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Polychlorinated Biphenyls (PCBs): A Legacy of Contamination in Michigan's Rivers

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POLYCHLORINATED BIPHENYLS (PCBs):
A LEGACY OF CONTAMINATION IN MICHIGAN'S RIVERS

By

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Abstract

Polychlorinated biphenyls (PCBs) are ubiquitous contaminants worldwide and are the most frequent contaminant at US and bi-national Great Lakes areas of concern (AOCs). This study evaluated existing evidence to answer the questions: *how does total PCB contamination compare between fish species, are there spatial patterns in PCB contamination in fish species,* and *have our remediation efforts been effective?* Using multi-variate statistics (e.g. analysis of variance (ANOVA), principal component analysis (PCA), and multiple linear regression (MLR)), this research evaluated Michigan Department of Environmental Quality (MDEQ) fish contaminant monitoring data to attempt to answer the questions above.

PCB concentrations between the species were only significantly different when compared to carp ($p < 0.05$). There were no statistically significant differences between smallmouth bass, largemouth bass, and walleye. A congener analysis showed that there are similar general patterns in contamination but there is some nuance. For example, carp, smallmouth bass, and largemouth bass have significantly different concentrations of low and high molecular weight congeners ($p < 0.05$) but that is not the case for walleye ($p > 0.05$). This has implications for how we select suites of congeners used for “total PCB” quantification as well as toxicity.

Sources of PCBs were difficult to establish in Michigan’s rivers. It is clear that PCB concentrations in fish at AOC sites are higher than fish at non-AOC sites ($p < 0.001$). However, we were unable to determine definitively whether rivers were impacted by local or atmospheric sources of PCBs, but carp, largemouth bass, and walleye in Lake St Clair have similar congener profiles with high concentrations of lighter congeners. ANOVA and MLR showed that site status (AOC or non-AOC) is an important variable to consider when explaining the variance in PCB concentrations and in explaining PCB concentrations. Despite its statistical significance, it has little explanatory power in the ANOVA (partial $ή^2 = 0.017 – 0.040$) and has a low correlation to total PCB concentrations in the MLR (0.122, $p < 0.001$).

Evaluating the efficacy of remediation was done with limited data. A comparison of the quantification methodologies showed that combined trends often contradicted the more accurate congener-based trends in either direction or magnitude. The PCB half-lives ranged from 3.0 – 13.5 $year^{-1}$ at AOC sites and 0.64 – 17.5 $year^{-1}$ at non-AOC sites. These values are not different from the atmospheric half-lives.

Considered together, this work indicates the need for a better monitoring framework to facilitate a complete understanding of sources of PCBs to Michigan’s rivers and a sampling program with the spatial extent and frequency to evaluate remediation efforts. Additionally, PCB researchers at federal and state agencies, generally, should establish a standardized suite of PCB congeners used to quantify total PCB concentrations that will permit comparisons across studies.

1 Introduction

An environmental awakening in the 1970s was preceded by decades of liberal chemical application, culminating in ubiquitous effects on a global scale. Rachel Carson's book *Silent Spring* was the first accessible narrative about the environmental effects of excessive chemical use (Carson 1962). The scientific understanding unlocked by this book changed how humans interacted with the environment and signaled the beginning of an environmental movement that continues to evolve. Today we are reckoning with our history of using, processing, and discarding industrial products, byproducts, and waste into our waterbodies and on their shores. Hindsight has shown that these decisions have left a legacy of contamination globally, and polychlorinated biphenyls (PCBs) are an important part of the story of contamination in the Great Lakes basin. Used in industrial processes as lubricants, coolants, plasticizers, flame-retardants, and in carbonless copy paper, PCBs have far-reaching effects on the environment that continue to unfold.

The Great Lakes basin is home to more than 36 million people from two countries, eight states, two provinces, and approximately 125 sovereign Indigenous nations[1] (MI, WI, MN, Ontario maps). The industries and economies within the basin are as diverse as those who live here. Historically, the region has been the center of automotive, extractive, manufacturing, and agro-industries. Many of these industries are alive and well. Presently, the basin provides cultural ecosystem services (e.g. fishing, boating, and bird watching) that are an important economic contribution. In 2010, $15.4 billion of the US gross domestic product (GDP) was generated within the US Great Lakes shoreline counties (Allan et al. 2015). Under the treaties with the U.S. federal government, Indigenous nations retained the right to hunt, fish, and gather within ceded territories ("The Ways | Great Lakes Native Culture Language", accessed January 2017). The legacy of contamination within the basin affects the well-being of all of us who call this place home.

The general question that guided this research was *how are we doing?* Industrially contaminated locations within the Great Lakes basin are numerous and Michigan is no exception. Collectively, we have been aware of industrial contamination since the late 1960s. Since then international guidance documents (International Joint Commission) have encouraged progress and policy has funded cleanup projects. More than 40 years after the designation of Areas of Concern (discussed next), a reflection on and evaluation of the progress we have made seemed appropriate.

[1] There is not a centralized count for Indigenous and First Nations within the Great Lakes basin. This count is an approximation compiled from different sources. This ad-hoc approach subtly implies that some groups are worth identifying and some are not.

1.1 What are areas of concern?

Areas of Concern (AOCs) are geographic areas in the Great Lakes basin where local human activities resulted in beneficial use impairments (BUIs), changes in the chemical, physical, or biological integrity of the Great Lakes system (GLWQA 1987). The original Great Lakes Water Quality Agreement represented a commitment by the US and Canada to begin to address the contamination in the basin (GLWQA 1972). Since then there has been concerted effort within the basin to identify, prioritize, and remediate contaminated sites. Throughout the Great Lakes basin, 42 AOC sites were designated in either Canada or the US. Currently, there are 22 sites on the US side in addition to five bi-national sites. Of those 27 US-affiliated AOCs, 21 of them have PCB contamination making PCBs the most frequently occurring contaminant (Figure 1-1).

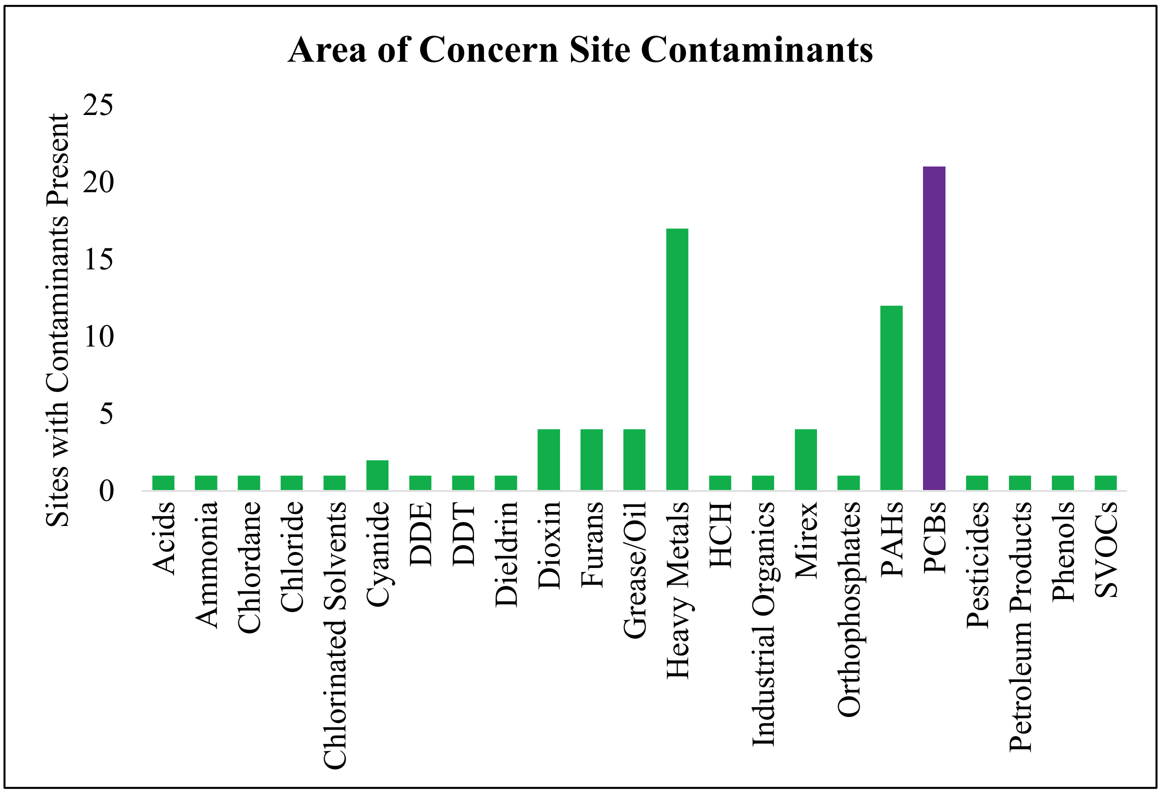


Figure 1-1 Contaminants present at US (and bi-national) Great Lakes Areas of Concern. PCBs are the most frequently occurring contaminant, present at 21 of the 27 sites.

Extensive PCB contamination is also an issue at AOC sites within Michigan and is associated with six of the twelve BUIs: restriction of fish and wildlife consumption, tainting of fish and wildlife flavor, fish tumors and other deformities, bird or animal deformities or reproduction problems, degradation of benthos, and restrictions on dredging activities. All eleven riverine AOC sites have PCB contamination (Figure 1-2). To develop a guidance document, the Michigan Department of Natural Resources and the Environment (MDNRE) and the Office of the Great Lakes (OGL) classified remedial actions as tier 1, tier 2, or tier 3 with removal and restoration actions being completed in the short term (0-3 years), midterm (3-5 years), or long term (5+ years), respectively (MDNRE 2010; MDEQ 2015). Typically, priority is given to tier 1 restoration activities although further actions can be prioritized based on risk to public health and the environment, reasonable costs, time to completion, state and local support, and percent of restoration achieved by implementing a specific remedial action (MDNRE 2010).

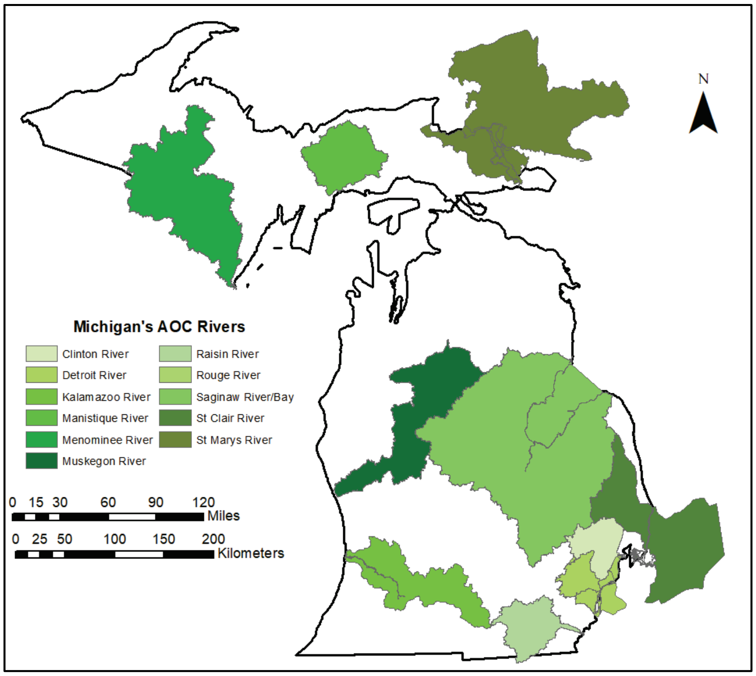


Figure 1-2 Watershed map for AOC rivers in Michigan.
All 11 of the sites reference PCB contamination as an issue.

Cleaning up the Great Lakes AOC sites has fluctuated as a policy priority. The International Joint Commission (IJC) was created in 1909 under the Boundary Waters Treaty between the United States and Canada (IJC website, accessed October 2018). This is a non-regulatory commission that represents a collaborative approach to transboundary issues in the Great Lakes, including toxics. Early on, the biennial reports addressed the progress (or lack thereof) in reducing toxics contamination in the basin. From 1993-2002 the IJC biennial reports brought up toxics and criticized both nations for their failure to address the problem (Langston 2017). Excuses for each nation's failure to eliminate toxic discharges followed each report. After the 2002 report, the IJC largely stopped discussing toxics (Langston 2017).

AOC sites were designated in 1987, and in 2004, the Legacy Act began to provide matching federal dollars for cleanup of contaminated sediment at U.S. AOC sites. To date, the EPA has invested over $338 million, with an additional $227 million from nonfederal partners (Legacy Act webpage, accessed October 2018). Touted as a success, the substantial investment in AOC site cleanup has led to some success. Four million cubic yards of contaminated sediments have been removed from 19 locations in nine US

AOC sites. Characterization of the extent of sediment contamination has occurred at another 23 locations.

Within the framework of our guiding question *how are we doing?*, it is important to be able to answer more specific questions such as, *have our remediation efforts been successful?* Successful remediation would mean that fish PCB concentrations were decreasing at a rate faster than in the atmosphere. Successful remediation also requires an understanding of the source of contamination. Understanding and quantifying the source of PCB contamination is another important piece of successful remediation. Spatial analysis was used to elucidate the question *are there spatial patterns in the PCB contamination in fish?*

1.2 What are polychlorinated biphenyls?

Polychlorinated biphenyls (PCBs) is the name of a group of human-made compounds that are persistent, bioaccumulative, and toxic (PBT). All three of these characteristics are important for understanding why PCBs are an ecological concern. Manufactured globally for use in industry, PCBs continue to be a global problem today, for many of the same reasons that they were so valuable to industry: they resist breakdown, even in extreme conditions (e.g. high heat, acidic or basic conditions, and reduction-oxidation reactions).

The molecular structure of the compounds are such that PCBs are difficult to break down, which is why they were such popular industrial compounds and why they continue to be a problem today. The generic molecular structure shows two aromatic rings, which form the backbone of the PCB molecule (Figure 1-3). Chlorine substitutions can occur in the ortho-, meta-, and para-positions, creating 209 unique arrangements known as congeners. Chlorines also add weight and stability to the compound. Chlorine is 35 times heavier and is less reactive than hydrogen. The outer valence level of chlorine is missing only one electron. Two chlorines can “share” an electron, creating an “electron cloud” around the molecule, and making reactions less likely. The central aromatic ring structure is more stable than a chain structure.

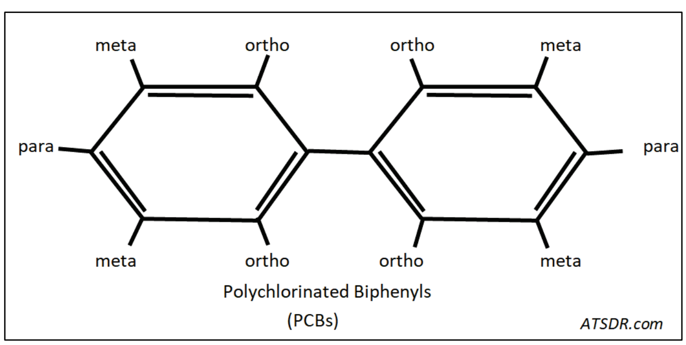


Figure 1-3 A schematic of a PCB molecule.

The octanol-water partition coefficient (K_{ow}) is a quantification of hydrophobicity, which is affected by the chemical structure. "Like dissolves like" is an easy way to describe solubility and is something we understand conceptually. When mixed, oil and water will quickly separate, creating distinct layers. This is because water is a polar solvent while the oil is a non-polar compound. Considering PCBs, we can understand their hydrophobicity on a conceptual level because we know they are oily and waxy substances. Based on the molecular structure, we know PCBs are non-polar, which means they will not dissolve in a polar solvent (e.g. water). Instead, PCBs are soluble in non-polar solvents (e.g. fat).

In the laboratory, the K_{ow} of a compound is quantified by using octanol, a laboratory-grade fat-surrogate. A known amount of PCB is put into a closed container with water and octanol. The ratio between the amount of the compound in the octanol and in the water is the K_{ow}. To facilitate comparison among many different compounds, the results are often reported on a log-scale. For PCBs, the log K_{ow} values range from 4.09 to 8.18 (Hawker and Connell 1988). This means that all PCBs are at least 10,000 times more likely to partition to octanol than water. This has implications for both persistence and bioaccumulation in food webs.

Not manufactured individually, PCB congeners were manufactured as mixtures known as Aroclors. Nine Aroclors were commonly used (1221, 1016, 1242, 1248, 1254, 1260, and 1262). Their nomenclature communicates the chlorine content, with the last two digits indicating percentage chlorine by weight (e.g. Aroclor 1242 is 42% chlorine by weight). The exceptions are 1016 and 1232 (Frame et al. 1996). PCBs were produced globally in amounts that exceeded one million tonnes; the US was responsible for producing about half of the global total and was one of the three countries to begin production in 1930 (Figure 1-4 and Figure 1-5; Breivik et al. 2007). The trade names vary by country (e.g. Aroclors in the US, Kanechlors in Japan, Sovol in the former USSR, Clophen in Germany, etc.), but all the mixtures contain many different congeners. Production in the US ended in 1977, and the USSR (Russia) was the last country to quit production in 1993 (Breivik et al. 2007). The US permits their continued use in closed systems; this is possible because of their persistence (PCBs can be distilled and reused for long periods). Industrial uses for Aroclors varied because the properties of the mixtures varied. Aroclors with a higher percent by weight of chlorine (e.g. Aroclor 1262) contained more of the heavier PCB congeners.

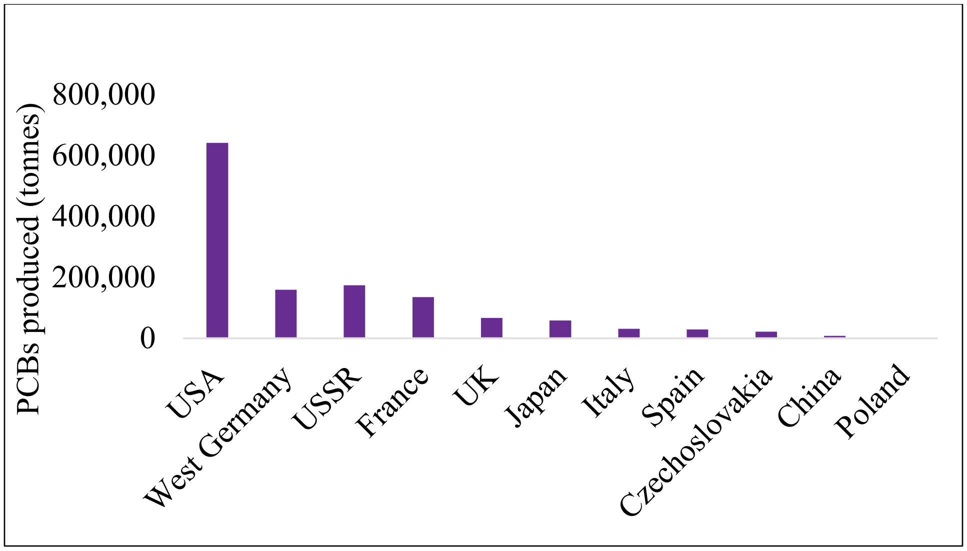


Figure 1-4 Total PCB production by country (in tonnes; Breivik et al., 2007).

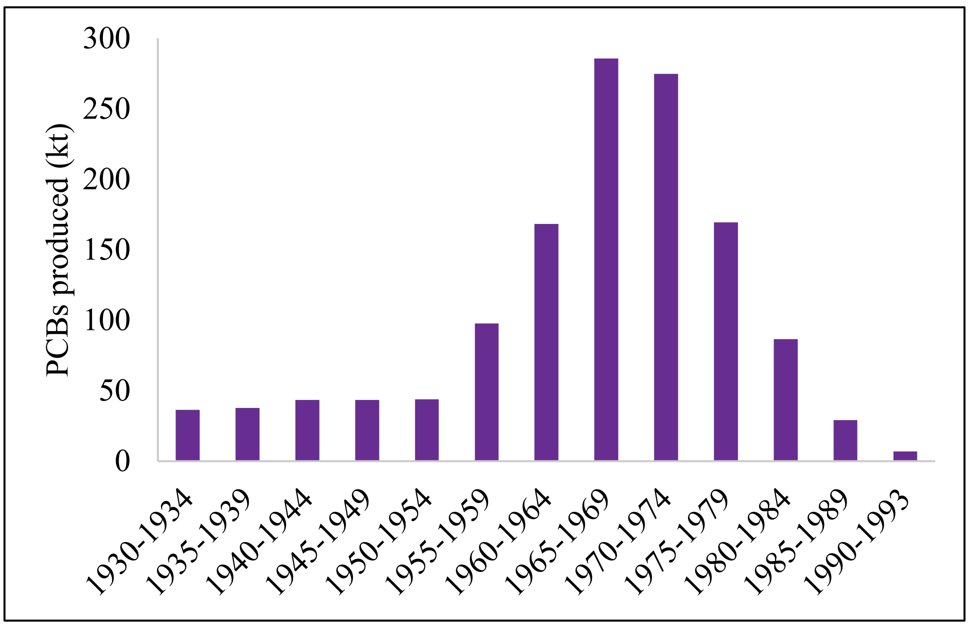


Figure 1-5 Global annual production of PCBs from 1930-1993 (Breivik et al. 2007).

Persistent, bioaccumulative, and toxic (PBT), PCBs have all of the characteristics of the pollutants banned under the Stockholm Convention. Opened for signatures in May 2001, the agreement articulated a global commitment to protecting human health and the environment by eliminating dangerous persistent organic pollutants (POPs) and supporting the transition to safer chemicals (*Stockholm Convention* 2001). The original contingent of compounds, known as the dirty dozen, included PCBs, and were targeted for elimination.

The PBT characteristics are intertwined and are largely related to the compound's structure. PCBs persist in the environment because of their specific chemical structure, resistance to degradation and refractory nature; they resist degradation, and are not very reactive. This persistence leaves them available for different environmental processes such as bioaccumulation.

Bioaccumulation refers to the tendency of a pollutant (i.e. PCBs) to build up in the tissue of organisms due to exposure to contaminated food, air, or water. For this to happen, intake must be greater than breakdown and elimination. Bioconcentration defines the uptake of a pollutant from water, generally across the gill surface for fishes with biomagnification referring to the increase in pollutant concentration that occurs between predator and prey. For compounds that are slowly eliminated or metabolized, concentrations will increase (biomagnify) in successively higher trophic levels in the food web. Since PCBs have log (K_{ow}) values that range from 4.09 to 8.18, we expect to see these persistent compounds accumulate in individual organisms and magnify up the food web (Hawker et al. 1988). Congeners with lower K_{ow} values tend to have lower chlorination and thereby a lower molecular weight, while higher K_{ow} congeners have more chlorine substitutions and are more likely to bioaccumulate (Figure 1-6). The relative importance of biomagnification relative to bioconcentration increases with the size of the organism and with trophic position.

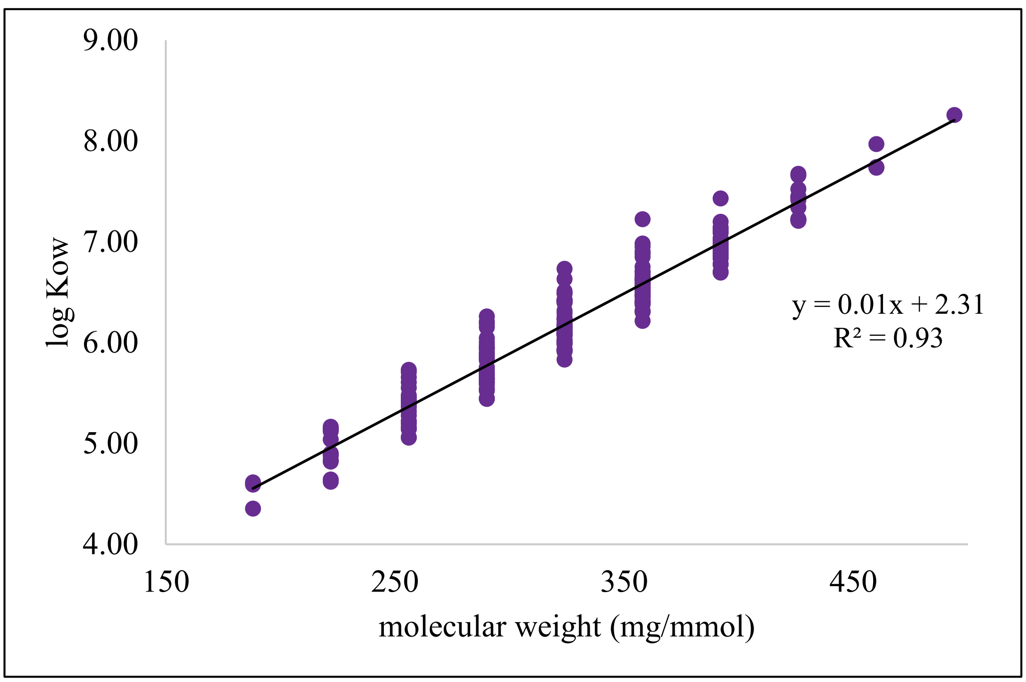


Figure 1-6 A plot of log Kow as a function of molecular weight. The clusters represent homologue groups, individual congeners with the same number of chlorine substitutions. (Frames 1997).

The 209 different chlorine arrangements, known as congeners, complicate the toxicity of PCBs. The positions of the chlorines translate to three types of PCB congeners: dioxin-like (DL), biotransformable, and non-dioxin-like (NDL). Dioxin-like congeners are non-ortho substituted, meaning there are no chlorines in the ortho-position, only chlorines in the meta- and para- positions. This molecular structure is like dioxins, and unsurprisingly it confers similar toxicity. Biotransformable congeners have an open meta- and para-position where enzymes can begin to break down the molecule. Non-dioxin-like congeners have structures that are unlike the others: there are chlorines in the ortho position, which contribute to the molecule's overall rigidity and non-planarity, and chlorines in adjacent positions inhibit the biotransformation of the molecule.

1.3 What is the environmental fate of PCBs?

As mentioned previously, the global production of PCBs ended in 1993 but because of their environmental cycling, the compounds continue to be an ecological concern (Perlinger et al. 2016). Different environmental processes affect the movement of PCBs including sedimentation, weathering, long-range transport, biotransformation, and bioaccumulation. Each of these processes will be discussed below, to provide an understanding of where PCBs end up and how they get there.

Sedimentation from lakes and oceans can represent a possible PCB loss from the environment, assuming the PCBs are buried in the sediments following sedimentation. The sedimentation rate largely determines burial, but hydrologic features such as flow also affect the accumulation of sediments and contaminants (Walters et al. 2008; Simmons and Wallschläger 2005). Sediment-bound PCBs record long-term trends and can indicate the PCB burial (Schneider et al. 2001). They might also represent a possible source of PCBs to the water column through resuspension, although recent work has shown that secondary emissions are significantly responsible for on-going sources of high molecular weight PCBs to Lake Superior (Khan 2018).

Spatial trends in sediment PCBs can provide evidence for localized loadings (e.g. Lake Huron and Georgian Bay) while a lack of a spatial trend can indicate atmospheric loading as an important source (e.g. Lake Superior; Gewurtz et al. 2008). Lake St Clair was determined to be a vector for contaminants, in large part because it is non-depositional. This feature, combined with its shallow depth and increased wave action during storms, results in sediments being contaminated to a lesser degree than in either Lake Erie or Ontario (Gewurtz et al. 2007). The low levels of contaminant concentrations made the determination of spatial trends and loading sources difficult.

Weathering refers to a change in the mixture of congeners present in the environment due to the combination of biological or chemical transformation, preferential partitioning in a multi-phase environment, and selective transport following partitioning. In the case of PCBs, it explains the modified Aroclor compositions based on the physical-chemical properties of the congeners in the mixture. Congeners with identical chlorination (i.e. homologues) partition similarly in the environment. Higher-chlorinated congers are more likely to adsorb to soils and sediments while the lesser-chlorinated congeners are more likely to volatilize which has the effect of concentrating congeners with similar chlorination (i.e. homologues). For example, the upper Great Lakes (Lakes Superior and Huron) have higher proportions of mono-/di-/tri-chlorinated congeners compared to Lake Ontario because of the atmospheric transport of lighter PCBs to the northern lakes (Gewurtz et al. 2008). Depositional areas had higher concentrations suggesting non-point sources, such as atmospheric deposition. This is an example of the global distillation of more volatile compounds. Alternatively, areas at lower latitudes might have a selective enrichment of heavy congeners since the lighter congeners volatilize out of the system. There is also a greater legacy of industrialization in lower Great Lakes.

For semi-volatile compounds like PCBs, secondary emissions can be quantitatively important and can prolong the lifetime in the environment long after primary emissions have ceased, for example, in Lake Superior (Khan 2018). The high latitude of the Great Lakes basin makes it vulnerable to this global distillation process. The Integrated Atmospheric Deposition Network (IADN) measurements reveal that gas-phase total PCBs over the lakes are decreasing, although there is a signal from in-use PCBs (Buehler et al. 2002; Hites 2018). Responses to policy changes can be seen relatively quickly in air and can therefore be used to evaluate the efficacy of such policies (Buehler et al. 2004). However, more vulnerable areas (i.e., high latitudes) receive most of the PCBs from outside the region (Friedman et al. 2016). This is especially true for the lighter, more volatile congeners.

Because Aroclors contain multiple PCB congeners, the composition of the mixture changes as it is mobilized through the atmosphere; homologues are transported through the atmosphere and deposited based on their volatility (Wania et al. 1996). The less mobile congeners will partition to other media (vegetation, soils) and become available for bioaccumulation. The hydrophobic properties of the PCB compounds are an important reason why low dissolved-phase concentrations persist in the lakes. PCB cycling in the lakes is an important process, and large lakes, like the Great Lakes, have the potential to become net sources of PCB contamination as atmospheric concentrations continue to decline (Meng et al. 2008; Baker et al. 1990; Jeremiason et al. 1994).

Biotransformation refers to the complete or partial metabolism of a compound. Once again, the structure of the PCB molecule influences the susceptibility of a congener to biotransformation. Ortho-chlorine substitutions and adjacent un-chlorinated positions represent congeners that are most susceptible to biotransformation (Kannan et al. 1995). This structure has also been shown to predict biotransformation in round gobies and smallmouth bass in Lake Erie (Kwon et al. 2006). Work has shown that bacteria in anoxic sediments can dechlorinate the more chlorinated homologues (octa-, nona-, deca-) (Magar et al. 2005a). Although dechlorination rates for individual congeners were not quantified, sediment cores indicated different sites have different rates (Magar et al. 2005b). Only seven congeners or co-eluting pairs had biotransformation rates quantified in fish: PCB-40, PCB 82-151, PCB-132, PCB-135, PCB-136, PCB-149-133, PCB-202-173 (Buckman et al. 2006). Currently, the MDEQ does not quantify hydroxylated PCBs

(OH-PCBs) which may lead to an underrepresentation of toxicity because research has shown that fish biotransform PCBs to hydroxylated forms (Buckman et al. 2006).

Bioaccumulation, discussed previously, is the tendency of a compound (i.e. a PCB) to build up in the tissues of organisms. The presence of PCBs in primary producers drive concentrations up the food web through biomagnification. The process of biomagnification is confounded by fish characteristics including sex, length, and lipid content that affect bioaccumulation, as well as the season (Gewurtz et al. 2011; Stapleton et al. 2002). Since the environmental fate of PCBs is driven by their chemical characteristics, similar compounds will behave similarly.

The biological fate of PCBs begins with and is driven by the water-phytoplankton flux (Dachs et al. 1999). When the air-water exchange flux is less than the water-phytoplankton exchange flux, the water concentrations are depleted unless there are local sources of PCBs. Biogeochemical cycling of suspended particles and phytoplankton in the seston affects PCBs; when there is more phytoplankton, there tends to be lower PCB concentrations (McCusker et al. 1999).

Both mussels and mayflies are good indicators of contamination in the water column and sediments, respectively. As sessile filter feeders, mussels ingest large volumes of water and mayflies live in and ingest primarily sediment and detritus. Gewurtz et al. (2000) found that in Lake Erie, the PCB contamination in mayfly larvae (13.46 μg/g, lipid normalized) was significantly greater than in *Dreissenia* mussels (6.53 μg/g, lipid normalized), amphipods (5.40 μg/g, lipid normalized), and crayfish (4.34 μg/g, lipid normalized). Mussels had greater PCB contamination than crayfish, but there were no significant differences between mussels and amphipods or crayfish and amphipods (Gewurtz et al. 2000). Invasive species stress ecosystems and can cause shifts in trophic dynamics. *Dreissena bugensis* (quagga mussels) and *Neogobius melanostomus* (round goby) are invasive species from the Caspian Sea region. Quagga mussels, as sessile filter feeders, focus PCBs in a pattern similar to historic sedimentation (Macksasitorn et al. 2015). Round gobies feed on quagga mussels and may increase the PCB transfer to higher predator species.

The trophic transfer of contaminants varies between organisms. In Lake Michigan the trophic transfer efficiency for PCBs in lake trout was 0.8 and it was 0.5 for Coho and Chinook salmon (Madenjian et al. 1998a; Madenjian et al. 1998b; Madenjian et al. 2002). Laboratory measurements indicated an efficiency close to 0.64 for mercury in white fish (Madenjian and O'Connor 2008). Trophic transfer efficiency did not appear to be affected by log K_{ow}, or degree of chlorination, although recent work found that there was less variability in the transfer efficiency factor (Madenjian et al. 1999; Kwon et al. 2006). PCB concentrations is also significantly correlated with trophic position, with higher trophic positions acquiring more contaminants (Houde et al. 2008).

The behavior of PCBs and organochlorine pesticides varies greatly between the Great Lakes. Annual changes in PCB concentrations in fish were significant in Lakes

Huron, Ontario, and Michigan (9.8 ± 3.8% for Lake Ontario to 15 ± 3.6% for Lake Michigan) (Chang et al. 2012). These authors attribute longer atmospheric half-lives in Lakes Superior and Huron as compared to Lakes Michigan and Ontario to physical properties such as volume and temperature.

The chemical structure and properties of PCBs are largely responsible for their environmental behavior. Understanding this behavior is important in the consideration of the *how are we doing* question. Ultimately, PCBs are globally distributed pollutants. With this ubiquity however, patterns are likely to emerge and assessment of the spatial patterns of PCBs can ultimately help us to identify the sources within specific boundaries. These spatial patterns combined with the variables that affect bioaccumulation means that different species will be affected differently. To understand the hazard to humans we must be able to also answer the question *how does total PCB concentrations compare between different species?*

1.4 What are the health effects of PCBs to humans?

Presently, most of our policies seek to mitigate negative health effects as defined by an absence of disease. Alternatively, WHO defines health as "… a state of complete physical, mental, and social well-being, and not merely the absence of disease or injury". These two ways of considering health lead to very different approaches for addressing PCB contamination. It is within the first health framework that the EPA characterizes risk by conducting risk assessments (RAs), separately for human and ecological health. Three factors are considered for these EPA-guided RAs, 1) the amount of chemical present in an environmental medium, 2) how much contact an organism might have with the contaminated medium, and 3) the inherent toxicity of the chemical (EPA website, accessed June 2018). This section will focus on the last two factors, a compound's toxicity and exposure.

Classified as toxic, PCBs affect health in a variety of sub-lethal ways, including as probable carcinogens (IARC; EPA; ATDSR). The three different categories of PCBs complicate the group's toxicity. Dioxin-like (DL) congeners are similar to polychlorinated dibenzodioxins (PCDDs) and polychlorinated dibenzo furans (PCDFs) with regard to their chemical structure. All three have chlorines on the ends of the molecule that enable them to bind strongly to the aryl hydrocarbon receptor (AHR), a protein associated with the metabolism of toxic compounds. Even within this category, the toxic response varies because the AHR regulates many different genes. There are immunological responses, dermatologic effects such as lesions and chloracne, as well as reproductive, developmental, endocrine, and hepatic effects (Yu 2014). Non-dioxin-like (NDL) congeners have toxicity that is not well characterized, which precludes the establishment of generally accepted risk quantification (Hamers et al. 2011). However, the toxicological effects of NDL congeners occur via multiple pathways not involving the AHR (i.e. endocrine disruption, neurotoxicity, immunological toxicity). Similarly, CYP450 enzymes metabolize biotransformable congeners (phase I metabolism) which make compounds more hydrophilic so that the body can eliminate them. During biotransformation, a PCB compound can be up- or down-regulated to create sub-lethal toxic effects (i.e. endocrine disruption and immunological toxicity). When a compound is up-regulated, it means it stimulates a cellular response while a down-regulated compound stifles a cellular response. This is an important consideration because the production of CYP450 enzymes relies on a cellular response, as does the initiation step for DNA replication.

Through animal research, reference doses (RfDs) for specific health endpoints are determined (Table 1-1) and extrapolated to humans. It is important to note that total PCBs determined by Aroclors (not congeners) are typically the basis for RfDs. Once it is determined that a concentration achieves an end point, a safety factor is applied (1-10) to account for sensitive individuals, species extrapolation, degree of severity in the clinical response, and duration of the study (MDCH 2012). In Michigan an RfD of 0.02 μg/kg*day of Aroclor 1254 is the basis for the fish consumption screening value. "This RfD provides screening values that might not account for health effects that result from dioxin-like activity that specific PCB congeners may have" (MDCH 2012).

Table 1-1 Different health endpoints and their respective reference doses (RfDs). A RfD is typically derived from animal studies and represents a threshold at which an adverse effect is not expected. The RfDs are based on Aroclor mixtures (MDCH 2012).

Health Endpoint	Reference Dose (RfD)	Species of Study
Cancer	0.04-2.0 mg/kg*day	Rats
Developmental Effects (neurological)	0.02 μg/kg*day	
Developmental Effects (Reduced Birth Weight)	0.07 μg/kg*day	Rhesus monkeys
Immunological Effects (inflamed Meibomian glands, decreased antibody response to sheep erythrocytes)	0.02 μg/kg*day	Cynomolgus monkeys

Toxic equivalency factors (TEFs) begin to consider the cumulative effects of exposure to multiple contaminants and are an important tool as we begin to recognize the risks associated with synergistic and/or antagonistic compounds. PCBs are only one of many compounds to which humans are exposed through fish consumption. Polychlorinated dibenzo dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs) are two important additional classes of compounds because of their common mode of action, binding to the Ah receptor. To facilitate inclusive risk assessment TEFs were developed, and quantify relative toxicity compared to tetrachlorodibenzo dioxin (TCDD). Since not all PCBs have this Ah-receptor toxicity, TEFs were only developed for the 12 that do (Table 1-2). The TEFs facilitate a comparison of toxicity between dissimilar compounds and provide a summation of "total toxicity", known as toxic equivalency (TEQ) (Equation 1-1).

$$\text{toxic equivalency factor} = \frac{\text{effective dose}_{50}\ \text{(compound)}}{\text{effective dose}_{50}\ \text{(TCDD)}} \qquad \text{Equation 1-1}$$

Table 1-2 Toxic equivalency factors (TEF) developed by the World Health Organization (WHO) (Van den Berg et al. 2006).

Congener Number	**TEF (1998)**	**TEF (2005)**
77	0.0001	0.0001
81	0.0001	0.0003
105	0.0001	0.00003
114	0.0005	0.00003
118	0.0001	0.00003
123	0.0001	0.00003
126	0.1	0.1
156	0.0005	0.00003
157	0.0005	0.00003
167	0.00001	0.00003
169	0.01	0.03
189	0.0001	0.00003

Fish are often touted as a low-fat protein source, rich in omega-3 fatty acids. Simultaneously, fish consumption advisories exist in all 50 states with PCBs being one of the most frequent culprits. In Michigan, statewide fish consumption advisories exist for 14 fish species because of mercury contamination, for one species (carp) because of only PCB contamination, and for one species (catfish) because of both chemicals (EPA 2011). Additionally, a knowledge gap exists pertaining to the omega-3 content of Great Lakes fishes, which precludes a risk-benefit analysis, an important decision-making tool for policy-makers and fish consumers alike (Turyk 2004).

Consumption of contaminated fish and seafood remains the predominant pathway of human exposure to PCBs, and a large amount of variability in consumption rates exist within geographic regions (EPA 2011). Self-reported fish consumption rates for Indigenous peoples are up to ten times greater than for the average consumer; however, average measured consumption was up to 60% lower than self-reported consumption (Dellinger 2004). Indigenous peoples are not the only communities known to consume fish regularly. Immigrant communities from places where fish and seafood are culturally important often bring these traditions with them when they immigrate to the US. First- and second-generation Asian American and Pacific Islander immigrants (AAPI) have been shown to consume more fish and seafood than accounted for in consumption rate guidelines (Sechena et al. 2003). Women from coastal regions also tend to have higher blood mercury levels (Mahaffey et al. 2009). In rural communities, consumption varied from 1-4 meals per month, but were usually higher during the summer months (Habron et al. 2008). This is a common feature of fish consumption, higher rates during the summer months. Within the fish consumption advisory framework, average fish consumption informs threshold concentrations and has the potential to underestimate the number and size of meals for some communities. An important note, fish consumption advisories are now fish consumption guidelines. I have chosen to use fish consumption advisory (FCA) as opposed to fish consumption guideline.

Within the "risk avoidance" framework of FCAs, effective communication regarding the risks is crucial. In Wisconsin, about 50% of Great Lakes fish consumers were aware of consumption advisories, but more men were aware than women (Ashizawa et al. 2005). Discrepancies in the perception of risk from fish consumption also exist among racial and income groups (Burger et al. 1999). In spite of this, a lack of knowledge is not the only reason people continue to consume fish. The FCAs are an example of policies that ignore many populations that "do not, cannot, or will not reduce risk by adhering to advisory recommendations" (O'Neill 2007; Gagnon 2016). A reconceptualization of the determinants of human health might eliminate FCAs as merely a tool for ensuring "informed consent" and using scientific language to quantify acceptable levels of risk, as it pertains to fish consumption (Arquette et al. 2002; Langston 2017). Instead, the new framework could facilitate the simultaneous and interconnected consideration of ecological and human health for EPA risk assessments, an expansion that might acknowledge its importance for many people (Evans et al. 1990; Wall Kimmerer 2013)

1.5 Research objectives

PCB contamination in fish provides a unique opportunity for exploring the intersection of science, policy, and community. The rate of PCB consumption is important knowledge for informing the creation of policies, both informal and formal, that regulate the cleanup and mitigation of PCB-associated risks. Communities within the basin are varied and have a diverse set of needs and expectations when it comes to contaminant levels in fish. This work focused generally on the question of *how are we* *doing?* with regard to PCB contamination in Michigan's rivers. To begin to answer this question it was broken down into three components: species differences, sources of contamination, and remediation efficacy. To measure our success, we must know how contamination compares among different species, where the PCBs are coming from, and if what we are doing is working.

By focusing on four species of interest (carp, smallmouth bass, largemouth bass, and walleye) from 2000 - 2015, we can evaluate a snapshot of portions of the food web. A comparison of both total PCB concentrations as well as congener profiles show us the magnitude and pattern of PCB concentrations. Determining the sources of PCBs and evaluating the efficacy of remediation go hand in hand. A clear understanding of sources of PCBs at a location provides direction for remediation work. Measuring PCB concentrations in fish over time demonstrates temporal patterns that can indicate whether the fish species have responded to the remediation efforts. Using a variety of multi-variate statistics, this study evaluated existing evidence to answer the questions: *How do PCB concentrations in different species and at different locations compare? Are there any patterns in PCB contamination in species that elucidate the source?* and *is there a decline in fish PCB concentrations at AOC sites?*

2 Methods

Statistical analyses are useful tools for discerning patterns and trends in environmental contamination and for observing its breadth and extent. The patterns and trends provide key information for developing solutions that protect human and ecological health. This section lays out the methodology for the analyses included in this body of work to address the overarching research objective of evaluating the efficacy of remediation efforts at AOC sites in Michigan. Specific questions include *how do PCB concentrations in different species and at different locations compare? Are there any patterns in PCB contamination in species that elucidate the source?* and *is there a decline in fish PCB concentrations at AOC sites?*

2.1 Data Source

Using data exclusively from the Michigan Department of Environmental Quality Fish Contaminant Monitoring program (FCMP) from 1987-2015, this work considered four species to compare PCB concentrations between species in different trophic levels. *Sander vitreus* (walleye) are top predators, *Micropterus dolomieu* (smallmouth bass) and *Micropterus salmoides* (largemouth bass) are mid-level predators; and *Cyprinus carpio* (common carp) are omnivores and often feed in benthic areas (Vander Zanden et al.1997). The PCB concentrations were quantified in smallmouth bass, largemouth bass, and walleye using skin-on filets while for carp skin-off filets were analyzed.

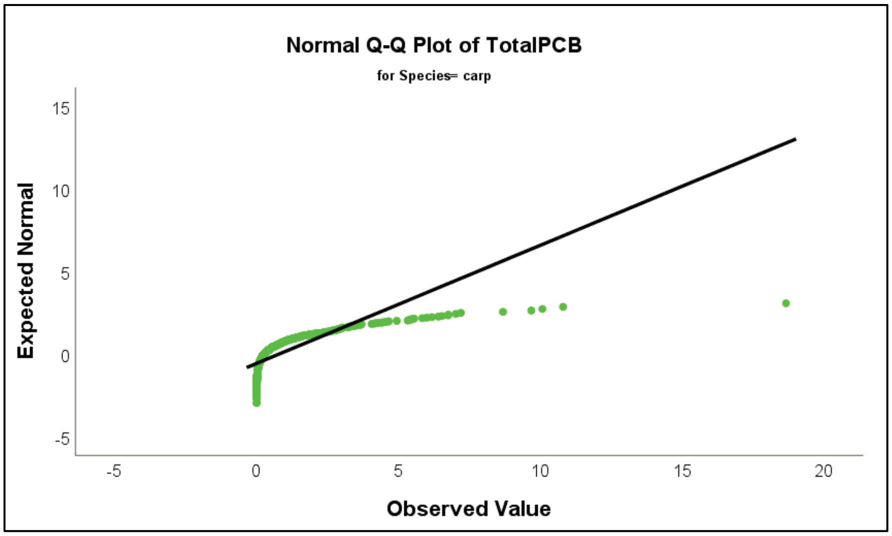
Michigan's FCMP is extensive, and fish are collected annually from waterbodies throughout the state. One of the contaminant classes they monitor is PCBs. Beginning in 1988 fish from waterbodies were collected and individually analyzed for PCB concentrations. Sampled waterbodies include rivers, inland lakes, impoundments, connecting channels, and nearshore Great Lakes areas. This work included fish samples caught in rivers, impoundments, and connecting channels, unless otherwise stated.

Pertinent MDEQ chemical analysis methodology is summarized here but can be found in more detail in the MDEQ report and MDCH health consultation document (MDEQ 2014; MDCH 2012). In Michigan, prior to 2000, total PCBs were calculated as total Aroclors (the sum of Aroclors 1242, 1248, 1254, and 1260). While the specific EPA method is not identified, the general method is outlined. A commercial Aroclor mixture acts as the standard and chromatogram peaks from the sample are matched to the Aroclor mixture. For the congener-based method, the chromatogram peaks of 83 individual congeners are summed and reported as a total PCB concentration.

In Michigan, 83 congeners are summed to calculate total PCB concentrations. Some of the congeners co-elute (e.g. PCB 37-42); this results in having the total PCB concentration include the concentration of both PCB 37 and PCB 42. A complete list of congeners analyzed is available in the MDEQ report. For the co-eluting congeners, the concentration of the individual congeners is not distinguished. However, in 2007, additional processing to include co-planar (dioxin-like) PCB concentrations began. These congeners are not included in the summed PCB concentration because of methodological differences. Congener concentrations below the detection limit (0.001 mg/kg) were assigned a K-code. Concentrations with unmet quantification limits (0.001 mg/kg) were assigned either an NQ- or J-code. For NQ-coded data, the concentrations were assigned a zero concentration. For J-coded data, the deviation from the quantification limit was determined to be insignificant and the concentration was set equal to the measured concentration. If all congeners included in the total PCB calculation (83 congeners) were below the detection limit, then the total concentration reported was less than the highest detection limit (0.001 mg/kg). For this analysis, all concentrations with a K-code were removed. There were no samples with an NQ-code. With regard to total concentrations, 139 samples were removed, 24 for carp, 51 for smallmouth bass, 54 for largemouth bass, and 10 for walleye. For all species, it can be assumed that the mean has not been greatly overestimated and the standard deviation has not been greatly underestimated because the number of K-coded samples removed is small relative to the total number analyzed (carp had 1095 samples, smallmouth bass had 491 samples, largemouth bass had 229 samples, and walleye had 232 samples). While this procedure eliminated any “not real” concentrations, it also truncated the distribution by removing any samples below the detection limit. Individual congener concentrations with a K-code were removed, keeping the actual fish sample in the data set.

2.2 Data Characteristics

Concentrations for all species were log transformed to ensure normality. Using the descriptive statistics function in SPSS, a normal QQ plot for species total PCB concentrations was used to assess normality of the distribution. Carp concentrations show a non-normal concentration distribution that becomes normal when concentrations are log-transformed (Figure 2-1).



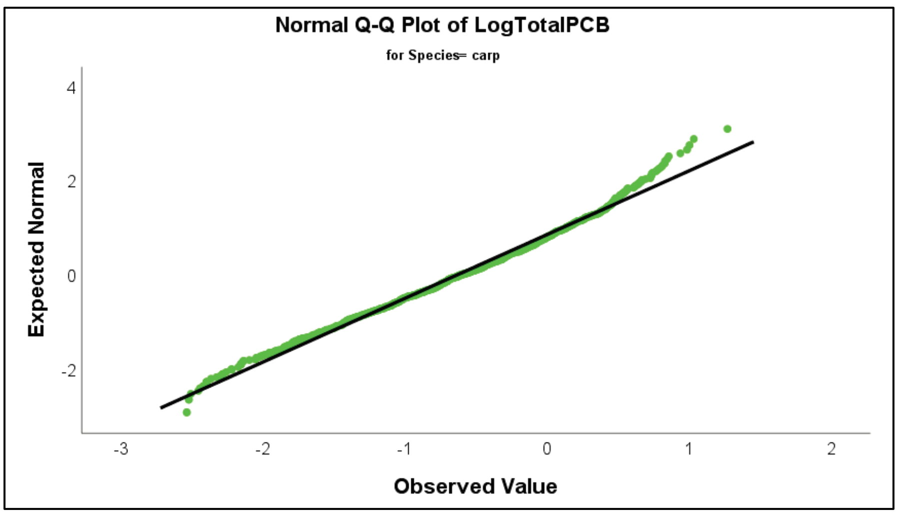


Figure 2-1 Normal Q-Q plots of total PCB concentrations for carp (green points compared to the normal distribution line (solid black). Un-transformed concentrations (top) are not normally distrbuted while log-transformed concentrations (bottom) are normally distributed. Data from MDEQ FCMP.

Fish lipid content was log-transformed to ensure normality, but fish length was normally distributed without a transformation (Figure 2-2 and Figure 2-3, respectively). To assess normality, normal QQ plots were qualitatively evaluated to decide if the data track a normal curve. Quantitatively, descriptive statistics demonstrate the appropriateness of the log-transformation of the data (Table 2-1). The improvement in the standard deviation of the data combined with the minimal skew provides evidence that these environmental data are normally distributed.

