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An Assessment of Polychlorinated Biphenyl Contamination in Fish from the Inland and Great Lakes of Michigan

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AN ASSESSMENT OF POLYCHLORINATED BIPHENYL CONTAMINATION IN
FISH FROM THE INLAND AND GREAT LAKES OF MICHIGAN

By

Emily C. Sokol

A THESIS

Submitted in partial fulfillment of the requirements for the degree of

MASTER OF SCIENCE

In Environmental Engineering

MICHIGAN TECHNOLOGICAL UNIVERSITY

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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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PREFACE

This dissertation is original, unpublished work. I, Emily Sokol, collected all data and conducted all analyses. My advisors, Dr. Urban and Dr. Perlinger, made corrections. Data summarized in Tables A.4 through A.8 were summarized by Kaitlin Reinl.

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ABSTRACT

Fish within the Great Lakes region of North America are an invaluable resource with economic and cultural significance. While these fish are vital, they contain chemical pollutants that are hazardous to human health. One such man-made group of chemicals, polychlorinated biphenyl compounds (PCBs), continue to be a problem long after the ban on production (1979).

The objective of this research thesis was to assess PCB contamination in fish within the Great Lakes Region. This objective was completed by determining the sources of PCB contamination, defining the ecosystem characteristics that significantly affect fish contamination, predicting when it will be safe to consume a desired amount of fish, identifying which water bodies have higher contamination, and determining if PCBs have significantly declined since the early 1990s.

The assessment of inland lake contamination revealed that lakes impacted by point sources of PCBs can be differentiated from lakes whose only source of PCBs is atmospheric. Principal Component Analysis of PCB concentrations in common fish species revealed that lakes impacted by local, point sources of PCBs had congener distributions in fish dominated by heavier congeners. Similar results were obtained for sites in the Great Lakes; PCBs in Lake Superior fish were found to be derived primarily from atmospheric deposition while the lower lakes had significant contributions from local sources.

It was discovered that deeper inland lakes had higher levels of fish contamination based on multiple linear regression analysis where mean depth was the best predictor of total PCB concentration in fish ($r^2=0.73$). The importance of developed watersheds to Great Lakes fish contamination was revealed using the same form of analysis. Lakes with lower primary production tended to have higher PCB contamination.

The use of a lake model to predict dissolved PCB concentrations from atmospheric concentrations and the EPA's Bioaccumulation and Aquatic System Simulator (BASS) to model food web dynamics predicted that if atmospheric concentrations continue to decline at the same rate, fish in Michigan's inland lakes will be safe to consume at a rate of 2 meals per day in roughly 20 years. For most sites in the Great Lakes, there has been a significant decline in PCB contamination since the early 1990s. However, the Great Lakes have a higher level of PCB contamination compared to inland Michigan Lakes.

This thesis research provides the public and scientific community an explanation of the trends in PCB contamination in the Great Lakes Region. Safer fish consumption habits according to PCB contamination are now possible without prohibiting the use of this resource. Modeling tools revealed what can be improved upon to adequately predict chemical accumulation in an aquatic ecosystem. The research provides a better and more comprehensive method to assess chemical contamination in fish so that the safety of humans and the environment can be secured for the future.

CHAPTER 1: LITERATURE REVIEW

1.1 Introduction

In order to complete an assessment of PCB contamination in the Great Lakes region, an understanding of the state of knowledge on PCB bioaccumulation is required. Persistent pollutant concentrations in a given ecosystem are affected by various physical and chemical characteristics. PCBs have an added complexity due to there being 209 PCB congeners, or unique chemical structures, in existence, where some are stable in the environment. Several studies across North America and Europe have attempted to identify the lake, watershed and food web characteristics that either adequately predict or have a significant effect on chemical accumulation in fish.

The health risks associated with hazardous pollutants are complex because of the many and various chemicals that bioaccumulate and the fact that each chemical affects human and animal health differently. Health risks associated with PCBs include developmental effects, immunological effects, reproductive effects and cancer. Examples of these include neonatal deficits in behavior, allergies, and rheumatoid arthritis (MDCH, 2012).

While this study focused on PCB accumulation, research has been conducted on a variety of hazardous chemicals (i.e. mercury, trace metals, PAHs, PBDEs). Some of these hazardous chemicals have properties similar to PCBs or act similarly in the environment (e.g. the ability to bioaccumulate, store easily in fat and/or resist biodegradation). Therefore, to assess the full range of potential environmental factors

affecting PCB accumulation, this review discusses research on any hazardous chemical bioaccumulation and corresponding significant environmental factors that may also affect PCBs. Modeling efforts to explain the movement of PCBs in water and the aquatic food web and contamination specifically in the Great Lakes Region are also discussed. The complexity of bioaccumulation models has increased as research has revealed the relative importance of environmental factors. It was proposed to determine which factors were deemed important from the literature, and to identify gaps that remain in our understanding of PCB bioaccumulation in the Great Lakes region. The environmental factors that are considered pertinent in the literature include: 1) the source of contamination, 2) physical and chemical lake and watershed characteristics, 3) global distribution, and 4) fish and food web characteristics.

1.2 Modeling Efforts

Since the 1980s, models have been developed and revised to accurately predict PCB concentrations in water, sediment and biota. There have been several lake water models developed for specific Great Lakes because PCB accumulation depends on the chemical and physical characteristics unique to a particular lake. Most models were designed for Lakes Superior, Michigan or Ontario and were focused on either air-water exchange or whole lake modeling that included sedimentation and resuspension (Jeremiason et al., 1994; Baker and Eisenreich, 1990; Hornbuckle et al., 1994; Mackay 1989; Mackay and Diamond, 1989; Rowe, 2009). These models have revealed that, due to sedimentation and resuspension, the internal cycling of PCBs

causes the recovery time to take longer for lakes than for the atmosphere. Over time, dead organisms and particles settle to the bottom of a lake, taking PCBs with them. However, with annual or multiannual turnovers, particles and PCBs can return to the water column from the sediment, and bioaccumulate once again. Thus, the major fraction of pollutants that settle out each year are due to this internal cycling and not to new inputs due to atmospheric loading (Larsson et al., 1998). In addition, the longer the hydraulic residence time, the longer the contaminant will remain in the lake.

Food web bioaccumulation and fish bioenergetics models have been developed in an attempt to account for all significant biota characteristics that affect contaminant accumulation. The level of complexity of these models continues to increase. The basis of the models has been either empirical or mechanistic, with the latter being much more complex and accurate. These models involve the combination of accumulation and loss of contaminants at each level of the food chain. Fish can gain or lose contaminants through respiration, consumption, metabolism, and excretion. Fugacity- based models include FISH from the Canadian Environmental Modelling Centre and FOODWEB by Campfens and Mackay (1997) (Mackay and Fraser, 2000). These models focus on individual fish, while more complex models have the ability to assess population dynamics (e.g., the United State Environmental Protection Agency's (U.S. EPA's) Bioaccumulation and Aquatic System Simulator (BASS)). The U.S. EPA has developed several models, including the Acute-to Chronic Estimation model (ACE), AQUATOX and BASS, to assess the exposure and

toxicity of contaminants (US EPA, 2014). For this assessment, EPA's BASS was used to predict the bioaccumulation of PCBs in fish in inland lakes. EPA's BASS uses three differential equations to determine the fate of pollutants, such as PCBs.

$$\frac{dB_f}{dt} = J_g + J_i - J_{bt} \quad [1.1]$$

$$\frac{dW_d}{dt} = F_d - E_d - R - EX - SDA \quad [1.2]$$

$$\frac{dN}{dt} = -EM - NM - PM \quad [1.3]$$

where B_f is the chemical body burden ($\mu\text{g}/\text{fish}$), W_d is the dry weight ($\text{g (dry wt)}/\text{fish}$) and N is the cohort population density. J is the net chemical exchange across gills (g), intestines from food (i) and chemical transformation rate (bt). The gains or losses of the chemical are from fish feeding (F_d), egestion (E_d), respiration (R), excretion (EX) and specific dynamic action (SDA). Population density is affected by the rate of emigration/dispersal (EM), non-predatory mortality (NM) and predatory mortality (PM). The combination of these three differential equations provides a detailed dynamic prediction of what occurs to a pollutant throughout the food web using bioaccumulation factors to explain the rate of chemical uptake in lower trophic organisms.

Another set of modeling software used widely is Ecopath with Ecosim. Used and continuously developed for almost 20 years, this software system has been widely used to assess marine food webs and applied to policies for fishery

communities. It uses the following two equations as the basis for the model (UBC Fisheries Centre, 2012):

$$\textit{Production} = \textit{catch} + \textit{predation} + \textit{net migration} + \textit{biomass} + \textit{other mortality} \quad [1.4]$$

$$\textit{Consumption} = \textit{production} + \textit{respiration} + \textit{unassimilated food} \quad [1.5]$$

The model uses biomass pools, which are similar to the cohorts in BASS, and links them to develop the entire food web. Some additions to the model include Ecospace and Ecotrace. Ecospace is a grid version of the program and has been used for protected areas in marine environments where detailed dimensions of food web dynamics are needed (UBC Fisheries Centre, 2012). Ecotrace is an addition that tracks contaminant movement (Razinkovas, 2007). This program has been used to study the movements of both mercury and PCBs (Booth and Dirk Zeller, 2005; Coombs, 2004).

1.3 Source of Contamination

To determine the relative significance of PCB sources, studies have turned to statistical analyses, including regression analyses to predict contamination levels, and component analyses to separate datasets based on variance. While all lakes are contaminated by atmospheric deposition, point sources can exist within a watershed, increasing the amount of contamination of the watershed. In addition, local contamination may have a different PCB congener distribution as these sites tend to

have heavier congeners that are less mobile in the environment. These point sources typically originate from sites where PCBs were improperly disposed of (i.e. contaminated sediment). Macdonald et al. (1991) used discriminant analysis to prove that one Ontario lake with known local sources had a significantly different ($p < 0.05$) PCB congener distribution in biota compared to other lakes in the region. Another study analyzed sediment cores by using Principal Component Analysis (PCA) and determined that certain locations in the Milwaukee Harbor Estuaries potentially had historical local sources (Rachdawong et al., 1997). Monosson et al. (2003) concluded that congener distributions in fish, compared using PCA and general linear model (GLM) profile analysis, can provide evidence of differences in sources along the Hudson River in the state of New York. The distribution of the prominent PCB congeners found in the environment could reveal that some inland lakes included in this study have unknown point sources.

Another form of factor analysis used to identify PCB contamination sources is positive matrix factorization (PMF). It has been successful in finding sources of PCB in sediment cores (Du et al., 2008; Bzdusek et al., 2006; Soonthornnonda et al., 2011). PCBs and particles settle out of the water column, forming distinct layers in sediment cores. These cores explain how the use of PCBs near the water body changed over time. Bzdusek et al. (2006) analyzed cores from a river that feeds into Lake Michigan. The two factors determined significant from PMF were specific Aroclor mixtures and a matrix that represented the dechlorination of an Aroclor mixture (Bzdusek et al., 2006). PMF was also used on sediment cores from four of

the Great Lakes to determine that 3 or 4 significant factors explained the variance among the samples. The factors were heavily influenced by specific Aroclor mixtures and some dechlorination. The analysis identified where and when PCB mixtures were used near the sites (Soonthornnonda et al., 2011). PMF is ideal for sediment core analyses; years of sedimentation can be broken down to identify the sources of PCBs over time using this matrix form of factor analysis (Soonthornnonda et al., 2011).

1.4 Lake and Watershed Characteristics

The loss of PCBs via volatilization can vary in magnitude, where lakes with larger surface areas can experience greater loss as well as deposition of PCBs. For most of the year in Lake Superior, volatilization dominates the loss of PCBs due to its larger surface area and climate (Hornbuckle et al., 1994; Baker and Eisenreich, 1990; Rowe et al., 2009). PCB water concentrations have declined since the 1980s, but the decline has slowed. Pearson et al. (1996) determined that the volatilization of PCBs from Lake Michigan has followed first order kinetics with a half-life of about 9 years. Lake Superior was also found to follow the same rate loss (Jeremiason et al., 1994). Due to this first-order rate tendency, the absolute magnitude of the annual loss is slowing and significant decreases in contaminant concentrations will take much longer than in the 1980s.

Another discussion in the literature involves the significance of watershed inputs to a lake system. Many hazardous chemicals undergo atmospheric deposition and enter a lake via runoff. However, the amount of chemicals entering a lake varies based on the land use in the watershed and pollutant chemical characteristics.

Jeremiason et al. (1991) performed a mass balance on two remote Canadian study lakes of varying productivity, finding that 60% of PCB inputs to the eutrophic lake were from the watershed during stratification. However, the overall propagated error for the mass balance was 90% over that time period, indicating that the watershed input could not be distinguished from zero. An assessment of the Delaware River watershed determined a pass-through efficiency of about 1% based on watersheds with no point sources of PCBs. It was concluded that this was likely due to the binding of PCBs to organic matter in the soil (Totten et al., 2006). A nearby study compared the watersheds of Chesapeake Bay and determined that the amount of commercial land within a watershed could explain 99% of the variance in PCB concentration in white perch; the greater the amount of developed land, the higher the total PCB contamination (King et al., 2004). According to the regression results of the study, the fraction of PCBs that remained in the fish when no developed land existed (the y-intercept) was -8.9 ng/g wet weight. This negative value reflects the significance of developed land to the model. More impervious surfaces and greater runoff rates of developed land were concluded to be the cause of this correlation (King et al., 2004). A study involving remote lakes in Ontario found 10% of total PCB loading to the lakes was from the watershed (Macdonald et al., 1991). Paul et al. (2002) conducted a similar analysis of Chesapeake Bay and other watersheds in the Northeastern United States; sediment contamination of metals, organics and polycyclic aromatic hydrocarbons (PAHs) increased as urban area increased in a given watershed. The y-intercept for the model was not provided (Paul et al., 2002).

Another Chesapeake Bay study had a similar conclusion on sediment contamination where the urban contribution of metals is from point sources. Atmospheric inputs were not considered (Comeleo et al., 1996). Analyses of Yukon lake sediments in Canada found that PCB concentrations were higher near more populated areas and PCB fluxes to sediments were lower in remote lakes. Glaciers likely had an effect on increasing the watershed inputs to small lakes at higher elevations (Rawn et al., 2001). In this assessment, the accumulation of PCBs was evaluated for Michigan's Upper Peninsula Inland lakes where much of the land is forested. It seems that, while study results vary, the magnitude of watershed PCB inputs to the lakes in this assessment may be assumed minimal ($\leq 10\%$) due to the undeveloped environment of the majority of watershed areas.

Studies have tried to determine the significance of trophic state on PCB contamination in lakes and biota by focusing on the extremes of lake productivity—eutrophic (highly productive) and oligotrophic (poorly productive). The lake productivity can have a positive effect on the amount of dissolved or particulate-bound PCBs. Regardless of the level of productivity in a lake, the dissolved form of a chemical is readily available for uptake at any level in a food chain. An interesting finding in one Canadian study was the discovery that the PCB congener distribution was maintained among lakes with varying trophic levels and sizes. This was attributed to larger lakes having greater deposition rates, but also larger losses due to sedimentation and volatilization (Macdonald et al., 1991). In a study looking at polybrominated diphenyl ethers (PBDEs) in biota (i.e. crab, fish, and porpoise) along

the western coast of Canada, the authors applied PCA and found that this organic pollutant had similar congener distributions across the large study area even though sampling locations varied greatly in characteristics (Ikonomou et al., 2002). This study revealed that water bodies with a wide variety of physical characteristics may not affect organic chemical accumulation in biota higher in the food chain.

It is theorized that more productive lakes lead to lower PCB concentrations in biota because increased particle deposition tends to decrease water concentrations as more PCBs sorb and also more biomass leads to dilution at the base of the food web. If the base of the food web contains lower PCB concentrations, then the effects of biomagnification would be less severe. Dachs et al. (2000) developed a model to explain the effects of eutrophication on the lake ecosystem. Air-water exchange, not settling fluxes, was determined to be most significant for phytoplankton concentrations, and increased with increasing phytoplankton biomass (Dachs et al., 2000).

There are, however, contrasting conclusions in the literature about the significance of lake trophic state on PCB concentrations in the lake and biota. A study comparing 19 Swedish lakes with no known point sources of contamination determined that sediment PCB concentrations were greater in eutrophic lakes than oligotrophic lakes. This was explained by the increased rate of organic matter-associated PCB settling in highly productive lakes. The total concentration of PCBs in each analyzed portion of the lakes (phytoplankton, zooplankton and fish) did not vary greatly among lake types, excluding the dissolved water concentration which

was 10% higher in oligotrophic lakes (Berglund et al., 2001a). An earlier study that compared two Canadian lakes that varied greatly in productivity also concluded that the settling of PCBs was greater in the eutrophic lake. In contrast to the aforementioned study, there was little difference in the dissolved PCB water concentration (the phase most readily absorbed by biota (Jeremiason et al., 1999)). A later study used the same Canadian lakes to study the addition of northern pike, a top predator, to the food chain. While the addition shifted the diet of lower trophic level organisms, the PCB concentrations did not vary greatly from original levels. Contaminant levels were lower in the eutrophic lake in all of the biota sampled (Kidd et al., 1999).

There have been many studies confirming the importance of lake trophic state on another hazardous pollutant, mercury. Lavoie et al. (2013) concluded that the concentration of mercury in aquatic food webs is highest in cold lakes with low productivity. There is less plankton biomass at the base of the food chain in a pristine lake, causing higher contaminant concentrations in organisms compared to plankton in eutrophic systems. Several other studies drew the same conclusion using similar techniques with stable isotopes for species trophic position determination and linear regression analysis to relate lake productivity to contamination (e.g. Kamman et al., 2003; Clayden et al., 2013; Chen et al., 2005; Driscoll et al., 2012).

A study including eight lakes ranging in surface area from 0.2 to 4800 km² in Ontario determined that these lakes did not have significantly different concentrations of dissolved PCBs even though lake sizes were very different and productivity varied

(Paterson et al., 1998). Similar conclusions to Berglund et al. (2001a) about settling rates were made by using a model developed for air-water exchange of PCBs in Lake Ontario. This study also noted an increased amount of deposition of PCBs into the eutrophic lake simulation due to higher settling rates (Dachs et al., 2000). Jeremiason et al. (1999) found that during times of stratification, there was net volatilization occurring from both lake productivity types while more volatilization occurred in the oligotrophic lake. A study using PCA and regression analysis for 33 lakes in Southern Ontario concluded that there were higher PCB concentrations in phytoplankton from oligotrophic lakes (Taylor et al., 1991). While there are more phytoplankton and microzooplankton per area in eutrophic lakes, the organisms have a lower lipid content, which reduces the amount of lipophilic PCBs being stored (Berglund et al., 2000a and Berglund et al., 2001b). Berglund et al. (2001b) did not see this trend found in phytoplankton reflected higher up in the food web. In contrast, a study of 61 southern Scandinavian lakes found lower PCB contamination in Northern Pike in more productive lakes. However, it was concluded that this was likely due to an increased growth rate of this species in the eutrophic lakes, not due to lower trophic level concentrations. The faster the growth rate, the faster the excretion of PCBs from an organism as well as the greater the growth dilution (Larsson et al., 1992). These studies point towards the conclusion that more productive lakes can reduce the amount of PCB exposure to biota, but the significance of this reduction varies. The trophic state of a lake may have an indirect effect on the level of contamination in higher trophic level organisms, but results fluctuate due to species

characteristics and lake location as dissolved water concentrations may not differ significantly.

Linear regression analysis is a statistical technique that has been used on a number of chemical pollutants to determine if there is a significant relationship between the contamination and any physical characteristics of the lake or watershed. McMurty et al. (1989) found a correlation using this technique between mercury in fish tissue and lake trophic indicators, lake area and watershed area in Ontario. The most significant correlation was with dissolved organic carbon, which increased with lake productivity ($r^2=0.60$, $p<0.05$). Multiple linear regression was also used with PCA to determine similar results for mercury contamination in biota in Nova Scotia (Clayden et al., 2013). The concentrations of methyl mercury in organisms closer to the base of the food web were correlated most strongly with pH, metal presence and lake morphometry (R^2 adjusted=0.348-0.730, $p<0.001$). Total concentrations of mercury in yellow perch were best predicted by wetland area (R^2 adjusted =0.020, $p<0.001$). This was not a surprise due to the ability of wetlands to convert mercury into the more toxic and bioavailable form. It was concluded that physical lake characteristics can play a large role in methyl mercury accumulation (Clayden et al., 2013).

Another physical lake characteristic that could affect PCB exposure is the amount of littoral zone in a lake. This could have a significant effect on feeding habits and therefore have an effect on the exposure of top predator fish. Pelagic feeding is associated with a longer food web because top predators consume more pelagic fish

than littoral organisms. Longer food webs lead to more bioaccumulation. Guildford et al. (2008) concluded that lake trout, which only feed in the pelagic zones, tend to have higher concentrations of PCBs because of the limited availability of littoral prey. Another study that sampled five of the same lakes, among others, found that polybrominated diphenyl ether (PBDE), another organic contaminant, increased in concentration in lake trout with increased benthic feeding (Gewurtz et al., 2011b). For mercury, Kidd et al. (2012) found inconsistent links between the level of contamination and benthic or pelagic feeding for lake trout. A study involving three river fish species found that detrital feeding increased the level of PCB contamination (Lopes et al., 2011). There may be a linkage between PCB concentrations in fish and littoral feeding habits, but many factors, including lake trophic state and food availability, can play a role in what fish consume and their level of exposure. In addition, fish of the same species in a given water body do not always have the same feeding habits (Vander Zanden et al., 2000).

1.5 Global Distribution

While production of PCBs was banned in the late 1970s due to the discovery of harmful health effects, the movement of these organic contaminants are still being studied today. All lakes throughout the world are affected by atmospheric deposition of PCBs. PCBs often undergo deposition and revolatilization multiple times, moving farther from the original source of production, use or contamination. This movement into the air and back to the earth's surface has been coined the grasshopper effect (Gouin et al., 2004). Light, or lower-chlorinated, PCBs can revolatilize more easily

due to their lighter weight, and they have been found to move to higher latitudes due to cooler air temperatures for deposition (Meijer et al., 2002). With warmer climates making volatilization easier, there is a chance that PCBs could be re-emitted and transported even farther north at greater concentrations in the future (Schmidt 2010).

Due to the grasshopper effect, there is a tendency for PCBs to move into higher latitudes and redeposit in lake ecosystems. Using linear regression, Houde et al.(2008) determined that there was a weak influence of latitude or longitude on lake trout PCB trophic magnification factors between Canadian lakes and lakes in the northeastern United States ($R^2=0.238$, $p<0.05$). Another study on mercury bioaccumulation was the first to show a significant positive relationship between the contaminant and latitude, likely because of temperature and lake trophic state differences across the large study region that included 205 aquatic food webs (Lavoie et al., 2013). Guildford et al. (2008) found lake area and latitude accounted for 73% of the variance in total PCB concentration in lake trout in 23 lakes in Canada and the eastern US. It would seem that in order to determine if latitude is significant, there needs to be a study completed at a larger scale (i.e., across continents) for PCB accumulation.

1.6 Fish and Food Web Characteristics

Similar to water concentrations, PCB concentrations in fish have been declining and can be explained using first order rate modeling. In a comparison of Great Lakes contamination from 1970 to 1998, the first order half-life of total PCBs in top predators ranged from 2.3 to 12.4 years ($R^2=0.61$ to 0.96 , $p<0.05$) (Hickey et

al., 2006). Lake Huron saw a slight increase in PCB contamination due to an increase in lipid content in lake trout from 1995 to 1998. There was a similar occurrence in Lake Superior when lake trout diet switched to lake herring in the early 1990s, but Lake Superior still has the lowest level of PCB contamination in fish among the Great Lakes (Hickey et al., 2006). Carlson and Swackhamer (2006) summarized the results of the U.S. Great Lakes Fish Monitoring Program (GLFMP), but only with samples from 1999 and 2000, which yielded no significant time trend of decline. However, the study did find that sites located in the same lake had significantly different PCB fish concentrations, suggesting the different diets among the same fish species lead to different PCB concentrations. Later, Carlson et al. (2010) summarized 34 years of monitoring efforts by the GLFMP. A significant decline in PCBs in lake trout and walleye has occurred since the 1970s. However, the rate of decline is slowing as concentrations have been significantly reduced (Carlson et al., 2006).

The differences in the food web may affect PCB bioaccumulation, but there has been debate over whether lipid content, which is affected by food web characteristics, is more important. The higher the lipid content, the more PCBs can be stored more easily in fish because this organic pollutant is lipophilic. Longer food webs result in fattier top predators because of their tendency to consume larger, fattier fish rather than the smaller organisms found in shorter food webs. Rasmussen et al. (1990) found that lake trout contamination can be explained by differences in the food chain, but that PCB content also increased with increasing lipid content. Trophic position can be affected by the food chain; the longer the food chain, the higher the

trophic position of top predators. Many studies have used stable isotopes to determine the trophic position of fish species and used different statistical methods to identify the factors that predict the level of contamination (Vander Zanden and Rasmussen, 1996; Borgå et al., 2004; McIntyre and Beauchamp, 2007). Some studies determined that trophic position was only significant in larger fish, using nitrogen isotope analysis to determine the exact trophic level of fish samples. Olsson et al. (2000) used a regression analysis to determine that perch in a Latvian lake only had strong correlations between increasing PCB concentrations and increasing trophic position if the samples were longer than 20 cm in their regression analysis. A later Norwegian study of multiple fish species, which used PCA and linear regression to expose trends, reached a similar conclusion. PCA divided fish species based on the measured tissue congener distribution into higher and lower trophic positions. This study revealed a trend that higher chlorinated PCB congeners increased in concentration with increasing trophic level using linear regression on the PCA components (Ruus et al., 2002). It was concluded in both studies that the significance of trophic level was an indication of contrasting characteristics of small and large fish of the same species. Smaller fish have a larger gill surface area to body weight ratio than larger fish which could increase their exposure from respiration rather than diet. This ratio may also be the cause of an increased loss of PCBs as well as a loss through excretion, causing the lower PCB concentrations. Metabolic differences could also be a factor with how quickly the organic contaminant is excreted (Ruus et al., 2002). The higher fat content, higher consumption of larger fish and smaller gill surface area to body

weight ratio of larger fish for a given species is the likely cause of trophic position being a more important factor (Olsson et al., 2000).

Other studies have shown contrasting views to Olsson et al. (2000) and Ruus et al. (2002). Using nitrogen isotope ratios to determine trophic position and backwards multiple linear regression, McIntyre et al. (2007) determined that age or length was more significant than trophic position for predicting PCB concentrations in a food web studied in the state of Washington ($r^2=0.419-0.829$, $p<0.002$). In addition, it was concluded that lipids were not significant in bioaccumulation according to a Pearson correlation between lipid content and total PCB concentrations for multiple food web species (McIntyre et al., 2007). It was recommended by Gewurtz et al. (2011a) to sample the larger size range of upper trophic level fish to find strong correlations between PCB concentration and length. A study on three lakes in the Yukon Territory used nitrogen isotope analysis and multiple linear regression to determine that the importance of trophic position depended on the fish species. Northern pike contamination was best explained by a combination of lipid content and trophic position ($r^2=0.81$, $p<0.01$) while burbot and lake trout concentrations were predicted by weight and trophic position ($r^2=0.87$ and 0.66 , respectively, $p<0.01$). Correlations with trophic position were only significant for lake trout when data were combined across lakes, but not for individual lake data (Kidd et al., 1998). Another study found similar complications for lake trout in four Arctic lakes in that trophic position could not explain PCB concentration differences due to nitrogen isotope inconsistencies. This points towards varying dietary

preferences in any given lake (Allen-Gil et al., 1997). Vander Zanden et al. (1996) designed food web classes in a trophic position model to represent the range of trophic positions for lake trout in an attempt to create a trophic structure without discrete trophic levels assigned. This model also accounted for omnivory and explained 85% of the variability between the lake types. In the same year, another study used ANCOVA and linear regression on lake trout in inland Ontario lakes and three of the Great Lakes to assess the interaction between food web structure, trophic position and lipid content. Regression analysis proved that lipid content could predict PCB contamination levels in all six lakes ($r^2=0.73$, $p<0.00001$). The longer the food web, the greater amount of lipid content in the species as well. Their conclusions posed the idea of an interplay between food web structures and lipid content which in turn similarly affected the accumulation of PCBs (Bentzen et al., 1996).

With the variability in lipid content dependent on the species, many other fish characteristics may affect contamination levels. In a comparison of rainbow trout and lake trout in Lake Michigan, Madenjian et al. (1994) determined that the longer life span and slower growth rate of lake trout led to higher PCB concentrations. Rainbow trout can reach the same size as lake trout in significantly less time, meaning the species has had less time to accumulate organic contaminants. In addition, the diet of rainbow trout was more diverse than that of lake trout, causing higher variability in dietary exposure compared to lake trout (Madenjian et al., 1994). Coho salmon, another top predator species in the Great Lakes, is more sensitive to changes in dissolved water concentrations because of its faster growth rate and metabolism.

While lake trout contaminant levels are built up over several years of exposure, coho salmon contamination reflects about 1 or 2 years of exposure (Pearson et al., 1996). It seems that the significance of food chain differences and other food web and fish characteristics on contaminant bioaccumulation is dependent on multiple factors including individual species physiology (i.e. lipid content, respiration rate, metabolism, and life span), food availability and dietary preference.

The relationship between level of contamination and lipid content of fish also becomes important when determining if the sex of the fish has significant effects on organic contaminant accumulation. The lipid content and weight of male and female fish can fluctuate before, during and after spawning. However, regression results for Gewurtz et al. (2011a) in Ontario found that walleye was the only species with a strong difference between sexes and PCB contamination while several other species were included in the study. Male walleye had higher fat content than their female counterparts. Fish length was determined to be a better predictor than lipid content for the highest trophic level predators, since size—not sex—is the cause of higher lipid content for the species as a whole (Gewurtz et al., 2011a). Madenjian et al. (2010) determined that male lake trout had a higher PCB content than females in Lake Ontario. The release of gametes was not the cause for this difference and their bioenergetics model could not explain the differences measured in the field. More research into food preferences and bioenergetics during spawning may be needed to understand the true effects of sex on PCB bioaccumulation (Madenjian et al., 2010). Upon further review of the literature on the effects of sex, Madenjian (2011)

concluded that one of three factors likely explained the differences between male and female contamination. Loss of PCBs during spawning and differences in habitat could only explain differences in few species and was not always significant. Differences in gross growth efficiency was concluded to affect all species to some extent and was the most significant factor for some. Males of a given species tend to need more energy to reach the same size and are more active than females. This review also recommended that bioenergetics models need to take these differences into account for more accurate modeling (Madenjian, 2011).

1.7 Great Lakes Region Contamination

Studies that compare inland lake contamination to the Great Lakes are uncommon. Typically, only the Great Lakes are studied because of their high priority in monitoring programs. However, for many people, especially indigenous people, all water bodies are important as a food source and hold cultural significance. Due to this varying level of contamination among species and pollutants, it is difficult to say whether fish from either the Great Lakes or inland lakes are safer. In the case of PCBs, the role of food web differences and its effect on lipid content are important. The Great Lakes tend to have much longer food webs than inland water bodies, which has been found to significantly affect lipid content and PCB concentrations, while the loading rates of contaminants are also higher for the Great Lakes (Bentzen et al. 1996). Bentzen et al. (1996) compared lake trout from inland Ontario lakes to the contamination in Lakes Superior, Huron and Ontario. It was determined that inland lake contamination was on average lower than that of the Great Lakes in the 1980s.

However, the contaminant levels in Lake Superior were significantly lower than the other Great Lakes as well as a portion of the inland lakes. The lower PCB contaminant levels were attributed to the colder Lake Superior water slowing fish metabolism (Bentzen et al., 1996). However, the opposite was observed for concentrations of methyl-mercury in fish in Lakes Michigan, Huron and inland water bodies (Carlson and Swachhamer, 2006). The different tendencies of PCBs and mercury accumulation in the water bodies were attributed to the significance of different lake and food web characteristics on bioaccumulation. In addition, toxaphene concentrations are highest in Lake Superior compared to the other Great Lakes (Carlson and Swachhamer, 2006). Toxaphene concentrations in lake trout from inland Ontario lakes were also lower than that of Lake Superior (Muir et al., 2004).

The discrepancies among inland water bodies and Great Lake contamination was assessed in more detail by Kannan et al. (2000). Siskiwit Lake, located on an island in Lake Superior where no point sources (i.e., a large quantity of PCBs originating from one small area) exist, was reported to have nine-fold higher levels of PCBs in lake trout than Lake Superior in the late 1990s if concentrations were lipid-normalized (Kannan et al., 2000). Local sources tend to have highly significant impacts on river systems. Of the 13 sites sampled throughout the State of Michigan and the Great Lakes, Kannan et al. (2000) found that the Detroit River, where local sources leach PCBs into the river, had the highest concentrations of PCBs.

An element that adds to the complexity of comparing lakes is the species present. Not all inland lakes contain the large, cold water fish species that the Great

Lakes have in abundance. In addition, different species accumulate PCBs differently because of unique traits (e.g. metabolism and growth rate). For example, Gerstenberger and Dellinger (2002) found that walleye were typically less contaminated with organic chemicals than lake trout and whitefish in the upper Great Lakes region.

1.8 Conclusion

Upon review of the literature related to chemical accumulation in fish, many questions are unanswered for the Great Lakes Region in terms of PCB contamination. Differentiating sources of PCBs to the region and linking important watershed and/or lake characteristics to contamination trends provides focus to remediation plans and healthier fishing/fish consumption habits. While the sources of contamination have been assessed in other regions, it has not been done so extensively for the Great Lakes Region. The importance of ecosystem characteristics has varied among studies. Few studies have shown unequivocally the effects of lake trophic state and fish diets on PCB accumulation. Understanding what food web and fish characteristics hold significance for PCB accumulation could explain why fish species have high variability in contaminant levels within the region and neighboring inland lakes. Applying modeling scenarios to evaluate some of these topics could provide more insight than could sampling efforts for the region.

The complexity of hazardous chemicals and their environmental processing has continued to challenge the scientific community. Continued study of such pollutants including PCBs is necessary for the protection of the environment and

human health. The development of models can do more for our understanding than sampling and analysis of contaminants alone. With continued efforts, our ability to combat hazardous chemicals will yield better protection of future generations.

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CHAPTER 2: INLAND LAKES ASSESSMENT

2.1 Introduction

An assessment of PCB contamination in Michigan's Upper Peninsula inland lakes was desired to determine: 1) if there is a distinct difference in PCB congener distribution in fish affected by different sources of contamination, 2) which lake ecosystem characteristics affect the level of PCB contamination in fish, 3) which lakes are most susceptible to PCB contamination and 4) when safely consuming a desired amount of fish could be possible. These objectives were completed by using statistical analyses on measured fish data provided by the Michigan Department of Environmental Quality and modeling tools.

Lakes can be impacted by two sources of PCBs: local, industrial contamination and atmospheric deposition. As considered here, industrial contamination is a point source of PCBs to the local watershed or lake due to negligent disposal of PCBs (i.e., contaminated soil and groundwater). In contrast, atmospheric deposition affects all lakes, and the PCBs can originate from another state or continent. In the literature, a form of principal component analysis (PCA) has been used to differentiate between these sources by comparing PCB congener distributions in fish (Macdonald et al., 1991; Rachdawong et al., 1997; Monosson et al., 2003). However, this type of comparison has never been done for this study region where most of the lakes have never been tested for local, point sources of PCBs.

Lakes have unique physical and chemical characteristics that can significantly affect the bioaccumulation of chemical contaminants. For example, the amount of particulates or dissolved organic matter in a lake will affect the concentration of a dissolved contaminant that is readily available for uptake by fish through respiration. In regards to mercury, a hazardous pollutant that also bioaccumulates, wetlands can alter it into its more toxic form (Clayden et al., 2013). The purpose of comparing lake ecosystem characteristics was to see if any characteristics could be used to estimate or to predict the total concentration of PCBs in fish. The significance of watershed inputs of PCBs to lakes has varied in previous studies (Jeremiason et al., 1991; Paul et al., 2002; King et al., 2004; Totten et al., 2006). There has been strong evidence that the trophic state of a lake can significantly impact the amount of PCBs to which fish are exposed (Macdonald et al., 1991; Paterson et al., 1998; Kidd et al., 1999; Dachs et al., 2000; Ikonomidou et al., 2002). A form of multiple linear regression (MLR) has been performed to determine the lake characteristics that can best predict, and therefore have the most effect on, bioaccumulation of various chemical pollutants (McMurty et al., 1989; Clayden et al., 2013). For the first time in this study, MLR analysis was used on inland lakes in the study region to determine which ecosystem characteristics (i.e., trophic state, lake size indicators, watershed area and wetland area) have the most impact on PCB contamination in fish.

