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Temporal Trends and Spatial Variabilities of PCB concentrations in Lake Trout from Lake Superior from 1995 to 2013

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TEMPORAL TRENDS AND SPATIAL VARIABILITIES OF PCB
CONCENTRATIONS IN LAKE TROUT FROM LAKE SUPERIOR FROM 1995 TO
2013

By

Hongyi Lin

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Preface

This thesis is original, unpublished work and will be submitted to a journal in the future. I, Hongyi Lin, collected all data and performed all analyses in this study. My advisors, Dr. Noel Urban and Dr. Judith Perlinger made the corrections.

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Receiving the master degree is not the end, but a new start in further academic life.

Abstract

It has been frequently reported that concentrations of PCBs in the Great Lakes fish have declined dramatically since their ban on production and use in 1979 in the United States, although some studies suggested that recent rates of decline are leveling off. In order to examine the temporal trends and spatial variabilities of PCB concentrations in lake trout (*Salvelinus namaycush*) from Lake Superior during the past two decades, statistical analyses were performed on fish sample data collected by two national agencies (U.S. EPA, Environment and Climate Change Canada) and three state agencies (Michigan Department of Environmental Quality, Minnesota Department of Natural Resources, Wisconsin Department of Natural Resources) from both the United States and Canada from 1976 to 2013. Because of a change in PCB analytical methodology in the mid-1990s, intercomparison between data recorded by the previous technique and the improved technique is not feasible.

Because most organochlorine compounds are easily bound to fatty tissues in fish, lipid content has been commonly considered as a predictor of PCB levels. Also, larger fish were assumed to have higher PCBs in their bodies. Multiple linear regression analyses, setting time, lipid content, and fish length as three independent variables, revealed that lipid content had little impact on PCB concentrations at all sites except Whitefish Bay since 1995, which is in contrast to some previous studies. However, a strong positive correlation between PCBs and fish length, in good agreement with previous research, was observed at all sites except Whitefish Bay over the same period.

It has been discovered that PCB concentrations vary among several sampling locations within Lake Superior. The general pattern was that the western sites had significantly higher concentrations than the eastern sites. When the entire historical record was analyzed, temporal trends were evident in all datasets. However, only at Keweenaw Point (U.S. EPA) was significant ($p = 0.0005$) declining trends in total PCB concentrations observed after 1995. In Wisconsin sites, the declining trend was marginal significant ($p = 0.04$) during the same period. In other locations, no temporal trends were found but large annual fluctuations occurred for unknown reasons. PCB concentrations at most sites have not achieved the reduction target of 100 ng/g ww for wildlife and human health protection established by the U.S. EPA. It is still difficult to predict when fish will be able to be consumed without limitation in this region.

Chapter 1: Literature Review

1.1 Introduction

   While this research focused on only one kind of contaminant (PCBs), one kind of fish (lake trout), and one lake (Lake Superior), it is still necessary to review other studies on different contaminants in all of the Great Lakes because some other toxicants have properties similar to PCBs and may act similarly in the environment. In order to get an overall assessment on contamination conditions in the Great Lakes, literature on a variety of persistent, bioaccumulative, and toxic substances (PBTs) in all the Great Lakes were reviewed in this study.

1.2 Persistent, bioaccumulative, and toxic substances (PBTs)

1.2.1 Overview of PBTs

   Persistent, bioaccumulative, and toxic substances (PBTs) consist of a series of toxic compounds that have high chemical stability and high mobility in the environment. They were identified to be hazardous to the environment and humans even at relatively low concentrations (U.S. EPA 2016a). The Great Lakes Binational Toxics Strategy signed by both the United States and Canada in 1997 classified PBTs into two categories, Level I and Level II. Currently consisting of 12 classes of contaminants, Level I contains the most toxic substances associated with some known serious environmental problems that give rise to primary concern and focus from the governments, including polychlorinated biphenyls (PCBs), mercury (including mercuric compounds), dioxins, hexachlorobenzene (HCB), mirex, and some other banned pesticides. Having relatively lower toxicity than Level I, Level II PBTs are those

substances having potential impacts on the environment, for instance, polycyclic aromatic hydrocarbons (PAHs), endrin, heptachlor, tributyl tin, etc. Level II currently contains 15 groups of toxicants but some of them may be elevated to Level I if they are recognized to have significant environmental concern (U.S. EPA and Environment Canada 1997).

The earliest research interest in PBTs was in the 1960s, during the period when PBTs were recognized as a significant threat to wildlife and human health (DeVault et al. 1996). PBTs were ubiquitous in the water, air, and fish in the Great Lakes region, causing concerns about their toxicity to the environment and engendering a number of research studies. Most of the Level I PBTs have been identified with relatively high concentrations during the last four decades, which advanced the development of monitoring programs in this region.

1.2.2 Polychlorinated biphenyl (PCBs) compounds

As one of the most commonly-observed PBTs, polychlorinated biphenyl (PCB) compounds, first synthesized in Germany over a century ago, are a class of synthetic organic chlorinated compounds that were widely used in coolants, adhesives, flame-retardants, dielectric fluids, and many other industrial applications during the early and middle 20th century (U.S. EPA 2016a). There are 209 congeners of PCBs identified by the International Union of Pure and Applied Chemistry (IUPAC) and the properties vary considerably due to different numbers and configurations of chlorine atoms. Most of them are light yellow viscous liquids with low solubility in water (< 0.5 mg/L, ambient temperature) (ATSDR 2000). In 1968, nearly 2,000 people in Japan got sick

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after consuming rice oil that was contaminated by PCBs. Concern about the high

environmental toxicity caused a ban on the manufacture of PCBs four years later

(UNEP 1999). Afterwards, most countries enacted regulations to restrict the production

and use of PCBs, including the United States' ban in 1979. Although PCBs have not

been produced for nearly 40 years in the U.S., an enormous amount of PCBs remains in

the environment due to their high chemical stability. The estimated cumulative global

PCB production was over 1.5 million tons before the global ban in the early 1990s, over

one third of which entered the environment through both use and disposal (Breivik et al.

2002). PCBs have been detected in different environmental media, including water,

atmosphere, soils, and biota. PCBs can bioconcentrate and biomagnify, i.e.,

bioaccumulate, through the food web like many other lipophilic contaminants. Thus fish

in higher trophic levels tend to have higher PCB concentrations. Currently, the average

total PCB concentrations in the Great Lakes water column are approximately 1 ng/L

(10^{-3} ppb) but total PCBs in top predator fish can be over 1000 ng/g (10^3 ppb)

(Hornbuckle et al. 2006). PCB concentrations can reach a six orders of magnitude

increase through the food chain. Long-term exposure to or uptake of PCBs could

increase the risk of diseases in the immune, reproductive, and nervous systems (Faroon

et al. 2003). Many species of fish from the Great Lakes are contaminated with PCBs,

resulting in promulgation of fish consumption advisories and guidelines issued by local

health officials (Madenjian, Ebener, and Sepúlveda 2015, Giesy et al. 1997, Bhavsar et

al. 2011). PCBs are highly resistant to degradation in the environment. PCBs can be

transferred into fish through three routes, including gills, epithelial/dermal tissues, and

food ingestion (Visha et al. 2015, Sadraddini et al. 2011). For top predators like lake

trout, Thomann and Connolly reported that nearly all of the PCBs uptake was from food rather than through the skin or gills (Thomann and Connolly 1984).
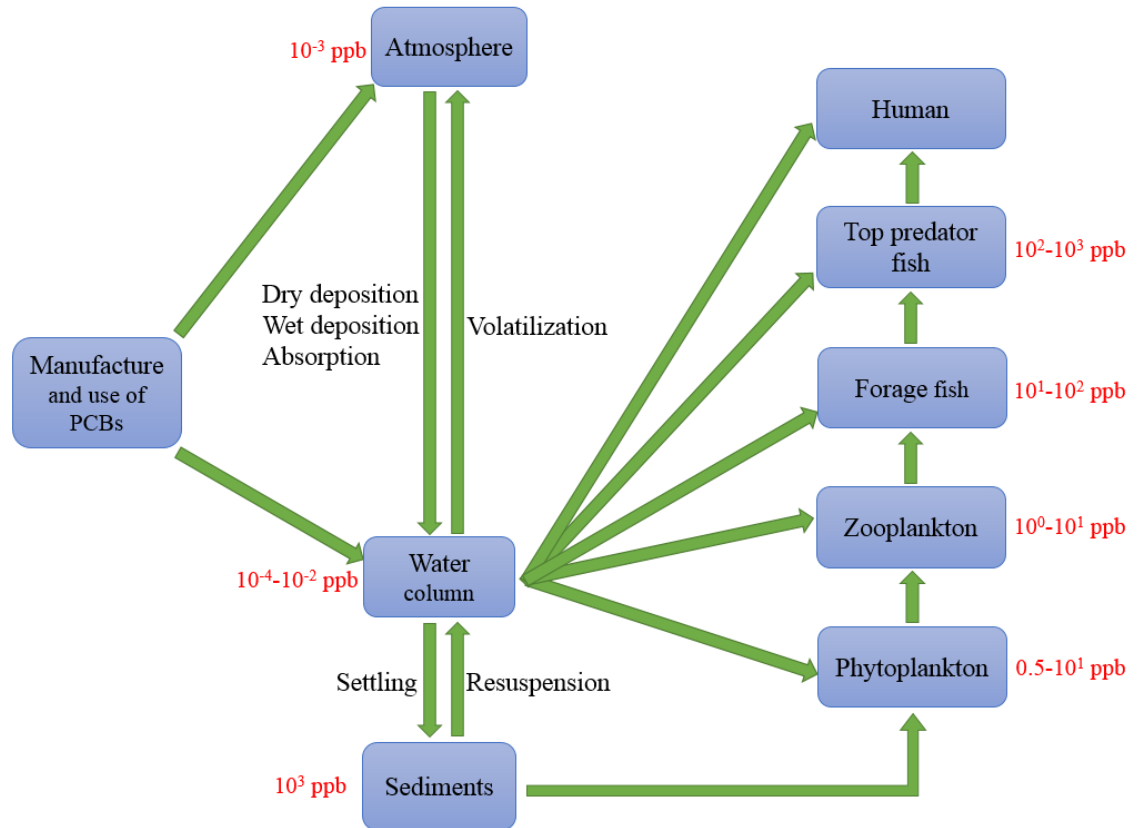
Figure 1-1. Cycling of PCBs between the environment and organisms. PCBs will bioaccumulate in biota and tend to bioconcentrate in fatty tissues. Throughout the food chain and food web, PCBs can biomagnify by several orders of magnitude.

1.3 Contaminant Levels in the Great Lakes

1.3.1 Overview of Contamination in the Great Lakes

The Laurentian Great Lakes, with a total surface area of 244,106 km^2, are the largest freshwater ecosystem on earth and account for about 21% of the world's surface freshwater (Sisson, Zacher, and Cayton 2007). Over 3500 species of wildlife and plants have been found in this region, making it one of the most biologically diverse areas in the world (Visha et al. 2015). Historically, the Great Lakes region was once the world's

most productive manufacturing region and hosted the greatest densities of coal, automobile, and synthetic industries in the early and mid-20th century. Large amounts of contaminants were released into the Great Lakes through human activities. Despite their large size, the ecosystem of the Great Lakes is still very fragile, and it has been contaminated with a variety of chemicals because of their extensive manufacture and use for over a half century. Since the Great Lakes Water Quality Agreement (GLWQA) was first signed by both the United States and Canada in 1972 and some subsequent regulations controlled the discharge of toxic substances (U.S. EPA 2016b), contaminant levels decreased dramatically during the 1970s-1980s in the Great Lakes region. However, some studies observed more moderate declining trends of PCBs and mercury in recent years (Bhavsar et al. 2007, Bhavsar et al. 2010, Zananski et al. 2011).

Lake Superior is the largest among the five Great Lakes. It has also been considered as the most pristine one because it has the lowest population in its catchment and the least industry along its shoreline. In Lake Superior, most contaminants tend to have lower concentrations in fish compared with the other four lakes (Carlson, DeVault, and Swackhamer 2010). There are, however, exceptions to this generality. Lake Superior has the highest mercury and toxaphene levels in fish of the five lakes, but the lowest PCB levels (Gerstenberger and Dellinger 2002).

1.3.2 PCBs from the atmosphere

Although industrial and agricultural activities contributed a lot to the loading of PCBs into the Great Lakes, the primary input of PCBs is from atmospheric deposition since the ban on manufacture and use in 1979 (Hornbuckle et al. 2006). Briefly, net loading

of contaminants from the atmosphere into the lake constitutes four physical processes, namely dry deposition, wet deposition, absorption, and volatilization. The first three terms are the inputs from the atmosphere while the last term is the loss from the lake. Absorption and volatilization are the two directions of gas transfer. Thus, the quantitative relationship can be expressed as follow (Blanchard et al. 2008, Hillery et al. 1998):

$$net\ atmospheric\ loading = dry\ deposition + wet\ deposition + absorption - volatilization$$

[Equation 1.1]

When it is incorporated in modeling calculations of monitoring programs, a detailed equation is used (Hoff et al. 1996), each term corresponds to the terms in Equation 1.1:

$$L = C_p R_p A + C_a \Phi_a v_d A + k_{ol}(1 - \Phi_a)C_a \left(\frac{RT}{H}\right)A - k_{ol}(1 - \Phi_w)C_w A$$

[Equation 1.2]

Table 1-1. Symbols in Equation 1.2 and their corresponding meanings.

Symbol	Quantity	Dimension
A	Area of the lake	m^2
C_p	Contaminant concentration in precipitation	kg/m^3
R_p	Precipitation rate	m/yr
C_a	Contaminant concentration in the atmosphere	kg/m^3
Φ_a	Fraction of the contaminant in particle phase in the atmosphere	dimensionless
v_d	Particulate deposition velocity	m/yr
k_{ol}	Air-water transfer coefficient	m/yr
R	Gas constant	atm·m^3/K/mol
T	Thermodynamic temperature	K
H	Henry's Law constant	mol/atm/m^3
Φ_w	Fraction of the contaminant in particle phase in the water	dimensionless
C_w	Contaminant concentration in the water	kg/m^3

According to the data from the Integrated Atmospheric Deposition Network (IADN), wet deposition fluxes of PCBs are a small portion of atmospheric deposition and do not differ significantly among the Great Lakes since 1992 even though fluxes in Lakes Huron and Ontario were slightly higher. Gas transfer is the dominant means of PCB loading, while volatilization has been demonstrated to be greater than absorption in most years. Annual atmospheric fluxes of PCBs to Lake Superior were approximately - 30 to 10 ng/m^2/day during 2000-2005 (negative values mean net output from lake and positive values mean net input to lake), indicating that currently the Great Lakes has turned from a sink of PCBs to a source (Blanchard et al. 2008). Although the general pattern of atmospheric deposition of PCBs is declining, a few increasing trends in absorption were still observed in the late 1990s in Lakes Superior and Erie (Buehler et al. 2001, Meng, Wen, and Sloan 2008).

1.3.3 PCBs in water column and sediment

Since PCBs are hydrophobic and have low solubility in water, concentrations in the water column of the Great Lakes are at the magnitude of pg/L or ng/L. During the past four decades, total PCB concentrations have declined by about two orders of magnitude from ~10 ng/L to ~0.1 ng/L in the water of Lake Superior (Hornbuckle et al. 2006). However, it should be noted that even at relatively low concentrations in the water column, PCBs can still accumulate to hazardous levels in fish through biomagnification. Calculations have shown that 50% of PCBs in the Lake Superior water column were transported to the benthic environment each year via settling particles (Hornbuckle et al. 2006).

1.3.4 PCBs in fish

As the world's largest freshwater system, the Great Lakes hosted prosperous fisheries from the late 19th century to the mid-20th century. However, the commercial fishery has been restricted in this region with the exception of a few areas in Lake Superior due to some ecological and environmental concerns. Local industries discharged PCBs, mercury, as well as other toxics into the environment during the 1950-70s, causing elevated contaminant concentrations in fish (Bhavsar et al. 2011). High contaminant levels in fish played an important role in the decline of the commercial fishery. For instance, increasing mercury concentrations in predatory fish from Thunder Bay contributed a lot to the closure of the local commercial fishery in the 1970s (O'Sullivan and Reynolds 2008). The study by Bhavsar *et al.* (2010) demonstrated that the consumption of fish from the Great Lakes was the major route for uptake of PCBs and other contaminants by people who lived near contaminant sources (Bhavsar et al. 2010).

Lake trout have been used as a surrogate species to monitor contaminant levels in the Great Lakes because it was difficult and expensive to determine the corresponding concentrations in the water column directly. In addition, investigations of contaminant levels in fish are useful to make and assess fish consumption advisories. Though few data on toxicant concentrations in the water column are available, some samples collected by the U.S. EPA indicated that the temporal trends of PCB levels were similar in the water column and lake trout (Huestis et al. 1996).

1.3.5 Mercury

Similar to many other PBTs, mercury is a contaminant of interest in the Great Lakes. There are three typical chemical forms of mercury in the environment, namely elemental [Hg(0)], ionic [Hg(II)], and organic forms. Mercury can cycle between different environmental media in these three chemical states through atmospheric deposition, volatilization, and other environmental processes. Similar to PCBs, the primary source of mercury in the Great Lakes basin is also atmospheric deposition (Cohen et al. 2004). Most concern focuses on methylmercury, an organic form of the contaminant. Methylmercury (MeHg) is usually generated from inorganic mercury in anaerobic environments such as sediments in a lake (Keating et al. 1997). The toxicity of methylmercury is much greater than its inorganic counterparts because organic mercury can be easily absorbed by humans through fish consumption. Though the toxicity of mercury has been recognized for decades, it was not included in the Great Lakes Fish Monitoring Program as a regular contaminant until 1999.

PCBs and mercury are the two major contaminants that limit the consumption of fish from the Great Lakes (Bhavsar et al. 2011). However, there are significant differences between these two contaminants. Unlike PCBs that have over 200 individual compounds, nearly all of the mercury found in fish is methylmercury (Bloom 1992). PCBs are bound to lipids in fish but mercury binds predominantly with protein in muscle tissue. Thus, lipid content has less impact on the mercury concentrations in the fish.

Zananski *et al.* performed three different types of regression analysis on the U.S.

EPA fish sample data (whole fish) from 1999 to 2009. They found significant spatial

differences between the paired sites in Lakes Superior and Huron but not in the other

three lakes. Total mercury concentrations in lake trout (walleye in Lake Erie) were

highest in Lake Superior and lowest in Lake Eire. This order was consistent with the

magnitude of atmospheric deposition. Both intra- and inter- lake spatial variability may

have resulted from different food webs, local mercury discharges, and water movement

patterns (Zananski et al. 2011). Although mercury concentrations in fish declined from

peak levels in the 1970s, currently the declining rates are levelling off and even

increasing trends were observed at some sites, especially in walleye from Lakes Ontario

and Erie (Bhavsar et al. 2010, McGoldrick and Murphy 2015).

1.3.6 Brominated Contaminants

As the bromine analogs of PCBs, polybrominated biphenyls (PBBs) were once used

commercially as flame-retardants in the early 1970s. They were banned in 1976 in North

America. Zhu *et al.* reported that for one of the major congeners, PBB-153, the

concentration in top predator fish (walleye from Lake Eire and lake trout from the other

four lakes) was almost unchanged from 1980 to 2000 in all of the Great Lakes except

Lake Huron, where concentrations declined from 39 to 17 ng/g lipid weight. It was in the

early 1980s that polybrominated diphenyl ethers (PBDEs) were used as replacements for

PBBs. The concentrations of total PBDEs in fish increased exponentially with time over

the same period in all the Great Lakes, from < 10 to around 1000 ng/g lipid weight. Lake

Superior had the longest doubling time of 2.8 years among all of the lakes for PBDE

concentrations in lake trout (Zhu and Hites 2004). Since both PBBs and PBDEs have

some similarities in chemical properties with PCBs, these brominated substances may

show similar time trends as their chlorinated counterparts.

