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FACTORS CONTRIBUTING TO ELEVATED CONCENTRATIONS OF MERCURY
AND PCBs IN FISH IN THE INLAND LAKES OF MICHIGAN'S UPPER
PENINSULA AND LAKE SUPERIOR

By

Mugdha Priyadarshini

A THESIS

Submitted in partial fulfillment of the requirements for the degree of

MASTER OF SCIENCE

In Environmental Engineering

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2018

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This thesis has been approved in partial fulfillment of the requirements for the Degree of
MASTER OF SCIENCE in Environmental Engineering.

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Abstract

Mercury (Hg) pollution adversely affects ecosystems and human health. Mercury in the form of methylmercury (MeHg) bioaccumulates in aquatic ecosystems, thereby affecting fish, fish-eating wildlife and humans. The goal of this research was to clarify the effects of environmental factors on MeHg concentrations in fish in the inland lakes of the Upper Peninsula of Michigan. Of the 74 lakes for which data were available, 56 had fish mercury concentrations above the water quality guideline. Multivariate statistical analyses indicated different factors affect fish Hg concentrations in large and small lakes.

Polychlorinated biphenyl (PCB) compounds are a class of persistent, bioaccumulative and toxic organic pollutants. Atmospheric deposition has been considered to be the major input of PCBs to Lake Superior. The objective of this project was to identify the source of PCBs to Lake Superior fish. Positive Matrix Factorization (PMF) identified multiple factors that contribute to the observed distribution of congeners. The congener distributions in air and fish were different from each other. Comparison of congener distributions in fish and sediments showed significant similarity, suggesting that the sediments are a source of PCBs to the fish.

1. Overview

Mercury and Polychlorinated Biphenyls (PCBs) are Persistent, Bioaccumulative and Toxic (PBT) contaminants. If concentrations are above those deemed safe for fish consumption, the consumption of fish with these contaminants becomes hazardous for human health (Sadraddini, Azim et al. 2011). In late 1960s and early 1970s, high concentrations of mercury and PCBs were seen in the Great Lakes Region whose toxic effects were then soon seen in humans. Mercury is a neurotoxicant that affects brain development and causes an increased risk of cardiovascular disease (Sadraddini, Azim et al. 2011), whereas chronic exposure to PCBs can cause major health effects such as reproductive effects like reduced conception and birth rates, effects on neurological, immune and endocrine systems and cancer. It is also important to know that within North America, mercury and PCBs are the most common causes for fish consumption advisories (Gewurtz, Bhavsar et al. 2011). This research seeks to identify the factors that are responsible for the concentrations of mercury and PCBs in fish.

Mercury is considered to be a local, regional and global environmental issue that has adverse health implications for humans and wildlife. Anthropogenic sources like burning of fossil fuels, mining, chlorine production, etc. are responsible for much of the mercury in the environment. Even after attempts to reduce mercury emissions, some parts of the world like India and China continue to burn fossil fuel (Gantner, Power et al. 2010). Atmospheric deposition is the major source of mercury to lakes; since there has been a decline in the emissions from the United States after 1990, long-range transport of

atmospheric Hg (due to its high residence time in air – 6 -18 months (Gworek, Dmuchowski et al. 2017)) from countries like India and China must be responsible for continued high rates of deposition. Even though the Lower Peninsula (LP) of Michigan has a higher rate of atmospheric Hg deposition compared to the Upper Peninsula (UP) (MDEQ, 2008), the fish mercury concentrations in the UP are higher than those in the LP (GLEC, 2003). This calls for further investigation of the lakes in the UP so that the factors causing high fish mercury concentrations can be identified. This research was a part of a big research project called managing impacts of global transport of Atmosphere-Surface Exchangeable Pollutants (ASEP) in the context of global change (<http://asep.mtu.edu/>) that aimed at identifying the factors and time required for recovery of lakes from mercury.

PCBs are a class of persistent organic pollutants that can cause major health effects in humans like cancer, and impairments of the neurological, endocrine and reproductive systems (Sadraddini, Azim et al. 2011). Atmospheric deposition is the major input of PCBs to Lake Superior (Eisenreich, Hollod et al. 1979, Capel and Eisenreich 1985, Baker and Eisenreich 1989, Baker and Eisenreich 1990), and since the ban on PCB production in 1979, the concentrations in air above Lake Superior have decreased causing a net emission from the lake to the air. This analysis was a part of the Great Lakes Air Deposition (GLAD) Project, the aim of which is to answer the question, “Are PCBs in air a major input to PCBs in fish within L. Superior?” If the answer to the question would be

yes, then more aggressive policies for removal of PCBs from the atmosphere would result in reductions in PCB concentrations in fish.

Even though both mercury and PCBs have a similar biomagnification pattern, they have different mechanisms of accumulation. The distribution and retention of PCBs is known to happen in the lipid content whereas, Hg exhibits a strong association with sulphur-rich protein. The mercury part of the research seeks to clarify the factors that affect methylmercury concentrations in the inland lakes in UP. Data for various parameters like pH, dissolved oxygen, wetland area, watershed area, etc., were first gathered from different sources. Using multivariate statistical tools like multiple linear regression and principal component analysis, factors that were affecting fish mercury concentrations were identified. The second part of the research deals with PCBs where the concentrations of congeners in air and lake trout samples were analyzed to identify the source of PCB contamination in lake trout. For this analysis, a tool known as Positive Matrix Factorization (PMF) was used.

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2. Mercury

2.1. Introduction

Mercury is a trace metal that has been used in thermometers, barometers, manometers, electrical switches and dental restoration. Three important forms of mercury include elemental mercury, organic, and inorganic mercury; the organic compound monomethylmercury (MeHg) is the most toxic to wildlife and humans. Inorganic divalent mercury can be converted to MeHg in low- oxygen environments (Ashizawa, Hicks et al. 2005, Rolfhus, Hall et al. 2011;www.briloon.org/mercuryconnections/GreatLakes). This conversion makes mercury highly bioavailable as it readily dissolves into membrane lipids (Yu, Driscoll et al. 2011, Clayden, Kidd et al. 2013). MeHg also bioaccumulates and biomagnifies as it goes up the food chain. The primary route for human exposure to mercury is fish consumption (Gantner, Power et al. 2010, Chen, Borsuk et al. 2014). Mercury can be emitted from natural sources (volcanoes, forest fires) and from various human activities such as fossil fuel combustion, waste incineration, metal smelting, mining, chlorine production, etc., (Gantner, Power et al. 2010). It is estimated that two thirds of the mercury currently in the environment is coming from human activities (Mason, Abbott et al. 2005). Currently, there are two important sources of mercury, i.e., new mercury and legacy mercury. Although the United States has reduced mercury emissions since 1990, new mercury continues to travel from distant sources. Legacy mercury is the mercury that was previously deposited in watersheds and that gets re-emitted to the atmosphere or gets mobilized to the surface waters (Chen and Herr 2010).

There have been numerous studies that identify the parameters affecting the concentration of MeHg in fish. The most important parameters are wetlands, DOC, and pH (Balogh, Swain et al. 2006, Clayden, Kidd et al. 2013, Clayden, Kidd et al. 2014). Wetlands have been identified as an important source of MeHg and play an important role in the mobility of Hg. There is often a positive correlation between MeHg and wetlands. In addition, low pH promotes bioavailability of Hg at the base of the food chain (Yu, Driscoll et al. 2011, Clayden, Kidd et al. 2013). While DOC is also among the important parameters, its effect can be either positive or negative. It can reduce the bioavailability of MeHg, when DOC binds with MeHg causing a reduction of bioaccumulation in lakes (Gorski, Armstrong et al. 2008). DOC can increase the concentrations of methylmercury when DOC stimulates abiotic methylation at very high DOC. (Chételat, Amyot et al. 2011). Total phosphorus is reported to have a negative impact on MeHg as greater lake productivity would result in growth dilution (Clayden, Kidd et al. 2013, Clayden, Kidd et al. 2014).

While the United States has decreased its Hg emissions since 1990, there are two important, ongoing sources of mercury (Gantner, Power et al. 2010). New mercury continues to reach the U.S. from distant sources such as China and India (Gantner, Power et al. 2010). Legacy mercury refers to that which has accumulated in watersheds and continues to be re-emitted to the atmosphere or mobilized to surface waters (Gantner, Power et al. 2010). With a large area/volume ratio, smaller lakes tend to have a higher mercury concentration compared to large lakes (Kidd, Muir et al. 2012, Zhang, Rygwelski et al. 2014).

As discussed earlier, atmospheric deposition is one of the major sources of mercury in lakes (Golden, Knightes et al. 2013), and even though it is known that the Lower Peninsula, MI (LP) has a higher atmospheric deposition compared to the Upper Peninsula, MI (UP) (MDEQ, 2008), the MeHg concentrations in fish are higher in the UP compared to the LP (GLEC, 2003). Hence, a study that clarifies the factors that affect MeHg in fish in the lakes in the UP is warranted.

Some of the factors that affect MeHg in lakes are latitude, land cover, elevation, and temperature. Some of these factors are uniform across the UP. This allows us to study other factors that could affect the concentrations of MeHg. Hence, the objective of this study was to identify the factors that are affecting Walleye Hg concentrations in the inland lakes of the UP. For this analysis, we hypothesized that fish Hg concentrations would most strongly be affected by pH, dissolved oxygen, watershed and wetland area.

2.2. Methods

The questions that are being posed in this study are:

1. What are the factors affecting fish mercury concentrations in the inland lakes in the Upper Peninsula of Michigan?
2. Is there a spatial pattern or trend in fish mercury concentrations in the UP?

This section includes information on the sources of Michigan Upper Peninsula fish mercury and lake/watershed features data, and methods used for collecting these data. It

then summarizes the statistical techniques that were used to identify the factors that affect fish mercury concentrations in inland lakes.

2.2.1. Study area

The area that was considered for this study is the Upper Peninsula of Michigan. The Upper Peninsula consists of 29% of the total land area of the state of Michigan, but has a total population of just 3% (Webster, Mackay et al. 1998). This means that it has a population density of just 7 people km⁻². Apart from the low population density, the Upper Peninsula has a uniform land cover (33.80% forested) (Calculated on GIS, data: <https://viewer.nationalmap.gov/basic/>) and climate. These reduce some of the common sources of variability. Of significance for mercury cycling, the Upper Peninsula has abundant wetlands; 30.2% of the land is covered with wetlands (Calculated on GIS, data: <https://www.fws.gov/wetlands/data/state-downloads.html>). Also, the Upper Peninsula of Michigan is very rich in lakes, with 16,851 lakes greater in size than one hectare (Calculated on GIS, data: <https://viewer.nationalmap.gov/basic/>). Of the many inland lakes of varied sizes, only lakes in which Walleye mercury concentrations had been measured were considered from the 15 counties in the Upper Peninsula. Figure 2.1 shows the locations of the lakes that are included in this study.

Figure 2. 1: Locations of lakes included in the study

2.2.2. Data collection

Data for 74 inland lakes in the Upper Peninsula, Michigan were collected for the parameters shown in Figure 2.1. Values of each parameter were identified for all 74 lakes.

Figure 2. 2: Parameters that were considered for the statistical analysis

As mentioned before, inorganic divalent mercury can be converted to MeHg in low-oxygen environments; hence for this analysis we gathered data for dissolved oxygen concentrations from the bottom of lakes. Parameters like pH, watershed area and wetlands were considered in this analysis because it is well known that wetlands can produce and supply MeHg to lakes and that the low pH caused by organic acids from wetlands can inhibit demethylation (Selvendiran, Driscoll et al. 2008). Parameters (total phosphorus, secchi depth and chlorophyll) representing trophic state were also considered for this analysis. It has been previously reported that more lake productivity causes growth dilution which results in lower mercury concentrations (Clayden, Kidd et al. 2013).

Methyl mercury concentrations in Walleye were collected from the Fish Contaminant Monitoring Program Online Database, which is maintained by the Michigan Department of Environmental Quality (MDEQ). Fish mercury concentrations for different lakes were measured in different years, and the concentration measurement timespan ranged from 1984 to 2013. For some lakes the data were available just for one year but, the lakes for which data were available for more than three years were analyzed to evaluate if the values were constant over time. This was achieved with the help of MeHg vs fish length scatter plots, the results of which are shown in Appendix A. The results indicated that the MeHg concentrations were comparable for most years. The data base contained values for fish length (cm), fish size (g) and fish methylmercury concentration (ppm).

To determine the length of fish most frequently caught, a histogram of fish lengths was created (Figure. 2.3); this histogram includes all fish collected for all 74 lakes. The most frequently caught size of fish (the mode) was 40-45 cm. The cumulative frequency curve indicates that this size class is also the median. Thus, for comparison among lakes, an average length of 42.5 cm was used as described below.

Figure 2. 3: A fish length histogram used to determine the most common size of fish collected

It is well known that fish Hg content depends on fish age (size). To compare the fish Hg contents among all 74 lakes, we chose to compare a common size of fish (viz., 42.5 cm). For each lake, a linear regression between fish length and fish Hg content was performed and used to calculate the fish Hg content of a 42.5-cm walleye. The number of fish per lake available for these regressions ranged from 2-151; correlation coefficients ranged from 0.0123-0.982 with three exceptions: Stanley Lake, Otter Lake and Gulliver Lake, where fish mercury concentration was negatively correlated with fish length. Of the 74 lakes in our dataset, seven were identified as reservoirs. These are Lake Michigamme (MeHg: 1.12), Michigamme Reservoir (MeHg: 0.68), Peavy Pond (MeHg: 0.58), Sunday Lake (MeHg: 1.04), Gogebic Lake (MeHg: 0.33), Deer Lake (MeHg: 0.84) and Lake Independence (MeHg: 0.55). Reservoirs are known to have high mercury content in fish.

The increased concentrations in reservoirs is attributed to bacterial methylation of Hg that is stimulated by decomposition of labile organic matter in recently flooded soils (Therriault and Schneider 1998). However, this duration of increased Hg concentrations is not clearly known because most of the reservoirs are monitored for a limited time (Bodaly, Jansen et al. 2007).

Data for total dissolved mercury was obtained from Michigan's water quality database (<http://www.mcgi.state.mi.us/miswims/>) and GLEC (2003). These data were available for 36 lakes in the UP of which 23 lakes overlapped with the fish Hg data set of 74 lakes.

Previous studies have shown that fish Hg content may be affected by lake trophic state, lake pH, DOC concentrations, and dissolved oxygen concentrations (Balogh, Swain et al. 2006, Selvendiran, Driscoll et al. 2008, Chen and Herr 2010, Chételat, Amyot et al. 2011). The water quality parameters chosen for this study included Secchi depth, chlorophyll and total phosphorus concentrations as indicators of lake trophic state; lake pH and near-bottom dissolved oxygen were also included because of their known effects on methylation and demethylation of mercury. Data were collected from a variety of sources including the state water quality database (<http://www.mcgi.state.mi.us/miswims/>), Soranno et al. (2015), EPA Storage and Retrieval - (https://ofmpub.epa.gov/storpubl/dw_pages.querycriteria) and GLEC, (2003).

The watershed and wetland areas were calculated using ArcGIS 10.4. To calculate the aforementioned areas, data was downloaded from the National Hydrography Dataset (NHD), a 1/3rd arc- second DEM (Digital Elevation Model), and the National Wetlands Inventory (NWI). This data was made available using the USGS TNM 2.0 Viewer-National Map Viewer (<https://viewer.nationalmap.gov/basic/>).

2.2.3. Statistical analysis

All data were first transformed by taking the natural logarithm. This was done to ensure normality of the data. Using the chi – square goodness of fit test, all transformed data were confirmed to be normally distributed (Appendix A). Linear regression was performed with Microsoft Excel to determine if any parameter was strongly correlated with methyl mercury concentration in fish. Also, using the statistical analysis software SPSS, multiple linear regression (MLR) (Clayden, Kidd et al. 2013, Clayden, Kidd et al. 2014) and principal component analysis (PCA) (Clayden, Kidd et al. 2013) were performed. SPSS has several methods for handling blocks of variables, which are as explained as below.

Enter: This method is also known as Forced Entry. In this method, all variables are included in the equation in a single step.

Remove: In this method, the variables in a block are removed simultaneously.

Stepwise methods: These methods are divided into three categories.

a. Stepwise: In this method one variable is added in every step. The criteria on which SPSS adds a variable is based on the p-value (i.e., the variable generating the lowest p-value is entered into the equation). Note that the variables that are already present in the equation are removed if their p-value is greater than the default limit after the inclusion of another variable.

b. Backward: This method works by the process of elimination. In this method, all variables are entered into the model initially and the variable with a p-value greater than α_{crit} (also known as p to remove) is eliminated at each step. This process of elimination stops after all p values are less than α_{crit} ¹.

c. Forward: This method works by the process of selection. In this method, no variables are entered initially. Instead, in each step the variable with the lowest p-value less than α_{crit} is entered. Once a variable is entered in the equation, the variable stays in the equation. This step was repeated, until more variables cannot be added (i.e., p values for remaining variables were all greater than α_{crit}).

Using any stepwise method would provide the same results, but, for this analysis, Backward MLR was used. Since Backward MLR works by the process of elimination, every time SPSS was run, the model eliminated a variable and SPSS reanalyzed the data until only statistically significant variables remained.

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¹ α_{crit} has a 15-20% cut-off if prediction performance is the goal. It does not have to be 5%.

In PCA, rotations are used with a goal of further analyzing the initial results and ultimately making the patterns of the loading clearer. For this analysis, quartimax rotation was used. This is a standard method for a non-orthogonal solution, which means that factors were allowed to be correlated. Two types of PCA were performed: the first one is where based on Eigen values the number of components were determined, and the second is where the number of components were fixed.

2.3. Results

2.3.1. Simple Linear Regression

In order to identify the parameters that were most strongly correlated to walleye Hg, simple linear regression was used (Figures 2.3 to 2.12). For this analysis, all parameters were transformed using natural logarithm to obtain normality of the data, and Walleye Hg concentration was used as the dependent variable. Table 2.1 summarizes the results of this analysis. The variables that were found to be significantly correlated with Walleye Hg content were pH ($p = 0.005$), watershed area: lake area ($p = 0.0033$) and dissolved organic carbon (DOC) ($p=0.0038$).

Table 2. 1: Independent Parameters with Regression Equation, R² and p-values

Independent Parameter	Regression Equation	R ² Value	P - value
pH	$y = -1.6272x + 2.4311$	0.158	0.001
Lake Area	$y = -0.0515x - 0.8088$	0.022	0.2143
Lake Depth	$y = -0.1157x - 0.5827$	0.040	0.089
Secchi Depth	$y = -0.2199x - 0.6522$	0.044	0.076
Total Phosphorus	$y = 0.0627x - 1.0335$	0.007	0.484
Chlorophyll Level	$y = 0.0406x - 0.9202$	0.004	0.579
Percent Wetlands	$y = 0.0648x - 1.0418$	0.013	0.332
Watershed Area: Lake Area	$y = 0.1374x - 1.2193$	0.115	0.003
Dissolved Oxygen	$y = 0.0119x - 0.8696$	0.002	0.712
Dissolved Organic Carbon	$y = 0.3669x - 1.6446$	0.117	0.004

The graphs for the dependent parameter (ln[Walleye Hg]) Vs. various independent parameters are shown below.

Figure 2. 4: Regression plot for Walleye Hg vs pH

Figure 2. 5: Regression plot for Walleye Hg vs Lake Area

Figure 2. 6: Regression plot for Walleye Hg vs Maximum Lake Depth

Figure 2. 7: Regression plot for Walleye Hg vs Secchi Depth

Figure 2. 8: Regression plot for Walleye Hg vs Total Phosphorus

Figure 2. 9: Regression plot for Walleye Hg vs Chlorophyll Level

Figure 2. 10: Regression plot for Walleye Hg vs % Wetland Area

Figure 2. 11: Regression plot for Walleye Hg vs Watershed Area: Lake Area

Figure 2. 12: Regression Plot for Walleye Hg vs Dissolved Oxygen

Figure 2. 13: Regression Plot for Walleye Hg vs Dissolved Organic Carbon

Simple linear regression was performed to identify factors that affected Walleye Hg. Figures 2.4 - 2.13 demonstrate that simple linear regression could not identify factors that strongly affected walleye Hg concentrations. Based on p-values, there was a significant relation between walleye Hg concentrations and pH, watershed area: lake area and DOC. Also, the regression coefficient (highest R^2 value = 0.1575 was observed for pH) was poor for most of the parameters, which means that the model explained little variability of the data around its mean. The processes of bioaccumulation and biomagnification of mercury in fish are complex, which means that a group of factors could affect them rather than one factor.