To determine which lakes are most susceptible to PCB contamination and when safe fish consumption may be possible, modeling tools were used to predict lake PCB concentrations and fish contamination. Previous lake models have been

developed for the Great Lakes region, but most have focused specifically on one lake (Baker et al., 1990, Mackay 1989, and Rowe 2009). For this study, a mass balance model was developed to determine the concentration of PCB congeners in any given lake. The only source of PCBs to the lake was assumed to be from the atmosphere; modes of atmospheric deposition include wet, dry particulate, and gas exchange. Calibrated using measured PCB water concentrations in Lake Superior, the model was used to estimate concentrations in other lakes that, in turn, were used to predict bioaccumulation. This model estimates PCB congener concentrations based on a wide range of lake chemical and physical characteristics so that it is not as restricted as previous models have been.

The U.S. Environmental Protection Agency's (EPA) Bioaccumulation and Aquatic System Simulator (BASS) was used to estimate PCB congener concentrations in fish at varying trophic levels in a given food web. Once the model was calibrated using Michigan Department of Natural Resources (MDNR) fish surveys, the model was adjusted to determine if any major change in food web structure had a significant effect on PCB concentrations in upper trophic level species. The proposed hypothesis was that the trophic position of a top predator, which is determined by the fish diet, significantly affects PCB accumulation.

EPA's BASS model has been used in many projects in the United States to study mercury, DDT and PCB bioaccumulation (US EPA, 2015). One such study assessed PCB accumulation in Lake Ontario Salmonids and used BASS's precursor, FGETS (Food and Gill Exchange of Toxic Substances) (Barber et al., 1991). The

bioaccumulation model was also used for PCB accumulation in creek systems (Marchettini et al., 2001). BASS has been applied to watershed studies (Johnston et al., 2011) and an assessment of fish mercury response time to atmospheric changes (Knights et. al., 2009). The great range of uses for this program, and the fact that it was recommended as an assessment tool to the State of Michigan (Exponent 2003), made it an appropriate tool for this analysis.

Lake ecosystem scenarios were developed using the models to determine the extent of PCB contamination in top predator fish. To encompass the wide range of possible lake types in the study region, the scenarios involved lakes that varied in size, trophic state and food web structure. The results of the scenarios helped to explain the importance of other biophysical factors affecting bioaccumulation and were used to determine which type of lake likely has the highest contamination in fish. Prediction of when safe fish consumption may be possible has never been estimated for inland lakes. These lake ecosystem scenarios and modeling tools have now made this possible.

2.2 Methods

2.2.1 Source of Contamination

In order to discriminate between fish impacted by a local source and those impacted by atmospheric sources, PCA was used on a set of lakes sampled by the Michigan Department of Environmental Quality (MDEQ) (Bohr, 2013). The MDEQ sampled and analyzed multiple fish species for total PCB concentrations and PCB

congener concentrations in 18 lakes across the state of Michigan's Upper Peninsula from 2000 to 2010 (Figure 2. 1). The samples were analyzed following the Great Lakes and Environmental Assessment Section Procedure 31 (Bohr and VanDusen, 2011).

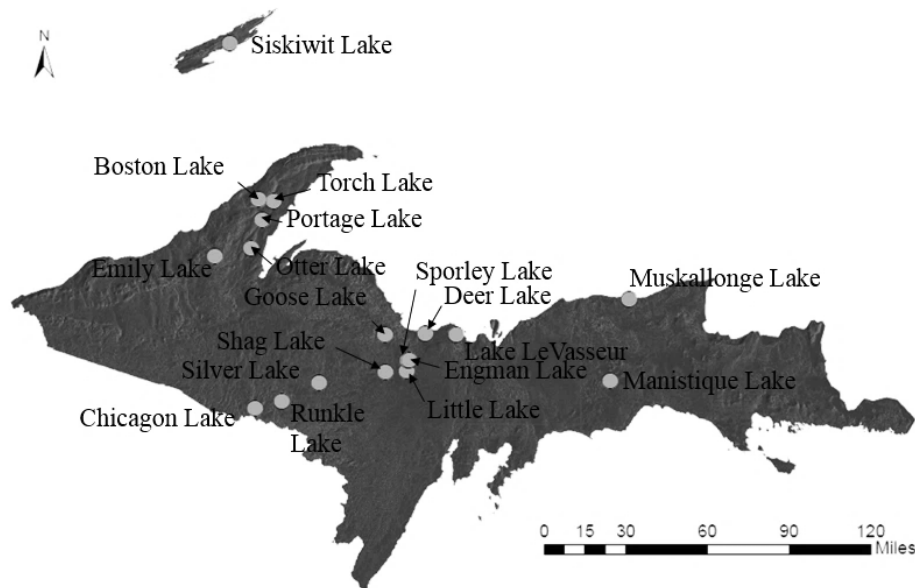


Figure 2. 1: Map of MDEQ sampled lakes from 2000 to 2010 in Michigan's Upper Peninsula.

PCA, with direct oblimin rotation, was performed using IBM® SPSS® Statistics 21 to determine if a statistically significant difference existed between fish contamination sources. PCA is a statistical method that uses the variance in observed data to simplify multiple variables into a reduced number of variables or principal components. These components are determined through transformations to account for the most variance among the datasets. Direct oblimin rotation is an oblique rotation and allows factors to not be orthogonal to make interpretation of results

easier. This method is widely used to observe similarities and differences in observed data.

For the analysis, concentrations of individual PCB congeners are treated as multiple variables for each lake. Congener concentrations above the detection limit were log-transformed for the analysis while congeners below detection limit were omitted from the analysis. By omitting congeners below the detection limit, the greatest contrast between sites could be interpreted. In addition, fish species (Northern Pike (*Esox lucius*) and Walleye (*Sander vitreus*)) were compared separately in the analysis to account for physiological differences (i.e. fat content, growth rate and relative size). The samples included in the analyses were between 40 to 50 and 50 to 60 cm in length for walleye and northern pike, respectively. Limiting the size of fish provided a better comparison among lakes because similar sizes and ages of fish have more comparable PCB concentrations (e.g. Olsson et al., 2000). Species comparisons were limited due to a lack of common species among all lakes. Due to this complication, three of the lakes could not be compared using PCA: Siskiwit Lake, Boston Pond and Chicagon Lake were sampled only for lake trout, white sucker and lake whitefish, respectively.

2.2.2 Ecosystem Characteristics

For lakes not impacted by local, industrial PCB contamination (Section 2.3.1) MLR was performed to determine if any lake characteristic(s) could predict the total concentration of PCBs in a given lake. Total concentration of PCBs, measured by the MDEQ, was calculated as the sum of all congeners above the detection limit. Both the

characteristics and the average total PCB concentrations for each lake were log transformed for the analysis. Lake fish sample concentrations were provided by the MDEQ (Bohr, 2013). Fish species included in the analysis were walleye, northern pike and lake trout. Values for lake characteristics used in the analysis can be seen in Table A. 1.

Lake characteristics included in the analysis were chosen based on their potential to affect fish PCB concentrations and data availability; lake characteristics used in the MLR included surface area, mean depth, maximum depth, trophic state, watershed area, wetland area, open water area within the watershed and the ratio of watershed area to lake surface area. The lakes determined from PCA to be only atmospherically impacted (Figure 2. 8) were used in the analysis so that the potential of local contamination did not skew the results. Siskiwit Lake was also included because there are no industrial sources on Isle Royale. Lipid-normalized total PCB concentrations in fish from each lake were used as the basis for fish PCB concentration in the analysis.

2.2.3.1 Lake PCB Model Description

A two-box model (Figure 2. 2) was designed to predict the PCB water concentration in inland lakes given rates of atmospheric inputs and lake characteristics. It was designed as a non-steady state model to illustrate the time required for the water column to react to a change in the atmospheric concentration of PCBs. This non-steady state approach contrasts with the previously published

QWASI (Quantitative Water Air Sediment Interaction) fugacity model, which was designed as a steady state model (Mackay and Diamond 1989).

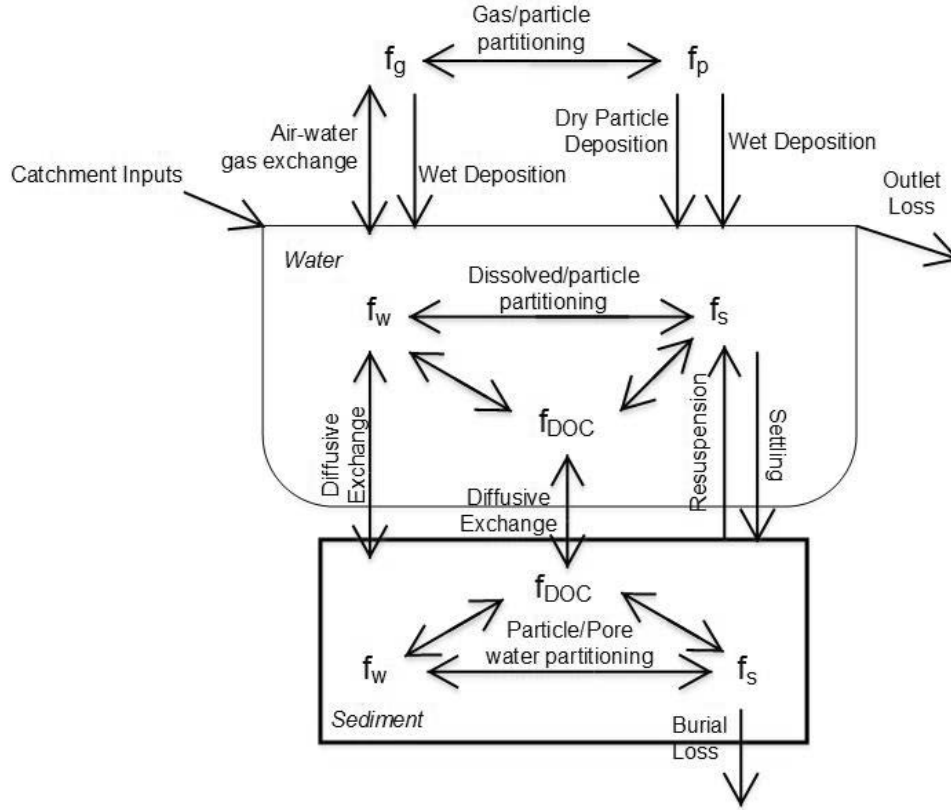


Figure 2. 2: Diagram of PCB water concentration model.

The differential equations used in this model were taken from Schwarzenbach et al. (2003):

$$\frac{dC_w}{dt} = J_w - k_{11}C_w + k_{12}C_s \quad [2.1]$$

$$\frac{dC_s}{dt} = J_s + k_{21}C_w - k_{22}C_s \quad [2.2]$$

$$J_w = J_{dry} + J_{pwet} + J_{gwet} + J_{aw} + J_{ws} \quad [2.3]$$

where J_s is assumed to be equal to zero for all lakes considered in this study. The “surface mixed sediment layer” (SMSL) model, provided by Schwarzenbach et al. (2003), was used as the basis of the model. Table 2. 1 and Table 2. 2 summarize all variables and equations used in the model.

Table 2. 1: List of all symbols and references used in the PCB lake model where M is mass, L is length and T is time (no entry under value means that the value varies for the PCB congener or lake).

Chemical Characteristics				
<i>Symbol</i>	<i>Quantity</i>	<i>units</i>	<i>value</i>	<i>Source</i>
C_a	PCB air concentration	M/L^3	-	IADN 2006 data
C_w	PCB water concentration	M/L^3	-	-
C_s	PCB soil concentration	M/L^3	-	-
D_{iw}, D_{jw}	Diffusivity of a compound in Water for compound of interest (i) and reference compound (j)	L^2/T	-	Schwarzenbach, 2003
D_{ia}, D_{ja}	Diffusivity of a compound in air for compound of interest (i) and reference compound (j)	L^2/T	-	Schwarzenbach, 2003
K_{oc}	natural organic matter-water partition coefficient	L^3/M	-	Schwarzenbach, 2003
K_{oa}	Octanol-air partition coefficient	unitless	-	Schwarzenbach, 2003
K_H	Dimensionless Henry's Law Constant	unitless	-	Paasivirta and Sinkkonen, 2009
K_{ow}	Octanol-Water Partition Coefficient	unitless	-	Paasivirta and Sinkkonen, 2009

M_i	molar mass of a compound	M/mol	-	Paasivirta and Sinkkonen, 2009
V_{iaw}	Air-water exchange velocity	L/T	-	Schwarzenbach, 2003
V_{ia}, V_{ja}	Mass transfer velocity of a compound in air	L/T	-	Schwarzenbach, 2003
V_{is}, V_{jw}	Mass transfer velocity of a compound in water	L/T	-	Schwarzenbach, 2003
f_w^{op}	dissolved fraction of PCB in open water	unitless	-	Schwarzenbach, 2003
f_s^{air}	PCB fraction sorbed to particles in air	unitless	-	Schwarzenbach, 2003
f_{DOC}	PCB fraction sorbed to DOC	unitless	-	Schwarzenbach, 2003
$C_{w,0}$	initial water concentration	M/L ³	-	-
$C_{s,0}$	initial sediment concentration	M/M	-	-
C_{ss}	steady state concentration	M/L ³	-	-
Atmosphere Characteristics				
<i>Symbol</i>	<i>Quantity</i>	<i>units</i>	<i>value</i>	<i>Source</i>
v_d	particle dry deposition velocity to lake	L/T	0.002 m/s	Rowe, 2009
$f_{oc,air}$	fraction of organic carbon in aerosol	unitless	0.1	Rowe, 2009
$f_{om,air}$	fraction of organic matter in aerosol	unitless	0.2	Rowe, 2009

TSP	atmospheric aerosol particle mass concentration	M/L ³	10 μg/m ³	Rowe, 2009
M _{air}	Average molar mass of air	M/mol	28.91 g/mol	Schwarzenbach 2003
\bar{V}_{air}	molar volume of air gasses	L ³ /mol	20.1 cm ³ /mol	Schwarzenbach 2003
f _d	fraction of time not raining or snowing	unitless	0.9	Rowe, 2009
Lake Characteristics				
<i>Symbol</i>	<i>Quantity</i>	<i>units</i>	<i>value</i>	<i>Source</i>
u ₁₀	Wind speed 10 meters above the water surface	L/T	-	CMX weather station data (NOAA GLERL, 2015)
A _o	Lake Surface Area	L ²	-	Table A. 2 or Table 2. 3
A _w	Watershed area	L ²	-	Table A. 2 or Table 2. 3
h	Lake Mean Depth	L	-	Table A. 2 or Table 2. 3
V	Lake Volume	L ³	-	Table A. 2 or Table 2. 3
TSS	Total Suspended Solids	M/L ³	-	Table A. 2 or Table 2. 3

f_{om}	fraction of organic matter in suspended solids	unitless	-	Table A. 2 or Table 2. 3
f_{oc}	fraction of organic carbon in suspended solids	unitless	-	Table A. 2 or Table 2. 3
DOC	Dissolved Organic Carbon in the water column	M/L ³	-	Table A. 2 or Table 2. 3
τ	residence time of the water body	T	-	-
r_{sw}^{op}	solid to water phase ratio	M/L ³	-	Schwarzenbach, 2003
K_d	distribution coefficient of suspended solids	L ³ /M	-	Schwarzenbach, 2003
K_{DOC}	partition coefficient for dissolved organic carbon	L ³ /M	-	Schwarzenbach, 2003
f_s^{op}	fraction sorbed to suspended solids in open water	unitless	-	Schwarzenbach, 2003
v_s	particle settling velocity	L/T	1.37 m/d	Noel Urban, personal communication
$Q_{pr (avg)}$	precipitation flow rate	L ³ /T	-	-
P	Annual Precipitation	L/T	0.83 m/yr	Current Results, 2015
Sediment Characteristics				
<i>Symbol</i>	<i>Quantity</i>	<i>units</i>	<i>value</i>	<i>Source</i>
f_{ocs}	Fraction of Organic Carbon in the sediments	unitless		Schwarzenbach, 2003
δ_{bl}	Aqueous boundary layer thickness	L	5×10^{-4} m	Rowe, 2009

<i>Symbol</i>	<i>Quantity</i>	<i>units</i>	<i>value</i>	<i>Source</i>
V_{sd}	Diffusive sediment-water exchange velocity	L/T		Schwarzenbach, 2003
K_d^{sc}	distribution coefficient of settled solids in sediment column	L^3/M		Schwarzenbach, 2003
μ_{res}	sediment resuspension rate	$M/L^2/T$	4×10^{-8}	Lake Superior Rowe, 2009
V_{sre}	sediment resuspension velocity	L/T	-	Schwarzenbach, 2003
ρ_s^{sc}	density of solids in sediment column	M/L^3	-	Schwarzenbach, 2003
r_{sw}^{sc}	solid to water phase ratio in sediment column	M/L^3	-	Schwarzenbach, 2003
Φ^{sc}	porosity of the sediment column	unitless	-	Schwarzenbach, 2003
V_{sedex}	Overall sediment-water exchange velocity	L/T	-	Schwarzenbach, 2003
f_w^{sc}	Dissolved fraction of PCB in sediment	unitless	-	Schwarzenbach, 2003
Z_{mix}	sediment mixing depth	L	0.01 m	Rowe, 2009.
m	mixed layer mass/area	M/L^2	-	Schwarzenbach, 2003
β	preservation factor of organic carbon in sediment mixing layer	unitless	0.0001	Noel Urban, personal communication, 2014.
η_p	particle scavenging efficiency	unitless	50000	Rowe, 2009.

Watershed Characteristics				
<i>Symbol</i>	<i>Quantity</i>	<i>units</i>	<i>value</i>	<i>Source</i>
$J_{dry,ws}$	Dry particle deposition onto watershed	$M/L^3/T$	-	Schwarzenbach, 2003
$J_{pwet,ws}$	particle wet deposition onto watershed	$M/L^3/T$	-	Schwarzenbach, 2003
$J_{gwt,ws}$	gas phase scavenging by precipitation onto watershed	$M/L^3/T$	-	Schwarzenbach, 2003
f_{ws}	fraction of chemical deposited on watershed that enters the lake	unitless	0.03	Totten et al. 2006
$V_{d,ws}$	particle dry deposition velocity to watershed	L/T	0.002 m/s	Rowe, 2009
C_{LS}	Concentration on leaf surface	M/L^3	-	Nizzetto and Perlinger, 2012
C_r	Concentration in leaf reservoir	M/L^3	-	Nizzetto and Perlinger, 2012
J_{sa}	Surface-air exchange flux	$M/L^3/T$	-	Nizzetto and Perlinger, 2012
J_{ra}	Reservoir-air exchange flux	$M/L^3/T$	-	Nizzetto and Perlinger, 2012
J_{ca}	Air-canopy exchange flux	$M/L^3/T$	-	Nizzetto and Perlinger, 2012
L	Leaf area	L^2	-	Nizzetto and Perlinger, 2012
k_{sa}	Air-surface mass transfer coefficient	L/T	-	Nizzetto and Perlinger, 2012

k_{ra}	Air-reservoir mass transfer coefficient	L/T	-	Nizzetto and Perlinger, 2012
K_{sa}	Surface-air dimensionless equilibrium partition coefficient	-	-	Nizzetto and Perlinger, 2012
K_{ra}	Air-leaf reservoir dimensionless equilibrium partition coefficient	-	-	Nizzetto and Perlinger, 2012
Constants				
<i>Symbol</i>	<i>Quantity</i>	<i>units</i>	<i>value</i>	<i>Source</i>
η	solution viscosity in centipoise	M/L/T	-	Schwarzenbach, 2003
R	Gas constant	8.314×10^{-3} kJ/mol/K		Schwarzenbach, 2003
T	Temperature	K	-	-
p	gas phase pressure	ML/T ²	1 atm	Schwarzenbach, 2003
TSI	Trophic State Index	unitless	-	Table A.2.1
t_{ss}	time to steady state	T	-	Schwarzenbach, 2003
Fluxes				
<i>Symbol</i>	<i>Quantity</i>	<i>units</i>	<i>value</i>	<i>Source</i>
J_w	sum of all input fluxes to lake	M/L ³ /T	-	Schwarzenbach, 2003
J_s	sum of all input fluxes to sediment	M/L ³ /T	-	Schwarzenbach, 2003
J_{dry}	dry deposition flux	M/L ³ /T	-	Schwarzenbach, 2003

J_{pwet}	particle wet deposition	$M/L^3/T$	-	Schwarzenbach, 2003
J_{gwet}	gas phase scavenging by precipitation	$M/L^3/T$	-	Schwarzenbach, 2003
J_{aw}	air-water exchange flux	$M/L^3/T$	-	Schwarzenbach, 2003
J_{ws}	watershed flux	$M/L^3/T$	-	Schwarzenbach, 2003
First Order Rates				
<i>Symbol</i>	<i>Quantity</i>	<i>units</i>	<i>value</i>	<i>Source</i>
k_{11}	sum of first order rate loss constants from the lake	T^{-1}	-	Schwarzenbach, 2003, see equation 2.1
k_{22}	sum of first order rate loss constants from the sediment	T^{-1}	-	Schwarzenbach, 2003, see equation 2.2
k_{12}	sum of first order rate loss constants from the lake	$L^3/M/T$	-	Schwarzenbach, 2003, see equation 2.1
k_{21}	sum of first order rate loss constants from the sediment	$L^3/M/T$	-	Schwarzenbach, 2003, see equation 2.2
k_{sedex}	resuspension transfer rate constant	T^{-1}	-	Schwarzenbach, 2003
$k_{a/w}$	removal rate to atmosphere	T^{-1}	-	Schwarzenbach, 2003
k_w	outflow loss rate	T^{-1}	-	Schwarzenbach, 2003
k_s	particle settling rate constant	T^{-1}	-	Schwarzenbach, 2003

Table 2. 2: List of equations used in the PCB lake model.

Equation Description	Units	Equation	Source	Eqn #
Flux Equations				
dry particle deposition flux	$\mu\text{g}/\text{m}^3/\text{yr}$	$I_{dry} = \frac{C_a f_s^{air} v_d f_d A_o}{V}$	Schwarzenbach et al. 2003	2.4
particle wet deposition	$\mu\text{g}/\text{m}^3/\text{yr}$	$I_{pwet} = \frac{\eta_p f_s^{air} Q_{pr} C_a}{V}$	Schwarzenbach et al. 2003	2.5
gas-phase scavenging by precipitation	$\mu\text{g}/\text{m}^3/\text{yr}$	$I_{gwet} = \frac{Q_{pr} (1 - f_s^{air}) C_a}{V K_H}$	Schwarzenbach et al. 2003	2.6
air-water exchange flux	$\mu\text{g}/\text{m}^3/\text{yr}$	$I_{aw} = \frac{v_{iaw} (1 - f_s^{air}) C_a A_0}{K_H * V}$	Schwarzenbach et al. 2003	2.7
watershed flux to lake	$\mu\text{g}/\text{m}^3/\text{yr}$	$J_{ws} = f_{ws} (J_{dry,ws} + I_{pwet,ws} + I_{gwet,ws} + J_{ca})$	Schwarzenbach et al. 2003	2.8
dry particle deposition onto watershed	$\mu\text{g}/\text{m}^3/\text{yr}$	$J_{dry,ws} = \frac{C_a f_s^{air} v_{d,ws} f_d A_{ws}}{V}$	Schwarzenbach et al. 2003	2.9
gas-phase scavenging by precipitation onto watershed	$\mu\text{g}/\text{m}^3/\text{yr}$	$J_{gwet,ws} = \frac{Q_{pr} (1 - f_s^{air}) C_a}{V K_H}$	Schwarzenbach et al. 2003	2.10
Air- canopy exchange flux	$\mu\text{g}/\text{m}^3/\text{yr}$	$J_{ca} = \sum_{i=1}^n (J_{ra(i)} + J_{sa(i)})$	Nizzetto and Perlinger, 2012	2.11

Reservoir-air exchange flux	$\mu\text{g}/\text{m}^3/\text{yr}$	$J_{ra} = \left(-2Lk_{ra} \left(C_a - \frac{C_{LS}}{K_{ra}} \right) \right) \times \frac{A_w}{V}$	Nizzetto and Perlinger, 2012	2.12
Surface-air exchange flux	$\mu\text{g}/\text{m}^3/\text{yr}$	$J_{sa} = \left(-2Lk_{sa} \left(C_a - \frac{C_{LS}}{K_{sa}} \right) \right) \times \frac{A_w}{V}$	Nizzetto and Perlinger, 2012	2.13
First-order rate constants and subcomponents				
Equation Description	Units	Equation	Source	Eqn #
sum of first order rate loss constants from the lake	yr^{-1}	$k_{11} = k_w + k_s + k_{sedex} + k_{a/w}$	Schwarzenbach et al. 2003	2.14
outflow loss rate (flushing)	yr^{-1}	$k_w = \frac{Q}{V}$	Schwarzenbach et al. 2003	2.15
particle settling rate constant (sedimentation)	yr^{-1}	$k_s = f_s^{op} \frac{v_s}{h}$	Schwarzenbach et al. 2003	2.16
resuspension transfer rate constant	yr^{-1}	$k_{sedex} = \frac{v_{sedex}}{h}$	Schwarzenbach et al. 2003	2.17
Overall sediment-water exchange velocity	m/s	$v_{sedex} = f_w^{sc} (v_{sd} + v_{sre})$	Schwarzenbach et al. 2003	2.18
Diffusive sediment-water exchange velocity	m/s	$v_{sd} = \frac{D_{iw}}{\delta_{bl}}$	Schwarzenbach et al. 2003	2.19

Equation Description	Units	Equation	Source	Eqn #
Sediment resuspension velocity	m/s	$v_{res} = \mu_{res} K_d^{sc}$	Schwarzenbach et al. 2003	2.20
removal rate to atmosphere	1/s	$k_{a/w} = f_w^{op} \frac{v_{iaw}}{h}$	Schwarzenbach et al. 2003	2.21
Dissolved fraction of compound in lake		$f_w^{op} = \frac{1}{(1 + r_{sw}^{op} K_d + K_{DOC}[DOC])}$	Schwarzenbach et al. 2003	2.22
solid to water phase ratio	kg/m ³	$r_{sw}^{op} = TSS$	Schwarzenbach et al. 2003	2.23
Distribution coefficient of suspended solids	m ³ /kg _{solid}	$K_d = f_{oc} K_{oc}$	Schwarzenbach et al. 2003	2.24
partition coefficient for DOC	m ³ /kg _{solid}	$\log K_{doc} = 0.94 \log K_{ow} - 0.29$	Schwarzenbach et al. 2003	2.25
chemical fraction sorbed to the particle in air		$f_s^{air} = K_p * TSP / (K_p * TSP + 1)$	Schwarzenbach et al. 2003	2.26
particle-gas partition coefficient		$\log K_p = \log K_{oa} + \log f_{om} - 11$	Schwarzenbach et al. 2003	2.27
natural organic matter-water partition coefficient	L/kg _{oc}	$\log K_{oc} = 0.74 \log K_{ow} + 0.15$	Schwarzenbach et al. 2003	2.28

Equation Description	Units	Equation	Source	Eqn #
sum of first order rate loss constants from the sediment as a function of the conc. in the sediment	yr ⁻¹	$k_{22} = \frac{1}{m} \left(\beta v_s r_{sw}^{sc} + \frac{v_{sedex}}{f_w^{sc} K_d^{sc}} \right)$	Schwarzenbach et al. 2003	2.29
solid to water phase ratio in the sediments	kg _{solids} /m ³	$r_{sw}^{sc} = \rho_s^{sc} * \frac{1 - \phi}{\phi}$	Schwarzenbach et al. 2003	2.30
density of solids in sediment	kg/m ³	$\rho_s^{sc} = f_{oc} + 2.5 - 2.5f_{oc}$	Schwarzenbach et al. 2003	2.31
porosity of the sediment		$\phi = \frac{K}{1 + \left(\frac{K - \phi_{min}}{\phi_{min}} \right) e^{-\phi_{max} f_{oc}}}$ $\phi_{min} = 0.6, K = \phi_{max} = 0.95$	Noel Urban, personal communication, 2014	2.32
sum of first order rate loss constants from the lake as a function of the conc. in the sediment	m ³ /kg/yr	$k_{12} = \frac{k_{sedex}}{f_w^{sc} K_d^{sc}}$	Schwarzenbach et al. 2003	2.33
distribution coefficient of settled solids	m ³ /kg _{solid}	$K_d^{sc} = f_{ocs} K_{oc}$	Schwarzenbach et al. 2003	2.34

Equation Description	Units	Equation	Source	Eqn #
Dissolved fraction of compound in sediment		$f_w^{sc} = \frac{1}{(1 + r_{sw}^{sc}K_d^{sc} + K_{doc}[DOC])}$	Schwarzenbach et al. 2003	2.35
sum of first order rate loss constants from the sediment	m ³ /kg/yr	$k_{21} = \frac{1}{m}(v_s f_s^{op} + v_{sedex})$	Schwarzenbach et al. 2003	2.36
mixed layer mass/area	kg/m ²	$m = z_{mix}(1 - Q^{sc})\rho_s^{sc}$	Schwarzenbach et al. 2003	2.37
fraction sorbed to suspended solids		$f_s^{op} = \frac{(r_{sw}^{op}K_d)}{(1 + r_{sw}^{op}K_d + K_{doc}[DOC])}$	Schwarzenbach et al. 2003	2.38
precipitation flow rate	m ³ /s	$Q_{pr} = P \times A_o \text{ for lake}$ $Q_{pr} = P \times A_w \text{ for watershed}$		2.39
Time to steady state	yr	$t_{ss} = \frac{6}{k_{11} + k_{22} - q}$ $q = \sqrt{(k_{11} - k_{22})^2 + 4k_{12}k_{21}}$	Schwarzenbach et al. 2003	2.40

In order to calculate the air-water exchange velocities of the PCB congeners, reference compounds were used to determine diffusivity and the velocity of the congener in air and water, provided a wind speed 10 meters above the surface (u_{10}) and air temperature. Equations from Schwarzenbach et al. 2003 were used:

$$\frac{1}{v_{ia/w}} = \frac{1}{v_{iw}} + \frac{1}{v_{ia}K_{ia/w}} \quad [2.41]$$

$$\frac{v_{iw}}{v_{jw}} = \left(\frac{D_{iw}}{D_{jw}} \right)^{0.67} \quad [2.42]$$

$$D_{iw}(cm^2s^{-1}) = \frac{13.26 \times 10^{-5}}{\eta^{1.14} \bar{V}_i^{0.589}} \quad [2.43]$$

$$\frac{v_{ia}}{v_{ja}} = \left(\frac{D_{ia}}{D_{ja}} \right)^{0.67} \quad [2.44]$$

Initially, carbon dioxide and water were used as the reference compounds for equations 2.41 and 2.44, respectively. Once the model was calibrated for Lake Superior, sulfur hexafluoride was used as the reference compound for small inland lakes to match the results of previous studies (Wanninkhof et al. 1985, Wanninkhof et al. 1987, Crusius and Wanninkhof 2003, Clark et al. 1995). The wind speed was also adjusted to account for the differences between large lakes and small inland lakes- 5 and 2.7 m/s, respectively. The diffusivity of a compound in air was determined by using the derivation of Fuller et al. (1966).

$$D_{ia} = 10^{-3} \frac{T^{1.75} \left[\left(\frac{1}{M_{air}} \right) + \left(\frac{1}{M_i} \right) \right]^{0.5}}{p \left[\bar{V}_{air}^{1/3} + \bar{V}_i^{1/3} \right]^2} \quad [2.45]$$

King and Saltzman (1995) provided the expression used for diffusivity of sulfur hexafluoride in water.

$$D_{SF_6w}(cm^2/s) = 0.029e^{-19.3/RT} \quad [2.46]$$

The water-film mass transfer velocity of carbon dioxide was calculated for each lake based on the average wind speed using the equation from Rowe (2009) which was based on the empirical relationship of Wanninkhof et al. (1985).

$$v_{CO_2}(cm/hr) = 0.45u_{10}^{1.65} \quad [2.47]$$

Schwarzenbach et al. 2003 provided the means to calculate the mass transfer velocity of water vapor in air.

$$v_{wa}(cm/s) = 0.2u_{10}(m/s) + 0.3 \quad [2.48]$$

Lake characteristics were determined by recorded measurements or estimated based on trophic state (Table A. 2). The trophic state index (TSI) and total suspended solids (TSS) were related to secchi depth by the following equations (Armongol et al., 2003):

$$TSI = 60 * 14.41 \ln(\text{Secchi Depth (m)}) \quad [2.49]$$

$$TSS = 9.61(\text{Secchi Depth (m)})^{-0.97} \quad [2.50]$$

In addition, hydraulic residence time (V/Q_{out}) was calculated using USGS (United States Geological Survey) gauge data (USGS, 2015). However, not all outlets were gauged for the lakes of interest. An average annual runoff was calculated for each USGS gauge in Michigan's Upper Peninsula that provided a mean flow and drainage area. An average runoff ($R_{ws} = 0.41$ m/yr) for the peninsula was assumed adequate to calculate the water retention time because the runoff from all gauges across the Upper Peninsula did not show any spatial trend (Figure A. 1 and Figure A. 2). Outflow was calculated as:

$$Q_{in} + P * A - E * A = Q_{out} \quad [2.51]$$

where P and E are average values of precipitation and evaporation (m/yr) and Q_{in} was calculated as $R_{ws} * A_{ws}$. This calculation assumes that groundwater flows into and out of the lakes are negligible. Results of the model can be seen in Figure A. 3.

2.2.3.2 Model Calibration

The model was calibrated using PCB congener concentrations measured in Lake Superior as a part of the Great Lakes Aquatic Contaminants Survey (GLACS) completed in 2006 (US EPA GLNPO, 2009). Particulate-bound and “aqueous” concentrations of PCBs were measured by GLACS; the sum of the two is assumed to equal total PCB concentration. Aqueous concentrations were measured by extracting the PCBs using XAD resin; this method measures all of the truly dissolved PCBs and a large fraction of the DOM-bound PCBs (US EPA GLNPO, 2009). The average aqueous concentration of PCBs from all sample locations was used for comparison with the model output. It was assumed that this was an accurate representation of the entire lake concentration where the only source of PCBs to the lake was from atmospheric deposition. Atmospheric PCB concentrations as the input to the model were based on IADN atmospheric measurements in Eagle Harbor in 2006 (IADN, 2006). Figure 2. 3 summarizes the calibration comparison. A Chi-Square Test of Goodness of Fit determined that the measured and modeled water concentrations were statistically similar at the 90% confidence level ($\chi^2 = (2, N=23) = 30.01, p > 0.10$). In this test, the null hypothesis states that the model is similar to the measured data where if $p > \alpha$, the null hypothesis cannot be rejected.

Volatilization was the most important removal mechanism for the model. Lighter PCB congeners had the highest rates of volatilization. Losses through flushing remained more consistent for all PCB congeners while sedimentation was more significant for heavier congeners (Figure A. 4 through Figure A. 6).

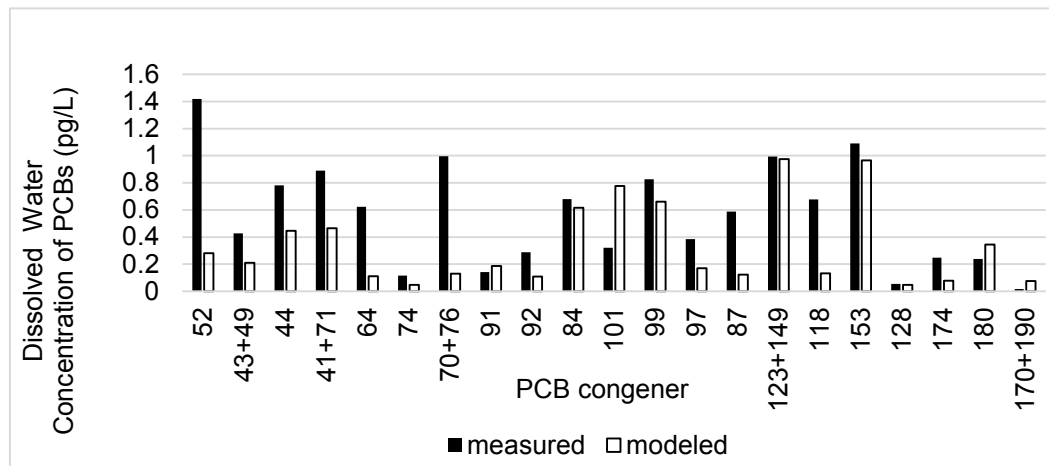


Figure 2. 3: Lake model calibration. Comparison of Lake Superior aqueous concentrations measured by the Great Lakes Aquatic Contamination Survey with model-predicted concentrations.