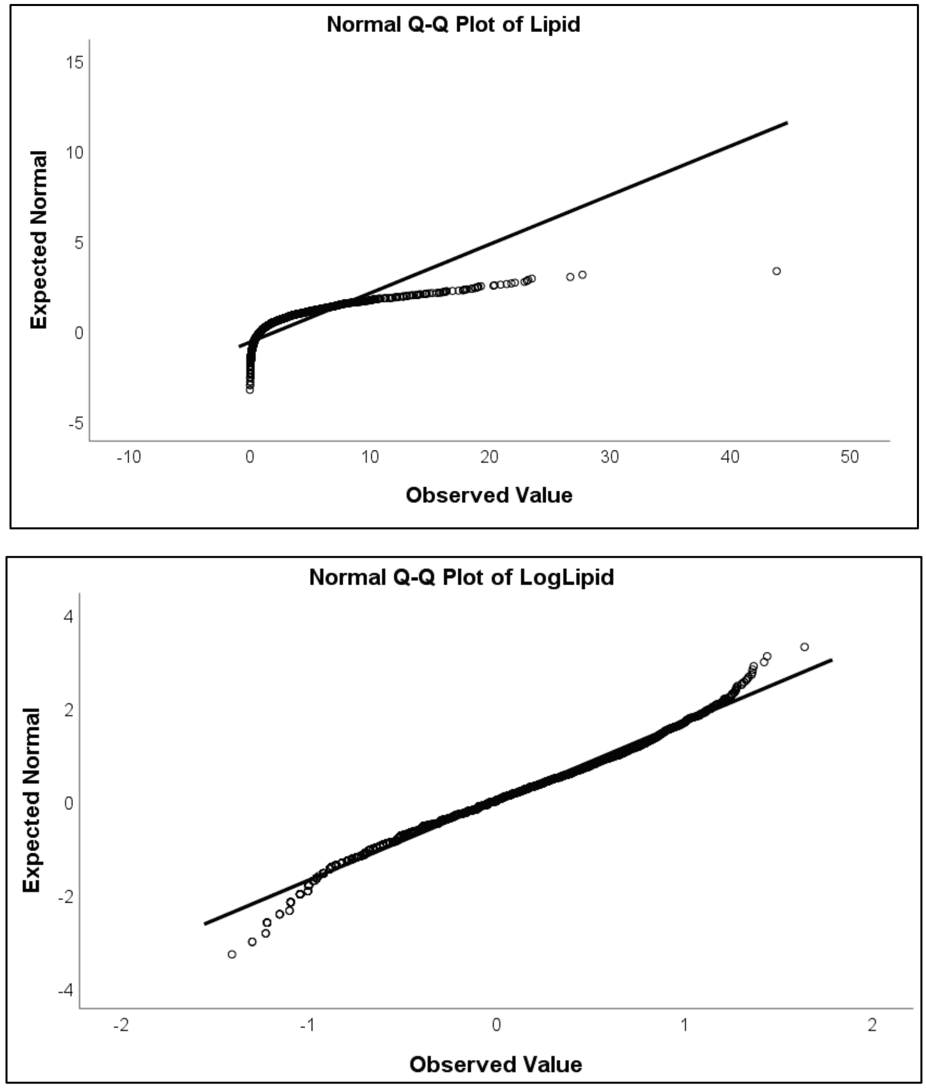


Figure 2-2 Aggregated lipid content for all species. Raw (top), log-transformed (bottom). The lipid contents are the points and the line represents a normal distribution. Data from MDEQ FCMP.

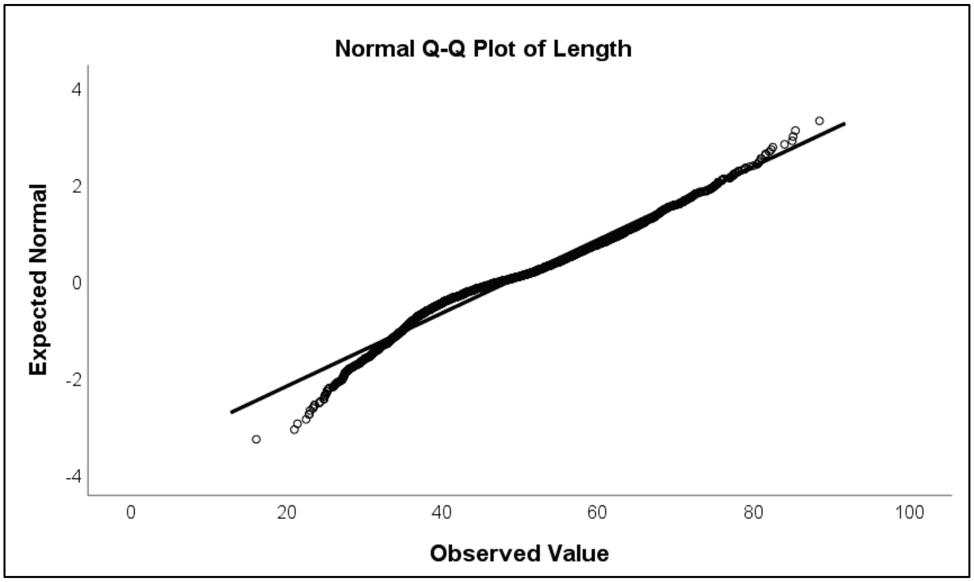


Figure 2-3 Aggregated lengths for all species. The lengths are the points and the line represents a normal distribution. Data from MDEQ FCMP.

Table 2-1 Descriptive statistics used to evaluate the appropriateness for the log-transformation of the lipid content in the MDEQ fish samples. Statistics calculated by IBM's SPSS.

	Lipid Content (% ww)	**Log Lipid Content**
Mean	2.42	0.01
Median	1.00	0.00
Skew	3.36	0.08
Standard Deviation	3.68	0.59

Box plots created in SPSS were used to determine outliers based on PCB concentrations grouped by species, sites status, lipid content category, and length category. The "outliers" and "extreme" values were the samples outside of the whiskers and were removed. The remaining dataset, with the outliers removed was used in the two-way ANOVAs and the multiple linear regression (MLR). All of the data, including the outliers, were included in the other analyses. See Appendix A for the box plots. The exclusion of both out and extreme concentrations did not significantly alter the amount of data for any of the species. Largemouth bass had six samples removed (3%) and carp had 19 samples removed (2%). Smallmouth bass and walleye had no outliers removed (Table 2-2).

Table 2-2 Fish samples before and after the removal of outliers. Carp and largemouth bass were the only species with any outliers and less than 5% of samples were removed. Data from MDEQ FCMP.

	Carp	**Smallmouth Bass**	**Largemouth Bass**	**Walleye**
n (all samples)	1095	491	229	232
n (outliers removed)	1076	491	223	232
Percent of Samples removed	2%	0%	3%	0%

In analyses that used length- or lipid-normalized concentrations, PCB concentrations were normalized to the length or lipid content for that sample. In other analyses, categories were created to organize fish samples based on lipid content or length. For this "binning" approach, the aggregated data from all species was used. While this approach disregards the unique fat differences between the fish species, it enables a comparison based exclusively on fat content. Lipid content was log-normally distributed, and length was normally distributed (Figure 2-2 and Figure 2-3, respectively).

In this work, entire watersheds were classified as Areas of Concern (AOCs) since it is fair to assume that both fish and the contaminants cross these invisible boundaries. The AOC sites as designated under the Great Lakes Water Quality Agreement (GLWQA), Annex 2 (statute 1972), often do not include the entire river. In fact, there are four rivers with only a portion of the river classified as an AOC (Table 2-3). For this work, AOC watersheds were considered an AOC site. For all four species, there was only one waterbody with samples outside of the AOC boundary; carp had one site on the Muskegon River, smallmouth bass had three sites on the Menominee River, largemouth bass had two sites on the Menominee River, and walleye had one site on the Menominee River that were outside of the EPA-defined AOC boundary.

Table 2-3 The boundaries of the AOC rivers in Michigan, as defined by the EPA.[2] Data from MDEQ FCMP.

AOC Waterbody	AOC Boundary
Clinton River	Entire watershed, including tributaries
Detroit River	Entire channel
Kalamazoo River	Entire river, below Morrow Dam
Manistique River	Last 1.7 miles of the river
Menominee River	Last 3 miles of the river
Muskegon River	1.5 miles of river, including Ruddiman, Ryerson, and Bear Creeks
Raisin River*	Last 2.6 miles of the river
Rouge River*	Entire watershed, including tributaries
Saginaw River*	Entire river
St. Clair River*	Entire channel
St. Mary's River	Entire channel

2.3 Determining the sources of PCB contamination

Principal Component Analysis (PCA)

Principal component analysis (PCA) is a multivariate statistical tool that reduces data into components (independent variables) that best describe the variance associated with the dependent variable (i.e. PCB concentrations or waterbody). A PCA assumes there is a relationship between the variables. When evaluating total PCB or congener concentrations, log transformed data were used. While the PCA is not sensitive to normality, the existence of outliers can influence the resulting components. Log transformation of concentrations addressed that problem. For the PCB source assessment, waterbody was the categorical variable and congener concentrations (averages for all the fish samples at any location) were the samples. To eliminate the influence of sites with much higher congener concentrations, relative log concentrations were used.

[2] Boundary maps and descriptions for the waterbodies with an asterisk (*) were obtained through the January 19, 2017 web snapshot because "… [the] EPA has allowed the publication of this page to lapse."

Using IBM's SPSS, the factor analysis program was used to evaluate MDEQ data based on samples' species, location, and congener concentration. For each of these applications, variables were excluded list wise, which excludes values by column (i.e. variable) instead of by case (i.e. fish sampled) (IBM 2017). A varimax rotation ensured components were orthogonal (perpendicular) and independent of each other to minimize communalities. A summary of the statistical outputs, including acceptable values, is shown below (Table 2-4).

Table 2-4 Statistical information from the SPSS factor analysis output.

PCA Statistic	Definition
Kaiser-Meyer-Olkin (KMO) Target: > 0.7	Evaluates if there are enough items predicted by each factor.
Bartlett's Test of Sphericity Target: < 0.05	Tests the assumption that the correlation matrix is significantly different from the identity matrix.
Communalities	Represents the relationship between each pair of variables before rotation. If many of the values are < 0.3 then the results are likely distorted.
Total Variance Explained	A table that divides the variance among the possible factors. When an eigenvalue is greater than 1.0 it indicates that the associated factor explains some of the variance better than the individual variable. This implies that there is common explanation that can be reached.
Scree Plot	A graphical representation of a factor's contribution to variance, and shows the value of the eigenvector.

Three different types of PCAs assessed log-transformed, non-normalized total PCB concentrations in different fish species; log-transformed, non-normalized total PCB concentrations at different locations; and non-normalized congener concentrations in different fish species. To compare PCB concentrations, total PCB concentrations, as determined by the MDEQ, were organized by species such that total PCB concentration ($\sum$ 83 congeners) were the variable and the individual fish were the samples.

To evaluate sources of PCBs, MDEQ data were organized such that waterbody name (e.g. Au Sable River) was the variable and the individual fish were the samples. To compare congeners, congener concentrations were organized to be the variable while the individual fish were the samples. This method considered exclusively common congeners, those present in ≥ 50% of samples. This somewhat arbitrary cutoff is justified by the objectives of the research and supported by literature showing that some congeners are more abundant in environmental media. The exclusion of less common congeners eliminated some of the noise in the data.

Ratio Analysis

Based on the unique uses for the different Aroclor mixtures, it was reasonable to expect patterns in fish PCB contamination based on the proximity to sources of industrial waste. To test for an Aroclor signature in fish PCB concentrations, lipid-normalized concentrations for carp and smallmouth bass were compared. Since the Aroclor characteristics are what led to the unique uses, it was expected that there would be an Aroclor signature in the fish PCB concentrations. We assumed that AOC sites with a paper mill legacy would have an Aroclor 1242 signature since the mixture was commonly used in carbon-less copy paper. We assumed the other AOC sites would have an Aroclor 1254 signature since the mixture was a general use mixture. A one-way analysis of variance (ANOVA) compared congener concentrations between the sites (i.e. paper mill AOC and non-paper mill AOC).

Congeners included in the analysis were selected due to their contrasting presence in one Aroclor compared to the other (Table 2-5). The first approach compared the ratio between the summed congener concentrations (Equation 2-1). The second analysis compared the ratio between the two Aroclors for each congener (Equation 2-2).

$$\text{Ratio} = \Sigma\ (\text{congeners}_{1242} / \Sigma\text{congeners}_{1254}) \qquad \text{Equation 2-1}$$

$$\text{Ratio} = \Sigma\ ((1242{:}1254) * \text{congener concentration}) \qquad \text{Equation 2-2}$$

Table 2-5 Congener presence in Aroclor 1242 and Aroclor 1254.

Congener	**Presence in Aroclor 1242 (%)**	**Presence in Aroclor 1254 (%)**
18	8.53	0.08
31	7.18	0.11
52	3.64	0.83
70	3.76	6.83
105	0.52	7.37
118	0.78	13.59
151	-	0.22

153	0.09	3.29
180	-	0.42

Spatial Analysis

Using ArcMap 10.5.1, averaged raw concentrations from the most recent sampling year were evaluated for latitudinal patterns (ESRI 2011). Fish PCB concentrations from samples in inland lakes and nearshore Great Lakes areas were included, as well as the data from rivers, impoundments, and connecting channels. Importing data into ArcMap required latitude and longitude for each sample, which were displayed using the global coordinate system (GCS, GCS_WGS_1984). Projecting the data into another coordinate system (i.e. NAD_1983_UTM_Zone_16N), specific to this region, allowed features from the Earth's curved surface to be projected onto a planar surface, while maintaining topology (Figure 2-4). All projected coordinate systems have some distortion. Sample location defined a sample site to maximize the number of sample sites (e.g. Lake Erie, Brest Bay). A qualitative assessment of the spatial sample distribution was done visually.

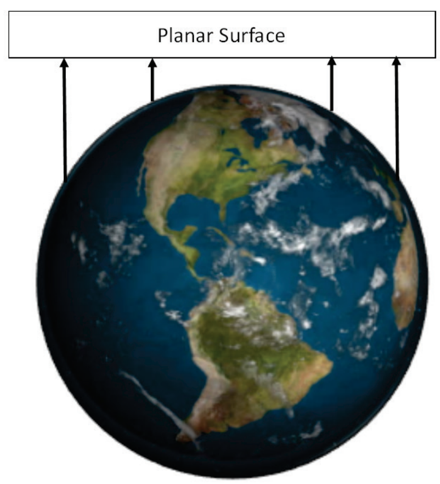


Figure 2-4 A schematic of the projection of the Earth, using a global coordinate system, to a planar surface, using an unspecified, user-selected projection system.
Image: www.videzzy.com, stock photo.

2.4 Evaluating the efficacy of remediation

Time Trend Analysis

As briefly mentioned earlier, methodologies for quantifying total PCB concentrations have changed over time. Initially, the MDEQ quantified total PCBs by summing Aroclor concentrations. Improvements in analytical ability have allowed for the quantification of individual congeners that are then reported as the summed total of congener concentrations. Time trends were determined by a linear regression of natural log-transformed, non-normalized total PCB concentrations as a function of sampling year. An evaluation of time trends for each sampled waterbody (e.g. Kalamazoo River) rather than for each sampled location (e.g. Kalamazoo River, Ceresco Impoundment) was done due to limited data availability at the sampled locations. Compositing locations allowed more trends to be evaluated. Prior to 2000, total PCBs were quantified as the sum of Aroclors. Discrepancies between the Aroclor and congener method exist so time trends were determined independently for Aroclor- and congener-based total concentrations (Priyadarshini 2018) as well as for all concentrations from both methods combined.

2.5 Comparing PCB concentrations

ANOVA- two-way

Using IBM SPSS, the univariate linear model was used to evaluate the single dependent variable, total PCB concentration, and to test H_0 that the variance among different populations are less than the variance within populations (IBM 2017). ANOVA assumes there is only one independent variable and the test requires that data meet three assumptions: that data are normally distributed, the samples are independent, and the variance among the data groups is similar. Below is a table that summarizes the statistical output used to evaluate the appropriateness and results of the two-way ANOVA (Table 2-6).

Table 2-6 Explanatory table for ANOVA statistics.

Summary Statistics	**Definition**
Count	A count of the number of samples in the data set, for each group (i.e. fish species).
Sum	The sum of the sample values, for each group.
Mean	The mean of the sample values, for each group.
Variance	The variance of the sample values, for each group.
ANOVA Statistics	**Definition**
Sum of Squares (SS)	$SS_{total} = \Sigma(x - \overline{x})^2$ The total SS can be partitioned into its source (i.e. within or between groups).

Degrees of Freedom (df)	df = (k-1)/(N-k) where k = number of groups and N = number of data entries
Mean Square (MS)	MS = SS/df The mean square can be partitioned into its source (i.e. within or between groups). $MSB = SS_{effect}/df$ and $MSW = SS_{error}/df$
F-statistic (F)	The ratio of two sample variances.
P-value	Denotes significance and the ability to reject H_0 when < 0.05.
Partial Eta Squared	The proportion of variance accounted for by an effect. partial $\acute{\eta}^2 = SS_{effect} / (SS_{effect} + SS_{error})$

Toxic Equivalency

The toxic equivalent concentration (TEC) represents the weighted sum of concentrations of multiple compounds that all exhibit a common mode of action; concentrations are weighted by their relative toxicity. The TEC is calculated using toxic equivalency factors (TEFs) established by the World Health Organization (WHO) in 1998 and updated in 2005. To be included in the TEF framework, a compound must meet four criteria: have a structural similarity to polychlorinated diphenyl dioxins (PCDDs) or polychlorinated diphenyl furans (PCDFs), bind to the aryl hydrocarbon (Ah-) receptor and elicit an AhR-mediated biochemical and toxic response, and be persistent and bioaccumulate (Van Den Berg et al. 1998).

Initially quantified in 1998, the TEFs were updated in 2005 following expert panel review of relative potency (REP) accompanied by expert judgement (Equation 2-3). The REP distributions were unweighted, and the expert judgement was preferred (Van den Berg et al. 2006). Updated TEF values are below (Table 2-7). The summation of all compounds' concentrations multiplied by the TEF's gives a toxic equivalent concentration (TEC; Equation 2-4). This equivalent concentration is useful because it translates disparate compound concentrations (i.e. PCBs, PCDF, PCDDs etc.) into the same units, allowing for a comparison of Ah-receptor toxicity contribution.

Table 2-7 TEFs for PCB congeners in 1998 and 2005. Factors were calculated using Equation 2-3 (below).

PCB	1998 TEF	2005 TEF
Non-ortho substituted PCBs		
77	0.0001	0.0001
81	0.0001	0.0003
126	0.1	0.1
169	0.01	0.03
Mono-ortho substituted PCBs		
105	0.0001	0.00003
114	0.0005	0.00003
118	0.0001	0.00003
123	0.0001	0.00003
156	0.0005	0.00003
157	0.0005	0.00003
167	0.00001	0.00003
189	0.0001	0.00003

Using the EPA's cancer RfD of 0.001 pg TEQ/kg*day RfD (0.000001 ng TEQ/kg*day), a threshold concentration was calculated to compare fish samples based on two different consumption rates. A less stringent threshold concentration calculated with the non-cancer RfD of 1 pg/kg*day was also calculated.

$$TEF_n = \frac{ED_{50}chemical_n}{ED_{50}TCDD} \qquad \text{Equation 2-3}$$

$$TEQ = \Sigma\, [PCB]_i * TEF_i \qquad \text{Equation 2-4}$$

$$threshold\ concentration = \frac{RfD * body\ weight}{consumption\ rate} \qquad \text{Equation 2-5}$$

Multiple Linear Regression (MLR)

Using IBM SPSS, backward stepwise regression analysis was used to develop a model that could predict total PCB concentrations with consideration for sample characteristics including lipid content, length, species, and site status (AOC or non-AOC) (IBM 2017). Log_{10}-transformed concentrations were used.

3 Results

3.1 PCB Concentrations: How do different species, locations, and congeners compare?

3.1.1 How do concentrations compare among different species?

A general understanding of the fish samples and their PCB concentrations, as well as their characteristics, is helpful. In general, carp are longer, fattier and have higher total PCB body burdens than smallmouth, largemouth, or walleye (Table 3-1). Carp have, on average, an order of magnitude higher total PCB concentration, and the maximum concentration is two orders of magnitude greater than that of the other three species. The concentrations are plotted on a box and whisker plot with minimum and maximum error bars (Figure 3-1). For these plots, outliers were not removed.

Table 3-1 Descriptive statistics for length, lipid content, and total PCB concentrations for four fish species with the outliers removed. (MDEQ FCMP data)

LENGTH (cm)	**carp**	**smallmouth**	**largemouth**	**walleye**
min	26.10	22.50	16.10	25.10
mean	58.05	36.31	35.59	47.23
median	57.70	36.20	35.90	45.60
max	88.50	52.07	52.60	72.10
lower 95% CI	57.46	35.82	34.88	45.99
upper 95% CI	58.65	36.80	36.29	48.46
LIPID (%)	**carp**	**smallmouth**	**largemouth**	**walleye**
min	0.10	0.04	0.50	0.10
mean	4.03	0.47	0.38	1.10
median	2.55	0.30	0.28	0.90
max	43.88	3.40	2.10	5.25
lower 95% CI	3.76	0.43	0.33	0.99
upper 95% CI	4.30	0.51	0.43	1.21
TOTAL PCB[3] (mg/kg ww)	**carp**	**smallmouth**	**largemouth**	**walleye**
min	< DL	< DL	< DL	< DL
mean	0.244	0.036	0.037	0.048
median	0.267	0.045	0.040	0.060
max	18.665	1.042	2.794	2.293

[3] In Table 3-1, DL abbreviates detection limit, not dioxin-like.

lower 95% CI	0.219	0.030	0.030	0.039
upper 95% CI	0.273	0.042	0.046	0.059

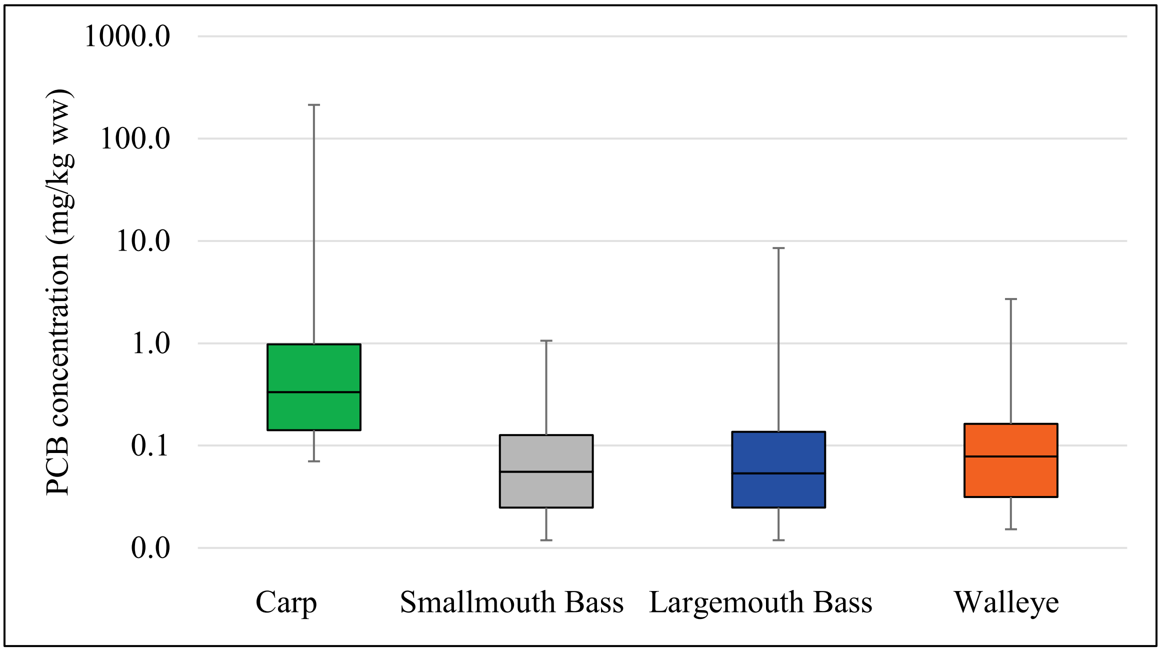


Figure 3-1 Box and whisker plots of total PCB concentrations in four species. Central lines are median values, boxes show quartiles, and whiskers show minimum and maximum values. Outliers were not removed.

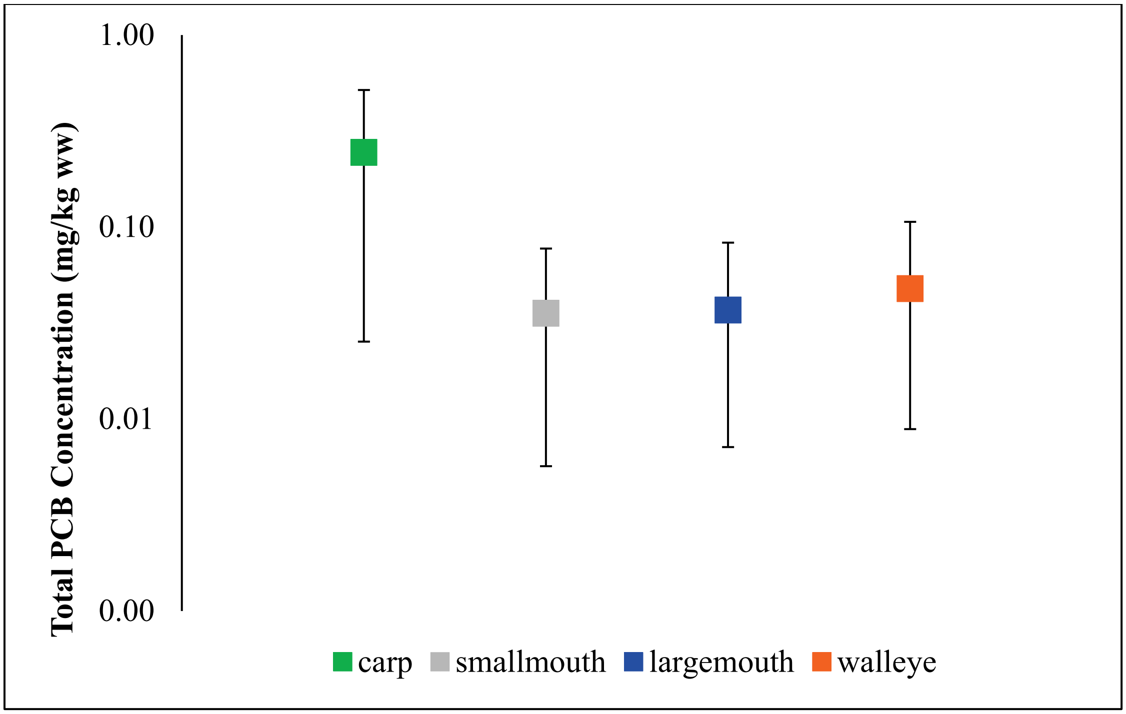


Figure 3-2 Mean PCB concentrations in the four species of interest. Bars represent 95% CI.

Diet can influence total PCB accumulation, and in larger fish it can represent the most important source of PCB contamination. Longer food webs and pelagic feeding tend to promote higher PCB concentrations (Guildford et al. 2008), although, especially in rivers, food webs vary greatly, even within the same waterbody (Vander Zanden et al. 1997). The excretion of PCBs does not exceed the intake of PCBs; however, growth can "dilute" the total body concentration. As benthic omnivores, carp root around in the sediment and consume macroinvertebrates as well as some incidental sediment. This is a possible reason for the higher PCB concentrations.

Lipid-normalized concentrations show that PCB concentrations in carp are an order of magnitude greater than in the other three species (Figure 3-3). Length-normalized concentrations show that carp concentrations are an order of magnitude greater than smallmouth bass and approximately two orders of magnitude greater than largemouth bass and walleye (Figure 3-4). Even when normalized to length and lipid, carp still had, on average, an order of magnitude greater total PCB body burden. Clearly, high concentrations in carp are not a result of size or lipid content. As with the non-normalized concentrations, carp appear to have roughly an order of magnitude more contamination than the other species. Accordingly, non-normalized concentrations were used in subsequent analyses unless otherwise stated.

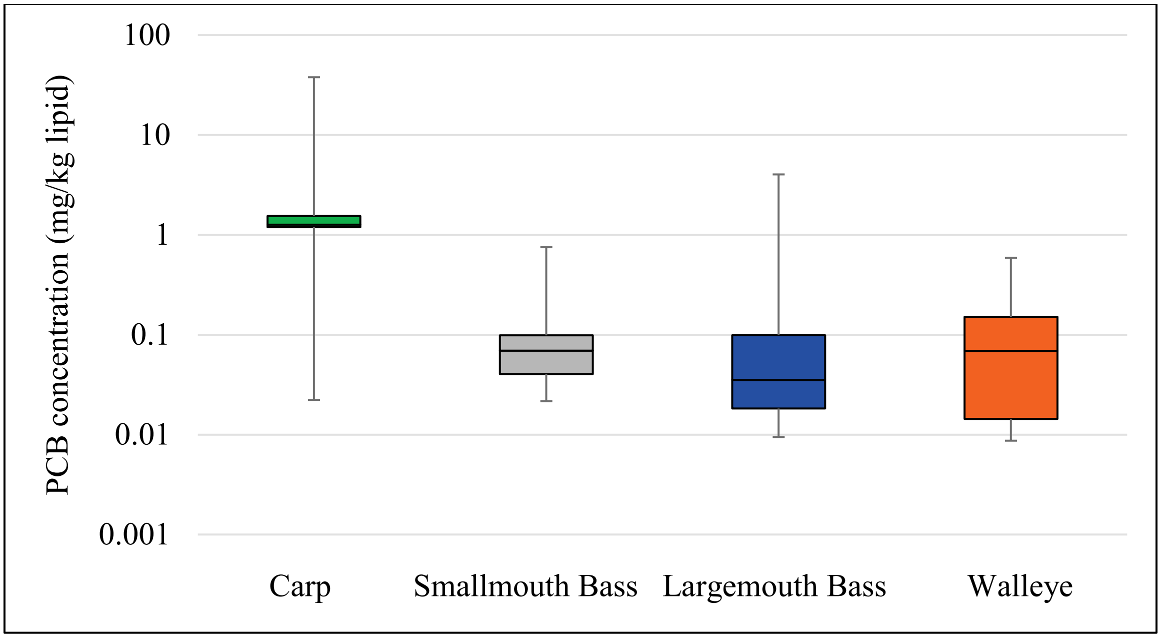


Figure 3-3 Lipid-normalized PCB concentrations for the species of interest. Fish were normalized to the lipid contents of the fish at the location where caught. Central lines are median values, boxes show quartiles, and whiskers show minimum and maximum values. Outliers were not removed.

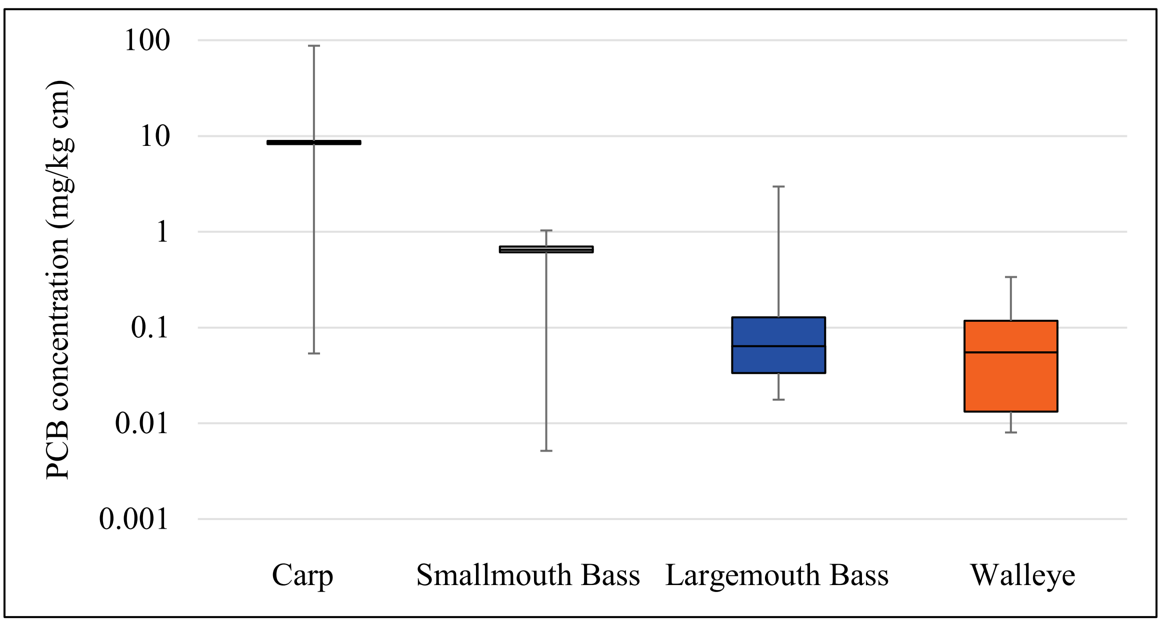
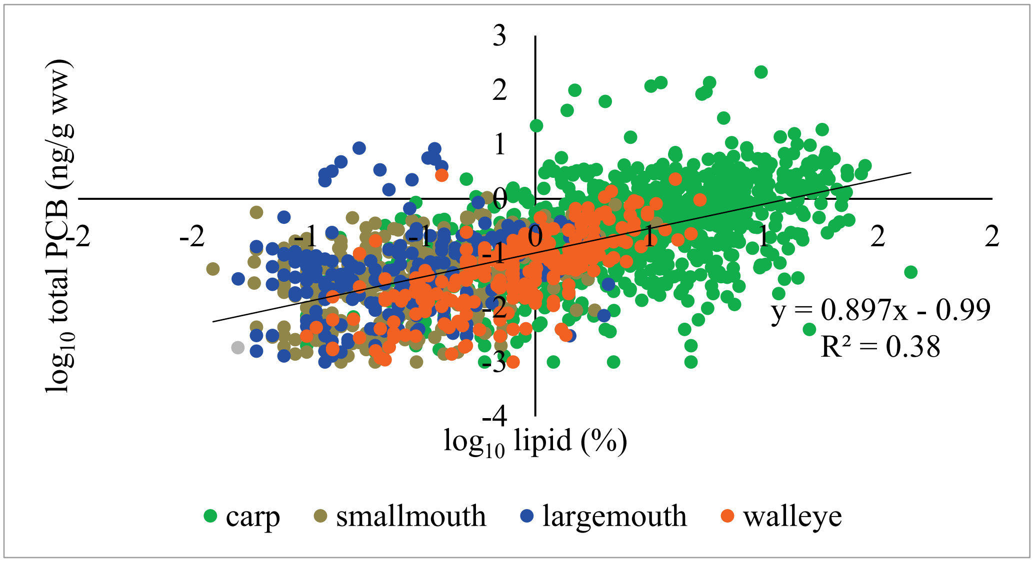


Figure 3-4 Length-normalized PCB concentrations for the species of interest. Fish were normalized to the lengths of the fish at the location where caught. Central lines are median values, boxes show quartiles, and whiskers show minimum and maximum values. Outliers were not removed.

While clear that neither length nor lipid content fully explain the PCB concentration differences among species, the regressions below show there are strong relationships with these variables. Regressions of PCB concentration on lipid content and length revealed that for all species, both slopes are different from zero and correlations are significant ($p < 0.001$) (Figure 3-5). The adjusted R^2 values for lipid content and length are 0.38 and 0.17, respectively. The regression between length and lipid is significant ($p < 0.001$) and the adjusted R^2 value is 0.44 (Figure 3-6).



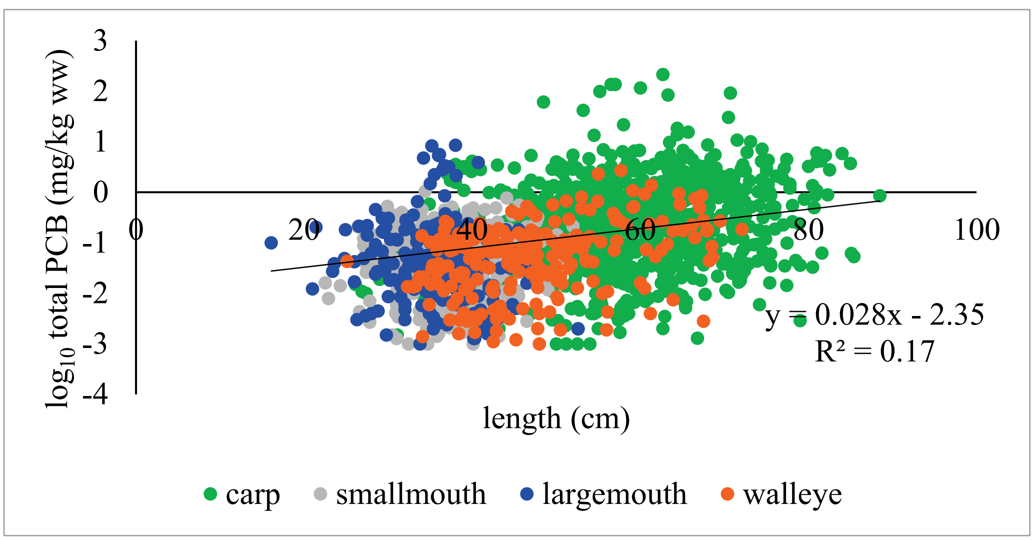


Figure 3-5 Linear regression for PCB concentration as a function of lipid content (top) and length (bottom). The different colors represent the different species. The regression line and R^2 value apply to all of the data in aggregate ($p < 0.001$).

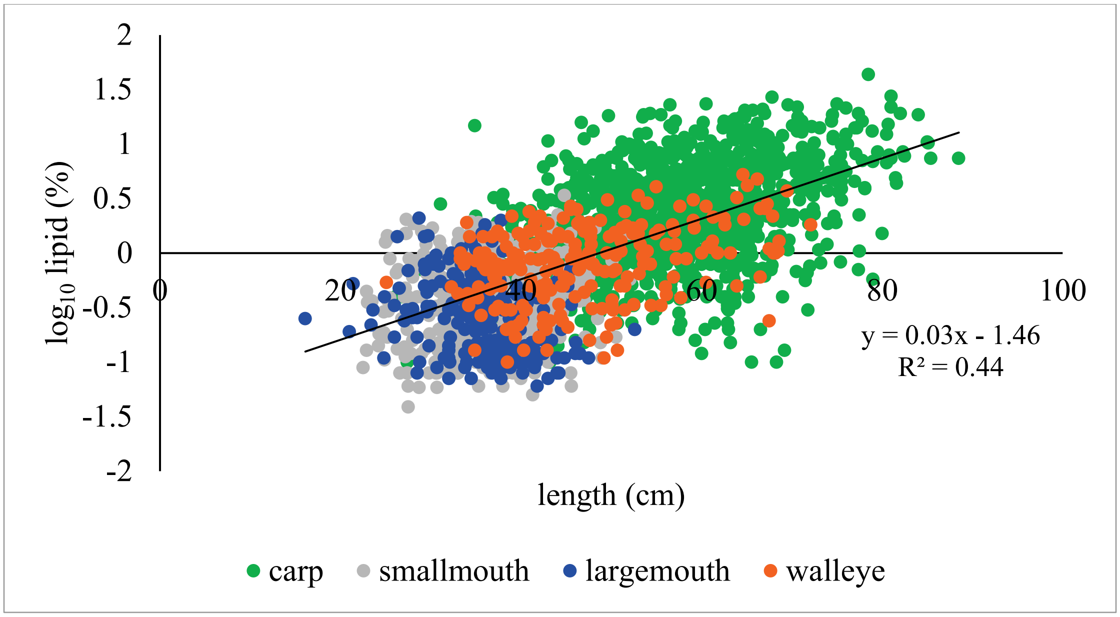


Figure 3-6 Linear regression with log lipid content as a function of length ($p < 0.001$).

Using PCA to elucidate the source of variance for total PCB concentrations in fish species proved difficult (Figure 3-7). In this analysis, fish species is the variable and log transformed total PCB concentrations were the samples. While the correlation matrix is significantly different from the identity matrix ($p < 0.05$), the KMO value was 0.510, which indicates the sampling may be inadequate due to pairs of variables not able to be explained by other variables. While 63.7% of variance was explained by the two components, the individual species results differed. Carp and largemouth bass were not explained well, based on the communalities (0.419 and 0.489, respectively), while smallmouth bass and walleye were much better explained (communalities of 0.745 and 0.894, respectively).

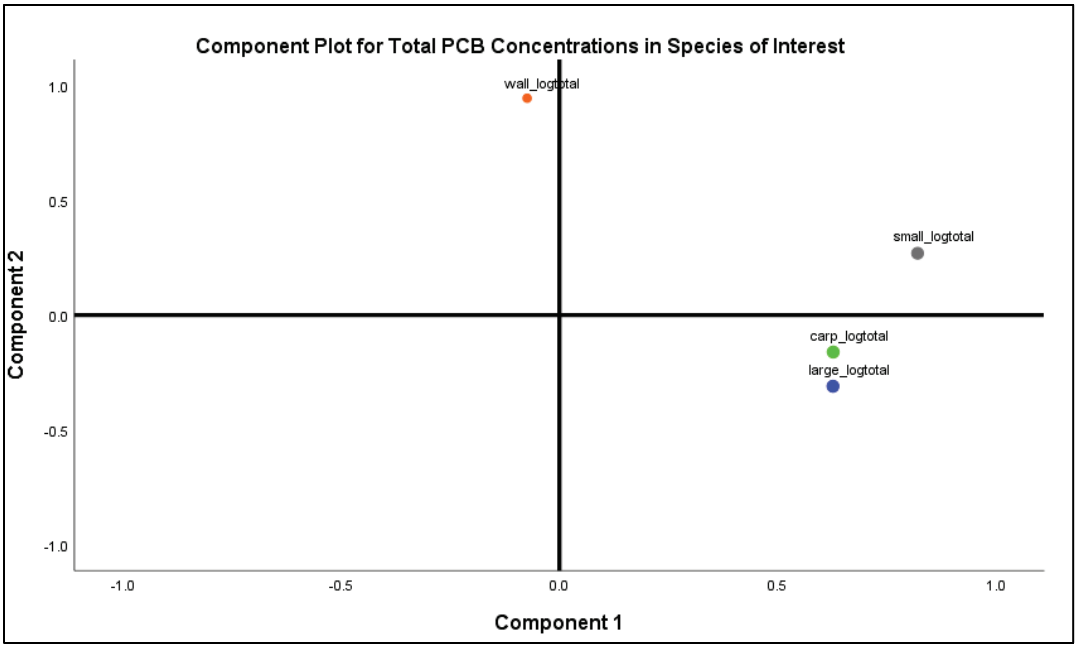


Figure 3-7 A PCA plot for PCB concentrations in fish species.

Species appears to be an important determinant of total PCB concentrations. Smallmouth bass and walleye were the two species best explained by this PCA. Smallmouth bass had a linear relationship between log total PCB concentration and component 1 while walleye had a linear relationship between log total PCB concentration and component 2 (Figure 3-8 and Figure 3-9, respectively). Even though carp and largemouth bass have component scores similar to smallmouth bass, those species are not well-explained by this PCA; therefore, it is unsurprising that no linear relationship exists between log total PCB concentration and component 1 score for either of the species. Plots for the other species-component combinations are in Appendix B.

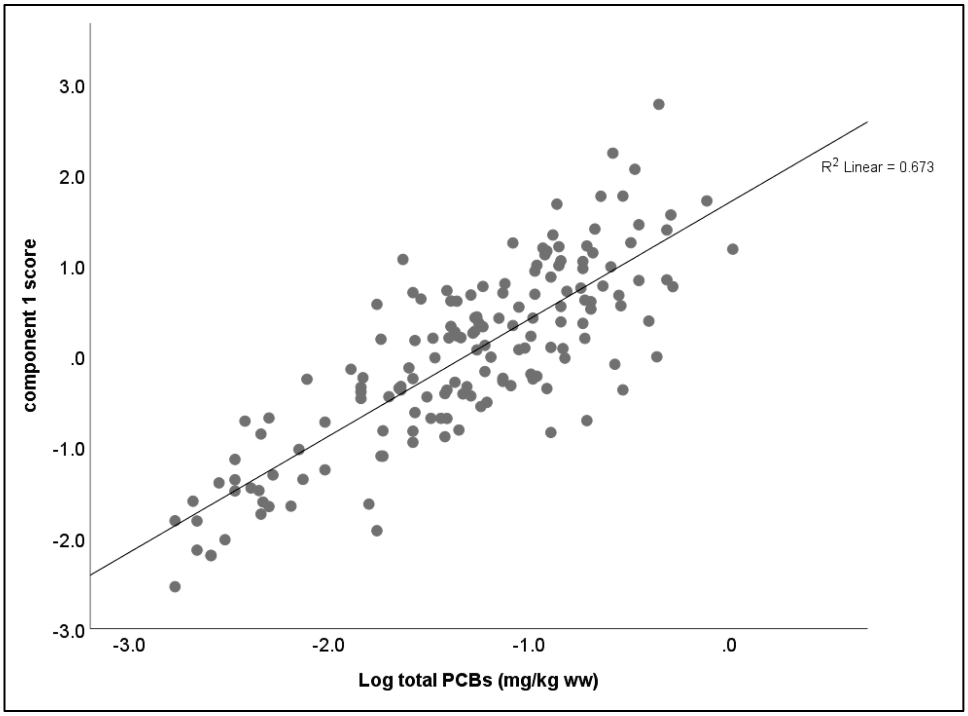


Figure 3-8 Smallmouth PCB concentration versus component 1 score. The strong linear relationship between total PCB concentration and the component 1 score indicates that smallmouth bass concentrations are well explained by component 1.

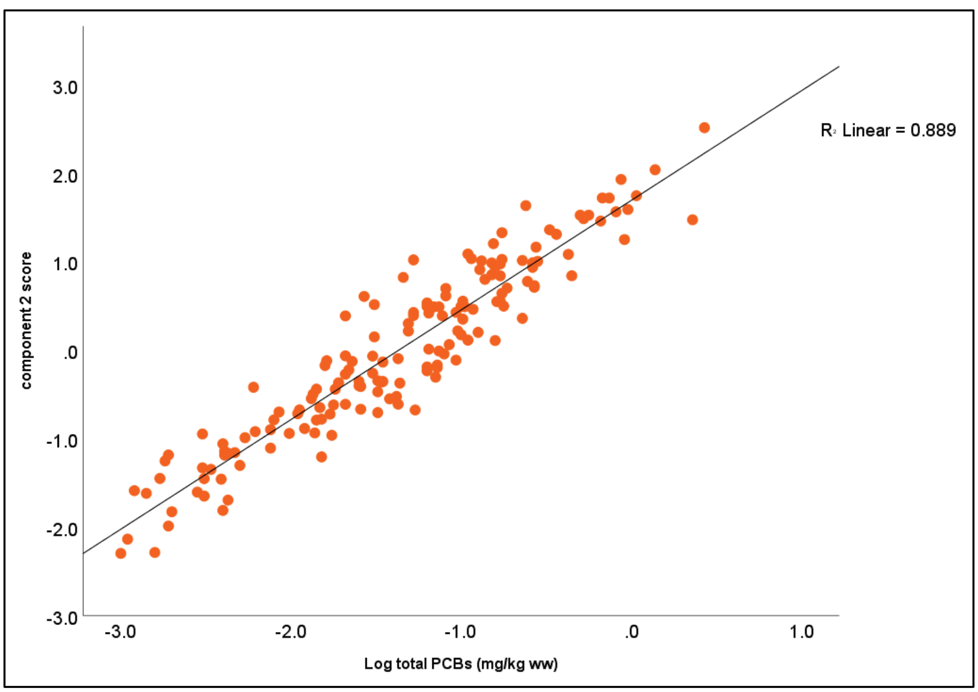


Figure 3-9 Walleye PCB concentration versus component 2 score. The strong linear relationship between total PCB concentration and the component 2 score indicates that walleye concentrations are well explained by component 2.

3.1.2 How do PCB concentrations compare between AOC and non-AOC sites?

Descriptive statistics for the species at AOC- compared to non-AOC sites indicate that for all species the total PCB body concentration is greater at AOC sites compared to non-AOC sites (Table 3-2). Among the species, the mean concentration is an order of magnitude greater at AOC sites compared to non-AOC sites for carp, smallmouth bass, and largemouth bass. The exception is walleye, where concentration in the fish at both site types is of the same magnitude.

Table 3-2 Descriptive statistics for length, lipid content, and total PCB concentrations for fish species at AOC and non-AOC sites, no outliers removed.

LENGTH	**carp AOC**	**carp non**	**small AOC**	**small non**	**large AOC**	**large non**	**wall AOC**	**wall non**
min	31.10	26.10	22.90	0.00	16.10	24.90	32.30	25.10
mean	58.74	57.36	36.67	35.84	34.61	36.99	49.65	43.62
median	58.40	57.15	36.60	35.70	35.40	36.50	49.27	42.80
max	85.00	88.50	52.07	49.00	47.50	52.60	72.10	61.21
LIPID	**carp AOC**	**carp non**	**small AOC**	**small non**	**large AOC**	**large non**	**wall AOC**	**wall non**
min	0.10	0.10	0.04	0.06	0.06	0.05	0.13	0.10
mean	3.84	4.21	0.44	0.52	0.31	0.46	1.27	0.81
median	2.38	2.80	0.29	0.40	0.23	0.30	1.00	0.70
max	27.72	43.88	3.40	2.05	1.45	2.10	5.25	3.10
TOTAL PCB [4] (mg/kg ww)	**carp AOC**	**carp non**	**small AOC**	**small non**	**large AOC**	**large non**	**wall AOC**	**wall non**
min	< DL	< DL	< DL	< DL	< DL	< DL	< DL	< DL
mean	3.18	0.57	0.10	0.07	0.51	0.05	0.18	0.10
median	0.47	0.18	0.05	0.04	0.07	0.02	0.07	0.04
max	215.05	15.62	1.04	0.49	8.42	0.38	2.72	1.08

A subsequent PCA that sorted species based on where they were caught (i.e. either at an AOC site or a non-AOC site; Figure 3-10) also proved to be inadequate. The correlation matrix was not significantly different from the identity matrix ($p > 0.05$) and the KMO value was 0.471 which indicates that the partial correlations are large compared to the ordinary correlation coefficients, which indicates that the variables are not linearly

[4] In Table 3-2, DL abbreviates detection limit, not dioxin-like.

related. The PCA explained only 44.3% of the variance and the site*species combinations varied greatly in their ability to be explained (Table 3-3).

Table 3-3 Communalities for the species*site combinations. Communalities quantify the proportion of variance explained by the variables. Values range from 0 to 1.

Carp AOC	Carp non	Small AOC	Small non	Large AOC	Large non	Walleye AOC	Walleye non
0.621	0.482	0.521	0.160	0.123	0.719	0.472	0.445

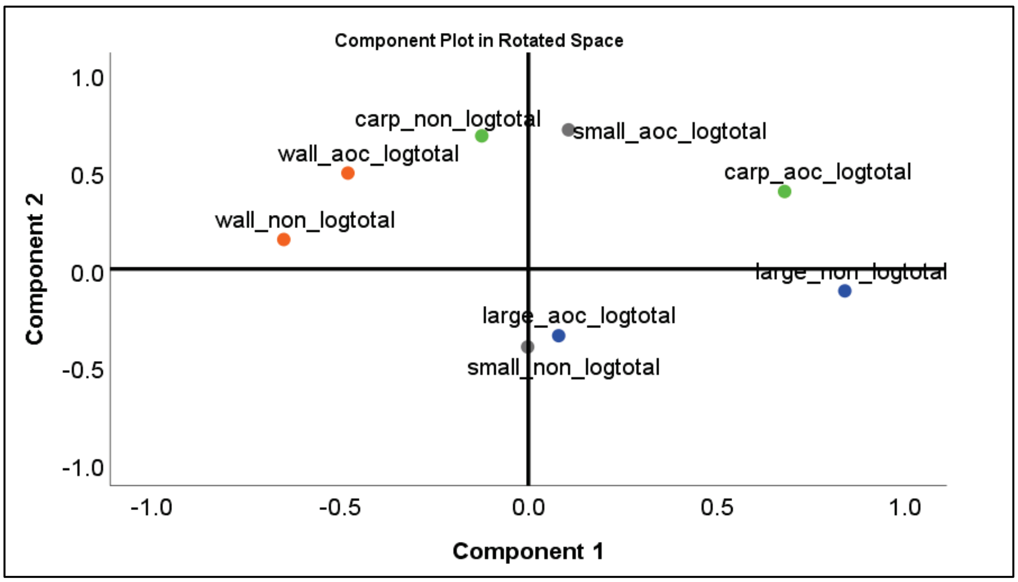


Figure 3-10 A PCA plot for PCB concentrations in fish species grouped into AOC and non-AOC sites.