2.3.2. Multiple Linear Regression

A MLR model may be used to explain the relationship between one dependent variable and two or more independent variables. For this particular analysis, a backward MLR

analysis was performed. The number of samples was 59, the regression coefficient (R^2) was 0.388, and the adjusted regression coefficient was 0.355. The adjusted R^2 value is altered from the R^2 value to account for the number of predictors in a model. Thus, the value would only increase if the term added would improve the model. Table 2.2 shows the standardized coefficients of variables that best predict the fish mercury concentration. The standardized coefficients indicate that all variables (dependent and independent) have a similar magnitude of impact. The magnitudes of the coefficients were then compared to see which one has a greater effect. Also, it is important to know that the larger beta coefficients are associated with lower p-values. From Table 2.2, it can be seen that as maximum depth and pH increase, walleye Hg concentration decreases, whereas as watershed area increases, walleye Hg concentration increases. When we tried to fit the regression model to our data, it was seen that the model predicted mercury concentrations higher (in some cases it was even 10-fold higher) than the known concentrations.

Table 2. 2: Factors that affect Walleye mercury concentration (N=59)

Parameter	Standardized Coefficients (Beta)	R^2 Values Obtained from Partial Regression Plots
(Constant)	2.99	
pH	-0.491	0.281
Watershed Area: Lake Area	0.388	0.156
Maximum Depth	-0.228	0.078

2.3.3. Principal Component Analysis

As mentioned before, there could be more than one factor that could affect walleye Hg concentrations. To interpret the data in a more meaningful manner, it was important to reduce the number of variables to a few to provide a more meaningful linear combination of variables. PCA can be used for such an analysis as it can identify pairwise correlations between variables. Each of these linear combinations of variables corresponds to a principal component. The PCA identified three components that, together, accounted for 68% of the total variance (Table 2.4). Component 1 identifies a positive correlation of watershed area and percentage wetland with Walleye Hg concentrations, which means that lakes with a big watershed and wetland area will have high Walleye Hg concentrations. Component 2 shows a negative relationship between pH and Walleye Hg concentration, and a positive relationship between lake area and Walleye Hg concentration. Component 3 is identified as dissolved oxygen (DO) and maximum lake depth, which indicates that Walleye Hg increases with an increase in DO and a decrease in maximum lake depth. These results further validate the results from the MLR analysis (section 2.3.2), with the exception of DO. A prior study indicates higher fish mercury concentrations are associated with lower DO concentration (Balogh, Swain et al. 2006).

Table 2. 3: Principal Components explaining the variance among the lakes

Component	Extraction Sums of Squared Loadings	
	% of Variance	Cumulative %
1	30.03	30.03
2	22.50	52.53
3	16.04	68.56

*Table 2. 4: Rotated Component Matrix
where the dark shaded areas indicate the values that correlate with different components, thus identifying the components by different parameters.*

Variable	Components		
	1	2	3
Watershed Area	0.842	0.461	
Watershed Area: Lake Area	0.796		-0.138
Percentage Wetland	0.743		
pH		0.737	-0.177
Lake Area	0.434	0.698	
Maximum Lake Depth		0.190	0.854
Dissolved Oxygen		0.319	-0.795
Secchi Depth	-0.523	0.309	0.546
Walleye Hg	0.356	-0.674	-0.202
Fish Mercury Concentration (Walleye)	0.019	0.052	0.06

Using component scores for the parameters, lake scores were calculated for all components. When the scores obtained for each component were plotted against each other (Figure 2.14) clusters of lakes were evident. The clustering was examined further by plotting component scores against lake area as shown below. Figures 2.15-17 contain two clusters of points, which indicate that the lakes within the individual clusters act similarly. Since the scores were plotted against lake area, the two clusters were based on lake size. Hence, for further analysis the lakes were separated into two groups, large lakes and small lakes.

Figure 2. 14: Component 3 Lake Score vs Component 2 Lake Score

Figure 2. 15: Component 1 Lake Score vs Lake Area

Figure 2. 16: Component 2 Lake Score vs Lake Area

Figure 2. 17: Component 3 Lake Score vs Lake Area

2.3.4. Grouping of lakes

Figure 2.18 shows a cumulative percentage plot that was used to identify the point of separation between large and small lakes. The point where the curve begins to flatten is the point of separation between large and small lakes. The point of separation was marked (the red dotted line in Figure 2.18) at 1.1 which corresponds to a lake area of ~ 3

sq. km. Thus, we separated the lakes into two size classes: large lakes (16 lakes $> 3 \text{ km}^2$) and small lakes (43 lakes $< 3 \text{ km}^2$).

Figure 2. 18: Cumulative percentage curve of log normally distributed Lake Area data

For further analysis, MLR and PCA were performed separately on the two data sets. The results are summarized below.

2.3.5. Statistical analysis of small lakes

2.3.5.1. Multiple Linear Regression

For this analysis, first all variables were natural log transformed. Multiple linear regression was performed on 43 lakes, and an R^2 of 0.572 (Adjusted $R^2 = 0.514$) was obtained. The results indicate that small shallow lakes with low pH and large wetland areas have higher Walleye Hg concentration.

Table 2. 5: Factors that affect Walleye Hg concentration (N=43)

Parameter	Standardized Coefficients (Beta)	R² Values Obtained from Partial Regression Plots
(Constant)	3.167	
Lake Area	-0.253	0.113
Maximum Lake Depth	-0.222	0.101
Total Phosphorus	0.327	0.177
Percentage Wetland	0.227	0.097
pH	-0.561	0.384

Partial regression plots are used when there is more than one independent variable for a single dependent variable. Comparing the graphs below with the ones plotted under simple linear regression, we observe that the R² values for the partial regressions are higher compared to the ones in simple linear regression. The partial regression plots for small lakes are shown below:

Figure 2. 19: Partial regression plot of Walleye Hg vs Lake Area

Figure 2. 20: Partial regression plot of Walleye Hg vs Maximum Lake Depth

Figure 2. 21: Partial regression plot of Walleye Hg vs Total Phosphorus

Figure 2. 22: Partial regression plot of Walleye Hg vs % Wetland Area

Figure 2. 23: Partial regression plot of fish mercury vs pH

2.3.5.2. Principal Component Analysis

The results of the PCA are summarized in Tables 2.6 and 2.7. From Table 2.6 it can be seen that PCA identified 4 components that accounted for 77% of the total variance.

Table 2. 6: Components explaining the variance in Hg concentration in fish in the small lakes

Component	Extraction Sums of Squared Loadings	
	% of Variance	Cumulative %
1	30.08	30.08
2	21.96	52.04
3	13.68	65.72
4	11.25	76.96

*Table 2. 7: Rotated Component Matrix
where the dark shaded areas indicate the values that correlate with different components, thus identifying
the components by different parameters.*

	Component			
	1	2	3	4
Watershed Area: Lake Area	0.872			
Wetland Area	0.788		0.11	0.502
Total Phosphorus	0.703	0.21	0.137	
Secchi Depth	-0.671	-0.404	0.296	0.126
Maximum Lake Depth		-0.842	0.128	0.182
Dissolved Oxygen		0.821		0.219
pH	0.182		0.915	
Fish Mercury Concentration (Walleye)	0.338	0.205	-0.703	-0.328
Lake Area	0.132		0.289	0.871
Chlorophyll	0.36	0.42	0.435	-0.521

PCA identifies components explaining variance in data, not only in Walleye Hg. From Table 2.7, it can be seen that component 1 could be identified as watershed characteristics and trophic state parameters. Component 2 (maximum lake depth) along with component 4 (lake area) identified parameters of lake morphology. Component 2 was also identified as DO. Component 3 represents a negative relation between Walleye Hg and pH.

2.3.6. Statistical analysis of large lakes

2.3.6.1. Multiple Linear Regression

For this analysis, the number of samples was 16, and an $R^2 = 0.439$ (Adjusted $R^2 = 0.352$) was obtained. Since Walleye Hg was positively correlated with watershed area and secchi depth it can be said that large oligotrophic lakes with a large watershed area have higher fish mercury concentration.

Table 2. 8: Factors that affect Walleye Hg concentration (N=16)

Parameter	Standardized Coefficients (Beta)	R² Values Obtained from Partial Regression Plots
(Constant)	-2.004	
Watershed Area:Lake Area	0.69	0.405
Secchi Depth	0.544	0.297

The partial regression plots for the parameters that were most strongly correlated to Walleye Hg in large lakes are shown below. The R^2 values indicate a much higher correlation compared to the simple linear regression which is because partial regression plots attempt to depict the effect of adding another variable to a plot having one or more dependent variable. Hence, it could be said that the Figure 2.23 is a regression plot for walleye Hg vs watershed area: lake area accounting for the effect of secchi depth.

Figure 2. 24: Partial regression plot of Walleye Hg vs Watershed Area: Lake Area

Figure 2. 25: Partial regression plot of Walleye Hg vs Secchi Depth

2.3.6.2. Principal Component Analysis

All variables for this analysis were first natural log transformed. The results of the PCA have been summarized in Tables 2.9 and 2.10. From Table 2.9 it can be seen that PCA identified 3 components that accounted for 71.89% of the total variance.

Table 2. 9: Components explaining variance in the large lakes

Component	Extraction Sums of Squared Loadings	
	% of Variance	Cumulative %
1	31.84	31.84
2	21.59	53.43
3	18.47	71.89

*Table 2. 10: Rotated Component Matrix
where the dark shaded areas indicate the values that correlate with different components, thus identifying the components by different parameters.*

	Component		
	1	2	3
Lake Area	0.184	0.234	0.774
Maximum Lake Depth	-0.263	0.805	0.051
Secchi Depth	-0.845	0.389	-0.136
Chlorophyll	0.817	0.107	0.048
Total Phosphorus	0.738	-0.287	0.259
Percentage Wetland	0.437	0.125	0.616
Watershed Area: Lake Area	0.681	0.043	-0.654
Dissolved Oxygen	0.123	-0.752	0.145
pH	-0.115	-0.904	-0.152
Fish Mercury Concentration (Walleye)	0.031	0.33	-0.691

From Table 2.10, it can be seen that component 1 was again identified as watershed and trophic state parameters. Component 2 identified parameters like maximum lake depth, pH and DO. It depicts a positive correlation of Walleye Hg and maximum lake depth and a negative correlation between Walleye Hg and DO and pH. Component 3 as watershed and wetland characteristics, lake area and walleye Hg.

2.4. Discussion

2.4.1. Factors that affect the concentrations of mercury in walleye in the Upper Peninsula of Michigan

Michigan's Upper Peninsula (UP) has features like low population density and low elevation with fairly uniform rainfall and landcover. Among the factors previously shown to affect methyl mercury (MeHg) concentrations in fish, topography, land cover and temperature (Stoor, Hurley et al. 2006, Golden, Knightes et al. 2013, Clayden, Kidd et al. 2014) are fairly similar across the UP. Hence, the impacts of other factors affecting MeHg bioaccumulation may be discernible. Table 2.11 summarizes the median and standard deviations of the UP lake and watershed characteristics that were evaluated in this study as potential predictors of MeHg in top predator fish.

Table 2. 11: Median and standard deviation of the parameters analyzed by multivariate statistics as potential predictors of Walleye MeHg concentrations

	Parameter		Median	Relative Standard Deviation
1.	Lake Area (km ²)	All Lakes	2.0	1.92
		<i>Small Lakes</i>	<i>1.2</i>	<i>0.62</i>
		<i>Large Lakes</i>	<i>6.4</i>	<i>1.10</i>
2.	Maximum Lake Depth (m)	All Lakes	9.1	0.67
		<i>Small Lakes</i>	<i>9.0</i>	<i>0.72</i>
		<i>Large Lakes</i>	<i>9.9</i>	<i>0.61</i>

	Parameter		Median	Relative Standard Deviation
3.	Secchi Depth (m)	All Lakes	2.7	0.43
		<i>Small Lakes</i>	2.7	0.47
		<i>Large Lakes</i>	2.4	0.41
4.	Chlorophyll (mg m ⁻³)	All Lakes	4.0	1.03
		<i>Small Lakes</i>	4.2	1
		<i>Large Lakes</i>	4.1	0.99
5.	Total Phosphorus (mg m ⁻³)	All Lakes	15.0	0.66
		<i>Small Lakes</i>	14.0	0.71
		<i>Large Lakes</i>	16.5	0.47
6.	Percentage Wetlands in Catchment	All Lakes	18.5	0.62
		<i>Small Lakes</i>	20.94	0.65
		<i>Large Lakes</i>	16.8	0.57
7.	Watershed Area: Lake Area	All Lakes	11.9	2.19
		<i>Small Lakes</i>	11.2	1.46
		<i>Large Lakes</i>	12.9	2.32
8.	Dissolved Oxygen* (mg/L)	All Lakes	5.7	0.83
		<i>Small Lakes</i>	4.8	0.92
		<i>Large Lakes</i>	7.0	0.61
9.	pH	All Lakes	7.7	0.11

10.	Walleye Hg (ppm)	<i>Small Lakes</i>	<i>7.6</i>	<i>0.11</i>
		<i>Large Lakes</i>	<i>7.9</i>	<i>0.10</i>
		<i>All Lakes</i>	<i>0.43</i>	<i>0.50</i>
		<i>Small Lakes</i>	<i>0.45</i>	<i>0.50</i>
		<i>Large Lakes</i>	<i>0.46</i>	<i>0.45</i>

Previous literature has shown that lake area can affect fish mercury concentrations (Gantner, Power et al. 2010), and this analysis found it to be a key variable for UP lakes; separation of lakes into two size classes enabled stronger statistical relationships to be determined for each size class than could be found for the entire data set. The median lake area was 1.95 km² which means most of the lakes that were considered in the analysis were small lakes, but the standard deviation indicates a large variation in lake size. The range of surface area for the small lake category was 0.24 – 3 km², which explains the low standard deviation. The surface area range for large lakes (n=16) was 3.2 – 53.1 km² which is a large range for just 16 lakes, that is reflected in the large standard deviation.

For small lakes, both PCA and MLR showed pH to have an inverse relationship with walleye Hg. Low pH inhibits demethylation and thereby allows accumulation of MeHg in lakes (Miskimmin, Rudd et al. 1992). Numerous previous studies have also found pH to be strongly related to fish Hg (Chtelat, Amyot et al. 2011, Rolfhus, Hall et al. 2011, Clayden, Kidd et al. 2013, Clayden, Kidd et al. 2014). Unlike some other regions, low

pH in UP lakes is due primarily to inputs of organic acids (humic and fulvic acids) from wetlands.

Wetlands present in the watershed area also serve as major sites of methylmercury production (St. Louis, Rudd et al. 1994, Hurley, Benoit et al. 1995, St. Louis, Rudd et al. 1996, Balogh, Swain et al. 2006, Selvendiran, Driscoll et al. 2008, Gantner, Power et al. 2010, Rolffhus, Hall et al. 2011, Clayden, Kidd et al. 2013, Golden, Knightes et al. 2013). A lake with a large watershed area and a higher percentage of wetlands present in the watershed will have a higher methylmercury concentration both due to MeHg runoff from the wetlands and to the low pH caused by organic acids generated in the wetlands. These interactions explain the impact of watershed and wetland areas that are observed in the large and small lakes.

Previous studies have shown that total phosphorus is inversely related to fish mercury concentrations (Clayden, Kidd et al. 2013, Clayden, Kidd et al. 2014). This means that fish Hg concentrations will be low in eutrophic lakes due both to growth dilution in the fish themselves, but, more importantly due to the dilution of Hg at the base of the food web by the increased algal density. In contrast, this study found that walleye Hg concentrations increase with increasing concentrations of total phosphorus. This anomaly is examined further below.

2.4.2. Role of wetlands in regulating MeHg bioaccumulation in area lakes

The Upper Peninsula of Michigan has an abundance of wetlands. Fully 30.2% of the total land cover is wetlands (Calculated in GIS, data: <https://www.fws.gov/wetlands/data/state-downloads.html>). Previous studies indicated that wetlands have a very important role in the concentrations of Hg in fish. This is because wetlands, while sinks for total mercury, nevertheless provide an environment for methylation. The process of methylation is complex and is a function of various physical and chemical conditions. Wetlands act as a net source of methylmercury (MeHg). Also, wetlands are a source of DOC and a contributor to low pH. Of the 74 lakes for which fish mercury concentrations were found, 37 also had total dissolved mercury concentrations in water available. As has been reported in other studies (Gantner, Power et al. 2010, Chételat, Amyot et al. 2011, Chen, Borsuk et al. 2014), there is no significant correlation ($r = 0.329$, $p = 0.332$) between fish mercury and total dissolved Hg in these lakes. The majority of the mercury in the water column may be bound to particles rather than being present in the dissolved phase and available for methylation (Clayden, Kidd et al. 2014). High dissolved Hg does not result in bioaccumulation if the lakes conditions are not conducive to methylation.

Figure 2. 26: Regression plot for Walleye Hg (MeHg) Vs total dissolved mercury (THg) in the 74 study lakes

Bayesian Multiple Linear Regression was performed with total dissolved Hg (THg) as the dependent variable. The regression analysis identified only dissolved organic carbon (DOC) as a significant predictor of THg. However, DOC was not a significant predictor for fish mercury. DOC has been described as an important parameter in previous studies (Selvendiran, Driscoll et al. 2008, Rolfhus, Hall et al. 2011, Golden, Knightes et al. 2013, Clayden, Kidd et al. 2014), and, as mentioned above, DOC was identified as an important predictor of THg in UP lakes. Hence further analysis in relation to DOC seems warranted.

PCA on SPSS has a function where the number of components can be restricted to the desired number. Figure 2.27 represents a 2-component plot for small lakes.

Figure 2. 27: Two-component PCA plot for small lakes

From the plot, it was seen that parameters that represent trophic state (total phosphorus, chlorophyll, Secchi depth) were all strongly weighted on component 1. However, wetland area (percent wetland) and watershed:lake area also were highly weighted on this component, but pH and fish mercury had relatively low weights on this axis. For further understanding of these parameters and the involvement of DOC, a correlation analysis was performed, the results of which are summarized in Table 2.12.

Table 2. 12: Pearson Correlation
The bold parameters indicate a significant correlation between the parameters and DOC

	Max Depth	Secchi Depth	Chlorophyll	Total Phosphorus	Percent Wetlands	Walleye Hg
<i>Large Lakes</i>	-0.277	-0.584¹²	0.129	0.053	0.905³	0.137
<i>Small Lakes</i>	-0.461³	-0.554³	0.267²	0.346³	0.640³	0.339²

From the table above, it was seen that for large lakes, DOC had no significant correlation with fish MeHg but was significantly correlated with percent wetland and trophic state parameters like Secchi Depth. Contrary to what was seen in large lakes, Walleye Hg and DOC were significantly correlated in small lakes. It was seen that DOC was also correlated to the trophic state parameters (secchi depth, total phosphorus, chlorophyll, etc.) identified in the PCA above. These correlations suggest that the effect of trophic state seen in the PCA analysis could potentially reflect the input of DOC from wetlands in the catchment.

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¹ Significant correlations with 90% confidence interval.

² Significant correlations with 95% confidence interval.

³ Significant correlations with 99% confidence interval.

2.4.3. Spatial Analysis

Figure 2. 28: Spatial distribution of fish Hg concentrations in lakes across the UP, Michigan

The spatial distribution of Walleye Hg in UP lakes was mapped (Fig. 2.28) using inverse distance weighting (IDW), a deterministic method of interpolation. The IDW suggests that the western UP lakes have slightly higher fish Hg than eastern UP lakes, but no north-south differences are observed although previous studies have indicated latitude to be a significant parameter in explaining fish mercury concentration (Clayden, Kidd et al. 2014). It was also seen that out of 74 lakes there were only 18 lakes that had Walleye Hg concentrations below EPA's water quality criterion (0.3 ppm). If the western UP is

separated from eastern UP at the eastern boundary of Marquette County, the western UP (56 lakes) has significantly higher fish Hg than does the eastern UP (t-test with unequal variance, $p = 0.01$).