2.2.4.1 EPA's BASS Model

EPA's BASS model is a program designed to predict the accumulation of a chemical in an aquatic food web. Each fish species is divided into cohorts to account for population dynamics. For model details see the BASS User's manual provided by the EPA (Barber, 2008). Fish input files and fish community files were provided by Mr. M. Craig Barber (personal communication, July 1st through September 22nd, 2014) of the Ecosystems Research Division of the EPA.

Lake characteristics were acquired from various sources. A mean lake temperature was calculated from the Online Lake Modeling System (Kirillin et al.,

2011). The concentrations of phytoplankton and zooplankton in Torch Lake were measured in a Michigan Tech course in 2000, 2002 and 2004, and used to determine an average (Urban, 2014). In addition, Torch Lake had passive samplers deployed in 2005 to measure the amount of dissolved PCBs; these water concentrations were used to determine the fit of BASS to measurements (MDEQ Water Bureau, 2006). The water concentrations were calculated from the passive sampler results by using the SPMD (semi-permeable membrane device) water concentration estimators from USGS Columbia Environmental Research Center (USGS CERC, 2010). Version 4.1 of the water concentration estimator was used because the 2005 SPMD study did not use performance reference compounds. For the other lakes, the concentrations of lower trophic level organisms were estimated based on lake characteristics and assumed constant for the simulations. Zooplankton (Z) and benthos (B) biomass were estimated using regression equations from Hanson and Peters (1984) by providing the total phosphorous concentration (TP), maximum lake depth (Z_{max}) and surface area (A_o) of the lake.

$$\log Z (mg/m^3, dry wt) = 0.989 \log TP - 0.158 \log Z_{max} + 1.13 \quad [2.52]$$

where TP and Z_{max} have units of mg/m^3 and meters, respectively. The regression coefficient for this relationship was 0.75 in the original study.

$$\log B (g/m^2, wet weight) = 0.742 \log TP - 0.158 \log A_o + 0.161 \quad [2.53]$$

where A_o has units of km^2 ; the regression coefficient was reported to be 0.59 (Hanson and Peters 1984). The regression used to calculate phytoplankton (*phyto*) biomass from total phosphorous (TP) was taken from Watson and Kalff (1981).

$$\log \text{phyto} (\text{mg}/\text{m}^3, \text{dry wt}) = 1.28 \log TP + 1.24 \quad [2.54]$$

where TP has units of mg/m^3 . Periphyton biomass was estimated using either secchi depth (*secchi*) or total phosphorous and the relationships from Shortreed et al., 1983.

$$\text{Periphyton} (\text{g}/\text{m}^2, \text{dry wt}) = 0.0161(\text{secchi}) + 0.375 \quad [2.55]$$

$$\text{Periphyton} (\text{g}/\text{m}^2, \text{dry wt}) = 0.0835 (TP) + 0.1479 \quad [2.56]$$

The regression coefficients reported for these relationships were 0.01 and 0.17, respectively. Secchi depth was measured in meters and TP in $\mu\text{g P/L}$.

Bioaccumulation factors for the lower trophic level organisms were estimated from linear regressions based on the octanol-water partition coefficient (unitless) of the PCB congener (Arnot and Gobas, 2006). These equations were used to set up the chemical exposure files.

$$\text{Autotrophs: } \log BCF = 0.21 + 0.71 \log K_{ow} \quad [2.57]$$

$$\text{Invertebrates: } \log BAF = 0.09 + 0.82 \log K_{ow} \quad [2.58]$$

where r^2 equals 0.88 for equation 2.57 and 0.55 for equation 2.58.

PCB congener chemical characteristics used in BASS were based on Paasivirta and Sinkkonen (2009). Lake characteristics (i.e. total phosphorus, secchi

depth) were found using the MDEQ's Michigan Surface Water Information Management System (MiSWIMS, 2015). Lake Fish Surveys were acquired from Patrick Hanchin at the Charlevoix Fisheries Station or directly from the MDNR fishery resource reports (MDNR, 2015). All inland lake fish PCB sampling and analysis data were attained from Joseph Bohr of the Water Resources Division at MDEQ (Bohr, 2013) for comparison with model output.

While BASS was a useful tool, it had limitations. The output analyzer was not capable of generating figures because of the many PCB congeners included in each simulation, and the total number of congeners included was necessary to adequately predict the total PCB accumulation. The newest operating system with which BASS was compatible was Windows XP which is no longer supported by the university. Due to these challenges, all figures were generated from individual project results in Microsoft Excel.

2.2.4.2 Model Calibration

To test the capabilities of BASS, a project file was developed for Torch Lake because PCB congener water concentrations were measured in this lake using passive samplers in 2006 which were used as the exposure input to the model (GLEC, 2006), and fish surveys were completed in 2007 and 2008 in this lake (Hanchin, 2013). In addition, the model was designated to use the FGETS (Food and Gill Exchange of Toxic Substances) modeling framework. This framework was chosen because fish surveys performed by the DNR did not provide adequate information to estimate population dynamics. Figures 2. 4 through Figure 2. 6 show the model output

generated in Microsoft Excel. The program was run for 10 years and used an average lake water temperature, depth and lower food web trophic level concentrations (i.e. zooplankton and periphyton). Table A. 9 summarizes the species included in the Torch Lake Simulation. All fish files and fish community files were provided by the EPA (C. Barber, personal communication, 2014). Only one fish species, walleye, had to be adjusted to fit measured data for weight to length ratios (Figure 2. 5) and the maximum age was extended from 7 years to 15 years to account for trends in Torch Lake (Hanchin, 2013). The fish files and fish community files provided by the EPA had typical diets for each species and all other fish parameters provided. All PCB congeners measured above detection limit in fish samples were included in the simulation. All PCB chemical characteristics used in the chemical property files were taken from Paasivirta and Sinkkonen (2009).

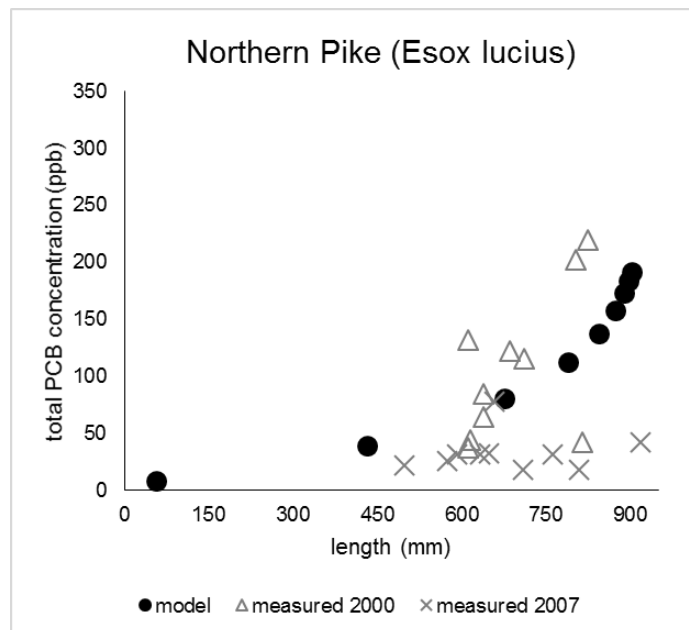


Figure 2. 4: EPA's BASS Torch Lake simulation northern pike output. Measured data from Bohr, 2013.

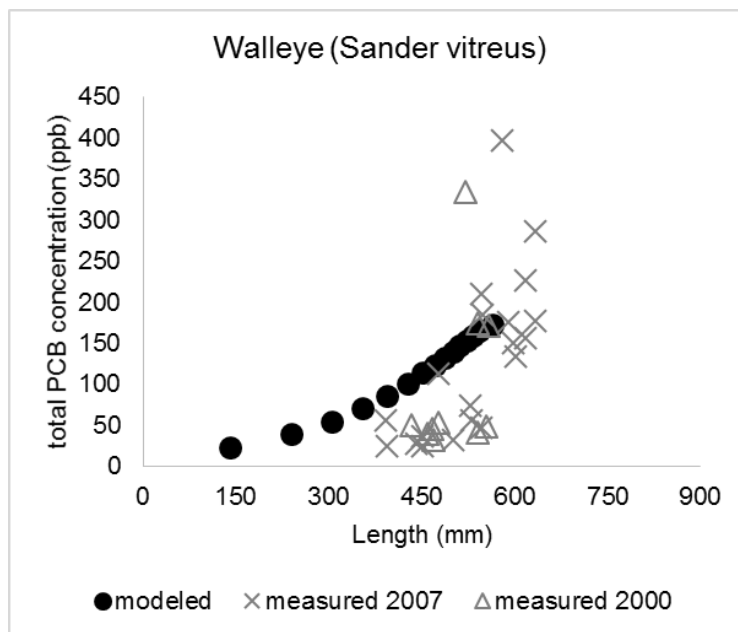


Figure 2. 5: EPA's BASS Torch Lake Simulation walleye output. Measured data from Bohr, 2013.

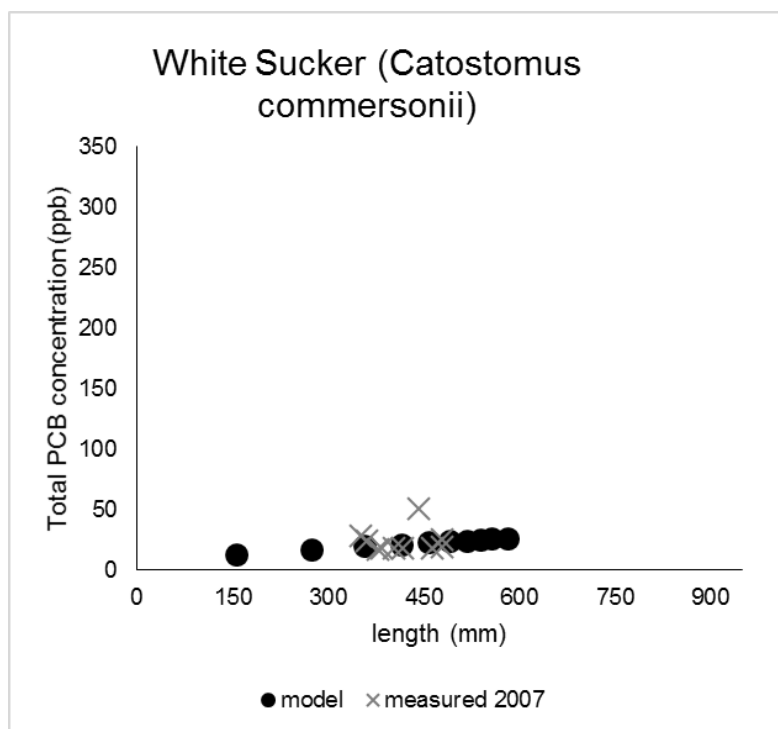


Figure 2. 6: EPA's BASS Torch Lake white sucker output. Measured data from Bohr, 2013.

Upon completion of the calibration using Torch Lake, the BASS model was used on Manistique Lake to evaluate the accuracy of the combined food web and lake models. Manistique Lake had walleye sampled for PCBs in 2003 by the MDEQ, but does not have any measured PCB water concentrations. Using the two models, the lake PCB model and EPA's BASS, to predict walleye concentrations revealed if the models could accurately predict PCB concentrations in a top predator fish species. All fish species included in the simulation are listed in Table A. 9. All fish files and fish community files were provided by the EPA (C. Barber, personal communication, 2014). The walleye fish file was adjusted in the same manner as for Torch Lake (Figure A. 4). Project file details can be found in Table A. 4. Figure 2. 7 shows the output of BASS for walleye from Manistique Lake. The lake PCB dissolved water concentrations used the same PCB atmospheric concentrations as the Lake Superior calibration inputs from IADN in 2006 over Eagle Harbor. This lake was also surveyed for fish species in 2003 and 2004 (Hanchin and Kramer, 2007).

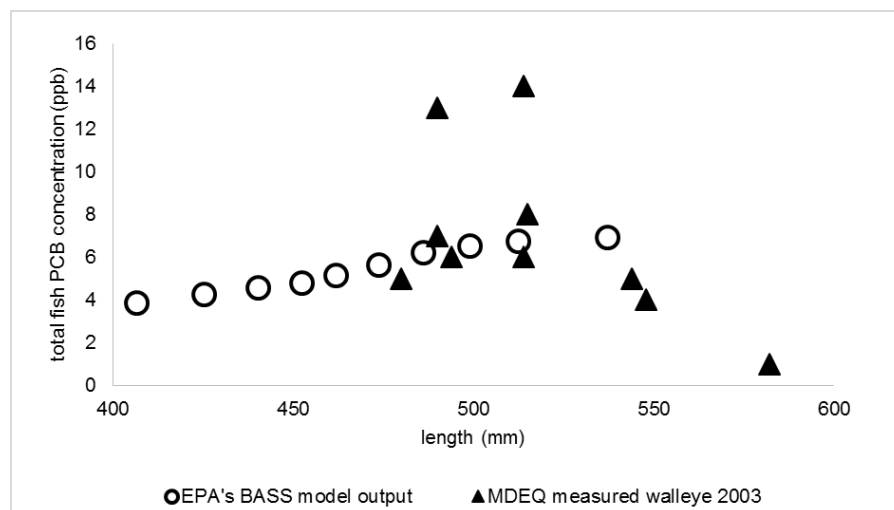


Figure 2. 7: Manistique Lake food web model output for walleye vs. measured MDEQ whole fish total PCB concentration from 2003 (Bohr, 2013).

2.2.5 Lake Ecosystem Model Scenarios

To understand the extent to which typical lake characteristics and corresponding food web structures affect PCB contamination, a set of lake scenarios that incorporated the scope of Michigan's Upper Peninsula lakes was developed. These scenarios were based on the typical lakes sizes from the Cheruvilil EPA-NLAPP 6-state lake-landscape database (Cheruvilil et al., 2013). The average characteristics for the four lake sizes were based on the 10th, 20th, 50th and 85th percentiles for the 135 Upper Peninsula lakes in the database (Table 2. 3).

Table 2. 3: Lake size category for lake/food web scenario development based on percentiles from Cheruvilil et al., 2013.

Lake Category	Mean Depth (m)	Surface Area (km2)	Watershed Area (km2)	Maximum Depth (m)
Seepage	2.5	0.5	8.8	9.0
Small	2.7	0.8	14.3	5.0
Medium	4.0	1.2	59.9	8.0
Large	6.5	2.2	70.5	10

Each lake size category was tested for the effect of trophic state by using the two extremes for lake productivity— oligotrophic and eutrophic. Lake characteristics used for lake productivity are listed in Table A. 2. In addition, the small lake category could contain lakes that may not have adequate streams for spawning, limiting the number of potential fish species. If there are not adequate streams for spawning, some benthic fish (e.g., suckers) and some top predators (e.g., northern pike) likely cannot sustain substantial populations within the lake. Therefore, two food web scenarios (one with and one without species that require tributaries for spawning) were

developed for the small lake category to account for this change in food web structure. The list of species included in each lake are summarized in Table A. 10. Species were chosen based on fish typically recorded to be abundant in the DNR fish surveys in the study region (Michigan DNR, 2015). The number of species present reflected the complexity of the food web and availability of different prey for top predators. Scenarios were chosen over using actual lake surveys due to the limited availability of recent fish surveys for lakes in the Upper Peninsula. The available fish surveys did not encompass the full range of lake sizes throughout the study area. Population dynamics were not included in BASS simulations due to the use of these theoretical scenarios. Details for each scenario project file are listed in Table A. 4. All fish files and fish community files were provided by the EPA (C. Barber, personal communication, 2014). Walleye fish files were adjusted according to the calibration adjustments (Figure A. 3).

2.2.6 Desired Fish Consumption

The Michigan Department of Community Health (MDCH) sets fish advisory limits for the state. Their basis for determining safe consumption limits was followed to determine a concentration of PCBs in fish that would ensure the safety of sensitive populations at a desired level of consumption. The MDCH defines sensitive populations as children under 15 and women between the ages of 15-45. This latter population has an average body weight (BW) of 65.4 kg. The most recent update for Fish Consumption Screening Values (FCSVs) sets the reference dose (RfD) as 0.02

µg/kg-day. This value was chosen to safely protect against harmful immune system effects caused by PCBs (MDCH, 2012).

A desired amount of fish consumption depends on the human population of interest as well as the fish species. It is important to set limits rather than ban consumption, as many groups desire to consume certain fish species. For the Keweenaw Bay Indian Community (KBIC), walleye have an important cultural significance. The KBIC is a local stakeholder in Michigan's Upper Peninsula who are concerned with safe fish consumption. Due to their traditions, there are certain times of the year when walleye are consumed at higher quantities than recommended by fish consumption advisories. During a recent talking circles event with the KBIC, the question of a desired amount of fish was posed to this stakeholder. The desired fish consumption was two meals of walleye/day, where one meal is equal to 8 ounces of fish (Gagnon, 2014).

The EPA provides an equation for determining the consumption limit used by the MDCH for safe human consumption (EPA, 2000):

$$\text{contamination amount} \left(\frac{\mu\text{g contaminant}}{\text{kg fish}} \right) = \frac{RfD \left(\frac{\mu\text{g}}{\text{kg-day}} \right) \times BW \text{ (kg)}}{\text{fish consumption (kg/day)}} \quad [2.59]$$

Using equation 2.56, 2.88 µg/kg (or 2.88 ppb) is the amount of PCBs in fish that is safe in order for the KBIC to consume their desired quantities.

$$\text{contamination amount} \left(\frac{\mu\text{g contaminant}}{\text{kg fish}} \right) = \frac{0.02 \left(\frac{\mu\text{g}}{\text{kg-day}} \right) \times 65.4 \text{ kg}}{0.454 \text{ (kg/day)}} = 2.88 \frac{\mu\text{g}}{\text{kg}} \quad [2.60]$$

2.3 Results

2.3.1 Source of Contamination

PCA identified two combinations of congeners that explained much of the differences among the lakes (i.e., divided them along two axis) on a per species basis (Figure 2. 8). Of the 18 lakes, only in Manistique Lake were PCB congener concentrations significantly correlated with both components ($p < 0.05$). The two components accounted for 90.1% and 90.9% of the total variance in the congener concentrations in northern pike (*Esox lucius*) and walleye (*Sander vitreus*), respectively. These species were the only possible options for comparison as no other species were common to all lakes. Based on regression factor scores, the PCB congeners that most affected component A were 138, 153 and 167 while component B was most affected by congeners 44, 49, 52, 66, 74, and 77. It is important to note that Goose Lake and Torch Lake were sampled for both walleye and northern pike. Knowing that Torch Lake's sediments are contaminated with PCBs, all lakes correlated with the same component (or axis) as Torch Lake have a likelihood of being locally, industrially impacted (Figure 2. 8 and Figure 2. 9).

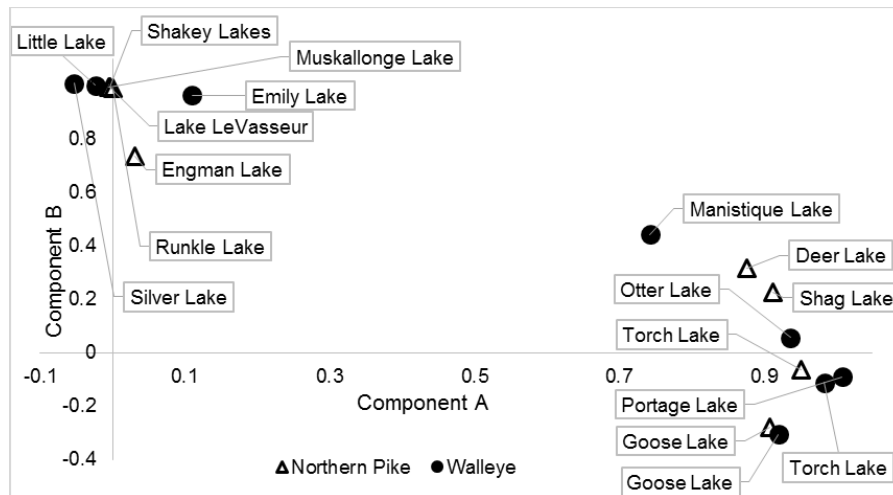


Figure 2. 8: PCA results. Each species were analyzed separately. The first component accounts for the most variance among the data. For the two analyses, the first component was not the same for lakes that contained both species. Therefore, component A consists of the first component for Walleye-sampled lakes and the second component for Northern Pike-sampled lakes (vice versa for component B) so that lakes sampled for both species correlated with the same component.

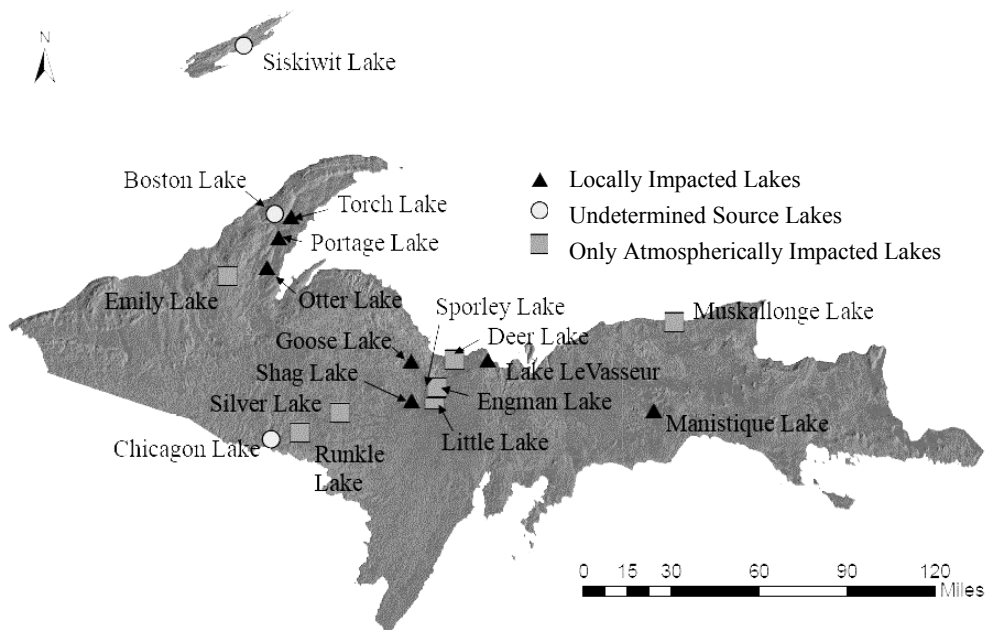


Figure 2. 9: Summary of Lakes categorized by means of PCA in terms of PCB source. Three lakes were not categorized due to the unique species sampled.

2.3.2 Ecosystem Characteristics

MLR analysis revealed mean depth to be the component that could most accurately predict PCB concentrations ($r^2=0.76$) (Figure 2. 10). Omitting mean depth from the analysis returned lake area as the next best predictor ($r^2=0.57$).

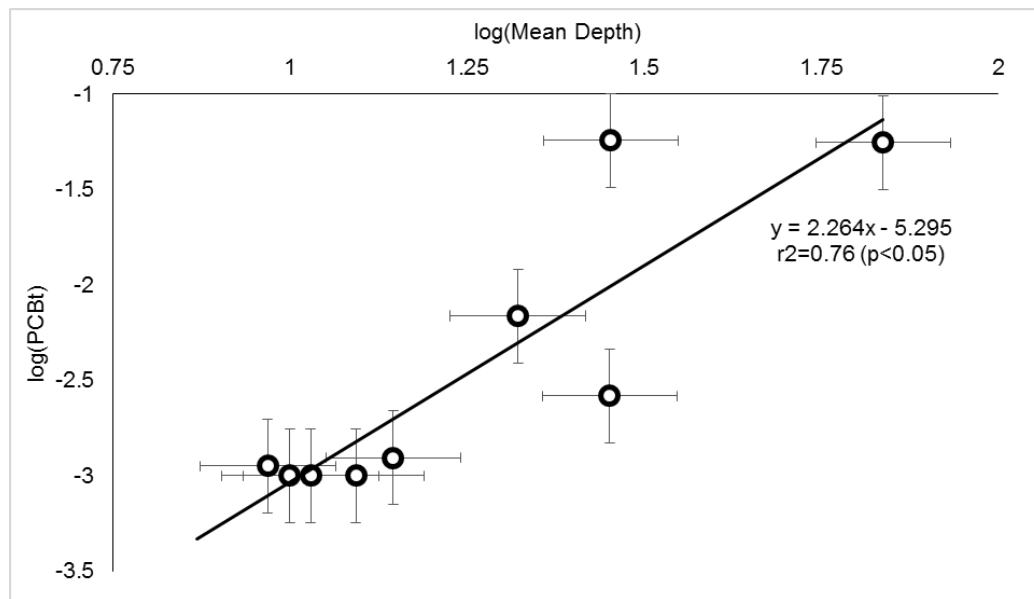


Figure 2. 10: Multiple Linear Regression Analysis results. Mean depth (ft) was determined to be the best predictor of total PCB concentration (PCBt) in sampled fish. Error bars represent standard error.

2.3.3 Ecosystem Model Scenarios

Figure 2. 11 through Figure 2. 14 show the output for selected species among the modeled scenarios. The models predict that oligotrophic lakes have higher PCB concentrations in fish while the smaller of the lake categories in each figure are more susceptible to high fish PCB concentrations as well.

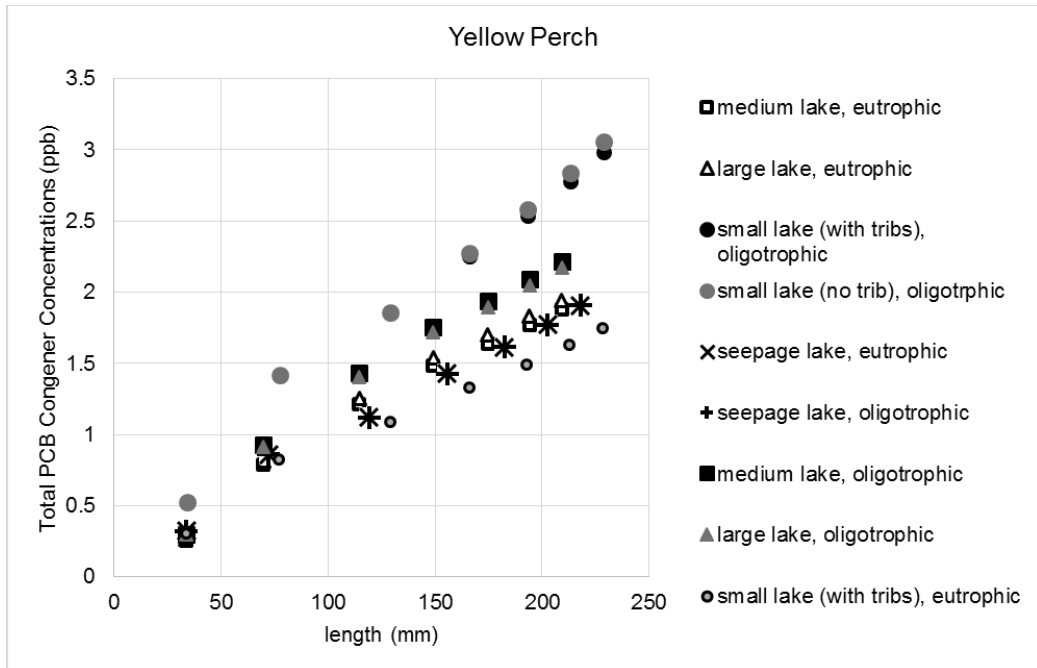


Figure 2. 11: EPA's BASS scenario outputs for yellow perch. Each lake scenario contained this species so that all lakes had one commonality.

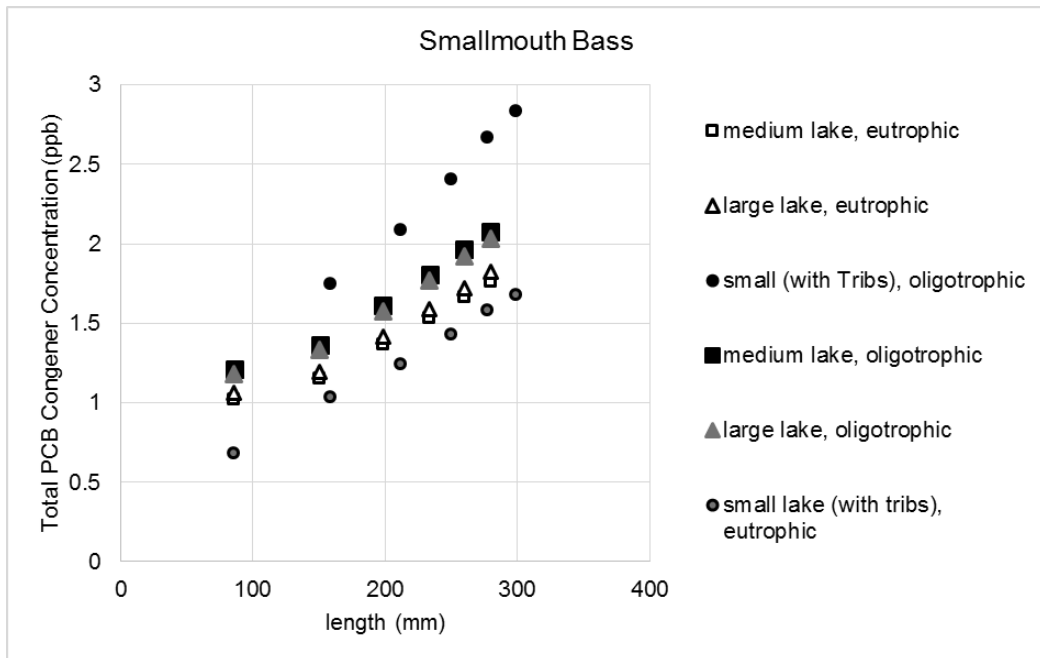


Figure 2. 12: EPA's BASS scenario outputs for smallmouth bass.

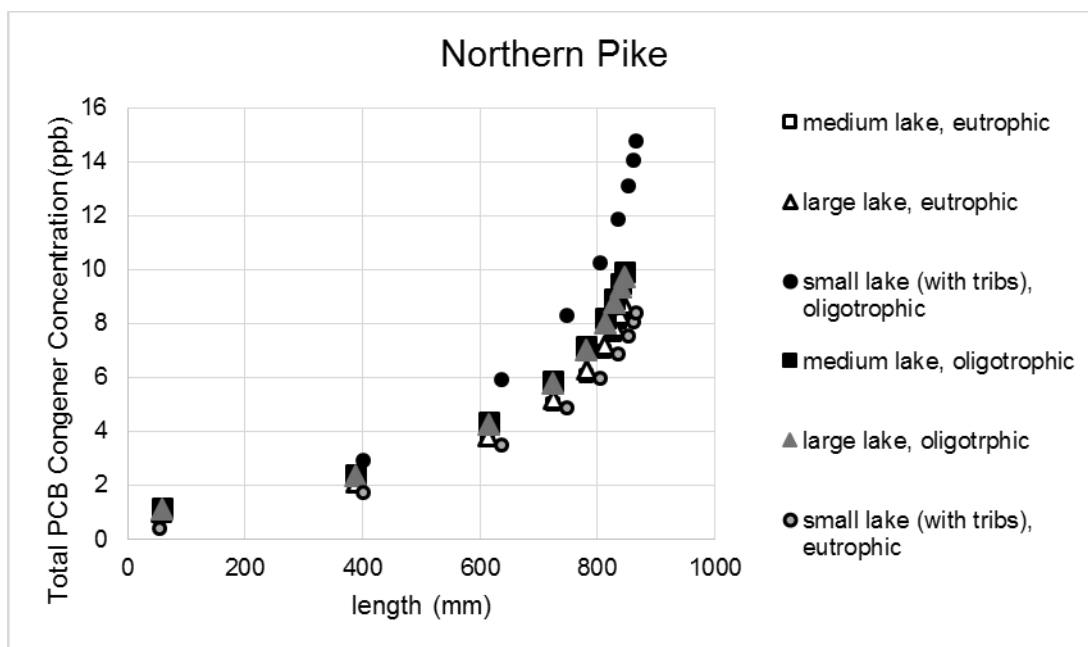


Figure 2. 13: EPA's BASS scenario output for northern pike.

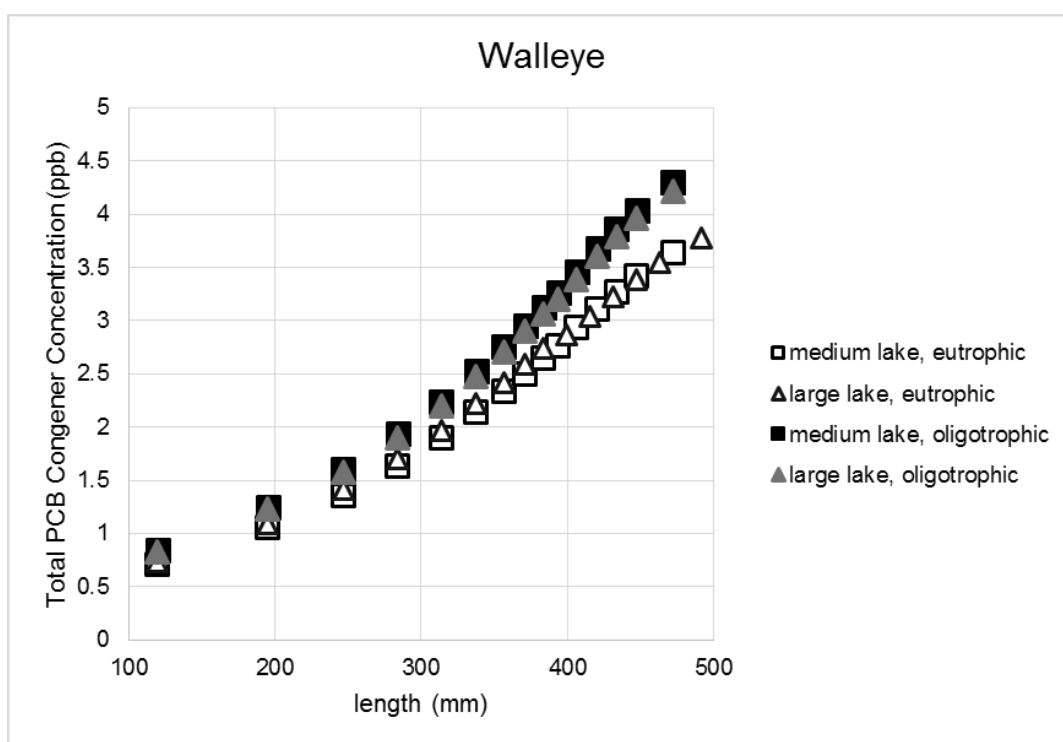


Figure 2. 14: EPA's BASS output for walleye.

A summary of the Cheruvelil EPA-NLAPP 6-state lake-landscape database was completed to determine the percentage of lakes in Michigan's Upper Peninsula that are most susceptible to high PCB contamination based on lake characteristics (Reinl, K., personal communications, 2015). Table A. 5 through Table A. 8 summarize all lakes in the database that had all characteristics needed for the analysis. Of the inland lakes in the Cheruvelil EPA-NLAPP 6-state lake-landscape database, 30 did not contain catchment size. For the 105 lakes that had all of the details necessary, it was determined that 15% of them were most susceptible to high PCB contamination in fish based on lake trophic state and lake size category (oligotrophic and small lakes). If this dataset reflects the distribution of lakes across the Peninsula, then roughly 600 lakes are likely to have high concentrations of PCBs in fish where the PCBs originated from atmospheric sources.

2.3.4 Desired Fish Consumption

In order to determine when in the future it may be possible to consume the desired amount of fish, the desired consumption of walleye was used as the threshold or end-goal. Using current atmospheric concentrations as the initial model input, the PCB lake model and EPA's BASS model were used to determine by how much atmospheric concentrations need to change in order for this safe consumption to be a reality. Manistique Lake (Figure 2. 15) and the theoretical scenario lake with the highest walleye PCB concentrations (Figure 2. 16) indicated that a drop of 42% in atmospheric PCB concentration from 2006 levels would be necessary to reach the target fish concentration.