To understand the relationships between the variables and PCB concentrations, one-way analysis of variance (ANOVA) was done. Length and lipid categories sorted the aggregated fish data for each variable. Length categories were small (1), medium (2), and large (3). Lipid content categories were lean (1), medium (2), and fatty (3). This allowed for the examination of the effect of each variable. One-way ANOVAs compare the variance between categorical data and are often coupled with t-tests to compare the means between those categories. A one-way ANOVA for the different categories (length, lipid, species and site status) showed that the variance was significantly greater between the groups than within the groups (i.e. PCB concentrations vary more among the different species than they do within a single species) (Table 3-4). T-tests (see Appendix B for tabulation) indicated that the mean PCB concentrations in the length and lipid categories as well as between the different sites were significantly different ($p < 0.001$). The species concentrations were significantly different between all the pairs except smallmouth bass compared to largemouth bass and largemouth bass compared to walleye ($p < 0.001$; $p > 0.05$, respectively).

Table 3-4 One-way ANOVA results comparing the log total PCB concentrations between the potential explanatory variables. The number of categories within a variable is in parenthesis below the variable name. F-statistics for the different categorical variables show that there is more variance between the categories than within a category. Calculations done using Microsoft Excel's data analysis tool pack.

	F-statistic	**p-value**
Length (3 Categories)	F (2, 1765) = 147.59	p < 0.001
Lipid (3 Categories)	F (2, 1761) = 414.59	p < 0.001
Species (4 Categories)	F (3, 1764) = 166.71	p < 0.001
Site Status (2 Categories)	F (1, 1766) = 34.10	p < 0.001

Unequal means among the different categories of the variables led to the desire to understand the interacting effects of these variables on total PCB concentrations, explored with two-way ANOVAs. While the one-way ANOVA evaluates variance with respect to only one variable, the two-way ANOVA evaluates variance with respect to two variables. To be effective, there must be approximately equal variances for the two variables. Use of log total PCB concentrations and characteristics (fish species, site status, length category, and lipid content category) resulted in Levene statistics that were significant, rejecting H_0 that groups have similar variances ($p < 0.028$). Despite the failed Levene's test, log PCB concentrations are normally distributed within each category, and Table 3-5 shows that there is a narrow range in variance within each category as well as across categories. Furthermore, the sample sizes for each category are large, ranging from 203 to 939, which further supports the decision to disregard the outcome of Levene's test and to interpret the two-way ANOVA results as valid. Of the six combinations, only three had no interaction effects ($p > 0.05$) meaning the variables are independent and we can interpret their effect on PCB concentrations Table 3-6 Table 3-6).

Table 3-5 Variance of log total PCB concentrations for each category.

Variance within species		**Variance within site status**		**Variance within lipid categories**		**Variance within length categories**	
Carp	0.599	AOC	0.724	Lean (1)	0.414	Small (1)	0.415
Smallmouth Bass	0.454	Non-AOC	0.619	Medium (2)	0.423	Medium (2)	0.615
Largemouth	0.491			Fatty	0.344	Large	0.548

Bass				(3)		(3)	
Walleye	0.492						

Table 3-6 Statistical output for the six two-way ANOVA combinations. The p-value evaluates the interaction effect. The three bolded and italicized combinations show no interaction effect ($p > 0.05$) and the results were interpreted.

Two-way ANOVA	**df**	**F-statistic**	**p-value**	**partial η^2**	**adjusted R^2**
site*species	***3***	***2.624***	***0.05***	***0.005***	***0.267***
site status	***1***	***40.620***	***< 0.01***	***0.023***	
species	***3***	***193.881***	***< 0.01***	***0.252***	
site*lipid	***2***	***1.824***	***0.16***	***0.002***	***0.407***
site status	***1***	***72.473***	***< 0.01***	***0.040***	
lipid	***2***	***562.481***	***< 0.01***	***0.395***	
site*length	***2***	***1.288***	***0.28***	***0.001***	***0.182***
site status	***1***	***29.041***	***< 0.01***	***0.017***	
length	***2***	***172.431***	***< 0.01***	***0.167***	
species*lipid	4	4.011	< 0.01	0.009	0.408
species	3	1.693	0.17	0.003	
lipid	2	114.732	< 0.01	0.118	
species*length	4	8.653	< 0.01	0.020	0.269
species	3	21.608	< 0.01	0.036	
length	2	18.002	< 0.01	0.020	
lipid*length	4	10.375	< 0.01	0.024	0.400
lipid	2	47.248	< 0.01	0.052	
length	2	1.104	0.33	0.001	

There are no significant interaction effects for site*species, site*lipid, or site*length. The estimated means plots for site*species shows that for all four species, the PCB concentrations were higher at AOC sites than at non-AOC sites (Figure 3-11). Since there were only two categories, a Tukey honest significance determination (HSD) could not be done, However, an independent t-test indicated that mean concentrations at AOC sites were higher than at non-AOC sites ($p < 0.001$). Regarding the species, Tukey HSD indicated mean PCB concentrations in carp are significantly greater than in the other three species ($p < 0.05$). However, there are no significant differences between the other three species. Generally, PCB concentrations were as follows: carp >> walleye > smallmouth bass ≈ largemouth bass.

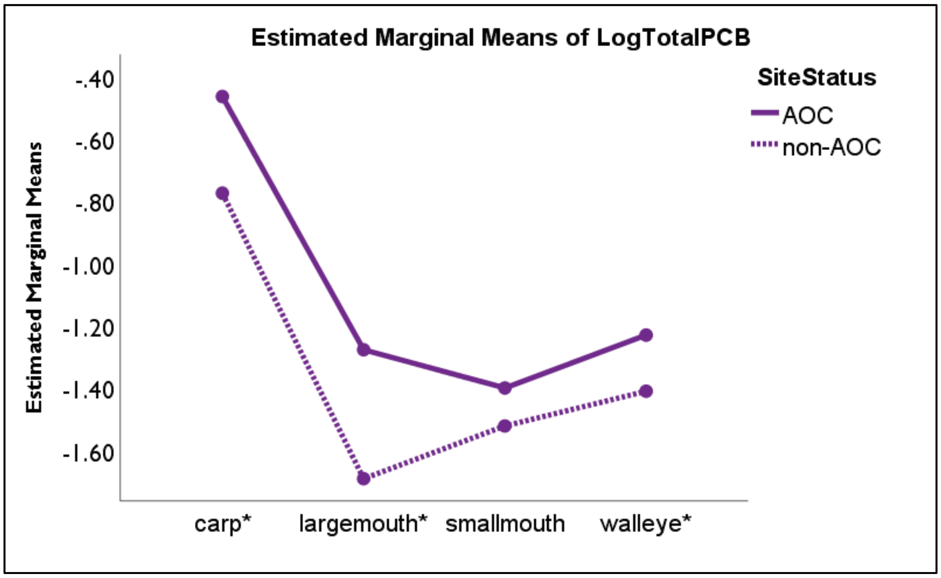


Figure 3-11 Estimated means plot of total PCB concentrations in fish species at AOC and non-AOC sites. Tukey HSD indicates that carp have higher PCB concentrations than the other three species but there are no statistically significant differences between the other three species. Asterisks (*) next to the fish species, indicate significant differences between AOC and non-AOC concentrations, for that species (determined using independent t-tests).

Below the estimated means plot (Figure 3-12) for site*lipid shows that for each of the three lipid content categories, PCB concentrations were higher at AOC sites than non-AOC sites, confirmed with an independent t-test, which shows that the differences are significant ($p < 0.001$).The plot also shows that PCB concentrations are higher, the fattier the fish ($p < 0.05$). Concentrations in fattier fish are higher than the other categories, regardless of site status. Thus the pattern is A3 > N3 > A2 > N2 > A1 > N1 where, for example, "A3" denotes AOC sites and lipid category 3.

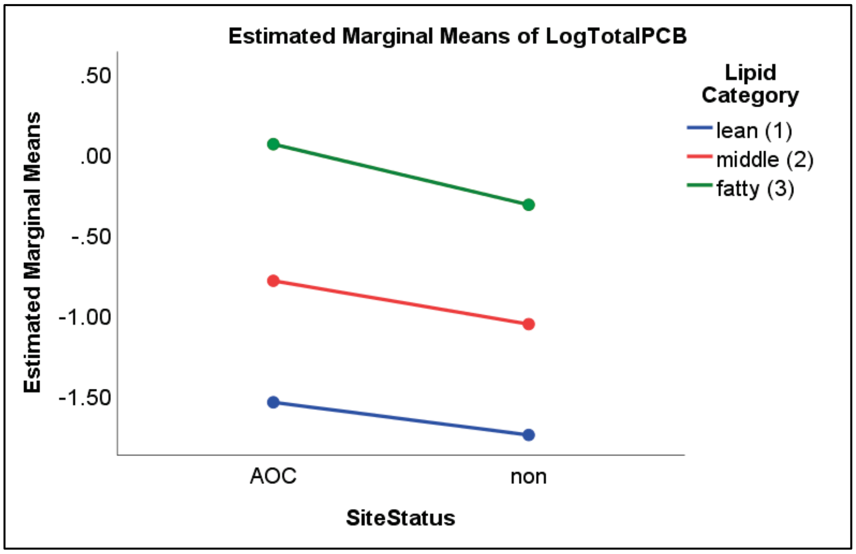


Figure 3-12 Estimated means plot of total PCB concentrations in fish of different lipid content at AOC and non-AOC sites. Category 1 = lean, category 2 = medium lipid, category 3 = fatty.

Below the estimated means plot for site*length shows that for each of the three length categories, PCB concentrations were higher at AOC sites than at non-AOC sites (Figure 3-13). Independent t-tests show that the difference is only significant for the small fish ($p < 0.001$). The plot also shows that PCB concentrations are higher, the longer the fish ($p < 0.05$). Based on significance, the following pattern emerges with regard to PCB concentrations: A3 > N3 > A2 ≈ N2 > A1 ≈ N1.

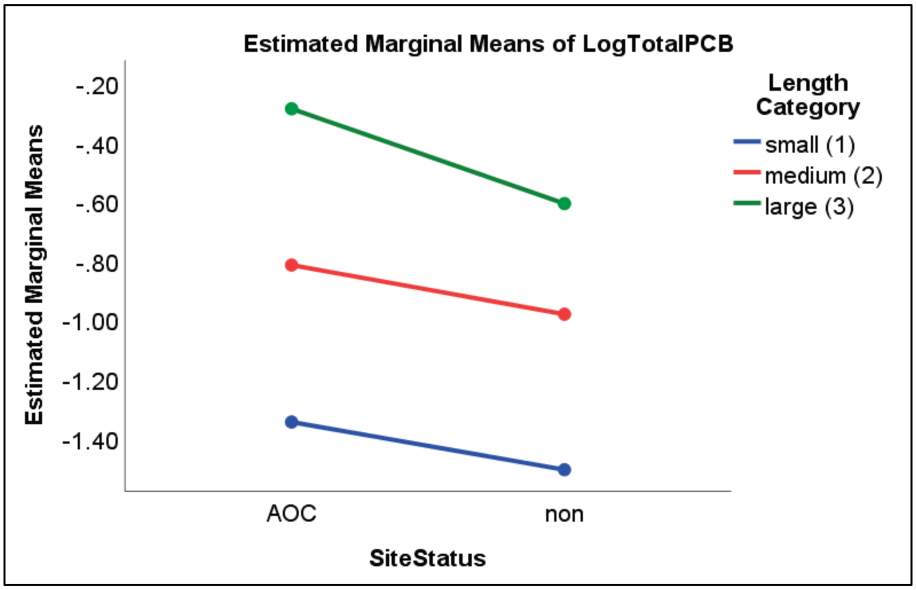


Figure 3-13 Estimated means plot of total PCB concentrations in length classes of fish at AOC and non-AOC sites. Category 1 = small, category 2 = medium, category 3 = large.

Partial η^2 is a measure of the proportion of variance explained by a given effect. The greater the value, the more variance explained. For all three of these scenarios (site*species, site*lipid, and site*length), the factor other than site status has much more relative impact on PCB concentrations (partial $\eta^2 > 0.166$) (Table 3-7). While it appears from simple linear regression (Figure 3-5 and Figure 3-6) that PCB concentrations depend on both length and lipid, the two-way ANOVA indicates that the interaction between lipid and length causes the correlation between length and PCB concentration (Table 3-7). Length does not explain any additional variance in PCB concentrations beyond what can be explained by variations in lipid content.

Because of the difficulty with the Levene's test, a two-way ANOVA with length- and lipid-normalized concentrations was attempted. Levene statistics failed to reject H_0 and indicated that the variance of PCB concentrations is equal across groups ($p > 0.05$), which permitted the interpretation of the ANOVA results (Table 3-7).

Table 3-7 Statistical output for the two-way ANOVAs with length and lipid normalized concentrations. The p-value indicates the significance of the interaction effect. Both combinations show no interaction effect ($p > 0.05$) and the results were interpreted.

Two-way ANOVA	df	F-statistic	p-value	partial η^2	adjusted R^2
Length Normalized PCB Concentrations					
species*site	3	0.305	0.822	0.004	0.004
species	3	1.147	0.331	0.016	
site	1	0.356	0.551	0.002	
Lipid Normalized PCB Concentrations					
species*site	3	0.293	0.830	0.004	0.008
species	3	0.607	0.611	0.008	
site	1	0.838	0.361	0.004	

For lipid-normalized log PCB concentrations, the estimated mean concentrations were higher, for all species, at AOC sites compared to non-AOC sites (Figure 3-14). Since there were only two site categories (AOC and non-AOC), a Tukey HSD test could not be done. However, an independent samples t-test indicated that mean concentrations at AOC sites are not significantly different from PCB concentrations at non-AOC sites for any species ($p > 0.05$). Additionally, the Tukey HSD did not show significant differences between any of the four species.

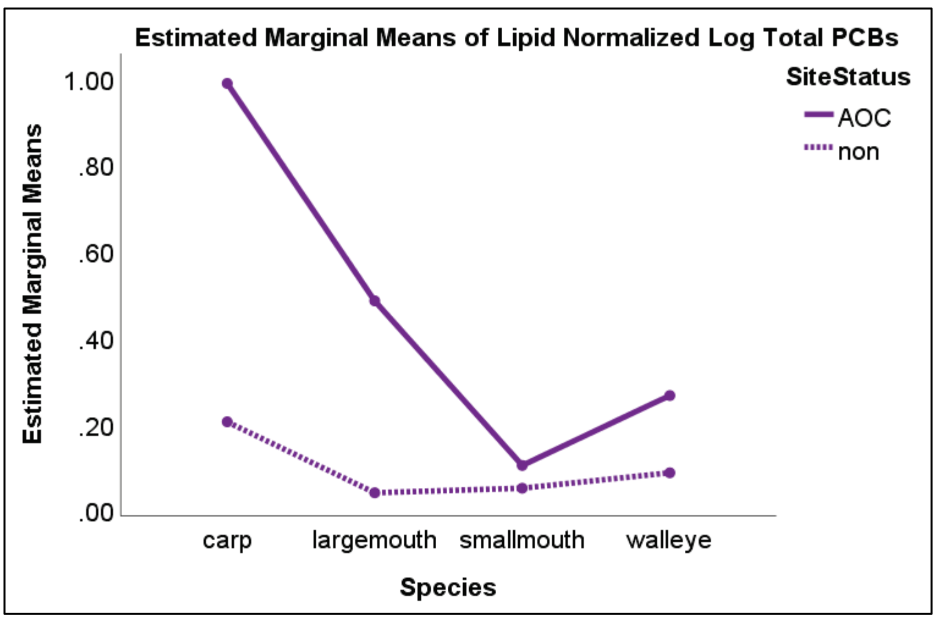


Figure 3-14 Estimated means plot of lipid normalized total PCB concentrations at AOC and non-AOC sites. A Tukey HSD test indicated that there are no statistical differences between AOC and non-AOC concentrations for any of the species ($p > 0.05$).

For length-normalized concentrations, the estimated mean concentrations were higher, for all species, at AOC sites compared to non-AOC sites (Figure 3-15). Since there were only two site categories (AOC and non-AOC), a Tukey HSD test could not be done. However, an independent samples t-test indicated that mean concentrations at AOC sites were not significantly different from PCB concentrations at non-AOC sites for any species ($p > 0.05$). Additionally, the Tukey HSD did not show significant differences between any of the four species.

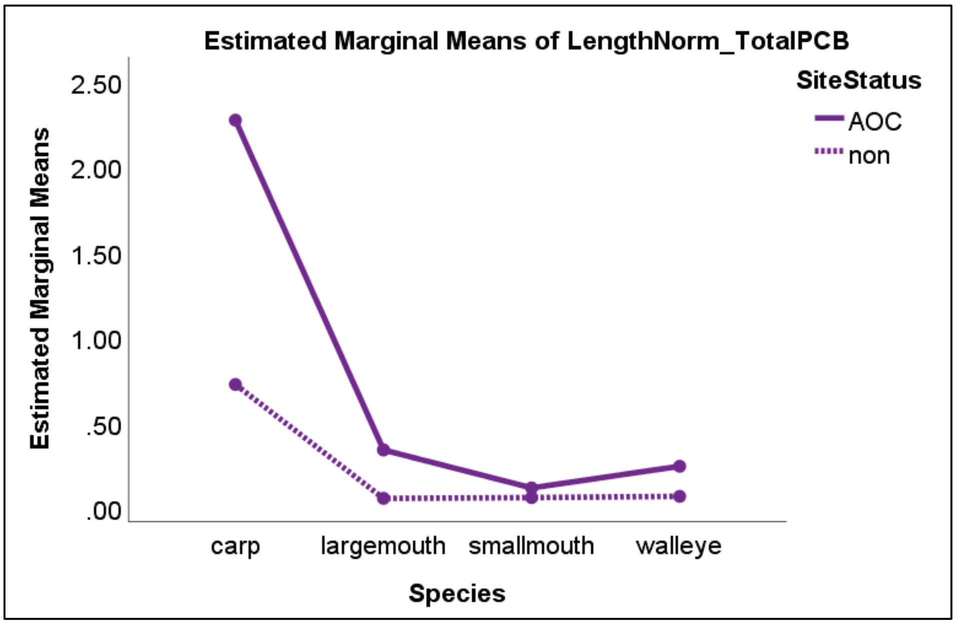


Figure 3-15 Estimatd means plot of length normalized total PCB concentrations at AOC and non-AOC sites. A Tukey HSD test indicated that there are no statistical differences between AOC and non-AOC concentrations for any of the species ($p > 0.05$).

Multiple linear regressions (MLRs) model relationships between a dependent variable (e.g. PCB concentrations in fish) and a set of independent variables (in this case, length, lipid content, site category). Stepwise regressions include variables in the model and then re-assess all variables to make sure they meet the inclusion criteria set by the modeler. Because site status is categorical, the model was set so that the coefficient represents the effect for AOC sites. There was a strong correlation (>21% of variance explained) between log total PCB concentration and log lipid content ($p < 0.001$) and length ($p < 0.001$) and a weak correlation (~1% of variance explained) with site status category ($p < 0.001$; Table 3-8). A strong correlation between length and lipid content is the most likely explanation for excluding length from the MLR model.

Table 3-8. Correlations between log PCB concentrations and possible explanatory variables.

	Log Total PCB	**Length**	**Site Status (0 = non, 1 = AOC)**	**Lipid Content**
Log Total PCB		0.461*	0.122*	0.673*
Length			-0.029	0.665*
Status Category				-0.113*
Lipid Content				
* indicates significance (p < 0.001)				

The regression equation that best explained the PCB concentration data included log lipid content and sites status (Equation 3-1). The standard error of the estimate was 0.577, and the standard deviation of PCB concentrations was 0.810, which indicates that the observed data vary less about the regression than about the mean. This is an indication of a useful model. Most of the samples fall within the 95% confidence intervals (Figure 3-16). The expected probability curve demonstrates that the residuals from the model are normally distributed (Figure 3-17).

$$[PCB] = -1.154 + (0.951 * log_{10}\ lipid\ content) + (0.323 * site\ status$$ Equation 3-1

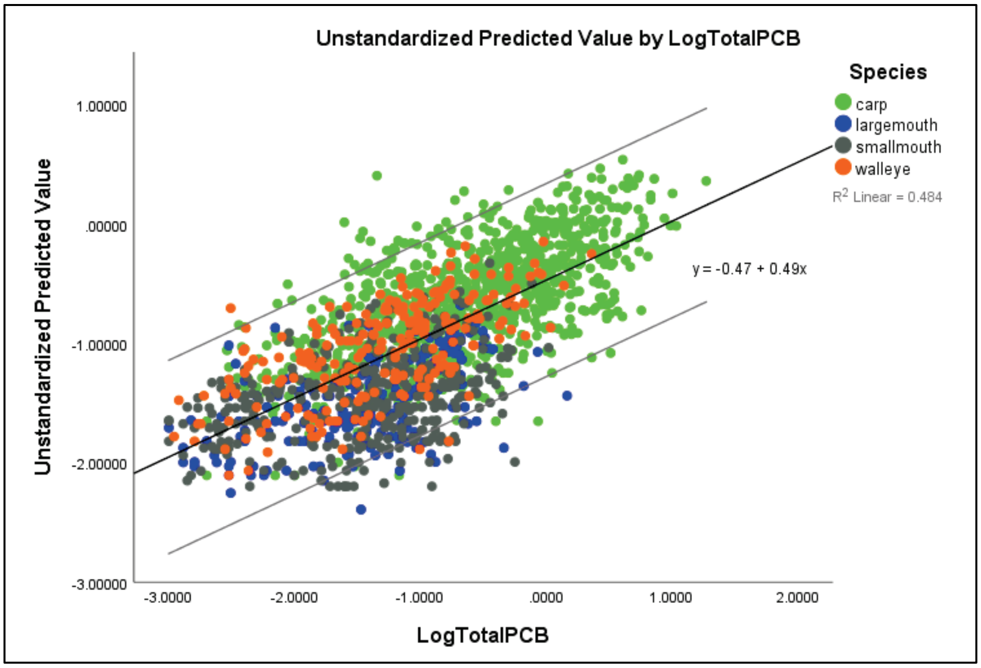


Figure 3-16 Predicted log total PCB concentrations as a function of measured log total PCB concentrations. Bands represent the 95% confidence intervals.

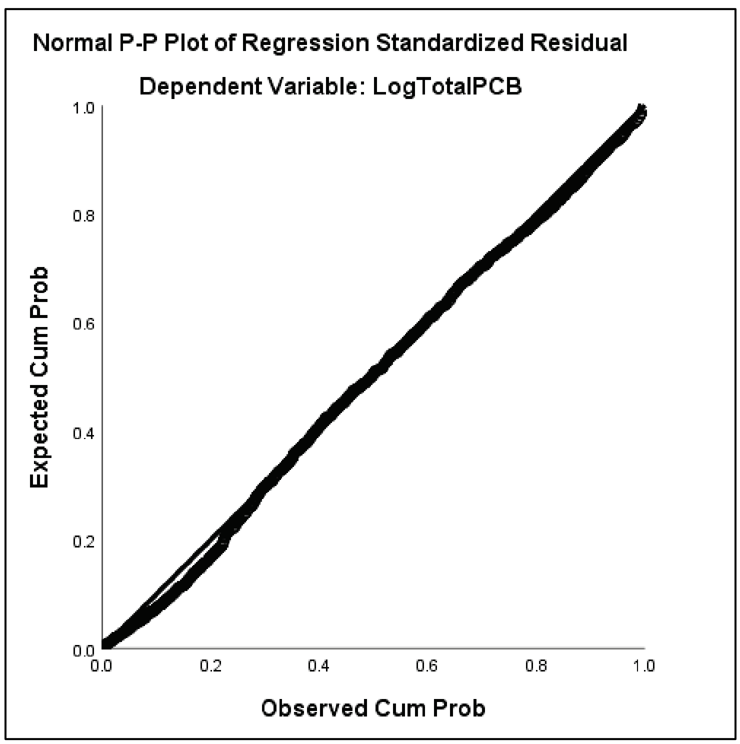


Figure 3-17 Probability plot of log total PCB concentrations based on the regression, Equation 3-1, above.

3.1.1 How do congener concentrations compare among different species?

The differences in congener profiles among different species and between the same species at different sites are indicative of factors beyond species and site status being important in understanding how fish assimilate PCBs. There were only five congeners or co-eluters that were present in at least 90% of fish samples (118, 138+163, 153, 170, 180). There was a total of 25 congeners or co-elutes that were present in at least 50% of fish samples (49, 52, 66+95, 77+110, 90+101, 97, 99, 105, 118, 128, 132, 138+163, 141, 146, 151, 153, 156, 170, 174, 177, 180, 182+187, 183, 194, 201). Additional congeners that were abundant in the different species are shown below (

Table 3-9).

Table 3-9 Common congeners (≥ 50% presence) in each species of interest. Twenty-five congeners were common in all four species and used in subsequent analyses.

Species	Congeners having 50% or greater abundance
Carp (51 congeners)	28, 44, 47, 49 52, 56+60, 64, 66+95, 70, 74, 77+110, 82, 84, 90+101, 91, 92, 97, 99, 105, 118, 126+178, 128, 130, 132, 135+144, 136, 137, 138+163, 141, 146, 151, 153, 156, 167, 170, 171, 172, 174, 177, 179, 180, 182+187, 183, 185, 193, 194, 195, 196+203, 199, 201, 206
Smallmouth Bass (27 congeners)	49, 52, 66+95, 77+110, 90+101, 97, 99, 105, 118, 128, 132, 138+163, 141, 146, 151, 153, 156, 170, 172, 174, 177, 180, 182+187, 183, 194, 196+203, 201
Largemouth Bass (25 congeners)	49, 52, 66+95, 77+110, 90+101, 97, 99, 105, 118, 128, 132, 138+163, 141, 146, 151, 153, 156, 170, 174, 177, 180, 182+187, 183, 194, 201
Walleye (33 congeners)	49, 52, 66+95, 70, 77+110, 87, 90+101, 92, 97, 99, 105, 118, 128, 132, 137, 138+163, 141, 146, 149, 151, 153, 156, 170, 172, 174, 177, 179, 180, 182+187, 183, 193, 194, 196+203, 201

A few individual carp and largemouth bass from Lake St Clair had orders of magnitude more contamination and were removed for the relative abundance comparison. The 25 most common congeners appear to have relatively similar patterns, but there are differences between species and AOC compared to non-AOC sites (Figure 3-18 and Figure 3-19, respectively).

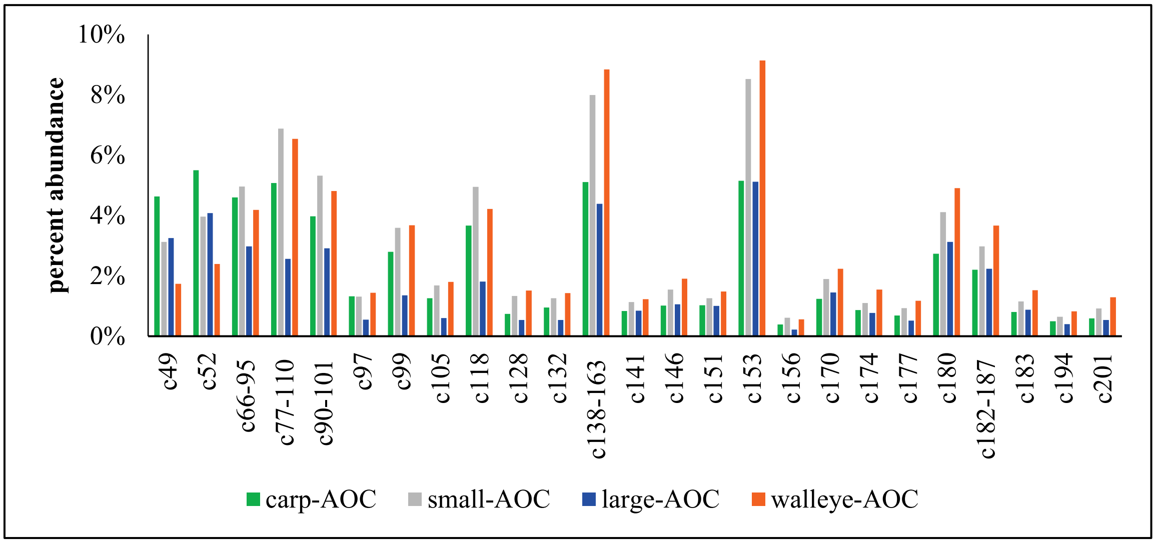


Figure 3-18 Congener profiles for the 25 common congeners in the four species at AOC sites.

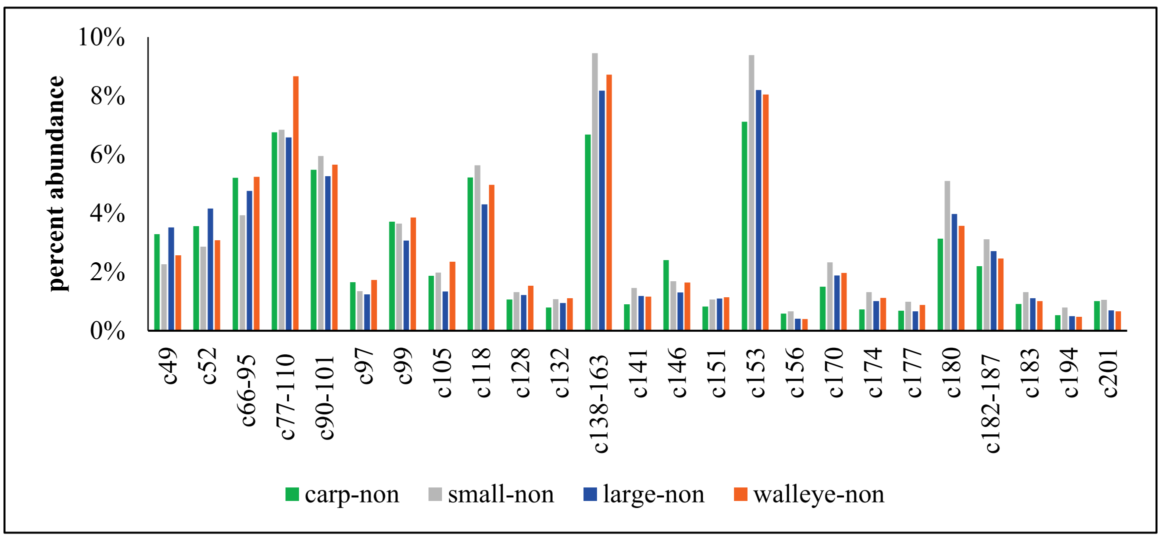


Figure 3-19 Congener profiles for the 25 common congeners in the four species at non-AOC sites.

A principal component analysis (PCA), using the 25 common congeners (present in $\geq$ 50% of fish samples) revealed that for all species, more than 89.5% of variance is explained by two components and more than 70.5% of variance is explained by one component (Table 3-10). The statistics in Table 3-10 show that for all species, PCA is an appropriate evaluation technique. The KMO scores are > 0.7, which indicates there are enough variables predicted by the components, the sphericity test indicates the correlation matrix is significantly different from the identity matrix, and the communalities are high.

Generally, the congeners with a higher log K_{ow} are best described by component 1 (carp, smallmouth bass, largemouth bass, and walleye represented by Figure 3-20, Figure 3-22, Figure 3-24, and Figure 3-26, respectively). Plotting component 1 score as a function of congener log K_{ow} confirmed the relationship (Figure 3-21, Figure 3-23, Figure 3-25, and Figure 3-27 for carp, smallmouth bass, largemouth bass, and walleye, respectively).

Table 3-10 Statistical measures; (output from SPSS) used to assess the appropriateness of PCA on a set of data. For all four species, KMO values exceed 0.7, which indicates variables are predicted by the components, the sphericity test is significant, indicating that the correlation matrix and identity matrix are different, and the communalities are high, indicating there is little distortion of the data.

	Kaiser Meyer Olkin (KMO) value	**Bartlett's Test of Sphericity**	**Variance Explained by component 1**	**Communalities**
Carp	0.915	39810.441 ($p < 0.001$)	77.37%	0.855-0.989*
Smallmouth Bass	0.879	8874.893 ($p < 0.001$)	73.58%	0.731-0.983
Largemouth Bass	0.805	3937.295 ($p < 0.001$)	70.57%	0.696-0.986
Walleye	0.895	7460.809 ($p < 0.001$)	84.29%	0.848-0.985
* For carp, PCB-201 was not well explained, communality was 0.129.				

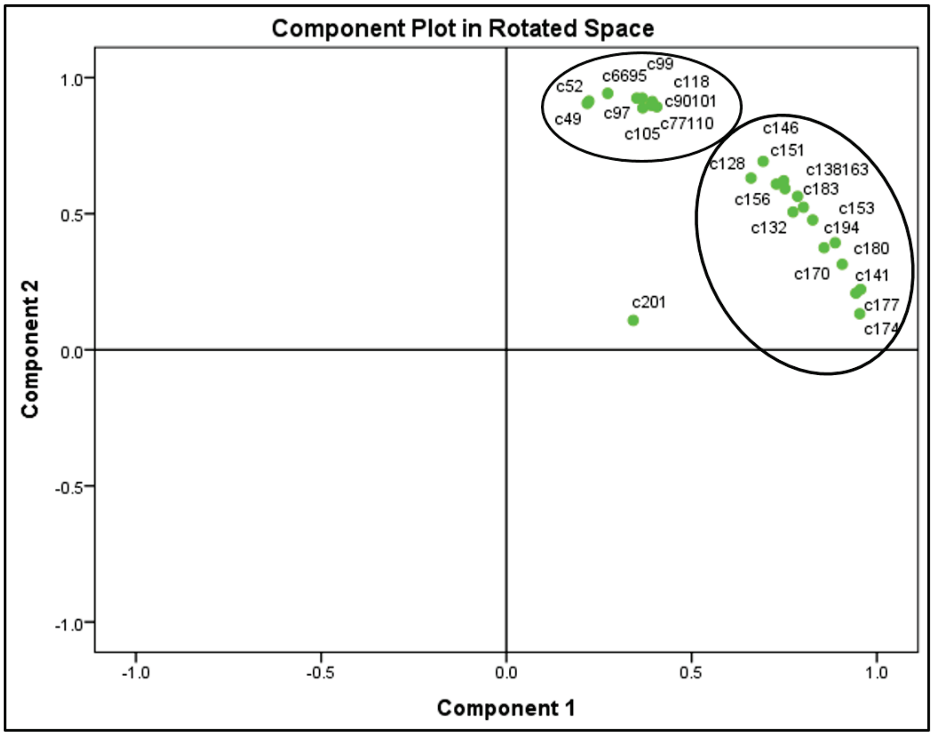


Figure 3-20 A PCA component plot for carp with common congeners, the 25 congeners that were present in at least 50% of all fish samples. With congener number as the variable and individual fish as the samples, 77.4% of the variance was explained by component 1.

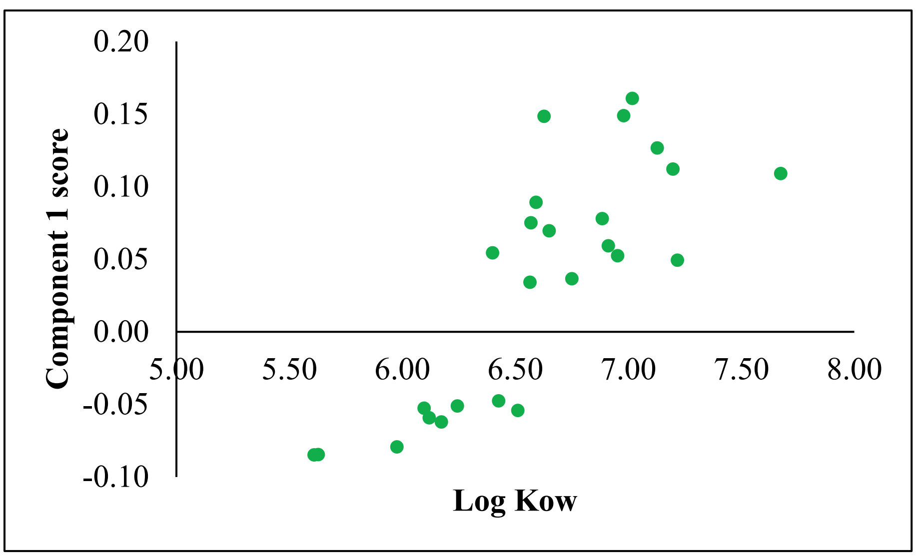


Figure 3-21 Based on the component 1 scores of the carp common congeners PCA (Figure 3-20), the component 1 score plotted as a function of log K_{ow}. Clustering shows that congeners with higher log K_{ow} values have a higher component 1 score.

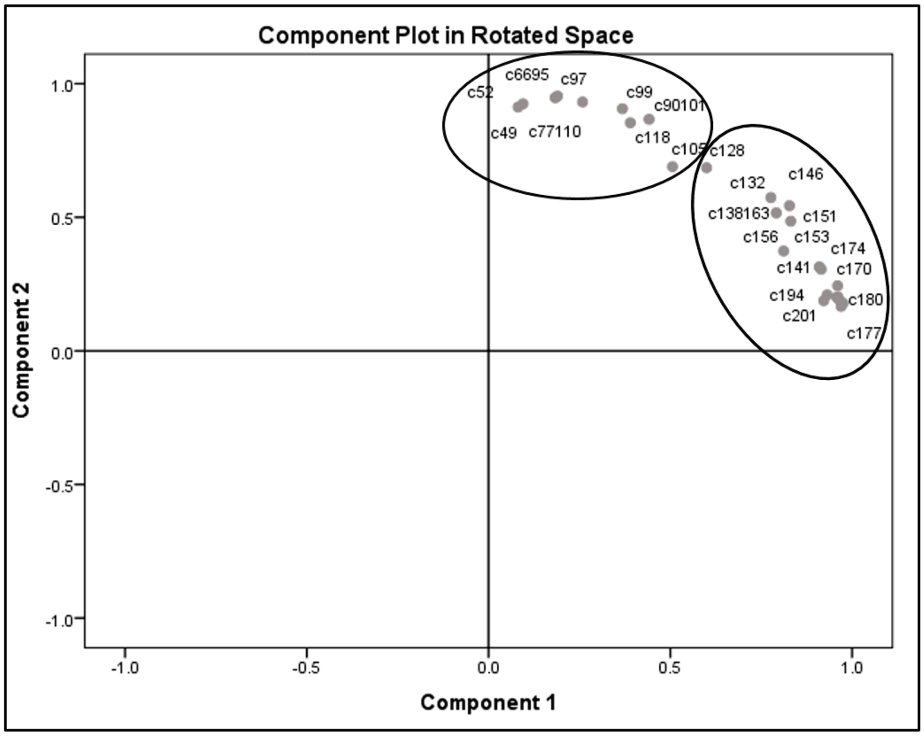


Figure 3-22 A PCA component plot for smallmouth bass with common congeners, the 25 congeners that were present in at least 50% of all fish samples. With congener number as the variable and individual fish as the samples, 73.6% of the variance was explained by component 1.

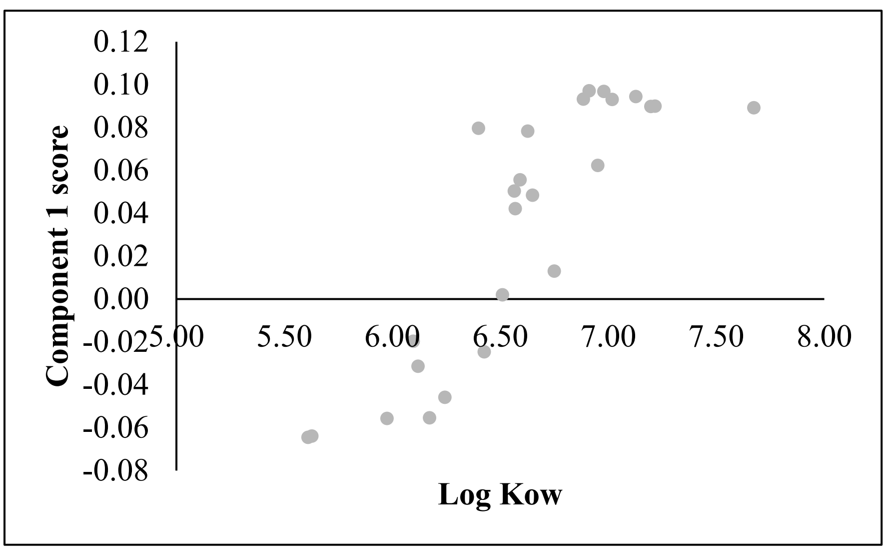


Figure 3-23 Based on the component 1 scores of the smallmouth bass common congeners PCA (Figure 3-22), the component 1 score plotted as a function of log K_{ow}. Clustering shows that congeners with higher log K_{ow} values have a higher component 1 score.

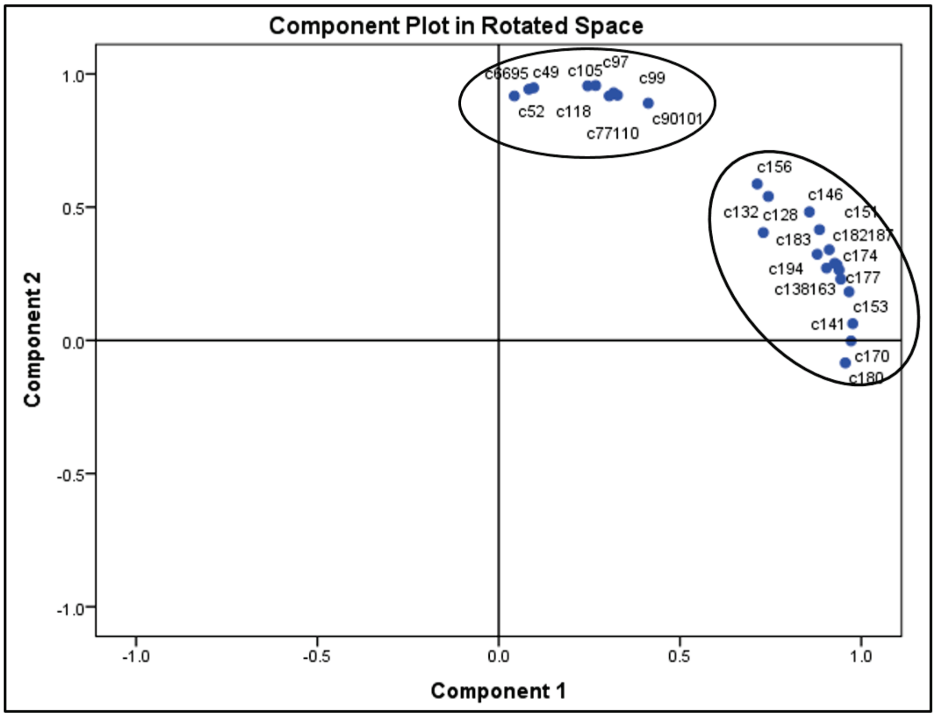


Figure 3-24 A PCA component plot for largemouth bass with common congeners, the 25 congeners that were present in at least 50% of all fish samples. With congener number as the variable and individual fish as the samples, 70.6% of the variance was explained by component 1.

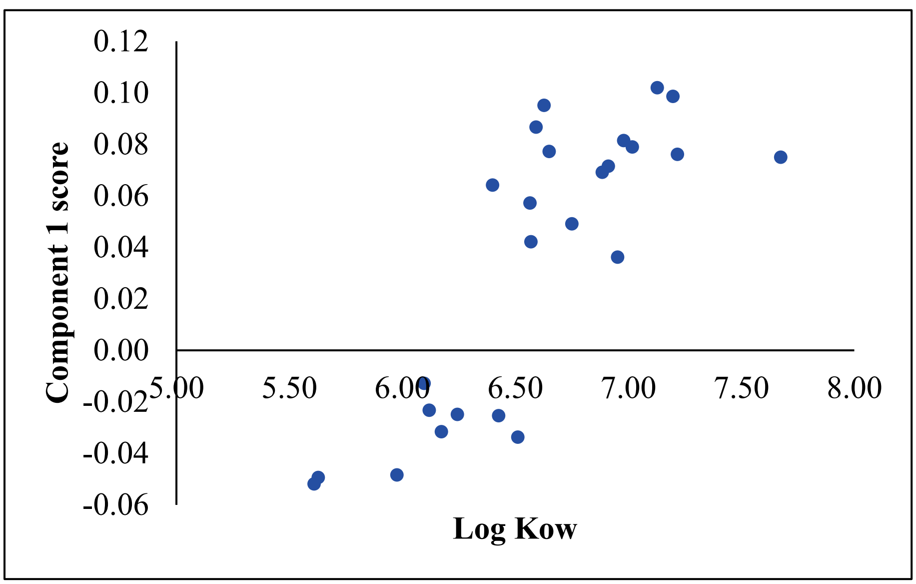


Figure 3-25 Based on the component 1 scores of the largemouth bass common congeners PCA (Figure 3-24), the component 1 score plotted as a function of log K_{ow}. Clustering shows that congeners with higher log K_{ow} values have a higher component 1 score.

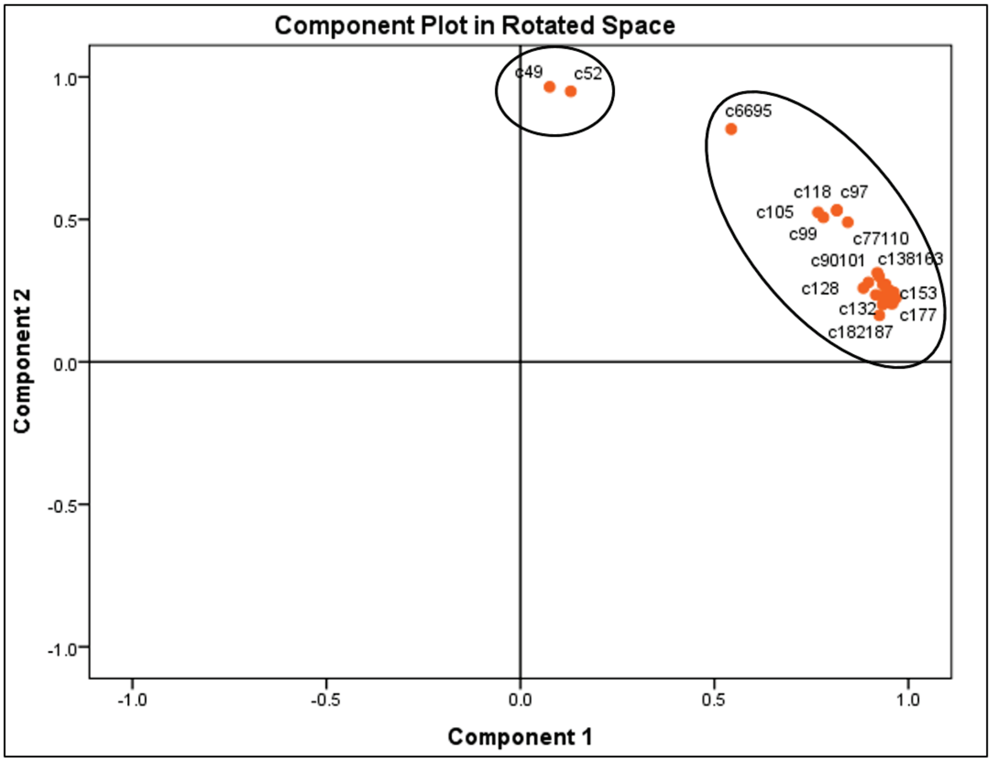


Figure 3-26 A PCA component plot for walleye with common congeners, the 25 congeners that were present in at least 50% of all fish samples. With congener number as the variable and individual fish as the samples, 84.3% of the variance was explained by component 1.

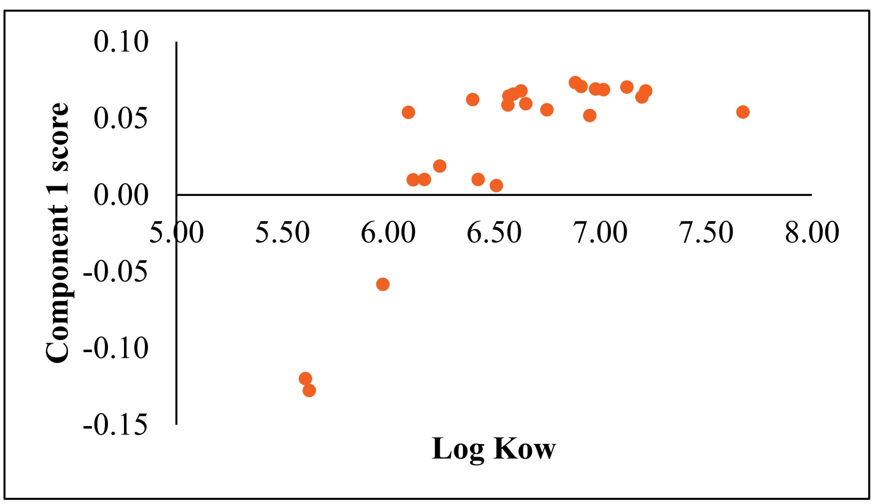


Figure 3-27 Based on the component 1 scores of the walleye common congeners PCA (Figure 3-26), the component 1 score plotted as a function of log K_{ow}. Clustering shows that congeners with higher log K_{ow} values have a higher component 1 score.

While 25 congeners were commonly occurring (present in ≥ 50% of samples), there are 109 congeners or co-elutes that are quantified by the MDEQ. By summing individual congener concentrations for a species at each site category (i.e. AOC or non-AOC), the relative abundance was calculated. For each species, the congener profile plots demonstrate differences between the site categories and the contribution of individual congeners to the total PCB concentration. Superficially, similarities emerge. For example, up until PCB-11 there is little contribution. Closer evaluation shows similarities between carp and largemouth bass (Figure 3-28 and Figure 3-30, respectively) and smallmouth bass and walleye (Figure 3-29 and Figure 3-31, respectively). Carp and largemouth bass appear to have a greater contribution from the lighter congeners compared to the other two species.

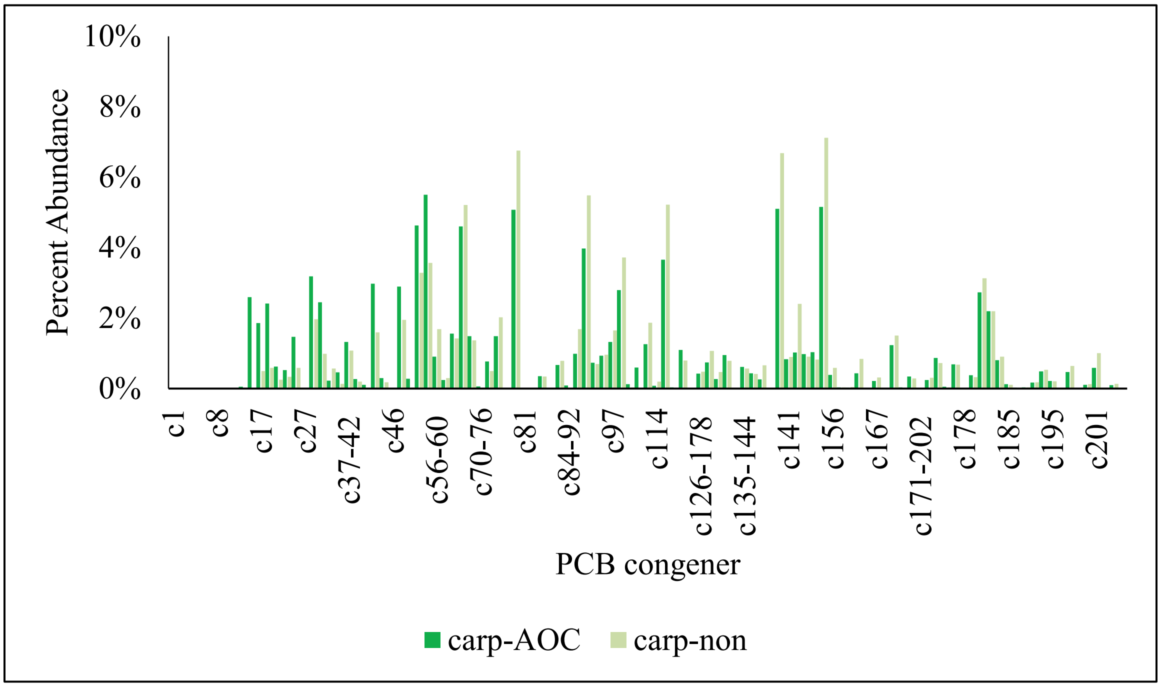


Figure 3-28 A congener profile comparison for carp at AOC sites and non-AOC sites. Congeners are organized by IUPAC number and represent an individual congener's percent contribution to the total PCB contamination. Relative abundance was determined by summing congener concentrations for all carp samples at the different site categories. Carp from Lake St Clair were excluded because of substantially higher concentrations.