Figure 2. 29: Hotspot analysis on fish mercury concentrations in lakes across the UP, Michigan

Hotspot analysis was conducted within Arc-Map to determine if individual lakes or clusters of lakes were statistically higher than the mean expected for that region (<http://desktop.arcgis.com/en/arcmap/10.3/tools/spatial-statistics-toolbox/hot-spot-analysis.htm>). The analysis identified the six individual lakes as hotspots as listed in Table 2.13.

Table 2. 13: Summary of lakes identified through Hotspot analysis.

Lake Name	County	Number of Neighbors	Confidence Interval
James Lake	Iron	29	99%
Lake Michigamme	Marquette	16	99%
Clearwater Lake	Gogebic	20	95%
Sunday Lake	Gogebic	10	95%
Deer Lake	Marquette	11	90%
Little Oxbow	Gogebic	14	90%

Of these, Deer Lake was an Area of Concern (AOC) which has now been restored and delisted. Deer lake received direct discharge of Hg from mineral assays (Swart 2014). Lake Michigamme has a large watershed (496 km²) of which 28% consists of wetlands; Knauer et al. (2011) attribute the high fish mercury in this lake to MeHg generated in the surrounding wetlands. Similarly, Sunday Lake has a large watershed (73 km²) of which 38% consists of wetlands. As discussed above, large watershed and wetland areas play an important role in the input of MeHg to lakes. James Lake has a markedly low pH (4.55) which has been reported previously to have a negative impact on Hg as it retards demethylation. The low pH may be an effect of acid mine drainage although no definitive evidence was found. The underlying cause for high Hg in Clearwater Lake is unknown. Little Oxbow Lake has a small watershed area (4.73 km²) with almost 31% area covered with wetlands. The large amount of wetlands could be the major source of MeHg to the lake.

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3. Polychlorinated Biphenyl (PCB) Compounds

3.1. Background of PCBs

A polychlorinated biphenyl-like chemical, a by-product of coal tar, was first discovered in 1865 and was synthesized in 1881. PCB compounds are a class of persistent, bioaccumulative and toxic organic pollutants. Their chemical structure consists of two benzene rings connected by a carbon-carbon bond. Based on the position and number of chlorine atoms present, there are 209 possible structures called congeners. In the year 1929, the Anniston Ordnance Company in Anniston, Alabama, U.S.A. began commercially producing PCBs in the form of Aroclors, which are a complex mixture that contain more than 80 congeners. Depending upon its composition, each Aroclor has a number, for example Aroclor 1242, Aroclor 1254, Aroclor 1260. The last 2 digits in these numbers indicate the percent by weight of chlorine in the mixture. However, Aroclor 1016 does not follow the same pattern as it contains 41% of chlorine by weight of the mixture.

Approximately 700,000 tons of PCBs, of which 625,000 tons were used domestically, were manufactured in the U.S. (Council 2001). They were widely used in plastics, transformers, capacitors, oil based paint, cable insulation, floor finish, carbonless copy paper, etc., . In 1966 the scientific community identified PCBs as an emerging problem (Jensen 1966), while in 1976 PCBs were found in the Great Lakes. In 1979, the U.S. Environmental Protection Agency (USEPA) banned the manufacture of PCBs, but allowed continuing use of PCBs in enclosed electrical systems (Council 2001).

In 2000, the total commercial harvest (which includes fishes like lake whitefish, yellow perch, walleye, lake trout, carp, etc.) had a value of > \$44 million (<http://www.miseagrant.umich.edu/downloads/fisheries/GLCommercialFinal.pdf>). But due to the presence of persistent, bioaccumulative and toxic chemicals, there had also been a decline in water quality parameters which caused a need for restrictions on fish consumption since the 1970s (Tilden, Hanrahan et al. 1997, Ashizawa, Hicks et al. 2005). Currently, there are fish consumption advisories for some types of fish in all of the Great Lakes. The Great Lakes states have a uniform fish consumption advisory approach where they quantify the amount of fish that can be safely consumed over a period. This limit is based on type and size of fish, location and contaminant level (Anderson, Amrhein et al. 1993, Turyk, Bhavsar et al. 2012).

Lake Superior has features like large surface area, low population and industrial activity in the watershed area and minimum tributary inflow, with more than 50% of its total water coming in the form of rain. Atmospheric deposition is the major input of PCBs to the lake (Eisenreich, Hollod et al. 1979, Capel and Eisenreich 1985, Baker and Eisenreich 1989, Baker and Eisenreich 1990, Gewurtz, Shen et al. 2008). Post-ban, PCB concentrations in air have decreased rapidly (Rapaport and Eisenreich 1988, Baker and Eisenreich 1990) but over time, this rate of decline has slowed, suggesting that a reversed air-water exchange process, resulting from PCB volatilization from Lake Superior, may be a source of PCBs to the overlying atmosphere (Baker and Eisenreich 1990, Perlinger, Simcik et al. 2004, Rowe 2009). The reversal of air-water exchange direction suggests that current policies are helping in reducing PCB concentrations in Lake Superior. Even

though Lake Superior is currently a source of PCBs to the air, to decrease PCBs in the Great Lakes, there may still be value in controlling atmospheric emissions because if the concentrations of PCB in air is the major source to PCBs in fish then reducing atmospheric deposition could result in lowering of PCB concentrations in Lake Superior. Hence identification of possible sources of PCBs in fish, and establishing a link between PCBs in the atmosphere and in fish, could not only help understand PCBs in the environment, it could help establish effective control policies.

Previous studies have used Positive Matrix Factorization successfully to identify sources for PCBs. (Rodenburg, Du et al. 2011) identified seven factors related to PCB contamination of ambient water samples as wastewater, storm water runoff and different Aroclors. Similarly, there have been other studies that have used PMF on PCBs in air and water and have identified the resolved factors as different Aroclors, wastewater, storm water, coal and wood combustion, etc. (Bzdusek, Lu et al. 2006, Du and Rodenburg 2007, Du, Belton et al. 2008, Saba and Su 2013, Aydin, Kara et al. 2014, Melymuk, Robson et al. 2014, Khairy, Muir et al. 2015). Hence for this analysis, EPA Positive Matrix Factorization (PMF) 5.0 was used to identify the possible sources of PCBs in air, water and fish. The objective of this study was to compare the concentration of PCBs in air and fish and to further identify if the concentration of PCBs in air could be a source of concentration of PCBs in fish. This helps determine if more aggressive policies are needed to make it safe to eat fish in the future.

3.2. Methods

The questions being answered in this part include:

1. Can the factors resolved by PMF for air, water and fish samples be identified as known Aroclors?
2. Are PCBs in air the major source of PCBs in fish?
3. Is there a need for more aggressive policies or are the current policies adequate to make it safe to eat fish in the future?

This section begins with discussing the thermodynamic data that were used to calculate concentrations of individual congeners in air, water and octanol in equilibrium with the eight known Aroclors (Frame, Cochran et al. 1996). These equilibrated samples were further used to study congener distributions. Furthermore, this section gives protocols for implementation of PMF including determination of the number of factors and identification of resolved factors.

3.2.1 Thermodynamic data

Thermodynamic data at 25°C were collected for all 209 congeners. The data included PCB number, number of chlorines, chlorine positions, molecular weight (g/mol), solubility (mol/m³), saturated vapor pressure (Pa) and octanol-water partition coefficient (K_{ow} , unitless) (René P. Schwarzenbach 2017). To obtain the other parameters, the following calculations were performed:

Sub-cooled liquid vapor pressure (P^*_L) at 25°C was calculated using the following expression:

$$\log P^*_L (25^\circ\text{C}) = -0.89L_i - 0.44S_i^2 - 5.43A_iB_i + 6.51 \quad (3.1)$$

Enthalpy of vaporization ($\Delta_{vap}H$) was calculated using the following expression:

$$\Delta_{vap}H = -8.79(\pm 0.07)\log P_L + 70(\pm 0.2) \quad [\text{unit: } \frac{\text{kJ}}{\text{mol}}] \quad (3.2)$$

Enthalpy of air-water exchange ($\Delta_{aw}H$) was calculated using the following expression:

$$\Delta_{aw}H = 17.3V_i + 1.4L_i - 0.73S_i + 33.6A_i + 43.5B_i + 8.4 \quad [\text{unit: } \frac{\text{kJ}}{\text{mol}}] \quad (3.3)$$

Enthalpy of octanol-water exchange ($\Delta_{ow}H$) was calculated using the following expression:

$$\Delta_{ow}H = 18.9V_i - 8.3L_i + 5.3S_i - 20.1A_i + 34.3B_i + 1.7 \quad [\text{unit: } \frac{\text{kJ}}{\text{mol}}] \quad (3.4)$$

Enthalpy of octanol-air exchange ($\Delta_{oa}H$) was calculated using the following expression:

$$\Delta_{oa}H = 1.6V_i - 9.7L_i + 6.0S_i - 53.7A_i - 9.2B_i - 6.7 \quad [\text{unit: } \frac{\text{kJ}}{\text{mol}}] \quad (3.5)$$

The air-water partition coefficient can be defined as the ratio of a chemical's equilibrium concentration in air phase to its concentration in the aqueous phase. Dimensionless Henry's law constant $K_{aw}(25^\circ\text{C})$ was calculated using the following expression:

$$\log K_{aw} = 2.55V_i - 0.48L_i - 2.07S_i - 3.67A_i - 4.87B_i + 0.59 \quad (3.6)$$

The octanol-water partition coefficient can be defined as the ratio of a chemical's equilibrium concentration in octanol phase to its concentration in the aqueous phase.

Octanol-water partition coefficient $K_{ow}(25^{\circ}\text{C})$ was calculated using the following

$$\log K_{ow} = 2.41V_i + 0.43L_i - 1.41S_i - 0.18A_i - 3.45B_i + 0.34 \quad (3.7)$$

The octanol-air partition coefficient can be defined as the ratio of a chemical's concentration in octanol phase to its concentration in the air phase. Octanol-air partition coefficient $K_{oa}(25^{\circ}\text{C})$ was calculated using the following expression:

$$\log K_{oa} = -0.04V_i + 0.91L_i + 0.66S_i + 3.49A_i + 1.42B_i - 0.25 \quad (3.8)$$

In the above equations, A_i , B_i , S_i , L_i , V_i , (where i congener number) are the Abraham solvation parameters where

A_i – Hydrogen bonding acidity

B_i – Hydrogen bonding basicity

S_i – Polarity/polarizability

L_i – Partitioning coefficient between gas phase and hexadecane

V_i – McGown volume

The polyparameter linear free energy relationships (pp-LFERs) in Equations 3.1 – 3.8 were obtained from Equation 8-19, 8-14, 9.27, 10-18, 10-17, 9-18, 10-10, 10-5 of (René P. Schwarzenbach 2017). To correct the parameters to temperatures other than 25°C , the

Van't Hoff equation along with the corresponding enthalpies estimated in Eqs. 3.1 – 3.5 were used.

$$\ln \frac{K_{i12}(T_2)}{K_{i12}(T_1)} = -\frac{\Delta_{12} H_i}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right) \quad (3.9)$$

These parameters were further used for the calculation of concentrations in air, water and octanol in equilibrium with Aroclors that will be discussed later in this section.

3.2.2. Collection and sorting of data

The percentage weights of all 209 congeners for Aroclors 1016, 1221, 1232, 1242, 1248, 1254, 1260 and 1260 were obtained from (Frame, Cochran et al. 1996). In the subsequent analyses, only selected congeners were used. The criteria for discarding congeners were: the weight percentage of the congeners were zero in all of the Aroclors, or the weight percentage of the congener with respect to the total congener weight was less than one percent for the major Aroclors produced in North America, i.e., Aroclors 1242, 1254 and 1260.

Initially Congener 11 was included in the analysis as it is present in paint (Hu, Martinez et al. 2008, Rodenburg, Guo et al. 2009). Later it was excluded, because a separate factor would have been needed to be invoked within PMF. If another factor (for Congener 11) were to be added, it would make the analysis more complicated, because the PCB 11 concentrations provided by IADN (air), GLACS (water and particulate) and EPA (fish) were almost always zero, and as a result PMF would try to assign it to several factors,

thereby increasing the noise in the analysis. Of the 209 congeners, only 60 congeners fit the criteria above.

The congeners that were present in each environmental sampling phase were compared with the list of 60 congeners that had fit the criteria listed above. Only the congeners common to multiple data sets were considered in the PMF analysis. The list of the selected congeners is presented in Table 3.1.

Table 3. 1: List of congeners in environmental samples that overlap with the 60 congeners present in all three major Aroclors at mole percentages greater than 1. Congeners in bold are present in all environmental phases (air, water, fish, sediment).

In this table, PCBs 4, 105, 132, 136 and 171 were all at mole present greater than 1% in Aroclor 1242, 1254 and 1260 but these PCBs were absent in all the environmental phases (air, water, fish, sediment)

Reduced Congeners	IADN (Air phase)	GLACS (Aqueous Phase)	GLACS (Particulate Data)	EPA (Fish Data)
4				
6	✓	✓	✓	✓
8				✓

Reduced Congeners	IADN (Air phase)	GLACS (Aqueous Phase)	GLACS (Particulate Data)	EPA (Fish Data)
15				✓
16	✓			✓
17				✓
18	✓	✓	✓	✓
22	✓	✓		✓
26	✓	✓		✓
28	✓			✓
31	✓			✓
32	✓			✓
33	✓			
37	✓	✓		
42	✓	✓	✓	✓
44		✓	✓	✓
48	✓			✓
49	✓			✓
52	✓	✓	✓	✓
56	✓			
60				✓

Reduced Congeners	IADN (Air phase)	GLACS (Aqueous Phase)	GLACS (Particulate Data)	EPA (Fish Data)
64	✓	✓	✓	✓
66	✓			
70				✓
71				✓
74	✓	✓		✓
82		✓	✓	✓
84		✓		
85	✓	✓	✓	
87	✓	✓	✓	✓
95	✓			✓
97	✓	✓	✓	✓
99	✓	✓	✓	✓
101	✓	✓	✓	
105				
110	✓			✓
118	✓	✓	✓	✓
128	✓	✓	✓	
132				

Reduced Congeners	IADN (Air phase)	GLACS (Aqueous Phase)	GLACS (Particulate Data)	EPA (Fish Data)
135				✓
136				
138				✓
141		✓	✓	✓
146		✓	✓	✓
149				✓
151		✓	✓	✓
153		✓	✓	✓
163				✓
170				✓
171				
174	✓	✓		✓
177		✓		✓
179				✓
180		✓	✓	✓
183		✓	✓	✓
187				✓
194	✓	✓	✓	✓

Reduced Congeners	IADN (Air phase)	GLACS (Aqueous Phase)	GLACS (Particulate Data)	EPA (Fish Data)
196				✓
199	✓			✓
203				✓

3.2.3. Congener distributions at equilibrium

Congener distributions that would be present at equilibrium with a single Aroclor were calculated for air, water and fish lipids (assumed to be 100% octanol).

Figure 3. 1: Four phases in equilibrium

To estimate the concentration in equilibrium, the following calculations were performed for each Aroclor:

$$\text{Number of moles (mole)} = \frac{\text{Average percent weight of } i \text{ in the aroclor}}{\text{Molecular Weight}} \quad (3.10)$$

$$\text{Mole fraction (\%)} = \frac{\text{Number of moles}}{\text{Total number of moles}} \cdot 100 \quad (3.11)$$

$$\text{Partial Pressure (Pa)} = \text{Mole Fraction} \cdot \text{Vapor Pressure} \quad (3.12)$$

$$\text{Concentration in Air } \left(\frac{\text{mol}}{\text{m}^3} \right) = \frac{\text{Partial Pressure}}{R \cdot T} \quad (3.13)$$

$$\text{Concentration in Water } \left(\frac{\text{mol}}{\text{m}^3} \right) = \frac{\text{Concentration in Air}}{\text{Air-water partition coefficient}} \quad (3.14)$$

$$\text{Concentration in Octanol } \left(\frac{\text{mol}}{\text{m}^3} \right) = \text{Concentration in Water} * \text{Octanol} - \text{Water partition coefficient} \quad (3.15)$$

3.2.4. PCB concentrations in various media in the Great Lakes region

The data for air, water and fish PCB concentrations was obtained from different sources that are mentioned below which was later used to run PMF. The air PCB concentration data for Lake Superior, Lake Michigan and Lake Erie for the years 2002-2015 were obtained from the Great Lakes Integrated Atmospheric Deposition Network (IADN). The dissolved and particulate phase PCB concentrations for Lake Superior (2006) and Lake Michigan (2003 -2005) were obtained from the Great Lakes Aqueous Concentrations Study (GLACS). The PCB concentration data for Lake Superior Trout (2003 – 2015) for the Apostle Islands and Keweenaw Point sampling stations were obtained from the U.S. Environmental Protection Agency (USEPA). The concentration data for sediments in Lake Superior (1986) were taken from (Baker and Eisenreich 1989). Data from (Song, Ford et al. 2004) were also examined, but too few congeners were listed in this publication.

3.2.5. Positive Matrix Factorization

3.2.5.1. Background

Positive Matrix Factorization (PMF) is a tool used for factor analysis where the sample data matrix is separated into two matrices: the factor contributions and the factor profile.

$$X = GF + E$$

The matrix X consists of sample concentrations. E is the matrix of residuals, i.e., the user provided uncertainty associated with the data. The data for these matrices are provided as input by the user. Matrix G, the factor contributions, and matrix F, the factor profiles, are PMF outputs. These outputs are derived by the model by minimizing the objective function Q.

$$Q = \sum_{i=1}^n \sum_{j=1}^m \left[\frac{e_{ij}}{s_{ij}} \right]^2$$

where n = observed samples

M = chemical species

e_{ij} = the difference between observations X
and model GF

s_{ij} = uncertainties

There are two versions of Q that are displayed for the runs, i.e., Q (true), which is the goodness of fit parameter calculated including all parameters, and Q (robust), which is the goodness of fit calculated by excluding points that did not fit the model. The run and seed number with the lowest Q (robust) value is considered the best solution (Norris G. 2014)

3.2.5.2. Logistics of working with PMF

PMF requires two files, sample concentration values and sample uncertainty values, as input. All files are accepted as either .csv (Comma-separated value), .txt (tab delimited), .xls or.xlsx (Excel Workbook). Also, PMF does not accept blank cells as inputs. The uncertainties file could be of two types. Concentration-based uncertainty files provide an estimate of uncertainty for all species. Equation-based uncertainty files use species-specific parameters to calculate uncertainties for each sample. Species for this analysis are the individual congeners in all environmental phases (air, water, particulate matter and fish).

Figure 3. 2: EPA PMF 5.0, Inputs GUI

For this analysis, concentration-based uncertainties were used because the equation-based uncertainties require knowledge of the Method Detection Limit (MDL), and the equation to calculate uncertainties is based on whether the concentration is greater or less than the MDL. In the data under consideration, several congeners had a value of zero as their concentration. It is unclear whether the zero value is due to the absence of a congener in a sample or because the concentration of the congener is much lower than the MDL and thus has been written as zero. Also, it is important to know that zero and negative values are not permitted in an uncertainty file.

For initiating a run, numerous parameters such as the following needed to be specified:

Number of runs: this must be an integer that specifies the number of runs that PMF needs to perform. These runs help in understanding the variation in Q. The recommended number of runs is 20.

Seed: this must be an integer that specifies the starting point of the iteration. The seed could either be chosen randomly, (i.e., as Random Start) or a seed number could be specified in the seed number box. The default is set to Random Start.

Number of factors: like other factor analysis techniques, PMF also suffers from the difficulty of determining the optimal number of factors. More information about this is provided in section 2.5 (Norris G. 2014).