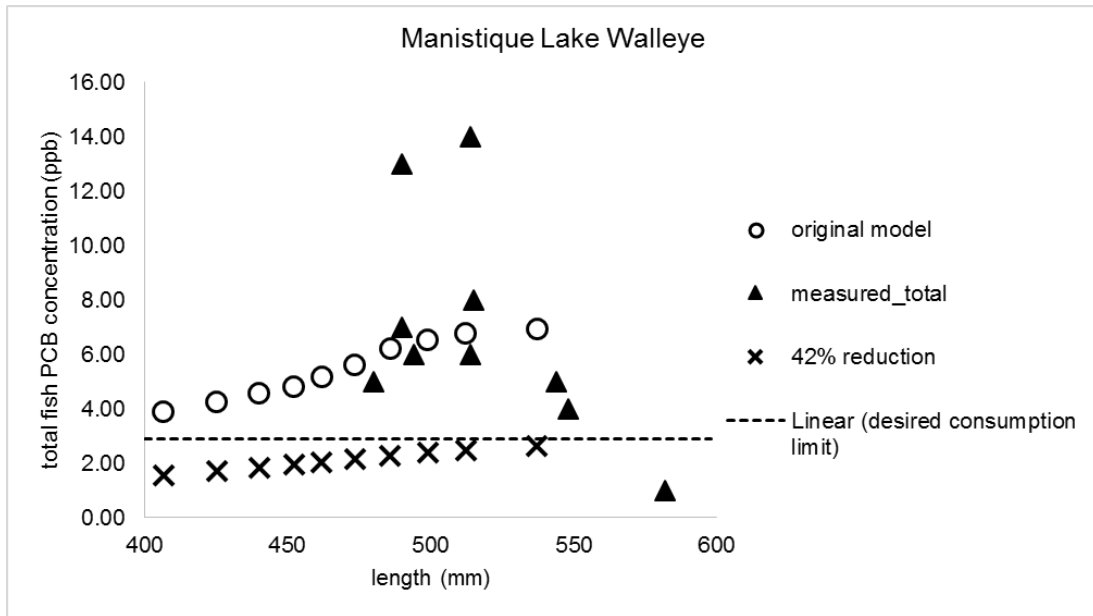


Figure 2. 15: EPA's BASS output for Manistique Lake walleye, measured DEQ data (Bohr, 2013) and reduced atmospheric PCB concentration in BASS. By reducing atmospheric concentrations of PCBs by 42%, the concentration in all sizes of walleye would drop below the desired fish consumption limit.

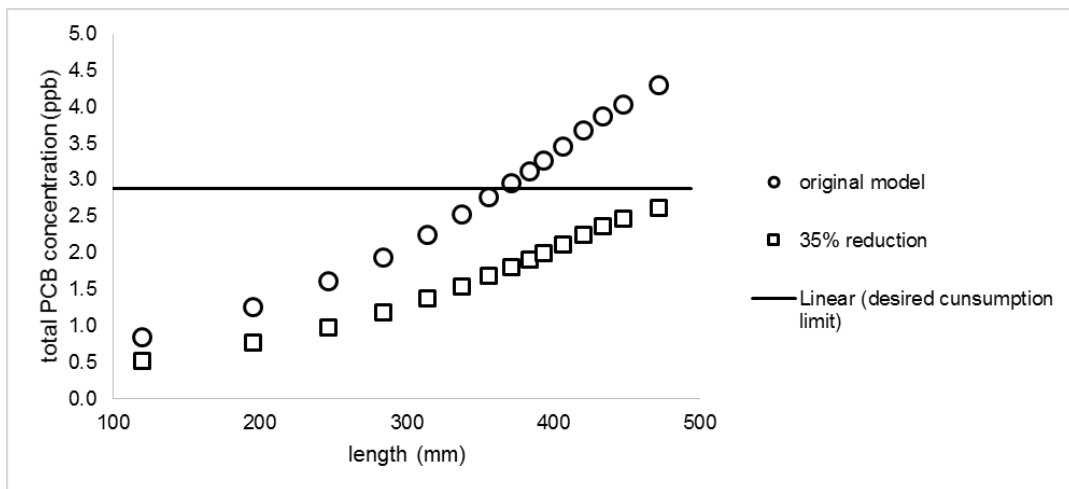


Figure 2. 16: EPA's BASS output for the medium oligotrophic lake. If atmospheric concentrations of PCBs were reduced by 35%, walleye of all sizes would be below the desired fish consumption limit.

2.3.5 Response Times of Lakes and Fish Species

As air concentrations of PCBs continue to decrease, a change in lake and biota concentrations follow. However, these responses are not immediately evident; it takes time for the lake and biota to re-equilibrate from the changed level of exposure.

Equation 2.40 was used to calculate the time to steady state (t_{ss}) for the PCB lake model (Schwarzenbach et al. 2003). The time to steady state for dissolved PCBs in Lake Superior and inland lakes ranged from 3.5 to 30 and 0.2 to 1.2 years, respectively. The time to reach steady state for PCBs in fish tissue (assuming steady state was reached once the contaminant concentration reached 95% of the final concentration) ranged between 4 and 7 years, depending on the fish species of interest (Figure 2. 17). Thus, a maximum of 37 years would be required for the heaviest congener to reach steady state in Lake Superior, and 8 years in a typical inland lake following a sudden drop in atmospheric concentrations.

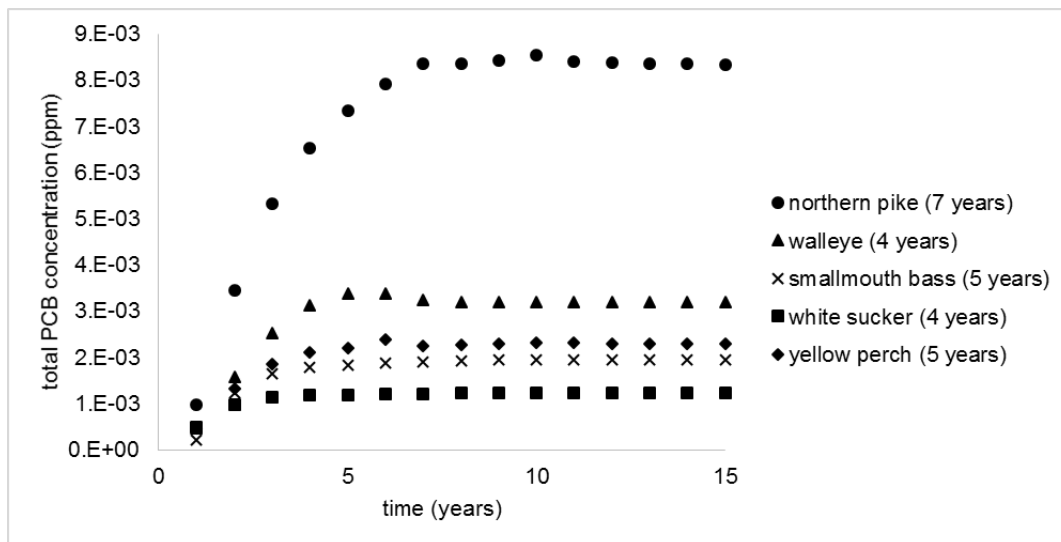


Figure 2. 17: Time to steady state for 5 common fish species in Michigan's Upper Peninsula Manistique Lake. The legend provides the time to steady state for each species in parenthesis.

2.4 Discussion

2.4.1 Source Determination

While it is widely accepted that PCBs impact all Michigan lakes through atmospheric deposition (MDEQ and US EPA Region 5, 2013), the extent of local, point source contamination is unknown. Other studies have used PCA to distinguish between PCB sources via congener distributions. A study of Milwaukee Harbor Estuaries and another of the Hudson River used congener distributions in the same manner to distinguish sources of PCBs (Rachdawong et al., 1997; and Monosson et al., 2003). Monosson et al. (2003) also found distinguishable PCB congener patterns, concluding that it was likely related to the source of contamination.

The results of the principal component analysis suggested that some inland lakes in Michigan's Upper Peninsula may have local sources of contamination. Only one sampled lake is known to have point sources of PCB contamination— Torch Lake (Mandelia, 2015) — both of which correlate to Component A in the PCA results. The fact that two lakes known to have local contamination had high scores on component A of Figure 2. 8 combined with the fact that heavier PCB congeners are weighted most heavily in component A, suggests that all lakes falling along this axis may be locally impacted. Fish from these lakes have relatively more of the heavier congeners; although food web factors cannot be ruled out, the presence of heavier congeners that are less likely to travel far from their original emission location via volatilization suggests that local contamination may exist in these lakes. To verify the existence of local sources, sampling (e.g., passive samplers spatially distributed

throughout the lake) would be required. It is important to note that Manistique Lake significantly correlated with both components. This lake was listed as PCB-impaired under the state-wide TMDL (total maximum daily load) (MDEQ and US EPA, 2013). It is interesting to note that Goose Lake also falls along the axis of local contamination. This lake has fish consumption advisories for selenium contamination caused by mining in Marquette County (MDEQ, 2009). The potential for local contamination of other chemicals associated with mining activities, including PCBs (Mandelia, 2015), could also be of concern for Goose Lake.

The use of PCA for source determination was limited to northern pike and walleye because these fish species were the most widely sampled species of the inland lakes. When comparing multiple species in the same analysis, there were no distinct groupings of lakes (not shown). This was likely due to differences in fish species characteristics that can significantly affect PCB accumulation (e.g., growth rate, size, trophic position, lipid content). This limited the number of lakes that could be included in the analysis. The lakes sampled by the MDEQ have public access. The sampling locations are not spread evenly across the Peninsula (Figure 2. 1); there seems to be a greater sampling preference for lakes in Marquette County where lakes have known point sources of chemical pollutants (e.g., Goose Lake has high selenium concentrations). The explanation for sampling preference is not known, but frequency of angler fishing and human population density around the lakes may be factors.

2.4.2 Ecosystem Characteristics

Linear regression analysis has been used to determine which ecosystem characteristics affect chemical bioaccumulation. Studies using regression analysis have found different factors to be more significant for mercury accumulation. Dissolved organic carbon (DOC), pH, lake morphometry and wetland area were considered significant factors for particular fish species (McMurty et al., 1989; and Clayden et al., 2013). While lake morphometry importance overlaps for PCBs and mercury, there seem to be many other lake properties influencing mercury accumulation. Since mercury can be transformed in a waterbody into its more readily available and toxic form (methylmercury), it is logical that chemical characteristics have a stronger effect on mercury. PCBs do not change as significantly. However, the concentration of DOC can have an effect on the concentration of dissolved PCBs (Berglund et al., 2001a).

It is important to note that not all physical lake characteristics could be included in the analysis because not all were measured across the peninsula. For example, in Michigan's Upper Peninsula, many lakes have a high concentration of dissolved organic carbon (DOC) and many are dystrophic, or contain high amounts of humic substances and organic acids. DOC affects the partitioning of PCBs in the water column, where higher DOC can reduce the concentration of dissolved PCBs which lessens the likelihood of bioaccumulation. Dystrophic lakes also have a lower visibility which reduces secchi depth, causing discrepancies in the true trophic status

of a lake. The concentration of DOC and the level of dystrophy in lakes is not well recorded by the State of Michigan and could not be well accounted for in this study.

Multiple Linear Regression (MLR) analysis was used to determine which lake characteristic(s) best predicted the total PCB concentration in fish within the nine lakes included in Michigan's Fish Contaminant Monitoring Program. The use of MLR to determine which lake physical or chemical characteristics adequately predict PCB or other persistent chemical accumulation in fish is typically done for one fish species only (e.g., Clayden et al., 2013; Ruus et al., 2002; Bentzen et al., 1996). Conducting MLR for just one fish species was not possible in this assessment because of the limited number of lakes and multiple species sampled in the study area. Only the nine lakes determined by PCA to have predominantly an atmospheric source of PCBs were included in this analysis. By including multiple species, additional sources of variability (trophic position, fish lipid content, fish age and growth rate) may contribute noise to the analysis and obscure the influence of lake characteristics. On the other hand, this approach identifies factors affecting all fish within a lake, not just factors affecting a single species.

While the number of lakes was limited, a strong correlation was observed between lake mean depth and PCB concentration ($r^2=0.73$, $p < 0.01$). In other words, the deeper the lake, the higher the PCB concentration in fish. The second best predictor, lake surface area ($r^2=0.569$), also points towards lake size as being of paramount importance. Several factors likely contribute to the influence of lake depth and surface area. A larger lake (surface area or depth) may have a longer

hydraulic residence time and slower flushing, allowing higher accumulation of PCBs within the lake water. PCB water concentrations in Lake Superior are most affected by atmospheric deposition, due to its large surface area (Rowe et al., 2009). A deeper lake may have a longer settling time and slower removal of PCBs by this mechanism as well. Larger lakes also have a higher likelihood of containing longer food webs, where top predators contain higher contaminant concentrations. For example, Rasmussen et al. (1990) found that lake trout contamination could be explained by food chain differences and lipid content. Larger lakes also have a greater likelihood of containing more pelagic feeding habitat, which Guildford et al. (2008) found to increase PCB contamination in lake trout. This conclusion is important for public understanding. With an awareness that fishing in smaller lakes with high primary production could reduce human exposure (as long as the small lakes have short hydraulic residence times), safer fishing habits could be taught/developed.

For the lakes excluded from the MLR analysis, which were those determined by PCA to have a high potential for local, industrial impacts, the regression equation under-predicts PCB concentrations in Torch Lake, Portage Lake, Otter Lake and Manistique Lake. For these lakes, the average measured total PCB concentration ranges from 1.4 to 4.3 times higher than what was predicted by the model. This provides additional confirmation that a local source of PCBs is impacting some lakes in Michigan's Upper Peninsula.

2.4.3 Ecosystem Model Scenarios

Due to the limited number of fish surveys available and the paucity of common species among the surveys, this study modeled lake categories to test the relative effects of lake characteristics on PCB accumulation in inland lakes. Recent fish surveys by the Michigan Department of Natural Resources (DNR) were limited in number and varied in regards to top predators and species presence. The small variability in fish community structure may be a reflection of the prevalence of stocking as well as the reality that commonly fished lakes span a narrow range of lake characteristics. However, the surveys do not provide information on the range of food webs in Michigan's Upper Peninsula. Lake size can significantly affect species richness and community composition (i.e., the common top predators). To include the full range of potential food webs, a variety of scenarios were modeled with EPA's BASS to assess PCB accumulation. The scenario analysis suggested that smaller oligotrophic lakes are likely to have fish with the highest levels of PCB contamination. It is not surprising that eutrophic systems have lower concentrations of PCBs in upper trophic level fish. These results are supported by existing literature: 1) the higher rate of settling in eutrophic systems reduces the level of exposure to the food web over time (Berglund et al., 2001a); 2) The level of contamination at the base of the food web is lower because of the greater amount of biomass (Kidd et al., 1999); and 3) the lipid content at the base of the food web is also lower in more eutrophic systems where there is greater competition for food, lowering the amount of PCBs that tend to accumulate in fatty tissue (Berglund et al., 2001b). Lake size has not been

deemed a significant factor in previous studies in which the level of PCB contamination in fish did not vary greatly while surface area and volume of the study lakes did (Paterson et al., 1998). Volatilization is the most significant rate of PCB loss for an inland lake according to the PCB lake model (Figure A. 4 through Figure A. 6). As the mean depth of a lake increases the rate of volatilization declines (Equation 2.18), indicating the potential importance of lake size. Volatilization varies more significantly for lighter congeners, settling is slightly more variable for heavier congeners and loss through flushing is similar for all congeners in the modeled inland lakes.

If the dataset of lakes used to develop the hypothetical scenarios is reflective of the distribution of lakes in Michigan's Upper Peninsula, 600 lakes are likely susceptible to high concentrations of PCBs in fish. Knowing this, it is important to understand what lakes would be best to avoid for fishing because of PCB exposure. The relatively small lakes with the lowest primary productivity have the highest PCB concentrations in fish according to theoretical modeling.

Due to the results of MLR analysis where mean depth explained a large amount of the variance in the dataset, the importance of physical characteristics may outweigh the significance of food web differences. The consideration of other physical lake characteristics may provide further explanation into the accumulation of PCBs that could not be evaluated here. One such characteristic is the frequency of turnovers. Shallower lakes can undergo multiple turnovers each year, re-exposing biota to PCBs that have undergone settling. The significance of these events is

unknown because the numbers of turnovers for inland lakes is unknown. For the inland lakes used in MLR, there was a positive correlation between mean depth and surface area. This overall increase in lake volume may also play a role in PCB exposure due to longer hydraulic residence times or colder depths for larger, older fish. Incorporating more physical data to the ecosystem scenarios and linear regression may explain more trends in total PCB contamination as well as links between physical characteristics that could not be evaluated in this study.

2.4.4 Response Times

Due to the internal cycling of PCBs within a lake and the turnover time of the fish community, a decline in fish contamination will not be seen instantly when atmospheric PCB concentrations decline. Depending on lake size and trophic state, the rate of removal of PCBs from the water column (i.e., burial and outflow loss) varies. According to the PCB lake model, the time to steady state can vary significantly between the Great Lakes and inland lakes. For Lake Superior, time to steady state for PCB congeners ranges from 3.5 to 30 years. For inland lakes, the time is much shorter, ranging 0.2 to 1.2 years.

The growth rate of a fish species affects how long it is exposed to PCBs before reaching a size suitable for human consumption. For example, coho salmon can reach the same length as lake trout in considerably less time due to their faster growth rates. Therefore, coho salmon typically have lower PCB content than lake trout of the same size (Pearson et al., 1996). According to the EPA's BASS model, the time to steady state for yellow perch, northern pike, walleye, and smallmouth bass

found in inland lakes in Michigan's Upper Peninsula is between 4 and 7 years. Thus, with the combination of lake and fish response times (ranging from 4.2 to 37 years), it could take about a decade after atmospheric concentrations decline for PCB content in fish to be positively affected.

Salamova et al. (2015) summarized the rate of decline of atmospheric PCBs in the Great Lakes Region according to measurements provided by the Integrated Atmospheric Deposition Network. It was determined that the half-life of total PCBs in the atmosphere was ~13.2 years over Eagle Harbor (Salamova et al., 2015). This halving time was used here to estimate how long it would take for PCBs to decline by 40% to reach desired fish consumption concentrations because Eagle Harbor air concentrations from 2006 were used to model the BASS ecosystem simulations. If atmospheric PCBs continue to decline at the same rate in Michigan's Upper Peninsula, and no new sources of PCBs are emitted to the atmosphere, atmospheric PCB levels will reach acceptable concentrations in about 8 years for Michigan's Upper Peninsula. With the additional response time for inland lakes and fish, it is estimated that PCBs will be below the desired fish consumption limit in about 20 years. The half-life of PCBs in the atmosphere of other locations in the Great Lakes region vary, ranging from about 12 to almost 19 years (Salamova et al., 2015). Thus, the time it will take for the entire Great Lakes Region to have safe fish for consumption according to PCB contamination could be longer than 20 years. Thus, the time it will take for the entire Great Lakes Region to have safe fish for consumption according to PCB contamination could be longer than 20 years.

2.4.5 Model Improvements

Some improvements or enhancements in EPA's BASS program would help to reveal the effects of other fish and ecosystems characteristics on PCB bioaccumulation. The predictions of periphyton, phytoplankton, zooplankton and benthos abundance (equations 2.49-2.55) have large uncertainty, but other predictive relationships are unavailable. The fish diets used in the BASS simulations were based on typical dietary habits for each species provided by Mr. M. Craig Barber of the EPA (personal communication, July 1st through September 22nd, 2014). Fish diets vary depending on changes in food availability seasonally, among lakes, and due to human impacts. In order to assess the effects of diet in Michigan's inland lakes, a more thorough analysis of inland fish dietary habits is needed. The range of dietary preferences could then be added as a new element to food web modeling and the theoretical scenarios. Typical diets for the study region could then be compared to the amount of littoral zone in a lake to determine if there is a significant difference in PCB accumulation due to a more pelagic or littoral diet. The effect of littoral feeding has been studied in lake trout producing conflicting results, while the consequences for other species have not been widely studied (Guildford et al., 2008; Gewurtz et al., 2011b; Lopes et al., 2011).

Accurate modeling of fish communities requires accurate measurements of population sizes. The scenarios used to test the effects of lake trophic state and lake size used FGETS because the differences in population that would be typical for each

lake size are unknown. More fish surveys in contrasting lake types would also determine the accuracy of the food webs used in the theoretical scenario analysis.

Most of the studies that have used the EPA's BASS were conducted on lakes near the east coast and in the southern United States. The predecessor to BASS, FGETS, was used to study PCB accumulation in Lake Ontario fish and indicated that gill exchange is more significant than previously thought (Barber et al., 1991). Other studies have used FGETS and BASS to assess PCB and mercury accumulation in the eastern half of the United States (Marchettini et al., 2001; Brockway et al., 1996; Johnston et al., 2011; VDEQ, 2005). Studies using the population dynamics capabilities in BASS are less common because of the need for more detailed information on a water bodies' ecosystem and the relative amount of time BASS has been available.

This is the first time EPA's BASS has been used for Michigan's Upper Peninsula inland lakes. While some fish species are found in both the Midwest and across the country, the growth rate, habitat preference and dietary preferences are likely different due to adaptation to the environment and differences in a given species' niche. This is the likely explanation for why the walleye fish file needed to be adjusted to adequately describe the size and maximum age of the species to match what was measured by the MDEQ.

EPA's BASS has a convenient output analyzer that, after running a project file, can produce figures depicting a range of model outputs. These outputs include comparisons of fish weight, length and age to the total concentration of the chemical

of interest, bioaccumulation factors, and species population. These figures can easily be produced for a single chemical. However, when assessing multiple PCB congeners at once, the output analyzer could not produce figures using available software; the amount of data was too great. The capabilities of the output analyzer need to be improved to accommodate the large number of PCB congeners.

According to the literature, effects of fish sex may not be significant for modeling accumulation except for walleye. In a comparison of multiple fish species common to Michigan's Upper Peninsula (i.e. whitefish, yellow perch, smallmouth bass and northern pike), Gewurtz et al. (2011a) recommended that individual fish consumption advisories be made for male and female walleye. It was concluded by Madenjian et al. (2011) that sex accumulation differences caused by gross growth efficiency affect all species, but the differences are moderate. Overall trends for sex differences are not necessary for incorporation in the BASS program due to the high variability in significance for most species; it would be an unnecessary effort until the significance has been proven crucial. However, it would be fascinating to see if walleye sex differences could be adequately explained using BASS.

2.5 Conclusion

The inland lakes assessment provided key insight into PCB contamination in the study region. Principal Component Analysis revealed that some lakes sampled by the Michigan Department of Environmental Quality may have point sources of contamination or are more susceptible to PCB accumulation. Multiple Linear Regression Analysis showed that mean depth was the best predictor of PCB

accumulation across lakes of varying characteristics and fish species. This revealed that the size of the lake can impact the bioaccumulation of PCBs. Additionally, lake food web modeling revealed that lake trophic state and hydraulic residence time have a significant impact as well. While all lakes in the study region are impacted by PCBs, 15% are most susceptible to higher contamination levels and are of greatest concern because of their physical characteristics. To avoid this higher exposure to PCBs, it is recommended not to fish in lakes with low primary productivity and long hydraulic residence times. With the response time of the inland lakes and fish species, it takes roughly 10 years for a change in atmospheric PCB concentrations to be seen in fish. With this time delay, and according to the measured rate of decline in atmospheric PCB concentrations, it will take roughly 20 years for inland lakes with no local point sources of PCBs in Michigan's Upper Peninsula to reach the level of consumption desired by local indigenous communities.

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CHAPTER 3: GREAT LAKES ASSESSMENT

3.1 Introduction

The Great Lakes are an abundant source of fish to consumers throughout the region. Their sheer size and unique characteristics provide a variety of habitats; the bay and littoral zones sustain multiple food webs within each Great Lake. Chemical contaminants are not spread evenly throughout each lake. The level of PCB contamination in fish varies widely due to local contamination (i.e. areas of concern and superfund sites), high emissions from urban areas, water currents and flow rates of rivers and bays (Zhang et al., 2008; Burniston et al., 2011).

To reduce human exposure to PCBs, it is important to understand which type of water body contains the safest fish for consumption. While there are always exceptions (e.g. local contamination), providing an overall recommendation for where it is best to fish can help to reduce risk while continuing to promote fishing in the State of Michigan. Evers et al. (2011) compiled a comparison of mercury in fillet fish samples in the Great Lakes and inland lakes in the Great Lakes Region. The comparison encompassed all species sampled from 2000 to 2008 from several monitoring efforts. It was concluded that mercury contamination was higher in fish from inland water bodies as compared to the Great Lakes. A similar comparison has yet to be made for PCBs.

While studies have been conducted on different lake sizes in the Great Lakes region and the corresponding PCB concentrations in fish, none have involved such a

large geographic extent for PCB contamination in Michigan involving so many fish species. Bentzen et al. (1996) compared PCB concentrations in a single species, lake trout, from the Great Lakes and a few inland Ontario lakes. This study expands on this earlier work by comparing the level of PCB contamination in multiple species from dozens of inland water bodies to the contamination found in the Great Lakes.

Since the ban on production and import of PCBs in 1970s, the level of contamination has declined in the Great Lakes. This decline has been documented through decades of sampling by the Great Lakes Fish monitoring Program (GLFMP). Carlson et al. (2010) summarized lake-wide trends in lake trout and walleye, showing that the rate of decline has been slowing in recent years. Other studies have also reported the decrease of PCBs in fish tissue (Borgmann and Whittle, 1991; Szlinder-Richert J. et al., 2009; Bhavsar et al., 2007), water (Jeremiason et al., 1994) and air (Hillery et al., 1997; Simcik et al., 1999; Salamova et al., 2015). Trend analyses typically utilize linear regression (Hillery et al., 1997; Simcik et al., 1999; Borgmann and Whittle et al., 1997). Exponential declines have also been reported (Jeremiason et al., 1994). Due to the efforts of the MDEQ, it was possible to see time trends of PCB contamination in Great Lakes fish for over two decades. Instead of an overall lake trend, the sites sampled revealed whether local clean-up efforts have been successful as well as if the decline in PCBs is statistically significant. Generally, time trends have focused on lake-wide confirmation that contaminants are declining. This analysis is unique because it focuses on specific locations where more remediation could reduce fish PCB contamination.

The MDEQ has been sampling fish for PCBs since the 1980s. Over time, the method for processing the fish has changed as technology has improved. Two analytical techniques have been used most frequently. The technique originally used to measure total PCB concentrations in biota was an Aroclor-based analysis. Aroclors are specific mixtures of PCBs designed by manufacturers and dominated by specific PCB congeners. Each Aroclor mixture was given a numerical ID indicating the weight percentage of chlorine in the mixture (e.g., Aroclor 1242 had 42% chlorine). Originally, Aroclors were measured by gas chromatography using a packed column and an electron-capture detector. Individual congeners were not resolved by this method; rather, a broad peak for an aroclor mixture eluted from the column. Beginning in the 1980s, packed columns were replaced with capillary columns that did resolve many of the individual congeners. At that point, the congeners could be summed to yield total PCB concentration, or a statistical program could be applied to determine the best fit to the Aroclor mixtures (e.g., Capel et al. 1985). This method assumes that PCBs are not degraded over time or differentially transported and still reflect the original Aroclor mixture. The longer the PCBs are present in the environment, the lower the accuracy of this method due to congener transformation and environmental fractionation.

Improvements in analytical techniques (better chromatographic separation, congener-specific identification via mass spectrometry) have made it possible to detect each congener in a sample. While more expensive, the new analytical

techniques yield congener and total-PCB concentrations that are not inferred from original Aroclor mixtures (Sather et al., 2001).

Comparisons of the two methods have been conducted and have yielded variable results because there are multiple variants of both methods, ranging from the use of multiple Aroclor mixtures or the summation of selected PCB congeners. Sather et al. (2001) compared the techniques, using the sum of three Aroclor mixtures (1242, 1254 and 1260) and the sum of 206 PCB congeners from the congener analysis method. In this comparison, the two techniques were very comparable (regression slope=1.079, $r^2=0.96$). Another study (Connor et al. 2005) compared methods recommended by the U.S. EPA for Aroclor analysis and the NOAA method for total PCB congener analysis. The NOAA method involved the sum of a subset of PCB congeners and the use of a regression equation to calculate the total PCB concentration. It was determined that total PCB concentrations determined for Aroclors 1248, 1254 and 1260 were typically five-fold lower than those calculated by the NOAA congener method (Connor et al., 2005). In conclusion, it seems the two methods for PCB tissue analyses have varying levels of comparability depending on which version of each method is used.

The MDEQ has used the congener method to determine the total PCB concentration for over a decade. The total PCB concentration is calculated as the sum of all congener concentrations that are above the detection limit (MDEQ, 2010). Prior to the adoption of the congener method, an Aroclor method was used that determined

the total PCB concentration from different Aroclor mixtures. It was desired to determine if the decline in PCB concentration was significant over time and how comparable were the Aroclor and congener methods for estimating total PCB concentrations in fish.

The Great Lakes were cross-compared using statistical analysis to reveal why PCB contamination varies among them and what is causing the variations. Previous studies have linked highly urbanized watersheds with higher PCB contamination in local water bodies (King et al., 2004; Paul et al., 2002). The Great Lakes, due to their size, differ from inland lakes in physical, chemical and food web characteristics. Other research has shown that concentrations vary by location in each Great Lake (Dellinger, 2004; Bhavsar et al., 2007). Using Multiple Linear Regression (MLR) analysis, the best predictor of total PCB concentration in fish for inland lakes was determined to be mean depth (Section 2.3.2). It was desired to see which predictor(s) could explain PCB contamination in the Great Lakes by using the same statistical analysis. Multiple physical characteristics (i.e. secchi depth, watershed area, surface area, mean depth and maximum depth) were factored into the analysis as well as features that pertain to local contamination (i.e. population, population density and distance to a known local contamination source). The local contamination factors were included because, according to PCA results, many sites were concluded to be locally impacted (see Section 3.4.3). Population and population density are linked to the level of urbanization within a watershed. The amount of developed land within a watershed has been linked to higher PCB contamination in nearby waters in multiple

studies (King et al., 2004; Paul et al., 2002). It was desired to see if the same could be said for the sites sampled by the MDEQ (Figure 3. 1).

The objectives of this research were to: 1) provide an accurate comparison of inland lake versus Great Lake PCB concentrations in fish, 2) evaluate time trends for PCB concentrations in fish, and 3) assess the causes for variable contamination levels among the Great Lakes. The analyses and comparisons completed involved inland lakes from Michigan's Upper and Lower Peninsula and each Great Lake sampled by the Michigan Department of Environmental Quality (MDEQ). These analyses are important to enhance the understanding of how PCBs have affected the Great Lakes Region. These new results can help to focus remediation efforts to locations where significant improvements are still possible.

3.2 Methods

3.2.1 Great Lakes Region Contamination Comparison

To compare the PCB concentrations in inland and Great Lakes, data were compiled from the MDEQ's Fish Contaminant Monitoring Program (FCMP). Because the sampling and analyses for this program are planned and executed by a single group, the methods are consistent across all sites and over time. The FCMP samples multiple fish species throughout the state and along the shores of the Great Lakes (Bohr, 2015). The fillets are processed for multiple contaminants, including PCB congeners and total PCB concentration (Figure 3. 1). Skin-on or skin-off sampling depended on the species for fillet samples (MDEQ, 2014). The average total

PCB concentration for each fish species in each water body category since the year 2000 were lipid normalized to remove the variability of fat content from the comparison. The water body categories included inland lakes, rivers and the Great Lakes. The data were divided into subcategories: Michigan's Upper and Lower Peninsula's rivers and inland lakes, and each of the Great Lakes. Lake Ontario was not sampled because the database is for the State of Michigan's water bodies only. These subcategories were chosen to compare spatial differences in addition to the water body categories.

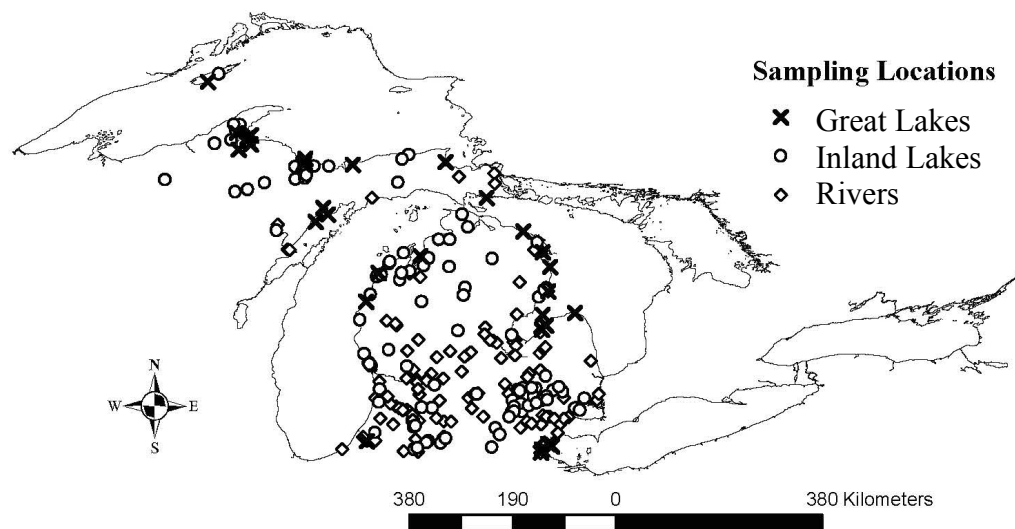


Figure 3. 1: MDEQ sampling locations (2000-2015) for edible fish monitoring program (data from Bohr, 2015).

3.2.2 Time Trend Analysis

The MDEQ has designated several sites in the Great Lakes and in inland water bodies for trend monitoring under their Fish Contaminant Monitoring Program (FCMP) (Figure 3. 2). For trend monitoring, whole fish rather than fillets are used.

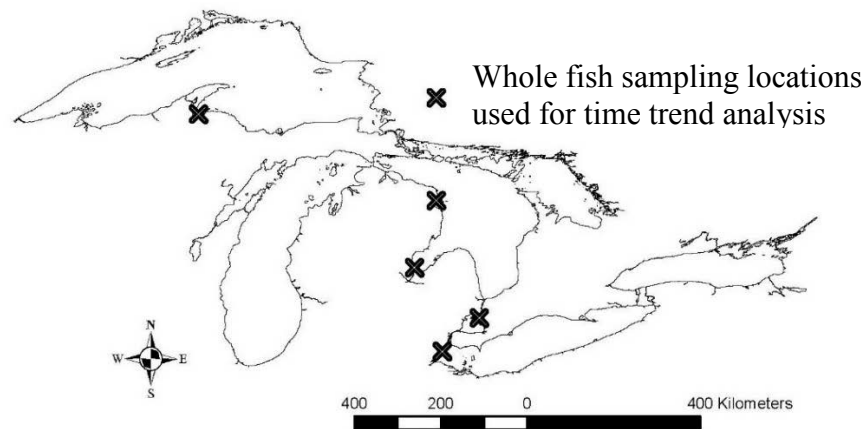


Figure 3. 2: Trend monitoring sites in the MDEQ Fish Contaminant Monitoring Program (MDEQ, 2015). The sites used in this analysis include Keweenaw Bay (lake trout), Thunder Bay (lake trout), Saginaw Bay (carp), Lake St. Clair (carp and walleye), and Brest Bay (carp and walleye).

Established in the 1980s, this program provides its fish contaminant data on the FCMP Online Database. The total PCB concentrations were used in this analysis (MDEQ, 2013). Conveniently, the MDEQ overlapped the use of both its Aroclor method and congener method for a few years in the 1990s, allowing for a direct comparison between the estimated total PCB concentrations. Five sites in the Great Lakes that had lake trout, carp and/or walleye samples were compared. There was at least one year of overlap between the two PCB analysis methods for each fish sampled. Linear regression analysis (General Linear Model (GLM) II) was used to quantify the relationship between results from both methods using fish analyzed during the overlapping years (generally 10 fish per site per year). Model II linear regression was used because neither the Aroclor method nor the congener method estimates of total PCB concentrations are free from measurement error. The resulting regression equations, one for each species from each site, were used to “convert” the

Aroclor method estimates of total PCB concentration to that of the newer, congener method (Figure B. 16 through Figure B. 22).

Time trend analysis was conducted by regressing (type I regression) total PCB concentration vs. time. Regressions were performed for each fish species in each location. To evaluate the effect of the change in methodology, regressions were performed using total PCB concentrations from both analytical methods and using the adjusted total PCB concentrations from the aroclor method with the results from the congener-specific method. For each fish species, total PCB concentrations were averaged for each year for use in the regression analysis.