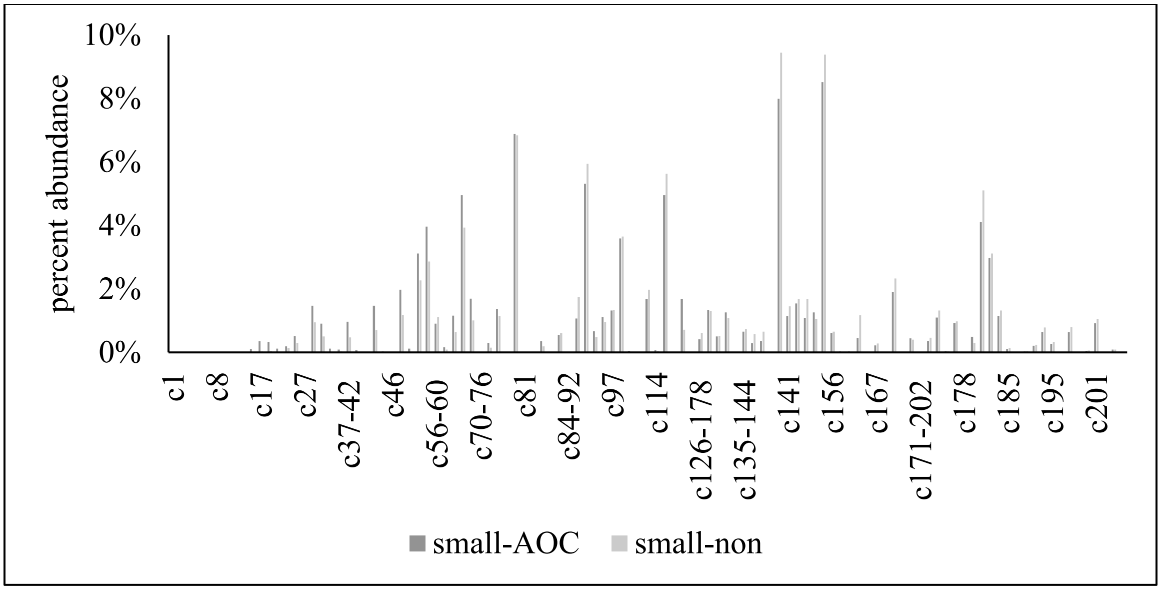


Figure 3-29 A congener profile comparison for smallmouth bass at AOC sites and non-AOC sites. Congeners are organized by IUPAC number and represent an individual congener's percent contribution to the total PCB contamination. Relative abundance was determined by summing congener concentrations for all smallmouth bass samples at the different site categories.

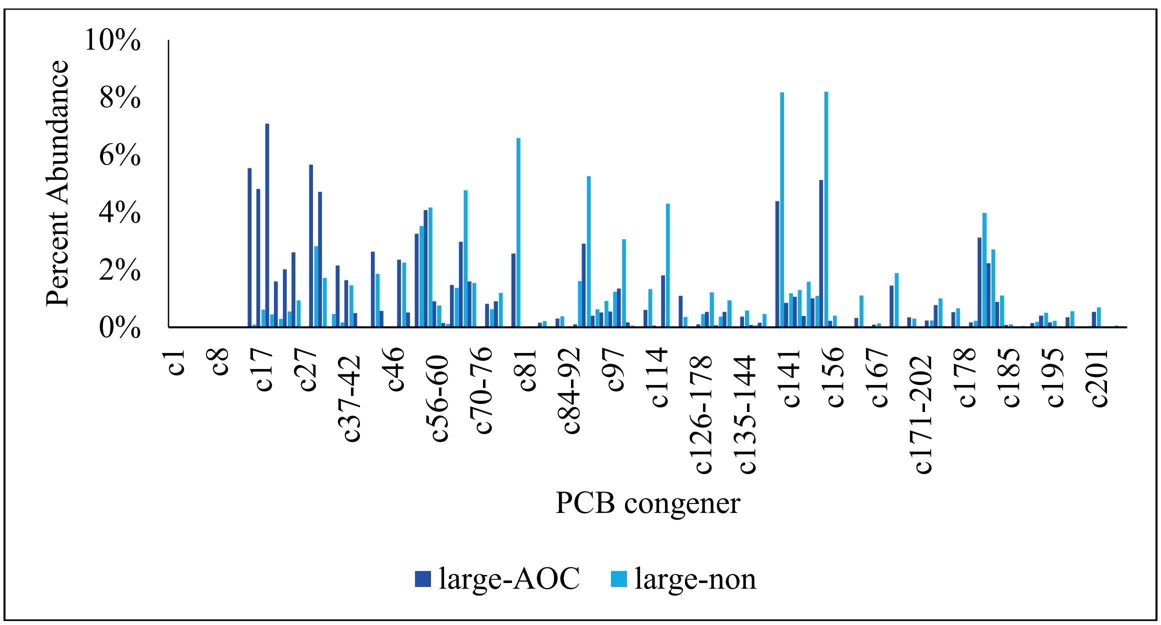


Figure 3-30 A congener profile comparison for largemouth bass at AOC sites and non-AOC sites. Congeners are organized by IUPAC number and represent an individual congener's percent contribution to the total PCB contamination. Relative abundance was determined by summing congener concentrations for all largemouth bass samples at the different site categories. Largemouth bass from Lake St Clair were excluded because of substantially higher concentrations.

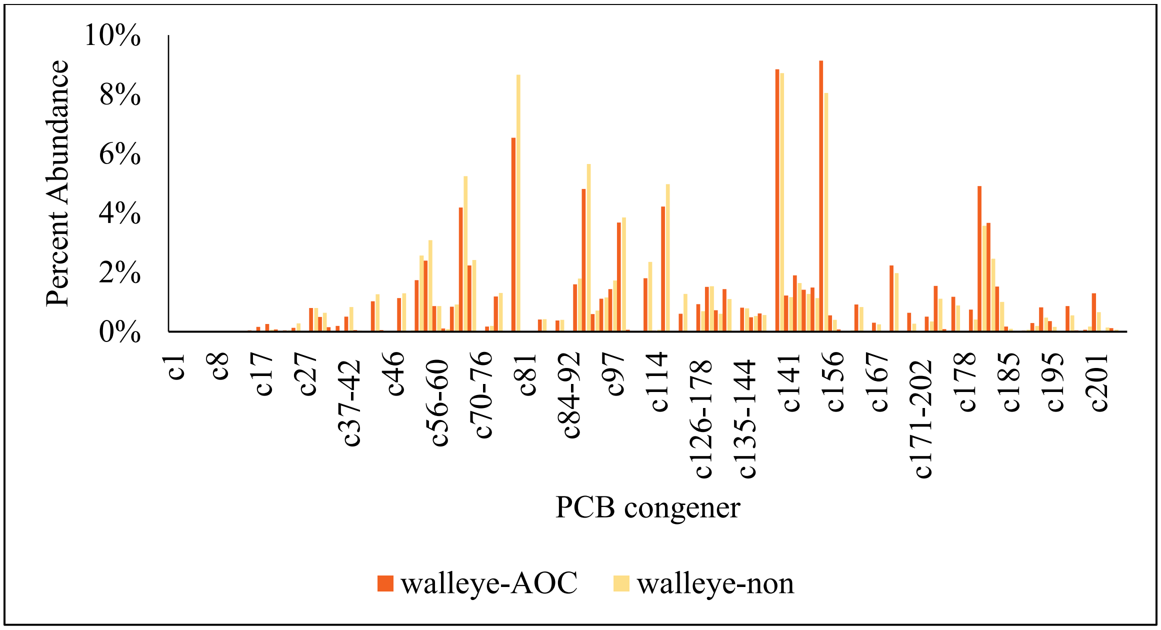


Figure 3-31 A congener profile comparison for walleye at AOC sites and non-AOC sites. Congeners are organized by IUPAC number and represent an individual congener's percent contribution to the total PCB contamination. Relative abundance was determined by summing congener concentrations for all walleye samples at the different site categories.

To assess this observation quantitatively, average congener concentrations were sorted into low (≤ PCB-100) and high congeners (> PCB-100). Independent t-tests, for each site*species combination, were done. Only walleye had no significant differences between the concentration of low and high congeners (Table 3-11). A paired t-test to compare average congener concentrations between AOC and non-AOC sites determined that there were significant differences between the congener concentrations at AOC and non-AOC sites for all four species ($p < 0.002$).

Table 3-11 Independent t-test results to compare low and high congener concentrations between species at both AOC and non-AOC sites.

	Significant differences between low and high congeners at AOC sites	**Significant differences between low and high congeners at non-AOC sites**
Carp	Yes, $p < 0.002$	Yes, $p < 0.002$
Smallmouth Bass	Yes, $p < 0.05$	Yes, $p < 0.05$

Largemouth Bass	Yes, $p < 0.001$	Yes, $p < 0.001$
Walleye	No	No

Using summed congener concentrations to calculate the percent of total PCBs, cumulative accumulation plots show a generally similar pattern; species have lower contributions of low congeners compared to high congeners (Figure 3-32). One largemouth bass sample from the Detroit River had two orders of magnitude more contamination than the other fish samples and was excluded from this analysis. While the general patterns are similar, there are obvious differences in accumulation patterns between the site*species combinations. Largemouth bass and carp at non-AOC sites appear to have a larger contribution of lower congeners to their total body concentrations compared to the other site*species combinations. Total body concentrations in carp are greater than the other three species, despite similar accumulation patterns (Figure 3-32). Figure 3-33 shows that carp, at both AOC and non-AOC sites, have an order of magnitude more contamination than the other species.

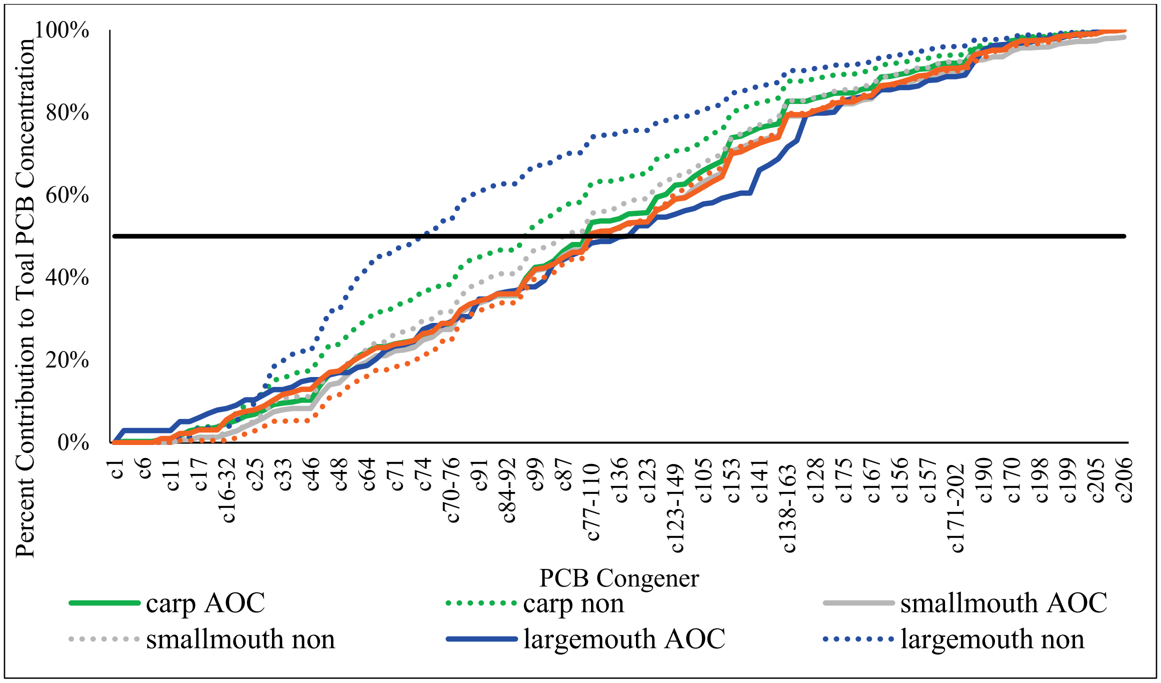


Figure 3-32 Cumulative percent accumulation plots for four species with AOC and non-AOC sites separated. Congeners are ordered by increasing log K_{ow}. One largemouth bass from the Detroit River that had surprisingly high concentrations of a few lighter congeners was removed from the analysis.

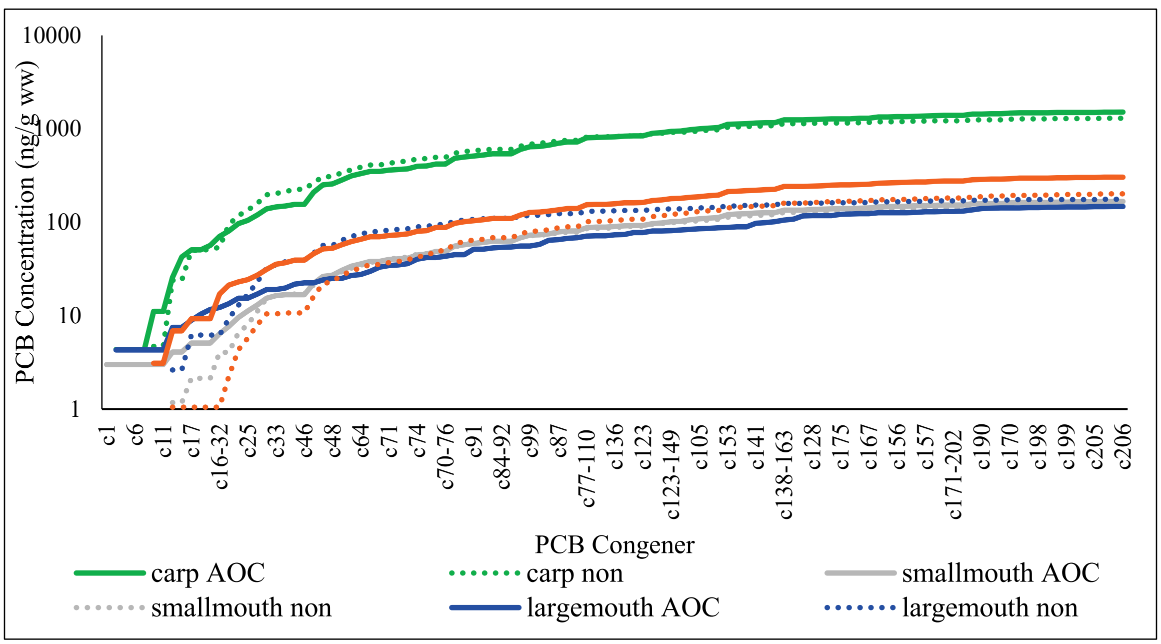


Figure 3-33 Cumulative congener accumulation plots for four species with AOC and non-AOC sites separated. Congeners are ordered by increasing log K_{ow}. One largemouth bass from the Detroit River that had surprisingly high concentrations of a few lighter congeners was removed from the analysis.

Toxic Equivalency Factors (TEFs): translating PCB concentrations into health endpoints

Dioxin-like (DL) compounds produce a specific toxic response by binding to the aryl hydrocarbon receptor (Ah-receptor). Twelve PCB congeners of all 209 are dioxin-like. As discussed earlier, each of them has a toxic equivalency factor (TEF) that enables comparison to or summation with other DL compounds. To evaluate the toxicity of the DL PCBs, a threshold concentration was calculated from the EPA's cancer reference dose of 0.001 pg TEQ/kg*day and the non-cancer reference dose of 1.0 pg/kg*day (Equation 2-5). When compared to calculated threshold concentrations most fish samples were above the most restrictive threshold (n = 1737) while few samples did not exceed any (n = 310; Figure 3-34). It is important to note that people who deviate from the consumption rate, weight, etc. have the potential to be above or below the average TEQ concentrations shown here. The implications of this are explored further in the discussion section.

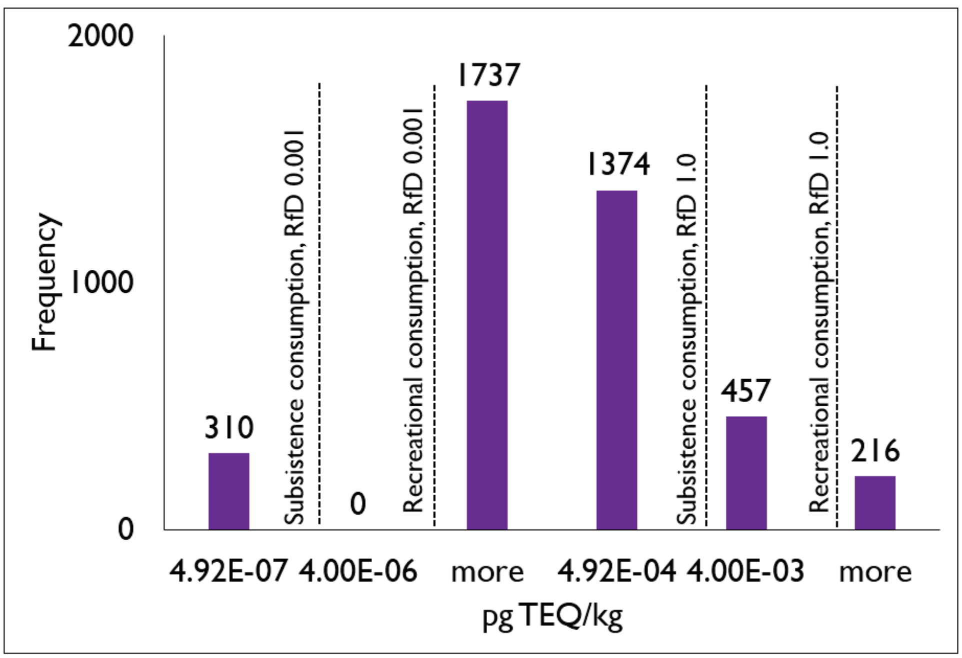


Figure 3-34 TEQ concentrations in fish compared to threshold concentrations based on a body weight of 70 kg. Two different consumption rates, 17.5 g/day for recreational anglers and 142.4 g/day for subsistence anglers. Two different endpoints the EPA's cancer RfD of 0.001 pg/kg*day and the non-cancer RfD of 1.0 pg/TEQ/kg*day.

Evaluation of individual congener contributions to TEQ concentrations shows that a few congeners contribute more of the total toxicity, and the contribution depends on species. The percent contribution to the TEC varies between species and between congener (Figure 3-35). While PCB-126 and PCB-169 have the highest TEFs (0.1 and 0.03, respectively), PCB-118 also contributes much of the toxicity (more than 20% for each species. This is likely because PCB-118 is more common congener in the fish than the other DL-PCB congeners

Table 3-12).

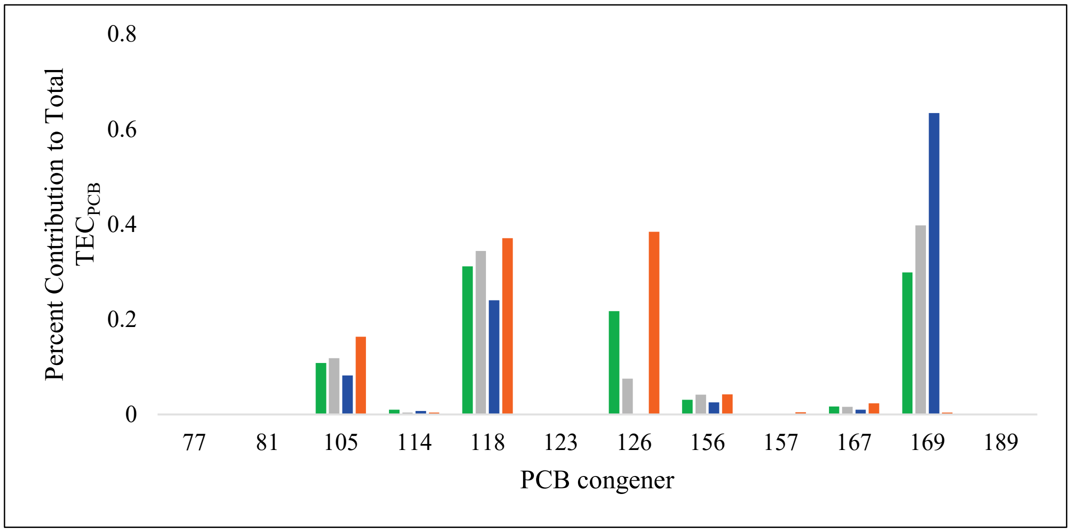


Figure 3-35 Percent contribution to total TEQ concentrations for PCBs. The TEC does not include dioxins or furans.

Table 3-12 Percent of fish samples containing each dioxin-like congener.

	Carp	Smallmouth Bass	Largemouth Bass	Walleye
PCB 77	11%	2%	0%	4%
PCB 81	7%	1%	0%	4%
PCB 105	79%	58%	64%	84%
PCB 114	28%	8%	14%	9%
PCB 118	88%	69%	91%	92%
PCB 123	11%	2%	0%	4%
PCB 126	10%	2%	0%	4%
PCB 156	74%	43%	49%	56%
PCB 157	16%	4%	0%	10%
PCB 167	61%	23%	22%	31%

PCB 169	7%	2%	2%	1%
PCB 189	0%	3%	2%	6%

3.2 Sources: Are there patterns in PCB contamination in fish species?

3.2.1 Carbonless copy paper compared to general use Aroclors

One-way ANOVAs evaluated whether carp and smallmouth bass exhibited Aroclor signatures associated with specific industrial uses. It was expected that AOC sites associated with a paper mill would have congener distributions similar to Aroclor 1242 since that mixture was used in carbonless copy paper. Conversely, other AOC sites were expected to have congener profiles more similar to Aroclor 1254, a general-use mixture. To evaluate the signature, two approaches were used. The first method summed the lipid-normalized concentrations of the nine Aroclor-representative congeners to create the ratio (Σ1242 congeners / Σ1254 congeners). The second approach calculated the ratio of a lipid-normalized congener's contribution to the Aroclor mixtures (e.g. PCB-18 had a ratio of 106.63, based on 8.83% in 1242 and 0.08% in 1254) and multiplied it by the lipid-normalized PCB concentration. Since the results were ambiguous, largemouth bass and walleye were not analyzed.

The first approach, using summed concentrations, indicated that there was more variance within a group (i.e. paper mill sites) than between groups (i.e. paper mill sites compared to non-paper mill sites) for both carp and smallmouth bass (Table 3-13). The second approach indicated that there was more variance between the groups than within a group. However, this was only significant for smallmouth bass (Table 3-13). It is likely that these results are confounded by the fact that Aroclor 1254 was also used in inking processes and presumably was also present at paper mill sites. Furthermore, transformers and capacitors were likely present at all sites.

Table 3-13 One-way ANOVA results to evaluate for the presence of Aroclor signatures in fish samples; lipid-normalized congener concentrations were used in two different comparisons.

	Approach 1 Σ ($congeners_{1242}$ / $Σcongeners_{1254}$)	**Approach 2** Σ ((1242:1254) * congener concentration)
Carp	$F (1, 44) = 0.32, p > 0.05$	$F (1, 44) = 1.46, p > 0.05$
Smallmouth Bass	$F (1, 25) = 0.34, p > 0.05$	$F (1, 25) = 5.15, p < 0.05$

3.2.2 Spatial patterns in PCB sources

Studies have shown that persistent organic pollutants (POPs) such as PCBs tend to accumulate at higher latitudes because of the temperature dependence of deposition and volatilization. Using the most recent data for each waterbody location, average concentrations were projected into a regional coordinate system, which includes Michigan (NAD_1983_UTM_Zone_16N). In evaluating spatial trends in inland waterbodies, data were insufficient for establishing reliable spatial trends in PCB contamination for all four species. For carp and largemouth bass (Figure 3-36a and Figure 3-36c, respectively) most fish samples were collected in the southern lower peninsula, at a latitude of approximately 43°N, which is close to the Saginaw River. For smallmouth bass (Figure 3-36b) there was an improvement (relative to carp) in the geographic spread in the lower peninsula, but sampling in the upper peninsula was sparse. For walleye, statewide coverage was even, but there were few data points and large areas without any samples (Figure 3-36d).

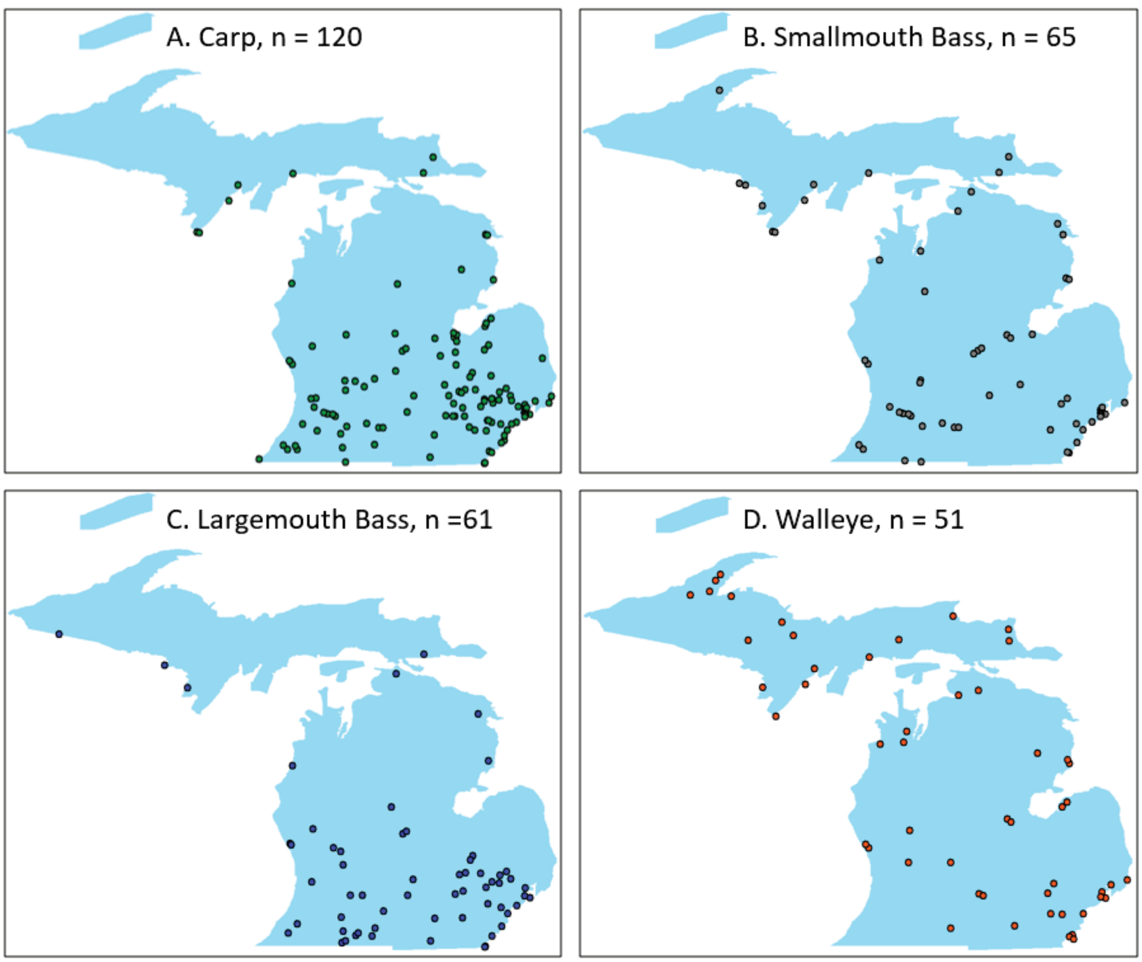


Figure 3-36 Maps of the sample locations in Michigan waters for A) carp, B) smallmouth bass, C) largemouth bass, and D) walleye. Sample locations are based on the MDEQ data from the fish contaminant monitoring program. (credit: MDEQ data)

PCA was used to differentiate between locally or atmospherically impacted sites; in this analysis, the unique waterbodies were the variables and the congener concentrations normalized to the total were the samples. Using relative concentrations as opposed to raw concentrations minimized the influence of sites with dramatically higher PCB concentrations. For the relative concentrations of PCB congeners in carp, two components explained only 48.11% of the total variance (Figure 3-37), and five components were necessary to explain 72.0% of the total variance. For smallmouth bass, only two components were extracted and explained 87.74% of the total variance (Figure 3-38). Neither species showed clear patterns in the site distribution.

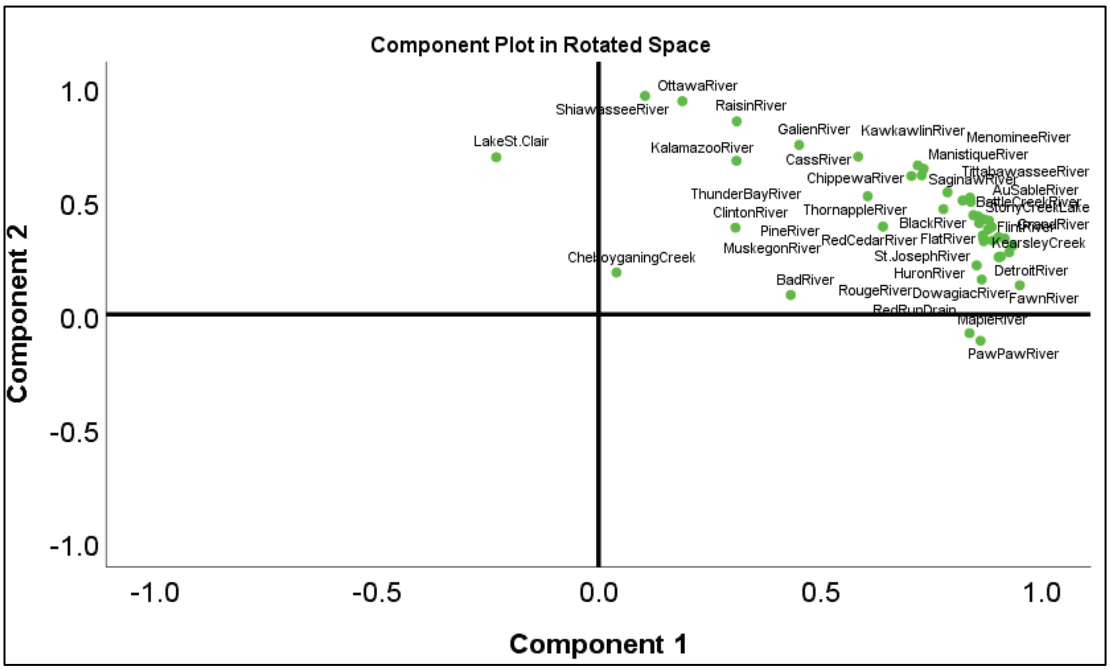


Figure 3-37 A PCA plot for Michigan water bodies with carp PCB data.

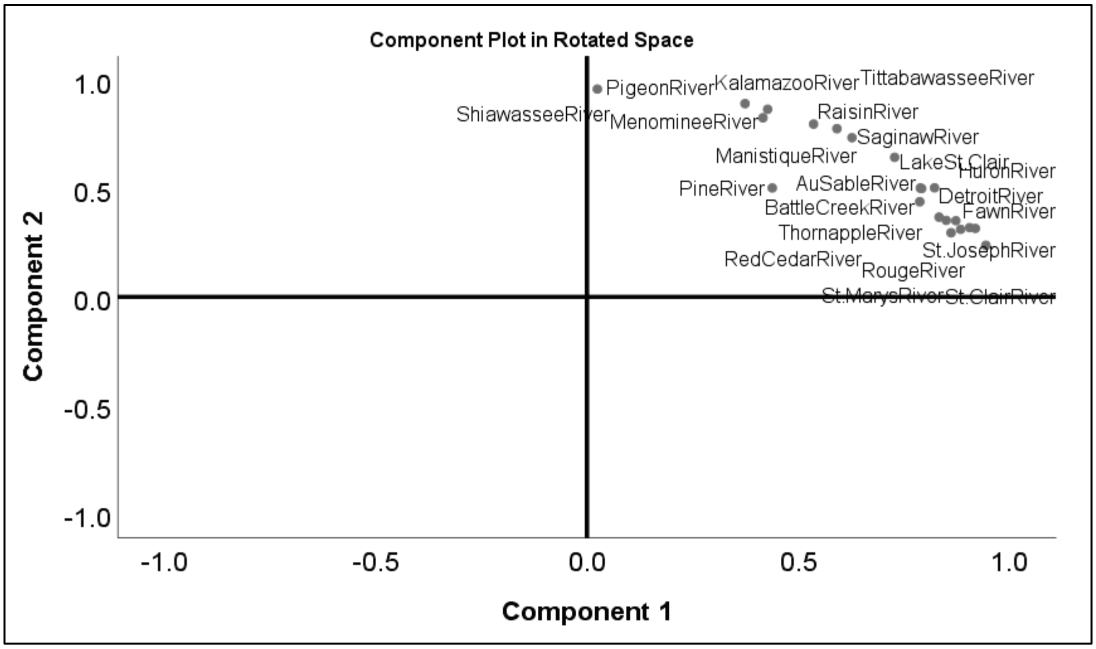


Figure 3-38 A PCA plot for Michigan water bodies with smallmouth bass PCB data.

For largemouth bass, two components explained 80.04% of the total variance in relative PCB concentrations, and there were three distinct groups of locations, but it is not obvious what either component represents (Figure 3-39). For walleye, two components explained 85.84% of the total variance in relative PCB concentrations (Figure 3-40). It appears that in walleye, the waterbody type explains the relative total PCB body burden; without Lake St. Claire, only one component was extracted.

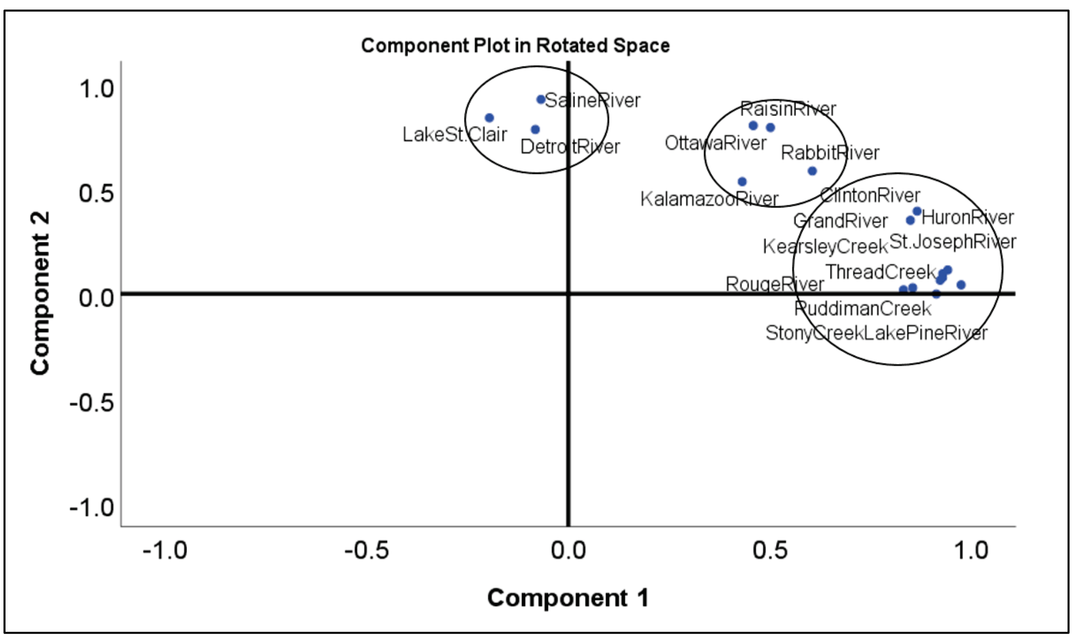


Figure 3-39 A PCA plot for Michigan water bodies with largemouth bass PCB data.

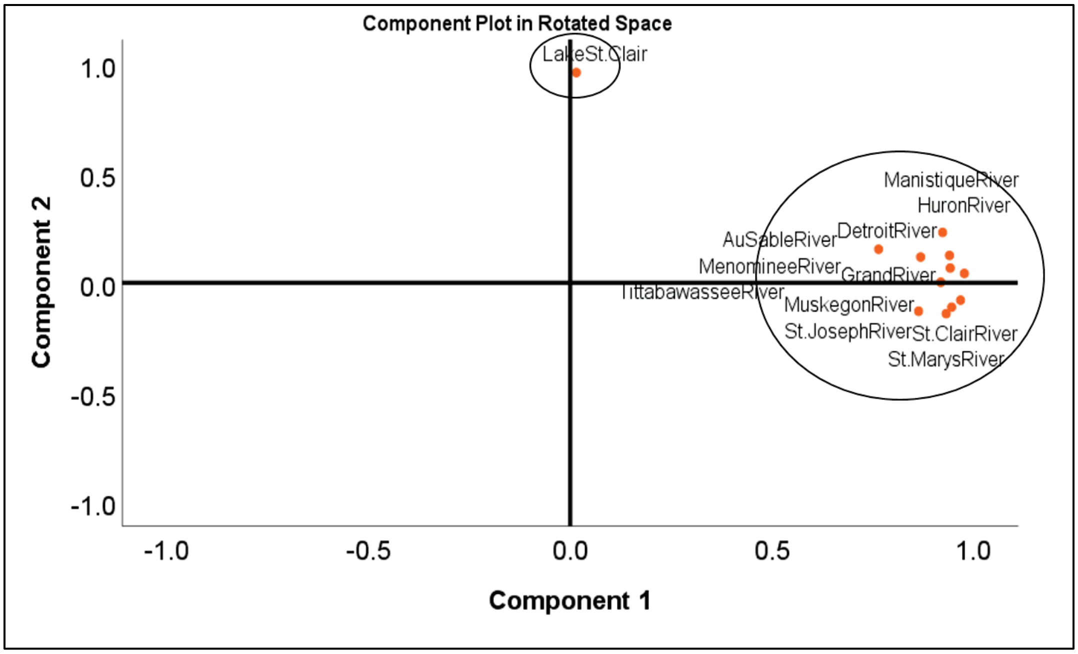


Figure 3-40 A PCA plot for Michigan waterbodies with walleye PCB data.

3.3 Efficacy of remediation, is our cleanup working?

Aroclor- and congener-based times trends

Analytical methods for total PCB quantification have changed through time. The Aroclor-based method used the peaks of a few, characteristic congeners to extrapolate to the total concentration of each Aroclor, and Aroclor concentrations were summed to yield total PCB concentration. The congener-based method sums the individually quantified congener concentrations. Because of the limited availability of data, to assess time trends in fish PCB concentrations in different waterbodies, location data were pooled. Waterbodies with at least three years of Aroclor-based totals or at least three years of congener-based data were included. To evaluate remediation efforts, raw concentrations were used to determine if time trends were significant. For the duration of Michigan's fish consumption monitoring program, this study determined total PCBs using both the Aroclor-based method as well as the congener-based method. Originally, the intention was to consider only the congener data because it is a more accurate estimate of PCB totals, but there were often insufficient data to determine time trends. When trend evaluation was possible, frequently only three years of data were present.

For carp, 19 waterbodies had enough data to evaluate time trends for either summation method. Of those, only nine waterbodies had sufficient data for time trend analyses for both the Aroclor and congener methods (Au Sable River, Detroit River, Huron River, Kalamazoo River, Lake St Clair, Menominee River, Raisin River, Rouge River, and St Joseph River). Summarized results are shown below (Figure 3-41 to Figure 3-49). The Au Sable River had a significantly decreasing trend for the aggregated data but not for either the Aroclor data or the congener data. The Detroit River had a significantly decreasing trend for the aggregated data and the congener data but not for the Aroclor data. The Huron River had a significantly decreasing trend for the aggregated data and a significantly increasing trend for the congener data; the Aroclor data did not have a significant slope. The Kalamazoo River and the Menominee River had significantly decreasing trends for all three data types while in Lake St Clair none of the trends were significant. The Raisin River had a significantly increasing trend for congener data but no significant trend for the aggregated data or the Aroclor data. The Rouge River had a significantly decreasing trend for the aggregated data but not for either the Aroclor data or the congener data. The St Joseph River had significantly decreasing trend for the aggregated and Aroclor data but a significantly increasing trend for the congener data. In summary, only two water bodies had consistent trends across all three sets of data. The other sites varied in their consistency across data sets.

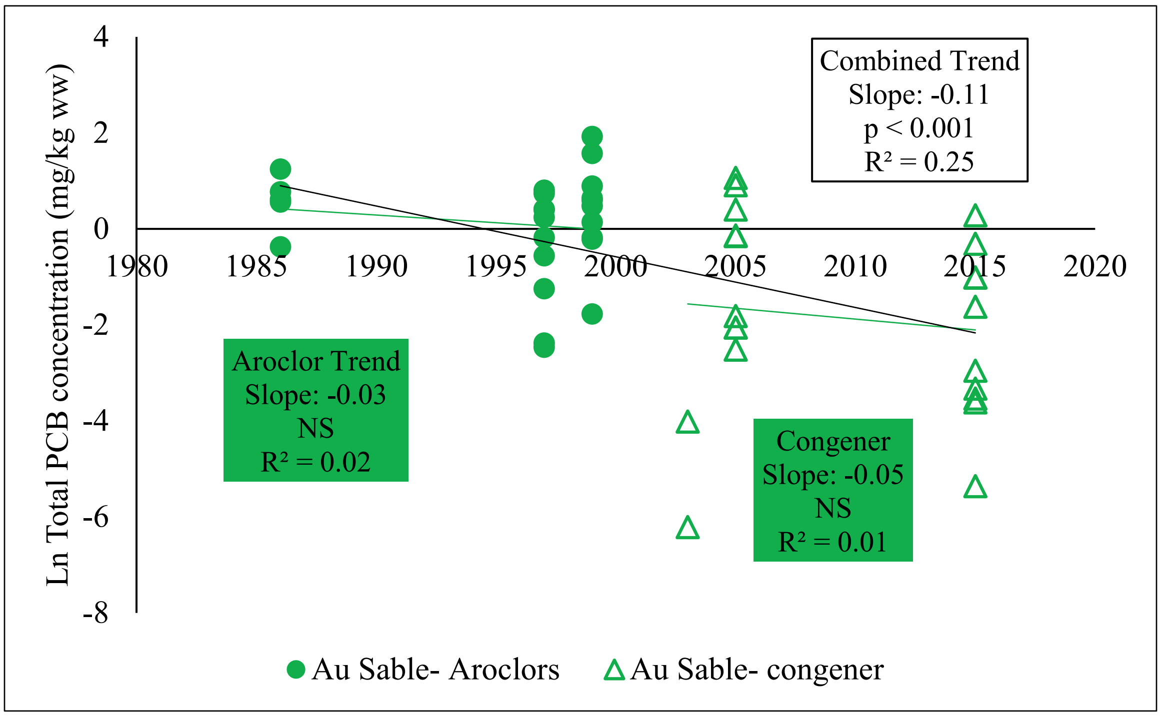


Figure 3-41 Temporal trends for total PCB concentrations in Au Sable River carp. Aroclor-based trends (closed circles) and congener-based trends (open triangles) are compared to the combined trend obtained by considering both sets of data comparable.

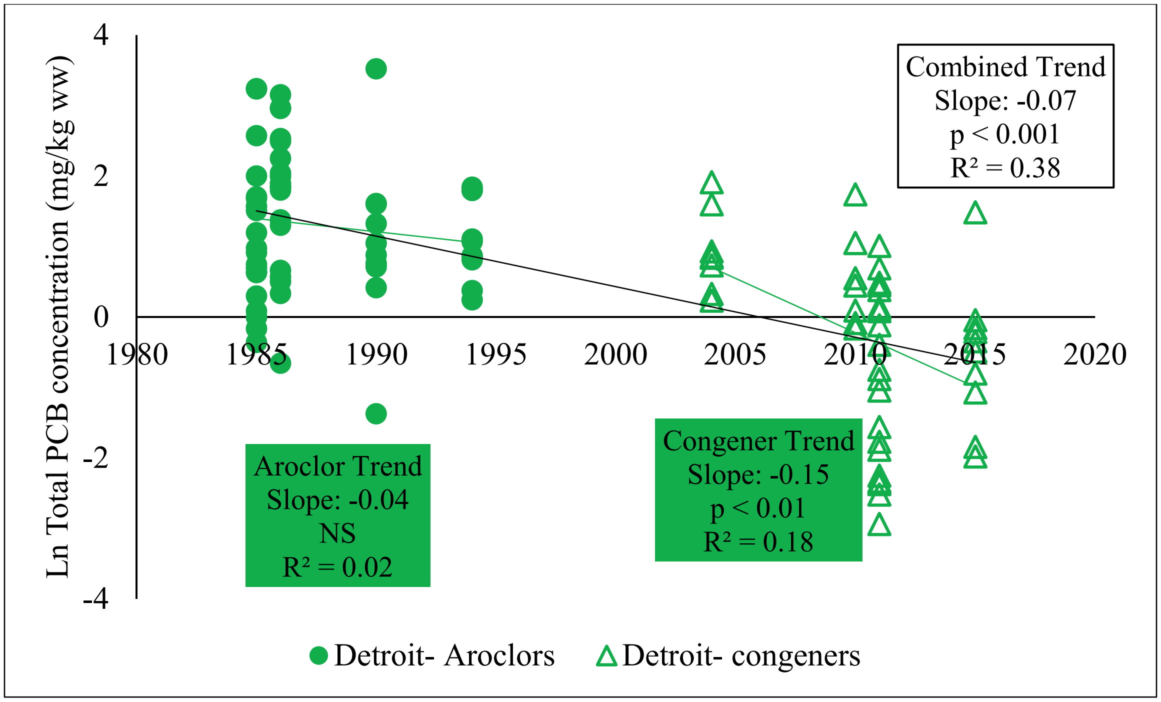


Figure 3-42 Temporal trends for total PCB concentrations in Detroit River carp. Aroclor-based trends (closed circles) and congener-based trends (open triangles) are compared to the combined trend obtained by considering both sets of data comparable.

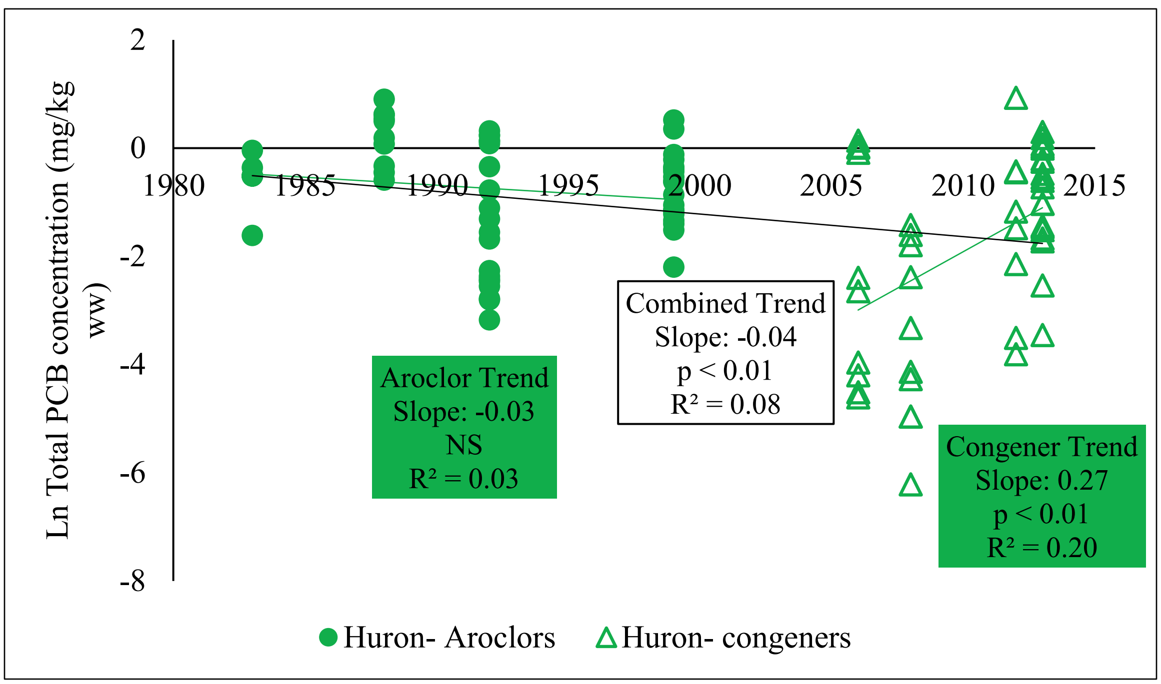


Figure 3-43 Temporal trends for total PCB concentrations in Huron River carp. Aroclor-based trends (closed circles) and congener-based trends (open triangles) are compared to the combined trend obtained by considering both sets of data comparable.

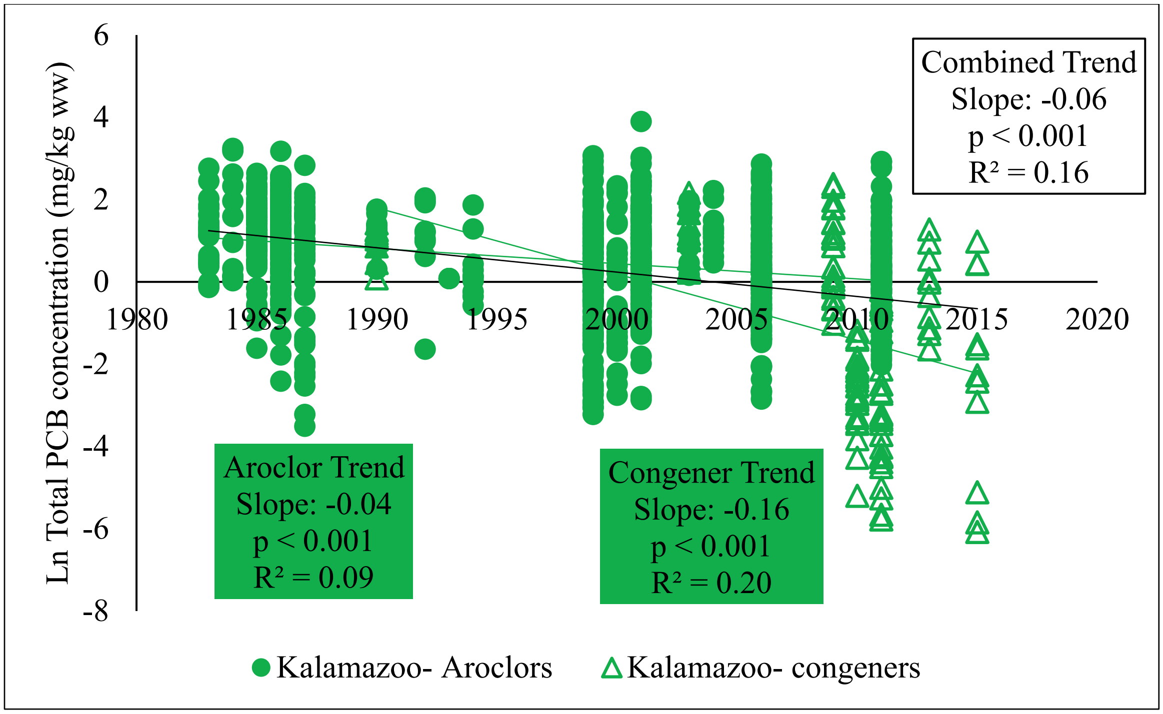


Figure 3-44 Temporal trends for total PCB concentrations in Kalamazoo River carp. Aroclor-based trends (closed circles) and congener-based trends (open triangles) are compared to the combined trend obtained by considering both sets of data comparable.

