45, 4475-4482.

Berg, M. V. D., L.Birnbaum, A. T. C. Bosveld, B. Brunstrom, P. Cook, and T. Zacharewski. 1998. Toxic Equivalency Factors for PCBs, PCDDs, PCDFs for Human and Wildlife. *Environmental Health Perspectives.* 106: 775-792.

Bidleman, T. F. Atmospheric processes-Wet and dry deposition of organic compounds are controlled by their vapor-particle partitioning. *Environ. Sci. Technol.* 1988. 22, 361-367.

Boate, A., G. Deteersnyder, J. Howarth, A. Mirabelli, and L. Peck. 2004. Chemistry of PCBs.

Breivik, K.; Sweetman, A.; Pacyna, J. M.; Jones, K. C. Towards a global historical emission inventory for selected PCB congeners - A mass balance approach-3.An update. *Sci. Total Environ.* 2007, 377, 296–307.

Carro, N., Garcia, I., Ignacio, M., Mouteira, A. Leverls and Distribution Patterns of Polychlorinated Biphenyl Congeners in Surface Sediments from Galicia Coast (North-Western, Spain) according to Granulometric Characteristics. *Environmental Technology*. 2002. 23, 919-930.

Cacela, D., Beltman, D.J., Lipton, J. Polychlorinated Biphenyl Source Attribution in Green Bay, Wisconsin, USA, using Multivariate Similarity among Congener Profiles in Sediment Samples. *Environmental Toxicology and Chemistry*, 2002, 21, 1591-1599.

de Voogt, P.; Brinkman, U. A. T. Production, properties and usage of polychlorinated biphenyls. In Kimbrough, R. D., Jensen, A. A., Eds. *Halogenated Biphenyls, Terphenyls, Naphthalenes, Debenzodioxins and Related Products*; Elsevier-North: Amsterdam, Holland, 1989.

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

Eisenreich, S. J.; Hollod, G. J.; Johnson, T. C. Accumulation of Polychlorinated Biphenyls (PCBs) in Surficial Lake Superior Sediments. Atmospheric Deposition. *Environ. Sci. Technol.* 1979. 30, 569-572.

Eisenreich, S. J.; Looney, B. B.; Thornton, J. D. Airborne organic contaminants in the Great Lakes ecosystem. *Environ. Sci. Technol.* 1981. 28, 20-38.

Eisenreich, S. J.; Capei, P. D.; Robbins, J. A.; Bourbonniere, R. Accumulation and Diagenesis of Chlorinated Hydrocarbons in Lacustrine Sediments. *Environ. Sci. Technol.* 1989, 23, 1126-1129.

Flynn, L.T., Kleiman, C.F. Public Health Concerns About Environmental Polychlorinated Biphenyls (PCBs). A Position Paper of the American Council on Science and Health. 1997.

Franz, T. P.; Eisenreich, S. J.; Holsen, T. M. Dry Deposition of Particulate Polychlorinated Biphenyls and Polycyclic Aromatic Hydrocarbons to Lake Michigan. *Environ. Sci. Technol.* 1998, 32, 3681-3688.

Francu, E.; Schwarzbauer, J.; Lana, R.; Nyvlt, D.; Nehyba, S. Historical Changes in Levels of Organic Pollutants in Sediment Cores from Brno Reservoir, Czech Republic. Water Air Soil Pollut. 2010, 209, 81-91.

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

Gioia, R.; Eckhardt, S.; Breivik, K.; Jaward, F.M.; Prieto, A.; Nizzetto, L.; Jones, K. C. Evidence for Major Emissions of PCBs in the west African Region. *Environ. Sci. Technol.* 2011, 45, 1349-1355.

Gotten, L. A.; Gigliotti, C. L.; Vanry, D. A.; Offenberg, J. H.; Nelson, E. D.; Dachs, J.; Reinfelder, J. R.; Eisenreich, S. J. Atmospheric Concentrations and Deposition of Polychlorinated Biphenyls to the Hudson River Estuary. *Environ. Sci. Technol.* 2004. 38, 2568-2573.