3.2.3 Source Identification

PCA was performed using IBM SPSS Statistics 22. Average, lipid-normalized congener concentrations were calculated for walleye and northern pike samples from each site where available (Bohr, 2015). The fish species were chosen so that they could be compared to the inland lake analysis. Two PCA analyses, one for each species, were performed. The analysis was limited to two factors to compare with inland lake results. Direct oblimin rotation was used as well. The congener distributions were limited to 34 congeners because those were above detection limits for the majority of samples. If a concentration was under detection limit for one of the 34 congeners considered, the value was set at the detection limit. Samples used in the analysis were limited to 40 to 50 cm and 60 to 70 cm in length for walleye and northern pike, respectively. This ensured that the samples were comparable in size. Age would have been used for this criteria had it been determined in the fillet

analysis. Table 3. 1 summarizes the sites and species used for the analysis. The inland lakes were the same water bodies as in the analysis for Michigan's Upper Peninsula (Section 2.2.1) and were included for further comparison of these distinct water bodies.

Table 3. 1: MDEQ sampling location used for PCA analysis (Bohr, 2015).

Water Body	Sampling Location	lat/long	Species
Lake Superior	Keweenaw Bay, L'Anse Bay	46.76/-88.45	northern pike
Lake Superior	Huron Bay	46.85/-88.26	walleye and northern pike
Lake Michigan	Little Bay De Noc	45.79/-87.05	walleye and northern pike
Lake Erie	Off Monroe	41.89/-83.33	walleye
Lake Erie	Western Basin	41.86/-83.27	walleye
Lake Michigan	Green Bay, Cedar River	45.56/-87.18	walleye
Lake Superior	Huron Bay	46.85/-88.26	walleye
Lake Superior	Tahquamenon River	46.56/-85.03	walleye
Lake Huron	Saginaw Bay, Bay Port	43.86/-83.37	walleye
Lake Huron	Saginaw Bay	43.78/-83.44	walleye

3.2.4 Ecosystem Characteristics

Average total PCB concentrations were calculated for each Great Lakes site sampled by the MDEQ for edible fish portion contamination. Site characteristics were used as independent variables in MLR analysis and correlation analysis to evaluate their contribution to the variability in average fish PCB concentrations at each site. MLR analysis was performed using IBM SPSS 22. Enough locations sampled walleye between 40 and 50 cm in length so that the analysis could be limited to one species. This eliminated confounding effects from multiple fish species. The nearest site of known local contamination, either an Area of Concern or Superfund

site, was factored into the analysis by calculating the distance from the potential source to the sampling site (Figure 3. 3). Physical characteristics of the bay or basin where fish were collected were used rather than characteristics for the entire Great Lake. The population factored into the analysis was estimated based on the area of each bay or basin's catchment area. Table B. 5 summarizes all details of site locations, variables and referenced information used for the analysis. All variables and concentrations were log-transformed for the analyses.

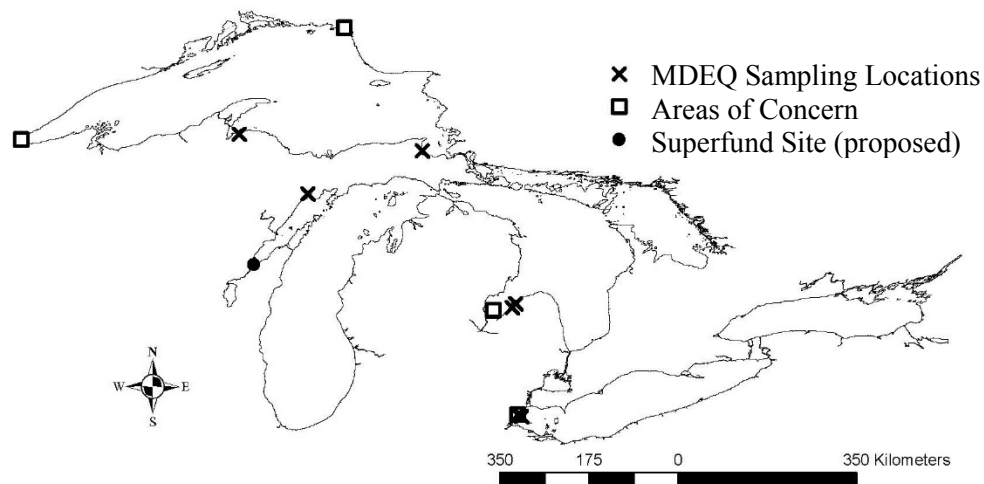


Figure 3. 3: MDEQ Great Lakes sites sampled for walleye between 2000 and 2015 along with the potential sources of known local PCB contamination that could affect the sites.

Stepwise forward and backward multiple linear regressions were compared to determine which variables explained more variance in fish PCB concentrations. Stepwise forward MLR finds the variable that explains the most variance and adds additional variables if any improve the outcome of the analysis. Backward MLR considers all variables initially and removes those that do not explain variance in the dependent variable or increase the total error of the analysis. Pearson Correlation

analysis was performed on all independent variables and the average total PCB concentrations in walleye.

3.3 Results

3.3.1 Great Lakes Region Contamination Comparison

Figure 3. 4 through Figure 3. 7 summarize the lipid normalized, average total-PCB concentration in fish sampled by the MDEQ for edible fish-portion monitoring since 2000. A Kruskal-Wallis test revealed that the variance is so large, that there was no statistical difference among them ($p>0.05$). Additionally, t-tests (pair-wise or assuming equal or unequal variance, as appropriate) led to the same conclusion for all groups ($p>0.05$). These statistical analyses were performed for both the common fish species among all groups and any common species between groups. These figures show only fish species commonly found in all three water body categories— inland lakes, rivers and the Great Lakes- for the most direct comparison. Figure B. 1 through Figure B. 9 summarize all species sampled in each water body category. Table B. 1 through Table B. 3 provide a more detailed summary of sampling (e.g., sampling sites and number of samples).

Among the Great Lakes, Lake Michigan had the highest PCB contamination, followed by Lake Huron; Lake Superior had the lowest contamination. The distribution of total-PCB concentrations among common fish species for each Great Lake was also determined (Figure B. 10 through Figure B. 15). The distributions, in the form of box plots, revealed that the level of contamination in individual fish

ranged from 0.2 ppm in lake trout to 14 ppm in carp. Lake Superior had the lowest variance in PCB concentrations for most fish species while the Great Lake with the highest variability differed among fish species. River fish typically had higher PCB concentrations than fish from inland lakes. It is important to note that these trends are not true for all fish species.

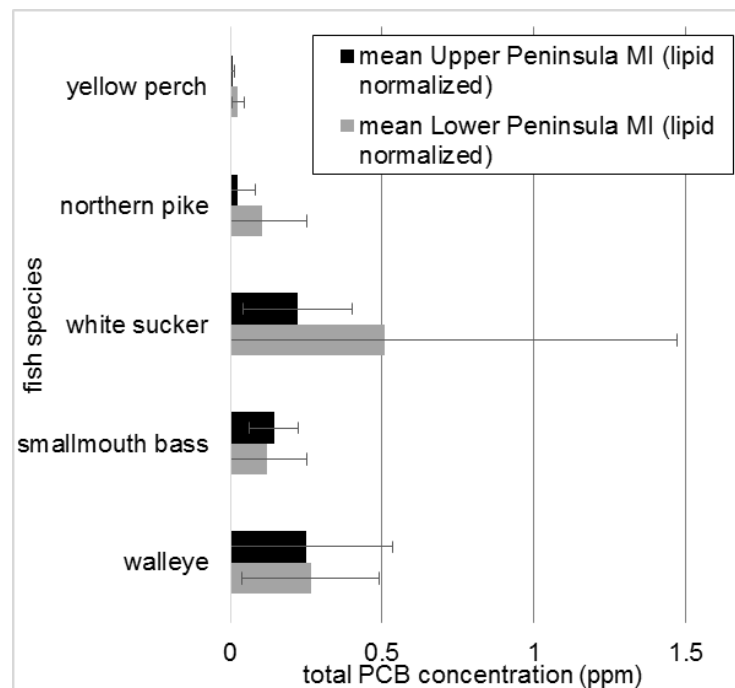


Figure 3. 4: MDEQ fish fillet data summary (2000-2015) of Michigan Rivers (Bohr, 2015). Data summarized in Table B. 1. Error bars indicate one standard deviation.

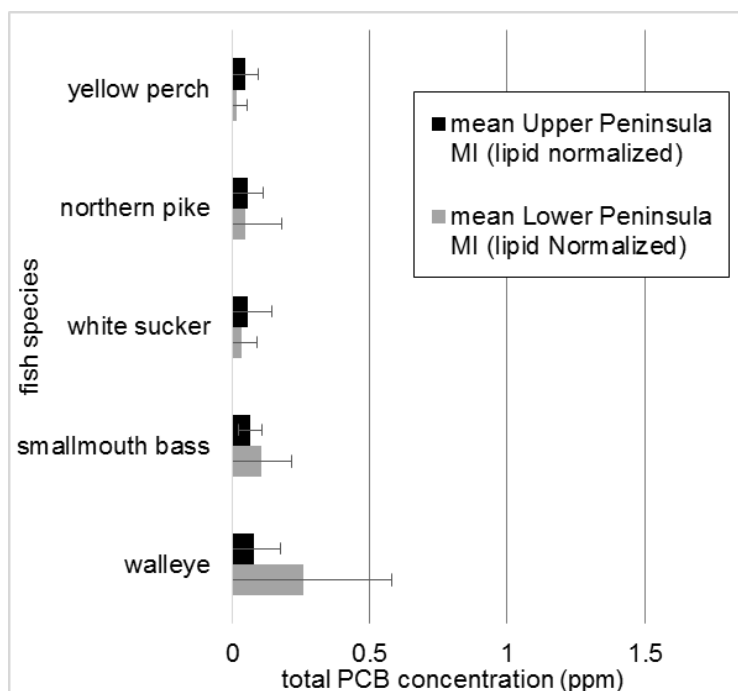


Figure 3. 5: MDEQ fish fillet data summary of Michigan inland lakes (Bohr, 2015). Data summarized in Table B. 1. Error bars indicate one standard deviation.

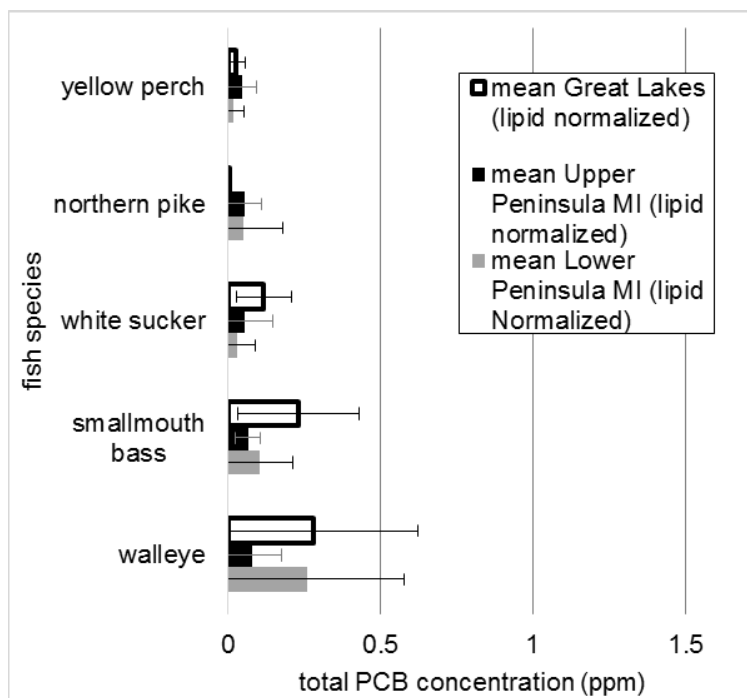


Figure 3. 6: MDEQ fish fillet data summary of inland lakes and Great Lakes (Bohr, 2015). Data summarized in Table B. 2 and Table B. 3. Error bars indicate one standard deviation.

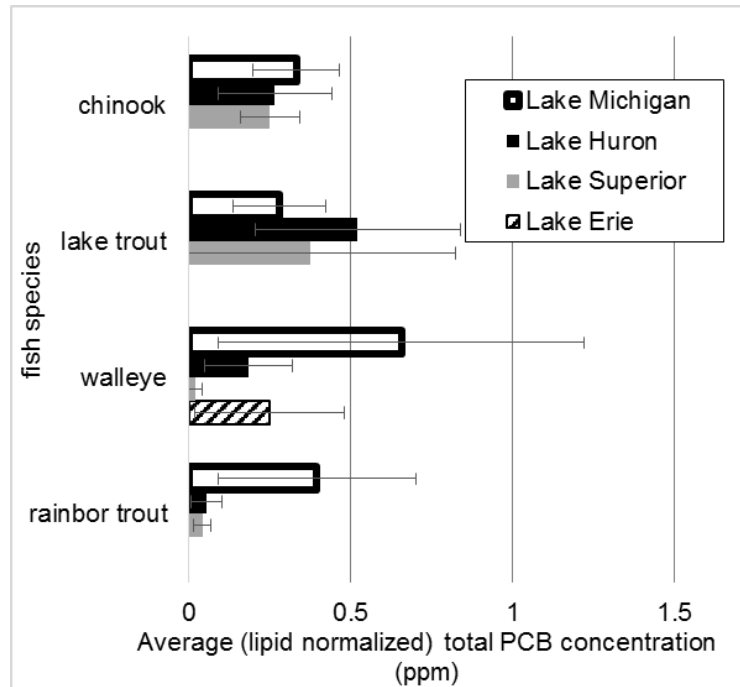


Figure 3. 7: MDEQ fish fillet data summary of Great Lakes (Bohr, 2015). Data summarized in Table B. 2 and Table B. 3. Error bars indicate one standard deviation.

3.3.2 Time Trend Analysis

Figure 3. 8 through Figure 3. 14 summarize the results of the comparison and time trend analysis. The regressions in these figures include all of the years where the congener method was used to calculate total PCB concentrations as well as the adjusted Aroclor method concentration estimates for any prior years. The difference between the Aroclor method and congener method ranged from ± 0.08 to 1.52 ppm, on average, for all sites and species. All declines in total PCB concentration were found to be statistically significant except for carp from Brest Bay in Lake Erie. After adjusting the PCB concentrations measured using the Aroclor method to be more, the rate of change in PCB concentration was reduced for most sites. Table 3. 2

summarizes the rate of change (i.e. the magnitude of slope change) caused by this adjustment.

Table 3. 2: Summary of differences in slope for all regressions in Figure 3. 8 through Figure 3. 14 from the original slope of decline.

Site Name	Great Lake	Fish Species	Magnitude of slope difference
Thunder Bay	Lake Huron	lake trout	5.5%
Lake St. Clair		walleye	7.0%
		carp	11%
Saginaw Bay	Lake Huron	carp	17%
Brest Bay	Lake Erie	walleye	61%
		carp	33%
Keweenaw Bay	Lake Superior	lake trout	-60%

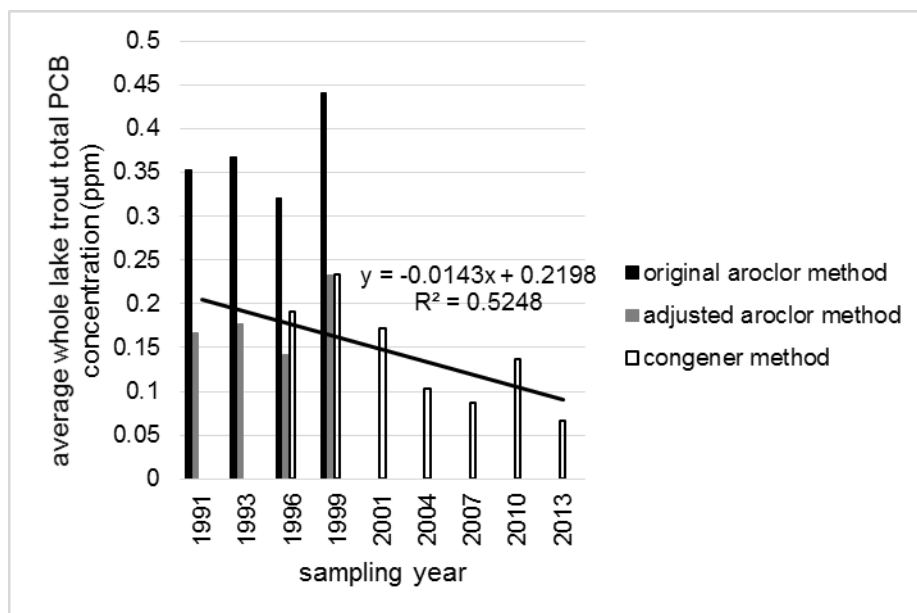


Figure 3. 8: Time trend analysis results for whole lake trout from Keweenaw Bay, Lake Superior (MDEQ, 2013). Pearson correlation $r = -0.726$, $p < 0.05$. Adjusted Aroclor method PCB concentrations were projected from regression analysis (See Figure B. 22). Total PCB concentrations were 44% to 53% lower according to the congener method compared to the Aroclor method.

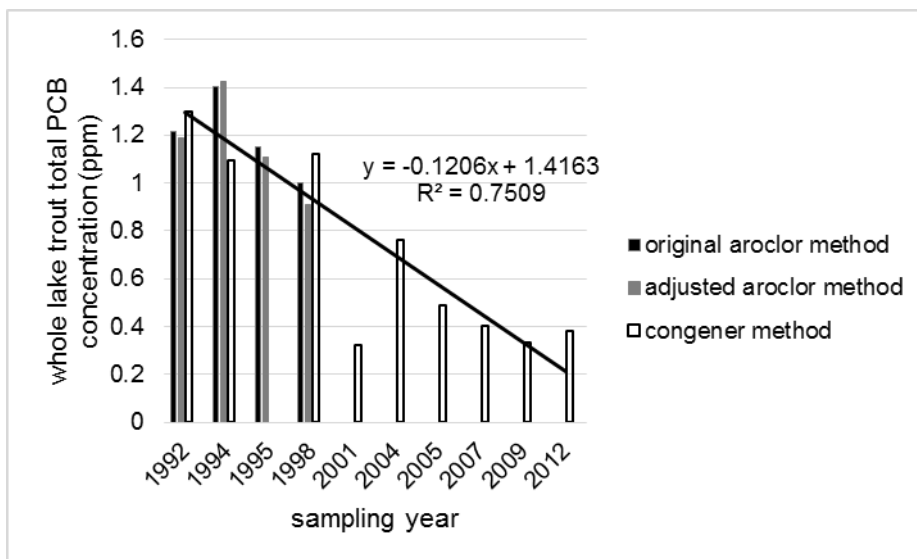


Figure 3. 9: Time trend analysis results for whole lake trout from Thunder Bay, Lake Huron (MDEQ, 2013). Pearson correlation $r = -0.87$, $p < 0.01$. Adjusted Aroclor method PCB concentrations were projected from regression analysis (See Figure B. 18). Total PCB concentrations were -9% to 2% lower according to the congener method compared to the Aroclor method.

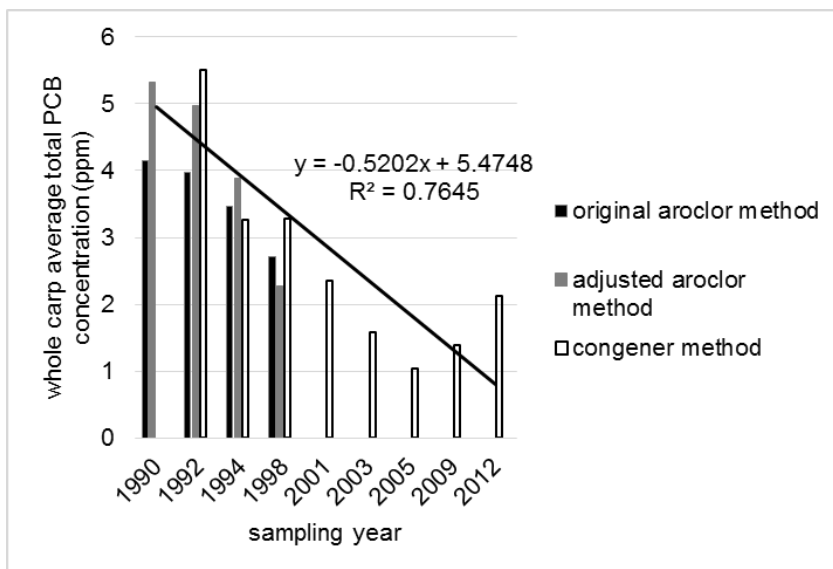


Figure 3. 10: Time trend analysis results for whole carp from Saginaw Bay, Lake Huron (MDEQ, 2013). Pearson correlation $r = -0.852$, $p < 0.01$. Adjusted Aroclor method PCB concentrations were projected from regression analysis (See Figure B. 19). Total PCB concentrations were -16% to 28% lower according to the congener method compared to the Aroclor method.

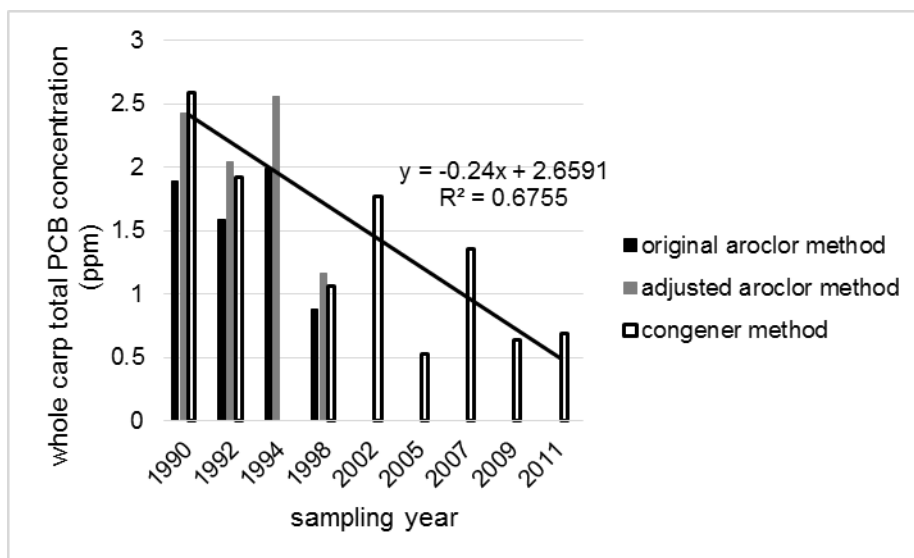


Figure 3. 11: Time trend analysis results for whole carp from Lake St. Clair (MDEQ, 2013). Pearson correlation $r = -0.839$, $p < 0.01$. Adjusted Aroclor method PCB concentrations were projected from regression analysis (See Figure B. 20). Total PCB concentrations were 29% to 31% lower according to the congener method compared to the Aroclor method.

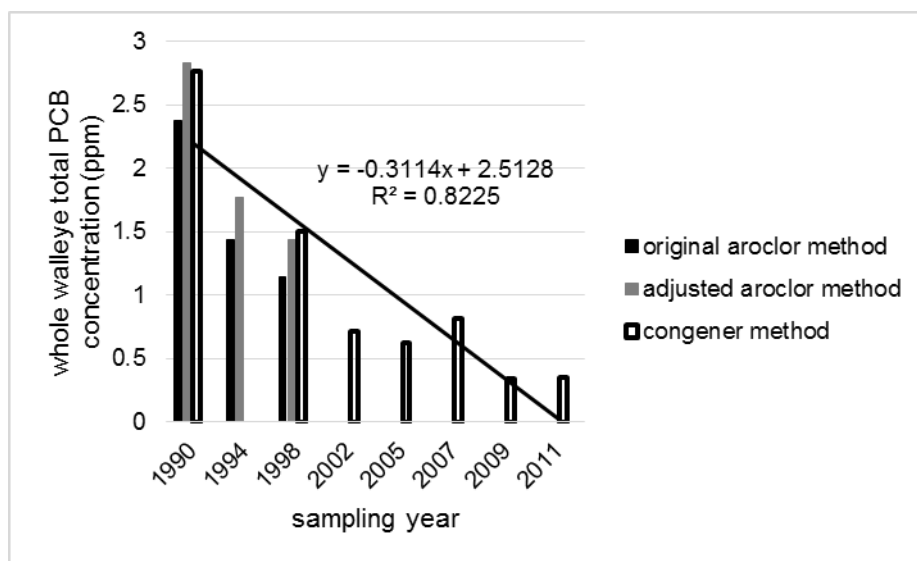


Figure 3. 12: Time trend analysis results for whole walleye from Lake St. Clair (MDEQ, 2013). Pearson correlation $r = -0.953$, $p < 0.01$. Adjusted Aroclor method PCB concentrations were projected from regression analysis (See Figure B. 21). Total PCB concentrations were 19% to 25% lower according to the congener method compared to the Aroclor method.

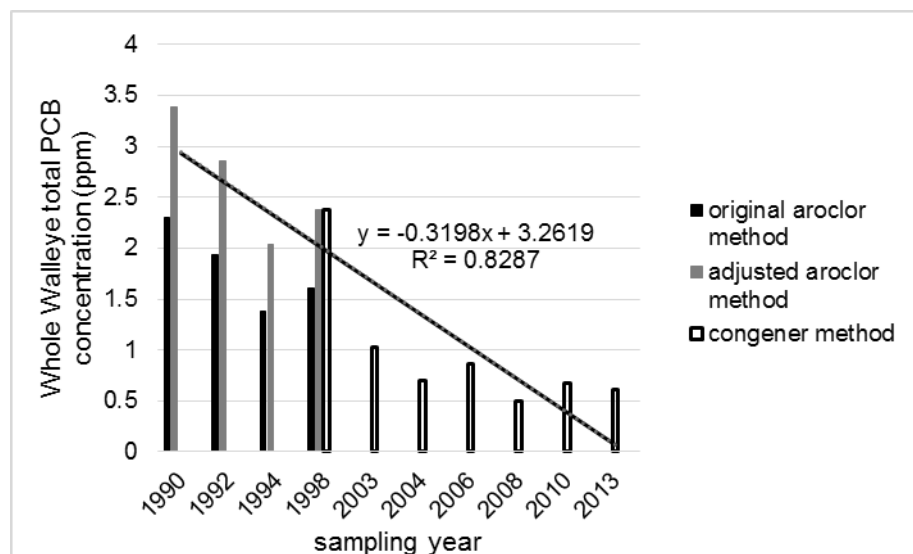


Figure 3. 13: Time trend analysis results for walleye from Brest Bay, Lake Erie (MDEQ, 2013). Pearson correlation $r = -0.935$, $p < 0.01$. Adjusted Aroclor method PCB concentrations were projected from regression analysis (See Figure B. 16). Total PCB concentrations were 47% to 48% lower according to the congener method compared to the Aroclor method.

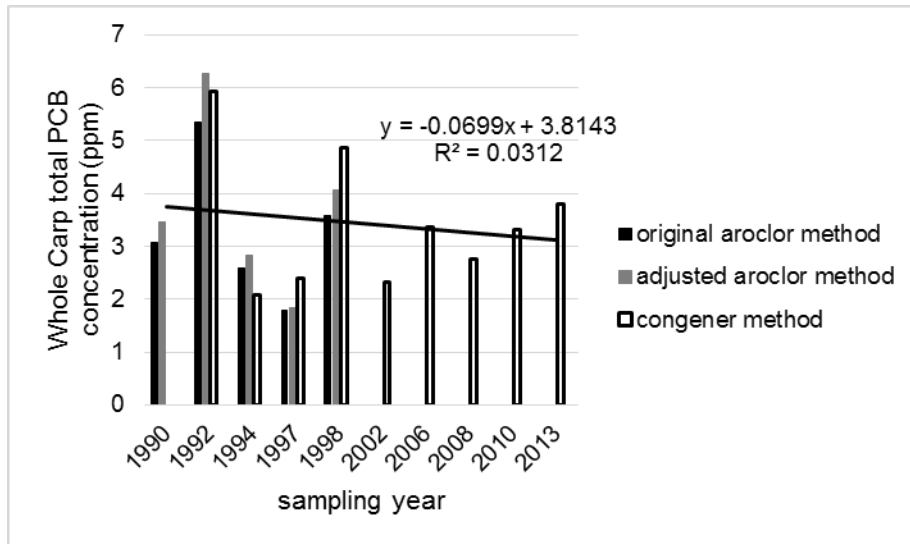


Figure 3. 14: Time trend analysis results for carp from Brest Bay, Lake Erie (MDEQ, 2013). Decline in concentration was not statistically significant. Adjusted Aroclor method PCB concentrations were projected from regression analysis (See Figure B. 17). Total PCB concentrations were 3% to 17% lower according to the congener method compared to the Aroclor method.

3.3.3 Source Identification

Based upon PCA, only three sampling locations— Manistique Lake (walleye), Lake Michigan’s Green Bay (walleye) and Lake Michigan’s Little Bay De Noc (northern pike)—had significant contributions from both components. Lake Superior was the only Great Lake where sites were designated as only atmospherically impacted (Figure 3. 15). 84% of the total variance was explained for walleye (component 1=63%) and 83% for northern pike (component 1=58%).

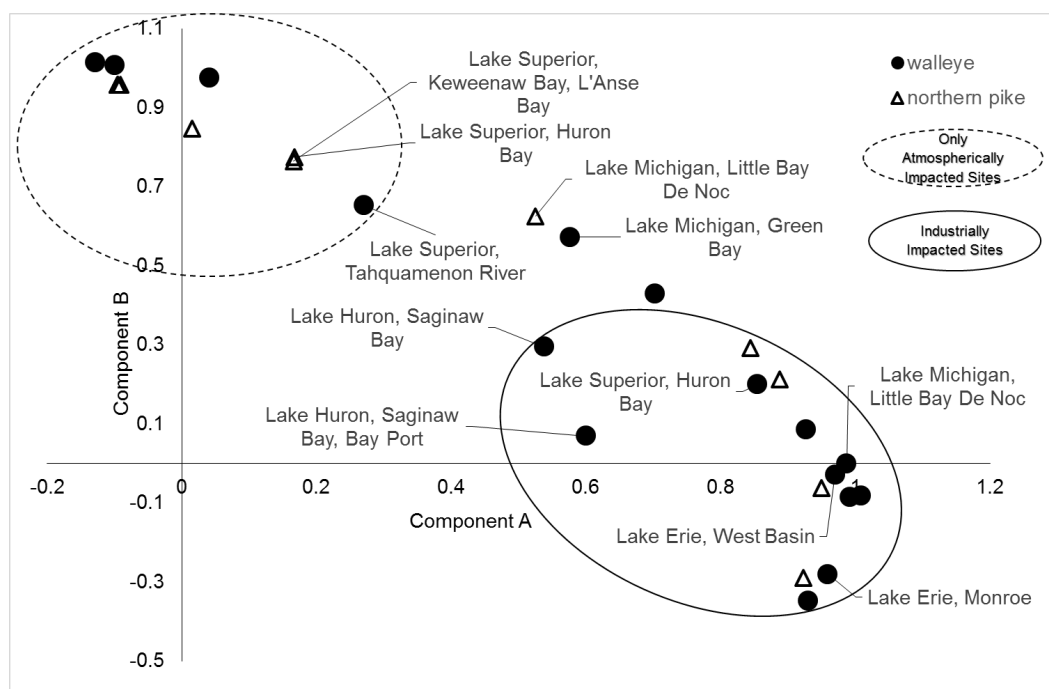


Figure 3. 15: PCA results comparing inland lakes from Michigan's Upper Peninsula to the Great Lakes (Bohr, 2015). Each species was analyzed separately. Component A consists of the first component for Walleye-sampled lakes and the second component for Northern Pike- sampled lakes (vice versa for component B). The component axes were altered so that the lakes sampled for both species (Goose Lake and Torch Lake) fell on the same axis. PCB congeners were weighted the same for both species in component B where lighter congeners were the most important; Component A was weighted by similar, heavy PCB congeners.

3.3.4 Ecosystem Characteristics

Of the two forms of MLR performed, backwards MLR produced the best fit; it explained more of the variance and had a lower standard error than the forward stepwise MLR analysis. Both forms of regression analysis had the same level of significance ($p < 0.006$). Stepwise MLR identified one variable (maximum depth) as the best predictor. The following equation is the result of the backward MLR analysis.

$$\log(\text{total PCB concentration (ppm)}) = 2.640 + 0.306 \log(\text{watershed area (km}^2\text{)}) - 2.747 \log(\text{max depth (m)}) - 0.628 \log(\text{population density}) \quad [3.1]$$

The watershed area, maximum depth and population density (human population over watershed area) accounted for 8.1%, 74.3% and 15% of the variance, respectively, for a total of 97.4% of the variance in fish PCB concentrations. The standard error of the analysis was reduced to 14.7% as opposed to 33% for the stepwise linear regression. Figure 3. 16 shows the fit of the backward MLR results to the measured total PCB concentrations at the site.

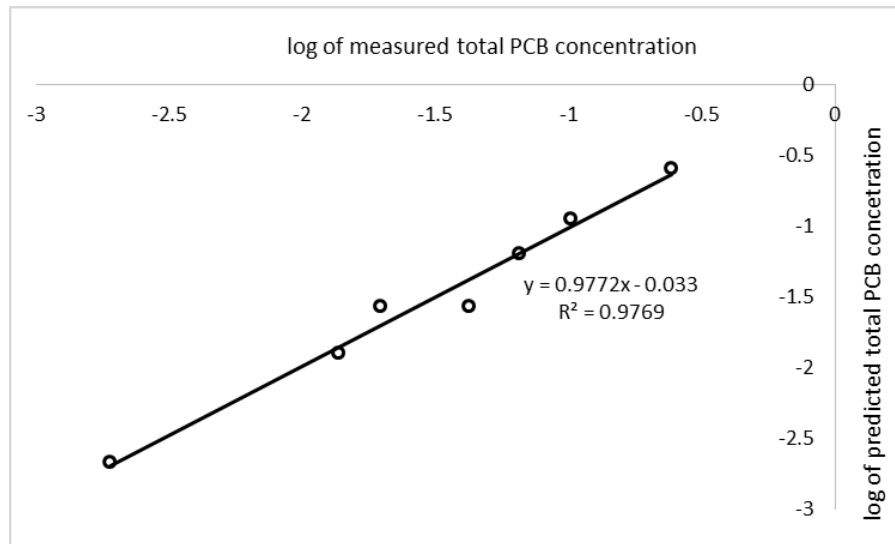


Figure 3. 16: Comparison of measured average total PCB concentrations (ppm) with those predicted by regression using three independent variables as selected by backwards MLR. Measured PCB data from MDEQ (Bohr, 2015).

Correlation analysis revealed six statistically strong correlations. Pairs of variables that were significantly correlated ($p < 0.05$) included population and distance to contamination, surface area and secchi depth, surface area and watershed area, and population density and population; factors that significantly correlated at the

99% confidence interval were population and watershed area, and total PCB concentration and maximum depth. Figure B. 23 shows the correlation matrix for all of the factors considered in the analysis. It is important to note that, according to the correlation analysis, one outlier exists for mean depth vs. total PCB concentration- the Tahquamenon River site in Lake Superior. Without this outlier mean depth was very significant ($r^2=0.80$).

3.5 Discussion

3.5.1 Great Lakes Region Contamination Comparison

Figure 3. 4 through Figure 3. 7 summarize the comparison of lipid normalized average total PCB concentrations in fish fillets of species from inland water bodies and the Great Lakes (sampling locations from Figure 3. 1). These figures were developed to compare the same species that were sampled from the different water body categories since 2000. It was determined that there was not a statistically significant difference between lake categories. There are some key points to glean from these figures. First, sampling efforts are not distributed evenly throughout the state and the Great Lakes. Less sampling, in regards to both the total number of samples and locations, has been completed for Michigan's Upper Peninsula relative to Lower Michigan. Second, sampling locations may not have been randomly distributed but preferentially located near to local contamination to assess cleanup efforts (e.g., the Kalamazoo and Detroit rivers have multiple sampling locations). Third, while the sampling locations in the Great Lakes are near shore, these are

locations where more fishermen are more likely to frequent. It becomes more expensive and less common to fish farther into the Great Lakes (Hoehn et al., 1996). In addition, many of the species sampled are more commonly found closer to shore.

According to the MDEQ dataset, among inland water bodies, four of the five comparable species had higher total PCB concentrations in rivers than in inland lakes. Three of the five fish species had higher contamination in Upper Peninsula rivers as compared to lakes, while all rivers in the Lower Peninsula had higher PCB contamination than the lakes. The PCB contamination in rivers may also reflect the non-random selection of sampling sites.

For three of the five species compared in Figure 3. 6, the Great Lakes had higher PCB concentrations in fish than those collected from inland lakes. However, it is important to look at each Great Lake individually (Figure 3. 7). Lake Michigan has always had the highest PCB contamination in fish, and Lake Superior has typically had the lowest (Carlson et al., 2010). Lake Ontario has historically had similar concentrations to those of Lake Michigan (Hickey et al., 2006). For this comparison, Lake Michigan had the highest total PCB concentrations for three of the four species compared in Figure 3. 7. The distribution of total PCB concentrations among sites can be seen in Figure B. 10 through Figure B. 15. Sites on Lake Erie and Lake Michigan tend to have the largest spread in sample concentrations. Among the fish types sampled, carp and lake whitefish have the highest and lowest levels of contamination, respectively. Overall, the Great Lakes tend to have higher PCB contamination in fish than inland lakes.