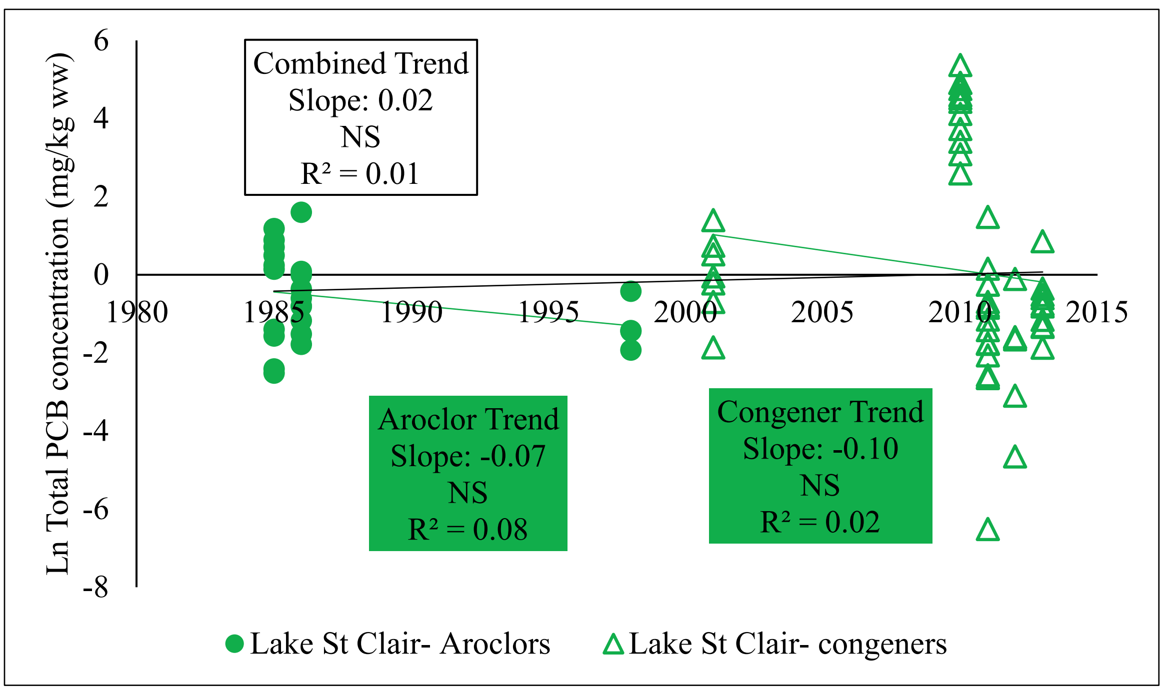


Figure 3-45 Temporal trends for total PCB concentrations in Lake St. Clair carp. Aroclor-based trends (closed circles) and congener-based trends (open triangles) are compared to the combined trend obtained by considering both sets of data comparable.

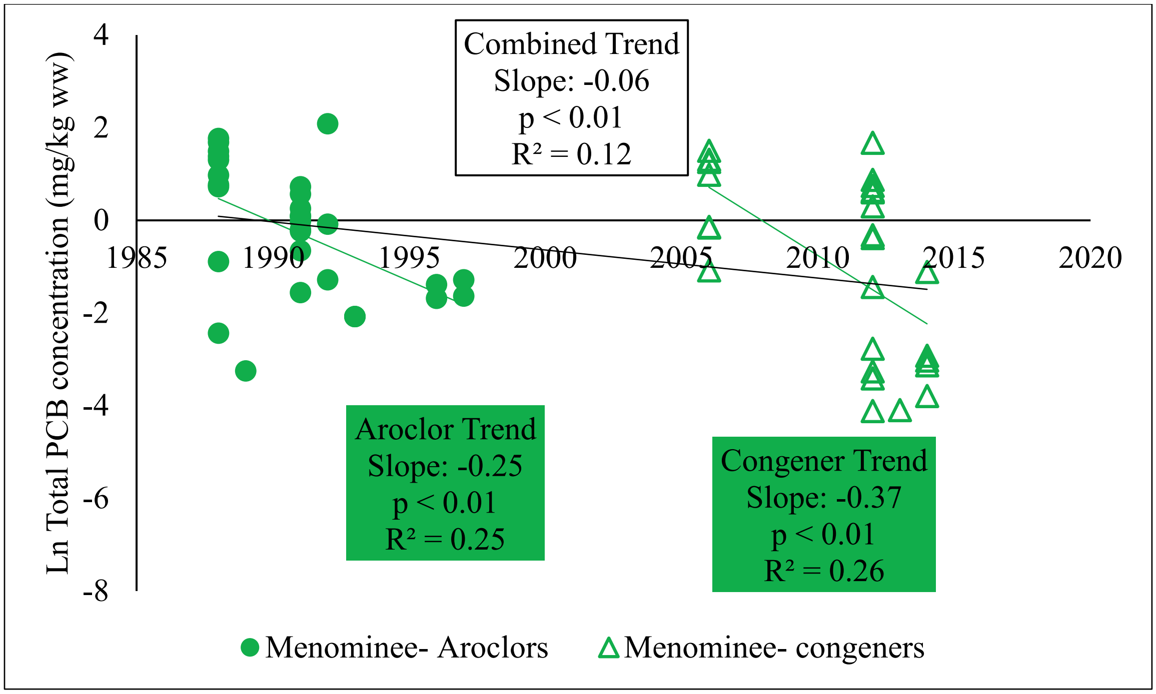


Figure 3-46 Temporal trends for total PCB concentrations in Menominee River carp. Aroclor-based trends (closed circles) and congener-based trends (open triangles) are compared to the combined trend obtained by considering both sets of data comparable.

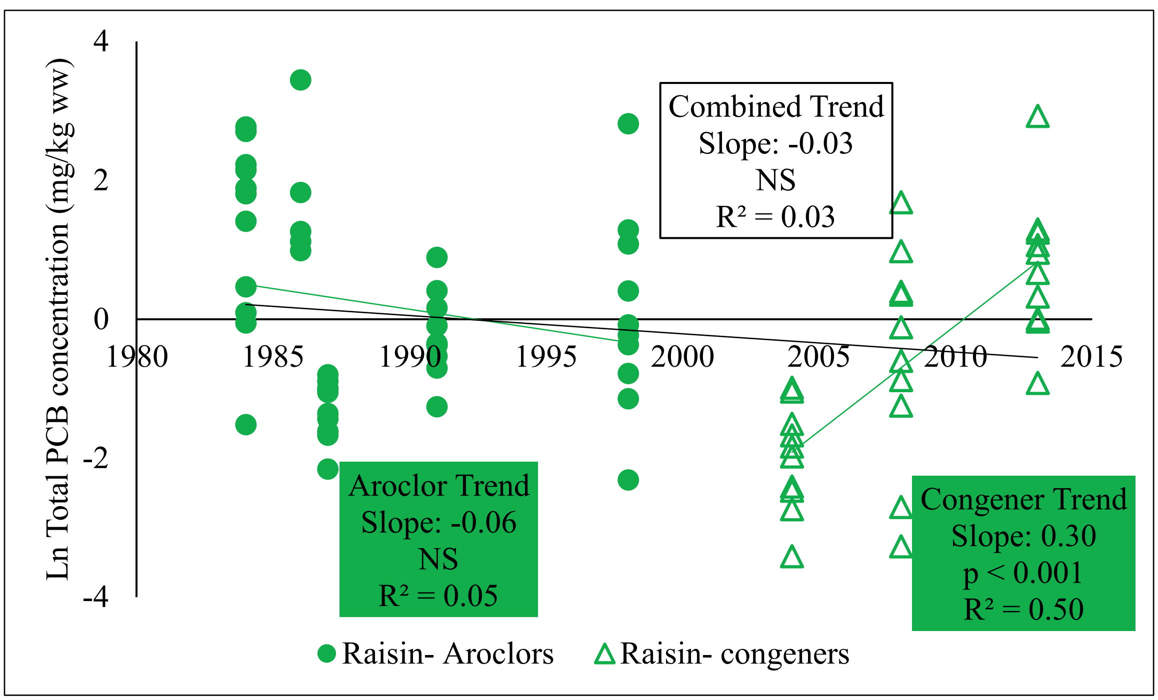


Figure 3-47 Temporal trends for total PCB concentrations in Raisin River carp. Aroclor-based trends (closed circles) and congener-based trends (open triangles) are compared to the combined trend obtained by considering both sets of data comparable.

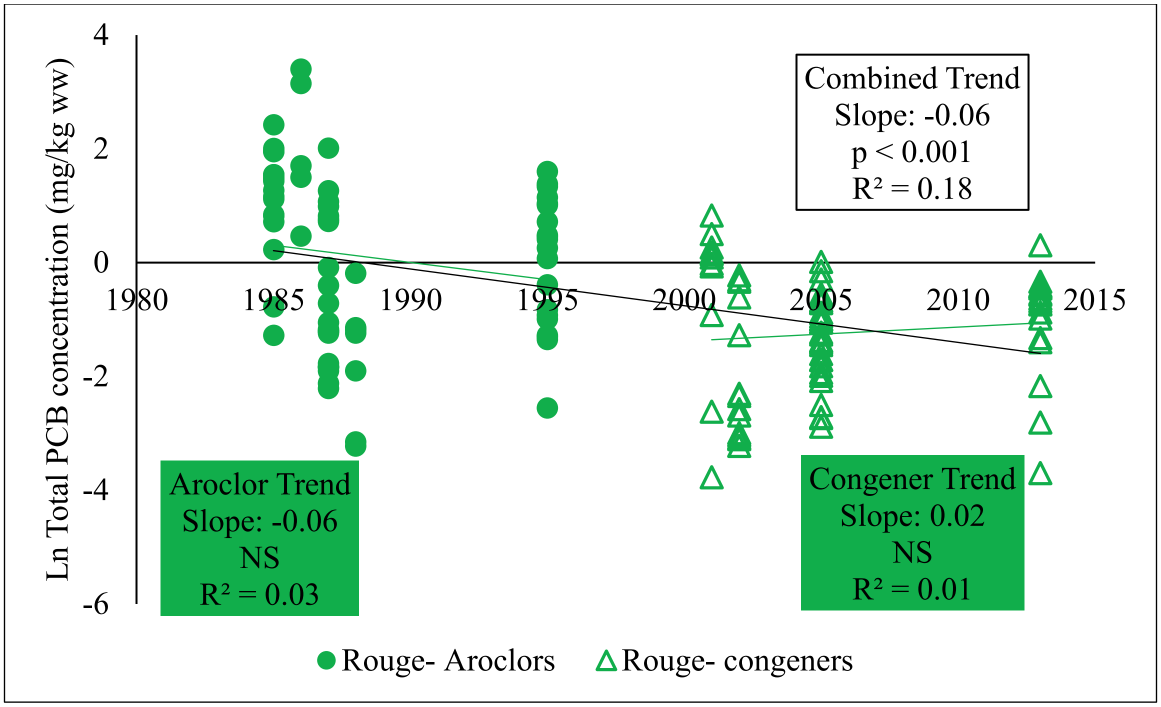


Figure 3-48 Temporal trends for total PCB concentrations in Rouge River carp. Aroclor-based trends (closed circles) and congener-based trends (open triangles) are compared to the combined trend obtained by considering both sets of data comparable.

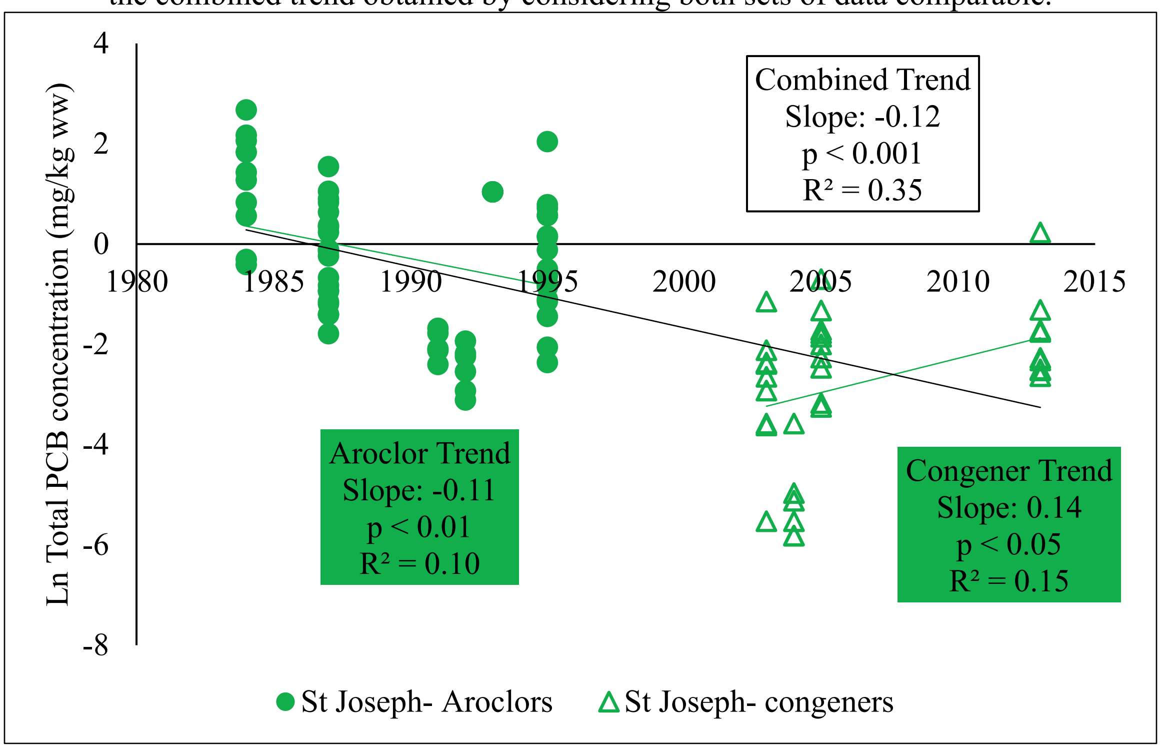


Figure 3-49 Temporal trends for total PCB concentrations in St. Joseph River carp. Aroclor-based trends (closed circles) and congener-based trends (open triangles) are compared to the combined trend obtained by considering both sets of data comparable.

For smallmouth bass, 13 waterbodies had enough data for a time trend analysis for either analytical method. Of those, only two waterbodies had sufficient data for time trend analyses with both the Aroclor and congener samples (Kalamazoo River and Lake St. Clair). Summarized results are shown below (Figure 3-50 and Figure 3-51). The Kalamazoo River had a significantly decreasing trend for the aggregated data as well as for the Aroclor data, but not for the congener data. Lake St Clair had significantly decreasing trends for all three data types (aggregated, Aroclor, and congener).

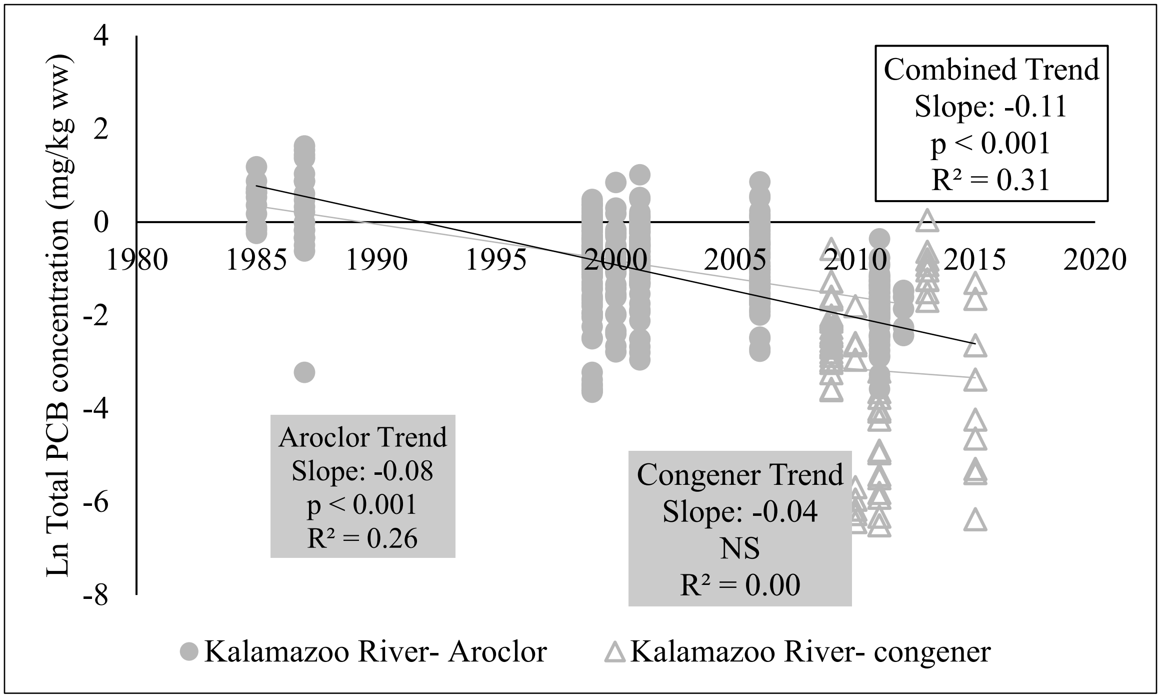


Figure 3-50 Temporal trends for total PCB concentrations in Kalamazoo River smallmouth bass. Aroclor-based trends (closed circles) and congener-based trends (open triangles) are compared to the combined trend obtained by considering both sets of data comparable.

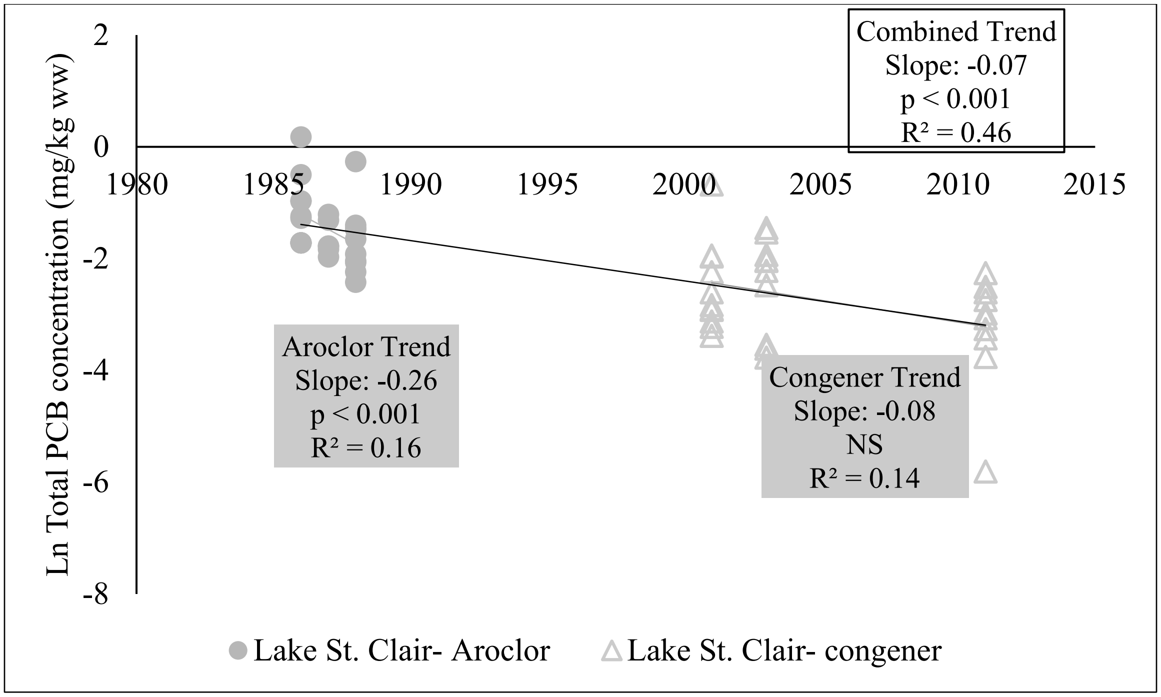


Figure 3-51 Temporal trends for total PCB concentrations in Lake St. Clair smallmouth bass. Aroclor-based trends (closed circles) and congener-based trends (open triangles) are compared to the combined trend obtained by considering both sets of data comparable.

For largemouth bass, six waterbodies had enough data for a time trend analysis for either analytical method. Of those, none had sufficient data for time trend analysis for both the Aroclor and congener samples. For walleye, 16 waterbodies had enough data for a time trend analysis for either analytical method. Of those, four waterbodies had sufficient data for time trend analyses for both the Aroclor and congener samples (Au Sable River, Grand River, Lake St Clair, and Menominee River). Summarized results are shown below (Figure 3-52 to Figure 3-55). The Au Sable River had a significantly decreasing trend for the aggregated data as well as for the Aroclor data, but not for the congener data. The Grand River had a significantly decreasing trend for the aggregated data and the congener data but not for the Aroclor data. Lake St Clair had a significantly decreasing trend for the aggregated data and the congener data but not for the Aroclor data. The Menominee River had a significantly decreasing trend for all three types of data.

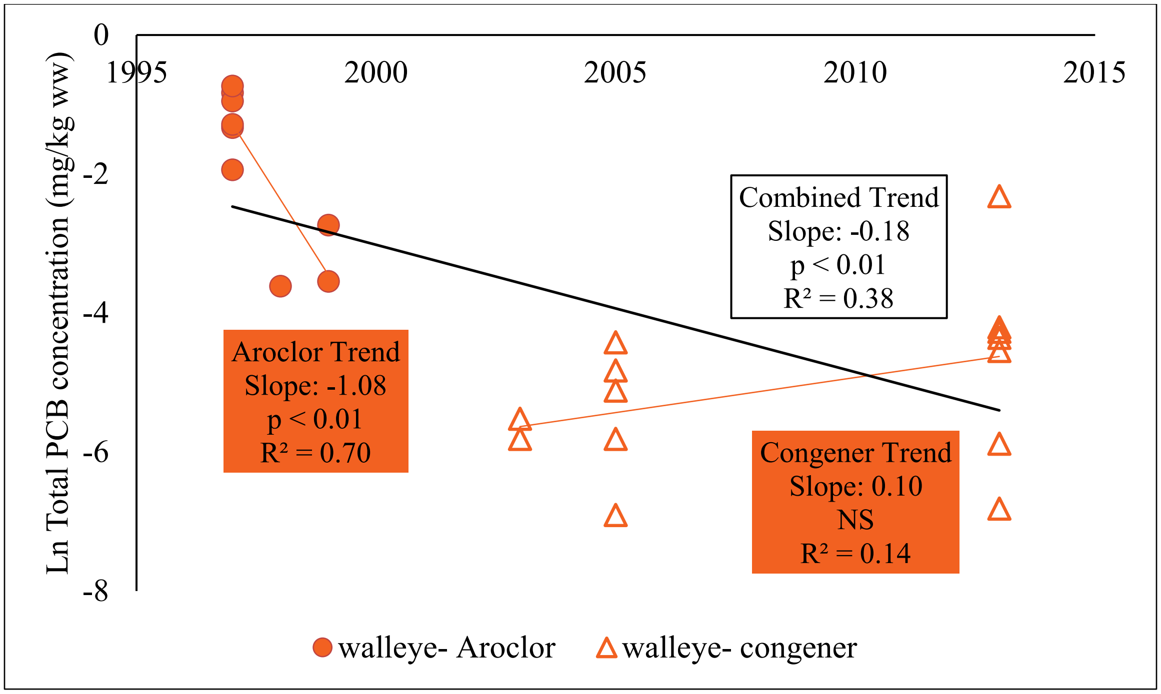


Figure 3-52 Temporal trends for total PCB concentrations in Au Sable River walleye. Aroclor-based trends (closed circles) and congener-based trends (open triangles) are compared to the combined trend obtained by considering both sets of data comparable.

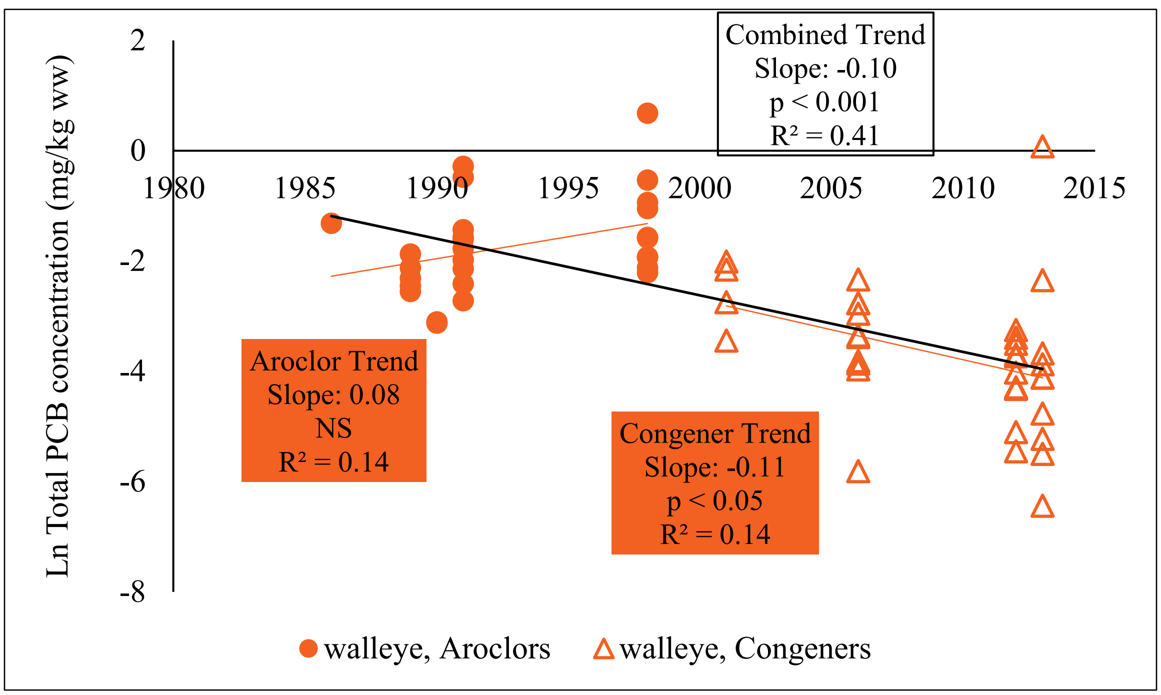


Figure 3-53 Temporal trends for total PCB concentrations in Grand River walleye. Aroclor-based trends (closed circles) and congener-based trends (open triangles) are compared to the combined trend obtained by considering both sets of data comparable.

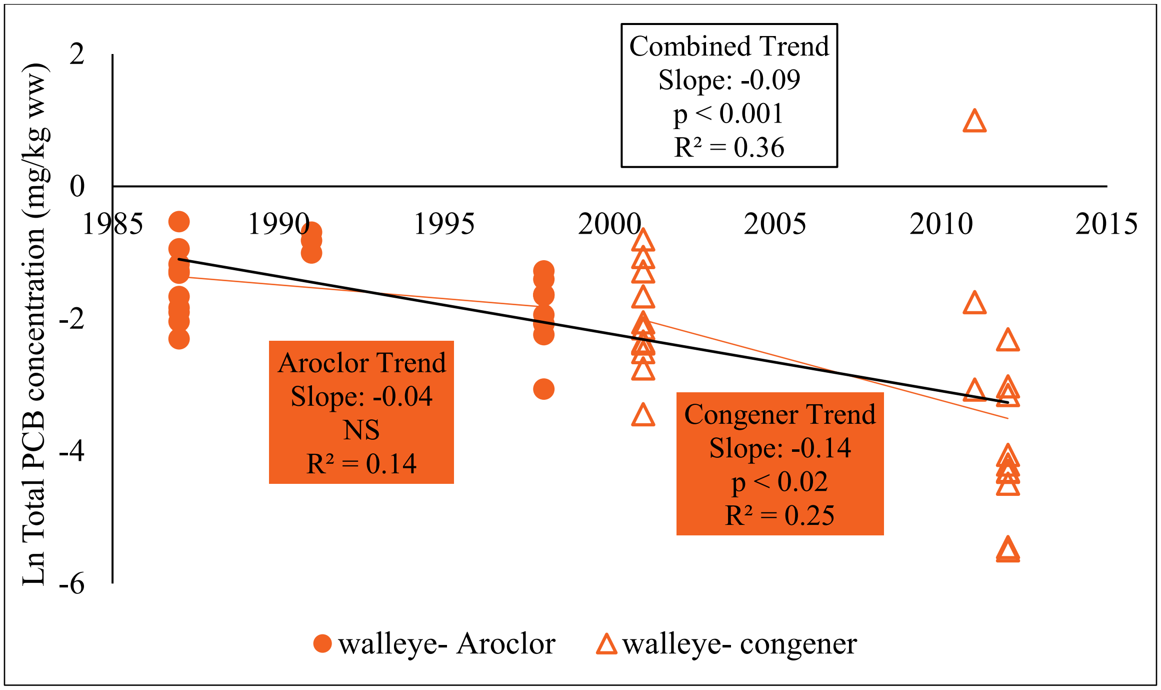


Figure 3-54 Temporal trends for total PCB concentrations in Lake St. Clair walleye. Aroclor-based trends (closed circles) and congener-based trends (open triangles) are compared to the combined trend obtained by considering both sets of data comparable.

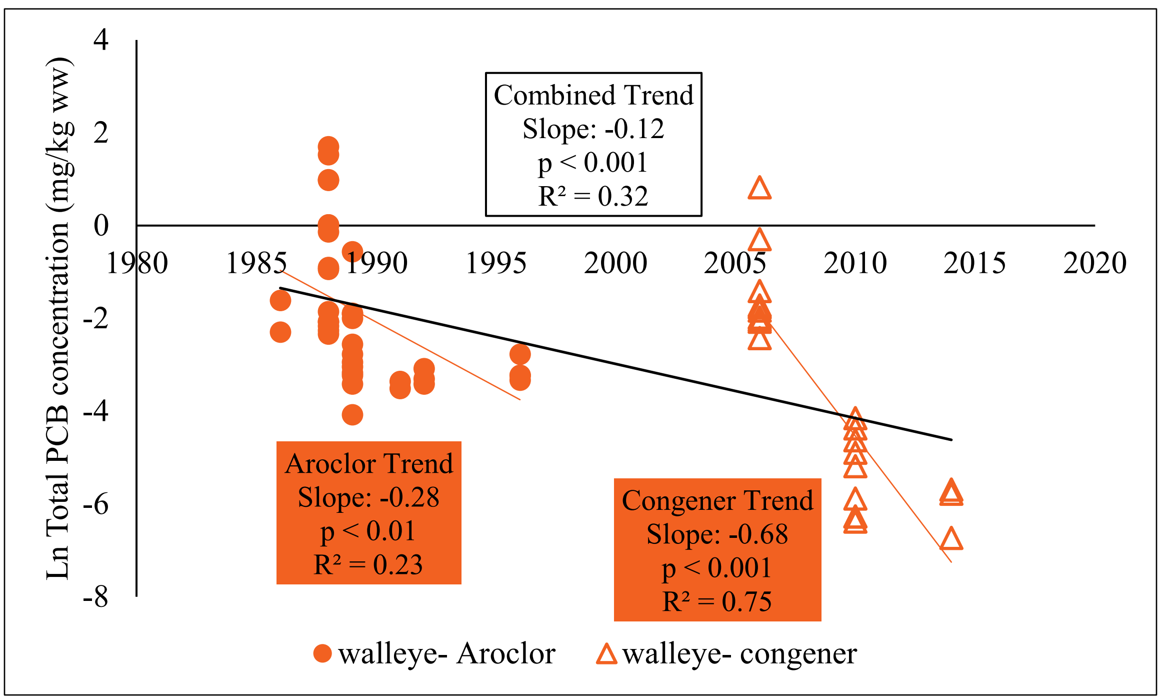


Figure 3-55 Temporal trends for total PCB concentrations in Menominee River walleye. Aroclor-based trends (closed circles) and congener-based trends (open triangles) are compared to the combined trend obtained by considering both sets of data comparable.

4 Discussion

PCBs are a legacy pollutant in Michigan and represent the most common contaminant at AOC sites within the state. Multiple threshold values apply to PCB concentrations in fish. The EPA uses regional screening levels (SLs) to represent the fish concentrations that can be “safely” consumed based on consumption rates, life expectancy, body weight, and the reference dose (RfD). Based on a body weight of 70 kg, a consumption rate of 17.5 g/d, a lifetime of 70 years, and a RfD of 2E-5 mg/kg*day, the SL for recreational fish consumers is 0.08 mg/kg. For sustenance fish consumers, the consumption rate is 142.4 g/d and the SL is 9.83E-3 mg/kg. In the state of Michigan, the target fish residue is 0.023 mg/kg and was determined based on a risk associated dose of 5E-6 mg/kg*day, a body weight of 70 kg, and a fish consumption rate of 15g/day. Below,

Table 4-1 and Figure 4-1 show that the sustenance SL is the most restrictive threshold value, with each species exceeding the limit in at least 78% of samples. Regardless of threshold value, carp exceed the limit in at least 75% of samples, with exceedance at 96% for the most conservative sustenance threshold value. The species histograms are included in Appendix B.

Table 4-1 The percent of fish that exceeded threshold values for the EPA and the State of Michigan. Based on the MI DEQ FCMP data, fish totals were compared to the three different threshold values. Outliers were removed from the samples.

	Sustenance Screening Level[5] (9.83E-3 mg/kg)	**Recreational Screening Level[6] (0.08 mg/kg)**	**MI’s Fish Tissue Residue Value[7] (0.023 mg/kg)**
Carp (n = 938)	96%	75%	90%
Smallmouth Bass (n = 363)	78%	33%	66%
Largemouth Bass (n = 203)	79%	32%	66%
Walleye (n = 227)		41%	69%

[5] Based on a body weight of 70 kg, a consumption rate of 142.4 g/d, a lifetime of 70 years, and a RfD of 2E-5 mg/kg*day

[6] Based on a body weight of 70 kg, a consumption rate of 17.5 g/d, a lifetime of 70 years, and a RfD of 2E-5 mg/kg*day.

[7] Based on Michigan’s TMDL, body weight of 70 kg, consumption rate of 15 g/d, and a risk associated dose of 5E-6 mg/kg*day.

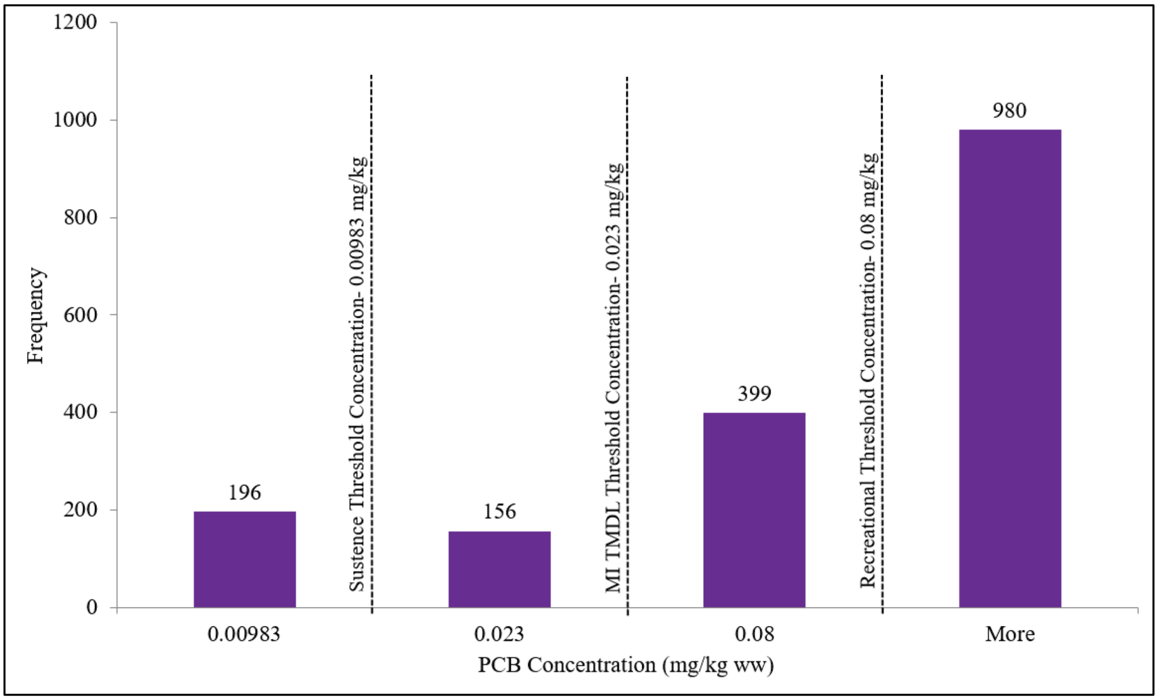


Figure 4-1 Fish samples from the MDEQ FCMP compared to three different regulatory threshold concentrations for PCB in fish. Data collected from MDEQ

Fish consumption represents the primary exposure route of toxicants to humans and varies greatly with region, income, race, and level of education (von Stackelberg et al. 2017). For example, Asian, Caribbean and Pacific Islander, Indigenous, multi-racial, and other non-Caucasian women in coastal areas often have higher blood-mercury levels than white women living inland (Mahaffey et al. 2009). In the Great Lakes region, fish are integral diet components in Ojibwe communities. Commercially, anglers fish for whitefish, lake trout, siscowet, herring, and salmon but also have hatcheries for walleye, perch, lake trout, and coaster brook trout ("The Ways | Great Lakes Native Culture Language", accessed January 2017). Spearfishing for walleye is a culturally significant practice that provides a connection to ancestors as well as an important protein source. Rural, suburban, or urban residency appears to have little influence on fish consumption (Lauber et al. 2017). The four species considered in this analysis are all caught recreationally or in commercial harvests, an important consideration as we explore possible PCB concentrations to which people might be exposed through fish consumption ("History of State-Licensed Great Lakes Commercial Fishing,", accessed May 2018).

In Michigan, we are never further than ten miles from a waterbody. In addition, 15% of Michiganders live in poverty (census, accessed June 2018). In Michigan's UP, food insecurity is a major concern for many (WUPDH 2018). Fish embody an accessible and bountiful foodstuff that is affordable. Given the positive relationship between fish consumption and income as well as non-Caucasian ethnicity, FCAs are a manifestation of environmental injustice.

The EPA does not make specific recommendations for fish consumption for freshwater anglers or Native Americans, because the consumption rates ranged from 5-51 g/day for freshwater anglers and the limited geographic extent of the surveys prevented the generalization of consumption across all tribes (EPA 2011). Dellinger (2004) found that actual consumption was much lower than the self-reported consumption (11.2 g/day versus 60 g/day, respectively). Accurately quantifying fish consumption rates is important in the consideration of body burdens and the consideration of toxicological effects. However, desired fish consumption might be a more appropriate management consideration since fish consumption advisories (FCAs) presuppose a willingness and ability to follow them (ASEP project 2013; Gagnon 2016; O'Neill 2004). Michigan Areas of concern (AOCs) represent an effort to prioritize cleanup within the Great Lakes basin. With annual PCB monitoring beginning in 1988 and AOC site designations established in 1987, followed by extensive remediation work and federal funding to help clean up, an assessment of *how are we doing*? seemed appropriate. To begin to answer this enormous question, specific research questions were used to guide the work: *are we able to determine the sources of PCB contamination?, have our remediation efforts been successful?*, and *how does PCB contamination compare between species, sites, and congeners?* The organization of this section attempts to answer those questions, in that order. The four species of interest include carp, smallmouth bass, largemouth bass, and walleye, selected because of their different trophic levels. The four species have other important differences that provide opportunities to understand better the patterns in PCB contamination in species, location, and congeners (Table 4-2).

Table 4-2 Important species characteristics for the species considered in this work. Length, lipid content, and PCB concentrations are the minimum and maximum based on the MDEQ fish contaminant monitoring program data with the outliers removed.

	Carp	**Smallmouth Bass**	**Largemouth Bass**	**Walleye**
Diet	Omnivore	Piscivore	Piscivore	Piscivore
Mean Trophic Level[7]	3.0	4.0	4.1	4.4
Typical age (years)[7]	28[8]	9[9]	10[10]	15[11]
Length (cm)	26 - 88	22 - 52	16 - 52	25 - 72
Lipid content (%)	0.1 - 43.9	0.04 - 3.4	0.5 - 2.1	0.1 - 5.2
Range of PCB concentrations (mg/kg ww)	< DL – 18.67	< DL – 1.04	< DL – 2.79	< DL – 2.29
Dominant congeners (> 90% abundance)	66-95, 77-110, 90-101, 97, 99, 105, 118, 128, 138-163, 141, 146, 151, 153, 156, 170, 177, 180, 182-187, 183, 194, 196-203, 201	118, 138-163, 153, 170, 180	77-110, 90-101, 99, 118, 128, 138-163, 153, 170, 180, 182-187, 183	118, 138-163, 153, 170, 180
([7]Vander Zanden et al. 1997; [8]Brown et al. 2005; [9]Paragamian and Colbe 1975; [10]Allen et al. 2002; [11]Colby and Nepszy 1981)				

4.1 PCB comparisons: What is the status of fish PCBs in Michigan?

Many factors affect PCB accumulation in fish, the most relevant one being exposure, which depends first on whether PCB contamination is present. PCBs are present worldwide, so we can expect all organisms to have had, or continue to have, exposure to them. Within the environment, different compartments (e.g. air, water, sediments, and biota) have varied PCB concentrations. In 1993, the dissolved fraction of PCBs in Lakes Superior, Michigan, Huron, and Ontario were approximately 100%, 62%, 52%, and 68% respectively (Anderson et al. 1999). In addition to differences in concentration between the compartments, PCBs also vary spatially within each compartment (e.g. biota). Previous work has shown that not only is PCB contamination an issue in Michigan, but also an issue on a regional, national, and global scale. Different fish species vary in their susceptibility to PCB contamination due to their unique habitat and physical characteristics. This work considered PCB contamination from multiple perspectives to gain insights into total PCB concentrations in different species as well as congener concentrations and toxicity. This section answers the questions: *are PCB concentrations highest in top predators*? and *are congener profiles the same for each species*?

4.1.1 PCB concentrations: How do they compare between different species?

PCBs are hydrophobic compounds, typically found in condensed organic environmental media (i.e., sediments and lipids). They also have relatively high octanol-water partition coefficients or log K_{ow} values, ranging from 4.46-8.18. The K_{ow} is often used to describe a compound's tendency to bioaccumulate (Hawker et al. 1988). This results in biomagnification through the food web because prey accumulate PCBs more quickly than they can be eliminated. Given the chemical properties of PCBs and their global distribution, it is not surprising that most of the fish samples had PCB concentrations above the detection limit.

The invasions by Ponto-Caspian region species (e.g. the *Dreissenid* mussels and round goby) have altered lotic and lentic ecosystems systems within the Great Lakes basin. In Lake Erie, *Dreissenid* mussels create a shunt for PCBs to the near-shore benthic area (Kwon et al. 2006). In the Hudson River, the populations of some fish species fluctuated due to *Dreissenid* proliferation (Strayer et al. 2004). Of these three Ponto-Caspian Sea region species, only the *Dreissenids*' PCBs correlated with sediment PCB concentrations, which has implications for the fish that feed on them (Macksasitorn et al. 2015).

Carp in Michigan's inland waters had the highest concentrations, with an order of magnitude more contamination than the other species (Figure 3-1). This distinction exists even when concentrations are lipid- and length-normalized (Figure 3-3 and Figure 3-4, respectively). As omnivores, carp feed on not only *Dreissenid* mussels and sediments, but also macroinvertebrates, that could constitute approximately half of their diet (Gido et al. 2007).

Although controlled thermodynamically, biomagnification can raise biota-sediment accumulation factors (BSAFs) above what log K_{ow} would predict (Morrison et. al. 1996). Additionally, work has shown that log K_{ow} is associated with longer half-lives, but recent work suggests that bioaccumulation in zooplankton is greater than what would be predicted based on log K_{ow} (Borgå et al. 2005). This means that concentrations in both macroinvertebrates and zooplankton might be higher than expected. Considered together, the diet of carp presents unique exposures that might contribute to their higher concentrations.

Invasive species can alter food web dynamics, which can ultimately affect how contaminants move through the system. Round gobies are an important food source to the piscivores. After their detection in Lake Erie in (1999), it was clear for young of the year smallmouth bass, gobies were at least 30% of the diet, indicating a quicker (i.e. younger) transition to a piscivorous diet (Steinhart et al. 2004). In Lake Ontario, round goby constitutes a high percentage of stomach content biomass for smallmouth bass and largemouth bass but were also present in the stomach content biomass of walleye (Taraborelli et al. 2010). However, despite a trophic link between quagga mussels and round goby, there was no significant correlation between their PCB concentrations (Macksasitorn et al. 2015). This apparent disconnect could explain why carp have significantly more PCB contamination than the other three species, while there are no significant differences between smallmouth bass, largemouth bass, or walleye PCB contamination ($p > 0.05$). Additionally, while these three species are piscivores, their trophic position does not differ significantly (Table 4-2).

The cumulative PCB accumulation plot (Figure 3-32Figure 3-32) shows that the pattern of accumulation is approximately linear with respect to log K_{ow} but clearly shows the magnitude of difference between carp and the other three species (Figure 3-33). This relationship suggests that carp do not have a completely separate and unique source of PCBs, but that they simply accumulate more of them. However, when we pick out the congener number that corresponds to approximately 50% PCB accumulation, we see that there are differences between species as well as sites (Table 4-3Table 4-3). As mentioned previously, carp are omnivores and consume sediments during feeding. Since heavier congeners tend to accumulate in the sediments, if sediments were a dominant PCB source, then we might expect to see that in the accumulation plot. In general bottom dwellers (e.g. carp, suckers, and catfish) have higher PCB concentrations than predator fish (e.g. smallmouth bass, largemouth bass, and walleye; (Stahl et al. 2009). This might point to characteristics such as age or bioenergetics as responsible for higher PCB accumulation in carp.

Table 4-3 For each species, at both site categories, the mid-point PCB congener and it's log K_{ow}.

	Congener	Log Kow
Carp AOC	PCB 77-110	6.24
Carp non	PCB 90-101	6.10
Smallmouth Bass AOC	PCB 77-110	6.24
Smallmouth Bass non	PCB 81	6.21
Largemouth Bass AOC	PCB 151	6.40
Largemouth Bass non	PCB 100	5.93
Walleye AOC	PCB 77-110	6.24
Walleye non	PCB 77-110	6.24

4.1.2 PCB concentrations: How do congener profiles and toxicity compare between species and location?

Accurate PCB quantification is critical for studying and understanding PCB contamination. Also, important, are sufficient numbers of congeners for quantifying "total PCBs". Previous studies have listed the congeners most important. McFarland and Clarke (1989) determined that 36 congeners, classified into five groups, were the most environmentally relevant based on the frequency of occurrence, relative abundance, and potential for toxicity. In 1998, the European Union Community Bureau of Reference recommended that the International Council for the Exploration of the Sea (ICES) monitor seven PCB congeners (28, 52, 101, 118, 138, 153, and 180) as environmental indicators (Webster et al. 2013). The B7 group of indicator congeners is used in biomonitoring by the National Center for Environmental Health at the CDC. More recently, a study on the toxicological effects of PCBs found that the not often monitored PCB-168, contributes significantly to the toxicity of PCBs (Hamers et al. 2011). Yet another subset of congeners are the 12 dioxin-like congeners that have an associated toxic equivalency factor (TEF) (Van den Berg et al. 2006). Other work has highlighted the difference in the subsets of congeners used to quantify "total PCBs" and the difficulties that arise when comparisons are made across the literature (Gandhi et. al. 2015). This work compared congener profiles between different species to assess the appropriateness of a single subset of congeners to describe the "total PCBs" in different species and quantified the DL-toxicity based on the 12-DL congeners.

While the congener profiles were similar between the four species, t-tests indicate differences between low molecular weight congeners (< PCB-100) and the high molecular weight congeners (> PCB-100) for carp, smallmouth bass, and largemouth bass, but not for walleye (Table 3-11). Comparing individual congeners at AOC and non-AOC sites show that there are differences (Figure 4-2, Figure 4-3, Figure 4-4, and Figure 4-5). This is an important finding because studies rarely quantify total PCBs based on all 209 congeners.

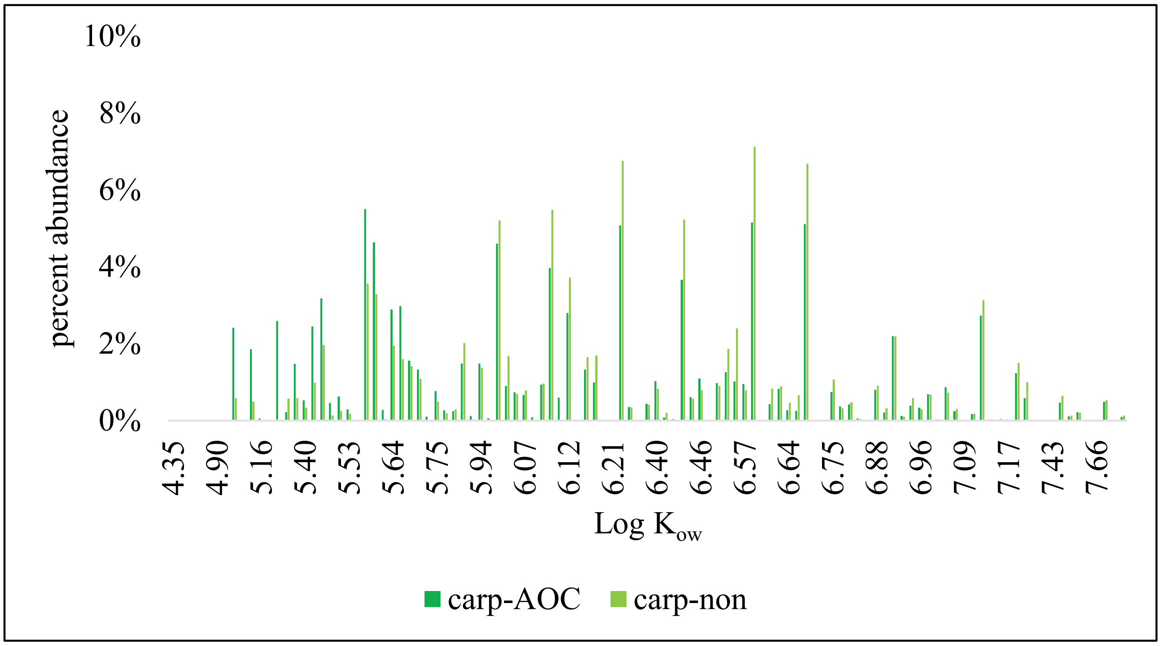


Figure 4-2 A congener profile comparison for carp at AOC sites and non-AOC sites. Congeners are organized by log K_{ow} and represent an individual congeners percent contribution to the total PCB contamination. Relative abundance was determined by summing congener concentrations for all samples at the different site categories.

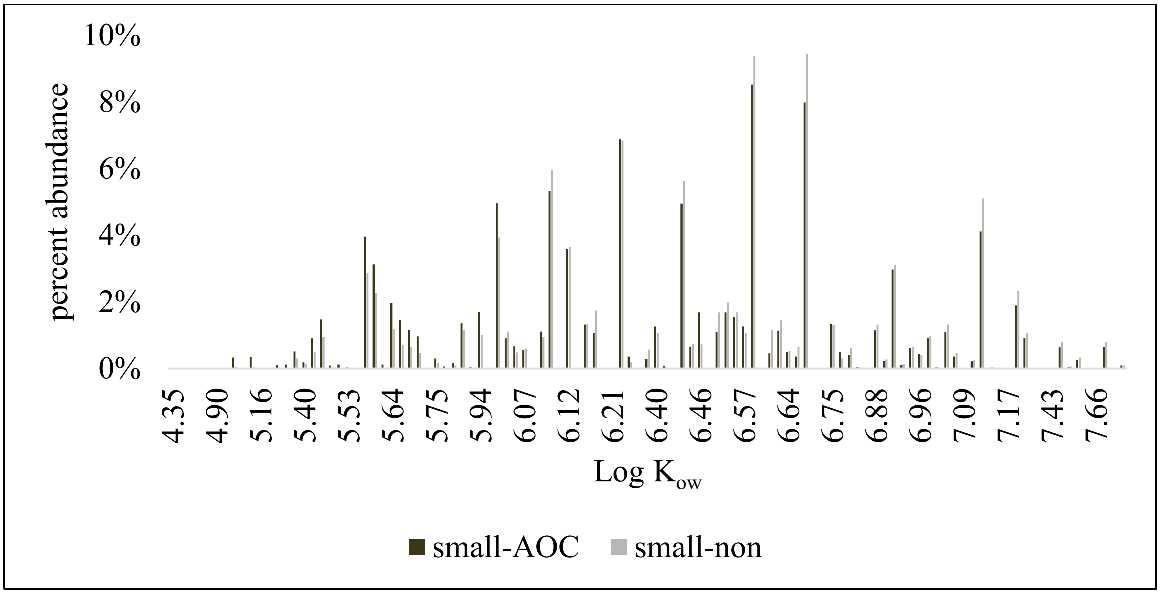


Figure 4-3 A congener profile comparison for smallmouth bass at AOC sites and non-AOC sites. Congeners are organized by log K_{ow} and represent an individual congeners percent contribution to the total PCB contamination. Relative abundance was determined by summing congener concentrations for all samples at the different site categories.