3.2.5.3. Output of PMF

Profiles/ Contributions: There are two graphs for each factor. One graph displays the factors profile. The top graph of Figure 3.3 depicts the concentrations distributed to each factor which is represented by a pale blue bar and a logarithmic scale y-axis on the left-hand side. The percent of species is represented by red dots. The second graph represents the concentration per sample for each sample.

Figure 3. 3: Profiles/Contributions

Factor Fingerprints (e.g., Figure 3.4): This graph depicts a stacked bar chart which consists of the concentration in percent for each congener contributing to each factor. PMF also generates various output files that contain information like records or model

inputs, model diagnostics and concentrations, normalized concentrations, profiles, and residual analysis for each run. This plot gives a visual representation of the contributions of each factor.

Figure 3. 4: Factor fingerprints

3.2.6 Trial Run

To understand more about the working of PMF, a trial run was performed. The samples used for this run were mixes of known percentages of Aroclors 1242 and 1260; the Aroclors had been equilibrated with air, so the concentrations used as inputs were concentrations in air. Information about these samples is provided in Table 3.2:

Table 3. 2: Percentages of air concentration in Aroclor 1242 and 1260

<i>Sample No.</i>	<i>Aroclor 1242</i>	<i>Aroclor 1260</i>
1	100	0
2	0	100
3	90	10
4	60	40
5	50	50
6	40	60
7	10	90

The PMF program was to identify only two factors, and random seed numbers were used to see how well the model predicted the known factors. Independently, the congener concentrations were calculated in Microsoft Excel. This helped to facilitate a comparison visually and to perform a paired t-test to compare data. When the aforementioned data was run on the EPA PMF program for different runs, and there were two different results that were generated. The plots generated using these two different results were shown in Figures 3.5 and 3.6, while the plot made using Excel is shown in Figure 3.7.

Figure 3. 5: Factor fingerprints for EPA PMF 5.0 for data in Table 3.2

Figure 3. 6: Factor fingerprints for EPA PMF 5.0 for data in Table 3.2

Figure 3. 7: Plot made in Excel for data from Table 3.2

A paired t-test was performed on the results obtained from the different runs. These runs were then compared to the concentrations that were calculated in Excel. The results shown in Table 3.3 demonstrate that the $t \text{ stat} < t \text{ critical (two-tail)}$ for both runs at 95% confidence which indicates that the concentrations of factor components obtained from PMF (both runs) are not significantly different from the concentrations of factor components (congeners) obtained from Excel.

Table 3. 3: Results of the t- paired test

t-paired test for the PMF generated result in Figure 3.5	t Stat	-0.12
	t Critical two-tail	2.00
t-paired test for the PMF generated result in Figure 3.6	t Stat	-0.98
	t Critical two-tail	2.00

Another study was done to examine the effect of seed number. The aim of the study was to see if using random seed numbers and specifying seed numbers (e.g., Seed numbers 1-10) would yield different results. To do this, the concentrations in air for Aroclors 1242 and 1260 were mixed in known percentages as summarized in Table 3.2. Then the model was first run for random seed numbers followed by a run for seed numbers 1-25. There were two different results as seen for the analysis shown in Figures 3.5 and 3.6. Figure 3.8 shows the frequency of seed numbers that were used for the run whose factor fingerprints are shown in Figure 3.5, while Figure 3.9 shows the frequency of seed numbers that were used for the run whose factor fingerprints are shown in Figure 3.6. The analysis demonstrates that there is no way to predict which fingerprint is observed for a particular seed number. Also, it should be noted that, from the paired t-test, it is known that the results for both the cases are correct. Thus, the seed numbers can be either random or specified.

Figure 3. 8: A histogram of seed numbers that produced the results shown in Figure 3.5

Figure 3. 9: A histogram of seed numbers that produced results shown in Figure 3.6

From figures it can be seen that there was no particular range/pattern of seed numbers that predicted a particular type of result. Hence seed numbers could be either random or specific. For this analysis, seed numbers. were kept random so that a wide range of numbers and their possible results could be analyzed to obtain the lowest Q (robust) values.

3.2.7. Determination of number of factors

The number of factors should provide clear and meaningful results as well as reduce matrix dimensionality as much as possible. Clear and meaningful implies that the factors represent known sources (e.g., Aroclors). Different investigators have used different approaches to determine the optimal number of factors. These approaches are described here.

In (Du, Belton et al. 2008, Rodenburg, Du et al. 2011) the PMF model was run for 3 to 9 factors and seed numbers 1-10. The optimal factor was the one for which the model

produced Q (robust) values that were equal to the theoretical Q (true) values. (Khairy, Muir et al. 2015) also stated that the number of factors that causes the Q (robust) values to be equal to Q (true) values would be the optimal number of factors.

The method used by (Du and Rodenburg 2007) examines Q (true) values as a function of number of factors. To do so, PMF was first run for 3 to 9 factors and seed numbers 1-10 (to ensure that the program is considering global and not a local minimum). On a plot of Q (robust) versus number of factors, the point where the curve started to flatten out was considered to be the optimal number of factors.

A third method was used by Brinkman et al. (2006). This method is similar to the previous one, except that the maximum mean and maximum standard deviation of scaled residuals ($Scaled\ Residual = Residual/Error\ estimate\ of\ the\ residual$) were used instead of Q. These values were calculated for a number of factors so that they could be plotted against number of factors. The optimal number of factors was considered to be a point immediately after a large incremental reduction in maximum mean and maximum standard deviation.

In this study, the optimal number of factors was determined by running PMF for 2-7 factors for 10 random seed numbers. Once the results were obtained, approaches 2 and 3 explained above were used individually and a common value was identified as the optimal number of factors.

3.2.8. PMF Run

Once the optimal number of factors is identified, PMF was run for different environmental medias. Initially air samples (throughout the year. The air samples were also separated by seasons i.e., summer air samples (June – July – August) and winter air samples (December – January – February)

The GLACS data has two parts i.e., XAD resin media and glass filter fiber (GFF) media. The XAD resin media consists of filtered water samples and this data was considered as the water samples while, the other data was considered as the particulate matter data.

Furthermore, the dish samples were available for two locations i.e., Apostle Island and Keweenaw Point. All resolved factors were identified as Aroclors at various temperatures like 25°C and 4°C. The summer air samples were identified as Aroclors at 15°C and winter air samples were identified as Aroclors at -4°C. The sediment data did not have enough number of samples to run PMF, hence the average sediment samples were compared with average fish concentration from the two locations.

3.2.9. Identification of resolved factors

The resolved factors were identified using two methods. First, cosine similarity was employed. It measures the similarity between two multivariate vectors by calculating the cosine θ , where θ is the angle between the two vectors. The cosine θ is 1 when the vectors have high similarity and is 0 when the vectors have no similarity. It is also important to know that this method considers the relative proportions of the variables and

not their magnitudes (see <http://www.minerazzi.com/tutorials/cosine-similarity-tutorial.pdf>).

Pearson Correlation coefficients also were calculated as a measure of the similarity of factors with congener distributions in known sources. Both methods were used to compare the distribution of congeners within factors generated by PMF to the concentrations of congeners in Aroclors equilibrated to the appropriate phase at environmentally-relevant temperatures such as 25 ° C, 4 ° C, 15 ° C (Summer) and -4 ° C (Winter).

Also, cumulative distribution plots were used to compare congener distributions among the different types of environmental samples (air, water, fish, sediments). PCB congener concentrations in air (IADN) and water (GLACS) were equilibrated with the octanol phase and then compared with concentrations in fish and sediments with the help of cumulative percentage plots.

3.3. Results

3.3.1. Determination of number of factors

As described in Section 3.2.6, PMF was run for 2 to 7 factors using 10 random seed numbers. From the results, a plot of Q (robust) vs number of factors was constructed to identify the point where the curve starts to flatten. Also, using scaled residuals, maximum mean and maximum standard deviation were calculated, that were similarly plotted as a

function of the number of factors to identify the point where there was a large incremental reduction of the dependent variable. The abscissa value where the drop in ordinate occurred was considered to indicate the optimal number of factors.

With both methods, it was difficult to identify the exact point where the curve starts to flatten (Fig. 3.10). The largest change in slope was observed at five factors, and hence five was considered to be the optimal number of factors. The data were further divided into two sets: winter data for the months December, January and February, and summer data for the months June, July and August. As shown below, congener patterns were different in summer and winter. Hence, air data were analyzed separately for summer and winter.

Figure 3. 10: Q (robust) vs number of factors (IADN data)

In Figures 3.13 and 3.12 there are two points that could be considered as the point of optimal number of factors: 4 and 6 respectively. From the percent change in slope observed in Figure 3.11, the curve seems to flatten at the fifth factor. The optimal number of factors was considered to be four.

Figure 3. 11: Q (robust) vs number of factors (winter IADN data)

Table 3. 4: Percent change in slope

No. of Factors	% change in slope
2	
3	81.6%
4	29.52%
5	59.8%
6	18.15%
7	17.76%

Figure 3. 12: Maximum standard deviation vs number of factors (winter IADN data)

Figure 3. 13: Maximum mean vs number of factors (winter IADN data)

From Figures 3.14, 3.15, and 3.16 and the percent change in slope observed in Figure 3.14, it can be concluded that the optimal number of factors was four.

Figure 3. 14: Q (robust) vs number of factors (summer IADN data)

Figure 3. 15: Maximum standard deviation vs number of factors (summer IADN data)

Figure 3. 16: Maximum mean vs number of factors (summer IADN data)

From the percent change in slope observed in Figures 3.17 and 3.18, the optimal number of factors for the aqueous PCB concentration data was 5 and optimal number of factors for the particulate PCB concentration data was 4.

Figure 3. 17: Q (robust) vs number of factors (water GLACS data)

Figure 3. 18: Q (robust) vs number of factors (particulate GLACS data)

From the percent change in slope observed in Figure 3.19, it was unclear whether the optimal number of factors were either four or five. Also, from Figures 3.20 and 3.21, the point after the large incremental change was claimed to occur at five factors. Hence, the optimal number of factors was considered to be 5.

Figure 3. 19: Q (robust) vs. number of factors (fish – Apostle Island)

Figure 3. 20: Maximum standard deviation vs number of factors (fish - Apostle Island)

Figure 3. 21: Maximum mean vs number of factors (fish – Apostle Island)

The point after the large incremental change in Figures 3.23, 3.24 and from the change in slope observed in Figure 3.22, the optimal number of factors was considered to be five.

Figure 3. 22: Q (robust) vs. number of factors (fish - Keweenaw Point)

Figure 3. 23: Maximum standard deviation vs number of factors (fish - Keweenaw Point)

Figure 3. 24: Maximum mean vs number of factors (fish –Keweenaw Point)

3.3.2. Identification of resolved factors

3.3.2.1. Air

Figure 3. 25: Factor fingerprint for Air

Figure 3. 26: Factor fingerprint for air in summer (15°C)

Figure 3. 27: Factor fingerprint for air in winter (-4°C)

The analysis of the air samples obtained from IADN data was conducted for four different temperatures. 25°C and 4°C were selected for the dataset that included all the months of the year, while -4°C was considered for the winter months (Dec-Jan-Feb), and 15°C was considered for the summer months (Jun-Jul-Aug). By examining the congener distribution, it was seen that most of the congeners present in the air were the “lighter” congeners. Considering the congeners below PCB 100 to be “lighter” congeners, 23 of 30 congeners present in the IADN data were found to be “light” congeners. Figures 3.25, 3.26, and 3.27 depict the factor fingerprints at their respective temperatures. These fingerprints represent the relative contribution of each factor for every congener. The percentage contributions were calculated for all the resolved factors as shown in Tables 3.4, 3.4, 3.6 and 3.7.

Table 3. 5: Cosine similarity and percent contributions for resolved factors in air (IADN) samples at 25°C

Conc. Air (25°C)	Factor 1	Factor 2	Factor 3	Factor 4	Factor 5
Aroclor 1016	0.81	0.72	0.3	0.54	0.3
Aroclor 1221	0.09	0.93	0.02	0.04	0.02
Aroclor 1232	0.46	0.98	0.16	0.3	0.16
Aroclor 1242	0.81	0.74	0.3	0.54	0.3
Aroclor 1248	0.92	0.43	0.41	0.72	0.4
Aroclor 1254	0.7	0.32	0.85	0.55	0.75
Aroclor 1260	0.25	0.34	0.4	0.23	0.44
Aroclor 1262	0.85	0.73	0.47	0.58	0.45
Percentage	47.17%	22.07%	16.90%	3.20%	1.05%

Table 3. 6: Cosine similarity and percent contributions for resolved factors in air (IADN) samples at 4°C

Conc. Air (4°C)	Factor 1	Factor 2	Factor 3	Factor 4	Factor 5
Aroclor 1016	0.81	0.72	0.3	0.54	0.3
Aroclor 1221	0.09	0.93	0.02	0.04	0.02
Aroclor 1232	0.46	0.98	0.16	0.3	0.16
Aroclor 1242	0.81	0.74	0.3	0.54	0.3
Aroclor 1248	0.92	0.43	0.41	0.72	0.4
Aroclor 1254	0.7	0.32	0.85	0.55	0.75
Aroclor 1260	0.25	0.34	0.4	0.23	0.44
Aroclor 1262	0.85	0.73	0.47	0.58	0.45
Percentage	47.17%	22.07%	16.90%	3.20%	1.05%

Table 3. 7: Cosine similarity and percent contributions for resolved factors in summer air (IADN) samples at 15°C

Summer Air Conc (15°C)	Factor 1	Factor 2	Factor 3	Factor 4
Aroclor 1016	0.54	0.67	0.57	0.65
Aroclor 1221	0.25	0.07	0.05	0.11
Aroclor 1232	0.44	0.38	0.32	0.39
Aroclor 1242	0.55	0.67	0.58	0.65
Aroclor 1248	0.53	0.81	0.7	0.79
Aroclor 1254	0.75	0.82	0.71	0.75
Aroclor 1260	0.35	0.36	0.3	0.33
Aroclor 1262	0.66	0.76	0.66	0.74
Percentage	19.60%	28.64%	35.71%	16.06%

Table 3. 8: Cosine similarity and percent contributions for resolved factors in winter air (IADN) samples at -4°C

Winter Air Conc (-4°C)	Factor 1	Factor 2	Factor 3	Factor 4
Aroclor 1016	0.7	0.79	0.79	0.52
Aroclor 1221	0.06	0.07	0.71	0.05
Aroclor 1232	0.39	0.43	0.87	0.29
Aroclor 1242	0.7	0.78	0.81	0.52
Aroclor 1248	0.85	0.9	0.64	0.65
Aroclor 1254	0.63	0.7	0.57	0.87
Aroclor 1260	0.27	0.26	0.43	0.38
Aroclor 1262	0.74	0.83	0.84	0.64
Percentage	6.32%	42.11%	31.56%	20.01%

To identify the resolved factors, first, the congener pattern of the resolved factors was compared to the congener patterns of 8 Aroclors. But doing so did not account for weathering, and hence the Aroclor congener concentrations were calculated to be in equilibrium with the appropriate phase (e.g., gaseous for the IADN air samples) as discussed in Section 3.2.3. In the case of the air PCB concentrations, they were adjusted for the process of volatilization as described in Methods. The Aroclors that had a similar chlorine content could also have an overlap in congeners because all Aroclors were manufactured by a similar bulk process. (Sather, Ikonomou et al. 2001) considered this situation and determined that Aroclors 1221, 1242, 1254 and 1260 were sufficiently independent, whereas the other Aroclors were linear combinations of the independent Aroclors. While trying to identify the resolved factors, it was deemed not necessary that

each factor be assigned an independent Aroclor; it was possible that a factor could identify as a combination of 2 or more Aroclors. Hence for comparison purposes, all 8 Aroclors were considered.

Cosine similarity was used to identify the Aroclor to which each factor was most similar. As described in Methods section 3.2, high similarity was seen when the cosine theta value approached a value of one. For this analysis, if $\cos \theta$ was greater than 0.8 a factor was ascribed to the corresponding Aroclor.

Based on the PMF results from the air data at 25°C and 4°C, we can infer that Factor 3 (16.9% of total) represents Aroclor 1254. Factor 1 resembles Aroclors 1242, 1016 and 1262 (Factor 1 represents 47% of the total PCBs). Aroclor 1016 has 41% chlorine content, which is very similar to Aroclor 1242 (Sather, Ikonomidou et al. 2001). As mentioned Factor 1 resembles Aroclor 1242, 1016 and 1262, it represents a mixture of light and heavy congeners which makes it fairly difficult to interpret the factor. Our interpretation is that this factor accounts for noise. Factor 2, representing 22% of the total PCBs, resembles Aroclors 1221 and 1232. According to (Sather, Ikonomidou et al. 2001), Aroclor 1221 is also independent from Aroclors 1242, 1254 and 1260, and Aroclor 1232 is a 50:50 mixture of 1221:1242. Hence, Factor 2 was interpreted as representing Aroclor 1221. From the above it was seen that Factors 1, 2 and 3 accounted for 86.14% of the total percent contributions. While the remaining two factors sum up to 13.86% of the total, there were no Aroclors that were similar to any of these factors. As

mentioned earlier, Lake Superior is majorly susceptible to atmospheric deposition and because the area has low population density and low industrial activities, it is unlikely other sources are affect PCB concentrations in Lake Superior. Thus, it could be said that these factors were mostly noise.

For the summer air data at 15°C, Table 3.7 indicates that Factor 2 accounts for heavier congeners, i.e., Aroclors 1248 and 1254. According to Sather, Ikonomou et al. (2001), Aroclor 1248 contains 67% of Aroclor 1242 and 33% of Aroclor 1254. The factor accounted for 29% of the total. Similarly, for winter air data at -4°C, Table 3.8 indicates that Factor 1 (6.3% of total) and Factor 2 (42% of total) both represent Aroclor 1248. Factor 4 (20.01% of total) also represents heavier congeners, specifically, Aroclor 1254. Factor 3 (32% of total) consisted of a combination of light and heavy congeners; evidently, the signal unexplained by other factors had contributions from both light and heavy congeners. We assume that this factor represents unexplained noise because no source would have this signal. Thus, for the winter data, 68% of the total can be explained by Aroclors.

3.3.2.2. Water

Figure 3. 28: Factor fingerprint for water (XAD data)

PMF analysis was run on dissolved phase (XAD) concentrations obtained from GLACS data; for the source assessment, Aroclors were equilibrated with water at 25°C (to simulate summer) and 4°C (to simulate winter). The GLACS data were divided into two parts: the XAD resin media, which consists of the water sample after it was filtered, and the glass fiber filter (GFF) media, which is the particulate data (discussed in detail later). While looking at the congener distribution in the XAD data, 16 of 28 congeners were found to be the lighter congeners, i.e., congeners below IUPAC number 100. Figure 3.28 shows factor fingerprints for the GLACS water data that represent the contributions of each factor for every congener. For comparison purposes, Aroclor concentrations in water phase were calculated using air-water partition coefficients and vapor pressures. Solubility was not used to calculate the Aroclor concentrations in water phase because

polyparameter linear free energy relationships were used to calculate the other coefficients and using the same would help maintain uniformity. These concentrations are obtained for the eight Aroclors and then compared to the congener patterns of the five factors obtained from PMF. From Table 3.8, it was seen that at 25°C Factor 1 (22.7% of total) resembles Aroclor 1262 which according to (Sather, Ikonomou et al. 2001) resembles Aroclor 1260. Factor 2 (16.5% of the total) resembles Aroclor 1242 and 1248. As discussed earlier, Aroclor 1248 resembles 67% of Aroclor 1242 and 33% of Aroclor 1254. Hence, Factor 2 can be said to be the effect of Aroclor 1242. As seen in Table 3.9, the same trend is seen at 4°C. For both the temperatures, only 39.2% of the total PCB concentrations can be explained as originating from Aroclors. When comparing the distribution of congeners in the air and water it was seen that although the IADN air data consisted mostly of the lighter congeners, the water data consisted of primarily heavier congeners.