By using the general categories for lake types, there was not a statistically significant difference between them. These categories ignore the important differences in lake characteristics that affect PCB accumulation in fish, which were determined in Chapter 2 and 3. This finding only emphasizes the importance of taking lake and ecosystem characteristics into account when determining where it is best to consume fish from.

The results for PCBs contrast with those of Evers et al. (2011) who assessed mercury contamination of the Great Lakes and inland lakes. That study compared all species represented in multiple databases. In comparing multiple fish species, it was determined that inland lakes had higher mercury contamination in fish than the Great Lakes. This comparison focuses on a smaller number of species that are found in all categories of water bodies. By doing so, the confounding effects of varying species metabolism, fat content, and other biophysical characteristics are reduced. The use of only one database helps to reduce noise resulting from different sample handling and analysis protocols.

3.5.2 Time Trend Analysis

The MDEQ has made an exemplary effort to assess PCB contamination in fish in the Great Lakes since the inception of the Fish Contaminant Monitoring Program in 1988.. The consistency with site and species sampling made it possible to see time trends in PCB concentrations in whole fish samples. Several sites have had continuous sampling since the early 1990s. Time trends for seven combinations of

fish type and sampling site were summarized to determine whether there has been a significant decline in PCB concentration over time.

Of the sites summarized, carp from Brest Bay in Lake Erie were the only fish population where the decline in PCB concentration was not statistically significant (Figure 3. 14). Interestingly, walleye from the same site have had a significant decline in PCB levels since 1990. This trend may correlate with cleanup efforts at a nearby Area of Concern, River Raisin, where high PCB contamination still exists in the sediment (US EPA, 2013b). Carp is a benthic fish species that has high fat content compared to other species. Its feeding habits could expose it to a greater amount of PCBs over its lifetime as compared to walleye, a pelagic feeding species. Carp migrate up rivers. The local contamination in a major river nearby could explain the insignificant decline in PCB concentrations. In contrast, the walleye have lower lipid content (1.5 to 15% in walleye vs. 1 to 32% in carp from Lake Erie from the MDEQ whole fish monitoring dataset) and consume prey higher in the food chain. These habits lead to most walleye PCB exposure originating in the water column, not the sediment. Water concentrations of PCBs have declined throughout the Great Lakes region (Carlson et al., 2010; Jeremiason et al., 1994) due to their ban, volatilization and sedimentation. Thus, it was not surprising to see a significant decline in PCB concentration for pelagic fish species.

Keweenaw Bay in Lake Superior was the only site where the adjusted total PCB concentrations reduced the rate of change in concentration since the start of fish sampling (Figure B. 22 and Figure 3. 14). There has been concern that the Aroclor

method overestimated total PCB concentrations. According to this assessment, it cannot be stated that the Aroclor method systematically overestimated total-PCB concentrations as performed by the MDEQ and its contractors.

A summary of the EPA's Great Lakes Fish Monitoring Program (GLFMP) showed that the half-lives of several chemicals (e.g. PCBs, DDT, PBDEs) have increased since the mid-1980s with the rate constants becoming less negative (Carlson et al., 2010). Hickey et al. (2006) stated that mean levels of PCBs in lake trout are reaching irreducible levels in Lakes Michigan and Huron. Continued sampling efforts will provide evidence of improvements from clean-up efforts. The sites that are not reaching safe levels should be targeted for remediation, focusing efforts where they are most needed.

The time-series data show that PCB concentrations do not decline smoothly in all locations. The noise in the time-series data could have multiple, overlapping causes. It has been documented that some top predators go through a major shift in diet due to food availability (Hickey et al., 2006). This shift can alter fat content, affecting the amount of PCBs that are stored for the lifespan of the fish. For example, Lake Superior lake trout have gone through major diet changes since the 1980s. The change to a fattier diet led to an increase in PCB accumulation in the early 1990s (Hickey et al., 2006). In addition, the size of the fish sampled over time has changed. While it is important to be consistent, there is no guarantee that the same size and age will be available during a sampling event. Finally, the time of year that sampling occurred can have an effect. Some fish species build up more fat during spawning

season (Madenjian, 2011), which can skew total PCB concentration estimates over time.

Salamova et al. (2015) investigated trends in atmospheric concentrations of PCBs from 1991 to the present in the Great Lakes Region. Samples for atmospheric PCB concentration measurement were collected every 12 days by the Integrated Atmospheric Deposition Network (IADN). The total concentration of PCBs in the vapor phase declined at a relatively similar rate across the region. The half-life of PCBs in the air ranged from one to two decades. While there were exceptions to these trends at certain sites, the slow rate of decline was concluded to be caused by local source emissions to the atmosphere. The decline in atmospheric PCBs is reflected in a decline in fish contamination in so far as most of the sites had a significant decline in PCB levels over the same time period. Using the same calculations used by Salamova et al. (2015) to calculate the half-life of total PCB concentration in fish, it was determined that the half-life for PCBs in fish ranged from 7 to 11 years. The estimate of half-life in air and fish was calculated over the same time period. It is interesting that the rate of decline in air and fish are similar. The sites where atmospheric concentration half-lives were longer were assumed to be affected by local sources. Similarly, the presence of continuing, local PCB sources are likely the cause of the lack of a decline in PCB in carp in Brest Bay of Lake Erie.

3.5.3 Source Identification

The MDEQ has sampled fish fillets from multiple locations in the Great Lakes since 2000, some of which are closer to local, industrial sources at the mouths of

rivers (Figure 3. 1, See Table B. 4 for Great Lake sites details). For example, Green Bay, which is connected to Lake Michigan, is known to have high fish PCB concentrations due to historical pulp and paper mill disposal of PCBs along the rivers that feed into the bay (EPA, 2015). The MDEQ has three sampling sites within Green Bay, possibly chosen to monitor the effects of these potential local sources. Similarly, Saginaw Bay, connected to Lake Huron, has PCB sediment contamination that is of concern for fish consumption advisories (EPA, 2013).

To identify which Great Lakes sampling locations were impacted by local PCB contamination sources, PCA was used in the same manner as for the inland lakes source analysis (Figure 2.2) and both the inland lakes and Great Lake sites were used in the Great Lakes PCA to compare contaminant sources. The same PCB congeners were significant in both the inland lake and Great Lakes PCAs- congeners 44, 49, 52, 66, 74, 77, 138, 153 and 163. The ratios of light congeners to heavy congeners was lower for locally impacted lakes in both inland and Great Lakes; inland, and Great Lakes follow the same trend in congener patterns (Table B. 6). On average, the sites determined to have a local source of PCB contamination had fish PCB concentrations that were an order of magnitude higher than those that had only atmospheric sources (Lake Superior sites).

Only two locations on Lake Michigan, Little Bay De Noc (northern pike) and Green Bay (walleye) sites, had significant contributions from both local and atmospheric sources of PCBs. Only the three sites from Lake Superior were determined to be impacted by atmospheric inputs alone. Several of the other sites are

near Areas of Concern or Superfund sites with known PCB contamination in the sediment and/or water column (Table B. 5). As was observed in the inland lake PCA source analysis (Section 2.3.1), component A was influenced most by heavier congeners, indicating the likelihood of local impacts.

There was one major outlier in the PCA analysis- walleye from Huron Bay in Lake Superior were categorized as being affected by local contamination. Northern pike from the same location correlated with the atmospheric source component. Two PCB congeners, 153 and 138, were higher in the walleye sampled from Huron Bay. These congeners played a significant role in defining sites with local contamination. However, the concentration of these congeners were not as high as at other sites in the Great Lakes; walleye from Huron Bay had 2 to 24 ppm less of these congeners than did other sites.

Other studies have used similar statistical techniques to evaluate PCB sources. Discriminant analysis, an earlier form of PCA, revealed significant differences in PCB congener distributions among biota of lakes in Ontario ($p < 0.05$) (MacDonald et al., 1991). Studies on the U.S. east coast found similar results, linking known local sources to fish contamination in nearby estuaries (Rachdawong et al., 1997; Monosson et al., 2003). These results support the conclusions made here that this form of analysis can provide evidence of the impact of local contamination sources on PCB accumulation in fish in the Great Lakes Region. Analyses like these may be beneficial in determining where sampling and clean-up efforts should be focused.

3.5.4 Ecosystem Characteristics

To assess what environmental factors had the most impact on PCB accumulation in fish for the MDEQ sample locations in the Great Lakes, correlation analysis, multiple linear regression and principal component analysis were applied for a number of characteristics (Table B. 5). Unlike the inland lake MLR analysis, some additional factors were considered to assess the effects of human activities. These characteristics included the human population within the watershed and the distance to a source of known local contamination acknowledged by the state or federal government. These were not considered in the inland lake analysis because population density did not vary greatly for the lake watersheds, and the location of local source impact sites was unknown. Population and population density were considered to observe the potential for human impact on the watershed and the movement of PCBs. It has been concluded in the literature that the more urbanized a watershed, the greater the amount of PCBs that impact a local water body (King et al., 2004; Paul et al., 2002). The distance to contamination was used to evaluate whether known sites of sediment contamination affect the PCB contamination in the fish. The characteristics used to describe the sites were not based on the entire Great Lake, but rather, on the bay or basin. The assumption being tested was that local factors were responsible for the heterogeneity among sites. Consideration of multiple fish species in the analysis would have increased the number of data points, but would likely have introduced additional noise due to interspecies differences in metabolism and trophic

position. While it was not possible to use one species for the inland lake analysis, it was possible to use walleye alone for this Great Lakes assessment.

Stepwise MLR revealed that maximum depth alone was the best predictor of total PCB concentration in walleye ($R^2=0.807$, $p<0.01$). Backward MLR identified three characteristics (watershed area, maximum depth, and population density) as the best predictors explaining 8%, 74%, and 15% of the total variance, respectively. It was important to assess the results of both methods to consider all of the variables initially in the analysis. In both cases, maximum depth was the best predictor where, as the depth of the site increased, the total PCB concentration decreased. In the case of inland lakes, mean depth can be linked to food chain differences as larger inland lakes have a potential for more complicated food webs (Guildford et al., 2008). For the sites in the Great Lakes, predatory fish could have a habit of feeding in the littoral zones near the sampling sites within the bays or basins and may not leave to feed elsewhere in the lakes. This would indicate the existence of unique food webs for each embayment. However, the relationship of depth to PCB contamination is inverted compared to inland lakes (Figure B. 24); as the depth of the bays and basins in the Great Lakes increase, the concentration of PCBs in fish decline. This result might be explained by the amount of littoral zone in each bay or basin and MDEQ sampling sites. Top predators sampled from the Great Lakes were caught at shallow depths, close to shore. These fish likely have a tendency to feed at shallower depth (the littoral zone). Many of these shallow bays and basins could be impacted by local contamination (i.e. AOCs, superfund sites or unknown sources); according to the

source analysis that used PCA (Section 3.3.3), the presence of local contamination is likely. Therefore, this feeding habit increases the level of exposure due to local sources even though littoral feeding habits may cause a shorter food web and less bioaccumulation, as discovered by Guildford et al. (2008). The area of littoral zone of these sites in the Great Lakes and the feeding habits at the time of fish sampling are unknown. Further research could reveal a link between feeding habits and depth in the Great Lakes. Conducting a similar regression analysis with fish collected farther from shore may reveal a different relationship between PCB concentrations and depth.

The correlation analysis revealed a few statistically strong links between the characteristics used in the MLR analysis. The most notable of these correlations is that of population and distance to contamination ($p < 0.05$), where the greater the population in the watershed, the closer the site is to local PCB contamination. These results, along with the MLR analysis, are not statistically robust due to the low number of sites used in the analysis; more sites could provide additional significant correlations. The backward MLR results included population density as an important factor. These analyses link the PCB concentration in the fish to more populated, developed land and the nearby contamination sources. King et al. (2004) and Paul et al. (2002) drew similar conclusions with regards to more developed land resulting in more PCBs and other chemicals entering New England estuaries because of increased runoff and emissions. A study of lakes in the Yukon Territory found higher PCB sediment concentration near populated areas (Rawn et al., 2002). Highly populated

areas typically contain chemically contaminated sites where industry utilized easy access to waterways for waste disposal. These areas also have more impermeable surfaces, leading to increased chemical runoff. As PCBs continue to redeposit, these surfaces allow them to enter water bodies more efficiently. These compounding factors, population/urban area and local sources, are likely the cause of the chemical contamination trends in the Great Lakes.

A singular outlier, the Tahquamenon River in Lake Superior, caused MLR to exclude mean depth in the analysis results (Figure B. 23). The mean depth for this outlier was estimated based on the bathymetry of the corresponding bay. It is important to note that, had this outlier not existed, it is likely that mean depth would have been just as significant in the analysis for the Great Lake sites as it was for inland lakes.

3.6 Conclusion

The analyses herein were completed in an effort to enhance the understanding of organic contaminants in the Great Lakes Region. It was concluded that the Great Lakes have higher PCB concentrations in fish than do inland lakes. Time trend analysis suggested that local remediation efforts have been successful in reducing PCBs, and that the decline in fish concentration is statistically significant for most sites. The exception to this trend is a site near an Area of Concern where sediment is contaminated with PCBs (Brest Bay, Lake Erie). Sources of contamination, either atmospheric or point sources, can be differentiated through the use of PCA. Sites where heavier PCB congeners are prevalent in fish indicate local contamination.

Focusing remediation efforts on these sites could increase the rate of ecosystem recovery and reduce human exposure to PCBs. Multiple linear regression revealed the importance of depth in relation to total PCB concentration in fish, which may be linked to food chain complexity and local source impacts. There is considerable heterogeneity in fish PCB concentrations among different sampling sites. The cause for this heterogeneity in the level of PCB contamination is, in part, due to the effects of urbanization. The more densely populated and industrialized a watershed, the more local sources of PCBs exist that can enter the lake through runoff or atmospheric transport. Therefore, focusing remediation efforts on more densely populated areas would improve ecosystem health across the Great Lakes Region. There is a need for continued remediation in the Great Lakes Region in order to reduce PCB levels in fish to below consumption advisory limits more quickly. The sooner we reach a time where PCBs and other persistent pollutants are no longer a concern, the better the ecosystems and livelihoods of future generations will be.

3.7 References

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CHAPTER 4: OVERALL CONCLUSIONS

The research herein revealed some notable explanations for trends in PCB contamination in fish in the Great Lakes Region. These trends involved the assessment of recorded data and model simulations. Practical implications and recommendations can be gleaned from these efforts in order to reduce the risks of polychlorinated biphenyl exposure.

Through the use of Principal Component Analysis (PCA), it was determined that differentiating between two sources of PCBs to a lake- atmospheric and local, point sources- was possible. Lakes impacted by both atmospheric and local, point sources contain fish with higher concentrations of heavier PCB congeners and PCA found this distinction statistically significant. Knowing this, it would be possible for government entities to focus clean-up efforts on lakes where local sources have not been confirmed, but contain fish with this type of contamination pattern. This could speed the recovery of the ecosystems where actions may still take an effect. Future work into the use of this method would be to compare results to other geographic regions to determine if the same PCB congeners are significant or if PCA would require an adjustment for different locations based on potential local contamination sources.

Other research results revealed what lakes may be most impacted by PCB contamination due to their physical and food web characteristics. For inland lakes, lake mean depth was very significant in explaining PCCB concentrations in fish using

Multiple Linear Regression (MLR) analysis; as mean depth in an inland lake increased, the level of total PCB contamination in fish increased. According to these results, it would be best to fish in inland lakes with shallow depths where no local contamination exists. However, the opposite trend was true for sites in the Great Lakes; as maximum depth increased, the concentration of PCBs in fish declined. It was unexpected that inland lakes and Great Lakes sites did not follow the same trend. A possible explanation could be due to the near-shore sampling of fish in the Great Lakes practiced by the Michigan Department of Environmental Quality (MDEQ). Fish of the same species in the Great Lakes have different feeding habits and metabolisms depending on the depth of water they inhabit. Higher food availability with the combination of higher local PCB contamination in the nearshore may cause this higher accumulation, skewing the trend identified by MLR analysis. Future work could involve looking at this trend across a larger geographic region to determine if the significance of depth is more of a worldwide trend. In addition, using another dataset for fish in the Great Lakes where sampling sites are farther from the nearshore may reveal trends similar to those found in inland lakes.

Trophic state also had significant effect on lake modeling scenarios that tested food web dynamics; lakes with more primary productivity had lower PCB contamination in fish. This may be due to the overall dilution of PCBs at the base of the food web. These finding could implicate what lakes are best to consume fish from- inland lakes with higher primary productivity may have safer fish. Future modeling work should include a better summary of possible top predator diets and

more seasonal changes in the water column in order to more accurately explain the significance of food web differences.

In comparing lake categories in the MDEQ fish monitoring dataset (i.e. upper and lower peninsula inland and Great Lakes sites), it was concluded that the Great Lakes have higher PCB contamination in fish than inland lakes. However, this conclusion may be skewed due to the effects of local, point sources on several of the sites sampled in the Great Lakes. A limited number of common species were sampled among the lake categories, making the direct comparison less statistically significant. For future efforts, it would be beneficial to include multiple datasets in the comparison to encompass a larger array of species and a larger number of samples. However, using datasets where laboratory processes were similar would be critical so that comparisons are accurate.

Through the use of the modeling tools and the literature, it was determined that it may be safe to consume a desired amount of fish from lakes in Michigan's Upper Peninsula in 20 years. This estimate was determined with the assumption that no local contamination existed in the lakes simulated; the existence of local contamination would increase the recovery time of the ecosystem. Efforts into modeling lake ecosystems in Michigan's Lower Peninsula may result in a longer time period till safe consumption may be possible as sources of PCBs, either atmospheric or local, may be more prevalent.

APPENDIX A

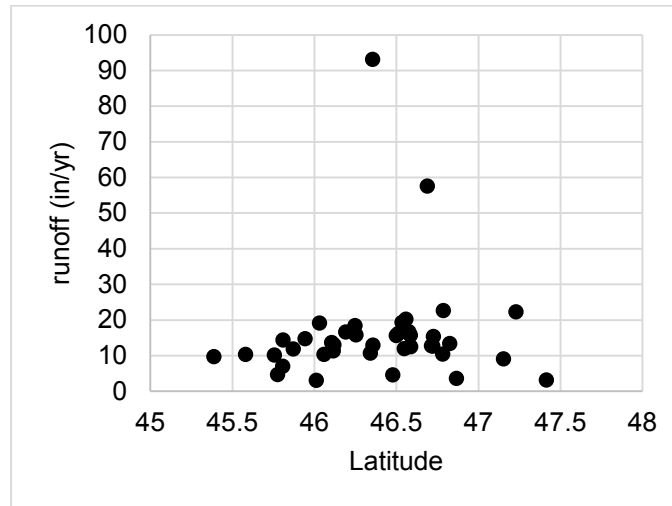


Figure A. 1: Plot of annual average runoff from USGS rain gauge data vs latitude (USGS, 2015). Average runoff equals 16.3 in/yr.

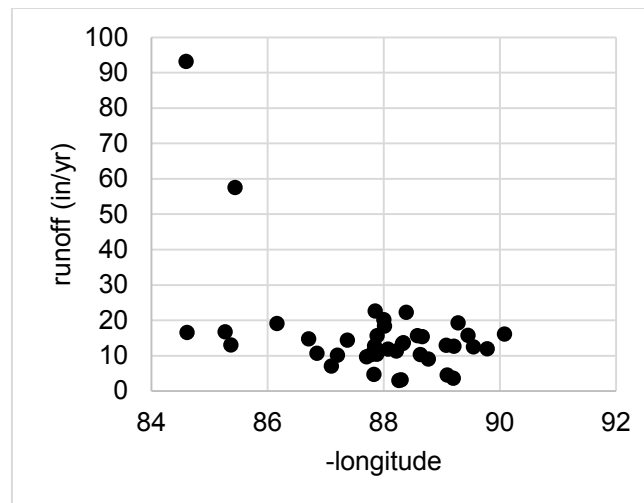


Figure A. 2: Plot of annual average runoff from USGS rain gauge data vs longitude (USGS, 2015). Average runoff equals 15.2 in/yr.

Table A. 1: Summary of lake characteristics used in multiple linear regression analysis and principal component analysis. Wind speed was 2.7 m/s for all inland lakes.

Lake Name	Lat/long	Surface Area ¹ (acres)	Mean Depth ² (ft)	Max Depth ² (ft)	Lake Trophic State ⁵	Watershed Area ³	Wetland Area ⁴ (acres)	Open Water Area ¹ (acres)	Ratios ⁶	PCBt ⁷ (ppm)
Boston Lake	47.171/-88.529	73	1	6	e	1760	802	74	24	0.0010
Chicago Lake	46.057/-88.505	1083	36	115	o	7767	1125	1201	7	0.0110
Deer Lake	46.529/-87.687	266	34	60	m	1587	69	280	6	0.0100
Emily Lake	46.859/-88.855	60	28	90	o	457	26	66	8	0.0026
Engman Lake	46.337/87.329	48	11	36	m	348	30	50	7	0.0010
Goose Lake	46.471/-87.519	406	9	15	e	9057	1349	463	22	0.1825
Little Lake	46.277/-87.346	460	14	50	m	5689	235	787	12	0.0012
Manistique Lake	46.237/-85.776	10346	10	25	m	58131	20381	17044	6	0.0076
Muskallonge Lake	46.670/-85.630	762	10	20	e	11436	569	973	15	0.0010
Otter Lake	46.913/-88.574	863	18	29	e	425538	8391	1659	493	0.0276
Portage Lake	47.069/-88.493	10808	28	59	m	136271	19819	13745	13	0.0572
Runkle Lake	46.102/-88.301	80	12	50	m	2049	825	179	26	0.0010
Shag Lake	46.268/-87.510	195	49	30	m	1084	51	195	6	0.0145
Silver Lake	46.203/-88.018	108	9	23	m	1053	122	113	10	0.0011
Siskiwit Lake	48.002/-88.792	4008	69	151	o	13153	1526	4615	3	0.0557
Sporley Lake	46.333/-87.340	77	21	42	m	377	17	90	5	0.0069
Torch Lake	47.168/-88.413	2401	56	100	m	45891	5798	2515	19	0.1268

Determined using ESRI® ArcMap™ 10.1 with data from ¹Michigan Department of Technology, Management and Budget (CTMB) geographic data library (CMTB, 2002), ² the Michigan Department of Natural Resources (DNR) bathymetry maps (MDNR, 2015), ³United States Geological Survey (USGS) National Map Data (USGS, 2014), ⁴ or US Fish and Wildlife's National Wetland Inventory (FWS, 2015). ⁵ Fuller and Taricska, 2012. ⁶Ratio of Watershed Area: Lake Area. ⁷Lipid normalized total PCB concentration from all samples taken from the MDEQ (Northern Pike, Walleye Lake Trout or Splake) (Bohr, 2013).

Table A. 2: Lake Characteristics based on trophic state (Armengol et al., 2003).

Trophic State	Trophic State Index (TSI)	TSI Selected	Secchi Depth Selected m	TSS, mg/L	f _{om}	DOC, mg/L	f _{ocs}
Oligotrophic	<30	20	16	0.653	0.1	1	0.03
Mesotrophic	40-50	45	3	3.311	0.25	2.5	0.05
Eutrophic	50-60	55	1.5	6.485	0.5	4	0.08

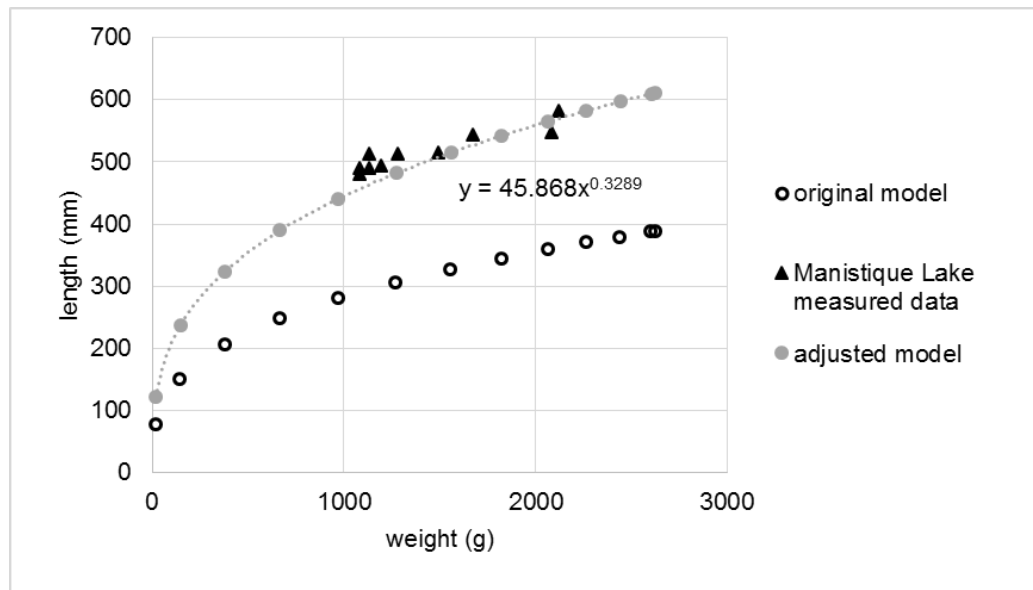


Figure A. 3: Adjustments made to walleye length to weight ratios in the fish file provided by the EPA (personal communications, Craig Barber 2014). Manistique Lake measured walleye data from Bohr, 2013.

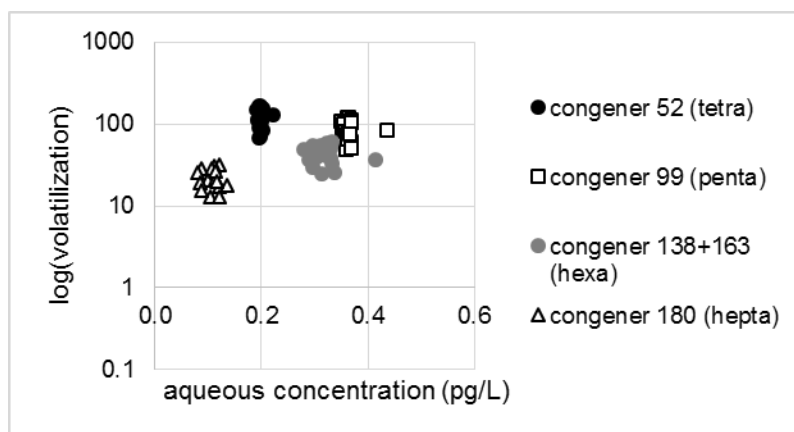


Figure A. 4: Summary of volatilization loss rates for four PCB congeners in the PCB lake model (chlorination level of each congener is in parenthesis). Lakes included are all ecosystem scenario lakes, Manistique Lake, Muskallonge Lake, Little Lake and Sporley Lake.

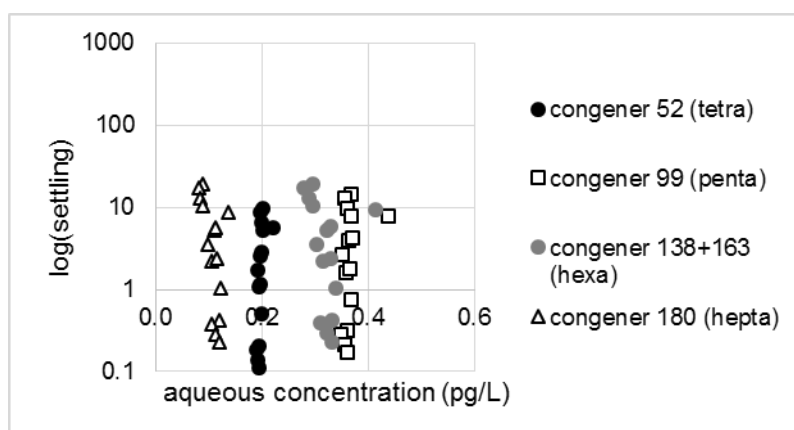


Figure A. 5: Summary of first order settling loss rates for four PCB congeners in the PCB lake model (chlorination level of each congener is in parenthesis). Lakes included are all ecosystem scenario lakes, Manistique Lake, Muskallonge Lake, Little Lake and Sporley Lake.

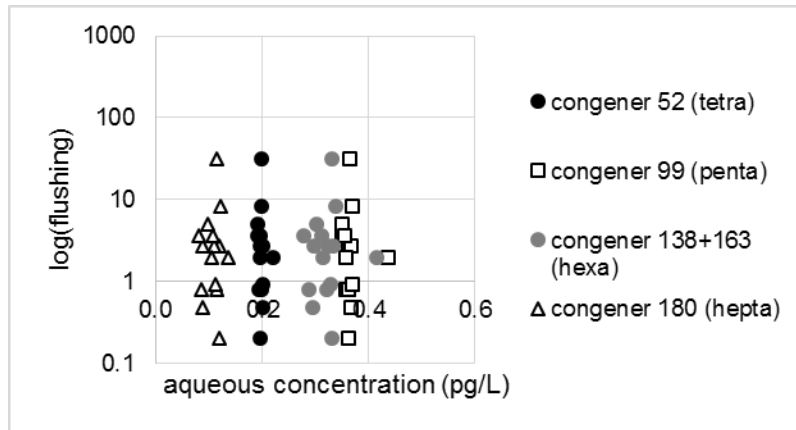


Figure A. 6: Summary of flushing (outflow) loss rates for four PCB congeners in the PCB lake model (chlorination level of each congener is in parenthesis). Lakes included are all ecosystem scenario lakes, Manistique Lake, Muskallonge Lake, Little Lake and Sporley Lake.

Table A. 3: Summary of lake characteristics for the PCB lake model. Variables are defined in Table 2. 1.

Lake Name	A _o (m ²) ¹	h (m) ¹	Secchi Depth (m) ²	Residence Time ³	A _w (m ²) 4	Runoff flow rate (m ³ /s) ⁵	ρ _s ^{sc} (kg/m ³) ⁶	φ ⁷	r _{sw} ^{sc} (kg/solids/m ³) ⁸	annual precipitation n (m/yr) ⁹	Q _{pr} (m ³ /s) ¹⁰	μ _{res} (kg/m ² /s)) ¹¹
Muskallonge Lake	3E+06	3.0	2.1	0.5	4.6E+07	16.1	2125	0.65	1141	0.92	0.09	1.6E-04
Mansitiqu Lake	4E+07	3.0	2.4	1.1	2.4E+08	81.7	2313	0.63	1383	0.92	1.22	1.3E-04
Sporley Lake	3E+05	6.4	6.7	3.2	1.5E+06	0.5	2313	0.63	1383	0.74	0.01	4.7E-05
Little Lake	2E+06	4.3	4.3	0.9	2.3E+07	8.0	2313	0.63	1383	0.74	0.04	7.3E-05
Lake Superior	8E+10	149		172.3	1.3E+11	2251.4	1760	0.85	311	0.73	1900.5	1.6E-05

¹Estimated from bathymetry maps from the Michigan DNR (MDNR, 2015); ²See Table A.1; ³Calculated from runoff and lake volume; ⁴Estimated in ArcMap 10.1 using DEM data from the USGS National Map Viewer (USGS, 2014);

⁵Calculated from USGS gauge data, estimated watershed area and lake volume; ⁶Table 2.2; ⁷Table 2.2; ⁸Table 2.2;

⁹Estimated from climate data (NOAA, 2015); ¹⁰Estimated from annual precipitation and lake surface area; ¹¹Table 2.2 and a resuspension flux of 0.017 g/cm²/yr from Mandelia (2015).

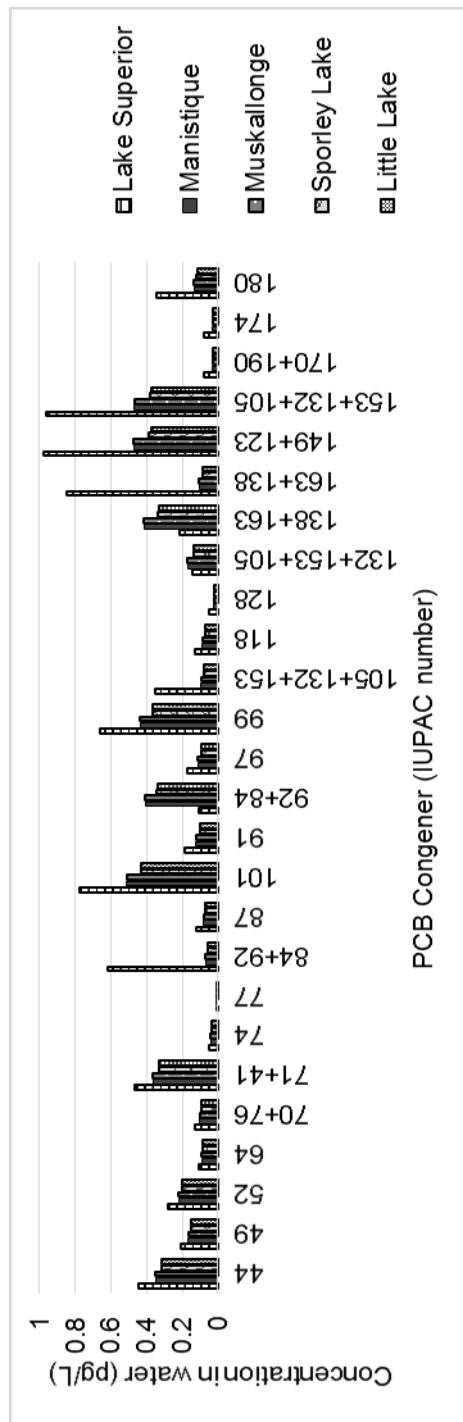


Figure A. 7: PCB water model output summary of selected PCB congeners and lakes from Michigan's Upper Peninsula.

Table A. 4: Summary of inputs for EPA's BASS project files ('eutro' is eutrophic, 'oligo' is oligotrophic).

parameter	Lake										
	Manistique Lake	Torch Lake	seepage oligo	seepage eutro	small (no tribes)	small (with tribes) oligo	small (with tribes) eutro	medium oligo	medium eutro	large oligo	lake eutro
Annual Outputs	1	1	1	1	1	1	1	1	1	1	1
Length of Simulation (years)	15	10	10	10	10	10	10	10	10	10	10
start month	April	April	April	April	April	April	April	April	April	April	April
temperature (deg C) ¹	10	13	9	9	10	10	10	8	8	8	8
water depth (m) ²	7.6	25	9	9	5	5	5	8	8	10	10
Benthos ³ (g(dw)/m ²)	3.03E-04	2.00E-03	0.00308	0.01772	3.50E-03	3.50E-03	1.96E-02	2.89E-02	1.67E-02	1.92E-03	1.10E-02
Insects ⁴ (g(dw)/m ²)	2.00E-03	2.00E-03	0.002	0.002	2.00E-03	2.00E-03	2.00E-03	2.00E-03	2.00E-03	2.00E-03	2.00E-03
Periphyton ⁵ (g(dw)/m ²)	0.149	2.00E-03	0.3989	2.80638	0.1992	0.1992	2.8064	0.39891	2.80638	0.39891	2.8064
Phytoplankton ⁶ (g(dw)/L)	1.40E-05	1.05E-06	7.11E-05	1.46E-03	3.76E-07	3.76E-07	1.46E-03	7.11E-05	1.46E-03	7.11E-05	1.46E-03
Zooplankton ⁷ (g(dw)/L)	2.13E-04	7.2E+01	0.0283	0.29218	3.42E-04	3.42E-04	3.21E-01	2.88E-02	2.98E-01	2.78E-02	2.87E-01

¹Kirillin et al., 2011; ²Lake Surveys (Hanchin et al., 2013; Hanchin and Kramer 2007) or estimated based on percentiles from Cheruvil et al., 2013 (Table 2. 3); ³Equation 2.46; ⁴BASS Default; ⁵Equation 2.48 or 2.49; ⁶Equation 2.47 or 2.50; ⁷Equation 2.45.

Table A. 5: Summary of all lakes in the Cheruvellil EPA-NLAPP 6-state lake-landscape database that fell under the “very small” category (Reinl, K., personal communications, 2015).