1.4 Models of Fish Contaminant Dynamics

1.4.1 First-order Decay Model

It has been found that many substances that are metabolized or degraded in the

environment follow a first-order decay model. Analyses of contaminant trends in early

data fit well with the common first-order decay model. For instance, total PCBs in lake

trout from Lake Michigan from 1974 to 1982; total DDT in lake trout from Lake

Michigan from 1970 to 1982 (DeVault et al. 1986) follow such a trend:

$$c_t = c_1 e^{-kt} \qquad \text{[Equation 1.3]}$$

where c_1 and c_t are the contaminant concentrations at the beginning and at time t,

respectively, and k is the first-order decay rate constant. An asymptote, c_0, is added to

the first-order model, representing an irreducible baseline concentration of contaminant

in the environmental (Stow et al. 1995):

$$c_t = c_1 e^{-kt} + c_0 \qquad \text{[Equation 1.4]}$$

Based on the with-asymptote model, a combination of two individual first-order

models was also used (Hickey, Batterman, and Chernyak 2006):

$$c_t = c_1[f e^{-k_1 t} + (1 - f)e^{-k_2 t}] + c_0 \qquad \text{[Equation 1.5]}$$

Where *f* is the fraction of c_1 attributable to the slow process and (1-*f*) is the fraction of c_1 attributable to the fast process, and k_1 and k_2 are the first-order rate constant for the slow and fast processes, respectively.

1.4.2 Two-segment Piecewise Linear Regression

The segment piecewise linear regression has its own advantages when the independent variables are clustered into different groups. For those contaminants that did not increase or decrease monotonically during the monitoring programs, it can be used to find out the temporal trends before and after the breakpoint. A common two-segment piecewise linear model is (Monson 2009):

$$\ln(c_t) = \frac{\alpha_1(T - t) + \alpha_{min}(t - t_{min})}{T - t_{min}}, t_{min} \leq t \leq T$$

$$\ln(c_t) = \frac{\alpha_{min}(t_{max} - t) + \alpha_2(t - T)}{t_{max} - T}, T \leq t \leq t_{max}$$

[Equation 1.6]

Where *T* is time of the breakpoint, α_1 and α_2 are the coefficients before and after the breakpoint, respectively, t_{min} and t_{max} are the beginning and end of the data used in calculation, respectively. Zananski et al. (2011) applied two-segment piecewise linear regression in total mercury concentrations in top predatory fish from the Great Lakes and found that temporal trends were distinct from the simple linear regression or quadratic regression.

1.4.3 Dynamic Linear Modeling (DLM)

Being distinct from traditional static regression analyses, dynamic linear modeling (DLM) has the parameters that shift with time. The estimates are influenced only by

prior and current data rather than subsequent information. Moreover, outliers and missing data have little impact on the results of DLM. Each DLM consists of an observation equation and several system equations (Petris, Petrone, and Campagnoli 2009). Considering fish length and lipid content as covariates, Sadraddini *et al.* and Visha *et al.* used the following equations to analyze temporal trends of PCBs and mercury in lake trout and walleye from the Great Lakes (Sadraddini et al. 2011, Visha et al. 2015):

Observation equation:

$$\ln(C_{ti}) = \text{level}_t + \beta_{t1}\ln(\text{length}_{ti}) + \beta_{t2}\ln(\text{lipid}_{ti}) + \Psi_{ti} \qquad \Psi_{ti} \sim N(0, \Psi_t)$$

[Equation 1.7]

System equations:

$$\text{level}_t = \text{level}_{t-1} + \text{rate}_t + \omega_{t1} \qquad \omega_{t1} \sim N(0, \Omega_{t1}) \qquad \text{[Equation 1.8]}$$

$$\text{rate}_t = \text{rate}_{t-1} + \omega_{t2} \qquad \omega_{t2} \sim N(0, \Omega_{t2}) \qquad \text{[Equation 1.9]}$$

$$\beta_{t1} = \beta_{t1-1} + \omega_{t3} \qquad \omega_{t3} \sim N(0, \Omega_{t3}) \qquad \text{[Equation 1.10]}$$

$$\beta_{t2} = \beta_{t2-1} + \omega_{t4} \qquad \omega_{t4} \sim N(0, \Omega_{t4}) \qquad \text{[Equation 1.11]}$$

$$\frac{1}{\Omega_{tj}^2} = \frac{\zeta^{t-1}}{\Omega_{1j}^2}, \ \frac{1}{\Psi_t^2} = \frac{\zeta^{t-1}}{\Psi_1^2} \qquad t > 1, j = 1,2,3,4$$

$$\text{level}_1, \text{rate}_1, \beta_1 \sim N(0,10000) \qquad t = 1$$

$$\frac{1}{\Omega_{tj}^2}, \frac{1}{\Psi_t^2} \sim G(0.001,0.001) \qquad \text{[Equation 1.12]}$$

Table 1-2. Symbols in DLMs (Equation 1.7-1.12) and their corresponding meanings.

Symbol	Quantity
t	Time
C_{ti}	Contaminant concentration at time t in the individual sample i
level_t	Mean contaminant concentration at time t accounting for the covariance with fish length and lipid content
rate_t	Rate of change of the level variable
length_{ti}	Fish length at time t in sample i
lipid_{ti}	Fish lipid content at time t in sample i
β_{t1}	Length regression coefficient
β_{t2}	Lipid content regression coefficient
Ψ_t, ω_{ti}	Error terms for time t
ζ	Aging of information with the passage of time

Chapter 2: Assessment of PCBs in lake trout from Lake Superior[1]

2.1 Introduction

PCBs are one of the major pollutants accumulated in fish from the Great Lakes, and have led to most restrictions in fish consumption in this region. Fish monitoring programs were established by several governmental agencies from both the United States and Canada in the Great Lakes region in the 1970s. These programs aimed to assess the temporal trends and spatial variabilities of contaminant levels in the lakes, as well as to provide reliable information for regulatory officials to issue fish consumption advisories for local residents.

Lake Superior, the largest among all five Great Lakes, is also the largest freshwater lake in the world by surface area (82,100 km^2), and contains nearly half of the water from the Great Lakes. Contaminants will remain in this lake for many years because of its relatively long retention time of 191 years (Minnesota Sea Grant 2016). Adverse effects of PCBs on human health and the environment first drew the attention of the public in the early 1960s. The environment of the Great Lakes has been contaminated by PCBs, thus health officials issued fish consumption advisories for local residents.

Fish, especially top predators like lake trout and walleye in the Great Lakes, are often selected as indicator organisms for evaluating the contaminant levels and trends in the aquatic system because they reflect the bioaccumulation of contaminants. Unlike analyzing sediment, because they move around, fish may indicate the contaminant level

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[1] The material contained in this chapter is in preparation for submission to a journal.

in a relatively larger area than other organisms that do not move around. At the same time, lake trout have high abundance on the lake scale. All these advantages make lake trout an ideal indicator organism of contamination in the Great Lakes.

However, different agencies have different mandates, and, consequently, different methodologies for monitoring contaminants. The U.S. EPA and ECCC monitor fish to detect trends over time; both agencies collect and analyze PCBs in whole fish. Both Minnesota and Wisconsin DNRs focus primarily on protecting the health of fish consumers. These agencies measure PCBs in skin-on fillet because humans usually eat only the fillet part of fish. The U.S. EPA is the only agency that composites individual fish before PCB analysis. Although composite samples could provide more representative information on the fish population and reduce the cost of chemical analysis, some individual fish characteristics, such as size and age, may not be reflected in the composite samples. In addition, using composite samples data could underestimate the variance when performing statistical analysis (Gewurtz et al. 2011). Analytical methodologies also differ, and PCB concentrations measured by the different agencies are not directly comparable.

Our research extracted all available fish sample data about PCB concentrations in lake trout in Lake Superior generated from two national agencies (United States Environmental Protection Agency, and Environmental and Climate Change Canada), as well as three state agencies from the Great Lakes states (Michigan Department of Environmental Quality, Minnesota Department of Natural Resources, and Wisconsin Department of Natural Resources) during the period of 1978-2013. Previous analyses of

the U.S. EPA and Canadian data have suggested that, after a rapid decline in concentrations in the 1970s and 1980s, concentrations have leveled off (Huestis et al. 1996, DeVault et al. 1996). In order to evaluate temporal trends and spatial variabilities in PCB concentrations in lake trout from Lake Superior over the past two decades, we analyzed fish sample data from all datasets after 1995.

2.2 Methods

In order to assess PCB trends and to determine what factors may affect PCB levels in the Great Lakes fish, fish contaminant data from two national agencies (U.S. EPA, Environment and Climate Change Canada), and three state agencies (Michigan Department of Environmental Quality, Minnesota Department of Natural Resources, Wisconsin Department of Natural Resources) were collected. We assess PCB temporal trends and spatial variabilities in lake trout from Lake Superior by performing statistical analyses on these five data sources.

2.2.1 Fish Sample Data Collection

Multiple contaminants in Great Lakes fish have been monitored by national and state/provincial agencies from both the U.S. and Canada since the 1970s. Besides sampling locations, the numbers of fish caught, methods of fish preparation, as well as PCB analytical techniques differed greatly among the agencies. Following are detailed descriptions of fish sampling protocols for each agency.

U.S. EPA

The Great Lakes Fish Monitoring Program (GLFMP) conducted by the U.S. EPA Great Lakes National Program Office (GLNPO) monitors trends in toxics in fish from

all of the Great Lakes (https://www.epa.gov/aboutepa/about-great-lakes-national-program-office-glnpo). To detect time trends, fish of the same size are collected every year, and the fish collection and preparation methodologies have remained unchanged since the program began. Lake trout (*Salvelinus namaycush*) were collected annually during late summer or early fall of 1978 to the present at two sampling locations in Lake Superior. Each location was sampled in alternate years since 1982. In odd years, fish were sampled at Keweenaw Point (offshore, deeper), and in even years fish were sampled in the Apostle Islands (nearshore, shallower). After measurement of individual fish characteristics (length, weight, gender, and age), whole fish were grouped into 10 composite samples of 5 individual fish each for the chemical analysis. PCB analyses were performed using gas chromatograph with electron capture detectors (GC-ECD) or mass spectrometer (GC-MS). Concentrations of total PCBs were reported as mixtures of Aroclors before the mid-1990s and were reported as the sum of 110 PCB congeners after then (Carlson and Swackhamer 2006). Results of the U.S. EPA's lake trout contaminant monitoring have previously been reported by DeVault *et al*. (1986; 1996), Carlson *et al.* (2006; 2010), Hickey *et al.* (2006), Chang *et al.* (2012), and Salamova *et al.* (2013), etc.

Environment Canada and Climate Change (ECCC)

The government of Canada started the Fish Contaminants Monitoring and Surveillance Program (FCMSP) in 1977 (Envrionment and Climate Change Canada 2014) (http://www.ec.gc.ca/scitech/default.asp?lang=en&n=828EB4D2-1#program). Fish sampling has occurred at a total of eight locations, but Thunder Bay-Pie Island and

Whitefish Bay were the only two locations that have sufficient data to perform rigorous

trend analysis. The number of fish caught ranged from 25 to 50 at each site in each

sampling year. Unlike the U.S. EPA, ECCC did not composite individual fish. Total

PCBs were quantified as Aroclor 1254 in whole fish. ECCC reported PCB

concentrations in μg/g ww with only one significant figure, which could lead to less

sensitivity in regression analysis, while other agencies had at least two figures. The

most recent available data were from 2013 for both sampling sites. Published

summaries of ECCC results include those of Bhavsar *et al*. (2007) and McGoldrick *et

al*. (2015).

Michigan DEQ

Michigan DEQ set up the Michigan Fish Contaminant Monitoring Program

(MFCMP) in the early 1980s (http://www.michigan.gov/deq/0,4561,7-135-

3313_3681_3686_3728-32393--,00.html). They analyzed three types of fish samples for

distinctive purposes. Whole fish samples were used to determine spatiotemporal trends

of contaminants, while fillet (edible portion) samples were used to develop fish

consumption advisories. Caged fish were not analyzed as much as the previous two

types but they provide more information on the sources of contaminants and track the

spatial distribution (Michigan DEQ 2013). Measurements of PCBs in fillet samples and

caged fish samples of lake trout from Lake Superior were too limited for the trend

analyses. Thus, only whole lake trout data were analyzed in this study. Michigan DEQ

collected 10 individual lake trout from Keweenaw Bay in late spring or early summer

(April or May) of each sampling year biennially or triennially since 1991. Unlike the

U.S. EPA, Michigan DEQ measured PCB concentrations in individual fish rather than in composite samples. The PCB analytical method was changed from Aroclors to congeners in 1996. However, both methods were applied in two sampling years (1996 and 1999) to enable comparison. Results from the Michigan DEQ monitoring program have been reported in unpublished state agency reports.

Minnesota DNR & Wisconsin DNR

Similar monitoring programs conducted by the states of Minnesota and Wisconsin started in 1976 and 1970, respectively (Monson 2009, Schrank 2011). The Minnesota DNR sampled fish at 15 locations in total, along the western shore of Lake Superior from Duluth to Clark Bay (Figure 2-2). The Wisconsin DNR had 17 sampling locations in four counties in the southwestern basin of Lake Superior. There were 4, 4, 8, and 1 sampling locations in the counties of Douglas, Bayfield, Ashland, and Iron, respectively (Figure 2-2). In general, less effort was made to collect fish of the same size each year. In addition to fish type, gender, size, and lipid content were also recorded by the states. Total PCB concentrations were reported in µg/g wet weight with two significant figures. Prior to 1990 and after 1990, the PCB analytical technique had a detection limit of 0.4 µg/g and 0.02 µg/g, respectively (Rasmussen, Schrank, and Williams 2014). Results of monitoring by these two agencies have been reported in Schrank *et al*. (2011).

Figure 2-1. Sampling locations of the U.S. EPA (Keweenaw Point, Apostle Islands), Michigan DEQ (Keweenaw Bay), and ECCC (Thunder Bay, Whitefish Bay) in Lake Superior.

2.2.2 Statistical analysis

Generally, PCBs can be analyzed and quantified by two approaches - either as mixtures of Aroclors or as individual congeners (Narquis, Hyatt, and Prignano 2007). In the mid-1990s, both the U.S. EPA and Michigan DEQ changed their analytical techniques for measuring total PCBs from the Aroclor method to the congener-specific method, resulting in difficulty in comparison between recent and historical data.

In contrast, the Environment and Climate Change Canada, as well as the two state agencies from the U.S., Minnesota DNR and Wisconsin DNR, quantified total PCBs as mixtures of Aroclors throughout the monitoring period, but the detection limit decreased from 0.4 μg/g to 0.02 μg/g in the early 1990s (Rasmussen, Schrank, and Williams 2014).

Aroclor method

Aroclors were the trade names of a series of mixtures of PCB congeners sold in the United States (Frame, Cochran, and Bøwadt 1996). An Aroclor mixture usually used a 4-digit number as its name, where the first 2 digits represented the biphenyl compounds, and the last 2 digits represented the percentage of chlorine by weight (ATSDR 2000). The Aroclor method was the original PCB analytical technique because the analytical capability to identify and quantify individual congeners was not available until the late 1970s. Now that individual congeners are quantified, total PCB concentrations can be calculated either as the sum of congeners (the result will depend on the number of congeners quantified), or by estimating 'Aroclor' concentrations from the specific congeners originally manufactured in each Aroclor. Among different agencies, varying statistical techniques are used to relate relative abundances of a variable numbers of congeners in a sample to the relative abundances in pure Aroclor standards to calculate Aroclor concentrations that are then summed to yield 'total PCB' concentrations. Although an anachronism, the Aroclor method is still widely used in PCB analysis because of its low cost and comparability with historical results. EPA Method 8082 is the typical Aroclor method using a capillary column in GC-ECD or GC-MS (EPA 2007). The Aroclor method overestimates the total PCB concentrations calculated from summing the measured congeners, because it assumes that all congeners present in the Aroclor standards behave identically in the environment and are present in environmental samples.

Congener-specific method

Because the toxicity of different PCB congeners varies a lot, determining PCBs as Aroclors may not provide sufficient information for environmental assessment. Besides, total PCB concentrations may get overestimated in the Aroclor method because some congeners might get double-counted on their gas chromatography patterns. With the improvements in analytical instrumentation, PCBs can be identified and quantified as individual congeners. Total PCB concentrations calculated with the congener method are much more accurate than the Aroclor method because the congener method includes only the PCB congeners actually in a sample. However, the expense of analyzing PCBs as congeners is approximately three times higher than that as Aroclors, resulting in some restrictions in applications (Bernhard and Petron 2001). In addition, most agencies have not published the health risk assessment of individual PCB congeners, making it unnecessary to quantify PCB congeners.

Data set description

Both the U.S. EPA and ECCC have a pair of sampling locations in different basins of Lake Superior. Although Michigan DEQ collected lake trout from various sampling locations, only in Keweenaw Bay were samples collected in multiple years. Hence, Keweenaw Bay was the only available location from the Michigan DEQ that could be used in trend analysis.

To evaluate if statistically significant differences exist between the individual sampling locations of the Minnesota DNR and Wisconsin DNR, one-way analyses of variance (ANOVA) were conducted for fish length, lipid content, and PCB

concentrations. Because ANOVA revealed no significant differences between sites for

PCB concentrations, we combined samples from all the sampling locations of

Minnesota DNR together as well as all sampling locations of the Wisconsin DNR.

Multiple Regression Analysis

Setting calendar year, fish length (using the arithmetic mean of 5 individual fish in

one composite for the EPA data) and fish lipid content (lipid content is not applicable

for the two EPA sites due to lack of data) as three independent variables, we performed

multiple linear regression on both original PCB concentrations and log-transformed

PCB concentrations for each data set using SAS to identify the covariates that could

affect PCB levels. The multiple regression models are shown in Equations 2.1 and 2.2.

Variables with a *p* value less than 0.05 were considered to be significant factors.

$$PCB = a_1(year) + a_2(length) + a_3(lipid) + \varepsilon$$

[Equation 2.1]

$$\log(PCB) = a_1(year) + a_2(length) + a_3(lipid) + \varepsilon$$

[Equation 2.2]

where a_1, a_2, and a_3 are the partial regression coefficients, and ε represents the

regression random error.

In multiple linear regression, if there is a significant linear relationship between two

or more independent variables, it will result in relatively large errors on estimates of

regression coefficients. Such interdependence is known as multi-collinearity, which is

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usually quantified as a variance inflation factor (VIF) in statistical analysis. VIF is

usually calculated by using the following formula:

$$\text{VIF}_i = \frac{1}{1 - R_i^2} \qquad \text{[Equation 2.3]}$$

Where VIF_i and R_i^2 are the variance inflation factor (VIF) and the coefficient of

determination (R^2) for the regression of the ith independent variable on all other

independent variables, respectively. Generally, if VIF is not greater than 5, the multi-

collinearity is weak; otherwise the multi-collinearity is high. In other words, we should

include only one of the multi-collinear independent variables in the multiple regression

analysis when VIF is greater than 5 (Nachtsheim et al. 2004). In this study, considering

the potential correlation between fish length and lipid content, if multi-collinearity is

significantly high between them, only the fish length would be included in multiple

regression analysis.