Haugen, J. E.; Wania, F.; Lei, Y. D. Polychlorinated Biphenyls in the Atmosphere of Southern Norway. *Environ. Sci. Technol.* 1999. 33, 2340-2345.

Harner, T. Organochlorine contamination of the Canadian Arctic, and speculation on future trends. *International Journal of Environment and Pollution*. 1997, 8, 51-73.

Harner, T.; Shoeib, M.; Diamond, M. L.; Stern, G. A.; Rosenberg, B. Using passive air samplers to assess urban-rural trends for persistent organic pollutants. 1. Polychlorinated biphenyls and Organochlorine Pesticides. *Environ. Sci. Technol*. 2004, *38*, 4474-4483.

Hafner, W. D.; Hites, R. A. Potential Sources of Pesticides, PCBs, and PAHs to the Atmosphere of the Great Lakes. *Environ. Sci. Technol.* 2003. 37, 3764-3773.

Heyvaert, A. C.; Reuter, J. E.; Slotton, D. G.; Goldman, C. R. Paleolimnological Reconstruction of Historical Atmospheric Lead and Mercury Deposition at Lake Tahoe, California- Nevada. *Environ. Sci. Technol.*2000. 34, 3588-3597.

Helm, P. A.; Milne, J.; Hiriart. B. V. Crozier, P.; Kolic, T. Lega, R.; Chen, T.; Macpherson, K.; Gewurtz, S.; Winter, J.; Myers, A.; Marvin, C. H.; Reiner, E. J. Lake-wide distribution and depositional history of current and past use persistent organic pollutants in Lake Simcoe, Ontario, Canada. *Journal of Great Lakes research.* 2011. 37, 132-141.

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

Hermanson, MH.; Christensen, ER.; Buser, DJ.; Chen, LM. Polychlorinated-Biphenyls in Dated Sediment Cores From Green Bay and Lake Michigan. *Journal of Great Lakes Research.* 1991. 17, 94-108.

Hoff, R. M.; Strachan, W. M. J.; Sweet, C. W.; Chan, C. H.; Shackleton, M.; Bidleman, T. F.; Brice, K. A.; Burniston, D. A.; Cussion, S.; Gatz, D. F.; Harlin, K.; Schroeder, W. H. Atmospheric deposition of toxic chemicals to the Great Lakes: A review of data through 1994. *Atmos.Environ*. **1996**, *30*, 3505-3527.

Hillery, B. R.; Basu, I.; Sweet, C. W.; Hites, R. A. Temporal and Spatial Trends in a Long-Term Study of Gas-Phase PCB Concentrations near the Great Lakes. *Environ. Sci. Technol.* 1997. 31, 1811-1816.

Howel, D. Multivariate data analysis of pollutant profiles: PCB levels across Europe. Chemosphere. 2007. 67, 1300-1307.

Holsen, T. M.; Noll, K. E.; Liu, S. P.; Lee,W. J. Dry Deposition of Polychlorinated Biphenyls In Urban Areas. *Environ. Sci. Technol.*1991. 25, 1075-1081.

Hu, D.; Martinez, A.; Hombuckle, K. C. Sedimentary records of non-aroclor and aroclor PCB mixtures in the Great Lakes. *Journal of Great Lakes research.* 2011. 37, 359-364.

Ikonomou, MG., Fernandez, MP., Knapp, W., Sather, P. PCBs in Dungeness crab reflect distinct source fingerprints among harbor/industrial sites in British Columbia. *Environ. Sci. Technol.* 2002. 36, 2545-2551.

Jimenez, J. C.; Dueri, S.; Eisenreich, S. J.; Mariani, G.; Skejo, H. Umlauf, G.; Zaldivar, J. M. Polychlorinated biphenyls (PCBs) in the atmosphere of sub-alpine northern Italy. *Environmental Pollution.* 2009. 157, 1024-1032.

Jiang, YF., Wang, XT., Zhu, K., Wu, MH., Sheng, GY., Fu, JM. Polychlorinated biphenyls contamination in urban soil of Shanghai: Level, compositional profiles and source identification. *Chemosphere*. 2011. 83, 767-773.