	Eutrophic		Mesotrophic		Oligotrophic	
	With Tribs	W/out Tribs	With Tribs	W/out Tribs	With Tribs	W/out Tribs
surface area (km²)	Count: 1 Minimum: 0.51571 Maximum: 0.51571 Mean: 0.51571 Standard Deviation: 0	Count: 2 Minimum: 0.33437 Maximum: 0.40746 Mean: 0.370915 Standard Deviation: 0.036545	Count: 3 Minimum: 0.24472 Maximum: 0.30823 Mean: 0.27988 Standard Deviation: 0.026371	Count: 7 Minimum: 0.20772 Maximum: 0.36911 Mean: 0.280894 Standard Deviation: 0.070398	NULL	Count: 5 Minimum: 0.20919 Maximum: 0.48061 Mean: 0.290774 Standard Deviation: 0.104469
mean depth (m)	Count: 1 Minimum: 1 Maximum: 1 Mean: 1 Standard Deviation: 0	Count: 2 Minimum: 2.1 Maximum: 3.3 Mean: 2.7 Standard Deviation: 0.6	Count: 3 Minimum: 1.9 Maximum: 3.3 Mean: 2.733333 Standard Deviation: 0.601849	Count: 7 Minimum: 2 Maximum: 5 Mean: 3.128571 Standard Deviation: 0.958741	NULL	Count: 5 Minimum: 1.3 Maximum: 5.1 Mean: 3.3 Standard Deviation: 1.384197
max depth (m)	Count: 1 Minimum: 3.048 Maximum: 3.048 Mean: 3.048 Standard Deviation: 0	Count: 2 Minimum: 6.401 Maximum: 15.545 Mean: 10.973 Standard Deviation: 4.572	Count: 3 Minimum: 5.182 Maximum: 12.5 Mean: 8.942 Standard Deviation: 2.990974	Count: 7 Minimum: 5.486 Maximum: 10.668 Mean: 8.098857 Standard Deviation: 1.947404	NULL	Count: 5 Minimum: 6.096 Maximum: 19.812 Mean: 11.2166 Standard Deviation: 4.591878
Catchment Area(km²)	Count: 1 Minimum: 19.26 Maximum: 19.26 Mean: 19.26 Standard Deviation: 0	Count: 2 Minimum: 3.29 Maximum: 7.098 Mean: 5.194 Standard Deviation: 1.904	Count: 3 Minimum: 9.422 Maximum: 137.047 Mean: 61.133 Standard Deviation: 54.841432	Count: 7 Minimum: 0.684 Maximum: 3.275 Mean: 1.541714 Standard Deviation: 1.029419	NULL	Count: 5 Minimum: 0.229 Maximum: 3.13 Mean: 1.2128 Standard Deviation: 1.011662
Percent of Total Lakes	1%	2%	3%	7%		5%

Table A. 6: Summary of all lakes in the Cheruvilil EPA-NLAPP 6-state lake-landscape database that fell under the “small” category (Reinl, K., personal communications, 2015).

	Eutrophic		Mesotrophic		Oligotrophic	
	With Tribs	W/out Tribs	With Tribs	W/out Tribs	With Tribs	W/out Tribs
surface area (km^2)	Count: 4 Minimum: 0.40197 Maximum: 1.87526 Mean: 0.806757 Standard Deviation: 0.618669	Count: 2 Minimum: 0.39313 Maximum: 0.42969 Mean: 0.41141 Standard Deviation: 0.01828	Count: 4 Minimum: 0.31739 Maximum: 0.60856 Mean: 0.453703 Standard Deviation: 0.117781	Count: 14 Minimum: 0.28278 Maximum: 0.83244 Mean: 0.50113 Standard Deviation: 0.180677	Count: 1 Minimum: 0.37157 Maximum: 0.37157 Mean: 0.37157 Standard Deviation: 0	Count: 5 Minimum: 0.23972 Maximum: 0.4961 Mean: 0.386282 Standard Deviation: 0.093823
mean depth (m)	Count: 4 Minimum: 1 Maximum: 4.5 Mean: 2.7 Standard Deviation: 1.262933	Count: 2 Minimum: 3.6 Maximum: 4.9 Mean: 4.25 Standard Deviation: 0.65	Count: 4 Minimum: 2.6 Maximum: 4.5 Mean: 3.55 Standard Deviation: 0.680074	Count: 14 Minimum: 1.6 Maximum: 6.4 Mean: 3.692857 Standard Deviation: 1.33388	Count: 1 Minimum: 4.5 Maximum: 4.5 Mean: 4.5 Standard Deviation: 0	Count: 5 Minimum: 2.5 Maximum: 7.4 Mean: 4.48 Standard Deviation: 1.884038
max depth (m)	Count: 4 Minimum: 3.048 Maximum: 14.935 Mean: 7.39125 Standard Deviation: 4.578906	Count: 2 Minimum: 9.144 Maximum: 18.288 Mean: 13.716 Standard Deviation: 4.572	Count: 4 Minimum: 7.315 Maximum: 13.411 Mean: 9.7535 Standard Deviation: 2.239786	Count: 14 Minimum: 3.048 Maximum: 15.24 Mean: 9.251429 Standard Deviation: 4.00072	Count: 1 Minimum: 15.2 Maximum: 15.2 Mean: 15.2 Standard Deviation: 0	Count: 5 Minimum: 7.01 Maximum: 27.432 Mean: 14.2036 Standard Deviation: 6.978871
Catchment Area(km^2)	Count: 4 Minimum: 12.813 Maximum: 62.979 Mean: 32.74525 Standard Deviation: 18.786577	Count: 2 Minimum: 0.738 Maximum: 3.515 Mean: 2.1265 Standard Deviation: 1.3885	Count: 4 Minimum: 9.505 Maximum: 23.452 Mean: 14.33025 Standard Deviation: 5.400411	Count: 14 Minimum: 0.887 Maximum: 6.936 Mean: 2.939357 Standard Deviation: 1.975333	Count: 1 Minimum: 10.034 Maximum: 10.034 Mean: 10.034 Standard Deviation: 0	Count: 5 Minimum: 0.466 Maximum: 2.616 Mean: 1.6532 Standard Deviation: 0.792359
Percent of Total Lakes	4%	2%	4%	13%	1%	5%

Table A. 7: Summary of all lakes in the Cheruvellil EPA-NLAPP 6-state lake-landscape database that fell under the “medium” category (Reinl, K., personal communications, 2015).

	Eutrophic		Mesotrophic		Oligotrophic	
	With Tribs	W/out Tribs	With Tribs	W/out Tribs	With Tribs	W/out Tribs
surface area (km²)	Count: 8 Minimum: 0.44545 Maximum: 2.00831 Mean: 1.171515 Standard Deviation: 0.526064	NULL	Count: 5 Minimum: 0.35333 Maximum: 1.34079 Mean: 0.889338 Standard Deviation: 0.386106	Count: 7 Minimum: 0.41913 Maximum: 1.58022 Mean: 1.035019 Standard Deviation: 0.361852	Count: 2 Minimum: 0.44308 Maximum: 0.48698 Mean: 0.46503 Standard Deviation: 0.02195	Count: 9 Minimum: 0.24207 Maximum: 0.79617 Mean: 0.441067 Standard Deviation: 0.157186
mean depth (m)	Count: 8 Minimum: 2.1 Maximum: 5.1 Mean: 3.2725 Standard Deviation: 0.929136	NULL	Count: 5 Minimum: 3 Maximum: 6.5 Mean: 4.1 Standard Deviation: 1.293058	Count: 7 Minimum: 3 Maximum: 5.2 Mean: 3.914286 Standard Deviation: 0.715998	Count: 2 Minimum: 5 Maximum: 5.8 Mean: 5.4 Standard Deviation: 0.4	Count: 9 Minimum: 4.6 Maximum: 9.9 Mean: 6.977778 Standard Deviation: 2.057927
max depth (m)	Count: 8 Minimum: 3.048 Maximum: 12.192 Mean: 8.071125 Standard Deviation: 3.343425	NULL	Count: 5 Minimum: 6.096 Maximum: 25.298 Mean: 11.2776 Standard Deviation: 7.171376	Count: 7 Minimum: 9.1 Maximum: 18.288 Mean: 13.013 Standard Deviation: 2.704447	Count: 2 Minimum: 12.192 Maximum: 16.764 Mean: 14.478 Standard Deviation: 2.286	Count: 9 Minimum: 7.62 Maximum: 32.004 Mean: 18.152556 Standard Deviation: 7.528123
Catchment Area(km²)	Count: 8 Minimum: 9.108 Maximum: 1948.278 Mean: 267.414875 Standard Deviation: 635.620074	NULL	Count: 5 Minimum: 9.632 Maximum: 58.344 Mean: 32.1304 Standard Deviation: 16.775817	Count: 7 Minimum: 1.983 Maximum: 8.641 Mean: 4.800857 Standard Deviation: 2.50613	Count: 2 Minimum: 12.103 Maximum: 65.439 Mean: 38.771 Standard Deviation: 26.668	Count: 9 Minimum: 0.207 Maximum: 3.598 Mean: 1.799111 Standard Deviation: 1.235286
Percent of Total Lakes	8%		5%	7%	2%	9%

Table A. 8: Summary of all lakes in the Cheruvellil EPA-NLAPP 6-state lake-landscape database that fell under the “large” category (Reinl, K., personal communications, 2015).

	Eutrophic		Mesotrophic		Oligotrophic	
	With Tribs	W/out Tribs	With Tribs	W/out Tribs	With Tribs	W/out Tribs
surface area (km²)	Count: 4 Minimum: 1.78923 Maximum: 3.63799 Mean: 2.709615 Standard Deviation: 0.711577	NULL	Count: 13 Minimum: 0.83186 Maximum: 9.71341 Mean: 3.371103 Standard Deviation: 2.232621	Count: 2 Minimum: 1.06354 Maximum: 1.86053 Mean: 1.462035 Standard Deviation: 0.398495	Count: 3 Minimum: 1.70744 Maximum: 5.88071 Mean: 3.458863 Standard Deviation: 1.768454	Count: 4 Minimum: 0.99996 Maximum: 3.00261 Mean: 1.8118 Standard Deviation: 0.820601
mean depth (m)	Count: 4 Minimum: 2.4 Maximum: 5.67 Mean: 3.9675 Standard Deviation: 1.321427	NULL	Count: 13 Minimum: 2.9 Maximum: 17 Mean: 6.047692 Standard Deviation: 3.739548	Count: 2 Minimum: 4.2 Maximum: 6.3 Mean: 5.25 Standard Deviation: 1.05	Count: 3 Minimum: 4.4 Maximum: 8.1 Mean: 6.233333 Standard Deviation: 1.510703	Count: 4 Minimum: 3.6 Maximum: 11.3 Mean: 7.775 Standard Deviation: 2.742604
max depth (m)	Count: 4 Minimum: 6.096 Maximum: 17.069 Mean: 10.668 Standard Deviation: 4.037983	NULL	Count: 13 Minimum: 6.096 Maximum: 37.49 Mean: 15.261769 Standard Deviation: 9.183044	Count: 2 Minimum: 14.63 Maximum: 15.24 Mean: 14.935 Standard Deviation: 0.305	Count: 3 Minimum: 9.144 Maximum: 21.336 Mean: 17.272 Standard Deviation: 5.747364	Count: 4 Minimum: 7.62 Maximum: 30.48 Mean: 22.479 Standard Deviation: 8.845438
Catchment Area(km²)	Count: 4 Minimum: 19.377 Maximum: 1814.632 Mean: 704.59875 Standard Deviation: 722.773745	NULL	Count: 13 Minimum: 10.486 Maximum: 286.111 Mean: 74.796154 Standard Deviation: 84.007929	Count: 2 Minimum: 2.107 Maximum: 5.542 Mean: 3.8245 Standard Deviation: 1.7175	Count: 3 Minimum: 9.631 Maximum: 22.779 Mean: 17.61 Standard Deviation: 5.723609	Count: 4 Minimum: 2.807 Maximum: 8.408 Mean: 5.308 Standard Deviation: 2.522359
Percent of Total Lakes	4%		12%	2%	3%	4%

Table A. 9: Summary of species included in Torch Lake and Manistique Lake food web modeling using EPA BASS.

Torch Lake	Manistique Lake
alewife (<i>Alosa pseudoharengus</i>)	brown bullhead (<i>Ameiurus nebulosus</i>)
black bullhead (<i>Ameiurus melas</i>)	northern pike (<i>Esox lucius</i>)
brown bullhead (<i>Ameiurus nebulosus</i>)	rock bass (<i>Ambloplites rupestris</i>)
common shiner (<i>Luxilus cornutus</i>)	shorthead redhorse (<i>Moxostoma macrolepidotum</i>)
longnose sucker (<i>Catostomus catostomus</i>)	silver redhorse (<i>Moxostoma anisurum</i>)
northern pike (<i>Esox lucius</i>)	smallmouth bass (<i>Micropterus dolomieu</i>)
pumpkinseed (<i>Lepomis gibbosus</i>)	walleye (<i>Sander vitreus</i>)
rainbow smelt (<i>Osmerus mordax</i>)	white sucker (<i>Catostomus commersonii</i>)
rock bass (<i>Ambloplites rupestris</i>)	yellow perch (<i>Perca flavescens</i>)
silver redhorse (<i>Moxostoma anisurum</i>)	
smallmouth bass (<i>Micropterus dolomieu</i>)	
trout-perch (<i>Percopsis omiscomaycus</i>)	
walleye (<i>Sander vitreus</i>)	
white sucker (<i>Catostomus commersonii</i>)	
yellow perch (<i>Perca flavescens</i>)	

Table A. 10: Species present in each lake size category for the lake/food web scenarios.

Lake Size Category				
Seepage	small (no tribs)	small (with tribs)	medium	large
bluegill (<i>Lepomis macrochirus</i>)	bluegill (<i>Lepomis macrochirus</i>)	black bullhead (<i>Ameiurus melas</i>)	black bullhead (<i>Ameiurus melas</i>)	black bullhead (<i>Ameiurus melas</i>)
pumpkinseed (<i>Lepomis gibbosus</i>)	pumpkinseed (<i>Lepomis gibbosus</i>)	bluegill (<i>Lepomis macrochirus</i>)	bluegill (<i>Lepomis macrochirus</i>)	bluegill (<i>Lepomis macrochirus</i>)
rock bass (<i>Ambloplites rupestris</i>)	rock bass (<i>Ambloplites rupestris</i>)	northern pike (<i>Esox lucius</i>)	brown bullhead (<i>Ameiurus nebulosus</i>)	brown bullhead (<i>Ameiurus nebulosus</i>)
yellow perch (<i>Perca flavescens</i>)	yellow perch (<i>Perca flavescens</i>)	smallmouth bass (<i>Micropterus dolomieu</i>)	longnose sucker (<i>Catostomus catostomus</i>)	longnose sucker (<i>Catostomus catostomus</i>)
smallmouth bass (<i>Micropterus dolomieu</i>)	smallmouth bass(<i>Micropter us dolomieu</i>)	pumpkinseed (<i>Lepomis gibbosus</i>)	northern pike (<i>Esox lucius</i>)	northern pike (<i>Esox lucius</i>)
		rock bass (<i>Ambloplites rupestris</i>)	pumpkinseed (<i>Lepomis gibbosus</i>)	pumpkinseed (<i>Lepomis gibbosus</i>)
		white sucker (<i>Catostomus commersonii</i>)	rock bass (<i>Ambloplites rupestris</i>)	rock bass (<i>Ambloplites rupestris</i>)
		yellow perch (<i>Perca flavescens</i>)	shorthead redhorse (<i>Moxostoma macrolepidotum</i>)	shorthead redhorse (<i>Moxostoma macrolepidotum</i>)
			smallmouth bass (<i>Micropterus dolomieu</i>)	smallmouth bass (<i>Micropterus dolomieu</i>)
			trout-perch (<i>Percopsis omiscomaycus</i>)	trout-perch (<i>Percopsis omiscomaycus</i>)
			walleye (<i>Sander vitreus</i>)	walleye (<i>Sander vitreus</i>)
			white sucker (<i>Catostomus commersonii</i>)	white sucker (<i>Catostomus commersonii</i>)
			yellow perch (<i>Perca flavescens</i>)	yellow perch (<i>Perca flavescens</i>)

APPENDIX B

Table B. 1: Summary of MDEQ inland water body sampling from 2000-2015 (Bohr, 2015).

Fish Species	water body category	Peninsula	number of sites	number of samples
walleye	Inland Lake	Upper	8	111
		Lower	12	143
	River	Upper	3	78
		Lower	26	101
smallmouth bass	Inland Lake	Upper	1	19
		Lower	11	100
	River	Upper	3	59
		Lower	17	270
white sucker	Inland Lake	Upper	4	41
		Lower	11	106
	River	Upper	1	10
		Lower	14	232
northern pike	Inland Lake	Upper	9	116
		Lower	13	120
	River	Upper	2	16
		Lower	13	166
yellow perch	Inland Lake	Upper	3	26
		Lower	2	80
	River	Upper	2	19
		Lower	2	30

Table B. 2: Summary of MDEQ Great Lakes sampling from 2000-2015 (Bohr, 2015).

Species	Lake Michigan	Lake Huron	Lake Superior	Lake Erie
rainbow trout	19	10	9	
walleye	26	20	38	21
lake trout	10	20	29	
chinook	20	20	10	

Table B. 3: Summary of MDEQ Great Lakes sampling from 2000-2015 (Bohr, 2015).

Fish Species	number of samples	Great Lakes included
walleye	105	Erie, Michigan, Superior, Huron
smallmouth bass	74	Erie, Michigan, Huron
white sucker	20	Erie, Huron
northern pike	30	Michigan, Superior
yellow perch	49	Erie, Huron

Table B. 4: MDEQ Great Lakes sampling location summary for edible portion monitoring (Bohr, 2015).

Water Body	Sampling Location	lat/long	Species	lipid normalized average concentration (ppm)¹
Lake Superior	Keweenaw Bay, L'Anse Bay	46.76/-88.45	northern pike	0.002
Lake Superior	Huron Bay	46.85/-88.26	northern pike	0.004
Lake Michigan	Little Bay De Noc	45.79/-87.05	northern pike	0.004
Lake Erie	Off Monroe	41.89/-83.33	walleye	0.117
Lake Erie	Western Basin	41.86/-83.27	walleye	0.326
Lake Michigan	Green Bay, Cedar River	45.56/-87.18	walleye	1.135
Lake Michigan	Little Bay De Noc	45.79/-87.05	walleye	0.316
Lake Superior	Huron Bay	46.85/-88.26	walleye	0.023
Lake Superior	Tahquamenon River	46.56/-85.03	walleye	0.005
Lake Huron	Saginaw Bay, Bay Port	43.86/-83.37	walleye	0.227
Lake Huron	Saginaw Bay	43.78/-83.44	walleye	0.020
Lake Michigan	Grand Traverse Bay	44.99/-85.45	lake trout	0.281
Lake Superior	Isle Royale	47.88/-88.96	lake trout	0.097
Lake Superior	Munising	46.51/-86.57	lake trout	0.024
Lake Superior	Marquette	46.61/-87.35	lake trout	0.533
Lake Huron	Grindstone City	44.06/-82.89	lake trout	0.359
Lake Huron	Thunder Bay	45.06/-83.42	lake trout	0.707

¹See section 3.2.3 for calculation details.

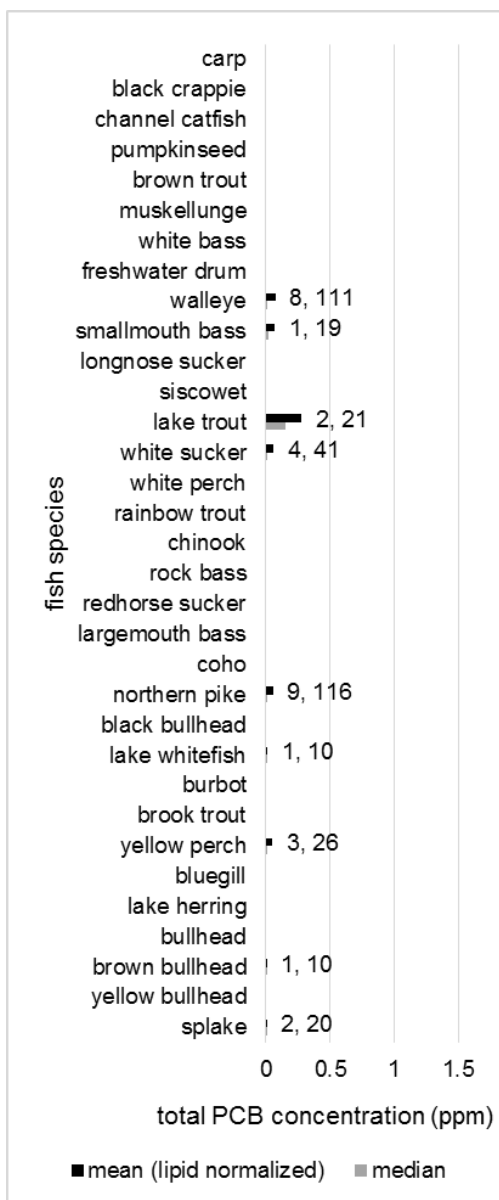


Figure B. 1: Summary of MDEQ fillet fish sample concentrations for Michigan's Upper Peninsula inland lakes from 2000-2015 (Bohr, 2015). Data summary: (number of sites, number of samples).

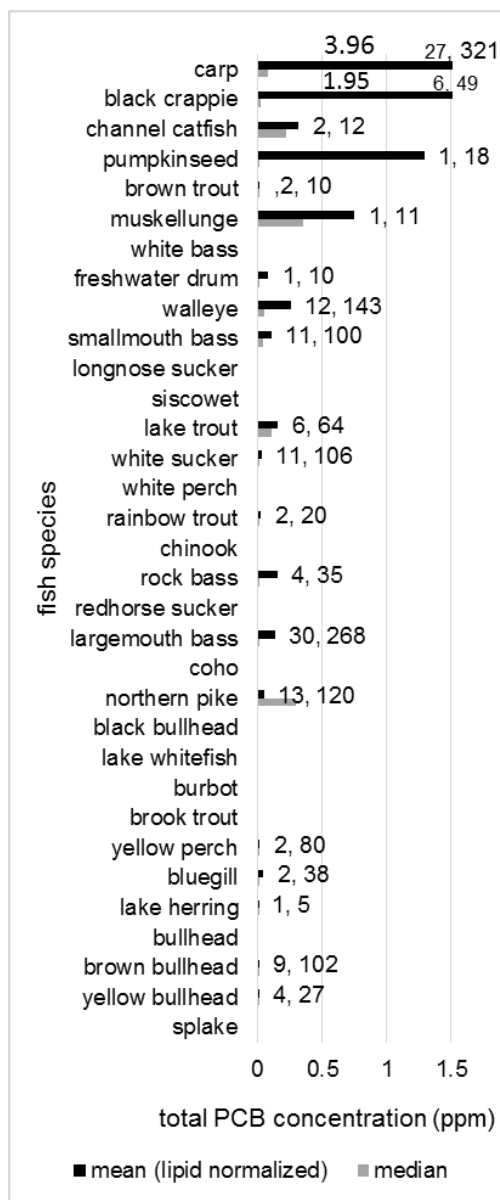


Figure B. 2: Summary of MDEQ fillet fish sample concentrations for Michigan's Lower Peninsula inland lakes from 2000-2015 (Bohr, 2015). Data summary: (number of sites, number of samples). Values exceeding 1.5 ppm indicated above respective bar.

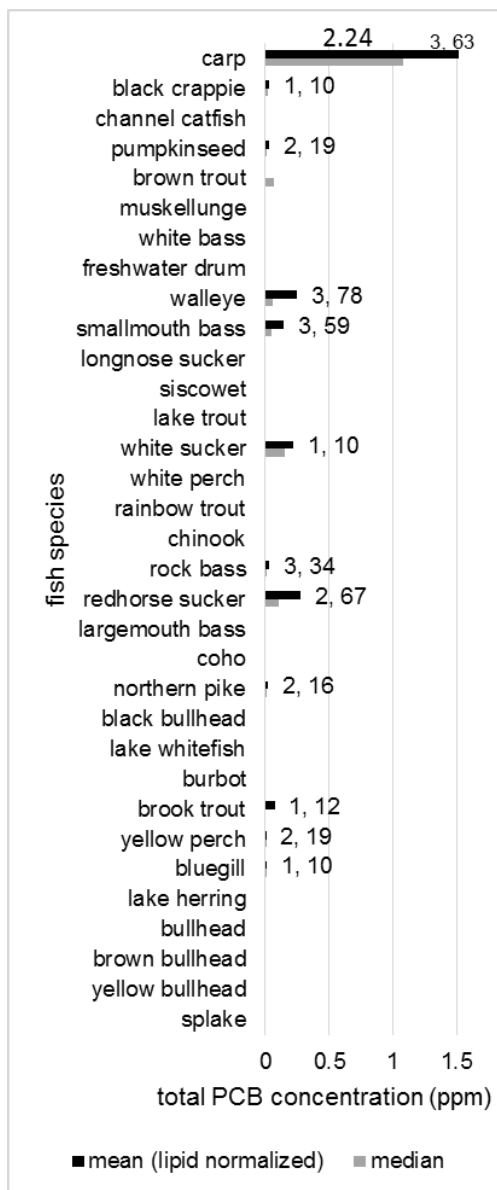


Figure B. 3: Summary of MDEQ fillet fish sample concentrations for Michigan's Upper Peninsula rivers from 2000-2015 (Bohr, 2015). Data summary: (number of sites, number of samples). Values exceeding 1.5 ppm indicated above respective bar.

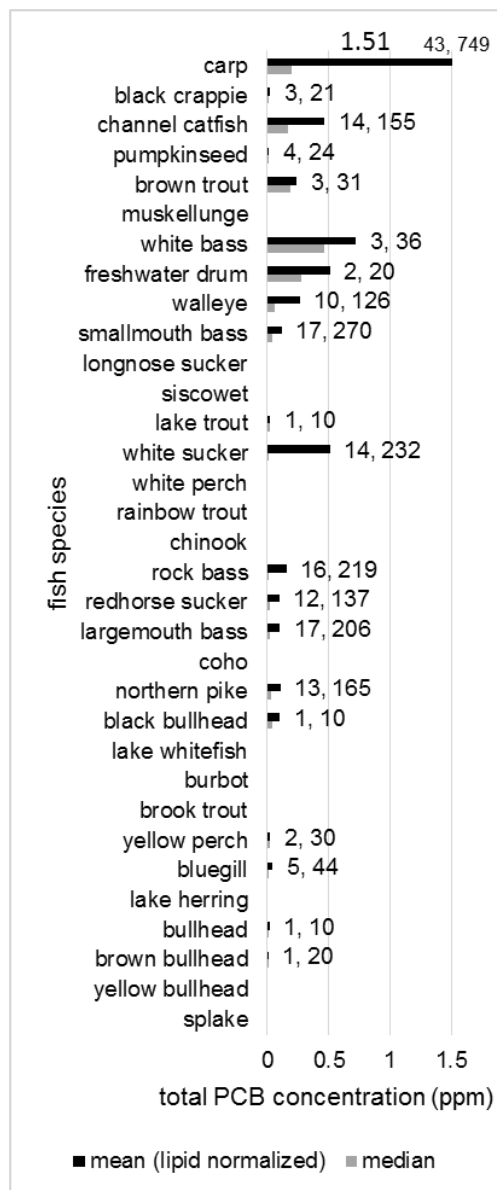


Figure B. 4: Summary of MDEQ fillet fish sample concentrations for Michigan's Lower Peninsula rivers from 2000-2015 (Bohr, 2015). Data summary: (number of sites, number of samples). Values exceeding 1.5 ppm indicated above respective bar.

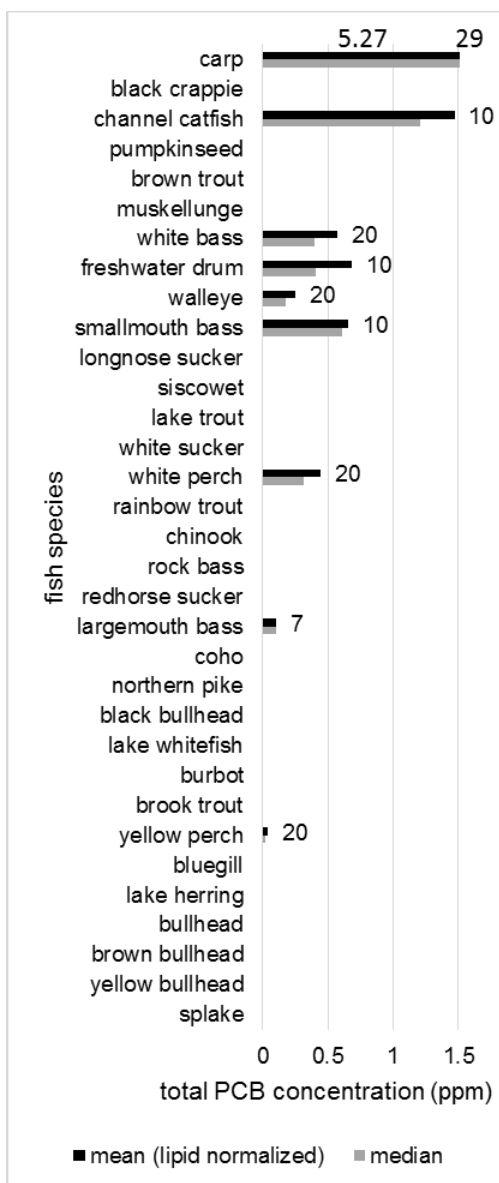


Figure B. 5: Summary of MDEQ fillet fish sample concentrations for Lake Erie from 2000-2015 (Bohr, 2015). Data summary: (number of samples). Values exceeding 1.5 ppm indicated above respective bar.

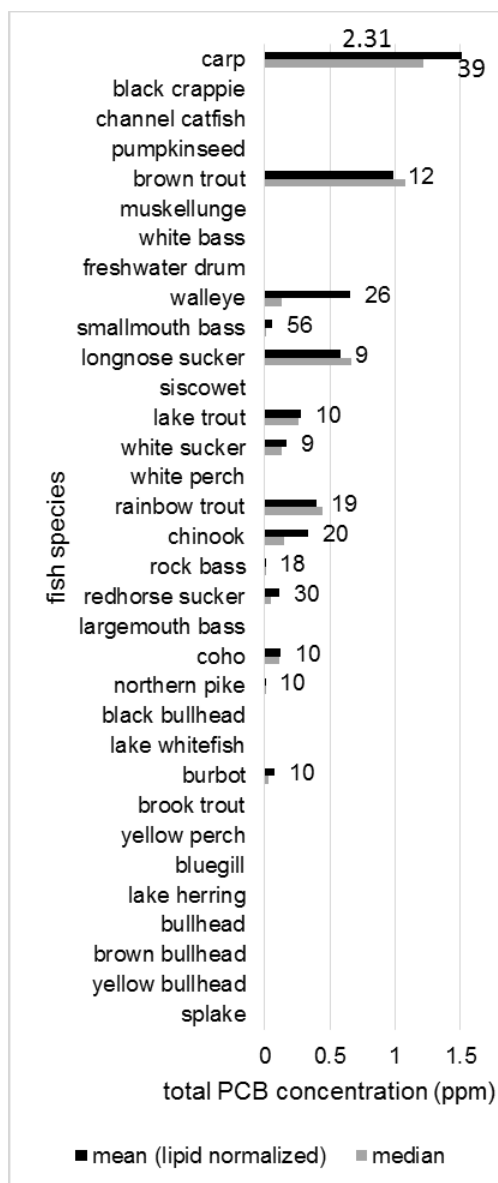


Figure B. 6: Summary of MDEQ fillet fish sample concentrations for Lake Michigan from 2000-2015 (Bohr, 2015). Data summary: (number of samples). Values exceeding 1.5 ppm indicated above respective bar.

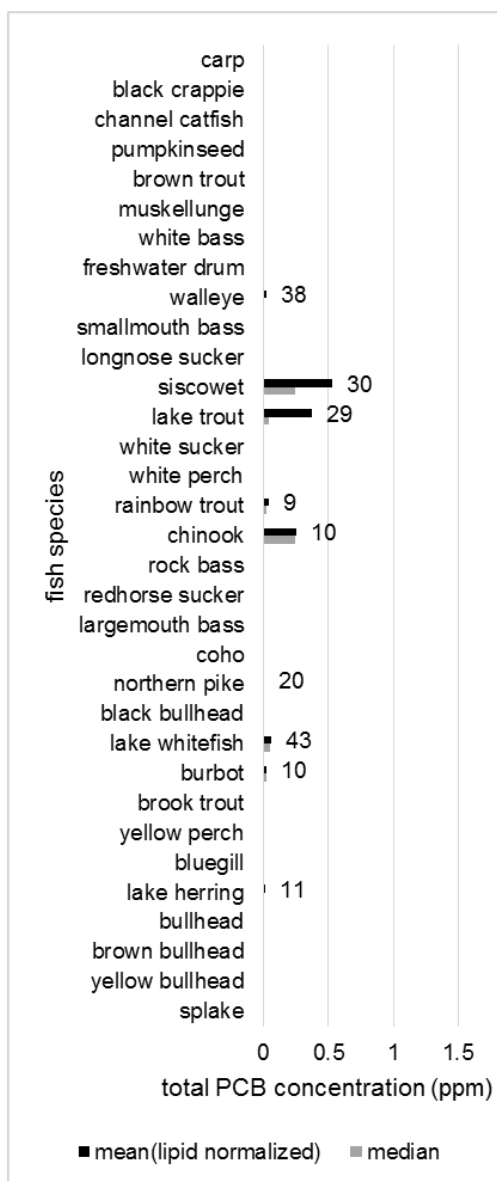


Figure B. 7: Summary of MDEQ fillet fish sample concentrations for Lake Superior from 2000-2015 (Bohr, 2015). Data summary: (number of samples).

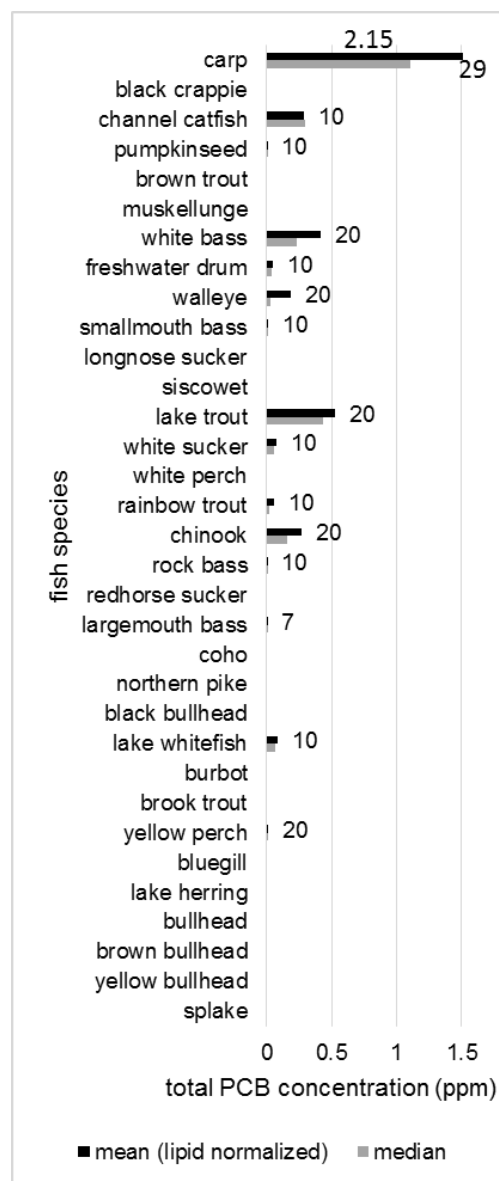


Figure B. 8: Summary of MDEQ fillet fish sample concentrations for Lake Huron from 2000-2015 (Bohr, 2015). Data summary: (number of samples). Values exceeding 1.5 ppm indicated above respective bar.