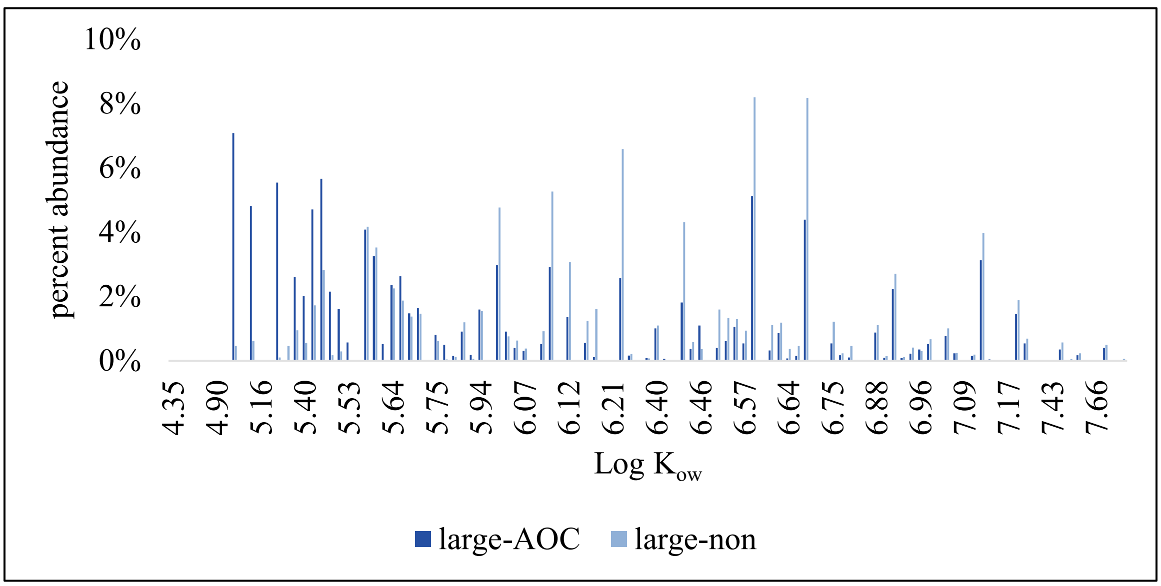


Figure 4-4 A congener profile comparison for largemouth bass at AOC sites and non-AOC sites. Congeners are organized by log K_{ow} and represent an individual congeners percent contribution to the total PCB contamination. Relative abundance was determined by summing congener concentrations for all samples at the different site categories.

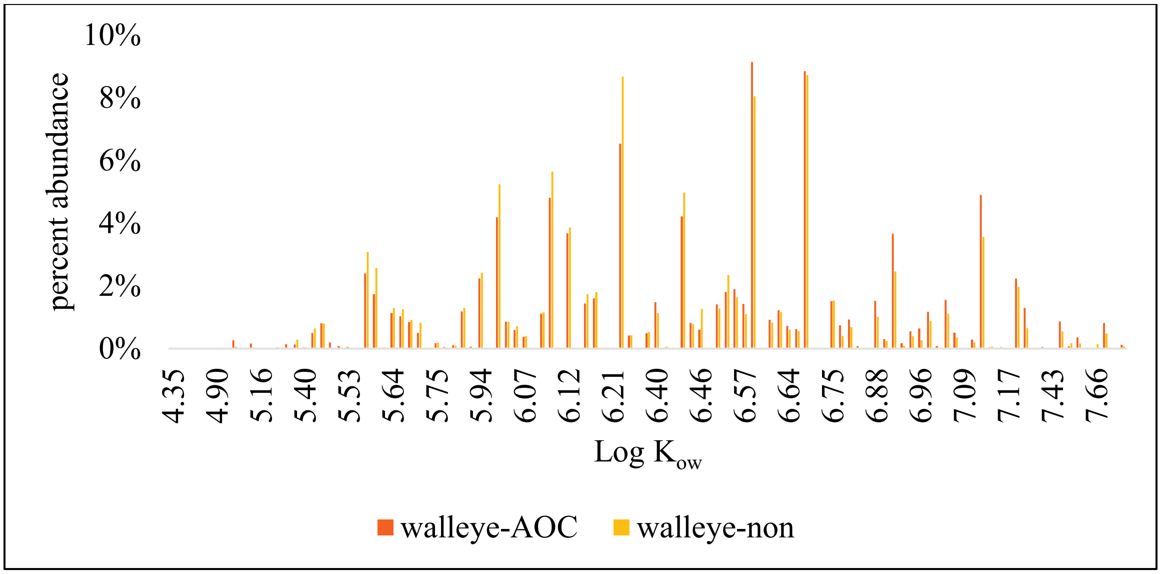


Figure 4-5 A congener profile comparison for walleye at AOC sites and non-AOC sites. Congeners are organized by log K_{ow} and represent an individual congeners percent contribution to the total PCB contamination. Relative abundance was determined by summing congener concentrations for all samples at the different site categories.

As shown previously, totals are based on subsets of different congeners, the selected congeners are not standardized, and studies frequently use different congeners. Even governmental agencies use different quantification methods. As stated previously, the MDEQ calculates PCB totals based on the summation of 83 congeners and co-eluting congeners while the EPA uses 19 congeners (“8082a,” n.d.). This variability not only makes comparisons difficult, it also has the potential to under- or over-estimate total concentrations, particularly if different species are under consideration. Furthermore, relying on only total PCB concentrations could ignore the potential differences in toxicity, depending on which congeners are present.

There are 12 congeners with dioxin-like (DL) toxicity that have been assigned toxic equivalency factors (TEF), which facilitates comparison of DL-PCB toxicity to that of polychlorinated dibenzo dioxins (dioxins) and polychlorinated dibenzo-furans (furans). Based on the MDEQ fish contaminant monitoring program data, only three of the DL-PCBs (PCB-105, PCB-118, and PCB-156) were common congeners (> 50% presence) while only five of the DL-congeners were present in the fish samples (105, 114, 118, 156, and 167). Using the EPA’s cancer screening level of 0.001 pg/kg*day, 85% of the species sampled exceeded the EPA cancer screening level of 4.92×10^{-7} pg/kg*day for subsistence anglers. Of all the fish samples, 11% exceeded the least restrictive limit, recreational anglers at the non-cancer RfD and 15% of the samples did not exceed any of the limits. The non-cancer RfD is 3 orders of magnitude greater than the cancer screening level, ranges between 1-10 pg/kg*day (globally) and is more widely used.

It is important to note that only DL-PCBs were included in this analysis. Dioxins and furans are, in many ways, similar to PCBs, including in their ubiquity (Bhavsar et al.

2008). This presents even greater challenges in preventing consumption of contaminated fish because the higher TEF values for dioxins and furans will mean even higher DL toxicity (Van den Berg et al. 2006).

4.1.3 Conclusions, What is the picture of PCBs in Michigan's rivers with respect to species and congeners?

The differences in PCB concentrations between carp and the other species were statistically significant. However, the differences in concentrations between smallmouth bass, largemouth bass, and walleye were not. Consideration of only total PCBs has the potential to mask the unique accumulation patterns for different species. Furthermore, since different congeners contribute more to the total PCB concentration for different species, selection of congeners is important to represent accurately PCB concentrations in different species. Lastly, DL PCB toxicity for subsistence anglers at the cancer screening level was exceeded in 85% of the fish samples. Only 15% of the samples did not exceed any PCB TEQ limit. It is almost certain that other DL compounds contribute toxicity, and their exclusion from the analysis underestimates the total toxicity.

4.2 Sources of PCBs: From where is Michigan's PCB problem coming?

Establishing sources of PCB contamination is a critical part of an effective remediation strategy. Positioned at the middle latitudes, the Great Lakes basin is vulnerable to atmospheric deposition of persistent organic pollutants (POPs) such as PCBs, and latitudinal patterns are likely (Wania and Mackay 1996). This vulnerability is exacerbated by colder water temperatures, which can extend a compound's persistence by inhibiting volatilization (Swackhamer et al. 1999). Previous work has used congener signatures to distinguish waterbodies that are affected by atmospheric deposition and those that are affected by local sources of PCBs (Macdonald and Metcalfe 1991; Sokol 2015). Rates of atmospheric deposition of PCBs are higher near large urban areas than in rural areas (Salamova et al. 2013; Salamova et al. 2015; Zhang et al. 1999), but if AOCs are a dominant source of pollution in the GL basin it is possible that they represent a local source of PCB contamination.

4.2.1 Do spatial patterns in the fish PCB concentrations exist?

Elucidating spatial trends in PCB contamination in Michigan rivers could refine our understanding of regional deposition trends. Sokol (2015) previously reported that PCB concentrations are higher in fish from Lower Peninsula lakes than from Upper Peninsula lakes. However, the disproportionate number of sampling sites located in the Lower Peninsula compared to the Upper Peninsula prevented refining this spatial analysis (Table 4-4). Carp had the greatest number of sample sites (n = 129) but also the least even distribution, with only 3% of sample sites in the UP. Smallmouth and largemouth bass had the same number of UP sample sites as carp but fewer total samples (n = 65 and n = 61, respectively). Walleye had the fewest samples sites (n = 51) but also the greatest number of UP sites (n = 12). Because of the skewed sampling, assessment of spatial trends was not pursued. To make this analysis worthwhile, more data in the northern LP and UP are required.

Table 4-4 Fish contaminant monitoring program sample sites (MDEQ). Stark differences exist between the numbers of sample sites in the Lower Peninsula (LP) compared to the Upper Peninsula (UP). This discrepancy precludes any spatial analysis. Data collected from the MDEQ.

	AOC sample sites	Non-AOC sample sites	UP sample sites	LP sample sites
Carp	46	83	4	125
Smallmouth bass	31	34	4	61
Largemouth bass	15	46	4	57
Walleye	17	34	12	39

Aroclors, congener mixtures manufactured by Monsanto, were used for specific purposes (i.e. Aroclors 1242 and 1260 were used for carbonless copy paper and inking, respectively). Aroclor 1254 was a more general use mixture and has been associated with use in transformers, capacitors, and hydraulic fluids (Frame et al.1996). While there is some overlap, each of the Aroclors had unique uses, so the congener pattern in the fish might provide evidence of which Aroclor was the source of the contamination. However, the absolute concentrations and the concentration ratios had such high variance that clear aroclor signatures could not be identified using a one-way ANOVA.

4.2.2 Are Michigan's rivers impacted by local or atmospheric sources of PCBs?

Understanding where Michigan's PCBs are coming from would allow strategic approaches to facilitate a better understanding of how our fish and our waters are becoming contaminated. Atmospheric deposition would indicate PCBs are coming to us from further away, while locally impacted waters would support the need for on-going work to clean up PCB-contaminated sites. Using PCA, relative PCB congener concentrations were used to assess Michigan rivers as either locally or atmospherically impacted by PCB contamination. Walleye and largemouth bass were the two species with obvious clustering (Figure 3-40 and Figure 3-39, respectively). The two clusters for walleye appear related to waterbody type, with 76.8% of the variance explained by the first component and an additional 9.0% explained by the second component. Three clusters for largemouth bass exist, but the causes of those clusters are not readily apparent. Component one explains 58.8% of the variance and the second component explains an additional 21.2% of the variance. For both species, component two explains Lake St Clair better.

Even though the PCA for carp did not exhibit any patterns, a few locations have similar congener profiles among the different species. Lake St. Clair is a waterbody with anomalously high concentrations in carp and largemouth bass. Additionally, lighter congeners dominate the congener profiles for carp, largemouth bass and walleye in Lake St. Clair (Figure 4-6, Figure 4-7, and Figure 4-8, respectively). For largemouth bass, the Detroit and Saline Rivers also clustered with Lake St. Clair, and, similarly, lighter congeners dominated the congener profiles for both of those locations. This could indicate a local source of contamination in Lake St. Clair since lighter congeners are more susceptible to weathering (Saba and Boehm 2011). More likely, atmospheric deposition is responsible for the abundance of lighter congeners since congener profiles of the air show more light congeners (Priyadarshini 2018). If the lighter congeners were coming from a local source of contamination, it is unlikely that the Saline River would be included in the clustering since it is not an AOC site.

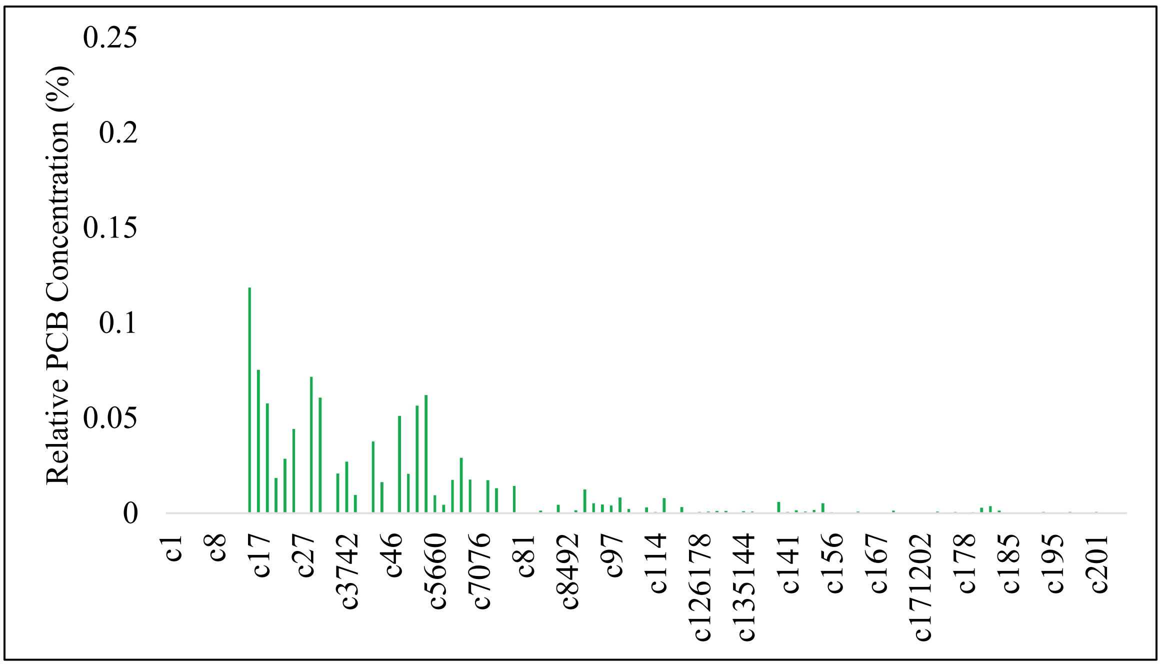


Figure 4-6 Congener profile for carp in Lake St. Clair. Data collected from MDEQ.

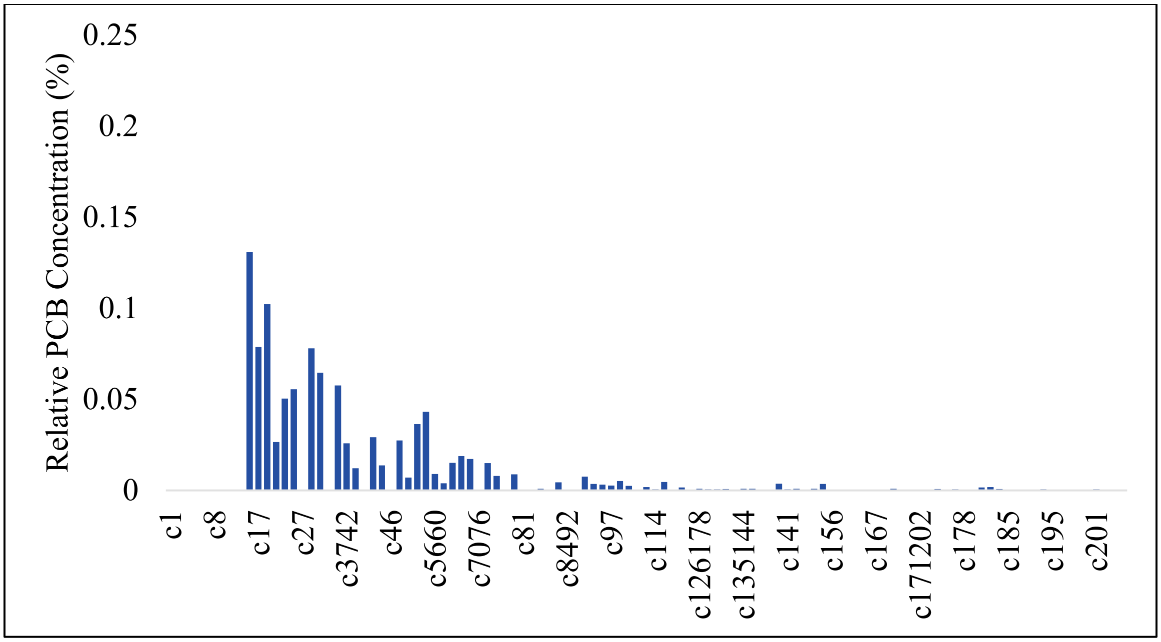


Figure 4-7 Congener profile for largemouth bass in Lake St. Clair. Data collected from MDEQ.

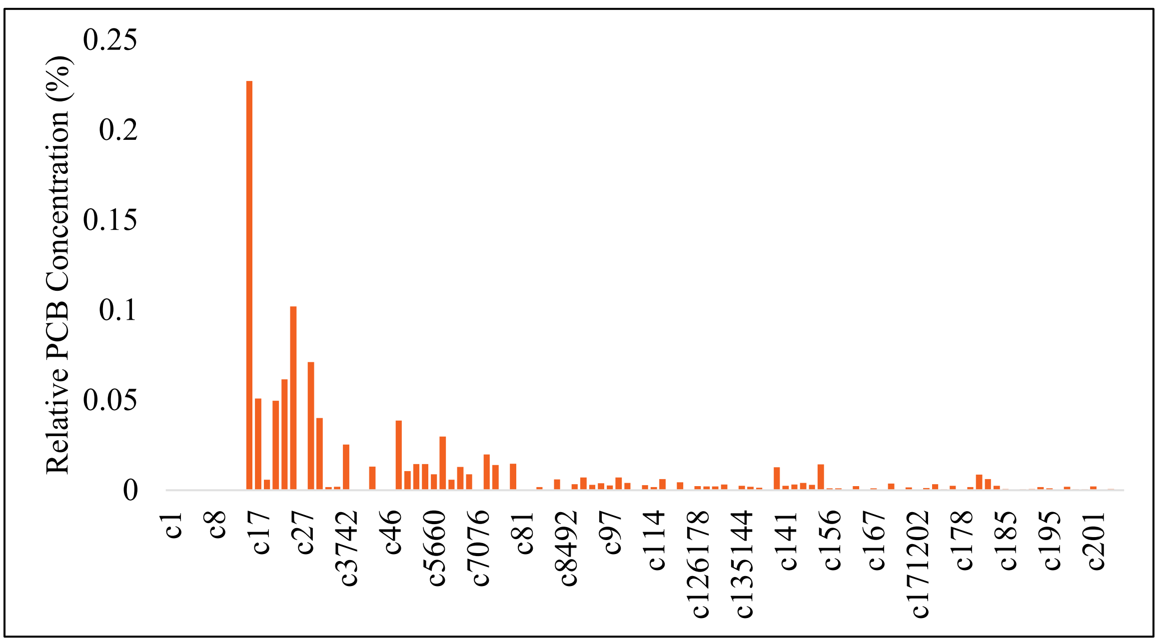


Figure 4-8 Congener profile for walleye in Lake St. Clair. Data collected from MDEQ.

4.2.3 Are AOCs sources of PCBs to the Great Lakes?

Multiple lines of evidence point to AOCs having a significant impact on fish PCB concentrations. A two-way ANOVA and t-tests showed that there were significantly higher concentrations in fish at AOC sites for carp, largemouth bass, and walleye (Figure 3-11). Although these differences are eliminated when lipid- and length-normalized concentrations were used, the majority of this work evaluates log-normalized data. Therefore, the discussion of AOC sites compared to non-AOC sites will as well (Figure 3-11). Lean fish at AOC sites have more contamination than lean fish at non-AOC sites, but less contamination than medium-fat fish (Figure 3-12Figure 3-12). The same relationship exists for length (Figure 3-13). Small fish at AOC sites have more contamination than small fish at non-AOC sites, but less contamination than medium-size fish. The similarity of these results makes sense when we consider the strong linear relationship between length and lipid content (Figure 3-6). It is possible that this alternating is confounded by the fact that carp are longer and fattier than the other species, which might be why the pattern emerges. The stepwise multiple linear regression (MLR) excluded length but showed the log lipid content and site status explained 49% of the variability of PCB concentrations in the species of interest (Figure 3-16). The correlation between log-transformed PCB concentration and site status was low (-0.113) but significant. Metcalfe et al. (1997) indicated that the Detroit River discharge increased the PCB burden of western Lake Erie zebra mussels.

4.2.4 Conclusion, What is the source of Michigan's PCBs?

This work was unable to determine the source(s) of PCBs to fish in Michigan's rivers. Most of the sample locations were in the Lower Peninsula and were often clustered, limiting the spatial extent of the data. Aroclor ratios showed that there was more variance within the site categories than between them, leaving unanswered the question of whether AOC sites have different PCB sources than non-AOC sites. Rivers best represent the intimate relationships between air, water, and sediment and allow partitioning between the different phases which might mask any previously existing source signature. In essence, it is possible that the PCBs in rivers are too highly weathered to be useful in source determination. The 2-way ANOVA shows that PCB concentrations are higher at AOC sites; this implicates AOC sites as a source of PCBs to downstream coastal areas. PCA provided evidence that for some species there is an atmospheric source of PCBs at a limited number of locations. Additional work is needed to establish the sources of PCBs to Michigan Rivers, work that will help AOC site managers to plan effective remediation strategies.

4.3 Efficacy of remediation, does the existing AOC framework allow us to assess our cleanup efforts?

Successful remediation of AOC sites depends on the BUI under consideration. For fish consumption advisories (BUI 1), sites have the option of accepting the state's criteria for delisting or developing a more stringent standard that is specific to that site (MDEQ 2015; MDNRE 2010). Generally, most AOC sites have opted to apply the state's criteria (Table 4-5) that give three options for the restoration criterion:

1. Fish consumption advisories in the AOC are the same as or less restrictive than the associated Great Lake or appropriate control site.
2. A comparison study of fish tissue contaminant levels demonstrates that there is not a statistically significant difference in fish tissue concentrations of contaminants causing fish consumption advisories in the AOC compared to a control site ($\alpha = 0.05$).
3. Analysis of trend data (if available) for fish with consumption advisories shows similar trends to other appropriate Great Lakes trend sites.

This portion of the work focused on evaluating the progress of our remediation work with an eye to the three de-listing criteria mentioned above. Qualitative analysis of acceptable control sites, a quantitative comparison of fish PCB concentrations, and a quantitative trend in fish PCB concentrations, it becomes clear that the current framework does not allow us to adequately evaluate the success of our remediation work.

4.3.1 AOC control sites: What is our reference?

All of the acceptable criteria allow for the comparison of PCB concentrations to an appropriate control site, including the associated Great Lake; most Michigan riverine AOC sites use one of the GLs as their control site (Table 4-5). The rationale for that choice is unclear. Lake size is an important consideration when comparing among lakes. Large lakes tend to have higher fish PCB concentrations than do smaller lakes (Sokol 2015) because of large surface areas for atmospheric deposition (e.g Eisenreich et al. 1981; Jeremiason et al. 1994), low nutrient concentrations resulting in lower fish growth rates, and long food chains (Muir et al. 2004). These differences are more exaggerated when we consider rivers, which can have even larger watershed to surface area ratios, higher nutrient concentrations (e.g. Meyer et al. 2005; Smith et al. 2005), and higher productivity (e.g. Randall et al. 1995).

Table 4-5 Michigan's river AOC sites with de-listing criteria for fish consumption advisories and the site's associated control site. [8]

	Restoration Criterion	**Associated Control Site**
Clinton River (Tewkesbury 2011)	When FCAs are the same as or less restrictive than associated GL or appropriate control site	Not mentioned
Detroit River (Esman and Bureau, n.d.)	Developing local criteria (will need MDEQ approval)	Not mentioned
Kalamazoo River (Riley and River 2012)	Accepted state's criteria, current FCA advisory in effect is more stringent than associated GL so comparison study of fish tissue contamination levels or trend data for FCA	Lake Michigan, Ceresco Reservoir (Superfund)
Manistique River ("Stage 2 Remedial Action Plan Manistique River Area of Concern" 2011)	"…PCBs in fish tissue from caged fish studies do not exceed background levels at the selected reference site" (p.9)	Manistique River watershed, above the dam
Menominee River (Mistak et al. 2012)	Not mentioned	Lake Michigan, Green Bay
Muskegon River (Swart 2011)	Accepted state's criteria, current FCA advisory in effect is more stringent than associated GL so comparison study of fish tissue contamination levels or trend data for FCA	Lake Michigan
Raisin River ("Stage 2 Remedial Action Plan River Raisin Area of Concern" 2012)	Accepted state's criteria, current FCA advisory in effect is more stringent than associated GL so comparison study of fish tissue contamination levels or trend data for FCA	Lake Erie
Rouge River (Badics et al. 2004)	"PCB concentrations meet state human consumption standards" (p.18)	Not mentioned

[8] The table was created from the most recent remedial action plan (RAP) report for each AOC site.

Saginaw River ("Stage 2 Remedial Action Plan for the Saginaw River/Bay Area of Concern" 2012)	Accepted state's criteria, current FCA advisory in effect is more stringent than associated GL so comparison study of fish tissue contamination levels or trend data for FCA	Lake Huron
St Clair River ("Volume 1 – Synthesis Report Volume 1 – Draft Synthesis Report" 2004)	"…perhaps the point at which AOC advisories are in some way comparable to open lake advisories." (p.49)	Lake Huron (mentioned as a comparison)
St Mary's River ("Stage 2 Remedial Action Plan Implementation Annex for the U.S. Waters of the St. Marys River Area of Concern" 2012)	Accepted state's criteria, current FCA advisory in effect is more stringent than associated GL so comparison study of fish tissue contamination levels or trend data for FCA	Lake Huron

The lack of a statistically significant difference in fish PCB concentrations between an AOC and non-AOC site is an appropriate justification for de-listing a FCA BUI. Results from this work show that a two-way ANOVA of log-transformed PCB concentrations showed significantly different concentrations between AOC and non-AOC sites for carp, largemouth bass, and walleye (Figure 3-11). These differences in fish PCB concentrations at AOC and non-AOC sites means it is unlikely that a single AOC site is equivalent to a single non-AOC site and therefore not ready to be de-listed.

4.3.2 Time trends: Are fish PCB concentrations decreasing?

Historically, concentrations of PCBs in the atmosphere above the Great Lakes basin have been decreasing (Buehler et al. 2002; Salamova et al. 2013; Salamova et al. 2015) in spite of signals from in-use PCBs (Hites 2018). The half-life for decrease in atmospheric PCB concentrations at the stations of the Integrated Atmospheric Deposition Network (IADN) range from 11.9 – 18.6 years (Salamova et al. 2015). The in-lake response also varies from 3.5 years to 12 years (Jeremiason et al. 1994; Khan 2018), but the lake concentrations are varied (Anderson et al. 1999). Due to the low organic carbon content of the Great Lakes water, PCB concentrations in air and water reflect the efficacy of policy changes (Buehler et al. 2004). In biota, the story is more complicated. As PBT compounds, PCBs bioaccumulate in organisms and exposure to PCBs depends on habitat, diet, trophic position, etc. Additionally, secondary emissions might contribute to the lag in lowered PCB concentrations in air compared to fish, as found for Lake Superior through dynamic lake mass balance modeling (Khan 2018). Half-lives for PCBs in Lake Superior fish for the period 1995 to 2015 ranged from 9.3 – 95.0 years (Lin 2016).

Quantifying total PCB concentrations is an important part of AOC monitoring and remediation work. Over time, analytical methods have evolved from the Aroclor-method, which quantifies total PCB concentrations by extrapolating Aroclor concentrations based on the peak of a few congeners, to the congener method, which quantifies individual congeners and then reports the total PCB concentration as the summation of the congeners. Quantification of individual congeners is more accurate because it can resolve some of the difficulties that arise in matching environmentally weathered samples to laboratory-grade Aroclor standards (Bernhard and Petron 2001; Gandhi et al. 2015; EPA 2008). The MDEQ FCMP switched from the Aroclor-method to the congener-method in 2000 and total PCB concentrations from both methods are considered equivalent despite the methodological differences. Using combined data (Aroclor- and congener-based total PCB concentrations) to determine time trends can be problematic because of issues with accuracy.

A comparison of Aroclor trends and congener trends often yields contradictory results. For example, no significant Aroclor total trend is observed but a significant congener-based trend is found in some fish in some locations (e.g. carp in the Detroit, Huron, and Raisin Rivers and walleye in the Grand River and Lake St Clair). In other locations a significant decreasing Aroclor-based trend but a significantly increasing or insignificant congener-based trend is observed (e.g. carp in the St. Joseph River and walleye in the Au Sable and Menominee River). This may result from comparing apples and oranges (results from two different analytical methodologies), or it may reflect the high temporal variability of the fish PCB concentrations that requires long-term data for accurate assessment of trends (Chang et al. 2012; Buehler et al. 2002)

Half-lives for PCBs in carp, smallmouth bass, and walleye varied (Table 4-6). The half-lives at AOC sites tend to be longer than at non-AOC sites. However, when aggregated, the half-lives at AOC sites are longer than at non-AOC sites, but the differences are not statistically significant ($p > 0.05$; Table 4-6).

Table 4-6 Total PCB half-lives in fish species at AOC and non-AOC sites. It is important to note that these averages only include the locations with a statistically significant slope.

	Site Status	Average half-life ($year^{-1}$) (combined/Aroclor/congener)
Carp	AOC (n = 6)	13.5 / 12.1 / 3.6
	Non-AOC (n = 3)	9.8 / 17.5 / 13.9
Smallmouth Bass	AOC (n = 2)	8.1 / 5.7 / 13.0
	Non-AOC (n = 0)	NA
Walleye	AOC (n = 2)	6.7 / 9.9 / 3.0
	Non-AOC (n = 2)	5.4 / 0.6 / 6.3

When averaged, PCB half-lives for all species at both AOC and non-AOC sites are statistically similar to the atmospheric half-lives (IADN data) and do not indicate that fish PCB concentrations are declining faster than the rate of atmospheric decline. A closer look shows that the story is more complicated. Firstly, there were only 2-4 statistically significant trends that were considered for any one of the species*site combinations. Considering the individual species*river combination the variation is obvious. For carp the half-lives ranged from 5.8 – 23.1 $year^{-1}$, smallmouth bass ranged from 2.7 – 17.3 $year^{-1}$, and walleye ranged from 0.6 - 17.3 $year^{-1}$. Together, this does not provide any evidence that cleaning up AOC sites is leading to a more rapid decrease in fish PCB concentrations. No apparent patterns or similarities in site characteristics and half-life exist.

Table 4-7 Time trends for carp in Michigan Rivers with at least 3 years of both Aroclor data and congener data. Aggregated data considers Aroclor and congener-based total to be comparable. NA indicates waterbodies where there was a positive half-life, indicating no apparent degradation of PCBs.

Carp	Combined Trends (years)	Aroclor Trends (years)	Congener Trends (years)
Au Sable River	$t_{1/2}$: 6.3 $p < 0.001$ $R^2 = 0.25$	$t_{1/2}$: 23.1 NS $R^2 = 0.02$	$t_{1/2}$: 13.9 NS $R^2 = 0.01$
Detroit River	$t_{1/2}$: 9.9 $p < 0.001$ $R^2 = 0.38$	$t_{1/2}$: 17.3 NS $R^2 = 0.02$	$t_{1/2}$: 4.6 $p < 0.01$ $R^2 = 0.18$
Huron River	$t_{1/2}$: 17.3 $p < 0.01$ $R^2 = 0.08$	$t_{1/2}$: 23.1 NS $R^2 = 0.03$	$t_{1/2}$: NA $p < 0.01$ $R^2 = 0.20$
Kalamazoo River	$t_{1/2}$: 11.6 $p < 0.001$ $R^2 = 0.16$	$t_{1/2}$: 17.3 $p < 0.001$ $R^2 = 0.09$	$t_{1/2}$: 4.3 $p < 0.001$ $R^2 = 0.20$
Lake St Clair	$t_{1/2}$: NA NS $R^2 = 0.00$	$t_{1/2}$: 9.9 NS $R^2 = 0.08$	$t_{1/2}$: 6.9 NS $R^2 = 0.02$
Menominee River	$t_{1/2}$: 11.6 $p < 0.01$ $R^2 = 0.12$	$t_{1/2}$: 2.8 $p < 0.01$ $R^2 = 0.25$	$t_{1/2}$: 1.9 $p < 0.01$ $R^2 = 0.26$
Raisin River	$t_{1/2}$: 23.1 NS $R^2 = 0.03$	$t_{1/2}$: 11.6 NS $R^2 = 0.05$	$t_{1/2}$: 2.3 $p < 0.001$ $R^2 = 0.50$
Rouge River	$t_{1/2}$: 11.6 $p < 0.001$ $R^2 = 0.18$	$t_{1/2}$: 11.6 NS $R^2 = 0.03$	$t_{1/2}$: NA NS $R^2 = 0.01$
St Joseph River	$t_{1/2}$: 5.8 $p < 0.001$ $R^2 = 0.35$	$t_{1/2}$: 6.3 $p < 0.01$ $R^2 = 0.10$	$t_{1/2}$: NA $p < 0.05$ $R^2 = 0.15$

Table 4-8 Time trends for smallmouth bass at Michigan Rivers with at least 3 years of both Aroclor data and congener data. Aggregated data considers Aroclor and congener-based total to be comparable.

Smallmouth Bass	Combined Trends (years)	Aroclor Trends (years)	Congener Trends (years)
Kalamazoo River	$t_{1/2}$: 6.3 $p < 0.001$ $R^2 = 0.31$	$t_{1/2}$: 8.7 $p < 0.001$ $R^2 = 0.26$	$t_{1/2}$: 17.3 NS $R^2 = 0.00$
Lake St Clair	$t_{1/2}$: 9.9 $p < 0.001$ $R^2 = 0.46$	$t_{1/2}$: 2.7 $p < 0.05$ $R^2 = 0.16$	$t_{1/2}$: 8.7 $p < 0.05$ $R^2 = 0.14$

Table 4-9 Time trends for walleye at Michigan Rivers with at least 3 years of both Aroclor data and congener data. Aggregated data considers Aroclor and congener-based total to be comparable. NA indicates waterbodies where there was a positive half-life, indicating no apparent degradation of PCBs.

Walleye	Combined Trends (years)	Aroclor Trends (years)	Congener Trends (years)
Au Sable River	$t_{1/2}$: 3.9 $p < 0.01$ $R^2 = 0.38$	$t_{1/2}$: 0.6 $p < 0.01$ $R^2 = 0.70$	$t_{1/2}$: NA NS $R^2 = 0.14$
Grand River	$t_{1/2}$: 6.9 $p < 0.001$ $R^2 = 0.41$	$t_{1/2}$: NA NS $R^2 = 0.14$	$t_{1/2}$: 6.3 $p < 0.05$ $R^2 = 0.14$
Lake St Claire	$t_{1/2}$: 7.7 $p < 0.001$ $R^2 = 0.36$	$t_{1/2}$: 17.3 NS $R^2 = 0.14$	$t_{1/2}$: 5.0 $p < 0.02$ $R^2 = 0.25$
Menominee River	$t_{1/2}$: 5.8 $p < 0.001$ $R^2 = 0.32$	$t_{1/2}$: 2.5 $p < 0.01$ $R^2 = 0.23$	$t_{1/2}$: 1.0 $p < 0.001$ $R^2 = 0.75$

4.3.3 Conclusions, Have our remediation efforts been successful?

The short answer is that we do not know, and this work outlined some of the reasons why that is the case. Great Lakes make poor control sites for riverine systems. They are inappropriate not only because of important habitat and food web characteristics differences, but also because PCB contamination is ubiquitous. Even the most remote habitats such as those of artic and sub-arctic polar bears (Verreault et al. 2005), harbor porpoises (Kleivane et al. 1995), and artic foxes (Wang-Anderson et al. 1993) have PCB contamination. AOC sites are assumed to be more contaminated than other non-AOC sites; none of the de-listing criteria requires the elimination of FCAs or PCB contamination. Instead, sites are remediated, with respect to FCAs, so long as fish at

AOC sites are not more contaminated than fish at a control site. Having the BUI de-listing criteria grounded in a comparison to other, often contaminated locations, makes clear that the standard is not whether a FCA exists or not, but whether it is similarly contaminated.

This perspective on AOC sites and their remediation, which were designated under the Great Lakes Water Quality Agreement, is at odds with the part of the agreement that states that the waters of the Great Lakes should "allow for human consumption of fish and wildlife unrestricted by concerns due to harmful pollutants" ("Great Lakes Water Quality Agreement" 2013). It also reiterates the importance of acceptable control sites. Habitat and food web characteristics affect concentrations in fish; so do time and space. Consistent, long-term data sets are important for establishing trends in fish PCB contamination and allow us to see the effects of in-use compounds. In Michigan, there is a long record of data, but methodological changes exist. These differences might inaccurately represent the fish response to policy changes and/or remediation efforts.

As a trans-national contaminant, the management and remediation of PCBs necessitates a similarly expansive approach (Perlinger et al. 2016; Gorman et al. 2016). At present, different agencies (and researchers) quantify total PCB concentrations using different methodologies that makes it nearly impossible to compare across studies. This methodological difference is exacerbated by the selection of different congeners to be included in the summation for total PCB concentrations. These methodological differences can under- or overestimate total PCBs in a given species, depending on whether the selected congeners are frequently present in the fish.

Contamination, fish, water, air, and predators do not acknowledge imaginary boundaries that surround AOC sites. Thus, these arbitrary boundaries do little more than focus the contamination and the subsequent effects onto a small area, irrespective of nearby areas that might also be receiving similar PCB inputs through atmospheric deposition. The lack of obvious positive effects of AOC site cleanup implies that localized sediment contamination is not prolonging fish body burdens of PCBs. This might also indicate atmospheric deposition is a primary source of PCBs throughout Michigan, which would further support a trans-national, collaborative approach to retiring in-use PCBs as well as cleaning up legacy contamination.

5 Conclusions

The original intention of this work was to assess the decades of remediation work to clean-up PCB contamination by examining the PCB concentrations in fish, using Michigan's rivers as an example. However, it was difficult to make these assessments, due in large part to the current management and monitoring strategies. As a result, the emphasis of this work shifted to assessing how we might use data to construct a successful monitoring program. Evaluating MDEQ data from the fish contaminant monitoring program, comparisons were performed between four species of interest: carp, smallmouth bass, largemouth bass, and walleye. Carp, an omnivore, had significantly higher PCB concentrations than the other three species but there were no significant differences among the other three species.

Significant differences in fish PCB concentrations exist between AOC and non-AOC sites, but lipid content is a better predictor of total PCB concentrations than is the presence of an AOC. Generally, fish at AOC sites have higher PCB concentrations than fish at non-AOC sites. Multi-variate statistics (analysis of variance (ANOVA), principal component analysis (PCA), and multiple linear regression (MLR)) evaluated the sources of contamination. The PCA indicated that for largemouth bass and walleye there might be a local source of PCB contamination at three sites due to congener profiles dominated by lighter congeners. However, PCA did not identify AOC sites as distinct from non-AOC sites. ANOVA and MLR both indicated the importance of site status (AOC or non-AOC) when explaining the variance in PCB concentrations and predicting PCB concentrations. However, in both analyses it had a relatively small contribution. For the MLR, site status was included in the regression equation despite the low, but significant, correlation (0.122).

Congener selection for analysis of PCBs in fish is important when quantifying total PCB concentrations. While the magnitude of contamination only differed for carp, there were differences in the accumulation of different congeners among all the species. That different species tend to accumulate different congeners is an important consideration anytime subsets of congeners are used to represent "total PCB" concentration. There is not currently a standard suite of congeners, although most subsets appear to be derived from the well-known list of environmentally dominant congeners. The creation of a standard subset of congeners for calculating "total PCB" concentrations would be valuable in that it would facilitate comparisons across a variety of studies. In the determination of a standardized congener subset, it is important to acknowledge that total body burden could be over or under represented based on the species being considered. Furthermore, the exclusive consideration of total PCBs ignores the potential differences in toxicity that might result from the inclusion or exclusion of particular congeners.

Trends at AOC and non-AOC sites were difficult to establish in part because of the methodological change that occurred in 2000. On average, half-lives at AOC sites were longer than non-AOC sites for the combined-trend, Aroclor-trend and congener trend, but only 2-4 sites were included in that average. Therefore, it is unlikely that those sites represent all others. Furthermore, the individual species*river combination shows how much the half-lives vary. For carp the half-lives ranged from 1.8 – 23.1 years, smallmouth bass ranged from 2.7 – 17.3 years, and walleye ranged from 0.6 – 17.3 years. Together, this does not provide any evidence that cleaning up AOC sites is leading to a more rapid decrease in fish PCB concentrations.

At present, current monitoring strategies make the evaluation of remediation efforts difficult. A quantitative analysis requires effective control sites and consistent quantification methodology. In Michigan, two different PCB quantification methodologies are treated equally and data are combined in order to establish time trends. The congener-based quantification method (post-2000) is more accurate than the previously used Aroclor-based method (pre-2000). The combined data results in significantly decreasing trends at most sites, in spite of contradictory results when only congener-based data are considered. Additionally, annual sampling occurs in one region such that sampled waterbodies are clustered and the minimum amount of time between two samples is five years. This precludes any spatial analysis of fish PCB concentrations and it also makes time trends difficult to establish since there are at least 15 years between three years of data. Considered together, our current monitoring strategy should be adjusted to more effectively evaluate the efficacy of remediation and to be better able to determine the sources of PCBs.

It is also important to consider the issues of fish consumption advisories and contaminated sites within the framework of environmental justice. Fish consumption varies among different populations and individual differences affect the toxicological response. Any time agencies determine acceptable levels of risk, there will always be those who are more vulnerable- either because of their ethnicity, their diet, their income, or their biology. For as long as FCAs are used a management tool, there will always be people marginalized. Therefore, modifying our monitoring program to be able to effectively establish PCB sources, evaluate the efficacy of remediation, and compile data from the many institutions should be of the utmost importance. Canada, specifically Ontario is on track to entirely phase out PCBs by the 2025 deadline articulated in the Stockholm Convention but the progress of such work in the US is unclear (Shu-Yin et al. 2018). The complete phase out of PCBs at a trans-national scale is important. The longer we postpone, the longer we use FCAs as Band-Aids to fix the problem of exposure to PCBs.

6 Recommendations to Strengthen Fish PCB Concentration Monitoring for Fish Consumption Advisory Assessment

This research project began as one that would evaluate the success of the AOC program by focusing on fish in Michigan's rivers. The Michigan Department of Environmental Quality uses the more accurate congener-based quantification method, analyzing for 83 congeners to quantify "total PCBs", more than any other Great Lakes state monitoring agency. In the end, however, as described in this thesis, it was difficult to conduct a rigorous evaluation, and the emphasis of the work shifted to assessing how we could use the fish PCB monitoring data and associated analyses to construct a more successful monitoring program. The following recommendations for improving fish contaminant monitoring programs would help them to inform fish consumption advisories (FCAs) and their delisting criteria in Michigan:

1. First, we must acknowledge that FCAs cannot protect everyone equally because of differences in diet and in susceptibility to contaminants.

2. Tandem PCB quantification at Michigan inland waterbody sample sites is needed to be able to effectively analyze historical trends in fish PCB concentrations. Options include quantifying total PCBs in archived samples based on the congener method or by quantifying total PCBs in future samples based on the Aroclor method.

3. A standardized suite of PCB congeners should be analyzed by all state and federal agencies to facilitate comparisons across jurisdictions. This suite should include the most environmentally prevalent dioxin-like congeners (77, 105, 118, 156), the remaining members of the B7 indicator group (138, 153, 180), the remaining members of the ICES-7 group (28, 52, 101), and other congeners present in at least half of the fish samples (49, 52, 66+95, 97, 99, 132, 141, 146, 151, 174, 177, 182+187, 183, 194, 201).

4. In choosing additional congeners for the quantification process, careful consideration should be given to the fish species being studied. In particular, for bottom-feeding fish it is desirable to include more low-molecular weight congeners (e.g., PCB congeners 28, 44, 47, 56+60, 64, 66+95, 70, 74, 82, and 84 are all congeners present in at least half of the carp samples).

5. More appropriate control sites are necessary for inland lake and river sites. Current convention allows for FCA de-listing through comparison of the inland waterbody fish concentrations with those collected from a selected Great Lake fish concentration However, lake size is an important consideration when

comparing among lakes because of greater atmospheric deposition, low nutrient concentrations, and longer food chains in the Great Lakes as compared to the smaller inland water bodies. These differences are more exaggerated for river sites, which can have larger watershed to surface area ratios, higher nutrient concentrations, and higher productivity as compared to inland lake sites (see section 4.3.1, page 91).

6. Because it is not evident that AOC sites are recovering faster than non-AOC sites, it is equally important to remove localized sources of PCBs to the atmosphere (e.g., from land-applied sewage sludge and transformer off-gassing), and thereby reduce PCB contamination from atmospheric deposition in all locations, as it is to remediate AOC sites.

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"8082a." n.d.

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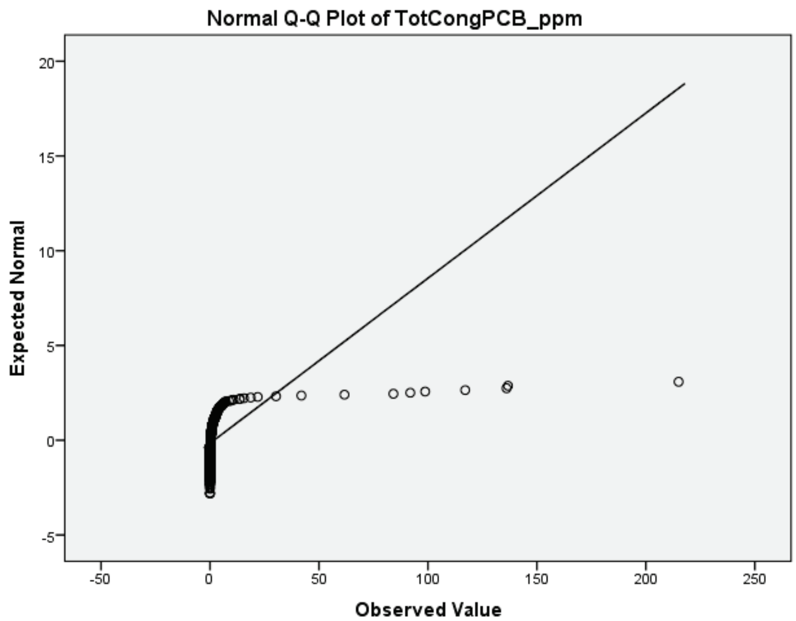
8 Appendix: additional methodological information

8.1 Normal QQ plots

Carp



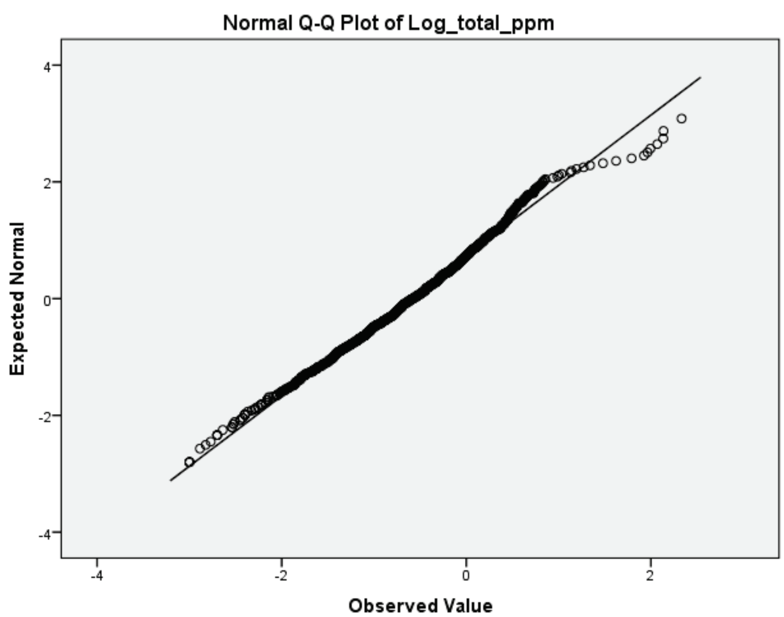
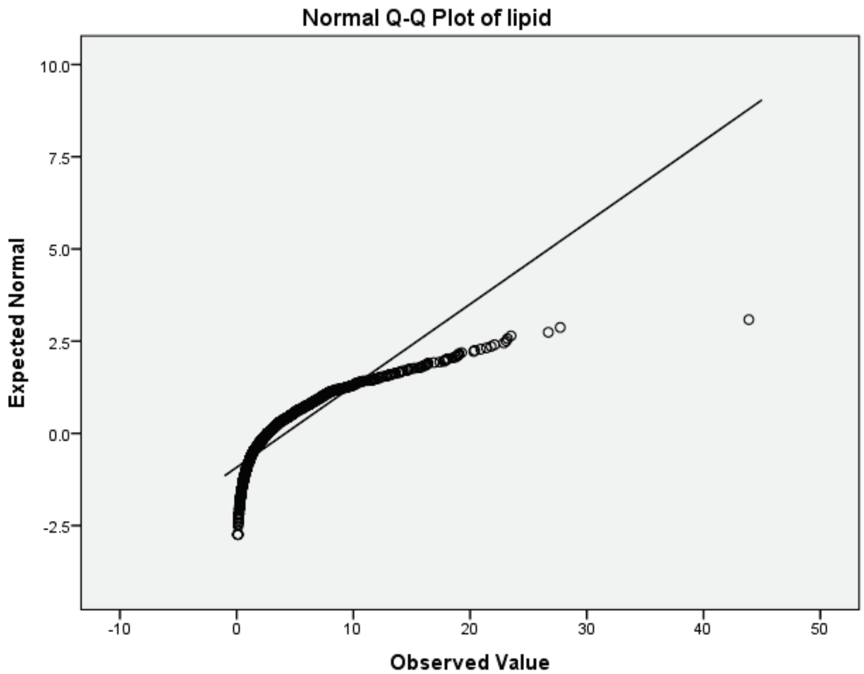


Figure 8-1 Total PCB concentrations in carp, raw (top) and log transformed (bottom). These plots were used to decide to use log transformed PCB concentrations.



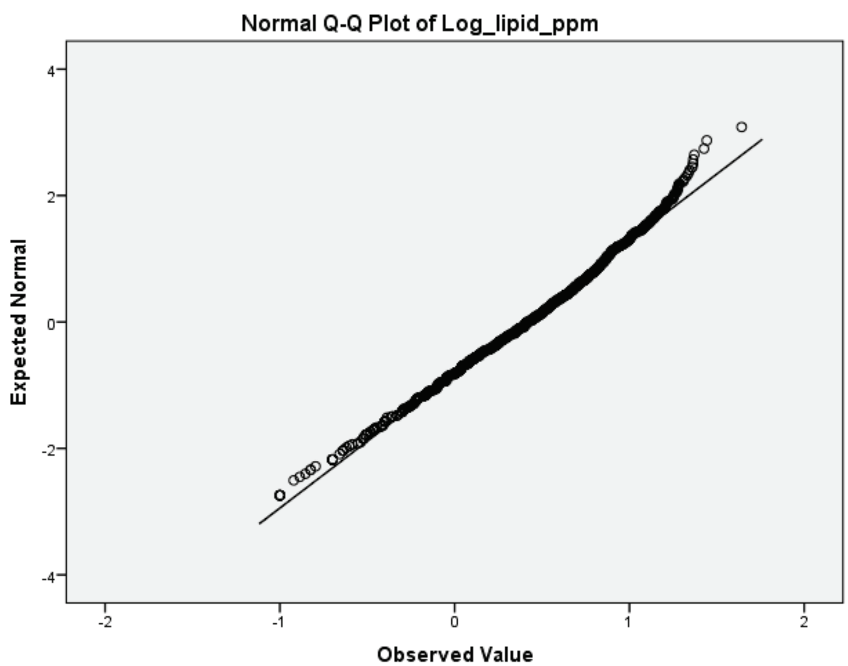


Figure 8-2 Lipid content in carp, raw (top) and log transformed (bottom). These plots were used to decide to use log transformed lipid content.