Khim, J.S., K. Kannan, D.L. Villeneuve, C. H. Koh and J.P. Giesy. Characterization of TCDD- and Estrogen-like Activity in Sediment from Masan Bay, Korea Using: 2. *In vitro* Gene Expression Assays. *Environ. Sci. Technol.*1999. 33:4206-42.

Krzanowski, W.J., 1988. Principles of Multivariate Analysis. Oxford University Press, Oxford.

Lee, WS., Chang-Chien, GP., Wang, LC., Lee, WJ., Tsai, PJ., Wu, KY., Lin, C. Source Identification of PCDD/Fs for various Atmospheric Environments in a Highly Industrialized City. *Environ. Sci. Technol*. 2004. 38, 4937-4944.

Lead, W. A.; Steinnes, E.; Jones, K. C. Atmospheric deposition of PCBs to moss (Hylocomium splendens) in Norwaybetween 1977 and 1990. *Environ. Sci. Technol.* 1996. 30, 424-530.

Magar, V.S., Johnson, G.W., Brenner, R.C., Quensen, J.F., Foote, E.A., Durell, G., Ickes, J.A., Peven-Mccarthy, C. Long-Term Recovery of PCB-Contaminated Sediments at the Lake Hartwell Superfund Site: PCB Dechlorination. 1. End-Member Characterization. *Environ. Sci. Technol*. 2005. 39, 3538-3647.

Motelay-Massei, A., Ollivon, D., Garban, B., Teil, MJ., Blanchard, M., Chevreuil, M. Distribution and spatial trends of PAHs and PCBs in soils in the Seine River basin, France. *Chemosphere*. 2004. 55, 555-565.

Muir, D. C. G.; Omelchenko, A.; Grift, N. P.; Savoie, D. A.; Lockhart, W. L.; Wilkinson, P.; Brunskill, G. J. Spatial Trends and Historical Deposition of Polychlorinated Biphenyls in Canadian Midlatitude and Arctic Lake Sediments. *Environ. Sci. Technol.* 1996. 30, 3609-3617.

Offenberg, J.; Simcik, M.; Baker, J.; Eisenreich, S. J. The impact of urban areas on the deposition of air toxics to adjacent surface waters: A mass budget of PCBs in Lake Michigan in 1994. Aquat. Sci. 2005. 67, 79-85.

Oliver, B. G.; Charlton, M. N.; Durham,;R. W.; Distribution, Redistribution, and Geochronology of Polychlorinated Biphenyl Congeners and Other Chlorinated Hydrocarbons in Lake Ontario Sediments. *Environ. Sci. Technol.* 1989, 23, 200-208.

Pearson, K., 1897. Mathematical contributions to the theory of evolution. On the form of spurious correlation which may arise when indices are used in the measurement of organs. Proceedings of the Royal Society 60, 489–498.

Rapaport, R. A.; Eisenreich, S. J. Historical Atmospheric Inputs of High Molecular Weight

Chlorinated Hydrocarbons to Eastern North America. *Environ. Sci. Technol.* 1988, 22, 931-941.

Robbins, J.A.; Edgington, D.N.; Kemp, A.L.W. Comparative 210Pb, 137Cs, and pollen geochronologies of sediments from Lakes Ontario and Erie. *Quaternary Research*. 1978, 10, 256-278.

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

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

Sittig, M., 1981. Handbook of Toxic and Hazardous Chemicals, Noyes Publications, New Jersey.

Strachan, W. M.; Eisenreich, S. J. Mass Balancing of Toxic Chemicals in the Great Lakes: The Role of Atmospheric Deposition. International Joint Commission workshop report, Scarborough, Ontario October 29-31, 1986; 1989

Sun, P.; Basu, I.; Blanchard, P.; Backus, S. M.; Brice, K. A.; Hulting, M. L.; Hites, R. A. Temporal and Spatial trends of Atmospheric Toxic Substances near the Great Lakes: IADN results through 2003. Environment Canada and the United States Environmental Protection Agency.

Sun, P.; Basu, I.; Hites, R. A.; Temporal Trends of Polychlorinated Biphenyls in Precipitation and Air at Chicago. *Environ. Sci. Technol.* 2006. 40, 1178-1183.