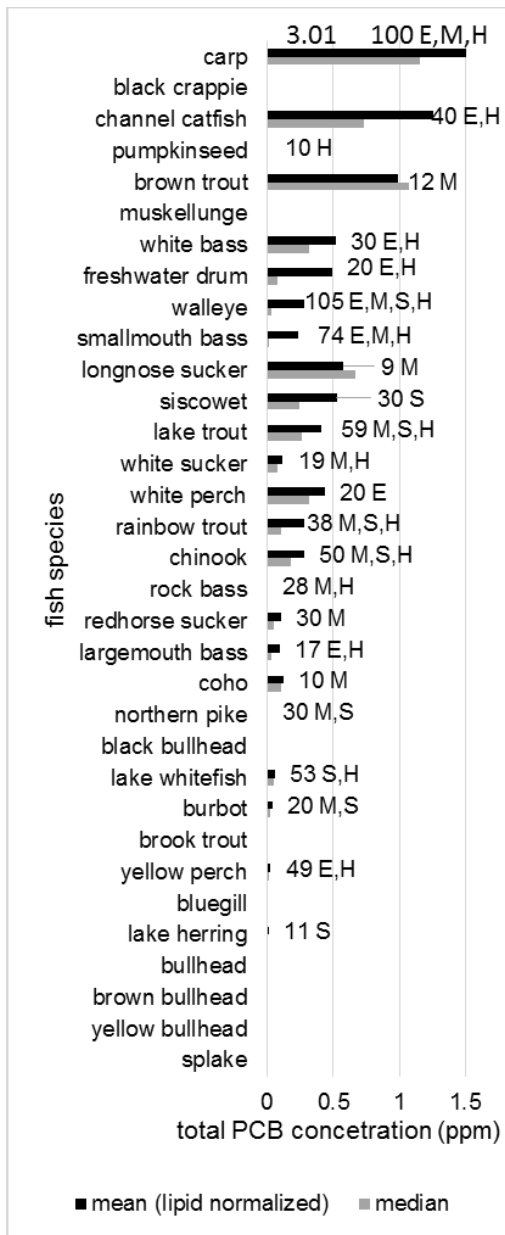


Figure B. 9: Summary of MDEQ fillet fish sample concentrations for all Great Lakes (excluding Lake Ontario) from 2000-2015 (Bohr, 2015). Data summary: (number of sites, Great Lake initial). Values exceeding 1.5 ppm indicated above respective bar

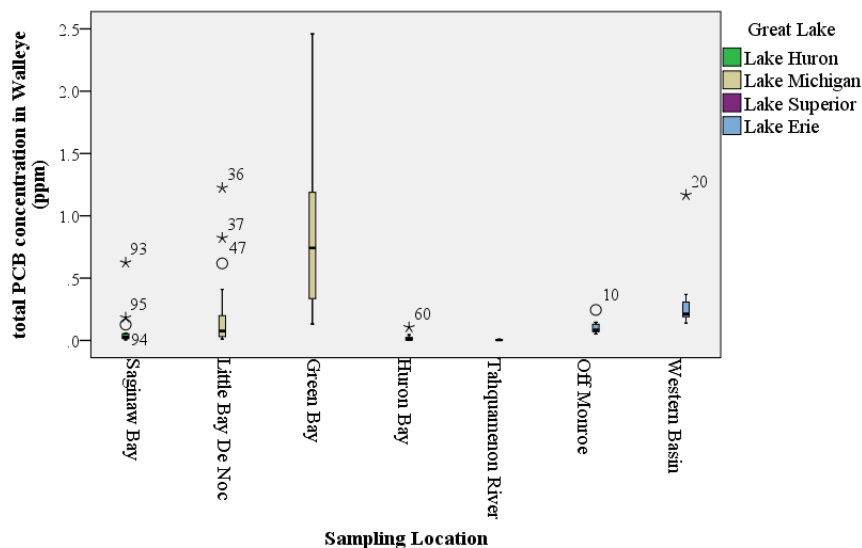


Figure B. 10: Summary of total PCB concentration distributions in walleye from MDEQ Great Lakes sampling sites (Bohr, 2015). See Table B. 4 for site details. Numbers indicate sample number (arbitrary), circles indicate outliers, stars indicate extreme outliers, error bars indicate the maximum and minimum (excluding outliers), and bars indicate the 75th percentile, median (line) and 25th percentile (from top down).

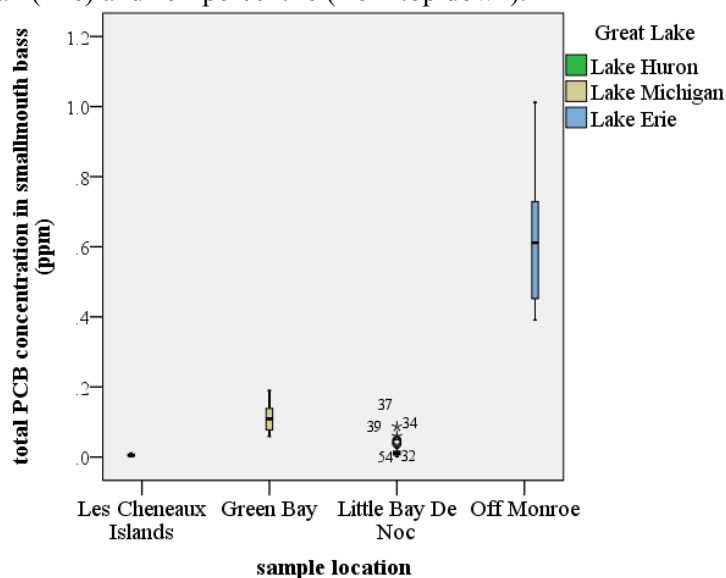


Figure B. 11: Summary of total PCB concentration distributions in smallmouth bass from MDEQ Great Lakes sampling sites (Bohr, 2015). See Table B. 4 for site details. Numbers indicate sample number (arbitrary), circles indicate outliers, stars indicate extreme outliers, error bars indicate the maximum and minimum (excluding outliers), and bars indicate the 75th percentile, median (line) and 25th percentile (from top down).

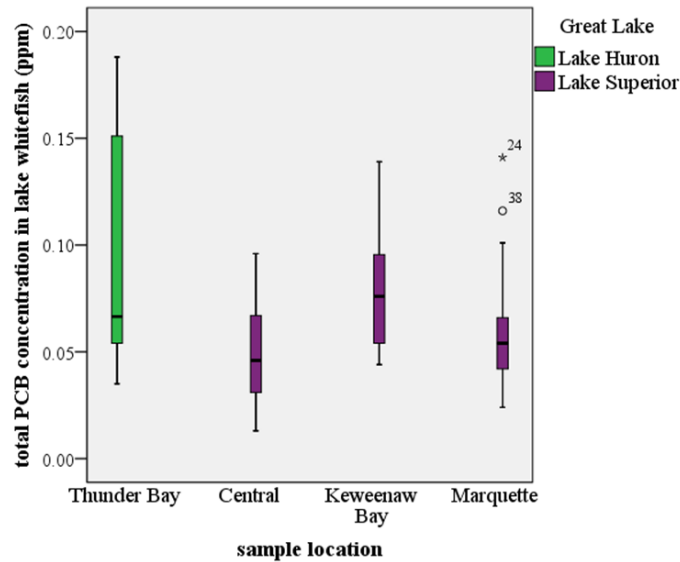


Figure B. 12: Summary of total PCB concentration distributions in lake whitefish from MDEQ Great Lakes sampling sites (Bohr, 2015). See Table B. 4 for site details. Numbers indicate sample number (arbitrary), circles indicate outliers, stars indicate extreme outliers, error bars indicate the maximum and minimum (excluding outliers), and bars indicate the 75th percentile, median (line) and 25th percentile (from top down).

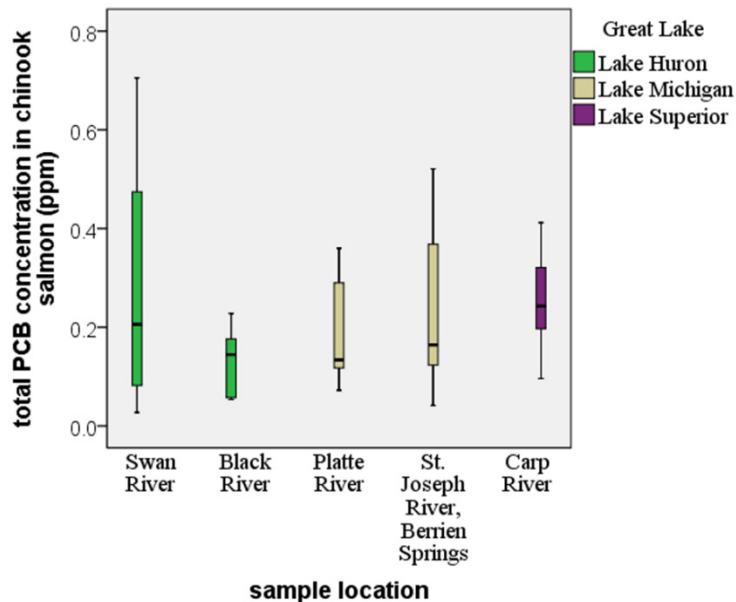


Figure B. 13: Summary of total PCB concentration distributions in chinook salmon from MDEQ Great Lakes sampling sites (Bohr, 2015). See Table B. 4 for site details. Numbers indicate sample number (arbitrary), circles indicate outliers, stars indicate extreme outliers, error bars indicate the maximum and minimum (excluding outliers), and bars indicate the 75th percentile, median (line) and 25th percentile (from top down).

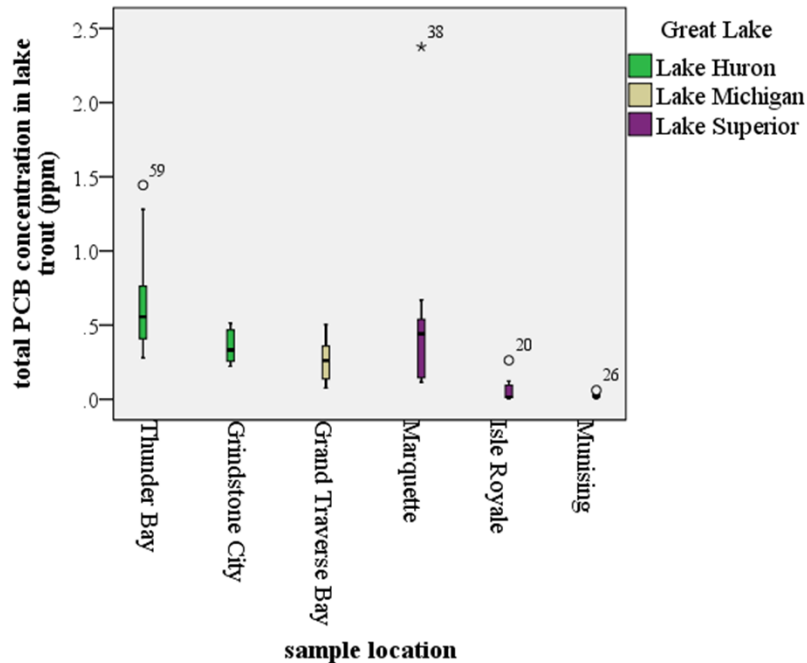


Figure B. 14: Summary of total PCB concentration distributions in lake trout from MDEQ Great Lakes sampling sites (Bohr, 2015). *See Table B. 4 for site details.* Numbers indicate sample number (arbitrary), circles indicate outliers, stars indicate extreme outliers, error bars indicate the maximum and minimum (excluding outliers), and bars indicate the 75th percentile, median (line) and 25th percentile (from top down).

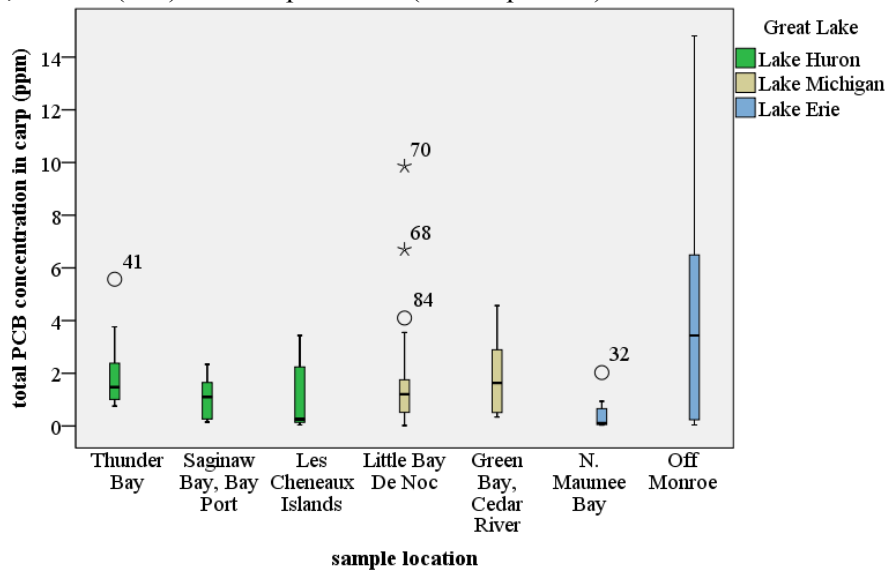


Figure B. 15: Summary of total PCB concentration distributions in carp from MDEQ Great Lakes sampling sites (Bohr, 2015). *See Table B. 4 for site details.* Numbers indicate sample number (arbitrary), circles indicate outliers, stars indicate extreme outliers, error bars indicate the maximum and minimum (excluding outliers), and bars indicate the 75th percentile, median (line) and 25th percentile (from top down).

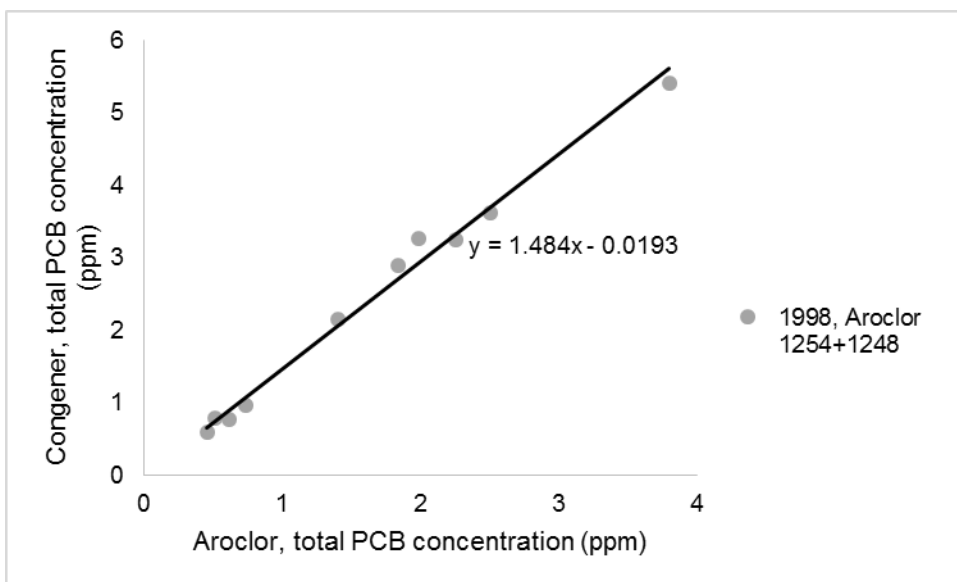


Figure B. 16: Aroclor method vs. congener method regression analysis for walleye in Brest Bay, Lake Erie (MDEQ, 2013). The legend indicates the year sampling occurred and which Aroclor mixture(s) were included in the total PCB concentration calculation.

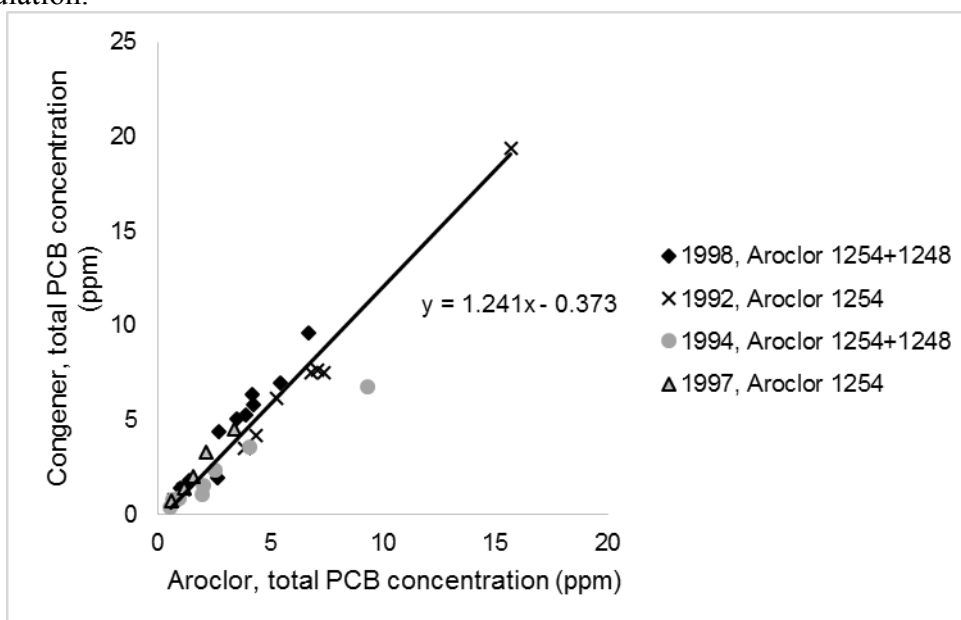


Figure B. 17: Aroclor method vs. congener method regression analysis for carp in Brest Bay, Lake Erie (MDEQ, 2013). The legend indicates the year sampling occurred and which Aroclor mixture(s) were included in the total PCB concentration calculation.

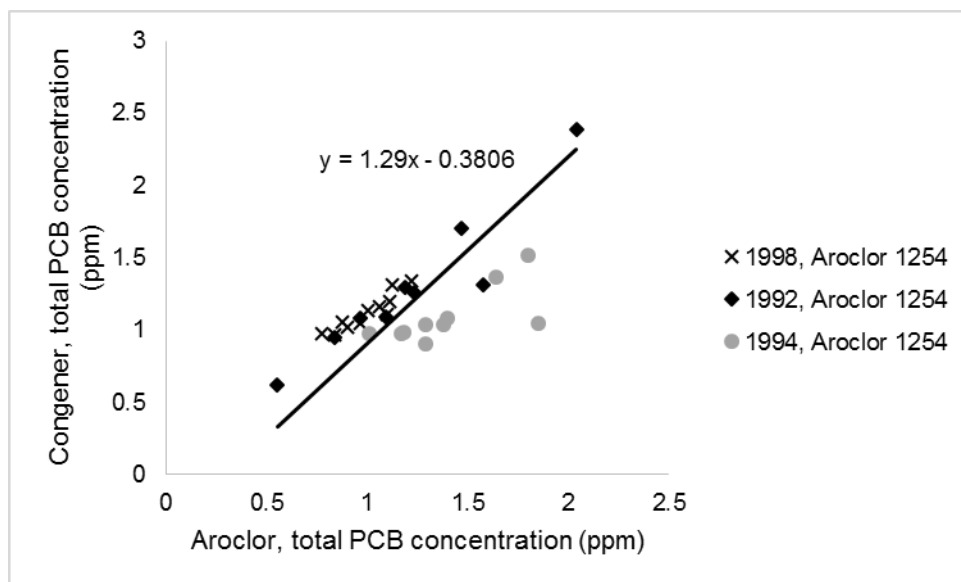


Figure B. 18: Aroclor method vs. congener method regression analysis for lake trout in Thunder Bay, Lake Huron (MDEQ, 2013). The legend indicates the year sampling occurred and which Aroclor mixture(s) were included in the total PCB concentration calculation.

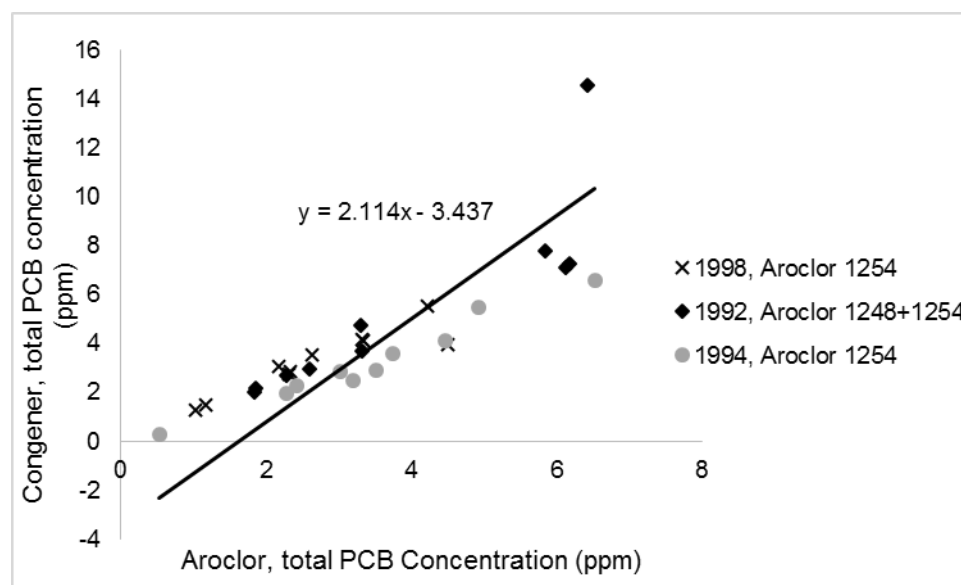


Figure B. 19: Aroclor method vs. congener method regression analysis for carp in Saginaw Bay, Lake Huron (MDEQ, 2013). The legend indicates the year sampling occurred and which Aroclor mixture(s) were included in the total PCB concentration calculation.

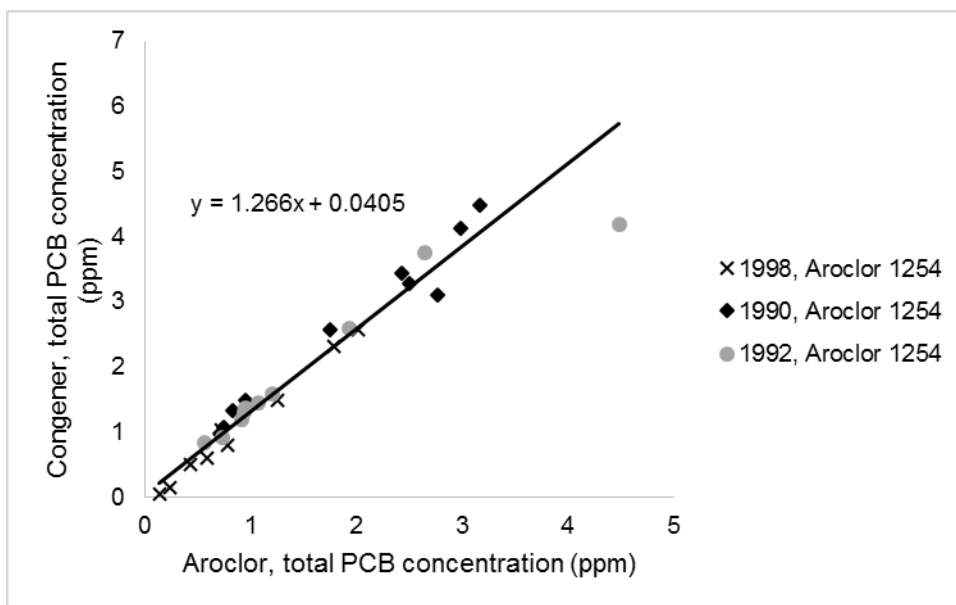


Figure B. 20: Aroclor method vs. congener method regression analysis for carp in Lake St. Clair (MDEQ, 2013). The legend indicates the year sampling occurred and which Aroclor mixture(s) were included in the total PCB concentration calculation.

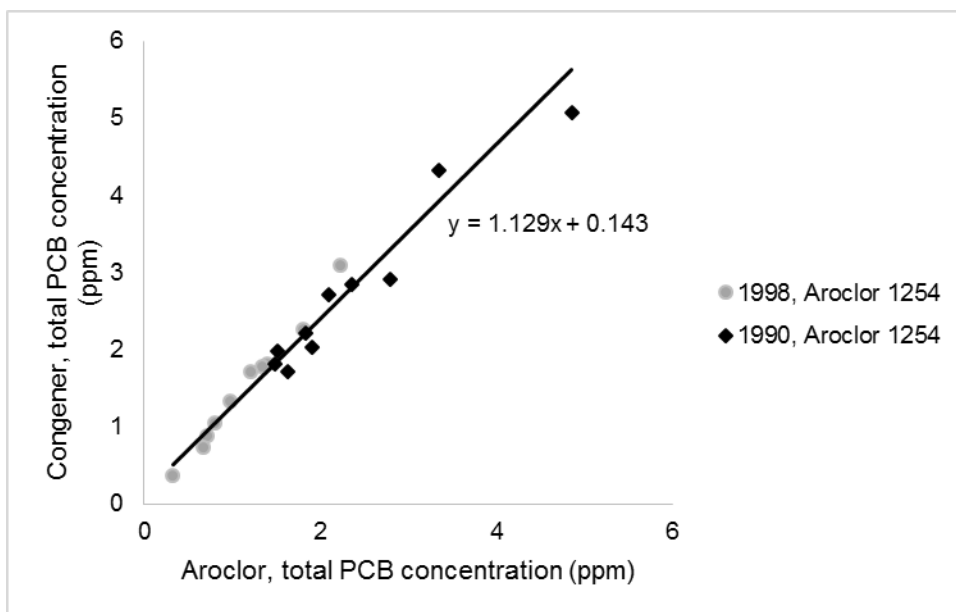


Figure B. 21: Aroclor method vs. congener method regression analysis for walleye in Lake St. Clair (MDEQ, 2013). The legend indicates the year sampling occurred and which Aroclor mixture(s) were included in the total PCB concentration calculation.

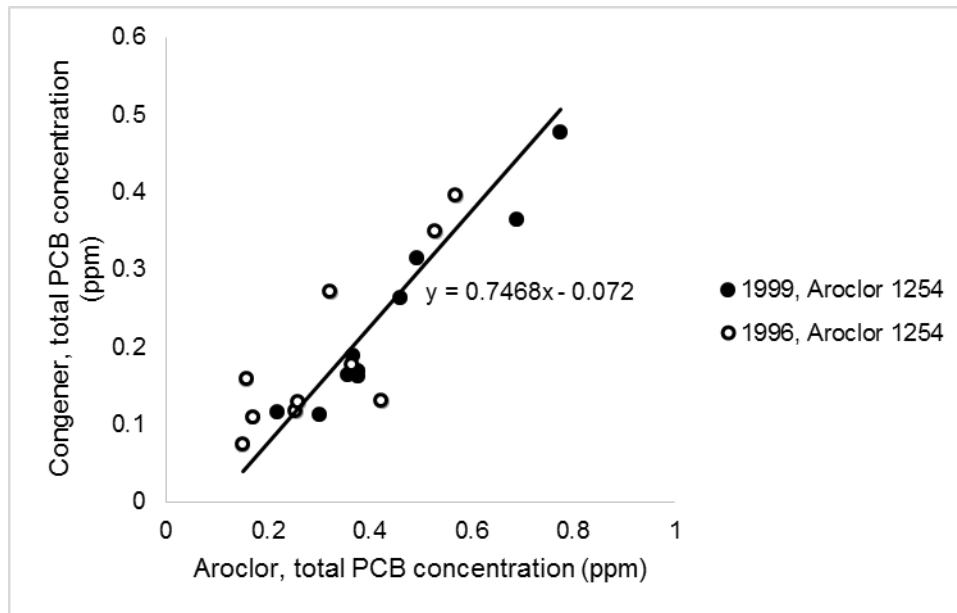


Figure B. 22: Aroclor method vs. congener method regression analysis for lake trout in Keweenaw Bay, Lake Superior (MDEQ, 2013). The legend indicates the year sampling occurred and which Aroclor mixture(s) were included in the total PCB concentration calculation.

Table B. 5: Great Lakes multiple linear regression analysis and correlation analysis inputs. Each table element has a respective footnote as reference. All values were log-transformed for analysis.

Great Lake Name	Site Name ¹	Latitude/ Longitude ²	secchi depth (m)	distance to contamination (km)	watershed (km ²)	population	Surface Area (km ²)	mean depth (m)	max depth (m)	Total PCB Conc. in walleye (ppm) ²³
Lake Superior	Huron Bay	46.84698/-88.25881	17.0 ³	203.0 ⁷	237.5 ¹²	2390 ¹⁹	42 ²⁰	21.3 ¹⁵	48.8 ¹⁵	0.014
Lake Superior	Tahquamenon River	45.55514/-85.0292	2.0 ³	368.0 ⁸	2046.1 ¹³	3648 ¹⁹	1004 ²⁰	12.8 ¹⁵	128.0 ¹⁵	0.002
Lake Erie	Off Monroe	41.89317/-83.3313	3.5 ⁴	0.5 ⁹	2776.5 ¹⁴	178577 ¹⁹	3600 ¹⁵	7.3 ²²	18.9 ²²	0.102
Lake Erie	Western Basin	41.8566/-83.2708	3.5 ⁴	6.7 ⁹	31908.7 ¹⁵	1797981 ¹⁹	3600 ¹⁵	7.3 ²²	18.9 ²²	0.244
Lake Michigan	Little Bay De Noc	45.79069/-87.05099	2.4 ⁵	88.0 ¹⁰	4032.6 ^{16,17}	28513 ¹⁹	4241 ²¹	15.8 ²¹	54.9 ¹⁵	0.066
Lake Huron	Saginaw Bay, Bay Port	43.85457/-83.3715	1.8 ⁶	0.001 ¹¹	22556.2 ¹⁸	1400000 ¹⁸	2960 ¹¹	14.6 ¹⁵	40.5 ¹⁵	0.043
Lake Huron	Saginaw Bay	43.783/-83.4362	1.8 ⁶	0.001 ¹¹	22556.2 ¹⁸	1400000 ¹⁸	2960 ¹¹	14.6 ¹⁵	40.5 ¹⁵	0.020

¹Site name based on walleye sampling site name (Bohr, 2015); ²Coordinates provided for sampling site (Bohr, 2015);

³Minnesota Sea Grant, 2013; ⁴Charlton, 2008; ⁵Qualls et al., 2013; ⁶MDEQ, 2006; ⁷US EPA, 2014; ⁸Environment Canada, 2011; ⁹US EPA, 2013b; ¹⁰US EPA, 2012; ¹¹US EPA, 2013c; ¹²Keweenaw Bay Indian Community, 2008; ¹³Waybrant and Zorn, 2008; ¹⁴River Raisin Watershed Council, 2015; ¹⁵ArcGIS 10.2 and maps (NOAA, 2013 and Great Lakes Information Network, 2015a and b); ¹⁶US EPA, 2013d; ¹⁷US EPA, 2013a; ¹⁸Saginaw Bay Watershed Initiative Network, 2015; ¹⁹Estimated from US Census Bureau (2015); ²⁰Estimated using Google Earth Pro (Google Inc., 2015); ²¹WICCI Green Bay Working Group, 2011; ²²Lake Erie Waterkeeper, 2015; ²³Lipid normalized total PCB concentration in walleye samples ranging from 40 to 50 cm in length (Bohr, 2015).

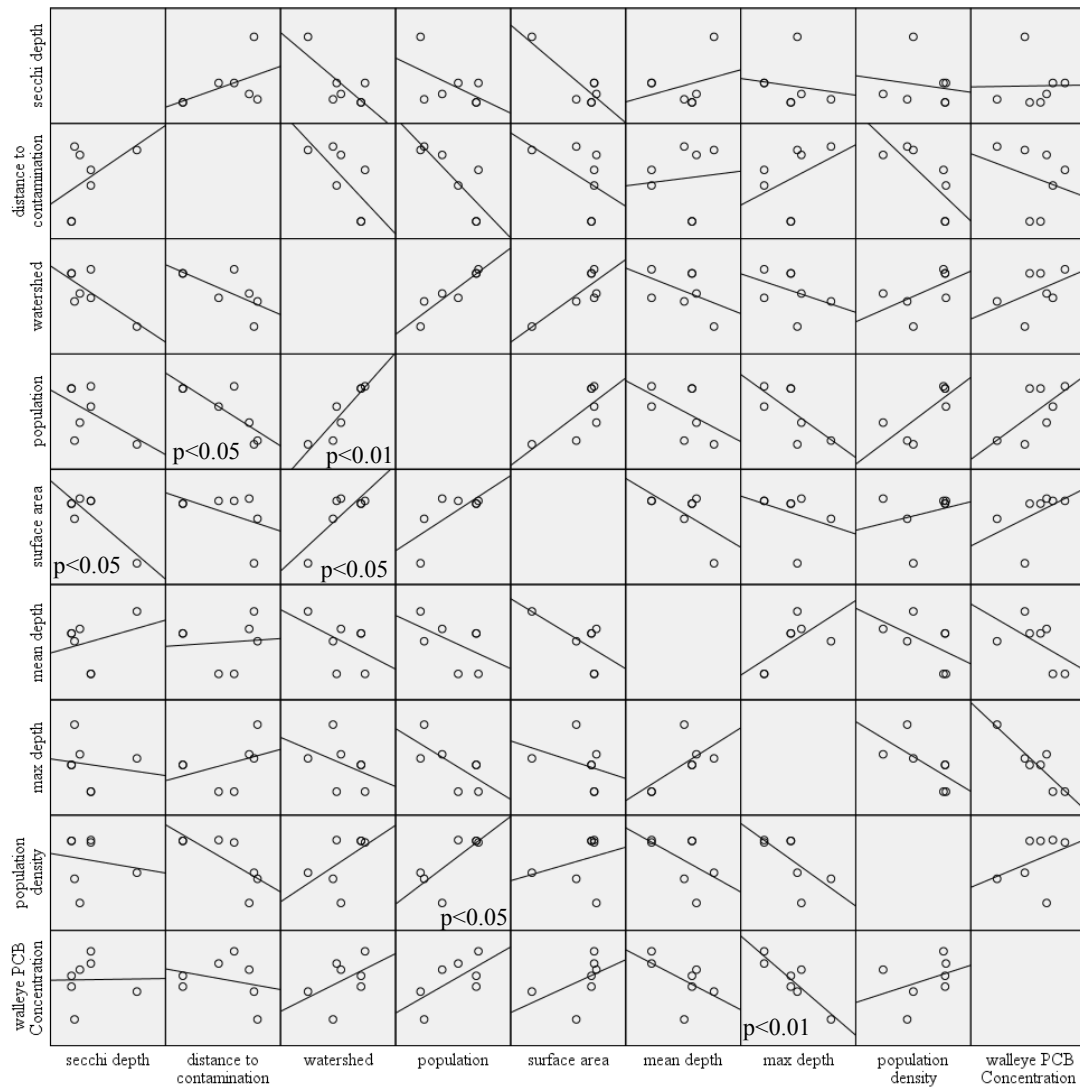


Figure B. 23: Correlation matrix of Great Lakes sites characteristics from Table B. 5. Six correlations were statistically significant (indicated by the significance levels).

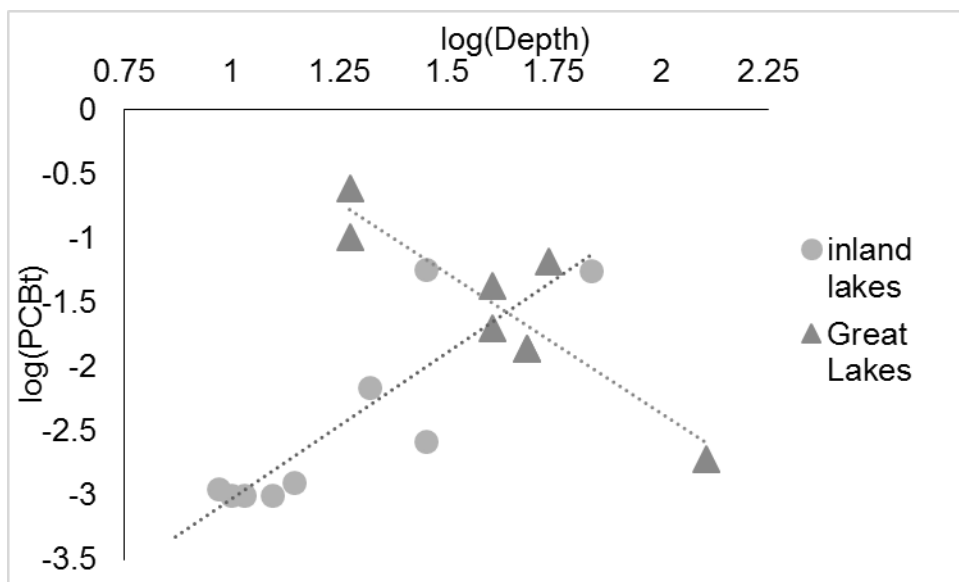


Figure B. 24: Comparison of mean depth from inland lakes and maximum depth from Great Lake sites vs. the total PCB concentration in fish used in MLR analysis.

Table B. 6: Ratios of average PCB congener concentrations that significantly impacted PCA- light congeners: heavy congeners. From Figure 3.15, Component B was most affected by congeners 44, 49, 52, 66, 74 and 77 (light congeners) while Component A was most affected by congeners 138, 153 and 163 (heavy congeners). 'Atm' stands for atmospherically.

	Great Lakes		Inland Lakes	
	atm impacted	locally and atm impacted	atm impacted	locally and atm impacted
min	0.68	0.20	0.06	0.07
max	0.89	0.49	1.50	1.40
average	0.77	0.33	1.08	0.45