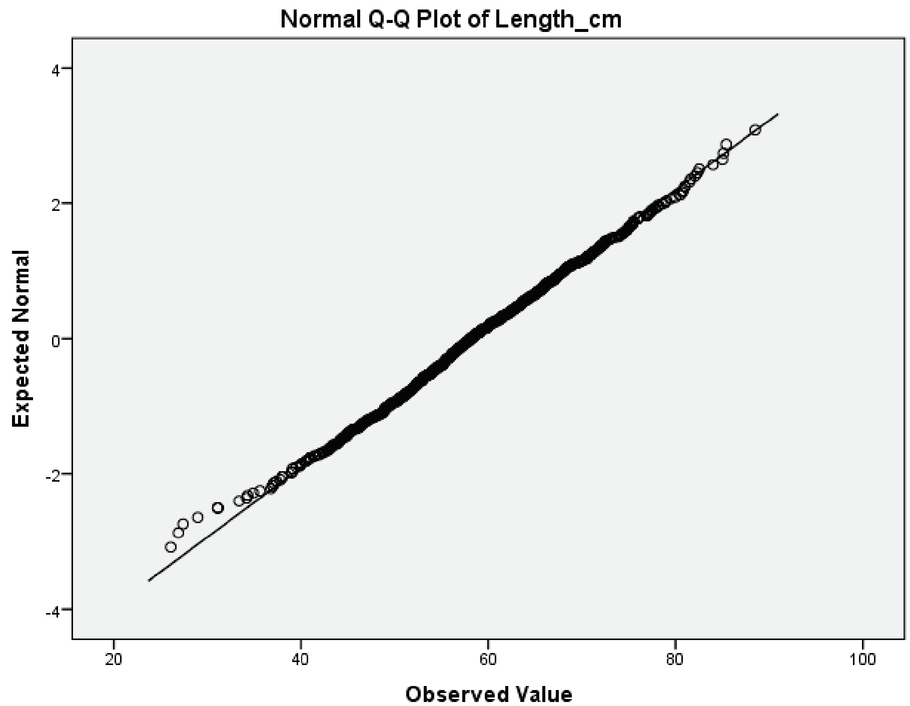
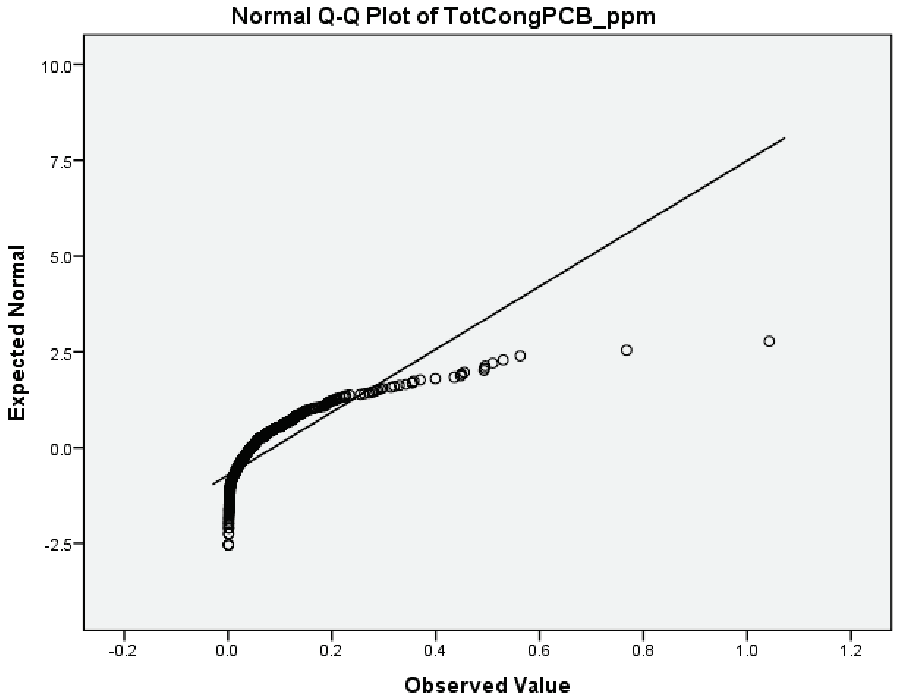


Figure 8-3 Length of carp, raw. This plot was used to decide to use un-transformed length.

Smallmouth bass:



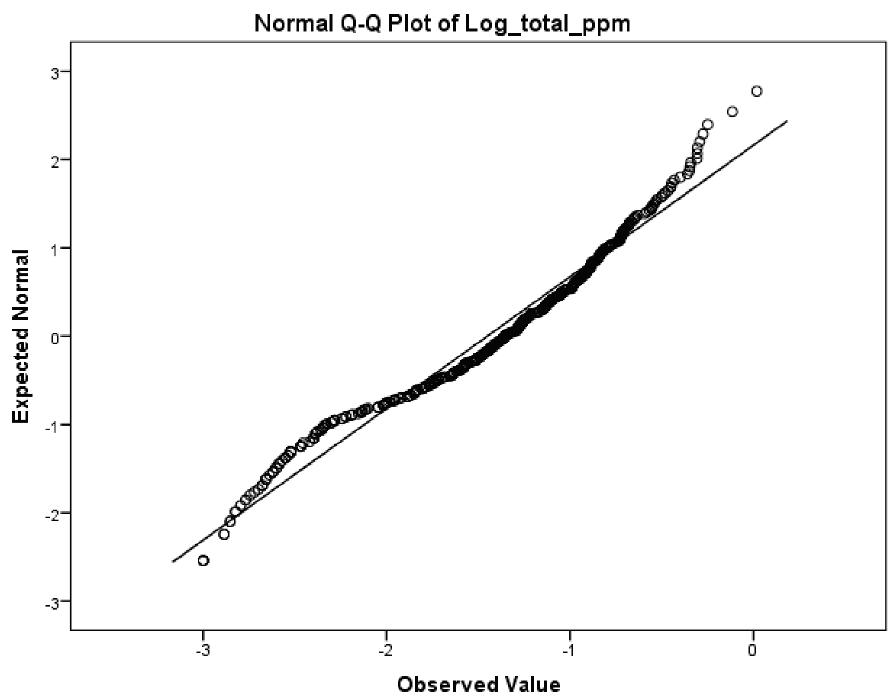
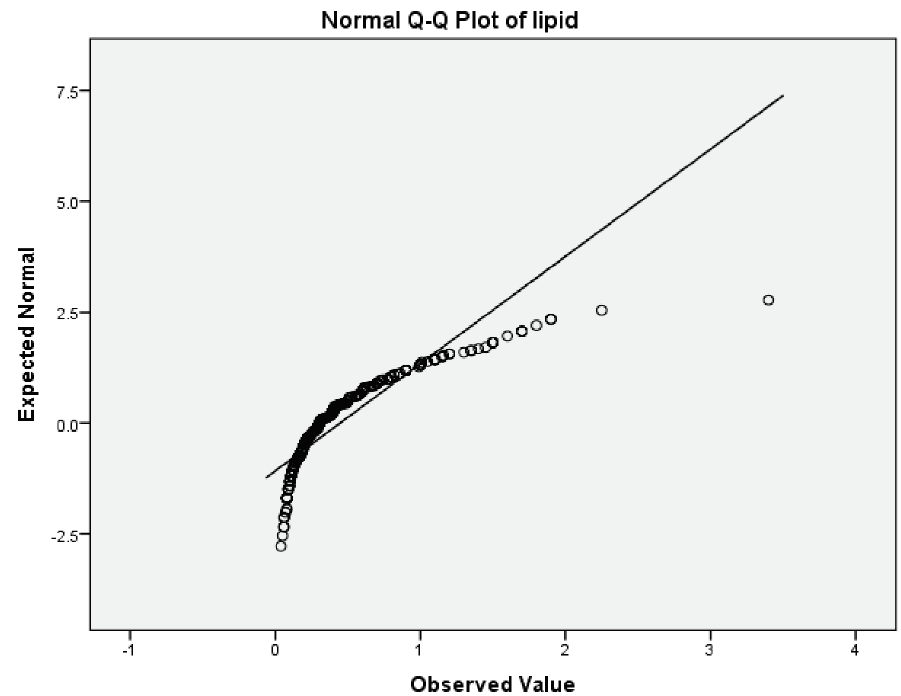


Figure 8-4 Total PCB concentrations in smallmouth bass, raw (top) and log transformed (bottom). These plots were used to decide to use log transformed PCB concentrations.



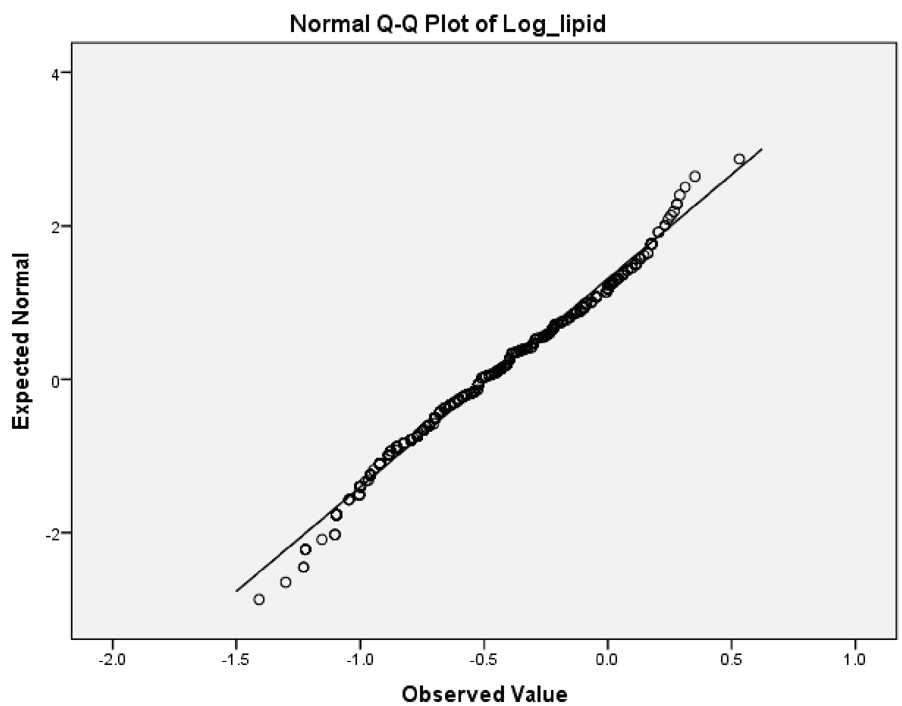


Figure 8-5 Lipid content in smallmouth bass, raw (top) and log transformed (bottom). These plots were used to decide to use log transformed lipid content.

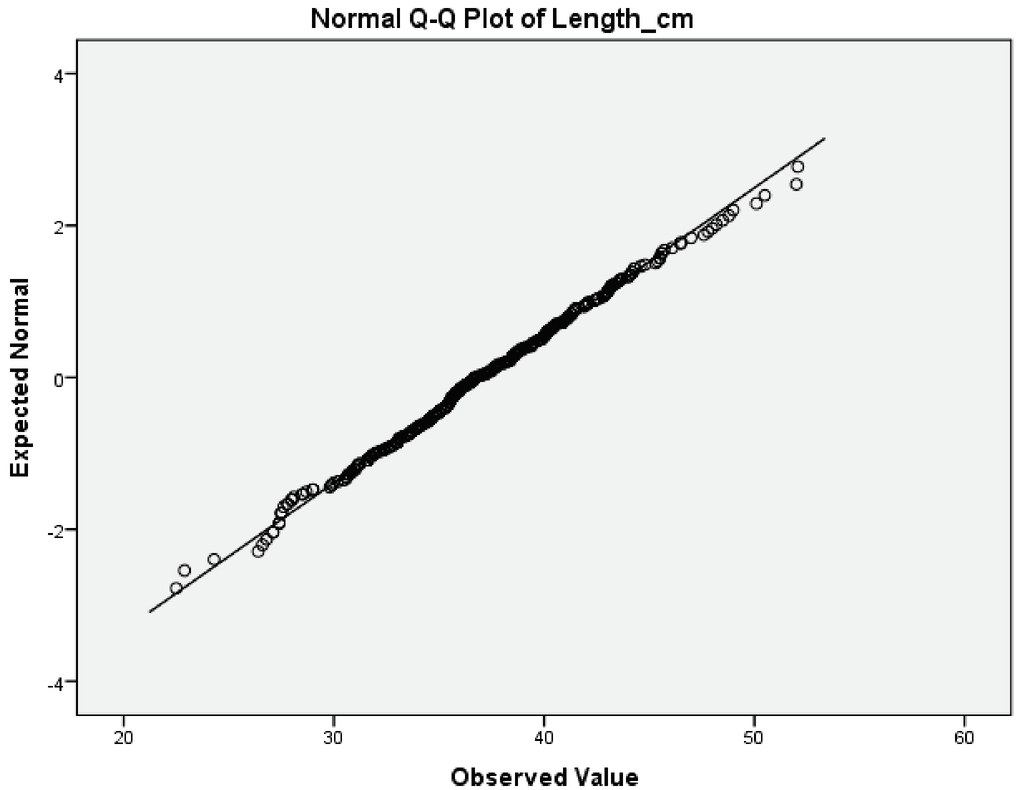
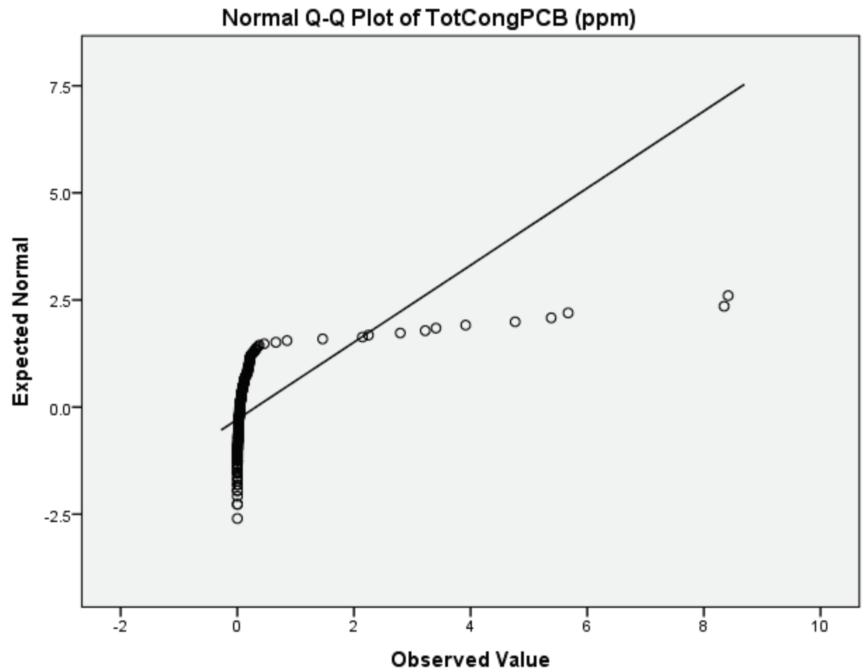


Figure 8-6 Length of smallmouth bass, raw. This plot was used to decide to use un-transformed length.

Largemouth bass



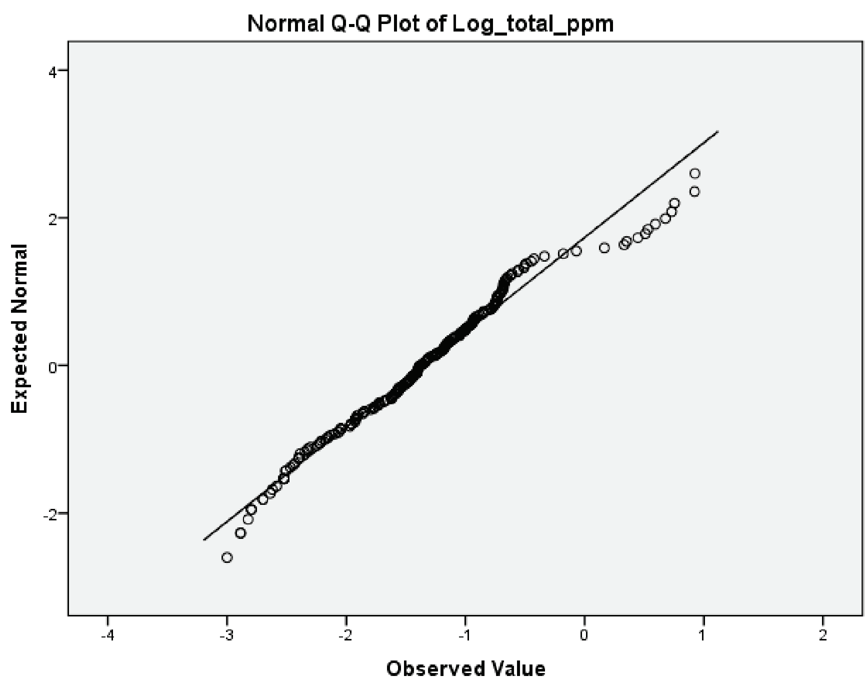


Figure 8-7 Total PCB concentrations in largemouth bass, raw (top) and log transformed (bottom). These plots were used to decide to use log transformed PCB concentrations.

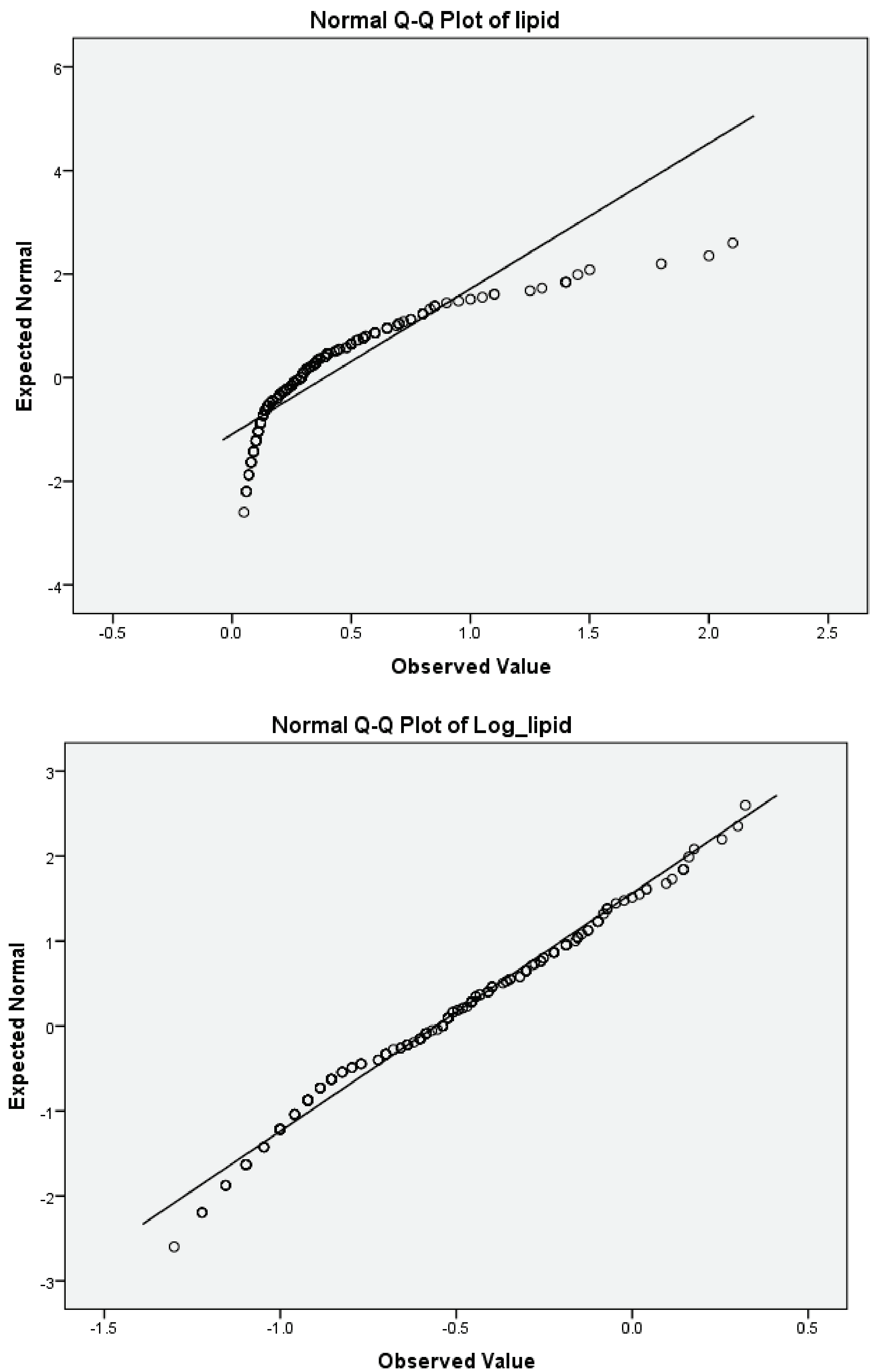


Figure 8-8 Lipid content in largemouth bass, raw (top) and log transformed (bottom). These plots were used to decide to use log transformed lipid content.

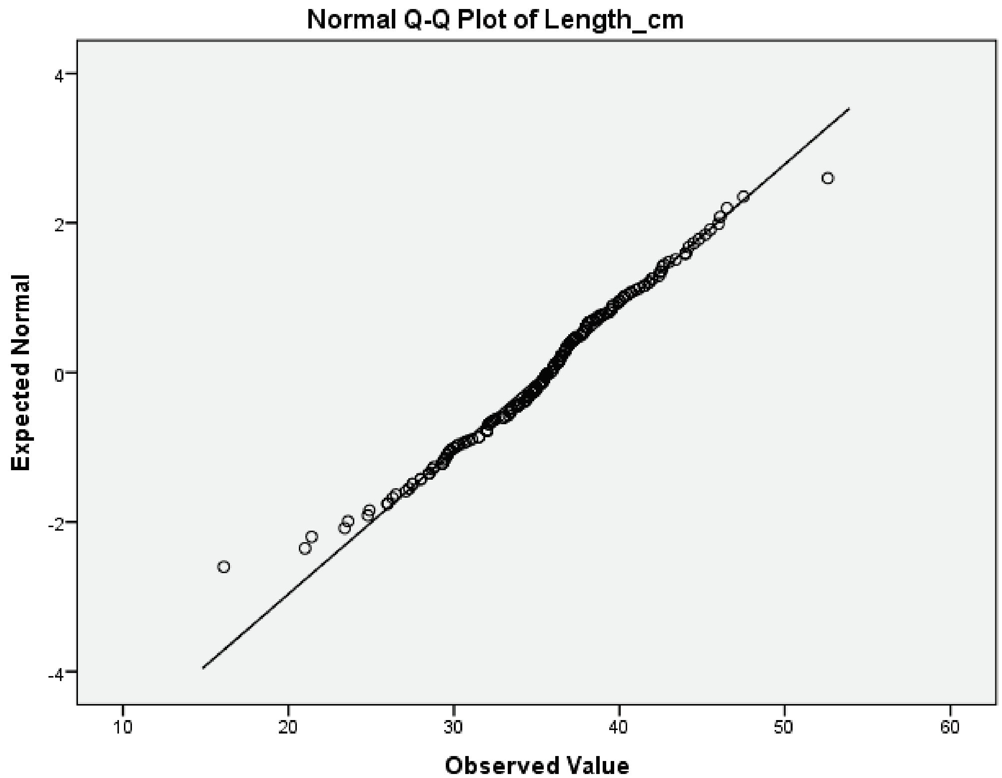
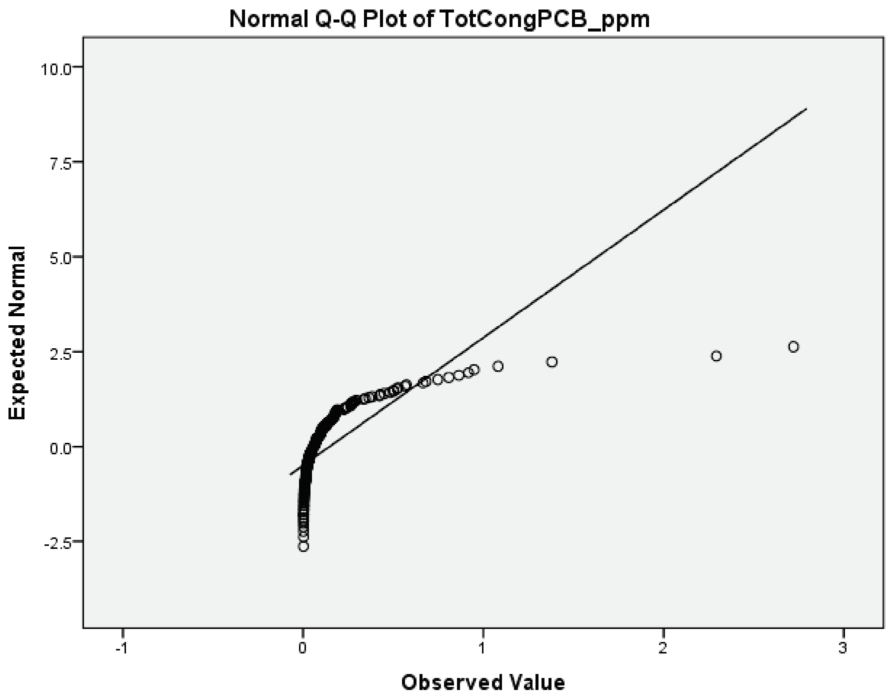


Figure 8-9 Length of largemouth bass, raw. This plot was used to decide to use un-transformed length.

Walleye



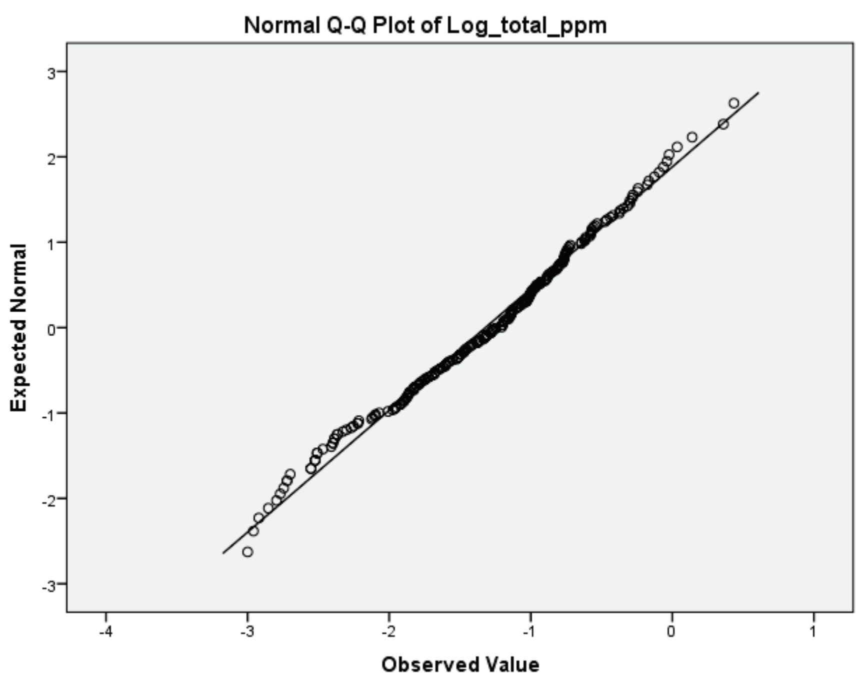


Figure 8-10 Total PCB concentrations in walleye, raw (top) and log transformed (bottom). These plots were used to decide to use log transformed PCB concentrations.

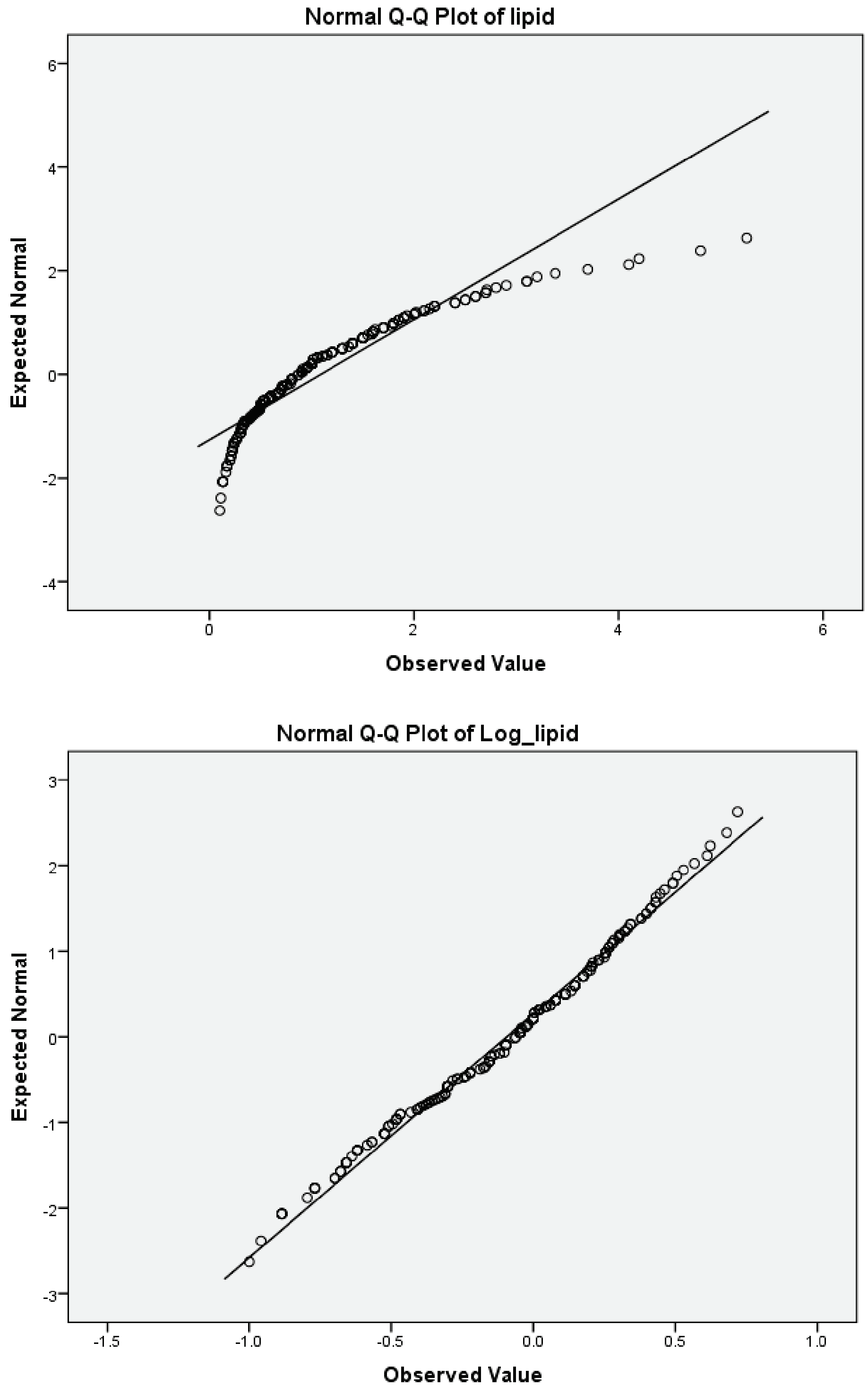


Figure 8-11 Lipid content in walleye, raw (top) and log transformed (bottom). These plots were used to decide to use log transformed lipid content.

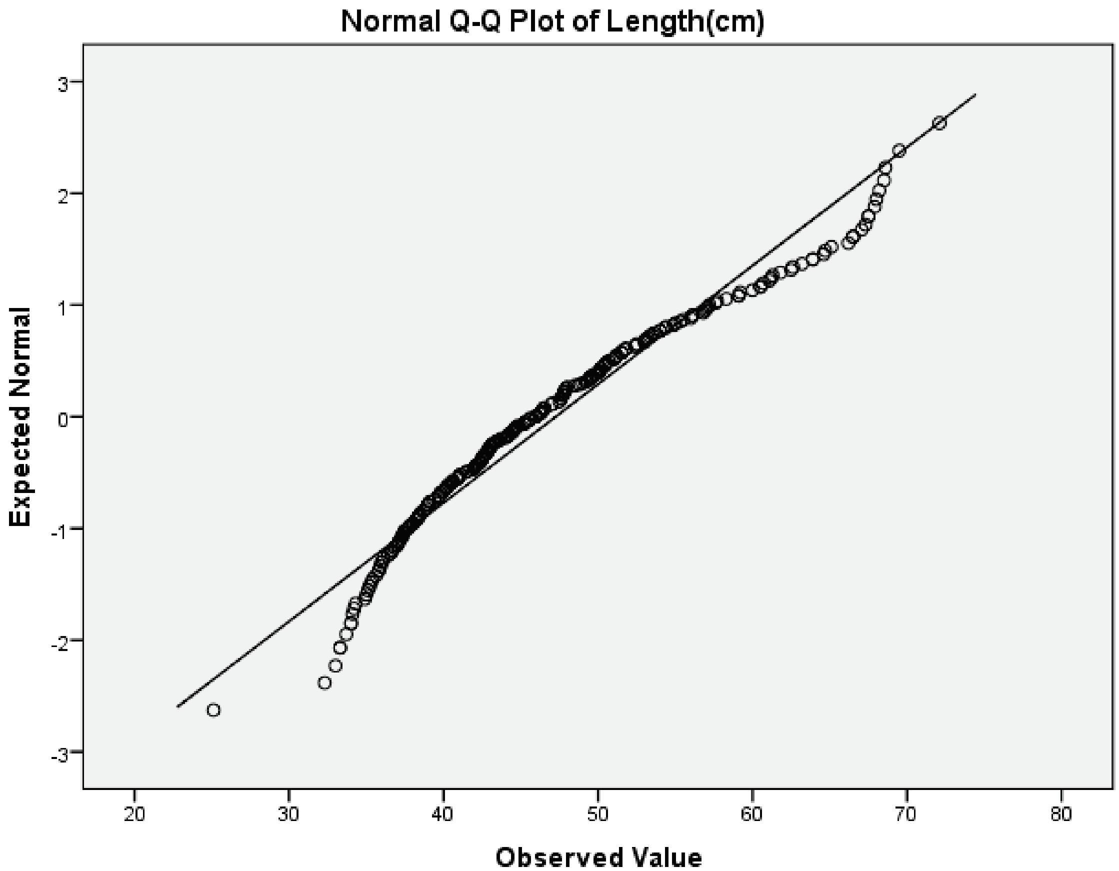


Figure 8-12 Length of walleye, raw. This plot was used to decide to use un-transformed length.

8.2 Box plots for determining outliers

Species

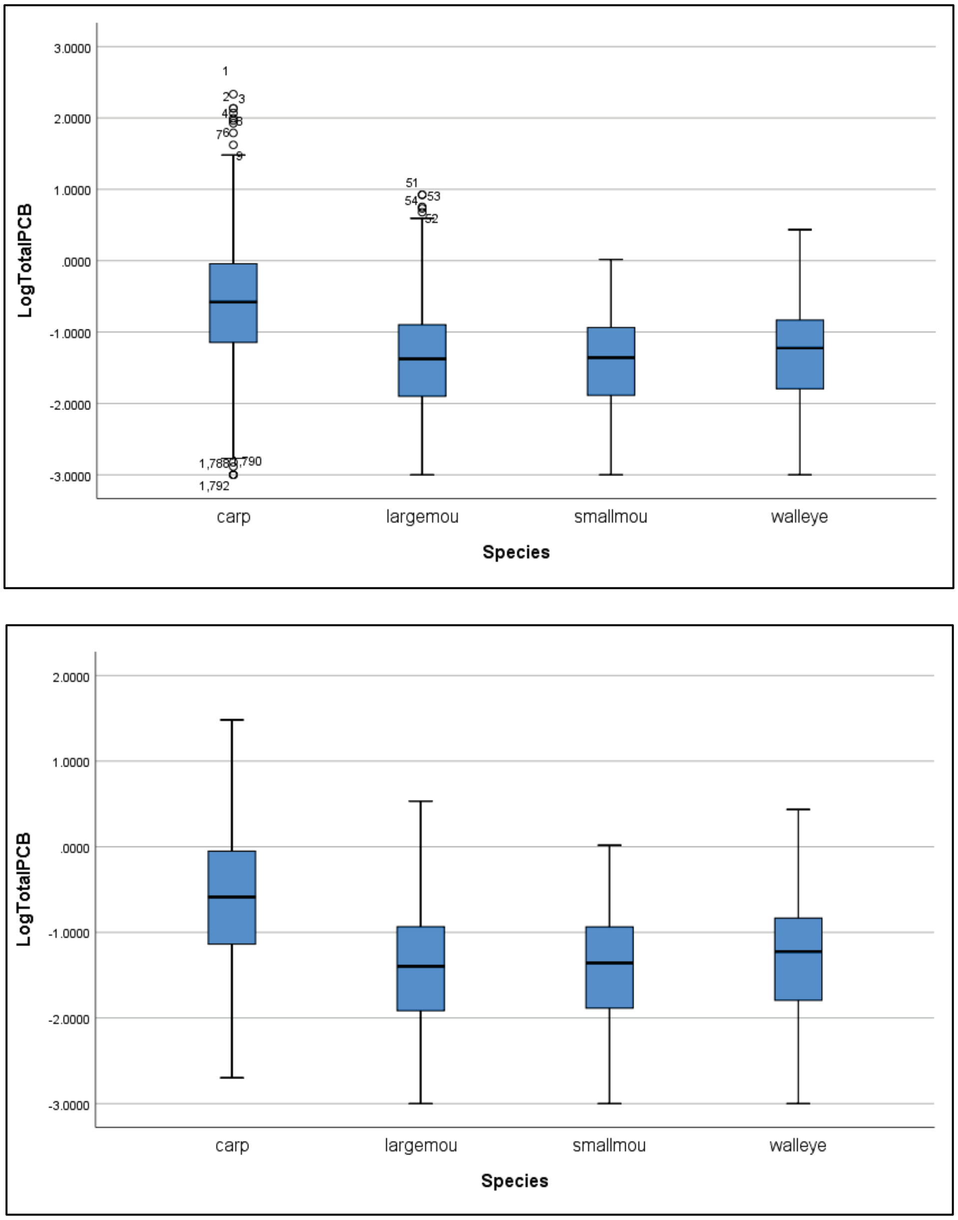
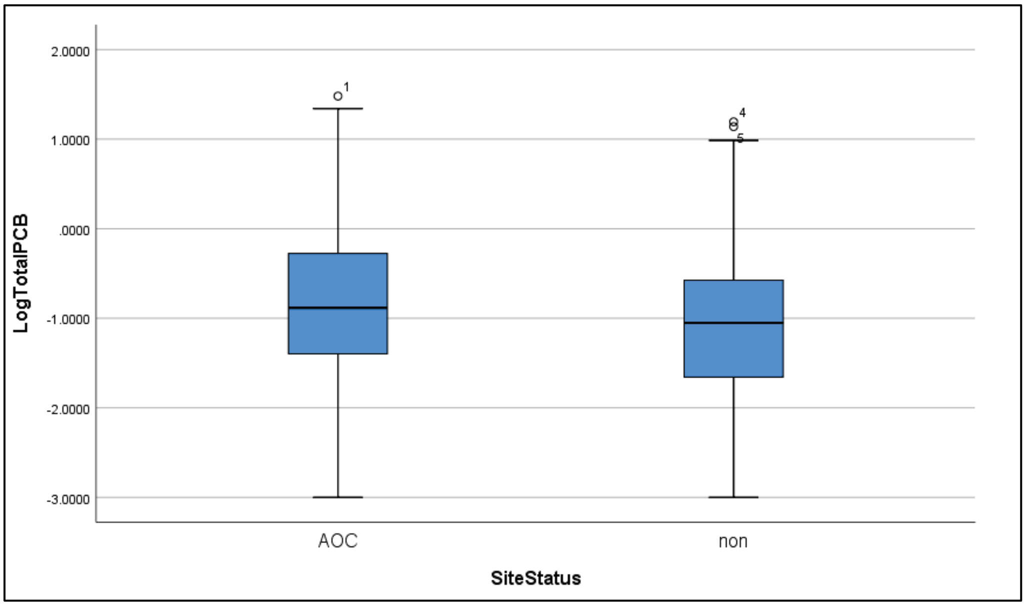


Figure 8-13 Box plots of log total PCB concentrations of fish of each species. All the data is included (top) and outliers removed (bottom).

Site status



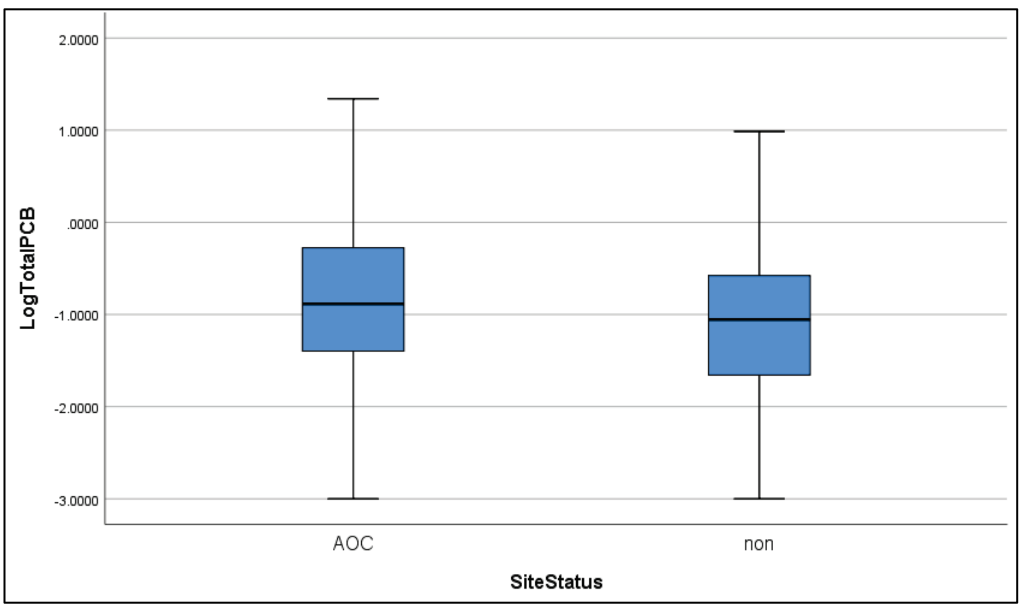
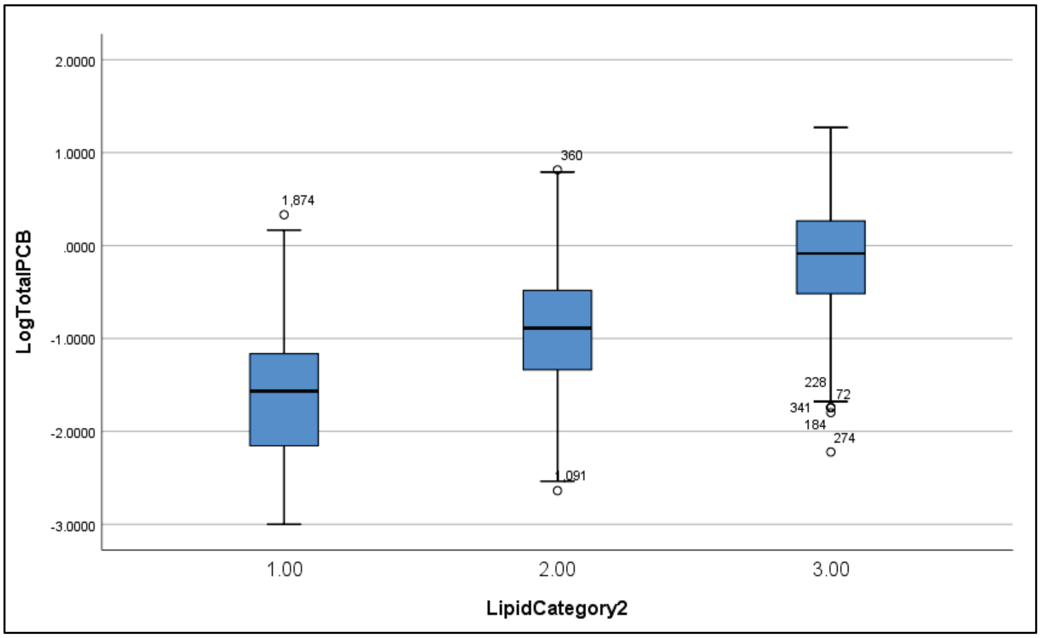


Figure 8-14 Box plots of log total PCB concentrations of the fish at each type of site. All the data is included (top) and outliers removed (bottom).

Lipid



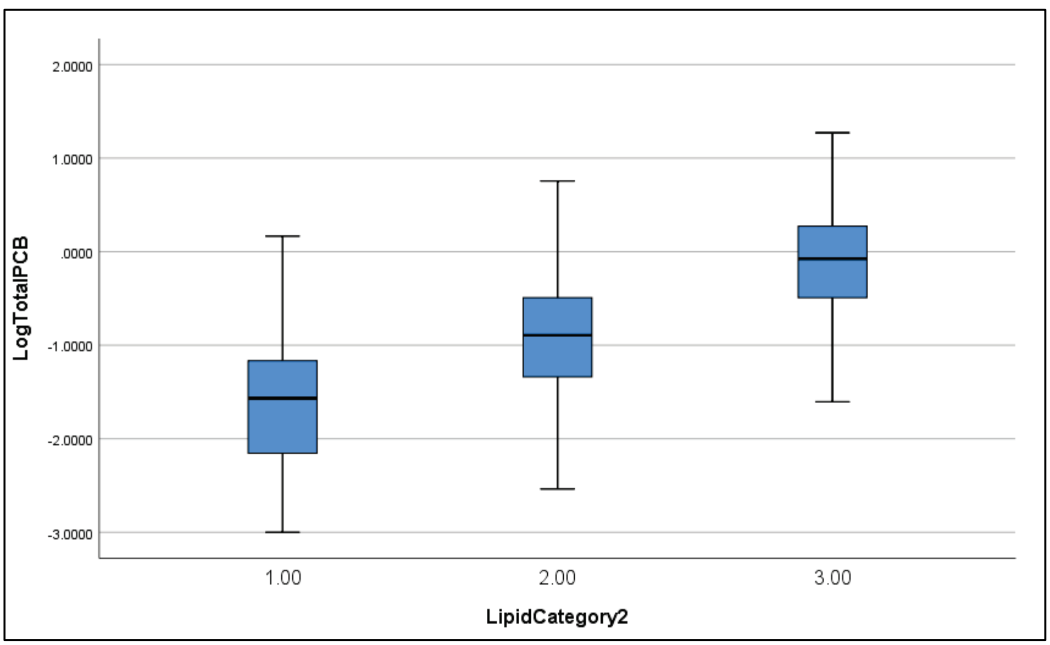


Figure 8-15 Box plots of log total PCB concentrations of the fish in each lipid category. All the data is included (top) and outliers removed (bottom).

Length

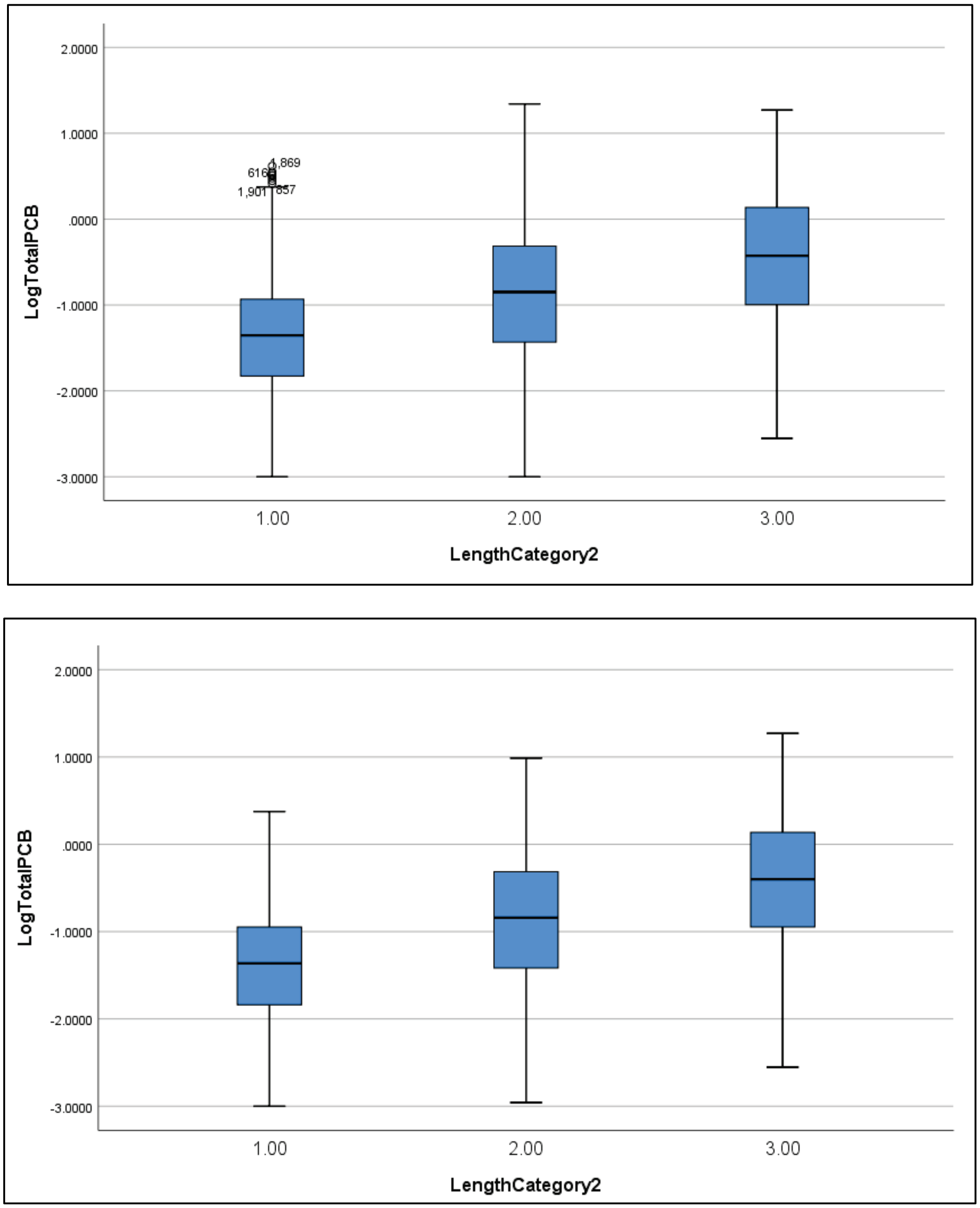
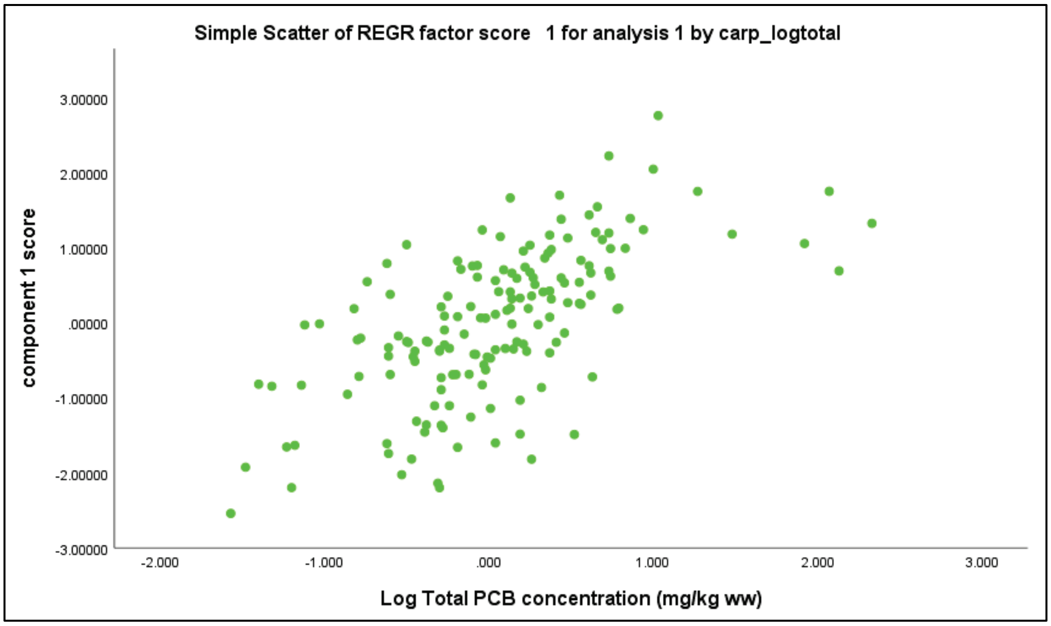


Figure 8-16 Box plots of log total PCB concentrations of the fish in each length category. All the data is included (top) and outliers removed (bottom).