Table 3. 9: Cosine similarity and percent contributions for resolved factors in water (GLACS) samples at 25°C

Conc. Water (25°C)	Factor 1	Factor 2	Factor 3	Factor 4	Factor 5
Aroclor 1016	0.64	0.81	0.46	0.23	0.5
Aroclor 1221	0.26	0.08	0.19	0.33	0.24
Aroclor 1232	0.5	0.47	0.36	0.33	0.41
Aroclor 1242	0.64	0.81	0.46	0.24	0.5
Aroclor 1248	0.55	0.84	0.61	0.37	0.63
Aroclor 1254	0.2	0.21	0.74	0.67	0.73
Aroclor 1260	0.5	0.2	0.47	0.36	0.41
Aroclor 1262	0.8	0.66	0.61	0.38	0.58
Percentage	22.70%	16.54%	26.15%	19.39%	15.22%

Table 3. 10: Cosine similarity and percent contributions for resolved factors in water (GLACS) samples at 4°C

Conc. Water (4°C)	Factor 1	Factor 2	Factor 3	Factor 4	Factor 5
Aroclor 1016	0.64	0.81	0.46	0.23	0.5
Aroclor 1221	0.26	0.08	0.19	0.33	0.24
Aroclor 1232	0.5	0.47	0.36	0.33	0.41
Aroclor 1242	0.64	0.81	0.46	0.24	0.5
Aroclor 1248	0.55	0.84	0.61	0.37	0.63
Aroclor 1254	0.2	0.21	0.74	0.67	0.73
Aroclor 1260	0.5	0.2	0.47	0.36	0.41
Aroclor 1262	0.8	0.66	0.61	0.38	0.58
Percentage	22.70%	16.54%	26.15%	19.39%	15.22%

3.3.2.3. Fish

Figure 3. 29: Factor fingerprint for Keweenaw Point

Figure 3. 30: Factor fingerprint for Apostle Island.

The data for fish were obtained from EPA for two locations: Keweenaw Point and Apostle Islands. These samples were compared with Aroclors equilibrated in octanol at 25°C and 4°C. Of the 47 congeners, 26 congeners were identified as “light” congeners (<

IUPAC number 100) which indicates that the congeners are distributed fairly evenly. Congener concentrations in octanol equilibrated with Aroclors were calculated from Aroclors in the water phase using octanol-water partition coefficients. These concentrations are obtained for the eight Aroclors and then compared with the five factors obtained from PMF. Tables 3.11 and 3.12 indicate cosine similarity values for Keweenaw Point at 25°C and 4°C. Factors 1, 3 and 4 (the three factors account for 90.5% of total) are comprised of heavier congeners, and are identified as similar to Aroclors 1260 and 1262.

Similarly, Tables 3.13 and 3.14 indicate cosine similarity analyses for Apostle Islands fish at 25°C and 4°C. Factors 2, 3 and 5 (all three factors account for 83% of total) are dominated by heavier congeners and are identified as similar to Aroclors 1260 and 1262.

Table 3. 11: Cosine similarity and percent contributions for resolved factors in fish (USEPA)-Keweenaw Point samples at 25°C

Fish Conc. In Keweenaw Point (25°C)	Factor 1	Factor 2	Factor 3	Factor 4	Factor 5
Aroclor 1016	0.01	0.15	0.02	0.13	0.17
Aroclor 1221	0	0.1	0.01	0.01	0.01
Aroclor 1232	0.02	0.1	0.02	0.08	0.1
Aroclor 1242	0.03	0.19	0.03	0.14	0.18
Aroclor 1248	0.1	0.37	0.03	0.14	0.17
Aroclor 1254	0.046	0.81	0.43	0.4	0.58
Aroclor 1260	0.82	0.61	0.82	0.81	0.78
Aroclor 1262	0.73	0.48	0.75	0.74	0.64
Percentage	46.64%	6.23%	37.17%	6.69%	3.10%

Table 3. 12: Cosine similarity and percent contributions resolved factors in fish (USEPA)- Keweenaw Point samples at 4°C

Fish Conc. In Keweenaw Point (4°C)	Factor 1	Factor 2	Factor 3	Factor 4	Factor 5
Aroclor 1016	0.01	0.15	0.02	0.13	0.17
Aroclor 1221	0	0.1	0.01	0.01	0.01
Aroclor 1232	0.02	0.1	0.02	0.08	0.1
Aroclor 1242	0.03	0.19	0.03	0.14	0.18
Aroclor 1248	0.1	0.37	0.03	0.14	0.18
Aroclor 1254	0.46	0.81	0.43	0.4	0.58
Aroclor 1260	0.82	0.61	0.82	0.81	0.78
Aroclor 1262	0.73	0.48	0.75	0.74	0.64
Percentage	46.64%	6.23%	37.17%	6.69%	3.10%

Table 3. 13: Cosine similarity and percent contributions for resolved factors in fish (USEPA)- Apostle Island samples at 25°C

Fish Conc. In Apostle Island (25°C)	Factor 1	Factor 2	Factor 3	Factor 4	Factor 5
Aroclor 1016	0.02	0.02	0	0.06	0.01
Aroclor 1221	0.01	0	0	0.01	0
Aroclor 1232	0.02	0.02	0.01	0.04	0.02
Aroclor 1242	0.04	0.04	0.02	0.07	0.03
Aroclor 1248	0.1	0.13	0.06	0.12	0.1
Aroclor 1254	0.45	0.48	0.38	0.21	0.46
Aroclor 1260	0.77	0.86	0.82	0.62	0.84
Aroclor 1262	0.64	0.77	0.74	0.73	0.73
Percentage	11.92%	20.02%	38.73%	4.71%	24.62%

Table 3. 14: Cosine similarity and percent contributions for resolved factors in fish (USEPA)- Apostle Island samples at 4°C

Fish Conc. In Apostle Island (4°C)	Factor 1	Factor 2	Factor 3	Factor 4	Factor 5
Aroclor 1016	0.02	0.02	0	0.06	0.01
Aroclor 1221	0.01	0	0	0.01	0
Aroclor 1232	0.02	0.02	0.01	0.04	0.02
Aroclor 1242	0.04	0.04	0.02	0.07	0.03
Aroclor 1248	0.1	0.13	0.06	0.12	0.1
Aroclor 1254	0.45	0.48	0.38	0.21	0.46
Aroclor 1260	0.77	0.86	0.82	0.62	0.84
Aroclor 1262	0.64	0.77	0.74	0.73	0.73
Percentage	11.92%	20.02%	38.73%	4.71%	24.62%

When the air, water and fish data were compared together, it can be observed that there were different Aroclors associated with each of the phases. Aroclors 1016, 1221 and 1242 were identified in the air data, whereas Aroclors 1260 and 1262 were identified in the fish. This suggests that the air was not the source for PCBs in fish. The next step was to identify the source. To do so, the particulates from the GLACS data was analyzed.

3.3.2.4. Particulate Matter

Table 3. 15: Cosine similarity and percent contributions for resolved factors in particulate (GLACS) samples at 25°C

Conc Particulate (25 °C)	Factor 1	Factor 2	Factor 3	Factor 4
Aroclor 1016	0.01	0.35	0.01	0
Aroclor 1221	0.01	0.35	0.01	0
Aroclor 1232	0.01	0.36	0.01	0
Aroclor 1242	0.01	0.41	0.01	0
Aroclor 1248	0.03	0.37	0.01	0.01
Aroclor 1254	0.44	0.62	0.11	0.26
Aroclor 1260	0.56	0.79	0.52	0.4
Aroclor 1262	0.21	0.66	0.31	0.21
Percentage	13.23%	18.54%	36.54%	31.69%

As discussed earlier, the particulate phase PCB concentrations were obtained from the GLACS data. The particulate data were compared with Aroclors equilibrated with DOC at 25°C. The water-equilibrated Aroclors were adjusted using organic carbon-water partition coefficients (K_{oc}). These concentrations were obtained for the eight Aroclors and then compared to the congener distributions of the four factors obtained from PMF. The results from Table 3.15 indicate that the Aroclors that have a higher content of the heavier congeners have a higher cosine similarity value in the comparisons with the particulate data. As mentioned for the preceding analyses, for a factor to be considered to resemble an Aroclor, $\cos \theta$ should be greater than 0.8. For the particulate data, none of the Aroclors met that criterion. The next step was to examine sediment PCBs to determine if it could be considered as a source of PCBs to fish and water.

Figure 3. 31: Factor fingerprint for particulates

Figure 3. 32: Cumulative concentrations of winter concentrations in air vs congener number

Figure 3.33: Cumulative concentrations of summer concentrations in air vs congener number

Figure 3.34: Cumulative concentrations in water vs congener number

Figure 3.35: Cumulative concentrations in fish in Apostle Island vs congener number

Figure 3. 36: Cumulative concentrations in fish in Keweenaw Point vs congener number

From Figures 3.32 – 3.36, it was seen that the congener distribution of cumulative concentration in air were different from the congener distribution of cumulative concentrations in fish. Hence, the concentrations of PCBs in air may not be the source to the concentrations of PCBs in fish. To further identify the source of PCBs in fish, we looked at the sediment data.

3.3.2.5 Sediments

The only sediment congener-specific PCB measurements located were from three cores analyzed by Baker et al. (1989). Additional congener-specific concentrations are reported by Li et al. (2004), but too few congeners are reported to be useful for this study. Three samples is inadequate for PMF analysis. However, average congener concentrations in sediments and fish (Apostle Islands and Keweenaw Point) were compared using other techniques.

Table 3. 16: Cosine Similarity Analysis of sediment concentrations and fish concentrations in Apostle Island and Keweenaw Point

	Apostle Island	Keweenaw Point
Cosine Similarity	0.84	0.86

There was a high similarity between the sediments and the Apostle Islands/Keweenaw Point fish (Table 3.16) as indicated by cosine θ analysis. Also, as discussed earlier, the fish congener concentrations were highly correlated with congener concentrations in Aroclor 1260. Bar charts and Pearson correlation coefficients were used for comparing fish and sediment concentrations with Aroclor 1260.

Table 3. 17: Pearson Correlation that compares sediment concentrations with concentrations of fish in Apostle Island and Keweenaw Point and Aroclor 1260¹

	Sediments	Apostle Island	Keweenaw Point	Aroclor 1260
<i>Sediments</i>	1			
<i>Apostle Island</i>	0.79*	1		
<i>Keweenaw Point</i>	0.81*	1.00*	1	
<i>Aroclor 1260</i>	0.73*	0.87*	0.84*	1

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¹ The * sign in table 3.17 indicates that these correlations are significant with a 99% confidence interval.

(a)

(b)

Figure 3. 37: Bar chart comparing fish PCB concentrations at (a) Keweenaw Point, and (b) Apostle Islands with sediment PCB concentrations and Aroclor 1260 composition

From Table 3.17, it is apparent that the fish, sediment and Aroclor 1260 concentrations are highly correlated with each other. From Figure 3.32 it can be seen that the congener distributions in fish and sediment were very similar to the concentrations in Aroclor 1260. Hence, it is possible that PCBs in fish were derived from PCBs in sediments.

3.3.3. Air concentrations adjusted to the octanol phase

Using the octanol-air partition coefficient, K_{OA} , the concentrations in the air phase (the IADN data) were used to calculate equilibrium concentrations in the octanol phase. This adjustment was done so that (1) the concentrations in air could be compared to the concentrations in air adjusted to equilibrium with the octanol phase (This comparison is useful to observe any change in the concentration of congeners based on the phases changes (weathering)); and (2) the concentrations in air adjusted to the octanol phase could be compared to the concentrations in fish. (If the concentrations in octanol phase and the fish are the same or nearly the same, it could help validate that the source of the PCBs in the fish is atmospheric deposition.)

3.3.3.1. Determination of the number of factors

From Figures 3.33, 3.34 and 3.35, no clear optimal number of PMF factors can be discerned. The optimum number could be 3, 4 or 7. From the change in slope in Figure 3.33, the optimal number of factors was 4. Figure 3.34 shows two optimal number of factors: 4 and 7. Figure 3.35 also shows two optimal number of factors: 5 and 7. Because

atmospheric deposition is the main form of input to Lake Superior, 7 factors seem unlikely. Hence, the optimal number of factors was considered as 4.

Figure 3. 38: Q (robust) vs number of factors (air in octanol phase) in summer

Figure 3. 39: Maximum standard deviation vs number of factors (air in octanol phase) in summer

Figure 3. 40: Maximum mean vs number of factors (air in octanol phase) in summer

From Figures 3.36, 3.37 and 3.38, it was also deduced that the optimal number of factors is 4.

Figure 3. 41: Q (robust) vs number of factors (air in octanol Phase) in winter

Figure 3. 42: Maximum standard deviation vs number of factors (air in octanol phase) in Winter

Figure 3. 43: Maximum mean vs number of factors (air in octanol phase) in winter

3.3.3.2 Identification of resolved factors

Summer:

Figure 3. 44: Factor fingerprint for summer air concentrations adjusted to equilibrium with octanol

From Table 3.18 it is observed that when PMF factors for concentrations of PCBs in air (in equilibrium with the octanol phase) were compared to Aroclor concentrations in the gas phase, PMF did not identify any factors that resemble Aroclors as determined with cosine similarity analysis. In contrast, when air samples equilibrated with octanol are analyzed by PMF and the factors compared with Aroclors equilibrated with octanol, factors did correspond with Aroclors. Table 3.19 shows that Factor 1 (24.9% of total) represents Aroclor 1260 whereas Factors 3 and 4 (together explain 52.3% of the total) resemble Aroclor 1254. This shows that if the air samples were equilibrated with the octanol phase, the octanol phase would have a higher abundance of heavier congeners. However, the distributions are still not the same as in the fish. Air samples equilibrated

with octanol had a contribution of 52.3% from Aroclor 1254 and 24.9% from Aroclor 1260. For fish samples, 90.5% of the total at Keweenaw Point and 83.4% of the total at the Apostle Islands came from Aroclor 1260.

Table 3. 18: Air (IADN) equilibrated with octanol phase compared with Aroclors in the air phase in summer

Summer Air Conc (15°C)	Factor 1	Factor 2	Factor 3	Factor 4
Aroclor 1016	0.01	0.22	0.06	0.09
Aroclor 1221	0	0.02	0.01	0.01
Aroclor 1232	0.01	0.13	0.03	0.05
Aroclor 1242	0.01	0.19	0.04	0.07
Aroclor 1248	0.03	0.35	0.11	0.14
Aroclor 1254	0.19	0.7	0.52	0.48
Aroclor 1260	0.15	0.39	0.44	0.35
Aroclor 1262	0.09	0.39	0.18	0.21
Percentage	24.88%	22.85%	26.39%	25.88%

Table 3. 19: Air (IADN) equilibrated with octanol phase compared with Aroclors in the octanol phase in summer

Summer Air Conc (15°C)	Factor 1	Factor 2	Factor 3	Factor 4
Aroclor 1016	0.03	0.38	0.09	0.14
Aroclor 1221	0.01	0.11	0.03	0.04
Aroclor 1232	0.04	0.41	0.13	0.17
Aroclor 1242	0.05	0.46	0.15	0.19
Aroclor 1248	0.12	0.66	0.35	0.36
Aroclor 1254	0.33	0.77	0.95	0.84
Aroclor 1260	0.25	0.32	0.4	0.67
Aroclor 1262	0.89	0.22	0.27	0.42
Percentage	24.88%	22.85%	26.39%	25.88%

Winter:

Figure 3. 45: Factor fingerprint for winter air concentrations adjusted to equilibrium with octanol

Tables 3.20 and 3.21 show that there is a similar interpretation for the winter data as for the summer data. From Table 3.21, Factor 1 represents Aroclor 1260 (31.04% of total). This means that even if air were equilibrated with octanol phase, there is only ~ 25-30% contribution that can be explained by Aroclor 1260 whereas in fish the contribution of Aroclor 1260 varies between 80 and 90%. This indicates that the PCBs in air are not the major source of the concentrations in fish.

Table 3. 20: Air (IADN) equilibrated with octanol phase compared with Aroclors in the air phase

Winter Air Conc (-4°C)	Factor 1	Factor 2	Factor 3	Factor 4
Aroclor 1016	0.01	0.35	0.19	0.09
Aroclor 1221	0	0.03	0.09	0
Aroclor 1232	0.01	0.19	0.15	0.02
Aroclor 1242	0.01	0.35	0.2	0.05
Aroclor 1248	0.02	0.51	0.23	0.09
Aroclor 1254	0.07	0.77	0.5	0.5
Aroclor 1260	0.05	0.49	0.52	0.4
Aroclor 1262	0.05	0.5	0.31	0.17
Percentage	31.04%	18.33%	8.58%	42.05%

Table 3. 21: Air (IADN) equilibrated with octanol phase compared with Aroclors in the octanol phase in winter

Winter Air Conc (-4°C)	Factor 1	Factor 2	Factor 3	Factor 4
Aroclor 1016	0.02	0.54	0.23	0.07
Aroclor 1221	0.01	0.14	0.13	0.03
Aroclor 1232	0.02	0.54	0.26	0.1
Aroclor 1242	0.03	0.61	0.27	0.13
Aroclor 1248	0.05	0.79	0.38	0.31
Aroclor 1254	0.15	0.62	0.63	0.95
Aroclor 1260	0.12	0.31	0.43	0.39
Aroclor 1262	0.87	0.2	0.66	0.39
Percentage	31.04%	18.33%	8.58%	42.05%

3.4. Discussion

3.4.1. Can PMF resolved factors for air, water and fish be identified as Aroclors?

As discussed in Section 3.1., numerous researchers have used PMF to analyze air, water and sediment samples and have successfully managed to identify all the resolved factors.

These factors in case of air and sediments have been successfully identified using profiles of unaltered Aroclor mixtures, volatilized Aroclor mixtures (using Equation 3.12), and emissions from combustion of coal and domestic burning of wood (Du and Rodenburg 2007, Khairy, Muir et al. 2015). For water samples, PMF resolved factors were compared with storm water, wastewater, and unaltered or volatilized Aroclors (Du, Belton et al. 2008, Rodenburg, Du et al. 2011). From the above, a couple of questions can be raised. One is if it was appropriate to compare air and water samples with unaltered Aroclor mixtures or to compare water samples with unaltered or volatilized Aroclor profiles. The other question that arises is whether in the United States domestic burning of wood can be considered as a major input? According to our understanding, it would be more appropriate to use volatilized Aroclor profiles for comparison with air samples, and to use water-equilibrated Aroclors for comparison with water samples. Hence, in this analysis, the concentrations in air, water and fish samples were compared with volatilized Aroclor mixtures, and aqueous or octanol-equilibrated Aroclor concentrations.

Contrary to what was seen in previous literature, we were able to identify some factors for each phase, but not all of them. From the cosine similarity values seen in Section 3.3.2.3, up to 3 factors were identified as Aroclor 1260 which accounts for 90.5% of the total PCBs in the fish samples in Keewenaw Point and 83% of the total PCBs in the fish samples in Apostle Island. None of the resolved factors in the particulate data could be identified as a known Aroclor.

3.4.2. Are PCB concentrations in air the major source of PCBs concentrations in fish?

To help answer the question above, it was important to know how the congener ratios vary among the various phases. The transformation of congeners was analyzed for two situations.

Comparison of air and fish PCB concentrations

The first piece of evidence to help answer the question above was seen in Sections 3.3.2.1 and 3.3.2.3; the cosine similarity analysis for the air and fish samples, respectively. It was seen that air samples (summer and winter) had a mixture of light and heavier congeners whereas the fish samples were dominated by heavier congeners, particularly those in Aroclor 1260.

Figure 3. 46: Comparison of concentrations in air and fish, which suggested that air was not the source of PCB concentrations in fish

Furthermore, Figure 3.46 shows that congeners below 97 represent ~80% of the cumulative concentrations in air samples whereas in case of fish samples congeners below 97 represents <20% of the cumulative concentrations. This indicates that more than 80% of concentrations in the fish samples and ~ 20% of the concentrations in air

samples were heavier congeners. Thus, it can be said that the concentrations of PCBs in air are not a major source concentration of PCBs in fish.