Spatial and Temporal Trends Analysis

Because PCBs can bioaccumulate in fish, it is assumed that older fish have higher

PCBs in their bodies. It is not simple to determine the fish age directly, thus fish length

is considered as a surrogate of fish age. A number of studies have indicated that PCB

concentrations in fish increase with fish size. Length and weight are both used to

represent fish size, but length is more commonly used in research (Miller 1994). All

PCB concentrations were first log-transformed before regression analysis to fit a normal

distribution. To determine if PCB concentrations have significant declines after 1995,

single linear regression analyses were employed on each of the seven datasets. PCBs

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were regarded to have decreased significantly if the regression had a negative, non-zero slope at the 95% confidence level. ANOVA and *t*-tests (pair-wise by year) of PCB levels were also run to compare the five datasets. Spatial variabilities might be attributable to differences in fish preparation techniques (whole fish vs. skin-on fillets) among agencies, differences in gender frequencies or local food webs among the sampling locations.

2.3 Results

2.3.1 Pooled Data

In order to determine if there were any statistically significant differences in PCB concentrations among individual sampling locations of the Minnesota DNR or Wisconsin DNR, one-way analysis of variance (ANOVA) was performed on fish length and PCB concentrations from these two agencies. Lake trout were collected at 15 and 17 sites during the period of 1976-2013 by Minnesota DNR and Wisconsin DNR, respectively. We selected data from a few sampling years that contained multiple sampling sites to perform ANOVA.

According to the results of ANOVA, few statistically significant differences (*p* value > 0.05) in PCB concentrations were found among individual sampling locations in either state (Table 2-1). Thus, data from the different sites were pooled in subsequent statistical analyses, respectively. Combined sites in Minnesota and Wisconsin were treated as single sampling locations.
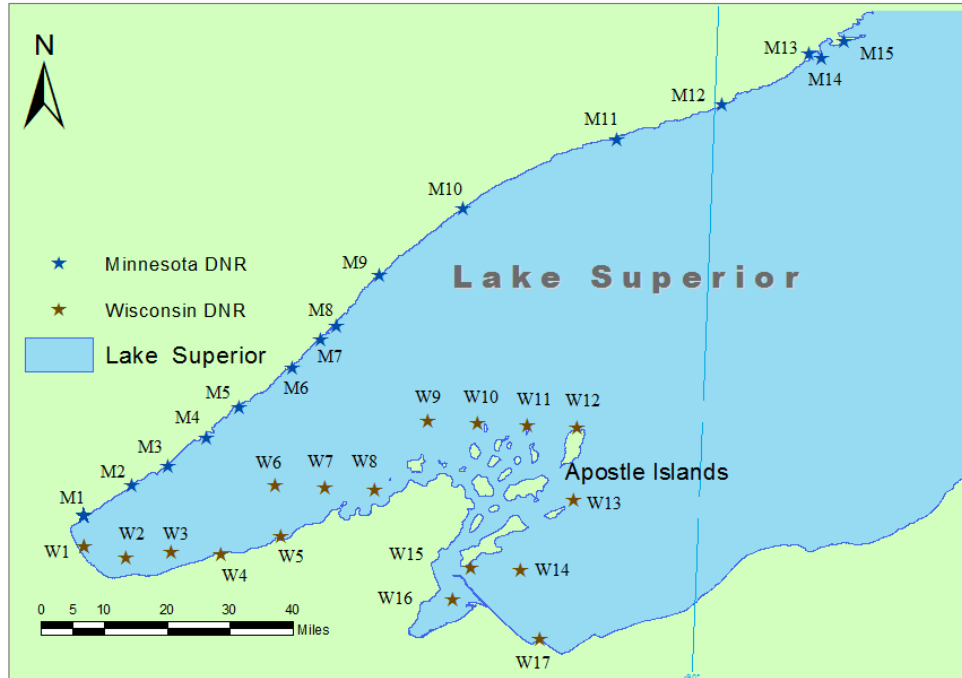
Figure 2-2. Individual sampling locations of Minnesota DNR. (M1: Coast Guard; M2: French River; M3: Knife Island; M4: Two Harbors; M5: Encampment Island; M6: Split Rock Point; M7: Beaver Bay; M8: Silver Bay; M9: Little Marais; M10: Tofte; M11: Grand Marais; M12: Hovland; M13: Grand Portage; M14: Hat Point; M15: Clark Bay); Wisconsin DNR (W1-W4: Douglas; W5-W8: Bayfield; W9-W16: Ashland; W17: Iron).

Table 2-1. Summary of ANOVA for fish length and PCB concentrations in individual sampling locations of Minnesota DNR and Wisconsin DNR.

Year	Sampling Locations	Fish Length (p value)	PCB Concentrations (p value)
Minnesota DNR			
1976	M2, M9, M12	NS[*] (0.72)	NS (0.43)
1985	M2, M6, M7, M11	NS (0.78)	NS (0.55)
1987	M2, M6, M11	NS (0.11)	NS (0.17)
1988	M2, M11, M13	**Sig[**] (0.0017)**	NS (0.15)
1996	M2, M3, M4, M5, M6, M10	NS (0.65)	NS (0.72)
2002	M1, M4, M6, M8	**Sig (0.0040)**	NS (0.35)
2010	M4, M8	**Sig (0.0426)**	NS (0.94)
Wisconsin DNR			
1976	W3, W7, W8	NS (0.58)	NS (0.92)
1984/85[***]	W1, W3, W4, W13, W15	NS (0.88)	NS (0.15)
1991	W2, W10, W12, W13, W14	NS (0.69)	NS (0.23)
1995	W2, W11, W13, W17	NS (0.07)	**Sig (0.0234)**
1997	W2, W3, W4, W11, W13, W14	NS (0.63)	NS (0.72)
1999	W2, W3, W4, W13, W14	NS (0.86)	NS (0.68)
2001	W3, W4, W6	NS (0.49)	NS (0.62)
2003	W2, W4, W10, W11, W13	NS (0.99)	NS (0.62)
2005	W3, W4, W10, W15	NS (0.68)	NS (0.31)
2007	W5, W10, W11, W13	NS (0.76)	NS (0.77)
2009	W3, W10	NS (0.60)	NS (0.43)
2011	W1, W7, W13	**Sig (< 0.0001)**	**Sig (0.0017)**
2013	W2, W4, W9, W10, W13, W14	NS (0.33)	NS (0.35)

[*]**NS** indicates that there are not significant differences among locations (p value > 0.05).

[**]**Sig** indicates that there are significant differences among sampling locations (p value < 0.05).

[***]Data of 1984 and 1985 from Wisconsin DNR were combined directly since the sample size of a single year was too small to perform ANOVA.

2.3.2 Changes in Analytical Technique for PCBs

The average total PCB concentrations in lake trout from Keweenaw Point (U.S. EPA) in the early 1990s were over 1000 ng/g ww but they decreased rapidly to 300 ng/g in 1995 (Figure 2-3). This drop was not a result of environmental processes, but an alteration in PCB measurement methodology from Aroclors to congeners at that time. A similar sharp decline was also observed in fish from the Apostle Islands, from 846 ng/g ww in 1984 to 400 ng/g ww in 1996 (Figure B-15). The Michigan DEQ also changed the analytical method for PCBs from Aroclors to congeners in 1996 (Figure 2-4). The PCB analytical techniques in the three other agencies remained consistent. These three agencies analyzed total PCBs as Aroclors since the beginning of their programs. It is unreasonable to compare the data before and after the change in analytical technique to determine the temporal trends of PCBs in the fish. In order to compare the data among different agencies, we focused on the data after 1995 from all datasets.

Michigan DEQ used both the Aroclor-based method and congener-specific method on the same samples in 1996 and 1999. Assuming that the total PCB concentrations determined by the two methods were linearly correlated, we performed single linear regression analysis on Aroclor method PCBs versus congener method PCBs using combined data of 1996 and 1999. A significant positive relationship was found with a slope of 0.60 ($p < 0.0001$, R^2=0.811). For data from Michigan DEQ, the congener method total PCB concentrations were 40%-50% lower compared to the Aroclor method (Figure 2-5) because the new method reduced the detection limit and measured only individual PCB congeners that were present in each sample.

Because the U.S. EPA did not determine total PCBs with both methods at the same time, it is not possible to establish the relationship between results from the two techniques for the U.S. EPA's data.
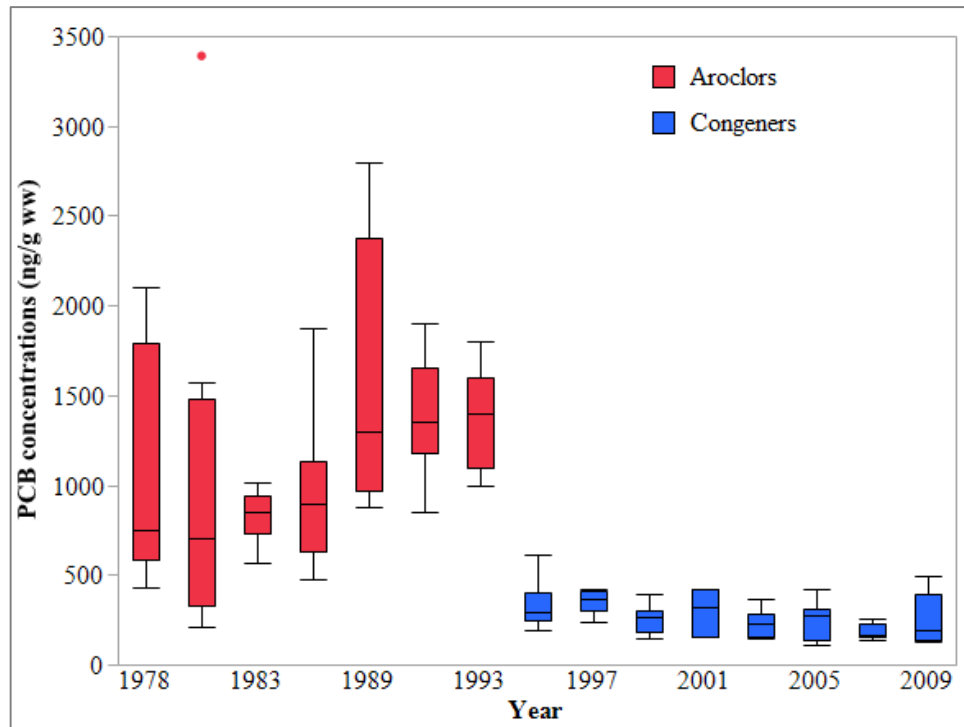
Figure 2-3. Total PCB concentrations in whole lake trout from Keweenaw Point (U.S. EPA, 1978-2009). The Aroclor method was used prior to 1995 and the congener method was applied since 1995 data. The horizontal line within the box represents the median while the whiskers represent the 5th percentile and 95th percentile, respectively.
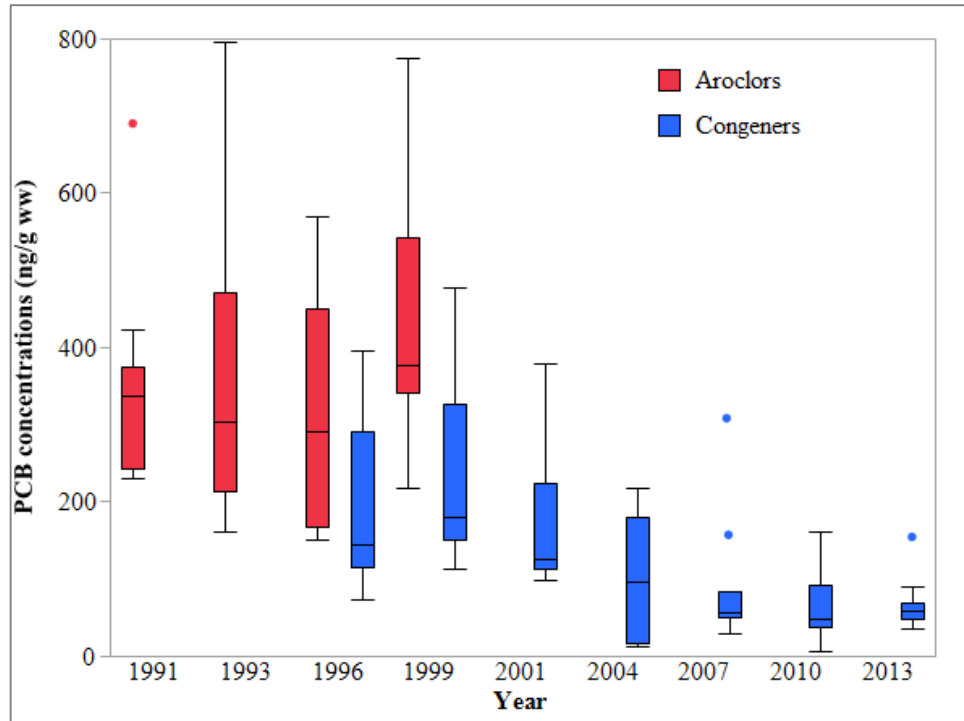
Figure 2-4. Total PCB concentrations in whole lake trout from Keweenaw Bay (Michigan DEQ, 1991-2013). The Aroclor method was used prior to 1996, and the congener method was applied after 1996. Both methods were used in 1996 and 1999. The horizontal line within the box represents the median while the whiskers represent the 5th percentile and 95th percentile, respectively.
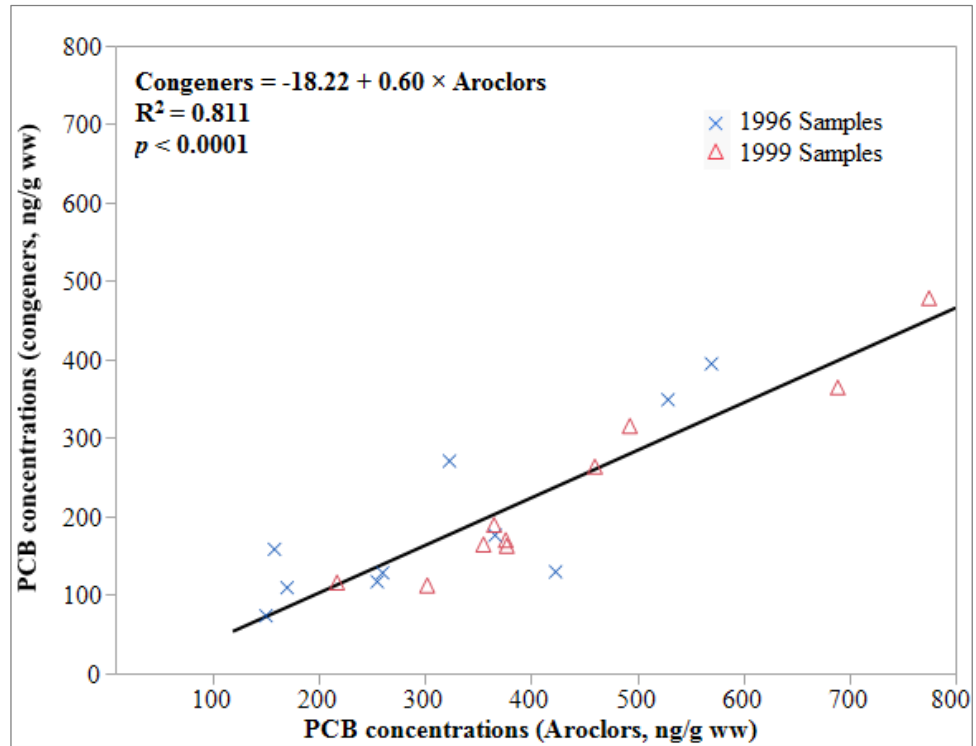
Figure 2-5. Linear regression between Aroclor method and congener method for total PCBs in lake trout from Keweenaw Bay (Michigan DEQ, pooled data of 1996 and 1999 samples).

2.3.3 Multiple Regression Analysis

The results of multiple linear regression analysis are summarized in Tables 4 and 5. There was a strong positive relationship between PCB concentrations and fish length in both whole fish and skin-on fillet samples according to the multiple regression results. The correlation was found at all sites except Whitefish Bay (Whitefish Bay p value = 0.82 while others < 0.05).

Lipid content was a significant predictor of PCB concentrations only in Whitefish Bay (Whitefish Bay p value < 0.0001 while others > 0.05). In other sites, lipid content had weak correlations with PCB concentrations, which is in contrast to previous research that showed lipid content to be an important regulator of PCB concentrations due to its high affinity for organic compounds (Rasmussen, Schrank, and Williams 2014). In general, lake trout in Whitefish Bay were relatively small (450-550 mm) compared with other locations (550-650 mm) after 1995. Fish lipid content was significantly higher in Whitefish Bay than at other sites, possibly a result of the existence of two different types of lake trout. Lean lake trout, typically found closer to shore have relatively low lipid content (around 10%), while the pelagic siscowet lake trout have much higher lipid content (25-40%).

Table 2-2. Summary of multiple linear regression analysis on original PCB concentrations.

Data Groups	Fish Preparation	Sampling Period	Predictor Variables	Estimates (*p* value)	VIF*
Keweenaw Bay EPA	Whole fish	1995-2009	Length Year	**1.1 (< 0.01)** **-9.3 (< 0.01)**	**1.0** **1.0**
Apostle Islands EPA	Whole fish	1996-2008	Length Year	**3.1 (< 0.01)** NS (0.95)	**1.1** **1.1**
Michigan DEQ	Whole fish	1996-2013	Length Year Lipid	**0.7 (0.01)** NS (0.38) NS (0.42)	**1.9** **1.8** **1.3**
Thunder Bay Canada	Whole fish	1997-2013	Length Year Lipid	**1.3 (< 0.01)** NS (0.14) NS (0.73)	**1.5** **1.2** **1.2**
Whitefish Bay Canada	Whole fish	1997-2013	Length Year Lipid	NS (0.82) NS (0.13) **8.4 (< 0.01)**	**1.6** **1.2** **1.5**
Minnesota DNR	Skin-on fillet	1996-2010	Length Year	**1.4 (< 0.01)** NS (0.10)	**1.0** **1.0**
Wisconsin DNR	Skin-on fillet	1995-2013	Length Year Lipid	**3.2 (< 0.01)** **-12.1 (0.04)** NS (0.73)	**1.2** **1.2** **1.2**

***Generally, multi-collinearity is weak when VIF < 5.

Table 2-3. Summary of multiple linear regression analysis on log-transformed PCB concentrations.

Data Groups	Fish Preparation	Sampling Period	Predictor Variables	Estimates (p value)	VIF *
Keweenaw Bay EPA	Whole fish	1995-2009	Length Year	**0.0017 (< 0.01)** **-0.0163 (< 0.01)**	**1.0** **1.0**
Apostle Islands EPA	Whole fish	1996-2008	Length Year	**0.0023 (< 0.01)** NS (0.86)	**1.1** **1.1**
Michigan DEQ	Whole fish	1996-2013	Length Year Lipid	**0.0031 (< 0.01)** NS (0.19) NS (0.13)	**1.9** **1.8** **1.3**
Thunder Bay Canada	Whole fish	1997-2013	Length Year Lipid	**0.0015 (< 0.01)** NS (0.11) NS (0.58)	**1.5** **1.2** **1.2**
Whitefish Bay Canada	Whole fish	1997-2013	Length Year Lipid	NS (0.60) **-0.0072 (0.01)** **8.4 (< 0.01)**	**1.6** **1.2** **1.5**
Minnesota DNR	Skin-on fillet	1996-2010	Length Year	**0.0023 (< 0.01)** **-0.0238 (< 0.01)**	**1.0** **1.0**
Wisconsin DNR	Skin-on fillet	1995-2013	Length Year Lipid	**0.0033 (< 0.01)** **-0.0161 (< 0.01)** NS (0.89)	**1.2** **1.2** **1.2**

*Generally, multi-collinearity is weak when VIF < 5.