9 Appendix: additional results

9.1 Species total v component plots



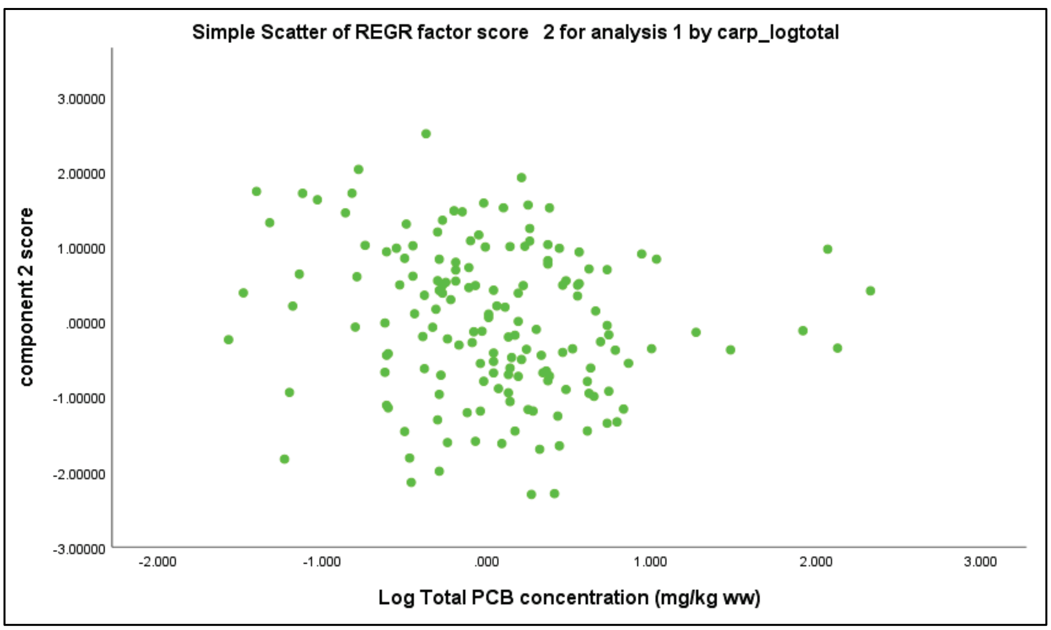


Figure 9-1 Carp PCB concentration versus component 1 score (top) and component 2 (bottom). The weak linear relationship between total PCB concentration and the component score indicates that carp concentrations are not well explained by either component.

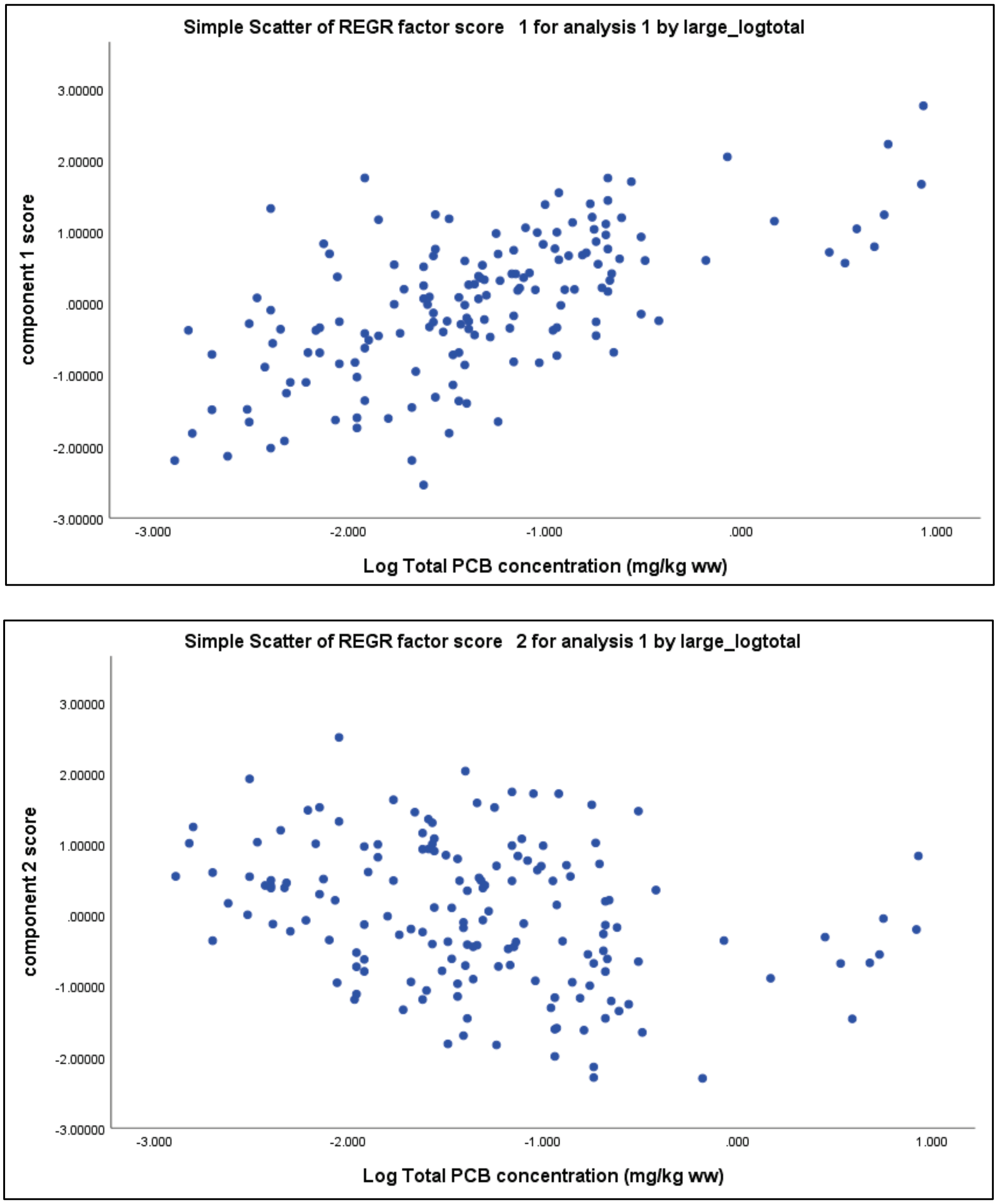


Figure 9-2 Largemouth bass PCB concentration versus component 1 score (top) and component 2 (bottom). The weak linear relationship between total PCB concentration and the component score indicates that carp concentrations are not well explained by either component.

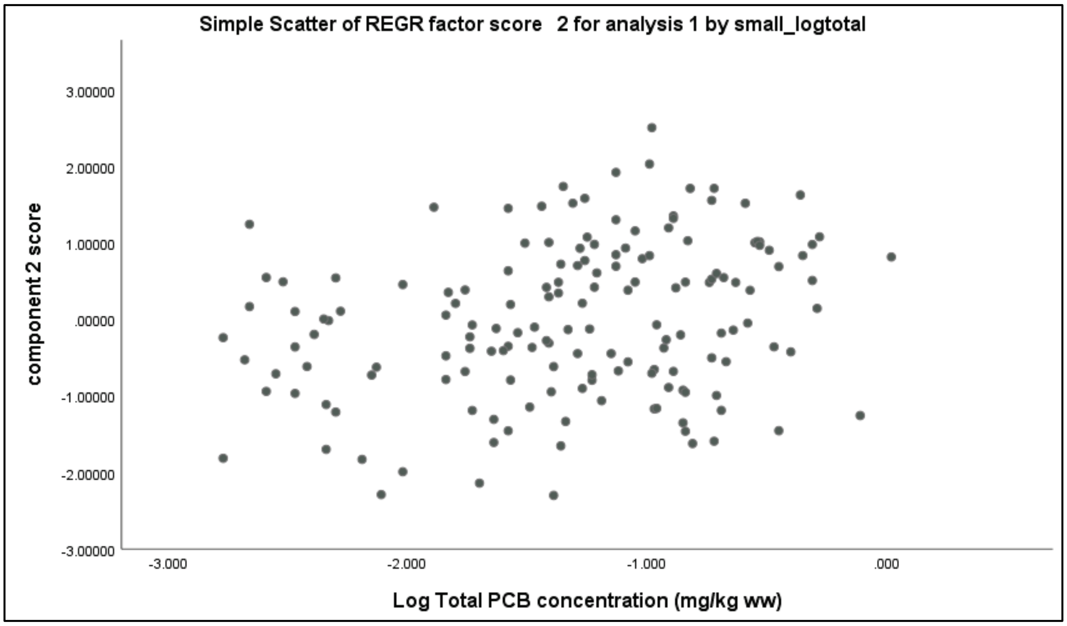


Figure 9-3 Smallmouth bass PCB concentration versus component 2 score. The weak linear relationship between total PCB concentration and the component score indicates that carp concentrations are not well explained by either component.

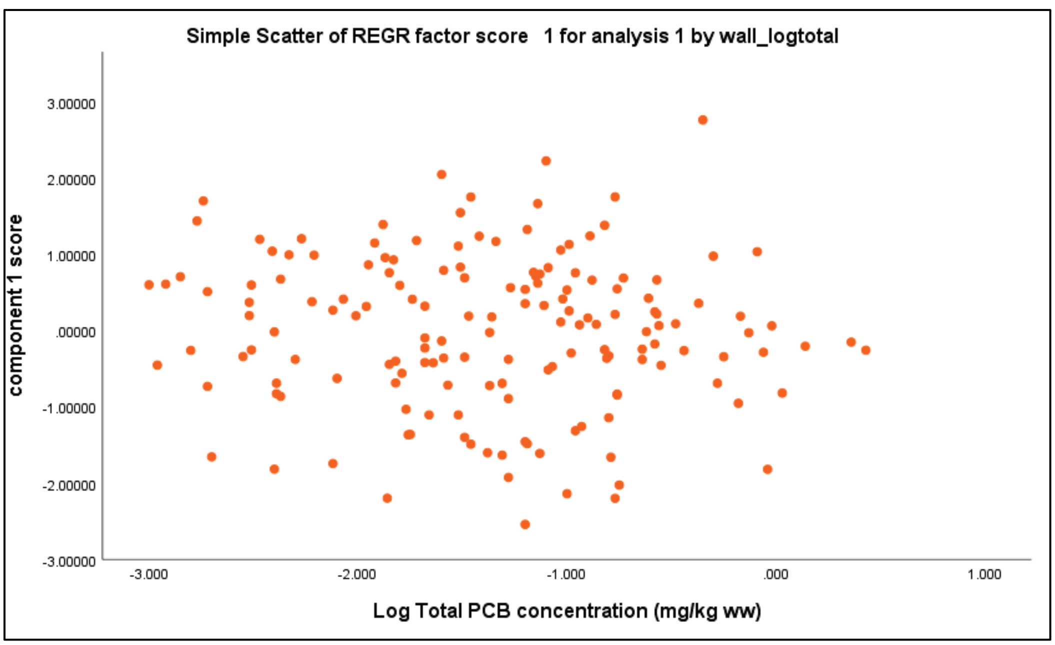


Figure 9-4 Walleye PCB concentration versus component 1 score. The weak linear relationship between total PCB concentration and the component score indicates that carp concentrations are not well explained by either component.

9.2 T-test results for PCB concentrations in length and lipid categories

Table 9-1 T-test results for comparing Log total PCB concentrations between fish in length category 1 to length category 2.

t-Test: Two-Sample Assuming Unequal Variances		
	Length1	*Length2*
Mean	-1.3936	-0.90954
Variance	0.480001	0.653812
Observations	530	958
Hypothesized Mean Difference	0	
df	1238	
t Stat	-12.1466	
P(T<=t) one-tail	1.86E-32	
t Critical one-tail	1.646085	
P(T<=t) two-tail	3.72E-32	
t Critical two-tail	1.961882	

Table 9-2 T-test results for comparing Log total PCB concentrations between fish in length category 2 to length category 3.

t-Test: Two-Sample Assuming Unequal Variances		
	Length2	*Length3*
Mean	-0.90954	-0.4493
Variance	0.653812	0.582132
Observations	958	280

Hypothesized Mean Difference	0	
df	477	
t Stat	-8.75817	
P(T<=t) one-tail	1.74E-17	
t Critical one-tail	1.648054	
P(T<=t) two-tail	3.47E-17	
t Critical two-tail	1.96495	

Table 9-3 T-test results for comparing Log total PCB concentrations between fish in length category 1 to length category 3.

t-Test: Two-Sample Assuming Unequal Variances		
	Length1	*Length3*
Mean	-1.3936	-0.4493
Variance	0.480001	0.582132
Observations	530	280
Hypothesized Mean Difference	0	
df	523	
t Stat	-17.2846	
P(T<=t) one-tail	1.39E-53	
t Critical one-tail	1.647772	
P(T<=t) two-tail	2.78E-53	
t Critical two-tail	1.96451	

Table 9-4 T-test results for comparing Log total PCB concentrations between fish in lipid category 1 to lipid category 2.

t-Test: Two-Sample Assuming Unequal Variances		
	Lipid1	*Lipid2*
Mean	-1.61289	-0.9224
Variance	0.46178	0.472891
Observations	482	955
Hypothesized Mean Difference	0	
df	975	
t Stat	-18.1128	
P(T<=t) one-tail	9.92E-64	
t Critical one-tail	1.646418	
P(T<=t) two-tail	1.98E-63	
t Critical two-tail	1.9624	

Table 9-5 T-test results for comparing Log total PCB concentrations between fish in lipid category 2 to lipid category 3.

t-Test: Two-Sample Assuming Unequal Variances		
	Lipid2	*Lipid3*
Mean	-0.9224	-0.21502
Variance	0.472891	0.459845
Observations	955	327
Hypothesized Mean Difference	0	

df	572	
t Stat	-16.2225	
P(T<=t) one-tail	2.88E-49	
t Critical one-tail	1.647522	
P(T<=t) two-tail	5.76E-49	
t Critical two-tail	1.96412	

Table 9-6 T-test results for comparing Log total PCB concentrations between fish in lipid category 1 to lipid category 3.

t-Test: Two-Sample Assuming Unequal Variances		
	Lipid1	*Lipid3*
Mean	-1.61289	-0.21502
Variance	0.46178	0.459845
Observations	482	327
Hypothesized Mean Difference	0	
df	701	
t Stat	-28.7485	
P(T<=t) one-tail	5.6E-121	
t Critical one-tail	1.64703	
P(T<=t) two-tail	1.1E-120	
t Critical two-tail	1.963354	

9.3 Tables with congener-component scores from local or atmospherically impacted sourcing PCA

Table 9-7 Component scores for individual congeners from the PCA used to evaluate whether carp in waterbodies were receiving local or atmospheric sources of PCBs. For the table to fit in the margins, component was shortened to comp.

CARP	Minimum Eigenvalue is 1					Only 2 factors allowed	
congener	comp 1	comp 2	comp 3	comp 4	comp 5	comp 1	comp 2
c1	-0.28632	-0.62363	-0.35967	-0.27629	-0.18779	-0.42997	-0.60659
c3	-0.28632	-0.62363	-0.35967	-0.27629	-0.18779	-0.42997	-0.60659
c0508	-0.26436	-0.59198	-0.37143	-0.32238	-0.19257	-0.44393	-0.56655
c6	-0.27995	-0.61445	-0.36308	-0.28966	-0.18918	-0.43402	-0.59497
c0709	-0.28632	-0.62363	-0.35967	-0.27629	-0.18779	-0.42997	-0.60659
c8	-0.28632	-0.62363	-0.35967	-0.27629	-0.18779	-0.42997	-0.60659
c11	-0.28632	-0.62363	-0.35967	-0.27629	-0.18779	-0.42997	-0.60659
c1127	-0.28632	-0.62363	-0.35967	-0.27629	-0.18779	-0.42997	-0.60659
c1517	-0.21848	-0.52586	-0.396	-0.41868	-0.20255	-0.4731	-0.48287
c1632	-1.69087	1.6129	0.23038	1.02059	-0.72466	-0.98379	0.74745

c17	-1.07501	1.41256	0.01933	-0.06986	0.51067	-0.98191	0.99215
c18	-1.04051	1.53536	-0.09393	0.38832	0.29045	-0.85803	1.09329
c22	-0.56658	0.24164	-0.17537	-0.0468	0.01247	-0.55996	0.06979
c25	-0.65918	0.41272	-0.19542	-0.45298	1.70494	-0.72151	0.40278
c26	-0.85596	1.23929	-0.14577	0.14614	0.3038	-0.80504	0.90539
c27	-0.28632	-0.62363	-0.35967	-0.27629	-0.18779	-0.42997	-0.60659
c28	-1.4063	3.21368	0.40915	-0.18884	1.84311	-1.2516	2.60929
c31	-1.20357	2.18353	0.37596	0.12224	0.38699	-0.93439	1.56601
c32	-0.36494	-0.0978	-1.45751	-0.90723	8.0931	-0.8549	0.99195
c33	-0.58018	0.13428	-0.19203	-0.05715	0.59136	-0.5295	0.03389
c3742	-0.61579	1.8324	0.1263	-0.1374	-0.26373	-0.72981	1.42738
c40	-0.47017	0.14645	-0.36333	-0.18782	0.41088	-0.60459	0.10017
c4171	-0.15262	-0.43093	-0.43126	-0.5569	-0.21687	-0.51497	-0.36277
c44	-0.39153	2.70709	-0.0006	0.00546	-0.54209	-0.71839	2.29066

c45	-0.45467	0.00498	-0.48153	-0.01993	0.37874	-0.56606	-0.01278
c46	-0.27403	-0.60592	-0.36625	-0.30208	-0.19047	-0.43778	-0.58418
c47	-0.88323	2.84971	0.4017	0.03224	-0.32418	-0.86742	2.20412
c48	-0.53126	-0.17526	-0.48729	0.46452	-0.27964	-0.44122	-0.29576
c49	-0.1607	3.78871	0.04531	-0.26059	-0.07081	-0.76387	3.41302
c52	0.25074	4.05779	-0.39985	0.07422	-0.58609	-0.62621	3.8097
c5660	0.35026	0.7258	-0.8922	0.32076	-0.68361	-0.2215	0.86191
c63	-0.19	-0.195	-0.39238	-0.29043	-0.06157	-0.43688	-0.16119
c64	-0.19796	1.37125	-0.17801	-0.28468	-0.16039	-0.56657	1.21939
c6695	2.41136	2.73444	-1.1823	0.21036	-0.62667	0.80324	3.45369
c70	0.56639	0.85806	-0.59811	-0.15773	-0.47512	-0.11503	1.04305
c7076	-0.20832	-0.51121	-0.40144	-0.44001	-0.20476	-0.47956	-0.46434
c71	-0.54414	0.79145	-0.03674	-0.327	0.35956	-0.64617	0.60504
c74	0.4997	1.14134	-0.1254	-0.68974	-0.42244	-0.17832	1.2199

c77	-0.28359	-0.61567	-0.36726	-0.25789	-0.19792	-0.4261	-0.59886
c77110	4.91647	0.81418	-1.90979	0.65157	-0.13494	2.76196	2.69964
c81	-0.27981	-0.61878	-0.35811	-0.28463	-0.19061	-0.42873	-0.60022
c8187	-0.28632	-0.62363	-0.35967	-0.27629	-0.18779	-0.42997	-0.60659
c82	-0.08065	-0.07478	-0.12977	-0.31947	-0.52796	-0.28123	-0.11434
c83	-0.28632	-0.62363	-0.35967	-0.27629	-0.18779	-0.42997	-0.60659
c84	0.21939	0.04712	-1.11049	0.45161	0.13096	-0.22336	0.32143
c8492	-0.17051	-0.45672	-0.42168	-0.51935	-0.21298	-0.5036	-0.3954
c87	1.36391	0.22651	0.95564	-2.59563	-0.02418	0.38562	0.5915
c90101	3.37614	0.55277	-0.41898	0.43556	-0.05681	2.355	1.68297
c91	-0.01323	0.15848	-0.34031	-0.02769	-0.36139	-0.24327	0.16712
c92	0.44555	0.00708	-0.84067	0.37229	-0.51652	0.01274	0.24131
c97	0.95348	0.03719	-0.3584	-0.50509	-0.23132	0.2854	0.41614
c99	2.46532	0.22663	-0.31513	-0.70767	-0.14853	1.31027	1.10211

c100	-0.4214	-0.37588	-0.20079	-0.09656	-0.12443	-0.40522	-0.45569
c101	0.076	-0.1014	-0.55369	-1.03678	-0.26659	-0.66033	0.05418
c105	1.11907	-0.17049	-0.07319	-0.75636	-0.23867	0.4801	0.23704
c114	-0.0289	-0.68184	-1.12899	0.48773	-0.32588	-0.32247	-0.47708
c118	3.65756	0.20482	0.21933	-1.46335	-0.1008	2.15421	1.41558
c123	-0.17159	-0.52224	-0.33864	-0.39233	-0.26775	-0.40302	-0.48317
c123149	-0.77289	-0.33462	-3.04053	7.2382	-0.137	0.89662	-0.32085
c126	-0.28489	-0.62175	-0.36088	-0.27142	-0.19042	-0.42798	-0.60467
c126178	-0.21115	-0.35936	0.48307	0.16607	-0.19734	0.2028	-0.52016
c128	0.59243	-0.64994	0.00949	-0.21655	-0.12596	0.43731	-0.40456
c130	0.14436	-0.40281	-0.31987	0.2118	-0.38585	0.06273	-0.3119
c132	-0.00606	-0.32931	0.72077	0.4175	-0.40704	0.56159	-0.50367
c134	-0.28632	-0.62363	-0.35967	-0.27629	-0.18779	-0.42997	-0.60659
c135144	0.14534	-0.33469	-0.30121	0.50304	-0.49022	0.17661	-0.277

c136	-0.20239	0.05329	1.03848	-0.25651	-0.96341	0.21061	-0.30985
c137	0.41072	-0.59125	-0.43153	-0.39205	-0.25814	-0.01296	-0.33413
c137176	-0.28632	-0.62363	-0.35967	-0.27629	-0.18779	-0.42997	-0.60659
c138163	3.80528	-0.41021	1.98414	1.9552	0.51407	4.71475	0.48214
c141	0.17018	-0.61151	0.47567	0.37997	-0.11242	0.60959	-0.62316
c146	0.15296	-0.82916	0.47206	-0.40051	4.59707	0.60983	-0.2776
c149	0.70779	-0.27205	1.9627	-2.03952	0.07937	0.73328	-0.28797
c151	-0.093	-0.38285	0.10908	1.06291	-0.15147	0.47362	-0.46597
c153	2.61052	-0.37433	3.56297	2.98565	1.986	5.16813	-0.06651
c156	0.16277	-0.56034	0.12546	-0.36965	-0.19429	0.10113	-0.48804
c157	-0.20073	-0.62911	-0.36253	-0.26555	-0.17097	-0.36234	-0.58125
c157200	-0.32594	-0.55646	-0.56913	0.34532	-0.29071	-0.32673	-0.55717
c158	0.24805	-0.4511	1.24646	-1.11692	-0.00251	0.42912	-0.51853
c158160	-0.28632	-0.62363	-0.35967	-0.27629	-0.18779	-0.42997	-0.60659

c167	-0.03386	-0.58086	-0.18647	-0.03229	-0.21769	-0.06297	-0.53043
c169	-0.24237	-0.64192	-0.45802	-0.21022	-0.20416	-0.41951	-0.59477
c170	-0.11179	-0.40339	1.57049	0.76326	0.00446	1.10242	-0.73834
c170190	-0.24641	-0.56611	-0.38104	-0.36006	-0.19647	-0.45534	-0.53381
c171	-0.32311	-0.4393	0.13603	0.31759	-0.20278	0.01582	-0.57198
c171202	-0.27172	-0.60259	-0.36749	-0.30693	-0.19097	-0.43925	-0.57997
c172	-0.25523	-0.55863	0.17855	-0.03109	-0.17459	-0.03715	-0.64833
c174	-0.29199	-0.42437	0.75147	0.68805	-0.1239	0.51182	-0.67261
c175	-0.33502	-0.54367	-0.16696	-0.19874	-0.2119	-0.34764	-0.59219
c177	-0.24939	-0.51764	0.60265	0.64105	-0.16078	0.45826	-0.71759
c178	-0.27456	-0.60668	-0.36597	-0.30098	-0.19035	-0.43745	-0.58514
c179	-0.26693	-0.47872	-0.14727	0.30913	-0.1946	-0.08618	-0.53434
c180	-0.366	-0.12807	4.70479	1.80732	0.42002	2.94927	-1.16666
c182187	-0.81665	-0.00793	2.87205	2.76152	0.16987	2.03445	-0.9278

c183	-0.27924	-0.46626	0.73575	0.57562	-0.08238	0.47547	-0.69426
c185	-0.31967	-0.53802	-0.0999	-0.1274	-0.20496	-0.27273	-0.59705
c189	-0.29913	-0.6039	-0.38501	-0.14118	-0.19104	-0.39972	-0.59428
c190	-0.3171	-0.53193	-0.29816	-0.09736	-0.18676	-0.36034	-0.55228
c193	-0.30156	-0.58037	-0.0084	-0.02646	-0.16805	-0.16196	-0.64763
c194	-0.39852	-0.51937	0.85095	0.22229	-0.10647	0.30765	-0.79147
c195	-0.3204	-0.50132	0.25219	-0.08026	-0.18713	-0.07655	-0.63067
c195208	-0.28112	-0.61615	-0.36245	-0.28719	-0.18892	-0.43327	-0.59712
c196203	-0.58814	-0.28657	1.70319	-0.23497	-0.43414	0.36349	-0.81877
c198	-0.2977	-0.60812	-0.31198	-0.19695	-0.19467	-0.38368	-0.60948
c199	-0.33125	-0.54913	-0.46773	0.33637	-0.16628	-0.27507	-0.55746
c201	-0.98143	0.31625	3.95137	-1.557	-1.34283	0.54015	-0.86531
c205	-0.25782	-0.61151	-0.33203	-0.2825	-0.18978	-0.3993	-0.59121
c206	-0.21462	-0.56365	-0.2762	-0.14392	-0.19964	-0.28927	-0.55081

c207	-0.28619	-0.6129	-0.37304	-0.24117	-0.20071	-0.42468	-0.59714

Table 9-8 Component scores for individual congeners from the PCA used to evaluate whether smallmouth bass in waterbodies were receiving local or atmospheric sources of PCBs.

SMALLMOUTH	Minimum Eigen value is 1	
	component 1	component 2
c1	-0.34147	-0.60125
c3	-0.34147	-0.60125
c0508	-0.34147	-0.60125
c6	-0.34147	-0.60125
c0709	-0.34147	-0.60125
c8	-0.34147	-0.60125
c11	-0.34147	-0.60125
c1127	-0.34147	-0.60125
c1517	-0.34147	-0.60125
c1632	-0.37427	-0.18411
c17	-0.39418	-0.00259
c18	-0.47411	-0.08169
c22	-0.36717	-0.41287
c25	-0.52789	0.01715
c26	-0.68438	0.49493
c27	-0.34147	-0.60125
c28	-1.2058	1.84075
c31	-0.74591	0.74256

c32	-0.40821	-0.38852
c33	-0.44929	-0.17646
c3742	-0.85765	1.01123
c40	-0.40351	-0.3408
c4171	-0.34147	-0.60125
c44	-0.6056	1.03487
c45	-0.36534	-0.54543
c46	-0.34147	-0.60125
c47	-0.79028	1.69003
c48	-0.19647	-0.43934
c49	-1.23268	2.75889
c52	-1.00223	3.17783
c5660	-0.78288	1.23168
c63	-0.52189	-0.08046
c64	-0.74574	0.875
c6695	-0.76223	4.37277
c70	-0.96131	1.69687
c7076	-0.34147	-0.60125
c71	-0.42552	-0.05969
c74	-0.95793	1.71091
c77	-0.34027	-0.59851
c77110	1.75182	4.04823
c81	-0.34137	-0.60103

c8187	-0.34147	-0.60125
c82	-0.20553	-0.26364
c83	-0.34147	-0.60125
c84	-0.34171	0.21245
c8492	-0.34147	-0.60125
c87	-0.11125	0.42068
c90101	1.5968	2.56692
c91	-0.43214	0.29993
c92	-0.4705	0.65614
c97	-0.13801	0.50486
c99	0.62802	1.90224
c100	-0.29171	-0.52622
c101	-0.34147	-0.60125
c105	0.16697	0.69751
c114	-0.29651	-0.34592
c118	1.09513	2.25425
c123	-0.33895	-0.5955
c123149	1.40013	-0.20771
c126	-0.34112	-0.60046
c126178	-0.00483	0.11543
c128	0.3956	-0.12304
c130	-0.06244	-0.25458
c132	0.34149	-0.23028

c134	-0.34147	-0.60125
c135144	-0.01697	0.07752
c136	0.03041	-0.15424
c137	-0.12793	-0.22508
c137176	-0.34147	-0.60125
c138163	5.05133	0.72614
c141	0.82102	-0.51862
c146	0.79361	-0.12379
c149	0.15337	0.02714
c151	0.55988	-0.2579
c153	5.44513	0.39227
c156	0.10481	-0.3653
c157	-0.2369	-0.59195
c157200	-0.35649	-0.48771
c158	0.11101	-0.30169
c158160	-0.34147	-0.60125
c167	-0.30555	-0.21099
c169	-0.31362	-0.56413
c170	1.40695	-0.59682
c170190	-0.34147	-0.60125
c171	0.10987	-0.47821
c171202	-0.34147	-0.60125
c172	-0.01854	-0.39195

c174	1.3025	-0.68196
c175	-0.28976	-0.55328
c177	0.59292	-0.45304
c178	-0.34147	-0.60125
c179	0.04684	-0.51771
c180	3.51618	-0.77492
c182187	2.53183	-0.54328
c183	0.83746	-0.59348
c185	-0.21167	-0.52989
c189	-0.32344	-0.59077
c190	-0.2335	-0.44307
c193	-0.04291	-0.56692
c194	0.41882	-0.45568
c195	0.03413	-0.56248
c195208	-0.34147	-0.60125
c196203	0.25884	-0.38479
c198	-0.32304	-0.55233
c199	-0.21467	-0.51989
c201	0.60091	-0.47073
c205	-0.29777	-0.57698
c206	-0.29377	-0.44656
c207	-0.34329	-0.58221

Table 9-9 Component scores for individual congeners from the PCA used to evaluate whether largemouth bass in waterbodies were receiving local or atmospheric sources of PCBs.

LARGEMOUTH	Minimum Eigenvalue is 1			Only 2 factors allowed	
	component 1	component 2	component 3	component 1	component 2
c1	-0.5154	-0.52094	-0.00586	-0.43826	-0.58464
c3	-0.5154	-0.52094	-0.00586	-0.43826	-0.58464
c0508	-0.5154	-0.52094	-0.00586	-0.43826	-0.58464
c6	-0.5154	-0.52094	-0.00586	-0.43826	-0.58464
c0709	-0.5154	-0.52094	-0.00586	-0.43826	-0.58464
c8	-0.5154	-0.52094	-0.00586	-0.43826	-0.58464
c11	-0.5154	-0.52094	-0.00586	-0.43826	-0.58464
c1127	-0.5154	-0.52094	-0.00586	-0.43826	-0.58464
c1517	-0.5154	-0.52094	-0.00586	-0.43826	-0.58464
c1632	-1.62719	3.10288	1.08353	-1.42947	2.6187
c17	-1.31676	2.58303	0.82166	-1.18192	2.19811
c18	-0.92565	2.23664	0.80987	-0.78911	1.92001
c22	-0.61797	0.49319	0.2739	-0.52896	0.34683
c25	-0.87072	1.25829	0.23574	-0.84639	1.0622
c26	-0.90043	1.8377	0.1667	-0.94908	1.63431
c27	-0.5154	-0.52094	-0.00586	-0.43826	-0.58464
c28	-0.51455	4.17982	-0.08291	-0.88053	4.01776
c31	-0.87366	3.31605	0.38998	-0.9791	3.04715
c32	-0.30419	-0.29736	-0.2162	-0.33198	-0.30208

c33	-0.55458	0.78254	0.39429	-0.4543	0.62009
c3742	-0.3023	0.76186	-0.41539	-0.49195	0.76353
c40	-0.47049	-0.01877	0.07472	-0.41331	-0.10011
c4171	-0.5154	-0.52094	-0.00586	-0.43826	-0.58464
c44	-0.10351	1.94151	-0.37252	-0.39588	1.93843
c45	-0.81193	0.57171	0.36784	-0.68551	0.37996
c46	-0.5154	-0.52094	-0.00586	-0.43826	-0.58464
c47	0.03916	1.93108	-0.53023	-0.31508	1.97406
c48	-0.50748	0.14661	0.2275	-0.4106	0.03209
c49	0.8323	2.87243	-1.04023	0.17026	3.09091
c52	1.12544	3.28558	-1.2048	0.352	3.56367
c5660	-0.16064	0.48224	-0.35663	-0.31454	0.50246
c63	-0.47175	-0.30577	-0.04311	-0.42915	-0.36222
c64	0.10599	0.9256	-0.34087	-0.09891	0.9727
c6695	2.64593	1.69152	-1.9115	1.67608	2.34378
c70	0.26968	1.39592	-0.60986	-0.07895	1.49823
c7076	-0.5154	-0.52094	-0.00586	-0.43826	-0.58464
c71	-0.55849	0.3517	-0.07629	-0.57995	0.27203
c74	0.33537	0.53823	-0.68253	0.03385	0.6818
c77	-0.5154	-0.52094	-0.00586	-0.43826	-0.58464
c77110	4.29692	0.47807	-2.05109	3.28162	1.42674
c81	-0.5154	-0.52094	-0.00586	-0.43826	-0.58464
c8187	-0.5154	-0.52094	-0.00586	-0.43826	-0.58464

c82	-0.26582	-0.37614	-0.10717	-0.25195	-0.39026
c83	-0.5154	-0.52094	-0.00586	-0.43826	-0.58464
c84	-0.26663	-0.23634	-0.09858	-0.26219	-0.2552
c8492	-0.5154	-0.52094	-0.00586	-0.43826	-0.58464
c87	0.26152	-0.38241	-0.28097	0.18307	-0.2907
c90101	3.14733	-0.13375	-0.98972	2.62109	0.49271
c91	-0.16108	-0.15602	-0.21949	-0.21167	-0.14221
c92	0.18484	-0.09031	-0.34757	0.06271	-0.00653
c97	0.57025	-0.33665	-0.42117	0.42027	-0.17817
c99	1.71072	-0.05326	-0.89698	1.30073	0.34267
c100	-0.50158	-0.42502	0.08657	-0.40236	-0.50329
c101	-0.5154	-0.52094	-0.00586	-0.43826	-0.58464
c105	0.78571	-0.4124	-0.44915	0.61915	-0.21565
c114	-0.47969	-0.4791	0.03379	-0.39504	-0.54463
c118	1.95545	-0.01441	-0.6151	1.62234	0.37323
c123	-0.5154	-0.52094	-0.00586	-0.43826	-0.58464
c123149	1.03458	-0.43277	-0.00644	1.00464	-0.26733
c126	-0.5154	-0.52094	-0.00586	-0.43826	-0.58464
c126178	-0.1615	-0.47999	0.06094	-0.08786	-0.50227
c128	0.58149	-0.54197	-0.20676	0.52199	-0.41035
c130	0.08836	-0.50345	-0.14555	0.0778	-0.45579
c132	0.31077	-0.4439	-0.25268	0.24425	-0.3478
c134	-0.5154	-0.52094	-0.00586	-0.43826	-0.58464

c135144	-0.13249	-0.36752	-0.05918	-0.11157	-0.36943
c136	-0.36572	-0.42575	0.00034	-0.30447	-0.47033
c137	0.0103	-0.51207	-0.20557	-0.01494	-0.46651
c137176	-0.5154	-0.52094	-0.00586	-0.43826	-0.58464
c138163	4.76837	-0.35101	-0.06269	4.47336	0.37798
c141	0.82223	-0.54347	-0.04111	0.80387	-0.4017
c146	0.88954	-0.49727	-0.06437	0.85487	-0.34293
c149	0.7026	-0.71266	0.1564	0.77413	-0.61549
c151	0.55241	-0.32878	0.00125	0.54668	-0.23888
c153	2.81411	0.45282	9.43972	5.80763	-0.60737
c156	0.00786	-0.51015	-0.1486	0.002	-0.47386
c157	-0.4475	-0.50404	-0.04739	-0.39033	-0.55154
c157200	-0.49895	-0.51978	0.06424	-0.3991	-0.59196
c158	0.17288	-0.54175	0.00118	0.21027	-0.50342
c158160	-0.5154	-0.52094	-0.00586	-0.43826	-0.58464
c167	-0.21744	-0.4962	-0.09163	-0.19074	-0.5027
c169	-0.51655	-0.51793	-0.00468	-0.4392	-0.58204
c170	0.77603	-0.41796	0.14362	0.81238	-0.31478
c170190	-0.5154	-0.52094	-0.00586	-0.43826	-0.58464
c171	-0.10081	-0.45208	-0.06598	-0.07674	-0.44622
c171202	-0.5154	-0.52094	-0.00586	-0.43826	-0.58464
c172	-0.26003	-0.47363	-0.05517	-0.22019	-0.49268
c174	0.43303	-0.53465	-0.06949	0.4291	-0.4467

c175	-0.47573	-0.52857	0.02	-0.39164	-0.59019
c177	0.01016	-0.30117	0.06998	0.06004	-0.30346
c178	-0.5154	-0.52094	-0.00586	-0.43826	-0.58464
c179	-0.22179	-0.49722	-0.04794	-0.17984	-0.51115
c180	1.914	-0.15904	0.52941	1.98599	0.04769
c182187	1.36268	-0.09844	0.38557	1.41556	0.04704
c183	0.40875	-0.40711	0.14602	0.46843	-0.35933
c185	-0.41552	-0.49048	0.0023	-0.34469	-0.54127
c189	-0.50357	-0.52186	0.02088	-0.41799	-0.58793
c190	-0.40225	-0.5128	-0.0187	-0.33743	-0.55782
c193	-0.30382	-0.48465	-0.04726	-0.25751	-0.5112
c194	-0.15857	-0.40329	0.09026	-0.08195	-0.43151
c195	-0.29627	-0.48296	-0.03864	-0.24766	-0.50977
c195208	-0.5154	-0.52094	-0.00586	-0.43826	-0.58464
c196203	-0.06484	-0.44774	-0.06761	-0.04401	-0.43637
c198	-0.51011	-0.42543	0.09961	-0.40587	-0.507
c199	-0.36548	-0.53327	-0.02926	-0.30479	-0.57068
c201	-0.0179	-0.36518	0.1049	0.05134	-0.3756
c205	-0.51447	-0.51525	0.00958	-0.43264	-0.58134
c206	-0.46168	-0.50866	-0.00559	-0.38897	-0.56467
c207	-0.5154	-0.52094	-0.00586	-0.43826	-0.58464

Table 9-10 Component scores for individual congeners from the PCA used to evaluate whether walleye in waterbodies were receiving local or atmospheric sources of PCBs.

WALLEYE	Minimum Eigenvalue is 1	
	component 1	component 2
c1	-0.6839	-0.42189
c3	-0.6839	-0.42189
c0508	-0.6839	-0.42189
c6	-0.6839	-0.42189
c0709	-0.6839	-0.42189
c8	-0.6839	-0.42189
c11	-0.6839	-0.42189
c1127	-0.6839	-0.42189
c1517	-0.6839	-0.42189
c1632	-0.59019	7.66158
c17	-0.55335	1.48713
c18	-0.35561	0.02274
c22	-0.58333	1.41464
c25	-0.48262	1.96055
c26	-0.41142	3.41604
c27	-0.6839	-0.42189
c28	-0.03644	2.4464
c31	-0.17627	1.29874
c32	-0.44724	-0.29311

c33	-0.54107	-0.19563
c3742	0.1021	0.84543
c40	-0.53928	-0.35697
c4171	-0.6839	-0.42189
c44	0.30615	0.70607
c45	-0.58372	-0.26533
c46	-0.6839	-0.42189
c47	0.31955	1.40454
c48	-0.48204	0.0906
c49	0.62772	0.85407
c52	0.82499	1.08926
c5660	0.23398	0.33632
c63	-0.4048	0.76676
c64	0.0274	0.1369
c6695	2.23954	1.27922
c70	1.01946	0.44864
c7076	-0.6839	-0.42189
c71	-0.43112	0.52113
c74	0.36743	0.54306
c77	-0.68069	-0.41892
c77110	3.81932	0.5651
c81	-0.68372	-0.42172
c8187	-0.6839	-0.42189

c82	-0.34551	-0.24703
c83	-0.6839	-0.42189
c84	-0.30907	-0.0693
c8492	-0.6839	-0.42189
c87	0.74217	-0.14001
c90101	2.6061	0.14898
c91	-0.15693	-0.16288
c92	0.32743	-0.06284
c97	0.29155	-0.10323
c99	1.96265	-0.36705
c100	-0.57738	-0.13074
c101	-0.6839	-0.42189
c105	0.64378	-0.35752
c114	-0.38221	-0.20818
c118	2.12938	-0.40072
c123	-0.68051	-0.41875
c123149	0.87277	0.77108
c126	-0.68314	-0.42118
c126178	0.26608	-0.36581
c128	0.36673	-0.52975
c130	0.11243	-0.30349
c132	0.25109	-0.09594
c134	-0.6839	-0.42189

c135144	0.08117	-0.07744
c136	0.09672	0.31987
c137	-0.12679	-0.40843
c137176	-0.6839	-0.42189
c138163	4.67059	-0.97307
c141	0.21496	-0.13195
c146	0.63296	-0.53013
c149	0.42996	-0.26435
c151	0.30285	-0.03434
c153	4.39956	-0.63556
c156	-0.18342	-0.39989
c157	-0.51166	-0.51743
c157200	-0.31681	-0.34611
c158	0.30049	-0.48311
c158160	-0.6839	-0.42189
c167	-0.17262	-0.36463
c169	-0.68381	-0.42181
c170	0.51774	-0.40044
c170190	-0.6839	-0.42189
c171	-0.04908	-0.32736
c171202	-0.6839	-0.42189
c172	-0.27854	-0.3784
c174	0.30102	-0.2327

c175	-0.47778	-0.42282
c177	0.12688	-0.18671
c178	-0.6839	-0.42189
c179	-0.18991	-0.31882
c180	1.7924	-0.40353
c182187	1.33695	-0.38484
c183	0.19504	-0.42943
c185	-0.51675	-0.39185
c189	-0.61659	-0.40352
c190	-0.44599	-0.37693
c193	-0.42928	-0.35217
c194	-0.18999	-0.43262
c195	-0.35971	-0.35016
c195208	-0.6839	-0.42189
c196203	0.00044	-0.27901
c198	-0.58184	-0.42166
c199	-0.44355	-0.41252
c201	-0.00547	-0.36862
c205	-0.61773	-0.40485
c206	-0.46025	-0.38157
c207	-0.67071	-0.42456

9.4 Histograms for total PCBs and threshold concentrations

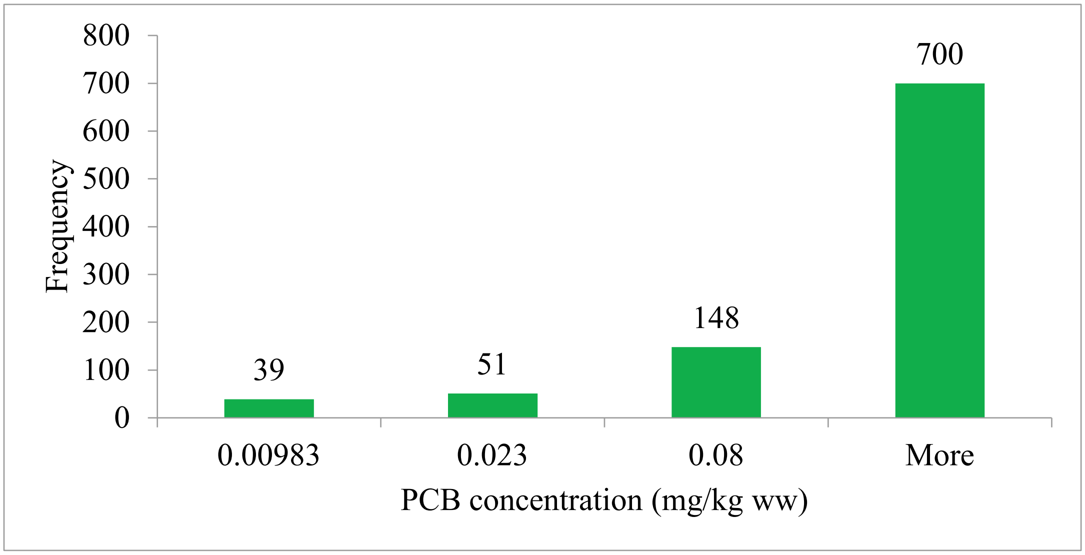


Figure 9-5 Histogram of carp PCB concentrations using the subsistence angler (9.83E-3 mg/kg), Michigan's TMDL (0.023 mg/kg) and recreational angler (0.08 mg/kg) threshold concentrations as the breakpoint.

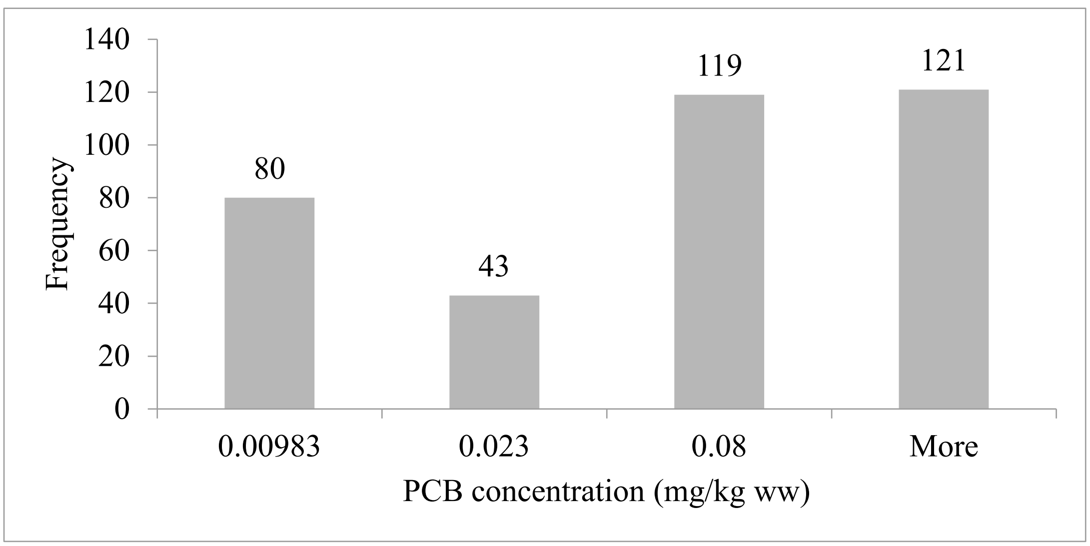


Figure 9-6 Histogram of smallmouth bass PCB concentrations using the subsistence angler (9.83E-3 mg/kg), Michigan's TMDL (0.023 mg/kg) and recreational angler (0.08 mg/kg) threshold concentrations as the breakpoint.

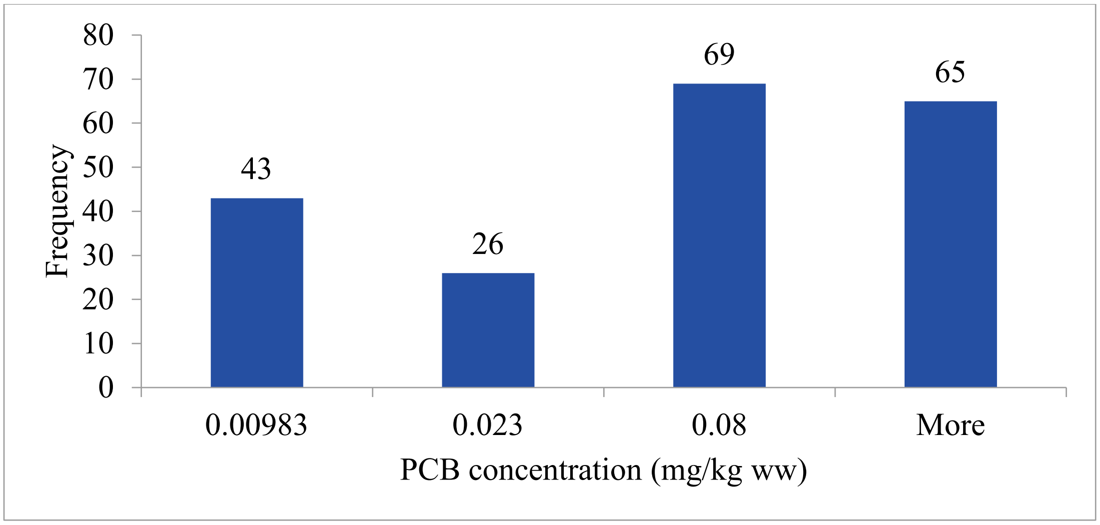


Figure 9-7 Histogram of largemouth bass PCB concentrations using the subsistence angler (9.83E-3 mg/kg), Michigan's TMDL (0.023 mg/kg) and recreational angler (0.08 mg/kg) threshold concentrations as the breakpoint.

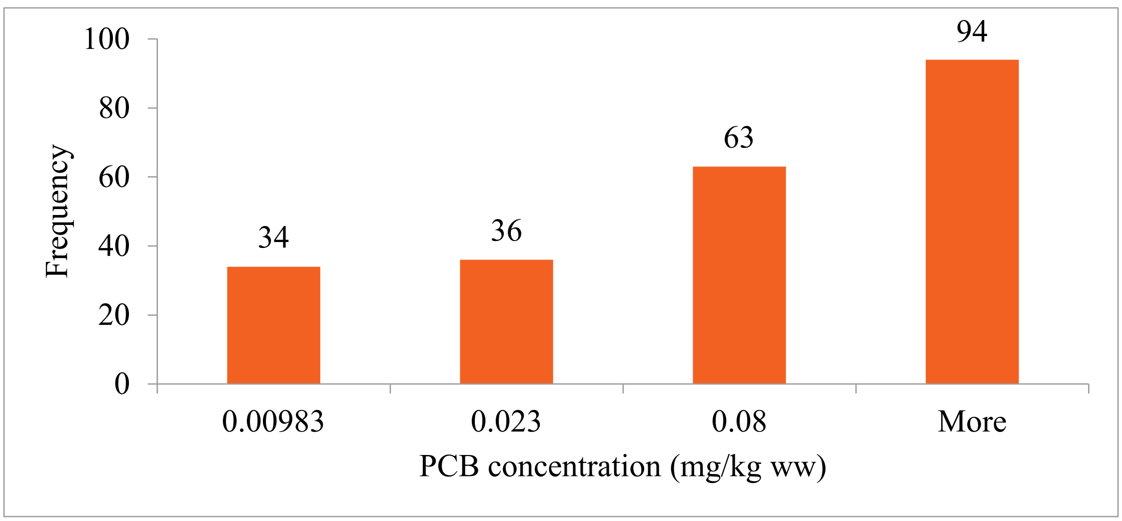


Figure 9-8 Histogram of walleye PCB concentrations using the subsistence angler (9.83E-3 mg/kg), Michigan's TMDL (0.023 mg/kg) and recreational angler (0.08 mg/kg) threshold concentrations as the breakpoint.