Comparison of air sample equilibrated with octanol phase and fish concentrations

As discussed in Section 3.3.3, by using the equilibrium constant, K_{OA} , the air sample (IADN) concentrations were equilibrated with the octanol phase. This was done so the concentrations of PCBs in the air and fish samples could be compared in the same phase. It is already seen that, in the fish samples, ~80-90% of the total contribution is from Aroclor 1260, whereas cosine similarity analysis results for air samples equilibrated with octanol phase in Section 3.3.3 indicate that ~73% of the total contributions were from Aroclor 1254 which means that even after equilibrating air with the octanol phase, the congener distribution in the two phases (i.e., air equilibrated with octanol phase and fish) are different.

Figure 3. 47: Comparison of cumulative concentrations in air equilibrated with octanol phase and fish

Further, from Figure 3.47, it can be seen that the cumulative PCB percentage for fish at congener 97 is < 20% whereas the cumulative percentage at the same congener for air

was ~40%. Hence, it could be said that in this scenario, concentrations in air samples equilibrated with octanol phase could explain only a third of the concentrations of PCBs that were seen in fish. These observations suggest that the congener distribution of PCBs in fish is distinctly different from that of air even if the phase change is taken into account. This renders it unlikely that PCBs in fish can all be derived from PCBs in air.

3.4.3. Comparison of sediment and fish concentration

Figure 3. 48: Cumulative percentage plot for sediments

Figure 3. 49: Cumulative percentage plot for fish at Apostle Island

Figure 3. 50: Cumulative percentage plot for fish at Keweenaw Point

Figure 3. 51: Comparison of PCB concentrations in sediments and Fish (both locations), which suggests that sediments are a major contributor of PCBs in fish

As discussed in the results in Section 3.3.2.5, sediments were identified as a potential source of PCB concentrations in fish. From Figures 3.48, 3.49 and 3.50, it can be seen that at congener 138 the cumulative percentage of PCBs is ~40% in fish whereas the cumulative percentage is 60% in sediments. From Figure 3.51, it is seen that the sediment cumulative concentration pattern is similar to the fish cumulative concentrations. Hence, the data indicate that sediments could be a major contributor to the PCB concentrations in fish. (Baker and Eisenreich 1989, Gewurtz, Shen et al. 2008) said that the rate of accumulation of sediments is low in Lake Superior, which may indicate a presence of legacy concentrations of PCBs. Based on the observation stated above, a more aggressive policy would probably show no immediate change/effect, but in the future it could help with the decline of concentrations of PCBs in fish. This is because the concentrations of PCBs in sediments are mainly legacy contaminants, which means that for the concentrations in sediments to reduce in the future, the current concentrations in air and water need to go down.

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4. Summary and Conclusions

In this project, I sought to determine the most influential factors for predicting fish Hg concentrations in inland lakes of Michigan's Upper Peninsula (UP). Approximately 74 lakes were identified for which both fish Hg and lake characteristics were available. Multi-variate statistics (Multiple Linear Regression, Principal Component Analysis) were applied to determine which lake characteristics were associated with high Hg concentrations. Results suggested that fish Hg is influenced by different factors in large ($> 3 \text{ km}^2$) and small ($< 3 \text{ km}^2$) lakes. In small lakes, the factors associated with elevated fish Hg included: pH, percentage wetland area in the catchment, total phosphorus concentration, maximum lake depth, and lake area. Among these variables, pH had the highest regression coefficient for the partial regression. The results indicate that small shallow lakes with low pH and large wetland area are likely to have elevated fish mercury. In large lakes, fish mercury was related to the watershed: lake area ratio and the secchi depth. Large eutrophic lakes with a small watershed area are likely to have low fish Hg concentrations.

Overall, many of the lakes had high fish Hg content. Fully 88% of the sampled lakes had fish Hg above EPA's criterion value of 0.3 ppm. This high percentage of impaired lakes suggests that the UP landscape is particularly susceptible to Hg deposition. This sensitivity is likely related to the high percentage of wetlands in the UP.

In this project I was trying to identify the source of concentrations of PCBs in fish samples in Lake Superior. Since atmospheric deposition is considered to be the major input of PCBs in Lake Superior, congener distributions of PCBs in air samples were

compared to the congener distributions of PCBs in fish samples to determine whether the air samples are a source of PCB concentrations in fish. To achieve the above, EPA's Positive Matrix Factorization (PMF) was used. Our results indicate that contrary to previous literature, we were unable to identify all factors that were generated by PMF as Aroclors. It was also seen that the air samples were identified as a mixture of Aroclors that indicated the presence of both light and heavy congeners whereas in case of fish samples, the factors were identified as Aroclor 1260 indicating the presence of heavy congeners. This brought us to the conclusion that maybe air samples are not a source of PCB concentrations in fish.

On further analysis of the sediment data, it was seen that the concentrations of PCBs in sediments could be a possible source of PCBs in fish samples. This suggests that the introduction of more aggressive emission control policies will not help in reducing PCB concentrations in fish.

Appendix A

Table A 1:Mercury, pH and lake morphology parameters in the lakes considered in this study

Lake Name	County	pH	Lake Area	Maximum Lake Area	Walleye Hg
Antoine Lake	Dickinson	8.6	3.00	7.62	0.184805
Au Train Lake	Alger	8.46	3.41	9.144	0.446249
Beatons	Gogebic	7.02	1.30	27.43	0.524
Beaufort Lake	Baraga	7.73	1.89	10.70	0.3951
Beaver Lake	Alger	8.1	3.17	11.9	0.364668
Bob Lake	Houghton	5.9	0.53	4.57	0.54535
Boot Lake	Schoolcraft	6.8	0.429	9.144	0.178105
Brevoort Lake	Mackinac	7.9	17.46	9.14	0.231895
Brule	Iron	8.06	0.97	6.10	0.606
Cable	Iron	7.07	1.35	8.84	0.52923
Caribou Lake	Chippewa	8	3.36	6.01	0.432966
Carney Lake	Dickinson	8.2	0.46	10.668	0.21359
Carp Lake	Chippewa	7.85	2.26	10.67	0.447079
Chaney Lake	Gogebic	7.525	2.01	6.10	0.43089
Chicagon	Iron	8	4.38	35.05	0.63073
Cisco L Chain	Gogebic	7.5	2.31	6.10	0.361
Clearwater	Gogebic	6.33	0.72	3.05	0.94
Craig Lake	Baraga	5.65	1.46	7.60	0.65489

Deer Lake	Marquette	-	3.67	18.3	0.849387
Duck	Gogebic	7.9	2.49	7.60	0.43895
Emily	Iron	8.03	1.32	9.75	0.47485
Emily Lake	Houghton	5.87	0.24	27.43	0.3776
Gogebic	Gogebic	8	53.12	10.67	0.33755
Goose Lake	Marquette	8.96	1.66	4.267	0.189438
Gratiot Lake	Keweenaw	7.8	5.88	21.336	0.46891
Gulliver Lake	Schoolcraft	8.3	3.56	8.534	0.469654
Hagerman	Iron	7.68	2.36	16.80	0.15452
Hamilton Lake	Dickinson	7.72	0.31	9.144	0.771191
Independence Lake	Marquette	7.86	7.52	9.1	0.559199
Indian	Iron	7.97	0.80	10.97	0.361
James	Iron	4.55	0.83	3.05	1.26
Kingston Lake	Alger	8.36	0.511	5.5	0.205932
Lac Viex Desert	Gogebic	7.302	17.82	11.58	0.199
Langford	Gogebic	8.33	1.95	3.05	0.68374
Little Lake	Marquette	7.5	1.86	15.24	0.218597
Little Oxbow	Gogebic	6.56	0.39	18.29	0.87687
Long	Iron	7.77	0.27	32.00	0.33518
Manistique Lake	Mackinac	8.25	41.86	6.096	0.3505288
Marion	Gogebic	6.63	1.20	12.19	0.624
Mendora Lake	Keweenaw	7.59	2.788	9.144	0.40842

Michigamme Lake	Marquette	6.25	17.36	21.30	1.122031
Michigamme Res.	Iron	6.68	19.70	15.2	0.68252
Millecoquins Lake	Mackinac	8.86	4.48	3.66	0.412078
Monocle Lake	Chippewa	6.8	0.6957	16.764	0.350297
Muskallonge Lake	Luce	9.13	3.19	6.096	0.610832
Nawakwa Lake	Alger	7.03	1.789	10.668	0.594155
North Manistique Lake	Luce	7.8	6.93	15.24	0.385471
Ottawa	Iron	8.24	2.14	27.43	0.24
Otter Lake	Houghton	8.2	3.63	8.84	0.57615
Parent	Baraga	6.73	0.74	3.00	0.446
Peavy Pond	Iron	8	9.50	-	0.5871
Perch	Iron	8	0.38	15.24	0.49356
Pike Lake	Luce	6.92	1.17	13.106	0.44855
Pomeroy	Gogebic	8.2	1.27	4.57	0.35828
Portage	Houghton	7.97	43.74	16.50	0.20545
Pretty Lake	Luce		0.195	20.7	0.222158
Rice Lake	Houghton	7.29	2.66	2.74	0.23213
Round Lake	Delta	8.4	1.95	17.069	0.217838
Silver lake	Dickinson	7.04	0.44	7.01	0.457043352
Six Mile Lake	Ontonogon	6.6	0.33	4.6	0.63337
South Groveland Lake	Dickinson	-	-	-	0.356351464
South Manistique Lake	Mackinac	7.86	16.75	8.8	0.218759

Stager	Iron	7.85	0.44	16.76	0.35402
Stanley	Iron	7.5	1.29	11.88	0.24536
Ste Kathryn	Iron	7.8	0.67	7.62	0.311
Sudden Lake	Ontonagon	-	0.16	4.6	0.54079
Sunday	Gogebic	7.2	0.90	2.10	1.04
Sunset	Iron	7.53	2.15	16.46	0.35423
Tamarack	Iron	7.67	1.34	5.50	0.557
Teal Lake	Marquette	7.6	1.96	9.75	0.245183
Thousand Island Lake	Gogebic	6.71	4.50	12.19	0.36457
Torch Lake	Houghton	7.13	9.71	37.49	0.20164
Winslow	Iron	7.63	1.05	7.60	0.497
Worm Lake	Baraga	7.13	2.59	2.10	0.46244

Table A 2: Watershed and wetlands characteristics, DOC and DO in the lakes considered in this study

Lake Name	County	Percentage Wetlands	Watershed Area: Lake Area	DOC	Dissolved Oxygen
Antoine Lake	Dickinson	4.86	3.29	8.0	0.1
Au Train Lake	Alger	15.26	85.60	5.2	-
Beatons	Gogebic	18.45	3.03	7.7	7.2
Beaufort Lake	Baraga	26.55	26.46	4.3	0.2
Beaver Lake	Alger	-	-	-	-

Bob Lake	Houghton	11.43	26.00	-	2.8
Boot Lake	Schoolcraft	37.50	7.65	-	0.1
Brevoort Lake	Mackinac	-	-	-	-
Brule	Iron	17.10	94.83	-	9.7
Cable	Iron	26.29	21.11	-	0.2
Caribou Lake	Chippewa	-	-	-	3.4
Carney Lake	Dickinson	5.52	3.15	11.0	2.25
Carp Lake	Chippewa	54.74	14.98	-	10.2
Chaney Lake	Gogebic	22.73	6.90	4.3	7.6
Chicagon	Iron	14.09	7.97	-	0.15
Cisco L Chain	Gogebic	34.97	54.43	-	-
Clearwater	Gogebic	1.20	2.50	13.0	5.7
Craig Lake	Baraga	30.91	20.72	-	5.7
Deer Lake	Marquette	23.53	70.71	7.8	0.1
Duck	Gogebic	21.47	8.12	6.8	7.6
Emily	Iron	22.48	41.89	-	9
Emily Lake	Houghton	6.28	8.64	6.0	10.3
Gogebic	Gogebic	25.60	9.40	7.0	7.8
Goose Lake	Marquette	12.02	18.90	-	0.1
Gratiot Lake	Keweenaw	6.19	5.52	13.0	0.2
Gulliver Lake	Schoolcraft	36.23	4.99	6.3	6.3
Hagerman	Iron	1.64	2.32	8.7	0.3

Hamilton Lake	Dickinson	20.65	86.84	-	8.1
Independence Lake	Marquette	8.86	42.03	-	7.8
Indian	Iron	2.39	4.21	-	8.4
James	Iron	4.08	2.94	3.0	7.4
Kingston Lake	Alger	1.32	11.82	-	-
Lac Viex Desert	Gogebic	14.78	4.56	-	0.2
Langford	Gogebic	34.84	6.03	-	0.3
Little Lake	Marquette	-	-	-	8.7
Little Oxbow	Gogebic	31.08	12.03	-	10.4
Long	Iron	2.00	1.86	-	5.7
Manistique Lake	Mackinac	39.84	6.97	8.2	3.68
Marion	Gogebic	18.46	14.49	-	0.2
Mendora Lake	Keweenaw	13.93	4.38	9.5	8.5
Michigamme Lake	Marquette	27.42	28.58	9.7	-
Michigamme Res.	Iron	25.86	40.92	5.8	9
Millecoquins Lake	Mackinac	19.78	31.85	-	0.14
Monocle Lake	Chippewa	-	-	-	0.2
Muskallonge Lake	Luce	7.44	16.42	11.5	0.4

Nawakwa Lake	Alger	33.27	8.33	4.8	3.8
North Manistique Lake	Luce	10.24	3.34	2.9	8
Ottawa	Iron	9.56	4.64	7.3	-
Otter Lake	Houghton	16.88	475.06	-	8.4
Parent	Baraga	-	-	-	0.2
Peavy Pond	Iron	-	-	5.2	4
Perch	Iron	33.59	152.92	8.5	2
Pike Lake	Luce	36.80	10.68	12.0	-
Pomeroy	Gogebic	36.15	15.54	5.2	7.2
Portage	Houghton	13.72	9.95	-	0.1
Pretty Lake	Luce	-	-	-	9.8
Rice Lake	Houghton	30.28	12.19	6.5	10.2
Round Lake	Delta	31.74	4.41	6.6	-
Silver lake	Dickinson	12.20	6.52	8.1	6.91
Six Mile Lake	Ontonogon	16.20	5.42	-	0.1
South Groveland Lake	Dickinson	-	-	14.0	-
South Manistique Lake	Mackinac	45.47	6.19	-	-
Stager	Iron	21.23	13.13		
Stanley	Iron	-	-	5.4	6.8

Ste Kathryn	Iron	-	-	-	0.1
Sudden Lake	Ontonogon	14.55	34.38	-	5.7
Sunday	Gogebic	37.82	80.40	7.2	-
Sunset	Iron	13.65	13.16	-	0.2
Tamarack	Iron	-	-	4.4	5.8
Teal Lake	Marquette	7.50	4.08	6.4	0.2
Thousand Island Lake	Gogebic	16.73	25.89	6.9	7.4
Torch Lake	Houghton	15.88	22.42	-	0.1
Winslow	Iron	34.88	16.47	27.0	-
Worm Lake	Baraga	44.64	23.50	8.0	7.2

Table A 3: Trophic state parameters in the lakes considered in this study

Lake Name	County	Secchi Depth	Chlorophyll Level	Total Phosphorus
Antoine Lake	Dickinson	4.57	3.9	11
Au Train Lake	Alger	2.286	6	20
Beatons	Gogebic	4.9	2.1	4
Beaufort Lake	Baraga	2.74	2	27
Beaver Lake	Alger	3.8	1.3	12
Bob Lake	Houghton	1.2573	4	8
Boot Lake	Schoolcraft	1.76	1.3	4

Brevoort Lake	Mackinac	3.2	1.7	13
Brule	Iron	0.914	13	35
Cable	Iron	1.67	1	15
Caribou Lake	Chippewa	1.8	3.6	16
Carney Lake	Dickinson	3.047	4.8	10
Carp Lake	Chippewa	4.88	3.2	10
Chaney Lake	Gogebic	1.83	10	24
Chicagon	Iron	4.57	2.4	20
Cisco L Chain	Gogebic	1.219	35	40
Clearwater	Gogebic	2.438	5.4	13
Craig Lake	Baraga	0.9	-	-
Deer Lake	Marquette	-	-	-
Duck	Gogebic	2.89	9.2	19
Emily	Iron	2.438	9	38
Emily Lake	Houghton	4.27	4.5	6
Gogebic	Gogebic	2.43	9	16
Goose Lake	Marquette	2.743	4	22
Gratiot Lake	Keweenaw	4.72	1.9	7
Gulliver Lake	Schoolcraft	2.26	4.2	22
Hagerman	Iron	5.334	4.5	5
Hamilton Lake	Dickinson	3.96	6.3	18
Independence Lake	Marquette	2.2	6.4	17

Indian	Iron	5.0292	2.4	13
James	Iron	2.74	1.1	8
Kingston Lake	Alger	2.89	5.6	11
Lac Viex Desert	Gogebic	1.4	5.9	38
Langford	Gogebic	1.51	5.9	43
Little Lake	Marquette	3.96	1.5	10
Little Oxbow	Gogebic	1.53	1.3	21
Long	Iron	2.74	5.8	22
Manistique Lake	Mackinac	2.4	4.2	21
Marion	Gogebic	3.35	3.7	9
Mendora Lake	Keweenaw	4.27	4	3.9
Michigamme Lake	Marquette	3.3528	4	12
Michigamme Res.	Iron	2.1	4	15
Millecoquins Lake	Mackinac	2.44	1	20
Monocle Lake	Chippewa	2.74	5.8	13
Muskallonge Lake	Luce	2.51	2.7	8
Nawakwa Lake	Alger	1.37	19.4	32
North Manistique Lake	Luce	5.2	2.6	9
Ottawa	Iron	4.11	1	38
Otter Lake	Houghton	1.37	24.79	31
Parent	Baraga	1.6	2	21
Peavy Pond	Iron	-	6.8	-

Perch	Iron	2.43	6.8	9
Pike Lake	Luce	2.13	4	10
Pomeroy	Gogebic	2	19	48
Portage	Houghton	4.57	3	10
Pretty Lake	Luce	-	-	-
Rice Lake	Houghton	2.59	2	10
Round Lake	Delta	3.96	4.3	6
Silver lake	Dickinson	4.2672	4	24
Six Mile Lake	Ontonogon	2.44	4	8
South Groveland Lake	Dickinson	-	-	-
South Manistique Lake	Mackinac	2.3	6	15
Stager	Iron	5.18	7.3	9
Stanley	Iron	3.05	2.3	22
Ste Kathryn	Iron	2.29	3.4	15
Sudden Lake	Ontonogon	-	-	-
Sunday	Gogebic	0.91	7.3	60
Sunset	Iron	3.66	3.7	10
Tamarack	Iron	1.22	9.4	24
Teal Lake	Marquette	3.9	1.9	17
Thousand Island Lake	Gogebic	3.81	3.9	11
Torch Lake	Houghton	3.04	0.5	53
Winslow	Iron	1.98	3.8	16

Worm Lake	Baraga	0.8	4.7	33

Table A 4: Average Walleye Hg and fish lengths in lakes for different years

Lake	County	Walleye Hg (PPM)	Fish Length (cm)	Year
Antoine Lake	Dickinson County	0.1967	41	1988
Antoine Lake	Dickinson County	0.2142	48.31	2005
Au Train Lake	Alger County	0.6048	52.76	2005
Au Train Lake	Alger County	0.3744	42.87	1987
Au Train Lake	Alger County	0.5625	40.57	1993
Beaufort Lake	Baraga County	0.34	38.16	1987
Beaver Lake	Alger County	0.334	39.3	2003
Bob Lake	Houghton County	0.69	49.37	2001
Boot Lake	Schoolcraft County	0.39875	51.87	2004
Brevoort Lake	Mackinac County	0.252	44.7	1989
Cable Lake	Iron County	0.528	40.3	1998
Caribou Lake	Chippewa County	0.58	52.3	1986
Carney Lake	Dickinson County	0.248	45.3	1989
Carp Lake	Chippewa County	0.39	39.83	1987
Chaney Lake	Gogebic County	0.397	48.54	1998
Chaney Lake	Gogebic County	0.49	48.65	2000