2.3.4 Normalization of PCB Concentrations

According to the results of multiple linear regression in Section 2.3.3, lipid content

was a poor predictor of PCB concentrations at nearly all sites. Lipid contents of lake

trout collected at different sampling locations were similar (Carlson and Swackhamer

2006). Hence, we did not normalize PCB concentrations to lipid content in this study.

It should be noted that fish lengths were different between groups, making it difficult

to compare PCB concentrations through years and locations directly. To minimize the

influence of fish length, PCB concentrations were normalized to fish length before

assessment of temporal trends and spatial variabilities. Both a linear model and power

model were applied to year-specific fish sample data to evaluate the relationship

between PCB concentrations and fish length.

Linear model:

$$PCB_L = aL + b \qquad \text{[Equation 2.3]}$$

Power model:

$$PCB_L = aL^b \qquad \text{[Equation 2.4]}$$

The power model is equivalent to another linear regression model after log-

transformation:

$$\ln(PCB_L) = \ln(a) + b\ln(L) \qquad \text{[Equation 2.5]}$$

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where PCB_L is PCB concentration (ng/g ww) at fish length L (mm). Constants a and b are estimated parameters in regression models. Site- and year-specific equations for both models are listed in Table A-5.

For data from all agencies during the period of 1976-2013, a significant positive relationship between PCB concentrations and fish length was observed in nearly half of the 98 year-specific data groups when using Equation 2.2 (47 of 98 tests, 48%). The power model (Equation 2.4) also resulted in the same percentage of positive relationships (48 of 98 tests, 49%). Thus, use of either model is appropriate, and we used the power model in subsequent analysis. The percentage varied dramatically among different sampling locations. The EPA and Michigan DEQ data showed fewer positive relationships when compared with data from the other three agencies. Only 27%, 17%, and 44% of the years exhibited positive relationships between PCBs and fish length for Keweenaw Point, Apostle Islands, and Keweenaw Bay, respectively. Positive relationships were observed in 59%, 53%, 54%, and 88% for Thunder Bay, Whitefish Bay, Minnesota DNR, and Wisconsin DNR, respectively (Figure 2-6). Such large differences can possibly be attributed to relatively large fish length range and sample size. Generally, the significance of positive relationships between contaminant levels and fish length increased with sample size and fish length range (Gewurtz, Bhavsar, and Fletcher 2011). The EPA and Michigan DEQ tried to collect lake trout in a narrow range in order to minimize the influence of fish length but ECCC and the two DNRs did not. In addition, the U.S. EPA and Michigan DEQ had only about 10 samples each sampling year while other agencies usually collected over 20 fish during the same sampling event.
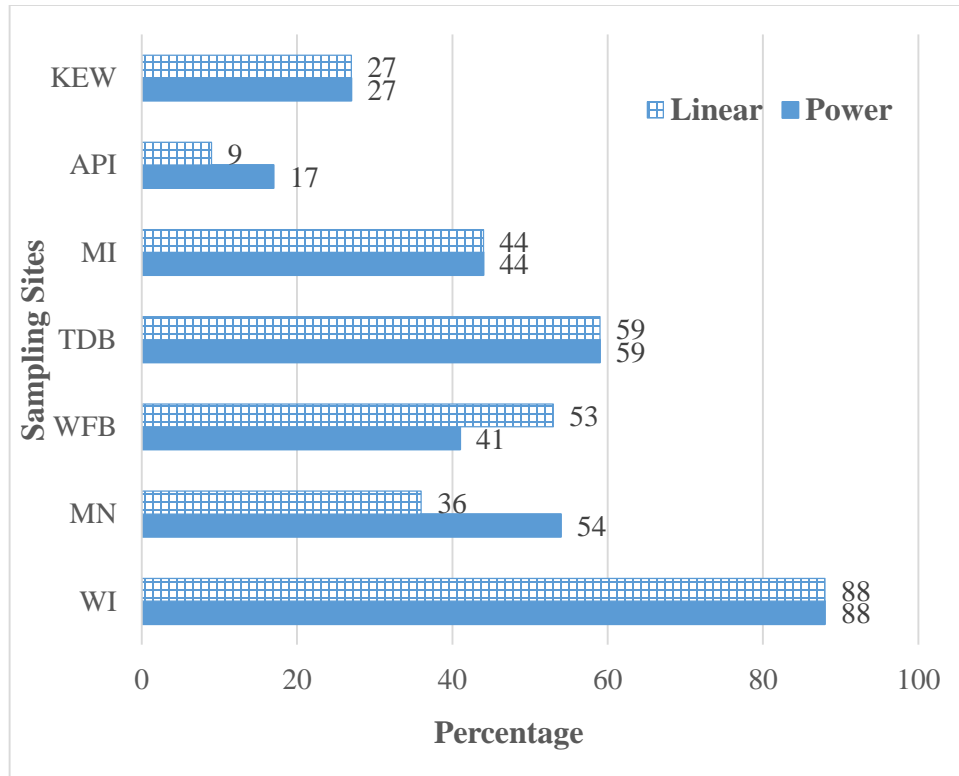
Figure 2-6. Percentage of cases that showed a significant relationship between PCB concentrations and fish length by both linear and power models. KEW-Keweenaw Point (U.S. EPA); API-Apostle Islands (U.S. EPA); MI-Keweenaw Bay (Michigan DEQ); TDB-Thunder Bay (ECCC); WFB-Whitefish Bay (ECCC); MN-Minnesota DNR; WI-Wisconsin DNR.

2.3.5 Fish Preparation Techniques

Since the techniques of fish preparation varied a lot among agencies, the spatial distributions of PCBs could partly be attributed to the differences between whole fish and skin-on fillets. In order to identify the variations and influences of different fish tissue types in spatial distribution analysis, lake trout collected from Apostle Islands (U.S. EPA, whole fish) were compared with those collected from Ashland County, Wisconsin (WI DNR, skin-on fillet; Figure 2-2, W9-W15). Since these two sampling locations are geographically close to each other, there are probably minor differences in food web structure, circulation pattern, historical input, and climate between them. As discussed previously, the U.S. EPA made an effort to collect fish of the same length, most of which were within in the range of 600-700 mm. However, the length of lake trout collected by Wisconsin DNR ranged from 340 mm to 940 mm over the 37-year period. The fish between 550 mm and 750 mm were selected in analysis from both agencies to minimize the influence of fish size. Since the U.S. EPA sampled only in even years in Apostle Islands while Wisconsin DNR sampled only in odd years in Ashland County since 1995, no data from the same year but only from adjacent years could be compared. It should also be noted that the PCB analytical methods changed from Aroclor to congener in the U.S. EPA monitoring program during the mid-1990s while Wisconsin DNR reported total PCBs as Aroclors through the period of the program. Generally, total PCB concentrations in whole fish samples appeared to be markedly greater than those in skin-on fillet samples by 2-4 fold. The change in PCB analytical methods had little impact on the general pattern of differences (Figures 2-7 & 2-8). The difference between the two agencies results from the affinity of PCBs for

lipids and the higher lipid content of whole fish as compared with fillets. Similar

differences were found between whole fish and fillets for other fish species and lakes,

e.g., coho salmon and rainbow trout from Lake Michigan and lake trout from Lake

Ontario (Amrhein, Stow, and Wible 1999).
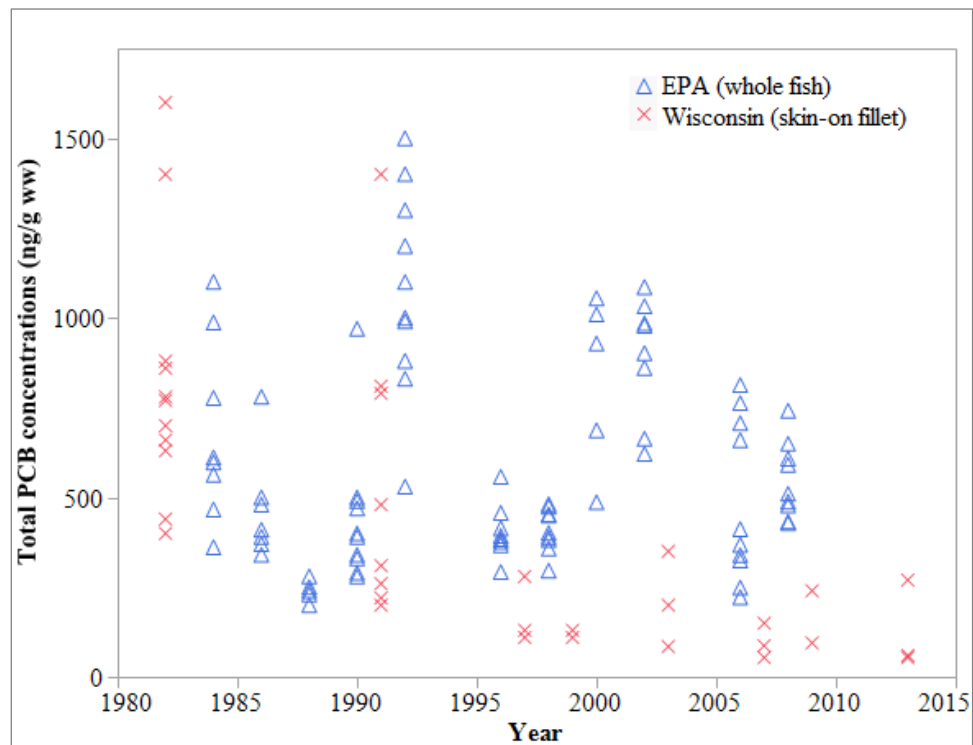
Figure 2-7. Comparison of total PCB concentrations in lake trout between whole fish samples and skin-on fillet samples for the whole period of monitoring programs. The EPA measured total PCBs as Aroclors prior to 1995 and changed to congener method after that. Wisconsin DNR measured total PCBs as Aroclors throughout the period.
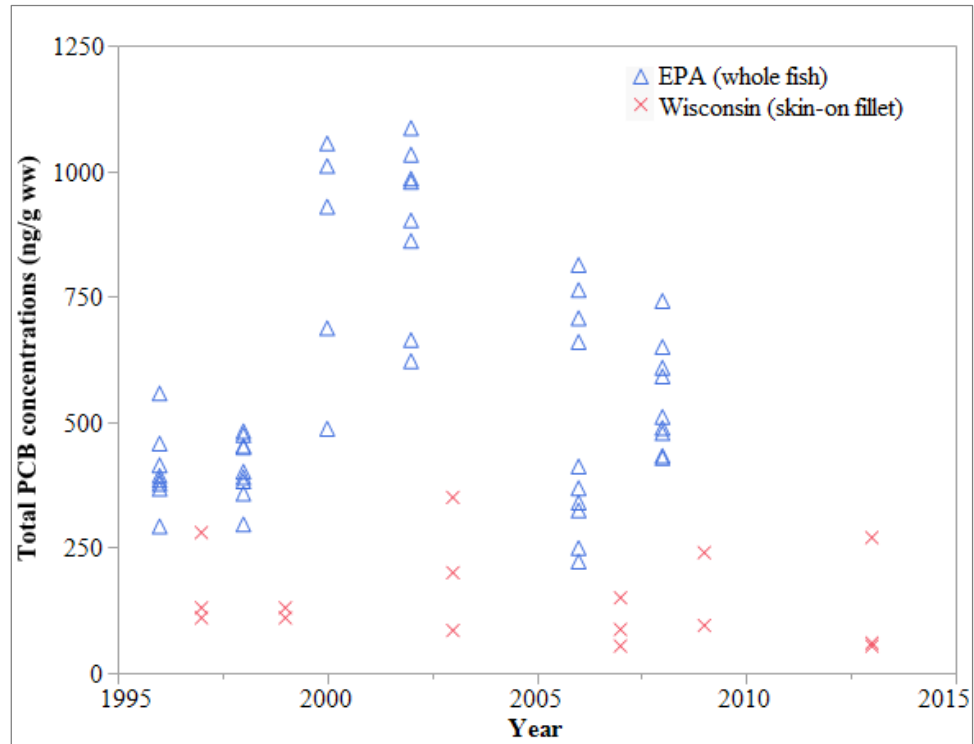
Figure 2-8. Comparison of total PCB concentrations in lake trout between whole fish samples and skin-on fillet samples since the change in PCB analytical techniques of the EPA program in 1995. The U.S. EPA measured total PCBs as the sum of 110 congeners and Wisconsin DNR measured them as Aroclors.

2.3.6 Temporal Trends

In order to minimize the influence of fish length, yearly average PCB concentrations from each agency were normalized to 600 mm, a common length of lake trout, by using the power model in Equation 2.5 before analyzing the temporal trends and spatial variabilities. PCB concentrations in lake trout from Lake Superior declined rapidly since the restriction on their production and use in 1979 in North America. The yearly average PCB levels before 1990 were approximately 2- to 3- fold higher than those after 1990 (Figure 2-9). While some of this apparent decline is due to changes in analytical methodology, it is not clear that all of the decline can be ascribed to that cause.

Unlike the historical rapid decline, downward trends of PCBs levelled off after about 1990. PCB levels in lake trout collected by the EPA and Michigan DEQ had a sharp decline in 1995 due to the shift in total PCB analytical technique from the mixture of Aroclors to sum of PCB congeners. Because the EPA did not determine total PCBs with both Aroclor and congener-specific methods for the same samples, it is not possible to analyze the temporal trends of the entire duration of the monitoring program. In order to assess the trends in different data sets, only samples collected after 1995 were analyzed from all five agencies.

At most sampling sites in Lake Superior, no statistically significant temporal trends in PCB levels in lake trout were found after 1995. Only 2 of 7 data sets showed statistically significant declines after 1995. Total PCBs in lake trout from Keweenaw Point decreased by approximate 25%, from 330 ng/g ww to 250 ng/g ww, during the period 1995-2009 (p value = 0.0005). Marginal significant declining trend was observed

in Wisconsin sites during the same period (p value = 0.04). In contrast, there were no significant trends in PCB concentrations in the other five data sets (p value = 0.95, 0.38, 0.14, 0.13, and 0.10 for Apostle Islands, Keweenaw Bay, Thunder Bay, Whitefish Bay, and Minnesota DNR, respectively). Abrupt changes in PCB concentrations were observed in several locations including Apostle Islands, Thunder Bay, Minnesota coastal waters, and Wisconsin coastal waters in the early 2000s for unknown reasons. Large yearly fluctuations in Wisconsin DNR data during the later 1970s and early 1980s may be attributed to large numbers of sampling sites and relatively small sample sizes each year. Our results are in good agreement with previous reported data. Decline rates of total PCBs diminished significantly compared with historical data (Table 2-4).

   Currently, at all sites, it is evident that total PCB concentrations in Lake Superior lake trout are still above the target of 100 ng/g ww established by EPA or 105 ng/g ww established by the Ontario Ministry of Environment and Climate Change (OMOECC) to protect wildlife and human health (OMOECC 2014). The large interannual fluctuations in PCBs observed at all sites make it difficult to predict the future conditions.

Table 2-4. Slopes of statistically significant temporal trends of PCB concentrations in lake trout from Lake Superior.

Sampling locations	Model type[*]	Period	Slope	*p* value	Reference
Keweenaw Point	1	1995-2009	**-9.3 yr⁻¹**	0.0005	This study
Wisconsin DNR	1	1996-2013	**-12.1 yr⁻¹**	0.04	This study
Keweenaw Point	2	1995-2009	**-0.0163 yr⁻¹**	0.0002	This study
	2	1991-2003	-0.0664 yr⁻¹	0.01	Carlson *et al*. 2010
	2	1999-2009	-0.02 yr⁻¹	NG[***]	Chang *et al*. 2012
Apostle Islands	2	1996-2008	NS[**]	0.86	This study
	2	1986-2002	NS	0.13	Carlson *et al*. 2010
	2	2000-2008	-0.06	< 0.05	Chang *et al*. 2012
Whitefish Bay	2	1997-2013	**-0.0073 yr⁻¹**	0.01	This study
Minnesota DNR	2	1996-2010	**-0.0238 yr⁻¹**	0.0037	This study
Wisconsin DNR	2	1996-2013	**-0.0161 yr⁻¹**	< 0.0001	This study
Keweenaw Point & Apostle Islands	2	1977-1990	-0.0434 yr⁻¹	< 0.05	DeVault *et al*. 1996
	2	1977-1998	-0.1292 yr⁻¹	< 0.01	Hickey *et al*. 2006
	2	1992-2010	-0.0219 yr⁻¹	NG	Salamova *et al*. 2013
OMOE sites	2	1978-2006	-0.0323 yr⁻¹	NG	Bhavsar *et al*. 2007

[*]Type 1 indicates the slope of original concentration versus time while type 2 indicates the slope of log-transformed concentration versus time.

[**]NS indicates that the slope is not statistically significant.