Sun, P.; Basu, I.; Blanchard, P.; Brice, K. A.; Hites, R. A. Temporal and Spatial Trends of Atmospheric Polychlorinated Biphenyl Concentrations near the Great Lakes. *Environ. Sci. Technol.* 2007, 41, 1131-1136.

Schuster, J. K.; Gioia, R.; Sweetman, A. J. Jones, K. C. Temporal Trends and Controlling Factors for Polychlorinated Biphenyls in the UK Atmosphere (1991-2008). *Environ. Sci. Technol.* 2010. 44, 8068-8074.

Schuster, J. K.; Gioia, R.; Breivik, K.; Steinnes, E.; Scheringer, M.; Jones, K. C. Trends in European Background Air Reflect Reductions in Primary Emissions of PCBs and PBDEs. *Environ. Sci. Technol.* 2010. 44, 6760-6766.

Schroeder, W. H.; Lane, D. A. The fate of toxic airborne pollutants. *Environ. Sci. Technol.*1988. 22, 240-246.

Shen, L., Wania, F., Lei, Y.D., Teixeira, C., Muir, D.C.G., Xiao, H. Polychlorinated biphenyls and polybrominated diphenyl ethers in the North American atmosphere. *Environmental Pollution*. 2006, 144, 434-444.

Shen, L.; Gewurtz, S. B.; Reiner, E. J.; MacPherson, K. A.; Kolic, T. M.; Khurana, V.; Helm, P. A.; Howell, E. T.; Burniston, D. A.; Brindle, I. D.; Marvin, C. H. Occurrence and sources of polychlorinated dibenzo-p-dioxins, dibenzofurans and dioxin-like polychlorinated biphenyls insurficial sediments of Lakes Superior and Huron. *Environmental Pollution.* 2009, 157, 1210-1218.

Swackhamer, D.L; Mcveety, B. D.; Hites, R. A. Deposition and Evaporation of Polychlorobiphenyl Congeners to and from Siskiwit Lake, Isle Royale, Lake Superior. *Environ. Sci. Technol.*1988. 22, 664-672.
Sweet, C. W.; Murphy, T. J.; Bannasch, J. H.; Kelsey, C. A.; Hong, J. Atmospheric Deposition of PCBs into Green Bay. *J. Great Lakes. Res.* 1993. 19, 109-128.

Strachan, W. M. J; Eisenreich, S. J. Mass balancing of toxic chemicals in the Great Lakes: The role of atmospheric deposition. International Joint Commission: Ontario , Canada, 1988.

Stern, G.A., Halsall, C.J., Barrie, L.A., Muir, D.C.G., Fellin, P., Rosenberg, B., Rovinsky, F.Y.A., Kononov, E.Y.A., Pastuov, B., 1997. Polychlorinated biphenyls in Arctic air. 1. Temporal and spatial trends: 1992e1994. *Environmental Science and Technology* 31, 3619e3628.

Wania, F.; Mackay, D. Global fractionation and cold condensation of low volatility organochlorinecompoundsin polar regions. *Ambio* **1993**, *22*, 10–18.

Wania, F., Su, Y., 2004. Quantifying the global fractionation of polychlorinated biphenyls. Ambio 33, 161-168.

You, H.; Ding, J.; Zhao, X. S.; Li, YF.; Liu, L. Y.; Ma, WL.; Qi, H.; Shen, JM. Spatial and seasonal variation of polychlorinated biphenyls in Songhua River, China. *Environ. Geocheml. Health.* 2011, 33, 291-299.

Zhang, H.; Eisenreich, S. J.; Franz, T. R.; Baker, J. E.; Offenberg, J. H. Evidence for Increased Gaseous PCB Fluxes to Lake Michigan from Chicago. *Environ. Sci. Technol.* 1999, 33, 2129-2137.

Zhang, H., Zhao, X., Ni, Y., Lu, X., Chen, J., Su, F., Zhao, L., Zhang, N., Zhang, X. PCDD/Fs and PCBs in sediments of the Liaohe River, China; Levels, distribution, and possible sources. *Chemosphere*. 2010. 79, 754-762.