Chicagon Lake	Iron County	0.435	50.125	1986
Chicagon Lake	Iron County	0.7038	44.07	1994
Chicagon Lake	Iron County	0.712	47.7	2008
Craig Lake	Baraga County	0.448	38.78	1989
Craig Lake	Baraga County	0.58	38.01	1991
Craig Lake	Baraga County	0.6694	41.14	2005
Deer Lake	Marquette County	0.971	47.83	1998
Deer Lake	Marquette County	1.15	47.24	1999
Deer Lake	Marquette County	0.659	46.65	2001
Deer Lake	Marquette County	1.06	48.84	2003
Deer Lake	Marquette County	0.4369	40.33	2008
Deer Lake	Marquette County	1.303	50.69	2011
Deer Lake	Marquette County	0.685	28.97	1990
Deer Lake	Marquette County	0.782	41.7	1993
Deer Lake	Marquette County	0.981	47.02	1996
Deer Lake	Marquette County	1.169	47.8	1997
Duck Lake	Gogebic County	0.5556	52.72	1986
Duck Lake	Gogebic County	0.571	48.36	1999
Emily Lake	Iron County	0.527	44.8	1988
Emily Lake	Houghton County	0.414	48.02	2002
Gogebic Lake	Ontonagon County	0.45	42.9	1985
Gogebic Lake	Ontonagon County	0.215	41.55	2002

Goose Lake	Marquette County	0.202	0.202	1988
Goose Lake	Marquette County	0.1836	0.18	2001
Gratiot Lake	Keewenaw County	0.524	43.76	2005
Gulliver Lake	Schoolcraft County	0.4855	45.42	1990
Gulliver Lake	Schoolcraft County	0.276	47.12	2003
Hagerman Lake	Iron County	0.249	50.4	1988
Hamilton Lake	Dickinson County	0.9337	50.93	1994
Kingston Lake	Alger County	0.4	52.575	2003
Lake Independence	Marquette County	0.481	0.48	1989
Lake Independence	Marquette County	0.701	0.7	1995
Lake Independence	Marquette County	0.5591	0.55	2005
Lake Independence	Marquette County	0.54	0.54	2014
Lake Mendora	Keewenaw County	0.544	44.04	2004
Lake Michigamme	Marquette County	1.05	41.25	1989
Lake Michigamme	Marquette County	1.123	42.25	2006
Langford Lake	Gogebic County	0.9444	50.83	1986
Langford Lake	Gogebic County	1.304	57.8	1994
Little Lake	Marquette County	0.264	46.04	2002
Little Oxford Lake	Gogebic County	0.807	39.76	2005
Long Lake	Iron County	0.6857	62.3	2007
Manistique Lake	Mackinac County	0.456	51.21	2003
Manistique Lake	Mackinac County	0.398	43.56	2013

Michigamme Reservoir	Iron County	1.0875	39.83	1984
Michigamme Reservoir	Iron County	0.54	41.16	1992
Michigamme Reservoir	Iron County	0.57	44.78	1995
Michigamme Reservoir	Iron County	0.5067	41.91	1998
Michigamme Reservoir	Iron County	0.654	43.34	2000
Michigamme Reservoir	Iron County	0.54	40.84	2008
Millecoquins Lake	Mackinac County	0.4322	47.77	1989
Millecoquins Lake	Mackinac County	0.7669	52	2006
Monacle Lake	Chippewa County	0.318	41	1986
Muskallonge Lake	Luce County	0.7468	44.07	2008
Nawakwa Lake	Alger County	0.772	47.02	1999
Nawakwa Lake	Alger County	0.532	42.3	2008
Nawakwa Lake	Alger County	0.628	46.75	1989
North Manistique Lake	Luce County	0.549	50.4	1989
Otter Lake	Houghton County	0.563	45.79	2000

Otter Lake	Houghton County	0.564	44.74	2010
Peavy Pond	Iron County	0.575	35.63	1984
Peavy Pond	Iron County	0.53	44.7	1997
Peavy Pond	Iron County	0.5157	38	1998
Perch Lake	Iron County	0.6108	44.12	1998
Perch Lake	Iron County	0.584	50.94	2006
Pike Lake	Schoolcraft County	0.5875	49.12	1989
Pomeroy Lake	Gogebic County	0.3367	40.3	1997
Pomeroy Lake	Gogebic County	0.397	45.37	1999
Portage Lake	Houghton County	0.2946	46.71	1988
Portage Lake	Houghton County	0.4466	50.82	2007
Pretty Lake	Schoolcraft County	0.48	50.03	2004
Rice Lake	Houghton County	0.39	49.28	1991
Round Lake	Delta County	0.4687	48.25	1987
Silver Lake	Dickinson County	0.585	45.96	2002
Six Mile Lake	Ontonagon County	0.628	42.4	1995
South Groveland Pond	Dickinson County	0.4463	49.73	2003
South Manistique Lake	Delta County	0.283	46.95	1988
Stager Lake	Iron County	0.329	41	2012
Stanley Lake	Iron County	0.225	44.25	1990

Stanley Lake	Iron County	0.24	47.34	2001
Sudden Lake	Ontonagon County	0.643	45.41	2001
Sunday Lake	Gogebic County	1.04	43.43	2003
Sunset Lake	Iron County	0.407	45.25	1998
Teal Lake	Marquette County	0.259	42.89	2004
Teal Lake	Marquette County	0.365	47.27	2005
Thousand Island Lake	Gogebic County	0.512	49.91	1999
Torch Lake	Houghton County	0.2433	42.33	1988
Torch Lake	Houghton County	0.416	50.25	2000
Torch Lake	Houghton County	0.8836	53.37	2007
Torch Lake	Houghton County	0.644	49.96	2013
Vermilac Lake	Baraga County	0.587	47.77	2001

Figure A 1: Walleye Hg vs fish length (Chicagon lake)

Figure A 2: Walleye Hg vs fish length (Michigamme Reservoir)

Figure A 3: Walleye Hg vs fish length (Peavy Pond)

Figure A 4: Walleye Hg vs fish length (Torch lake)

Figure A 5: Walleye Hg vs fish length (Craig lake)

Figure A 6: Walleye Hg vs fish length (Au Train lake)

Figure A 7: Walleye Hg vs fish length (Nawakwa lake)

Figure A 8: Walleye Hg vs fish length (Deer lake)

Figure A 9: Walleye Hg vs fish length (lake Independence)

Table A 5: Slopes and intercepts obtained from Walleye Hg vs fish length

Lake Name	County	Slope	Intercept
Cable Lake	Iron County	0.000561	0.505399
Chicagon Lake		0.005793	0.384549
Emily Lake		0.022674	-0.4888
Hagerman Lake		0.01196	-0.35379
Long Lake		0.017707	-0.41736
Michigamme Reservoir		0.038675	-0.96117
Peavy Pond		0.02176	-0.33768
Perch Lake		0.030138	-0.78732
Stager Lake		0.016678	-0.35479
Stanley Lake		-0.00347	0.392635

Sunset Lake		0.019189	-0.46129
Portage Lake	Houghton County	0.025595	-0.88236
Torch Lake		0.055489	-2.15664
Bob Lake		0.021032	-0.34849
Emily Lake		0.006595	0.097321
Otter Lake		-0.00458	0.770624
Rice Lake		0.023273	-0.75698
Sunday Lake	Gogebic County	-	-
Pomeroy Lake		0.016609	-0.3476
Little Oxford Lake		0.025561	-0.20948
Langford Lake		0.035958	-0.8445
Duck Lake		0.015737	-0.22987
Chaney Lake		0.000723	0.400162
Thousand Island Lake		0.019896	-0.48101
Beaufort Lake	Baraga County	0.012716	-0.14531
Craig Lake		0.023035	-0.32409
Vermilac Lake		0.023603	-0.5407
Gogebic Lake	Ontonagon County	0.01863	-0.45421
Six Mile Lake		0.053721	-1.64977
Sudden Lake		0.03506	-0.94925

Gratiot Lake	Keewenaw County	0.04347	-1.37858
Lake Mendora		0.087833	-3.32447
Caribou Lake	Chippewa Lake	0.015003	-0.20468
Carp Lake		0.020154	-0.40949
Monacle Lake		0.02115	-0.5486
Brevoort Lake	Mackinac County	0.009139	-0.1565
Manistique Lake		0.015654	-0.31478
Millecoquins Lake		0.026172	-0.70024
Round Lake	Delta County	0.043637	-1.63673
South Manistique Lake		0.014436	-0.39478
Boot Lake	Schoolcraft County	0.023524	-0.82167
Gulliver Lake		-0.02474	1.520978
Pike Lake		0.020974	-0.44283
Pretty Lake		0.034206	-1.23158
Muskallonge Lake	Luce County	0.086604	-3.-6984
North Manistique Lake		0.0207	-0.49427
Au Train Lake	Alger Lake	0.023368	-0.54689
Beaver Lake		0.009584	-0.04265

Kingston Lake		0.019262	-0.61272
Nawakwa Lake		0.027276	-0.56084
Antoine Lake	Dickinson County	0.008755	-0.18729
Carney Lake		0.012289	-0.3087
Hamilton Lake		0.01926	-0.04762
Silver Lake		0.036982	-1.11468
South Groveland Pond		0.012439	-0.1723
Deer Lake		0.033031	-0.55444
Goose Lake	Marquette County	0.001001	0.14689
Lake Independence		0.012146	0.042993
Lake Michigamme		0.04225	-0.67359
Little Lake		0.012798	-0.32533
Teal Lake		0.025969	-0.8585

Table A 6: The chi – square goodness of fit test results

<i>Parameter</i>	<i>P-Value</i>	<i>Normally Distributed</i>
Lake Area	<i>2.2991E-08</i>	<i>Yes</i>
Maximum Lake Depth	<i>1.5683E-11</i>	<i>Yes</i>
Secchi Depth	<i>1.3949E-09</i>	<i>Yes</i>

Chlorophyll	<i>4.6812E-13</i>	<i>Yes</i>
Total Phosphorus	<i>1.4997E-06</i>	<i>Yes</i>
% Wetland	<i>2.9369E-08</i>	<i>Yes</i>
Watershed Area: Lake Area	<i>1.6556E-12</i>	<i>Yes</i>
Dissolved Oxygen	<i>5.6207E-15</i>	<i>Yes</i>
pH	<i>1.2718E-07</i>	<i>Yes</i>
Walleye Hg	<i>1.9329E-06</i>	<i>Yes</i>

Table A 7 Pearson Correlation for big lakes (Part 1)

	Walleye Hg	Dissolved Oxygen	pH	Watershed Area: Lake Area	% Wetland
Walleye Hg	1	-0.158	-0.226	0.448	-0.187
Dissolved Oxygen	-0.158	1	0.557	-0.055	0.037
pH	-0.226	0.557	1	-0.009	-0.192
Watershed Area: Lake Area	0.448	-0.055	-0.009	1	-0.058
% Wetland	-0.187	0.037	-0.192	-0.058	1

Table A 8: Pearson Correlation for big lakes (Part 2)

	Lake Area	Max Lake Depth	Secchi Depth	Chlorophyll	Total Phosphorus
Lake Area	1	0.03	-0.164	0.209	0.119
Max Lake Depth	0.03	1	0.556	0.004	-0.312
Secchi Depth	-0.164	0.556	1	-0.619	-0.738
Chlorophyll	0.209	0.004	-0.619	1	0.477
Total Phosphorus	0.119	-0.312	-0.738	0.447	1

Table A 9: Pearson Correlation for small lakes (Part 1)

	Walleye Hg	Dissolved Oxygen	pH	Watershed Area: Lake Area	% Wetland
Walleye Hg	1	0.092	-0.544	0.243	0.195
Dissolved	0.092	1	-0.002	0.121	-0.064

Oxygen					
pH	-0.544	-0.002	1	0.127	0.115
Watershed Area:	0.243	0.121	0.127	1	0.532
Lake Area					
% Wetland	0.195	-0.064	0.115	0.532	1

Table A 10: Pearson Correlation for small lakes (Part 2)

	Total Phosphorus	Lake Area	Max Lake Depth	Secchi Depth	Chlorophyll
Total Phosphorus	1	0.183	-0.070	-0.523	0.273
Lake Area	0.183	1	0.093	0.073	-0.108
Max Lake Depth	-0.07	-0.093	1	0.423	-0.350
Secchi Depth	-0.523	0.073	0.423	1	-0.300
Chlorophyll	0.273	-0.108	-0.350	-0.300	1

Table A 71: Variable excluded from the analysis (big lakes) (MLR)

Model	Excluded Variable	Significance	R Square	Adjusted R Square
1	None		0.563	-0.093
2	Chlorophyll	0.941	0.562	0.062
3	Chlorophyll	0.940	0.560	0.176
	% Wetland	0.870		
4	Chlorophyll	0.925	0.558	0.264
	% Wetland	0.917		
	Total Phosphorus	0.852		
5	Chlorophyll	0.882	0.544	0.315
	% Wetland	0.932		
	Total Phosphorus	0.848		
	Lake Area	0.597		
6	Chlorophyll	0.864	0.504	0.324
	% Wetland	0.918		
	Total Phosphorus	0.836		

	Lake Area	0.698		
	Dissolved Oxygen	0.375		
7	Chlorophyll	0.505	0.456	0.320
	% Wetland	0.973		
	Total Phosphorus	0.664		
	Lake Area	0.908		
	Dissolved Oxygen	0.373		
	Maximum Lake Depth	0.323		
8	Chlorophyll	0.610	0.439	0.352
	% Wetland	0.886		
	Total Phosphorus	0.661		
	Lake Area	0.845		
	Dissolved Oxygen	0.660		
	Maximum Lake Depth	0.769		
	pH	0.547		

Table A 82: Variable excluded from the analysis (small lakes) (MLR)

Model	Excluded Variable	Significance	R Square	Adjusted R Square
1	None		0.604	0.496
2	Watershed Area: Lake Area	0.528	0.599	0.504
3	Watershed Area: Lake Area	0.605	0.595	0.514
	Dissolved Oxygen	0.569		
4	Watershed Area: Lake Area	0.757	0.583	0.514
	Dissolved Oxygen	0.545		
	Secchi Depth	0.328		
5	Watershed Area: Lake Area	0.662	0.572	0.514

	Dissolved Oxygen	0.591		
	Secchi Depth	0.405		
	Chlorophyll	0.325		

Table A 9: Component Score Coefficient Matrix for large lakes (PCA)

	1	2	3
Lake Area	0.046	0.113	0.379
Max Lake Depth	-0.041	0.320	0.040
Secchi Depth	-0.291	0.097	-0.020
Chlorophyll	0.325	0.111	-0.024
Total Phosphorus	0.250	-0.063	0.088
% Wetland	0.145	0.087	0.285
Watershed Area: Lake Area	0.308	0.074	-0.370
Dissolved Oxygen	-0.021	-0.309	0.067
pH	-0.109	-0.392	-0.068
Walleye Hg	0.079	0.144	-0.351

Table A14: Component Score Coefficient Matrix for small lakes (PCA)

	1	2	3	4
Lake Area	-0.011	0.134	0.028	0.593
Max Lake Depth	0.106	-0.494	0.014	0.035
Secchi Depth	-0.232	-0.118	0.161	0.037
Chlorophyll	0.101	0.171	0.373	-0.440
Total Phosphorus	0.259	0.026	-0.070	-0.003
% Wetland	0.388	-0.201	-0.023	-0.107
Watershed Area: Lake Area	0.311	-0.097	-0.038	0.307
Dissolved Oxygen	-0.106	0.516	-0.007	0.234
pH	0.058	-0.004	0.555	-0.123
Walleye Hg	0.142	0.013	-0.381	-0.115

Appendix B

Table B 1: Percent weight of Aroclor 1221¹

PCB No.	Aroclor 1221
1	35.8
2	3.81
3	20.44
4	6.19
5	0.74
6	3.82
7	1.7
8	12.34
9	1.74
10	0.8
11	0.16
12	0.59
13	1.12
14	0
15	4.18
16	0.31
17	0.34
18	0.78

---

¹ In the table, all the congeners after congener 118 were absent.

19	0.08
20	0.07
21	NM
22	0.26
23	
24	0.02
25	0.09
26	0.13
27	0.05
28	0.62
29	0.01
30	
31	0.6
32	0.17
33	0.48
34	
35	0
36	
37	0.19
38	
39	
40	0.04

41	0.03
42	0.09
43	
44	0.21
45	0.04
46	0.02
47	0.05
48	0.06
49	0.15
50	
51	0
52	0.22
53	0.04
54	
55	
56	0.12
57	
58	
59	0.01
60	0.07
61	
62	

63	0
64	0.1
65	
66	0.21
67	0
68	
69	
70	0.24
71	0.06
72	
73	
74	0.12
75	
76	0
77	0.01
78	
79	
80	
81	
82	0
83	
84	0.02

85	0.03
86	
87	0.04
88	
89	
90	
91	
92	0.02
93	
94	
95	0.05
96	
97	0.03
98	
99	0.04
100	
101	0.07
102	
103	
104	
105	0.05
106	

107	
108	
109	
110	0.05
111	
112	
113	
114	
115	
116	
117	
118	0.08

Table B 2: Percent weight of Aroclor 1232¹

PCB No.	Aroclor 1232	Aroclor 1232
1	15.21	15.84
2	1.98	1.94
3	10.36	10.2
4	5.32	5.38
5	0.49	0.5

---

¹ In the table, all the congeners after congener 187 were absent.

6	3.02	3
7	1.12	1.09
8	10.71	10.72
9	1.25	1.29
10	0.6	0.58
11		
12	0.35	0.35
13	0.73	0.72
14	0	0.02
15	3.24	3.19
16	1.79	1.79
17	1.83	1.82
18	4.89	4.83
19	0.46	0.47
20	0.42	0.42
21	NM	
22	1.62	1.62
23	0	0
24	0.08	0.08
25	0.37	0.37
26	0.75	0.74
27	0.12	0.12

28	3.92	3.89
29	0.05	0.05
30		
31	4.17	4.11
32	1.08	1.07
33	2.84	2.88
34	0.01	0.01
35	0.06	0.05
36		
37	1.15	1.12
38		
39		
40	0.4	0.36
41	0.36	0.35
42	0.66	0.69
43	0.12	0.09
44	1.81	1.81
45	0.47	0.45
46	0.19	0.19
47	0.49	0.49
48	0.61	0.62
49	1.37	1.36

50		
51	0.12	0.13
52	1.83	1.86
53	0.37	0.37
54	0	
55	0.05	0.05
56	0.93	0.92
57	0	0.01
58		
59	0.2	0.15
60	0.61	0.6
61		
62		
63	0.1	0.1
64	0.87	0.87
65		
66	1.74	1.71
67	0.09	0.08
68		
69		
70	1.9	1.9
71	0.54	0.54

72	0	
73		
74	0.92	0.92
75	0.02	0.02
76		
77	0.17	0.16
78		
79		
80		
81	0	
82	0.12	0.12
83	0.05	0.04
84	0.2	0.18
85	0.17	0.17
86	0.01	0.01
87	0.22	0.22
88		
89	0.05	0.05
90		
91	0.1	0.1
92	0.05	0.05
93		

94		
95	0.3	0.3
96	0.01	0.01
97	0.18	0.17
98		
99	0.21	0.21
100		
101	0.33	0.32
102	0.03	0.03
103		
104		
105	0.22	0.21
106		
107		
108		
109	0.03	0.03
110	0.38	0.38
111		
112		
113		
114	0.02	0.01
115	0.01	0.01

116		
117	0.01	0
118	0.29	0.28
119		
120		
121		
122		
123		
124	0	
125	0	0
126		
127		
128		
129		
130		
131		
132	0.02	0.02
133		
134		
135		
136		0
137		

138	0.06	0.05
139		
140		
141		
142		
143		
144		
145		
146		
147		
148		
149	0.05	0.05
150		
151	0.01	0
152		
153	0.05	0.05
154		
155		
156		
157		
158		
159		

160		
161		
162		
163	0.02	0.02
164		
165		
166		
167		
168		
169		
170		
171		
172		
173		
174		
175		
176		
177		
178		
179		
180	0.02	0
181		

182		
183		
184		
185		
186		
187	0.01	0

Table B 3: Percent weight of Aroclor 1016¹

PCB No.	Aroclor 1016	Aroclor 1016
1	0.52	0.54
2	0.02	0.03
3	0.15	0.16
4	3.62	3.66
5	0.17	0.15
6	1.64	1.69
7	0.29	0.3
8	8.29	8.31
9	0.58	0.59
10	0.23	0.23
11		
12	0.07	0.07

---

¹ In the table, all the congeners after congener 105 were absent.