[***]NG indicates that the values are not given.
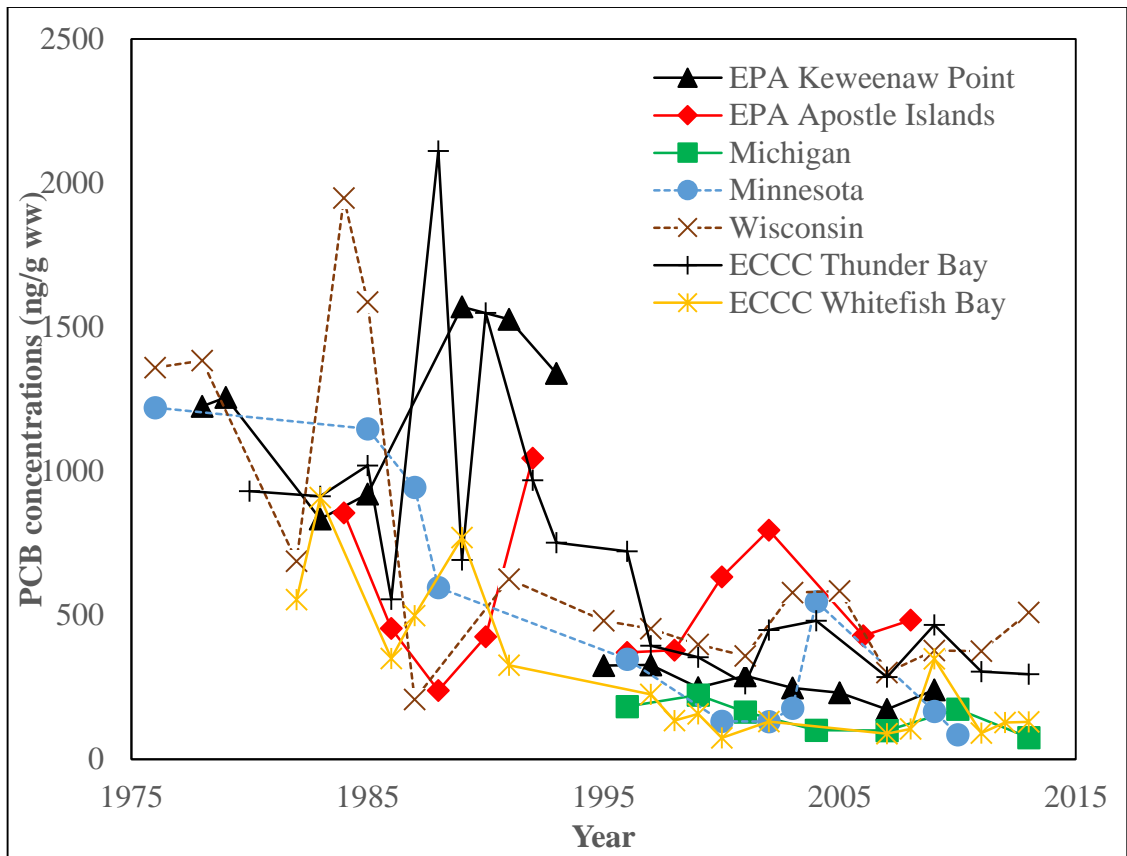
Figure 2-9. Temporal trends of average PCB concentrations sorted by sampling sites since 1976 (normalized to fish length). The solid lines represent whole fish and the dashed lines represent skin-on fillets.
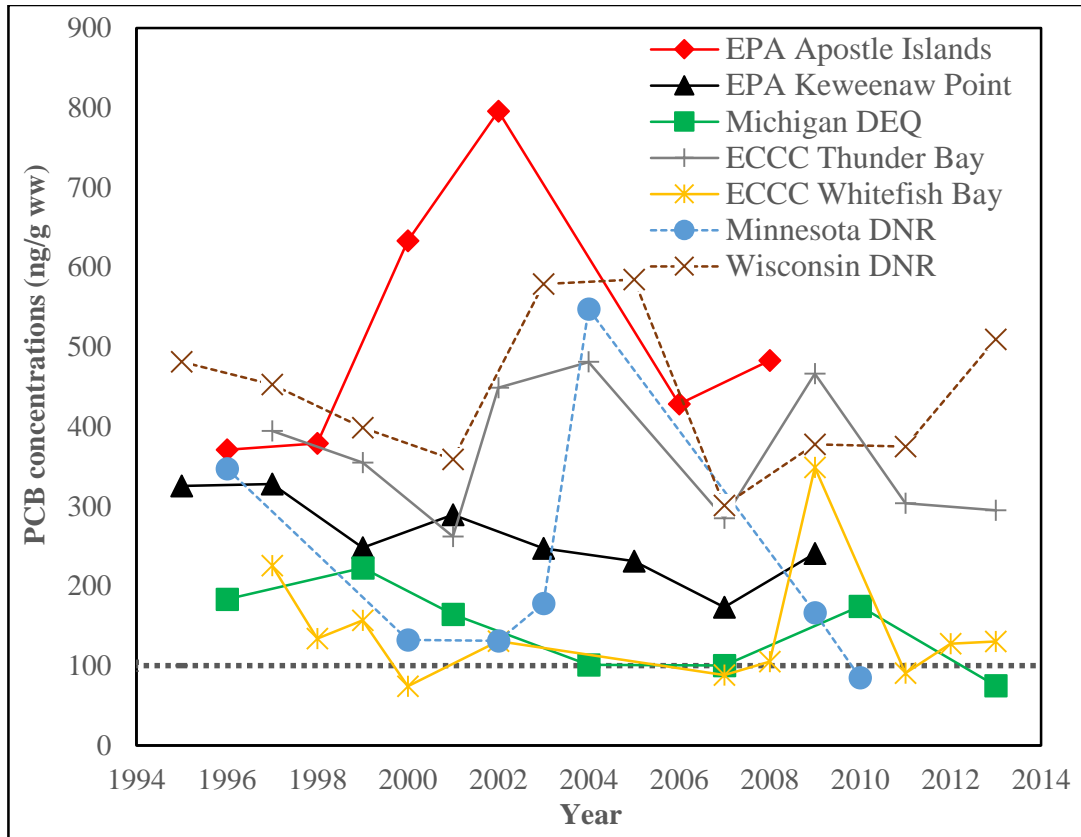
Figure 2-10. Temporal trends of average PCB concentrations sorted by sampling sites since 1995 (normalized to fish length). The solid lines represent whole fish and the dashed lines represent skin-on fillets. The horizontal dotted line represents the reduction target of 100 ng/g for wildlife and human health protection established by the EPA.

2.3.7 Spatial Variability

PCB levels in lake trout varied tremendously between different sampling locations in Lake Superior (Figures 2-9 & 2-10). After normalization to fish length at 600 mm by using Equation 2.5 (i.e., using a value of $L = 600$ in Equation 2.5), yearly average PCB concentrations of different agencies did not have an exact order. During the late 1970s and 1980s, interannual variations were too large to have a fixed order of total PCB levels among sites. In general, total PCBs in Apostle Islands lake trout tended to be the highest among all data sets after 1995, ranging from 400 ng/g ww in 1996 to 800 ng/g ww in 2002. Keweenaw Bay and Whitefish Bay had significantly lower PCB levels that were not greater than 200 ng/g ww in most years. There was no precise order of PCBs in the four other data sets that had relatively wide ranges in PCB concentrations, from ~150 ng/g ww to 550 ng/g. Few sites shared a similar pattern of temporal trends, which may reveal spatial differences within Lake Superior.

Although all agencies reported PCB concentrations in lake trout as 'Total PCBs', it should be noted that fish preparations and PCB measurement methods were different. Statistically significant inter-site differences were observed in the paired sampling locations by both the EPA and ECCC. Total PCB concentrations in Apostle Islands and Thunder Bay fish were greater than in fish from Keweenaw Point and Whitefish Bay, respectively (Figures 2-11 & 2-12). Overall, the western basin of Lake Superior had higher PCBs than the eastern basin, possibly as a result of previous industrial activity near the western shore (e.g., Duluth in Minnesota). Similar distribution was observed in walleye from Lake Erie, where the western half had higher PCB concentrations than the eastern half. Historical large amount of PCB point sources near the Detroit River

(upstream of Lake Eire) in the wester basin contributed to the downward gradient (Carlson and Swackhamer 2006).

Spatial differences were also evident even between locations that are geographically close to each other. For instance, total PCB concentrations in Wisconsin DNR fish samples were significantly higher than those in Minnesota DNR samples in recent years although these sites were close together and there was little difference between their analytical techniques.
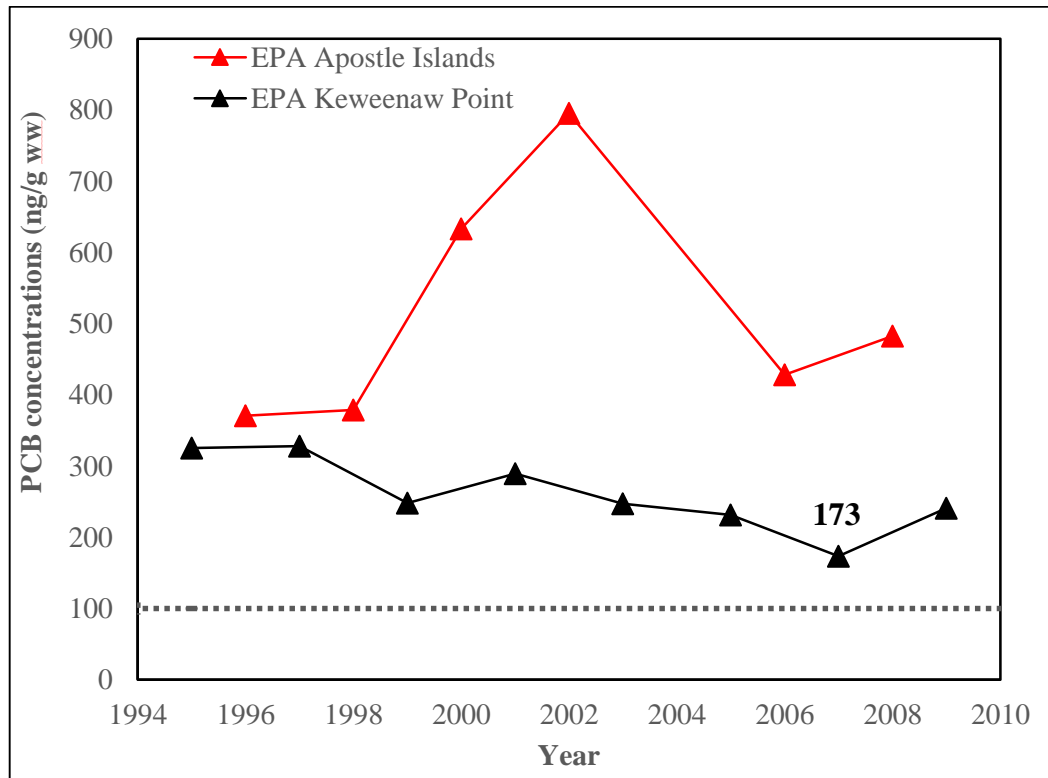
Figure 2-11. Yearly average PCB concentrations (normalized by fish length) in paired sampling sites by the U.S. EPA during 1995-2009. The horizontal dotted line represents the reduction target of 100 ng/g that established by the U.S. EPA.
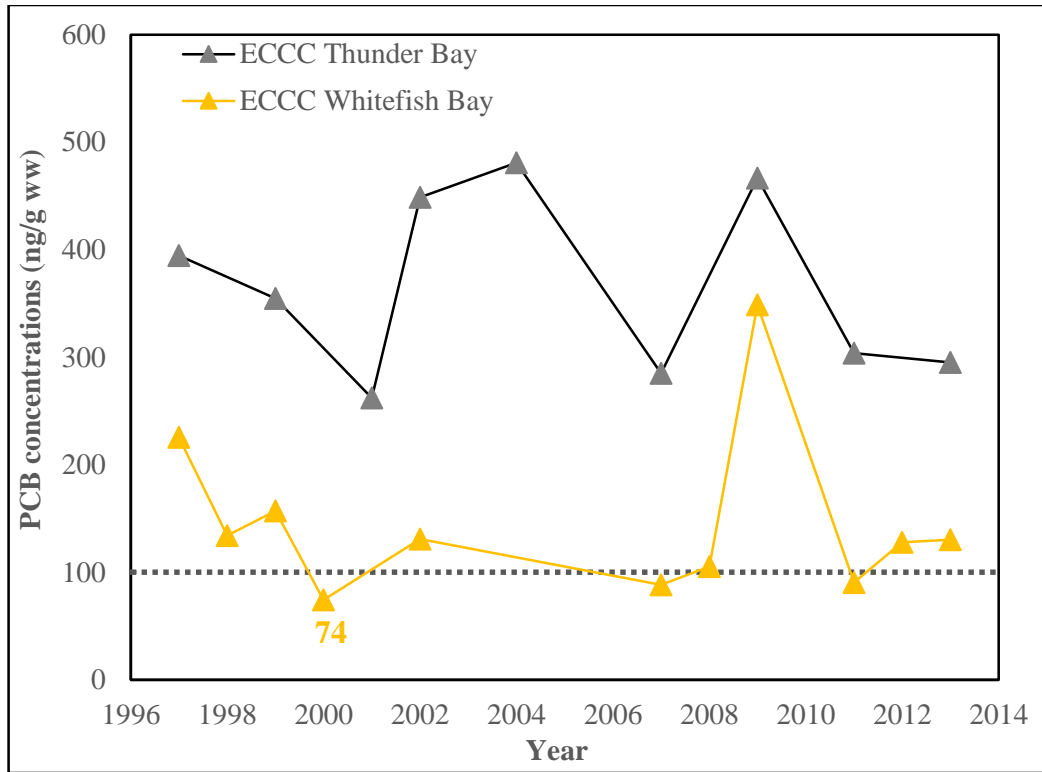
Figure 2-12. Yearly average PCB concentrations (normalized by fish length) in paired sampling sites by Environment and Climate Change Canada during 1997-2013. The horizontal dotted line represents the reduction target of 100 ng/g that established by the U.S. EPA.

2.4 Discussion

The five agencies that provided fish contaminant data sampled nearly the entire area of Lake Superior. Using such extensive long-term fish contaminant monitoring datasets allowed us to present a comprehensive analysis of trends in the PCB concentrations in Lake Superior fish. For data from the U.S. EPA, Michigan DEQ, and ECCC, total PCBs were measured in whole lake trout. The other two state agencies, Minnesota DNR and Wisconsin DNR, both analyzed PCBs using skin-on fillets of lake trout. Thus it is not expected that the concentrations reported by all agencies will be comparable. Generally, it has been observed that PCB concentrations are higher in whole fish samples than in fillets because of the lower lipid content in fillets (Gewurtz et al. 2011).

Previous studies generally have not reported significant within-lake spatial differences in PCB concentrations in fish from the Great Lakes. They combined different sampling locations in one single lake. For example, fish data of the two EPA sites, Keweenaw Bay and Apostle Islands, were pooled for analysis of temporal trends. (Hickey, Batterman, and Chernyak 2006, Salamova et al. 2013). An exception is lake trout from Lake Huron, where significant spatial differences were observed between the main basin, Georgian Bay, and North Channel (Paterson et al. 2016). However, significant spatial differences in PCB concentrations in lake trout from Lake Superior were found in our study. The spatial differences are probably not a result of regional trends in atmospheric deposition, the primary source of PCBs to the Great Lakes. There have been many hypotheses to explain why spatial distributions of PCB concentrations exist in Lake Superior. Carlson *et al*. pointed out that differences in food webs could contribute to such spatial patterns within the lake. Besides, water movement patterns

and local climate may be other explanations (Carlson and Swackhamer 2006). For instance, the paired sites of the EPA, Keweenaw Point and Apostle Islands, are offshore and nearshore locations, respectively. The paired sites by the ECCC, Thunder Bay and Whitefish Bay, are geographically far from each other. Local environmental conditions may play an important role in modifying the PCB levels (Schmidt, Vander Zanden, and Kitchell 2009, McGoldrick et al. 2010).

There were seven geographic areas where fish were sampled by the five agencies. Only two locations exhibited significant diminishing trends of total PCBs in lake trout after 1995. Currently, net atmospheric loading of PCBs is negative due to the large amount of volatilization (Blanchard et al. 2008). Thus, sediments have changed from a net sink of PCBs to a source by releasing PCBs into the water column (Pearson et al. 1996, Bhavsar et al. 2007). Therefore, PCB concentrations in fish may be affected strongly by internal conditions within the lake, particularly concentrations in sediments.

Although only a few significant temporal trends were observed after 1995, year-to-year fluctuations existed at most sites. Total PCBs in the Apostle Islands and the Minnesota and Wisconsin samples showed abrupt changes in the late 1990s and early 2000s. These abrupt changes might result from changes in food webs. A stable isotope study has shown that the diets of Lake Superior lake trout shifted several times in the 1990s, from leaner sculpins to fattier species like lake herring, and then back to the original lean diet (Whittle et al. 1997). Human activities, climate change, and invasive species can result in alterations of food web structure. Water temperature have increased by 2-3 °C in Lake Superior during the last 30 years. With increasing wind

speed and diminishing ice cover, volatilization rate of PCBs from the lake decreased, which contributed to the alteration in the air-water exchange of PCBs. Moreover, processes of partition of PCBs between water column and sediments, as well as bioaccumulation of PCBs by fish may also change (Hickey, Batterman, and Chernyak 2006, Carlson, DeVault, and Swackhamer 2010).

In order to reduce the uncertainty in data analysis, larger sample size is required especially for agencies like Minnesota DNR and Wisconsin DNR that collected fish at a number of sites. Because no spatial differences were found among these intra-agency sites, we advise sampling at fewer sites but with larger sample size at each site.

2.5 Summary and Conclusion

Total PCB concentrations were measured in lake trout from a number of sampling locations in Lake Superior by five different agencies from the U.S. and Canada since the 1970s. For the duration of the fish contaminant monitoring programs, concentrations of total PCB have declined markedly from approximately 1200 ng/g ww to < 300 ng/g ww at most sites. Fish from the Apostle Islands and Thunder Bay areas still have concentrations of 300 to 500 ng/g ww. Over the past 20 years, total PCB concentrations in lake trout have remained almost unchanged at most sites with the exceptions of Keweenaw Point and Wisconsin sites where significant declines were observed. Although the current PCB levels are much lower compared with historical values, total PCB concentrations in lake trout from Lake Superior are still generally above the reduction target of 100 ng/g ww established by the U.S. EPA. The absence of significant temporal trends and the large interannual variability in concentrations make

it difficult to predict when the target concentrations will be reached. Comparison of fish from across the lake suggested that fish in the western half might have higher total PCB concentrations than those in eastern half.

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Appendix A: Tables

Table A-1. Publications on temporal and spatial trends of contaminant levels in fish from the Great Lakes since 1980.

Authors & Published Year	Data Sources	Contaminants	Title of Paper
Hesselberg *et al* 1990	U.S. EPA	PCBs, DDT, dieldrin	Contaminant Residues in the Bloater (*Coregonus hoyi*) of Lake Michigan, 1969-1986
Miller *et al* 1994	U.S. EPA	OCs	Organochlorine Concentration Dynamics in Lake Michigan Chinook Salmon (*Oncorhynchus tshawytscha*)
DeVault *et al* 1996	U.S. EPA	PCBs, DDT, dieldrin, chlordane, toxaphene	Contaminant Trends in Lake Trout and Walleye from the Laurentian Great Lakes
Huestis et al 1996	U.S. EPA	PCBs, OCs	Temporal and Age-related Trends in Levels of Polychlorinated Biphenyl Congeners and Organochlorine Contaminants in Lake Ontario Lake Trout (*Salvelinus namaycush*)
Weis *et al* 2004	EC	Mercury	Mercury Concentrations in Fish from Canadian Great Lakes Areas of Concern: an Analysis of Data from the Canadian Department of Environment Database
Zhu *et al* 2004	U.S. EPA	PBDEs, PBBs	Temporal Trends and Spatial Distributions of Brominated Flame Retardants in Archived Fishes from the Great Lakes
Carlson *et al* 2006	U.S. EPA	PCBs, mercury, DDT, dieldrin, toxaphene, mirex, HCB	Results from the U.S. Great Lakes Fish Monitoring Program and Effects of Lake Processes on Contaminant Concentrations
Hickey *et al* 2006	U.S. EPA	PCBs, DDT, dieldrin, toxaphene, and mirex	Trends of Chlorinated Organic Contaminants in Great Lakes Trout and Walleye from 1970 to 1998
Bhavsar *et al* 2007	OMOE	PCBs	Are PCB Levels in Fish from the Canadian Great Lakes Still Declining?
Bhavsar *et al* 2010	OMOE	Mercury	Changes in Mercury Levels in Great Lakes Fish Between 1970s and 2007

Table A-1 (Continued)

Sadraddini *et al* 2011	U.S. EPA	PCBs, mercury	Temporal PCB and Mercury Trends in Lake Eire Fish Communities: a Dynamic Linear Modeling Analysis
Zananski *et al* 2011	U.S. EPA	Mercury	Mercury Temporal Trends in Top Predator Fish of the Laurentian Great Lakes
Chang *et al* 2012	U.S. EPA	PCBs, OCs	Temporal Trends of Polychlorinated Biphenyls and Organochlorine Pesticides in Great Lakes Fish, 1999–2009
Mahmood *et al* 2013	U.S. EPA	OCs	Fish Contamination in Lake Erie: an Examination of Temporal Trends of Organochlorine Contaminants and a Bayesian Approach to Consumption Advisories
Salamova *et al* 2013	U.S. EPA	PCBs, OCs	Post-1990 Temporal Trends of PCBs and Organochlorine Pesticides in the Atmosphere and in Fish from Lakes Erie, Michigan, and Superior
Rasmussen *et al* 2014	U.S. EPA	PCBs	Trends of PCB Concentrations in Lake Michigan Coho and Chinook Salmon, 1975-2010
McGoldrick *et al* 2015	U.S. EPA	PCBs, mercury, PBDEs, OCs	Concentrations and Distribution of Contaminants in Lake Trout and Walleye from the Laurentian Great Lakes (2008-2012)

Table A-2. Sampling locations and years of each agency.