13	0.24	0.25
14		
15	2.4	2.49
16	3.88	3.88
17	3.98	3.98
18	10.86	10.75
19	0.99	1.01
20	0.88	0.89
21		
22	3.5	3.51
23	0.01	0.02
24	0.16	0.17
25	0.72	0.72
26	1.57	1.59
27	0.51	0.5
28	8.5	8.57
29	0.1	0.1
30	0	0
31	9.32	9.26
32	2.37	2.37
33	6.21	6.19
34	0.03	0.03

35	0.05	0.06
36		
37	1.02	1.01
38		
39		
40	0.58	0.58
41	0.76	0.76
42	1.59	1.59
43	0.28	0.25
44	4.47	4.48
45	1.23	1.22
46	0.49	0.48
47	1.26	1.24
48	1.61	1.59
49	3.35	3.4
50	0.01	0.01
51	0.32	0.32
52	4.63	4.61
53	0.95	0.94
54	0.01	0.02
55		
56	0.07	0.06

57	0.01	0.01
58		
59	0.41	0.38
60	0.04	0.03
61		
62		
63	0.06	0.05
64	1.87	1.84
65		
66	0.39	0.36
67	0.06	0.06
68		
69	0	0
70	0.59	0.56
71	1.16	1.17
72	0	0
73	0	0
74	0.33	0.33
75	0.06	0.06
76		
77		
78		

79		
80		
81		
82		
83		
84	0.05	0.05
85	0	
86		
87		
88		
89		
90		
91	0.06	0.06
92		
93		
94		0
95	0.31	0.03
96	0.04	0.04
97	0	0.04
98		0
99	0.01	0.01
100		

101	0.04	0.03
102	0.04	0.04
103		
104		
105	0	

Table B 4: Percent weight of Aroclor 1242¹

PCB No.	Aroclor 1242	Aroclor 1242	Aroclor 1242
1	0.51	0.34	0.78
2	0.02	0.02	0.05
3	0.15	0.11	0.27
4	3.11	2.71	3.41
5	0.13	0.11	0.19
6	1.42	1.24	1.63
7	0.26	0.18	0.34
8	6.99	6.48	7.68
9	0.5	0.4	0.6
10	0.2	0.14	0.25
11			
12	0.06	0.04	0.09
13	0.2	0.17	0.27

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¹ In the table, all the congeners after congener 163 were absent.

14			
15	1.98	1.95	2.39
16	3.03	3.44	2.94
17	3.14	3.29	2.97
18	8.53	9.14	7.93
19	0.79	0.84	0.75
20	0.68	0.77	0.71
21			
22	2.71	3.08	2.73
23	0.01	0.01	0.01
24	0.13	0.13	0.14
25	0.57	0.61	0.6
26	1.21	1.38	1.24
27	0.4	0.44	0.39
28	6.68	7.31	6.6
29	0.08	0.08	0.09
30			
31	7.18	7.82	7.01
32	1.85	2.05	1.79
33	4.85	5.35	4.82
34	0.02	0.02	0.03
35	0.07	0.07	0.09

36			
37	1.86	2.19	2.05
38			
39			
40	0.77	0.79	0.72
41	0.69	0.69	0.65
42	1.13	1.25	1.17
43	0.18	0.19	0.16
44	3.6	3.63	3.42
45	0.93	0.91	0.84
46	0.37	0.38	0.33
47	0.97	0.92	0.91
48	1.18	1.17	1.19
49	2.59	2.6	2.38
50	0	0	0
51	0.25	0.23	0.22
52	3.64	3.47	3.47
53	0.75	0.71	0.68
54	0	0	0.01
55	0.09	0.11	0.1
56	1.8	1.85	1.8
57	0.02	0	0.03

58			
59	0.37	0.32	0.27
60	1.17	1.17	1.19
61			
62			
63	0.13	0.11	0.12
64	1.76	1.68	1.67
65			
66	3.38	3.38	3.4
67	0.15	0.17	0.16
68			
69			
70	3.76	3.7	3.73
71	1.04	1.06	1
72	0.01	0.01	0.01
73		0	
74	1.83	1.76	1.84
75	0.05	0.03	0.04
76	0.08	0.08	0.06
77	0.27	0.33	0.33
78			
79			

80			
81	0	0.01	0.01
82	0.29	0.22	0.28
83	0.12	0.09	0.12
84	0.46	0.35	0.43
85	0.36	0.24	0.32
86	0.03		0.04
87	0.52	0.38	0.49
88	0	0	
89	0.1	0.07	0.09
90			
91	0.24	0.17	0.23
92	0.06	0.09	0.13
93			0
94	0	0	0.01
95	0.68	0.51	0.64
96	0.03	0.02	0.03
97	0.43	0.31	0.41
98			
99	0.53	0.36	0.49
100			
101	0.78	0.57	0.71

102	0.08	0.05	0.07
103			
104			
105	0.52	0.37	0.52
106			
107			
108			
109	0.08	0.04	0.06
110	0.94	0.68	0.88
111			
112	0		
113			
114	0.05	0.03	0.05
115	0.04	0.03	0.05
116			
117	0.03	0.02	0.04
118	0.78	0.51	0.69
119			
120			
121			
122	0.01	0	0.02
123	0.03	0.02	0.03

124	0.03	0.02	0.03
125	0.02	0.02	0.02
126			
127			
128	0.04	0	0.02
129		0	
130			
131			
132	0.05	0.03	0.04
133			
134			
135			
136			0
137			
138	0.16	0.05	0.1
139			
140			
141	0.01	0	0
142			
143			
144			
145			

146			
147			
148			
149	0.07	0.04	0.06
150			
151			0
152			
153	0.09	0.04	0.05
154			
155			
156	0.02		
157			
158	0.02		0.01
159			
160			
161			
162			
163	0	0.02	0

Table B 5: Percent weight of Aroclor 1248¹

PCB No.	Aroclor 1248	Aroclor 1248
1	0.05	0.02
2		
3	0.01	
4	0.32	0.04
5	0	
6	0.13	0
7	0.02	
8	0.81	0.26
9	0.04	
10		
11		
12		
13	0.02	
14		
15	0.22	0.06
16	1.04	0.71
17	1.05	0.93
18	4.29	3.29
19	0.22	0.14

---

¹ In the table, all the congeners after congener 187 were absent.

20	0.14	0.08
21		
22	1.33	1.38
23		0
24	0	
25	0.11	0.04
26	0.4	0.23
27	0.12	0.07
28	3.59	5.57
29	0	0
30		
31	5.07	5.47
32	0.88	0.93
33	2.23	2.21
34	0	0
35	0	
36		
37	0.79	0.95
38		
39		
40	1.13	0.92
41	0.77	0.75

42	1.67	1.79
43	0.3	0.19
44	6.31	5.09
45	1.09	0.91
46	0.47	0.39
47	1.49	2.41
48	1.66	1.54
49	4.12	4.17
50		
51	0.3	0.31
52	6.93	5.58
53	1.05	0.88
54		0
55	0.06	0.05
56	3.16	3.19
57	0.02	0.02
58		
59	0.37	0.23
60	1.85	2.67
61		
62		
63	0.17	0.19

64	3.01	3.32
65		
66	5.84	7.22
67	0.13	0.1
68		
69		
70	7.28	7.39
71	1.67	1.86
72	0.02	0.01
73		
74	3.14	4.67
75	0.08	0.08
76	0.13	0.13
77	0.41	0.52
78		
79		
80		
81	0.01	0.02
82	0.81	0.62
83	0.26	0.2
84	1.26	0.91
85	0.98	1.14

86	0.11	0.09
87	1.45	1.11
88	0.02	0.02
89	0.2	1.67
90		
91	0.63	0.56
92	0.38	0.25
93	0.04	0.03
94	0.03	0.02
95	1.96	1.43
96	0.08	0.06
97	1.22	0.97
98		
99	1.47	1.81
100		
101	2.22	1.89
102	0.19	0.17
103	0.02	0
104		
105	1.6	1.45
106		
107		

108		
109	0.18	0.13
110	2.97	2.55
111		
112		
113		
114	0.12	0.12
115	0.11	0.11
116		
117	0.09	0.1
118	2.29	2.35
119	0.06	0.06
120		
121		
122	0.06	0.05
123	0.07	0.08
124	0.1	0.07
125	0.04	0.03
126	0	0
127		
128	0.12	0.08
129	0.02	

130	0.04	0.01
131		
132	0.15	0.14
133		
134		0.01
135	0.04	0.04
136	0.05	0.06
137	0.03	0.02
138	0.38	0.41
139		
140		
141	0.07	0.09
142		
143		
144		0.01
145		
146	0.04	0.05
147		
148		
149	0.24	0.33
150		
151	0.04	0.08

152		
153	0.23	0.43
154		
155		
156	0.06	0.04
157	0	0
158	0.04	0.04
159		
160		
161		
162		
163	0.06	0.08
164	0.02	0.03
165		
166		
167	0	0
168		
169		
170		0.08
171		
172		
173		

174		0.08
175		
176		
177		0.03
178		
179		0.02
180	0.02	0.21
181		
182		
183		0.06
184		
185		
186		
187		0.09

Table B 6: Percent weight of Aroclor 1254

PCB No.	Aroclor 1254	Aroclor 1254
1	0.02	
2		
3		
4	0.02	0.06
5		

6	0	0.02
7		
8	0.05	0.13
9		
10		
11		
12		
13		
14		
15	0.01	0.03
16	0.02	0.09
17	0.02	0.08
18	0.08	0.25
19		
20		
21		
22	0.02	0.04
23		
24		
25		
26	0	0.03
27		

28	0.06	0.19
29		
30		
31	0.11	0.28
32	0.01	0.05
33	0.05	0.16
34		
35		
36		
37	0.01	0.07
38		
39		
40	0.15	0.12
41	0.02	0.01
42	0.09	0.15
43		
44	0.67	2.31
45	0.02	0.05
46		
47	0.07	0.14
48	0.05	0.12
49	0.26	1.1

50		
51		
52	0.83	5.38
53	0.04	0.12
54		
55		
56	1.7	0.55
57		
58		
59	0	0.02
60	0.95	0.18
61		
62		
63	0.07	0.02
64	0.36	0.59
65		
66	3.56	1.01
67	0	
68		
69		
70	6.83	3.49
71	0.11	0.15

72		
73		
74	2.19	0.84
75		
76	0.03	0.02
77	0.2	0.03
78		
79		
80		
81	0	
82	1.53	1.11
83	0.56	0.48
84	1.58	2.32
85	2.49	1.28
86	0.1	0.06
87	3.41	3.99
88		
89	0.11	0.09
90		
91	0.53	0.93
92	0.57	1.29
93		

94	0	0.02
95	1.84	6.25
96	0.01	0.04
97	2.78	2.62
98		
99	4.53	3.02
100		
101	5.49	8.02
102	0.09	0.15
103		0.03
104		
105	7.37	2.99
106		
107		
108		
109	0.78	0.37
110	8.42	9.29
111		
112		
113	0.01	
114	0.5	0.18
115	0.37	0.2

116		
117	0.19	0.23
118	13.59	7.35
119	0.12	0.08
120		
121		
122	0.25	0.1
123	0.32	0.15
124	0.47	0.29
125	0.03	0.02
126	0.02	0
127		
128	1.71	1.42
129	0.39	0.38
130	0.5	0.6
131	0.14	0.19
132	1.5	2.29
133		0.11
134	0.2	0.37
135	0.28	0.61
136	0.24	0.7
137	0.52	0.42

138	5.95	5.8
139	0.14	0.15
140		
141	0.69	0.98
142		
143		
144	0.12	0.24
145		
146	0.45	0.67
147	0.02	0.1
148		
149	1.82	3.65
150		
151	0.22	0.69
152		
153	3.29	3.77
154	0.02	0.04
155		
156	1.13	0.82
157	0.3	0.19
158	0.9	0.81
159		

160		
161		
162		
163	0.7	1.03
164	0.31	0.4
165		
166	0.05	0.05
167	0.35	0.27
168		
169		
170	0.35	0.52
171	0.08	0.14
172	0.03	0.07
173		
174	0.14	0.34
175		
176	0	0.04
177	0.08	0.2
178		0.03
179	0.02	0.1
180	0.42	0.67
181		

182		
183	0.09	0.18
184		
185		
186		
187	0.09	0.25
188		
189	0	0.01
190	0.05	0.07
191		
192		
193		0.03
194		0.01
195		
196		
197		
198		
199		0.01
200		
201		
202		
203		0.02

204		
205		
206	0.03	0.03
207		
208	0.01	0.01
209		

Table B 7: Percent weight of Aroclor 1260

PCB No.	Aroclor 1260	Aroclor 1260	Aroclor 1260
1	0.03	0.03	0.01
2			
3	0		
4	0.03	0.03	0
5	0		
6	0.01	0.01	
7			
8	0.06	0.06	0
9			
10			
11			
12			
13			

14			
15	0	0.02	
16	0.02	0.02	0
17	0.02	0.02	0
18	0.07	0.07	0
19		0	
20			
21			
22	0.02	0.02	0
23			
24			
25			
26	0	0	0
27			
28	0.05	0.05	0
29			
30			
31	0.06	0.05	0
32	0.01	0.01	0
33	0.04	0.04	0
34			
35			

36			
37	0.01	0	0
38			
39			
40	0	0	
41		0	
42	0	0	0
43			
44	0.04	0.04	0.03
45	0	0	
46	0		
47	0	0	0
48	0	0	
49	0.01	0.02	0.01
50			
51			
52	0.27	0.25	0.21
53	0	0	0
54			
55			
56	0.02	0.02	0
57			

58			
59			
60	0.04	0.04	0.03
61			
62			
63			
64	0.01	0.01	0
65			
66	0.03	0.03	0.01
67			
68			
69			
70	0.04	0.04	0.05
71	0	0	0
72			
73			
74	0.05	0.05	0.04
75			
76			
77			
78			
79			

80			
81			
82			
83	0	0	0
84	0.11	0.12	0.1
85	0	0	0.02
86			
87	0.44	0.42	0.36
88			
89			
90			
91	0	0	0.01
92	0.34	0.32	0.25
93			
94			
95	2.56	2.54	2.27
96			
97	0.1	0.09	0.08
98			
99	0.03	0.04	0.06
100			
101	3.23	3.18	2.99

102			
103			
104			
105	0.22	0.21	0.23
106			
107			
108			
109	0	0	0
110	1.38	1.36	1.25
111			
112			
113	0		
114	0		0
115			0
116			
117			
118	0.51	0.5	0.45
119			
120			
121			
122			
123			

124	0	0	0
125			
126			
127			
128	0.56	0.55	0.5
129	0.15	0.14	0.12
130	0.23	0.22	0.21
131	0.08	0.07	0.05
132	2.84	2.96	2.91
133	0.08	0.06	0.06
134	0.36	0.36	0.31
135	1.14	1.09	1.02
136	1.48	1.45	1.44
137	0.02	0.02	0.02
138	6.47	6.41	6.73
139			
140			
141	2.62	2.68	2.57
142			
143			
144	0.61	0.61	0.61
145			

146	1.17	1.16	1.11
147			
148			
149	8.74	8.78	8.73
150			
151	3.04	3.04	3.03
152			
153	9.09	9.17	9.91
154			
155			
156	0.53	0.54	0.5
157	0.02	0.02	0.02
158	0.57	0.58	0.6
159			
160			
161			
162			
163	2.41	2.43	2.44
164	0.72	0.7	0.66
165			
166			
167	0.2	0.2	0.17

168			
169			
170	3.97	4.01	4.36
171	1.09	1.08	1.17
172	0.71	0.7	0.69
173	0.11	0.09	0.09
174	4.92	4.96	4.99
175	0.18	0.18	0.17
176	0.59	0.58	0.59
177	2.54	2.52	2.64
178	0.86	0.84	0.79
179	2.05	2.04	1.99
180	10.9	11.2	12.05
181	0	0	0
182			
183	2.33	2.35	2.56
184			
185	0.56	0.56	0.53
186			
187	5.44	5.37	5.39
188			
189	0.08	0.11	0.12

190	0.82	0.8	0.85
191	0.16	0.17	0.17
192			
193	0.54	0.49	0.57
194	2.11	2.06	2.03
195	0.86	0.81	0.85
196	1.02	1.03	1.21
197	0.07	0.07	0.07
198	0.1	0.11	0.09
199	1.87	1.86	1.6
200	0.26	0.26	0.23
201	0.25	0.25	0.23
202	0.36	0.36	0.28
203	1.5	1.45	1.25
204			
205	0.1	0.1	0.1
206	0.66	0.61	0.31
207	0.05	0.06	0.03
208	0.16	0.16	0.06
209			

Table B 8: Percent weight of Aroclor 1262

PCB No.	Aroclor 1262	Aroclor 1262
1	0.02	0.03
2		
3		0.01
4	0.07	0.04
5		
6	0.03	0.02
7		
8	0.15	0.08
9		0
10		
11		
12		
13		
14		
15	0.3	0.02
16	0.07	0.03
17	0.07	0.03
18	0.19	0.1
19	0.02	
20		

21		
22	0.06	0.03
23		
24		
25	0	0
26	0.03	0.01
27	0	0
28	0.15	0.08
29		
30		
31	0.16	0.08
32	0.05	0.02
33	0.13	0.07
34		
35		
36		
37	0.04	0.02
38		
39		
40	0	0
41	0	0
42	0.03	0.01

43		
44	0.1	0.05
45	0	0
46		0
47	0.1	0
48	0.1	0
49	0.7	0.04
50		
51		
52	0.17	0.11
53	0	0
54		
55		
56	0.04	0.02
57		
58		
59	0	
60	0.02	0.02
61		
62		
63		
64	0.04	0.02

65	0	
66	0.08	0.05
67		
68		
69		
70	0.12	0.07
71	0.02	0
72		
73		
74	0.06	0.04
75		
76		
77		
78		
79		
80		
81		
82		
83	0	0
84	0.05	0.03
85	0.03	0.01
86		

87	0.11	0.11
88		
89		
90		
91	0.01	0
92	0.07	0.09
93		
94		
95	0.87	0.99
96		
97	0.06	0.03
98		
99	0.06	0.03
100		
101	1.03	1.23
102		
103		
104		
105	0.18	
106		
107		
108		

109	0	0
110	0.36	0.42
111		
112		
113		
114		
115		
116		
117		
118	0.17	0.14
119		
120		
121		
122		
123		
124	0	0
125		
126		
127		
128	0.17	0.2
129	0.03	0.04
130	0.03	0.06

131		
132	1.07	1.35
133	0.03	0.05
134	0.11	0.14
135	0.67	0.65
136	1.02	0.99
137	0.01	0
138	2.33	3.14
139		
140		
141	1.63	1.69
142		
143		
144	0.41	0.41
145		
146	0.57	0.61
147		
148		
149	6.36	6.44
150		
151	3.14	2.81
152		

153	6.78	7.42
154		
155		
156	0.14	0.18
157	0	0
158	0.18	0.21
159		
160		
161		
162		
163	1.5	1.55
164	0.23	0.3
165		
166		
167	0.02	0.05
168		
169		
170	3.05	3.47
171	0.85	0.89
172	0.63	0.62
173	0.03	0.05
174	6.56	6.1

175	0.19	0.16
176	0.73	0.66
177	2.82	2.73
178	1.31	1.1
179	3.64	3.01
180	13.72	14.53
181		
182		
183	2.89	2.86
184		
185	0.93	0.81
186		
187	9.55	8.76
188		
189	0.03	0.04
190	0.74	0.77
191	0.13	0.13
192		
193	0.67	0.65
194	3.79	4.32
195	1.39	1.46
196	2.41	2.12

197	0.14	0.13
198	0.24	0.22
199	4.91	4.57
200	0.69	0.6
201	0.66	0.58
202	1.2	0.96
203	4.11	4.37
204		
205	0.16	0.18
206	1.19	1.33
207	0.17	0.18
208	0.29	0.26
209		