Agencies	Sampling Locations	Sampling Years	Analytical Techniques of Total PCBs
U.S. EPA	Keweenaw Point	1978, 1979-2009 (all odd years except 1981 and 1987)	Aroclor 1254 before 1995; Sum of 110 congeners after 1995.
	Apostle Islands	1984-2008 (all even years except 1994)	
ECCC (Canada)	Whitefish Bay	1982, 1983, 1986, 1987, 1989, 1991, 1997, 1998, 1999, 2000, 2002, 2007, 2008, 2009, 2011, 2012, 2013	Aroclor 1254
	Thunder Bay	1980, 1983, 1985, 1986, 1988, 1989, 1990, 1992, 1993, 1996, 1997, 1999, 2001, 2002, 2004, 2007, 2009, 2011, 2013	
Michigan DEQ	Keweenaw Bay	1991, 1993, 1996, 1999, 2001, 2004, 2007, 2010	Aroclor 1254 before 1996; Congeners since 1996.
Minnesota DNR	15 sites*	1976, 1985, 1987, 1988, 1996, 2000, 2002, 2004, 2009, 2010	Aroclors
Wisconsin DNR	17 sites*	1976, 1982, 1984, 1985, 1987, 1991, 1995-2013 (all odd years)	Aroclors

*For further information on sampling sites from MN DNR and WI DNR, see Table A-4.

Table A-3. The arithmetic means of fish length and PCB concentrations in lake trout in several locations in Lake Superior (95% confidence intervals in parentheses).

Year	Number of Samples	Fish Length (mm)	Lipid (%)	PCB Concentrations (ng/g wet weight)
Keweenaw Point (U.S. EPA)				
1978	12	532 (434, 629)	NA[*]	1086 (674, 1497)
1979	10	478 (364, 592)	NA	1001 (312, 1689)
1983	10	594 (576, 612)	NA	826 (725, 928)
1985	9	620 (603, 636)	NA	950 (630, 1270)
1989	10	614 (564, 665)	NA	1608 (1092, 2124)
1991	10	544 (517, 571)	NA	1385 (1154, 1616)
1993	10	614 (602, 626)	NA	1370 (1179, 1561)
1995[**]	10	615 (604, 626)	NA	334 (242, 425)
1997	9	648 (637, 660)	NA	354 (302, 407)
1999	8	603 (573, 634)	NA	250 (182, 318)
2001	3	614 (604, 625)	NA	296 (-42, 635)
2003	10	567 (556, 579)	NA	234 (180, 288)
2005	7	637 (625, 649)	NA	246 (144, 348)
2007	7	632 (616, 649)	NA	183 (142, 224)
2009	8	636 (612, 660)	NA	255 (138, 373)
Apostle Islands (U.S. EPA)				
1984	9	594 (572, 615)	NA	846 (428, 1264)
1986	8	602 (585, 618)	NA	455 (336, 574)
1988	10	603 (580, 626)	NA	240 (221, 259)
1990	10	629 (620, 639)	NA	446 (303, 589)
1992	10	616 (604, 628)	NA	1073 (865, 1281)
1996[**]	10	649 (633, 665)	NA	401 (352, 450)
1998	10	630 (613, 646)	NA	398 (350, 446)
2000	9	743 (725, 761)	NA	784 (607, 961)
2002	8	672 (654, 690)	NA	891 (750, 1032)
2006	10	681 (659, 703)	NA	486 (325, 646)
2008	9	680 (664, 697)	NA	548 (466, 629)
Keweenaw Bay (Michigan DEQ)				
1991	10	632 (617, 648)	15.6 (13.8, 17.3)	352 (257, 448)
1993	10	603 (578, 629)	16.5 (13.0, 20.0)	367 (216, 518)
1996[**]	10	624 (608, 639)	14.8 (12.2, 17.4)	191 (112, 269)
1999	10	630 (620, 640)	14.6 (12.2, 17.1)	234 (148, 319)
2001	10	629 (621, 637)	14.1 (11.5, 16.6)	172 (107, 238)
2004	10	608 (563, 654)	14.7 (12.9, 16.4)	103 (44, 162)
2007	10	522 (462, 583)	8.3 (7.0, 9.7)	87 (26, 148)

Table A-3 (Continued)

2010	10	469 (441, 496)	10.9 (8.4, 13.3)	136 (-47, 320)
2013	10	531 (479, 584)	12.2 (10.7, 13.7)	66 (42, 91)

Thunder Bay (ECCC)

1980	50	548 (522, 574)	18.7 (16.8, 20.6)	850 (755, 945)
1983	50	469 (444, 494)	11.8 (10.7, 12.9)	714 (613, 815)
1985	50	413 (385, 441)	9.1 (7.1, 11.1)	702 (549, 855)
1986	50	482 (462, 502)	10.5 (9.1, 11.9)	446 (381, 511)
1988	25	546 (514, 578)	11.4 (9.9, 12.9)	1920 (1615, 2225)
1989	35	444 (402, 485)	11.3 (9.5, 13.1)	511 (439, 584)
1990	52	485 (465, 505)	12.4 (11.2, 13.5)	1252 (1062, 1441)
1992	20	502 (480, 524)	15.2 (12.7, 17.8)	810 (642, 978)
1993	41	603 (585, 621)	13.2 (12.0, 14.4)	756 (607, 905)
1996	40	519 (496, 543)	18.8 (16.9, 20.7)	625 (494, 756)
1997	50	636 (608, 664)	16.6 (14.5, 18.8)	418 (337, 499)
1999	20	562 (537, 587)	18.9 (16.1, 21.7)	332 (238, 427)
2001	50	555 (535, 576)	14.4 (13.3, 15.5)	243 (191, 294)
2002	40	500 (476, 524)	14.6 (13.1, 16.2)	374 (284, 464)
2004	40	540 (525, 556)	13.1 (11.4, 14.9)	433 (290, 576)
2007	50	516 (501, 531)	13.7 (12.4, 15.1)	245 (206, 284)
2009	50	550 (530, 570)	15.6 (14.0, 17.1)	428 (362, 493)
2011	25	497 (465, 528)	14.4 (11.9, 17.0)	252 (192, 311)
2013	25	441 (422, 460)	11.4 (10.0, 12.9)	217 (166, 267)

Whitefish Bay (ECCC)

1982	46	476 (449, 503)	13.4 (10.6, 16.2)	439 (371, 507)
1983	35	583 (553, 614)	20.9 (18.7, 23.1)	883 (513, 1253)
1986	33	492 (473, 510)	12.6 (11.1, 14.1)	286 (230, 343)
1987	50	391 (372, 410)	8.1 (6.9, 9.4)	325 (277, 373)
1989	47	481 (464, 498)	17.6 (15.4, 19.7)	617 (506, 728)
1991	24	594 (550, 638)	12.0 (10.5, 13.5)	323 (242, 404)
1997	40	489 (469, 509)	16.5 (15.4, 17.6)	184 (145, 223)
1998	30	488 (456, 519)	13.0 (11.6, 14.4)	109 (80, 138)
1999	15	466 (439, 493)	16.5 (14.0, 18.9)	122 (105, 139)
2000	30	442 (417, 468)	11.0 (9.8, 12.3)	55 (45, 64)
2002	20	484 (460, 508)	10.7 (9.7, 11.8)	106 (82, 130)
2007	49	468 (449, 488)	9.2 (8.0, 10.3)	69 (56, 82)
2008	50	542 (522, 562)	13.6 (11.8, 15.4)	95 (77, 113)
2009	46	528 (515, 540)	19.4 (17.8, 20.8)	307 (262, 351)
2011	25	530 (511, 550)	18.1 (16.5, 19.7)	80 (66, 94)
2012	25	562 (542, 581)	19.8 (18.0, 21.7)	120 (72, 167)
2013	18	542 (500, 584)	25.6 (21.5, 29.7)	118 (98, 138)

Table A-3 (Continued)

Minnesota DNR				
1976	43	572 (547, 596)	11.2 (9.5, 12.8)	1163 (1037, 1289)
1985	15	579 (533, 626)	9.0 (7.6, 10.4)	1108 (319, 1897)
1987	20	626 (552, 701)	9.2 (7.9, 10.6)	986 (458, 1513)
1988	21	586 (526, 645)	7.2 (5.6, 8.8)	581 (271, 891)
1996	18	600 (536, 664)	7.7 (5.4, 10.0)	347 (197, 498)
2000	10	590 (524, 657)	10.4 (8.8, 12.1)	130 (87, 174)
2002	12	605 (506, 704)	NA[*]	132 (69, 196)
2003	3	742 (570, 913)	NA	220 (82, 358)
2004	6	831 (785, 877)	NA	758 (253, 1264)
2009	5	560 (372, 748)	NA	156 (-54, 365)
2010	5	564 (522, 606)	NA	80 (44, 116)
Wisconsin DNR				
1976	7	506 (445, 567)	12.4 (4.3, 20.6)	1147 (577, 1717)
1978	1	564	11.7	1300
1982	12	711 (685, 737)	13.7 (11.0, 16.3)	814 (589, 1039)
1984	7	596 (376, 816)	7.9 (2.7, 13.1)	1936 (-270, 4141)
1985	7	733 (631, 835)	12.0 (8.9, 15.2)	1939 (4, 3873)
1987	6	515 (463, 568)	8.2 (6.8, 9.6)	178 (142, 214)
1991	30	678 (632, 724)	11.0 (9.3, 12.6)	706 (481, 931)
1995	18	651 (587, 715)	10.8 (7.9, 13.8)	522 (250, 793)
1997	18	656 (590, 722)	9.6 (8.0, 11.2)	495 (273, 717)
1999	19	650 (578, 722)	9.5 (7.8, 11.1)	432 (212, 652)
2001	16	646 (578, 713)	8.5 (6.7, 10.3)	386 (186, 586)
2003	12	712 (549, 775)	10.1 (7.6, 12.5)	687 (274, 1010)
2005	10	672 (549, 795)	8.4 (6.4, 10.3)	655 (-62, 1372)
2007	9	718 (651, 785)	6.9 (5.5, 8.3)	360 (150, 571)
2009	15	703 (624, 782)	5.8 (4.4, 7.1)	443 (168, 716.8)
2011	14	719 (649, 789)	7.2 (5.5, 8.9)	449 (145, 754)
2013	20	722 (660, 783)	9.0 (7.6, 10.5)	612 (235, 989)

[*]NA indicates not analyzed.

[**]For the two sites of U.S. EPA, total PCBs were measured as a mixture of Aroclors prior to 1995 and were quantitated as congeners since then.

[***]For Keweenaw Bay (Michigan DEQ), total PCBs were measured as a mixture of Aroclors prior to 1996 and were quantitated as congeners since then.

Table A-4. Summary of individual sampling locations of Minnesota DNR and Wisconsin DNR.

Sampling Location ID	Sampling Locations Name	Sampling Years	Number of Samples*
Minnesota DNR			
M1	Coast Guard	2002	2 (0)
M2	French River	1976	14 (0)
		1983	1 (1)
		1985	2 (0)
		1987	12 (0)
		1988	11 (0)
		1996	6 (0)
		2004	1 (0)
M3	Knife Island	1996	4 (0)
M4	Two Harbors	1996	1 (0)
		2002	3 (0)
		2004	5 (0)
		2009	5 (0)
		2010	4 (1)
M5	Encampment Island	1996	2 (0)
		2010	1 (1)
M6	Split Rock Point	1983	1 (1)
		1985	5 (0)
		1987	2 (0)
		1996	1 (0)
		2002	4 (0)
		2010	1 (1)
M7	Beaver Bay	1985	4 (0)
M8	Silver Bay	2002	3 (0)
		2010	4 (2)
M9	Little Marais	1976	14 (0)
M10	Tofte	1996	4 (0)
M11	Grand Marais	1983	1 (1)
		1985	4 (0)
		1987	6 (0)
		1988	6 (0)
M12	Hovland	1976	15 (0)
M13	Grand Portage	1988	4 (0)
		2003	3 (0)
M14	Hat Point	1983	1 (1)
M15	Clark Bay	2000	10 (0)

Table A-4 (Continued)

Wisconsin DNR			
W1	Douglas-1	1985	1 (0)
		1987	1 (0)
		2011	4 (1)
W2	Douglas-2	1985	2 (0)
		1991	13 (0)
		1995	10 (1)
		1997	6 (0)
		1999	2 (0)
		2003	2 (0)
		2013	7 (0)
W3	Douglas-3	1976	2 (0)
		1978	1 (0)
		1985	1 (0)
		1997	2 (0)
		1999	7 (0)
		2001	2 (0)
		2005	2 (0)
		2009	10 (0)
W4	Douglas-4	1997	1 (0)
		1999	2 (0)
		2001	5 (0)
		2003	5 (0)
		2005	3 (0)
		2013	3 (0)
W5	Bayfield-1	2007	5 (1)
W6	Bayfield-2	2001	1 (0)
W7	Bayfield-3	1976	1 (0)
		2011	5 (0)
W8	Bayfield-4	1976	3 (0)
W9	Ashland-1	2013	1 (0)
W10	Ashland-2	1991	1 (0)
		2003	1 (0)
		2005	2 (0)
		2007	3 (0)
		2009	3 (0)
		2013	3 (0)
W11	Ashland-3	1995	1 (0)
		1997	1 (0)
		2003	3 (0)
		2007	1 (0)

Table A-4 (Continued)

W12	Ashland-4	1991	4 (0)
W13	Ashland-5	1982	10 (0)
		1984	2 (0)
		1985	3 (0)
		1991	5 (0)
		1995	2 (0)
		1997	1 (0)
		1999	2 (0)
		2003	1 (0)
		2007	1 (0)
		2011	5 (0)
		2013	5 (0)
W14	Ashland-6	1991	7 (0)
		1997	7 (0)
		1999	7 (0)
		2013	1 (0)
W15	Ashland-7	1982	2 (0)
		1984	5 (0)
		2005	3 (0)
W16	Ashland-8	2011	1 (1)
W17	Iron	1995	6 (0)

*Value in the parentheses represents the number of samples with total PCB concentration under the detection limit. These samples were not included in the data analysis.

Table A-5. Relationship between PCB concentrations and fish length.

Year	Linear model (p value)	Power model (p value)
Keweenaw Point (U.S. EPA)		
1978	$PCB_L = 3.31L - 673$ (0.0025)	$\ln(PCB_L) = 1.508\ln(L) - 2.58$ (0.0022)
1979	$PCB_L = 4.94L - 1363$ (0.0041)	$\ln(PCB_L) = 2.401\ln(L) - 8.14$ (0.0002)
1983	NS (0.16)	NS (0.16)
1985	NS (0.64)	NS (0.51)
1989	NS (0.69)	NS (0.67)
1991	NS (0.07)	NS (0.07)
1993	NS (0.40)	NS (0.37)
1995	NS (0.82)	NS (0.92)
1997	NS (0.45)	NS (0.44)
1999	NS (0.96)	NS (0.94)
2001	NS (0.50)	NS (0.42)
2003	$PCB_L = 3.68L - 1857$ (0.0043)	$\ln(PCB_L) = 9.098\ln(L) - 52.28$ (0.0032)
2005	NS[*] (0.26)	NS (0.39)
2007	$PCB_L = 1.94L - 1047$ (0.0373)	$\ln(PCB_L) = 6.430\ln(L) - 36.28$ (0.0338)
2009	NS (0.06)	NS (0.06)
Apostle Islands (U.S. EPA)		
1984	NS (0.05)	$\ln(PCB_L) = 7.930\ln(L) - 44.03$ (0.0380)
1986	NS (0.54)	NS (0.55)
1988	NS (0.98)	NS (0.94)
1990	NS (0.50)	NS (0.51)
1992	NS (0.42)	NS (0.49)
1996	NS (0.12)	NS (0.09)
1998	NS (0.85)	NS (0.89)
2000	NS (0.64)	NS (0.69)
2002	NS (0.57)	NS (0.65)
2006	$PCB_L = 5.04L - 2946$ (0.0270)	$\ln(PCB_L) = 7.213\ln(L) - 40.96$ (0.0272)
2008	NS (0.61)	NS (0.57)
Keweenaw Bay (Michigan DEQ)		
1991	NS (0.52)	NS (0.44)
1993	NS (0.81)	NS (0.74)
1996	NS (0.39)	NS (0.42)

Table A-5 (Continued)

Year		
1999	NS (0.27)	NS (0.24)
2001	NS (0.72)	NS (0.71)
2004	$PCB_L = 0.96L - 483$ (0.0152)	$\ln(PCB_L) = 8.575 \ln(L) - 50.78$ (0.0094)
2007	$PCB_L = 0.68L - 266$ (0.0324)	$\ln(PCB_L) = 3.044 \ln(L) - 14.80$ (0.0140)
2010	$PCB_L = 4.57L - 2008$ (0.0302)	$\ln(PCB_L) = 11.501 \ln(L) - 66.63$ (0.0111)
2013	$PCB_L = 0.34L - 116$ (0.0150)	$\ln(PCB_L) = 2.295 \ln(L) - 10.28$ (0.0100)
Thunder Bay (ECCC)		
1980	$PCB_L = -1.15L + 1485$ (0.0249)	$\ln(PCB_L) = -0.535 \ln(L) + 10.05$ (0.0444)
1983	$PCB_L = 2.55L - 480$ (< 0.0001)	$\ln(PCB_L) = 1.784 \ln(L) - 4.49$ (< 0.0001)
1985	$PCB_L = 3.25L - 644$ (< 0.0001)	$\ln(PCB_L) = 1.887 \ln(L) - 4.96$ (< 0.0001)
1986	NS (0.13)	$\ln(PCB_L) = 0.932 \ln(L) + 0.25$ (0.0345)
1988	NS (0.23)	NS (0.09)
1989	$PCB_L = 1.13L + 9$ (< 0.0001)	$\ln(PCB_L) = 0.894 \ln(L) + 0.75$ (< 0.0001)
1990	NS (0.08)	NS (0.09)
1992	$PCB_L = 5.42L - 1911$ (0.0004)	$\ln(PCB_L) = 2.746 \ln(L) - 10.44$ (0.0013)
1993	NS (0.09)	NS (0.08)
1996	$PCB_L = 2.48L - 664$ (0.0044)	$\ln(PCB_L) = 2.396 \ln(L) - 8.68$ (< 0.0001)
1997	$PCB_L = 1.85L - 756$ (< 0.0001)	$\ln(PCB_L) = 2.538 \ln(L) - 10.52$ (< 0.0001)
1999	NS (0.56)	NS (0.20)
2001	$PCB_L = 1.09L - 364$ (0.0014)	$\ln(PCB_L) = 2.196 \ln(L) - 8.60$ (0.0049)
2002	$PCB_L = 3.09L - 1169$ (< 0.0001)	$\ln(PCB_L) = 3.122 \ln(L) - 13.62$ (< 0.0001)
2004	NS (0.61)	NS (0.79)
2007	NS (0.67)	NS (0.47)
2009	$PCB_L = 0.92L - 79$ (0.0496)	NS (0.24)
2011	NS (0.79)	NS (0.32)
2013	$PCB_L = 1.14L - 287$ (0.0336)	$\ln(PCB_L) = 2.793 \ln(L) - 11.74$ (0.0029)

Table A-5 (Continued)

	Whitefish Bay (ECCC)	
1982	$PCB_L = 1.61L - 328 \ (< 0.0001)$	$\ln(PCB_L) = 1.540 \ln(L) - 3.48$ (< 0.0001)
1983	NS (0.21)	NS (0.23)
1986	$PCB_L = 1.65L - 525 \ (0.0009)$	$\ln(PCB_L) = 3.404 \ln(L) - 15.58$ (0.0002)
1987	$PCB_L = 1.53L - 273 \ (< 0.0001)$	$\ln(PCB_L) = 2.803 \ln(L) - 11.09$ (< 0.0001)
1989	NS (0.98)	NS (0.37)
1991	$PCB_L = 1.53L - 273$	$\ln(PCB_L) = 3.010 \ln(L) - 13.62$ (< 0.0001)
1997	NS (0.91)	NS (0.76)
1998	NS (0.56)	NS (0.64)
1999	$PCB_L = 0.33L - 32 \ (0.0487)$	NS (0.12)
2000	NS (0.20)	NS (0.25)
2002	$PCB_L = 0.48L - 128 \ (0.0300)$	NS (0.06)
2007	$PCB_L = 0.27L - 57 \ (0.0045)$	$\ln(PCB_L) = 1.283 \ln(L) - 3.75$ (0.0008)
2008	NS (0.24)	NS (0.43)
2009	$PCB_L = 2.00L - 748 \ (< 0.0001)$	$\ln(PCB_L) = 3.752 \ln(L) - 17.91$ (< 0.0001)
2011	NS (0.13)	NS (0.09)
2012	NS (0.94)	NS (0.60)
2013	$PCB_L = 0.26L - 22 \ (0.0206)$	$\ln(PCB_L) = 1.188 \ln(L) - 2.75$ (0.0065)
	Minnesota DNR	
1976	$PCB_L = 4.07L - 1166 \ (< 0.0001)$	$\ln(PCB_L) = 1.979 \ln(L) - 5.54$ (< 0.0001)
1985	$PCB_L = 4.63L - 1861 \ (< 0.0001)$	$\ln(PCB_L) = 4.024 \ln(L) - 18.96$ (0.0002)
1987	$PCB_L = 5.76L - 2624 \ (< 0.0001)$	$\ln(PCB_L) = 3.452 \ln(L) - 15.76$ (< 0.0001)
1988	NS (0.09)	NS (0.28)
1996	$PCB_L = 1.60L - 616 \ (0.0017)$	$\ln(PCB_L) = 3.738 \ln(L) - 18.42$ (< 0.0003)
2000	NS (0.05)	NS (0.06)
2002	NS (0.06)	$\ln(PCB_L) = 1.738 \ln(L) - 6.44$ (0.0291)
2003	NS (0.13)	NS (0.10)
2004	NS (0.09)	NS (0.05)

Table A-5 (Continued)

2009	NS (0.06)	$\ln(PCB_L) = 3.978\ln(L) - 20.51$ (0.0120)
2010	NS (0.94)	NS (0.91)

Wisconsin DNR

1976	NS (0.51)	NS (0.59)
1982	NS (0.11)	NS (0.05)
1984	$PCB_L = 9.48L - 3715$ (0.0012)	$\ln(PCB_L) = 3.729\ln(L) - 16.96$ (0.0009)
1985	$PCB_L = 17.17L - 10646$ (0.0055)	$\ln(PCB_L) = 6.364\ln(L) - 34.83$ (0.0047)
1987	$PCB_L = 0.63L - 147$ (0.0092)	$\ln(PCB_L) = 1.819\ln(L) - 6.18$ (0.0132)
1991	$PCB_L = 3.17L - 1445$ (0.0001)	$\ln(PCB_L) = 2.947\ln(L) - 12.90$ (< 0.0001)
1995	$PCB_L = 3.20L - 1562$ (0.0003)	$\ln(PCB_L) = 5.404\ln(L) - 29.22$ (< 0.0001)
1997	$PCB_L = 2.74L - 1309$ (< 0.0001)	$\ln(PCB_L) = 4.061\ln(L) - 20.52$ (< 0.0001)
1999	$PCB_L = 2.65L - 1290$ (< 0.0001)	$\ln(PCB_L) = 4.462\ln(L) - 23.33$ (< 0.0001)
2001	$PCB_L = 2.34L - 1127$ (0.0003)	$\ln(PCB_L) = 3.499\ln(L) - 16.95$ (< 0.0001)
2003	$PCB_L = 5.37L - 3138$ (0.0012)	$\ln(PCB_L) = 6.122\ln(L) - 34.08$ (0.0006)
2005	$PCB_L = 4.68L - 2494$ (0.0053)	$\ln(PCB_L) = 6.427\ln(L) - 36.36$ (< 0.0001)
2007	$PCB_L = 2.22L - 1231$ (0.0332)	$\ln(PCB_L) = 6.427\ln(L) - 36.36$ (0.0087)
2009	$PCB_L = 2.50L - 1312$ (0.0025)	$\ln(PCB_L) = 4.069\ln(L) - 21.02$ (0.0001)
2011	$PCB_L = 3.31L - 1933$ (0.0015)	$\ln(PCB_L) = 5.269\ln(L) - 29.12$ (0.0024)
2013	$PCB_L = 3.20L - 1698$ (0.0184)	$\ln(PCB_L) = 5.403\ln(L) - 29.73$ (< 0.0001)

[*]NS indicates that the relationship is not significance ($p > 0.05$).

Appendix B: Figures

Original total PCB concentrations (ng/g ww) vs. time (year). Slopes in the following figures are equal to the corresponding estimated values of year in multiple regression analysis in Table 2-2.
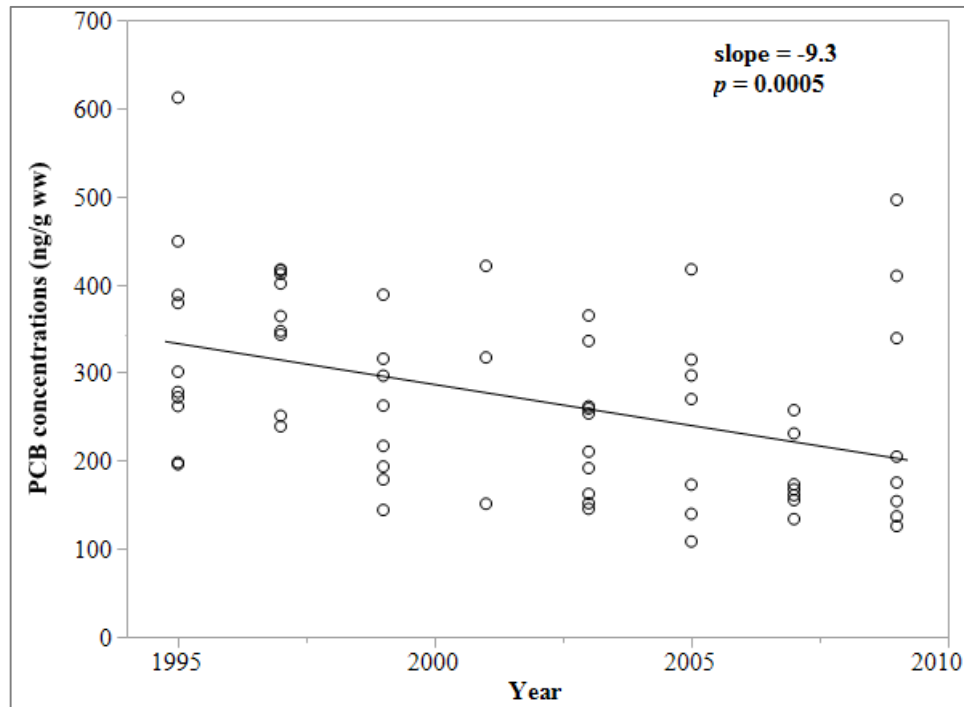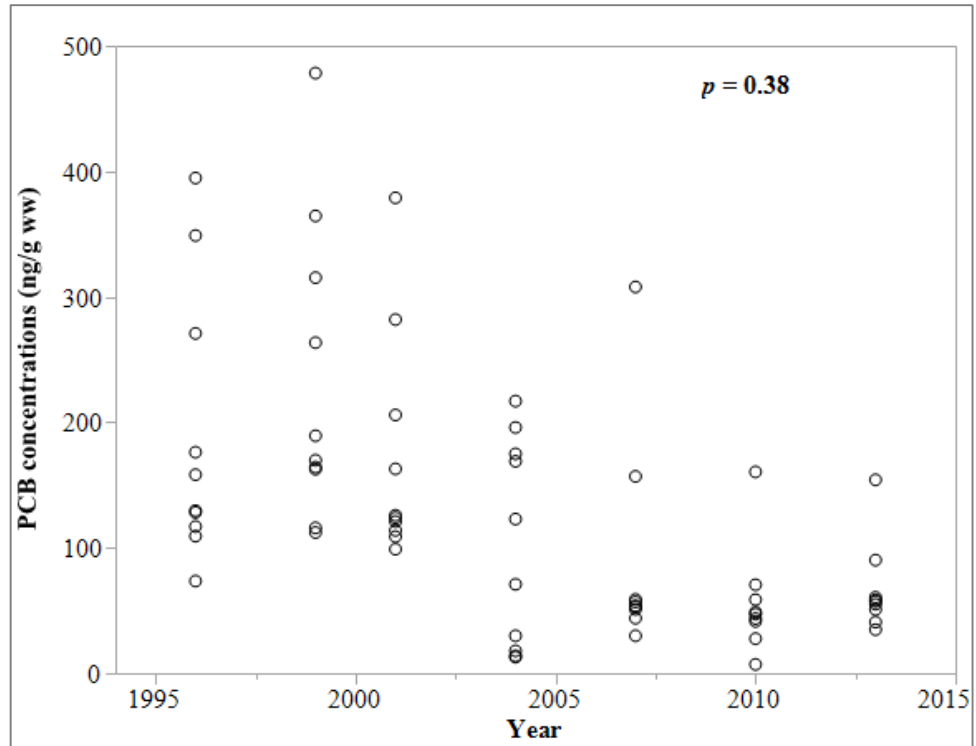

Figure B-1. Linear regression between total PCB concentrations versus time in lake trout from Keweenaw Point (U.S. EPA) from 1995-2009. The correlation is significant ($p = 0.0005$).
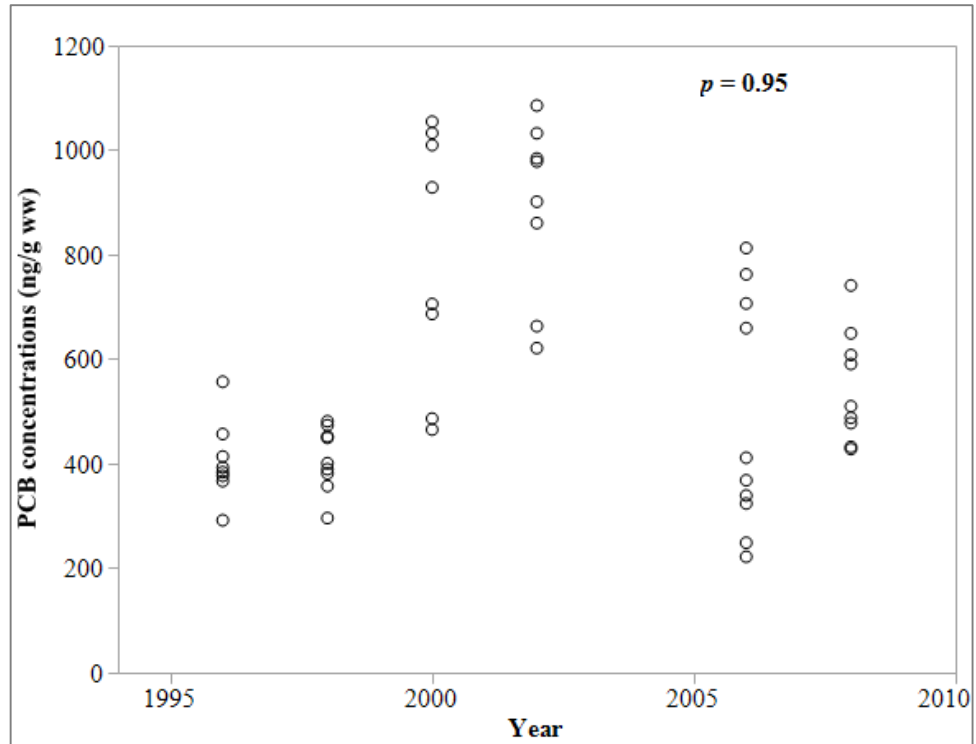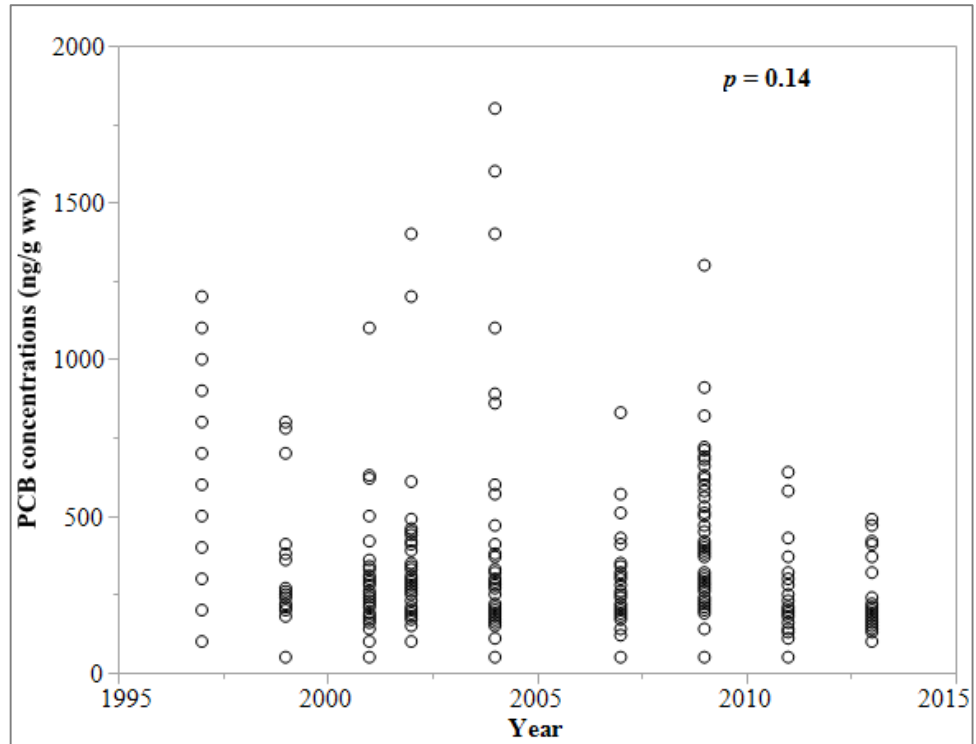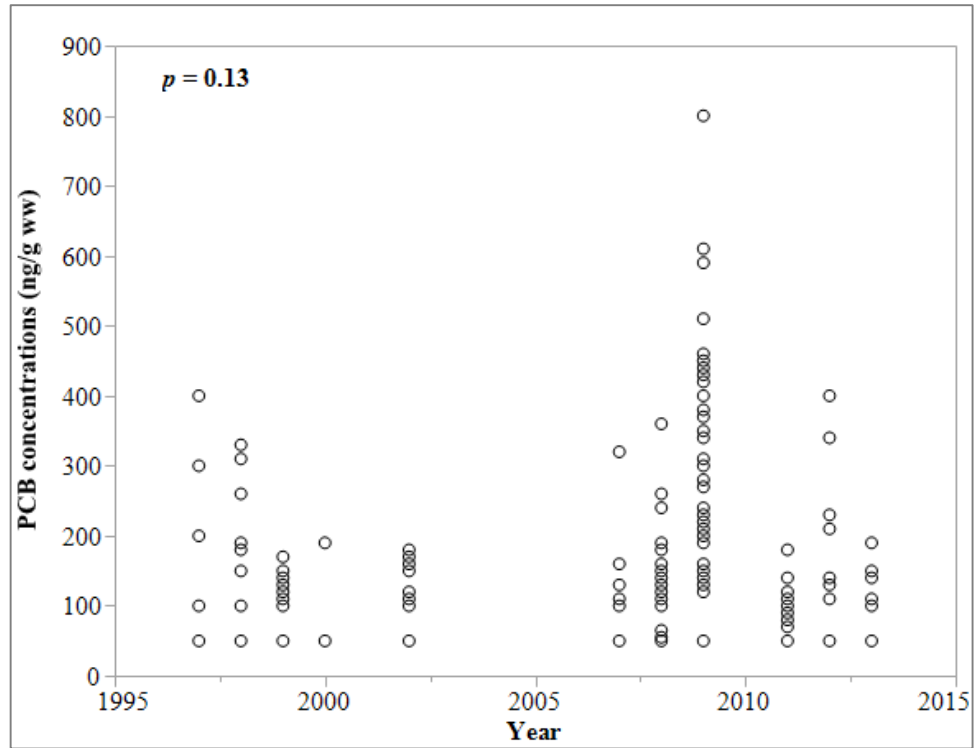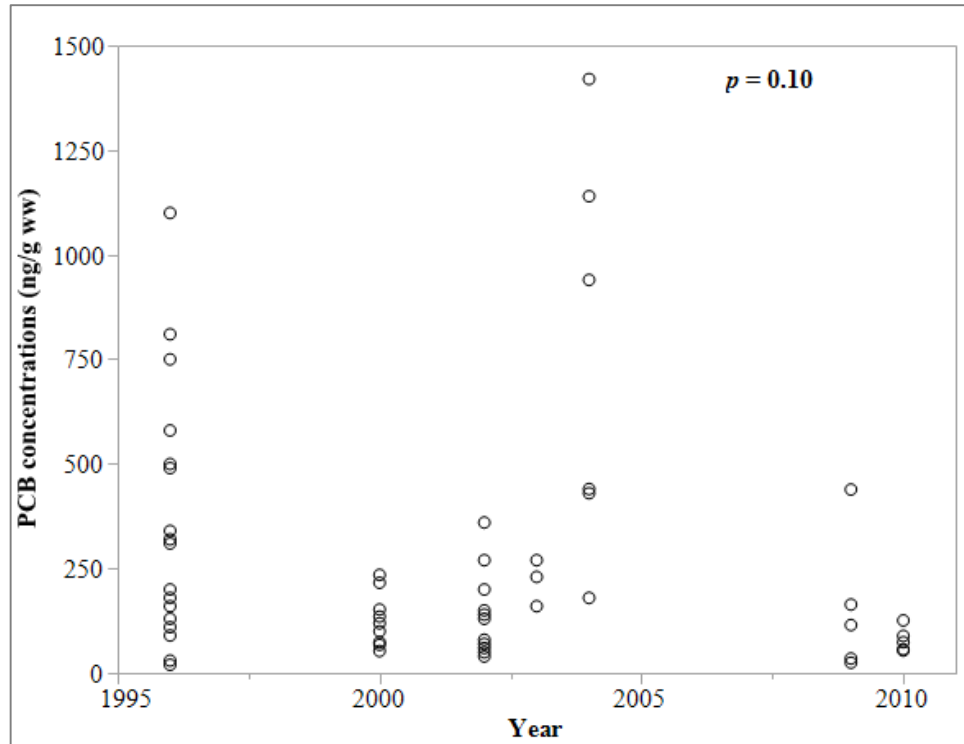
Figure B-2. Linear regression between total PCB concentrations versus time in lake trout from Apostle Islands (U.S. EPA) from 1996-2008. The correlation is not significant ($p = 0.95$).

Figure B-3. Linear regression between total PCB concentrations versus time in lake trout from Keweenaw Bay (Michigan DEQ) from 1996-2013. The correlation is not significant ($p = 0.38$).
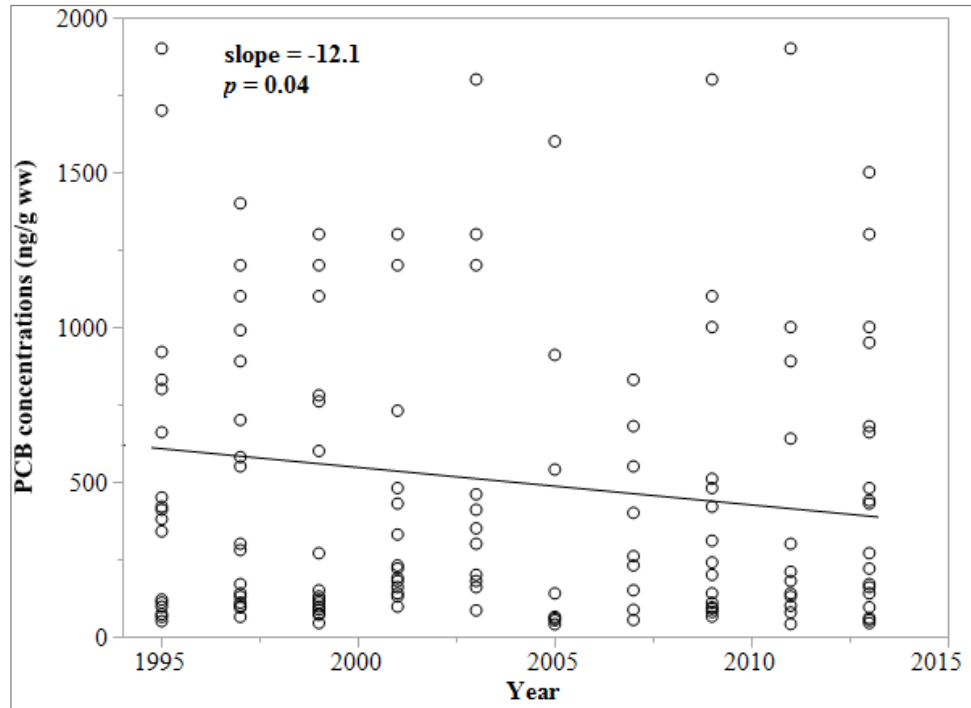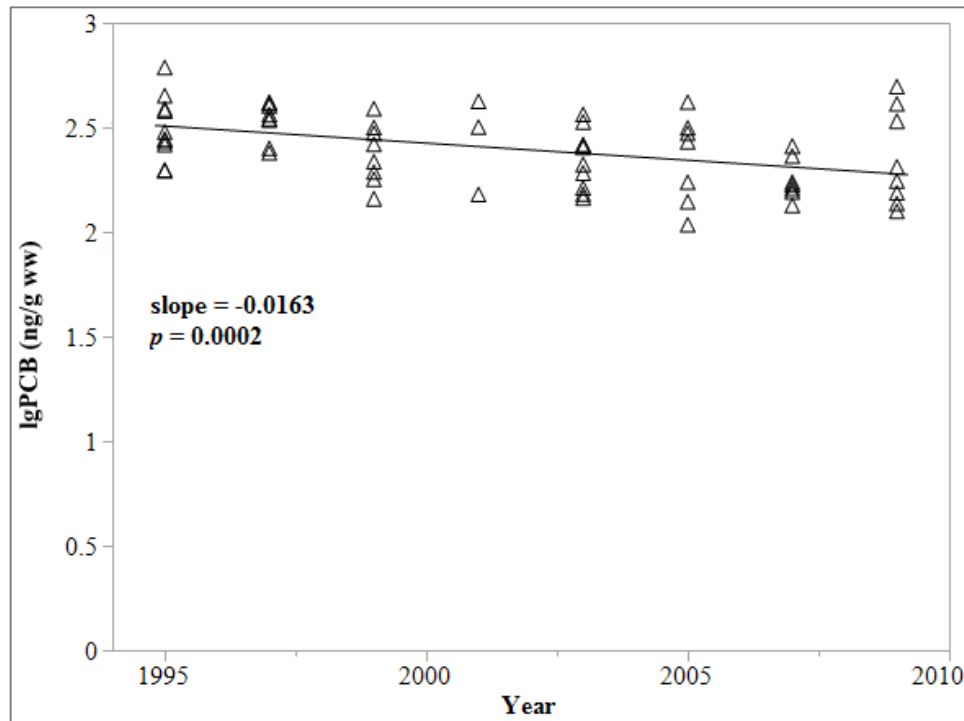
Figure B-4. Linear regression between total PCB concentrations versus time in lake trout from Thunder Bay-Pie Island (ECCC) from 1997-2013. The correlation is not significant ($p = 0.14$).

Figure B-5. Linear regression between total PCB concentrations versus time in lake trout from Whitefish Bay (ECCC) from 1997-2013. The correlation is not significant ($p = 0.13$).

Figure B-6. Linear regression between total PCB concentrations versus time in lake trout from Minnesota (MN DNR) from 1996-2010. The correlation is not significant ($p = 0.10$).

Figure B-7. Linear regression between total PCB concentrations versus time in lake trout from Wisconsin (WI DNR) from 1996-2013. The correlation is marginal significant ($p = 0.04$).

Only in Keweenaw Point and Wisconsin sites, the regression correlations are statistically significant.

Log-transformed total PCB concentrations (ng/g ww) vs. time (year). Slopes in the following figures are equal to the corresponding estimated values of year in multiple regression analysis in Table 2-3.
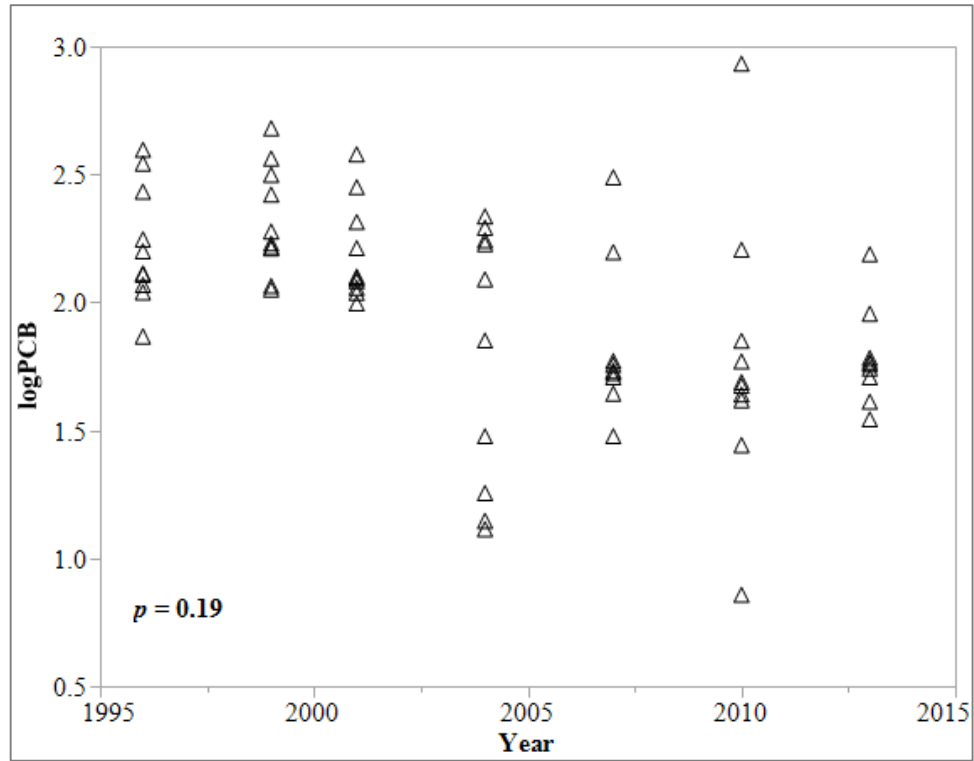

Figure B-8. Linear regression between log-transformed total PCB concentrations versus time in lake trout from Keweenaw Point (U.S. EPA) from 1995-2009. The correlation is significant ($p = 0.0002$).
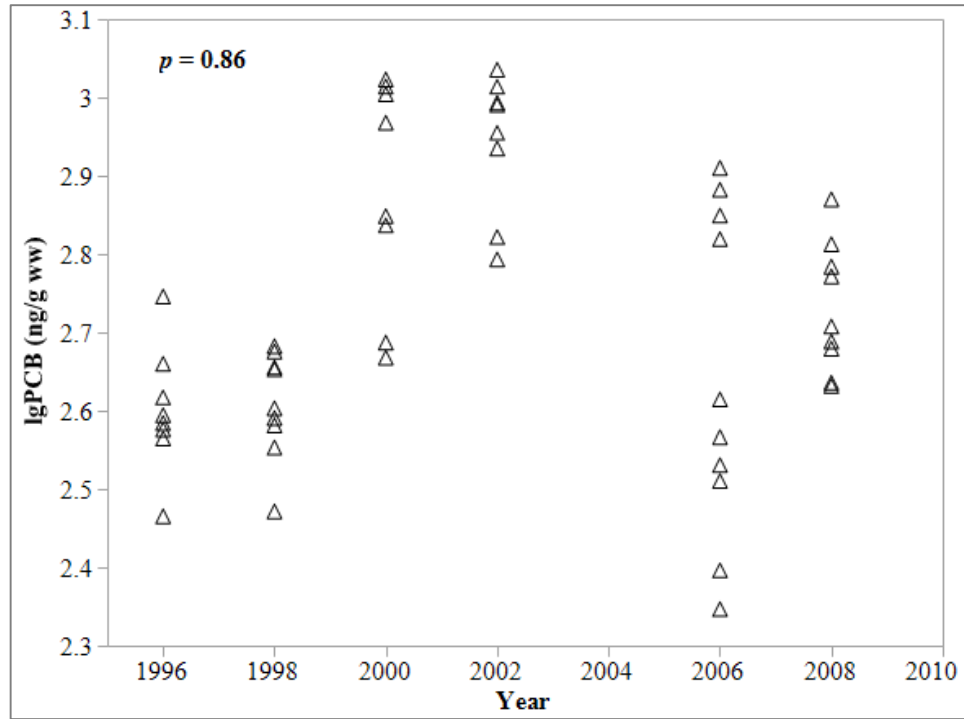
Figure B-9. Linear regression between log-transformed total PCB concentrations versus time in lake trout from Apostle Islands (U.S. EPA) from 1996-2008. The correlation is not significant ($p = 0.86$).

Figure B-10. Linear regression between log-transformed total PCB concentrations versus time in lake trout from Keweenaw Bay (Michigan DEQ) from 1996-2013. The correlation is not significant ($p = 0.19$).
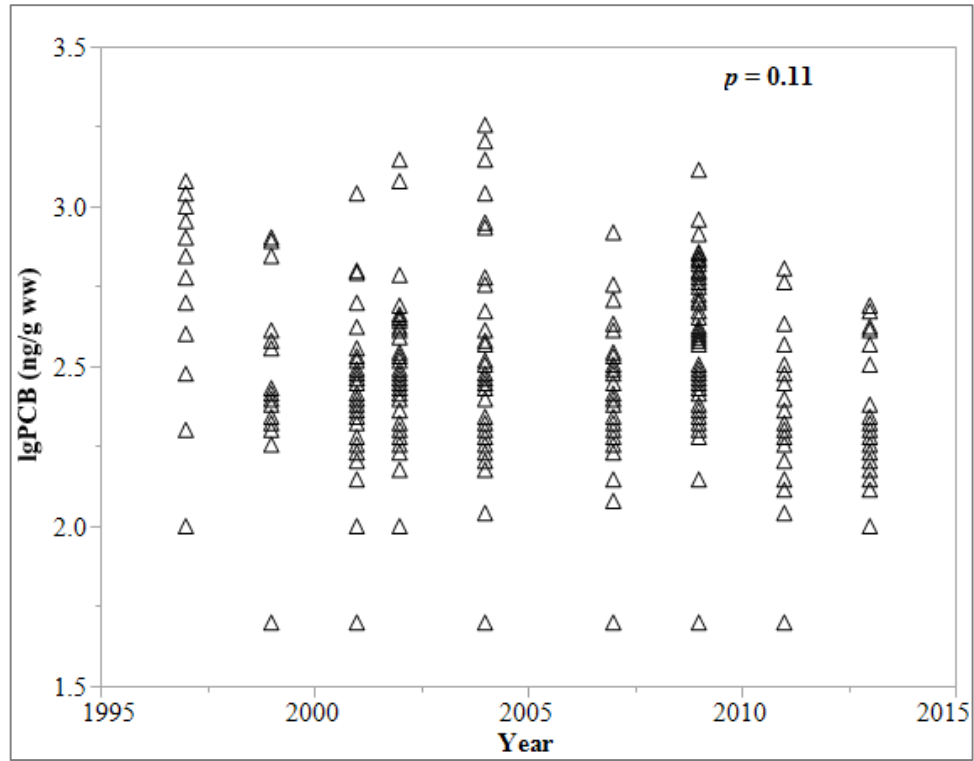
Figure B-11. Linear regression between log-transformed total PCB concentrations versus time in lake trout from Thunder Bay-Pie Island (ECCC) from 1997-2013. The correlation is not significant ($p = 0.11$).
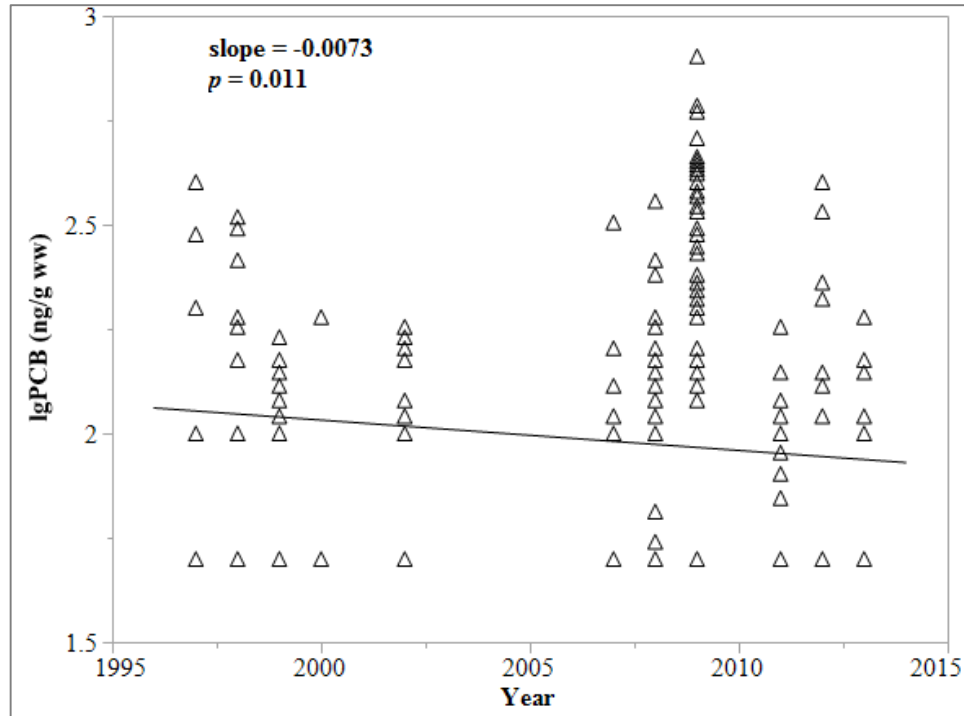
Figure B-12. Linear regression between log-transformed total PCB concentrations versus time in lake trout from Whitefish Bay (ECCC) from 1997-2013. The correlation is significant ($p = 0.011$).
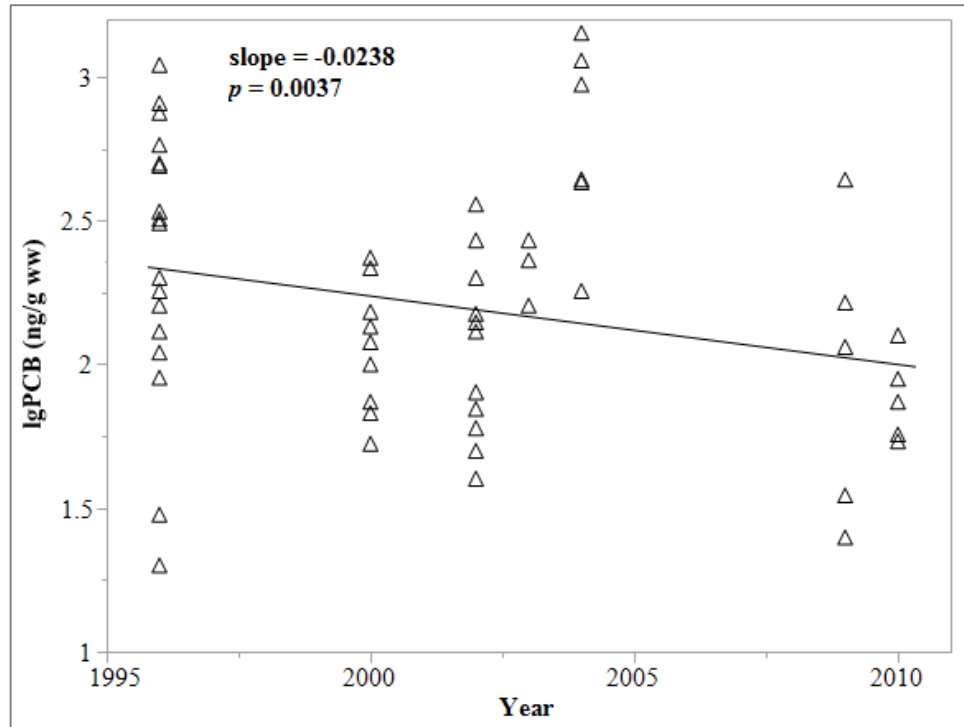
Figure B-13. Linear regression between log-transformed total PCB concentrations versus time in lake trout from Minnesota (MN DNR) from 1996-2010. The correlation is significant ($p = 0.0037$).
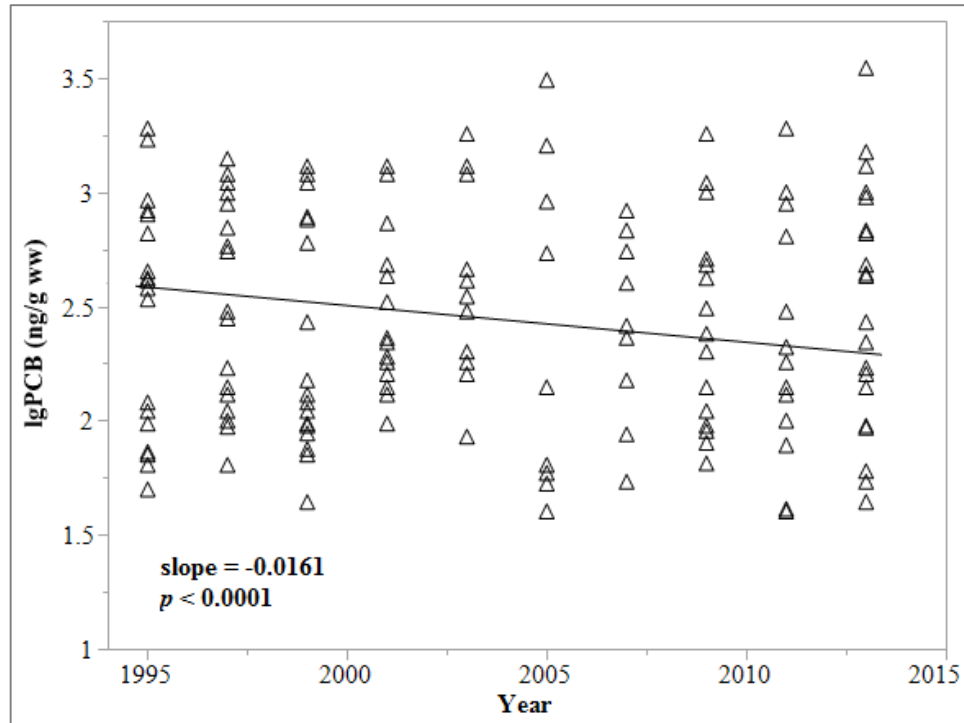
Figure B-14. Linear regression between log-transformed total PCB concentrations versus time in lake trout from Wisconsin (WI DNR) from 1996-2013. The correlation is significant ($p < 0.0001$).

In Keweenaw Point, Whitefish Bay, Minnesota sites, and Wisconsin sites, the regression correlations are significant.
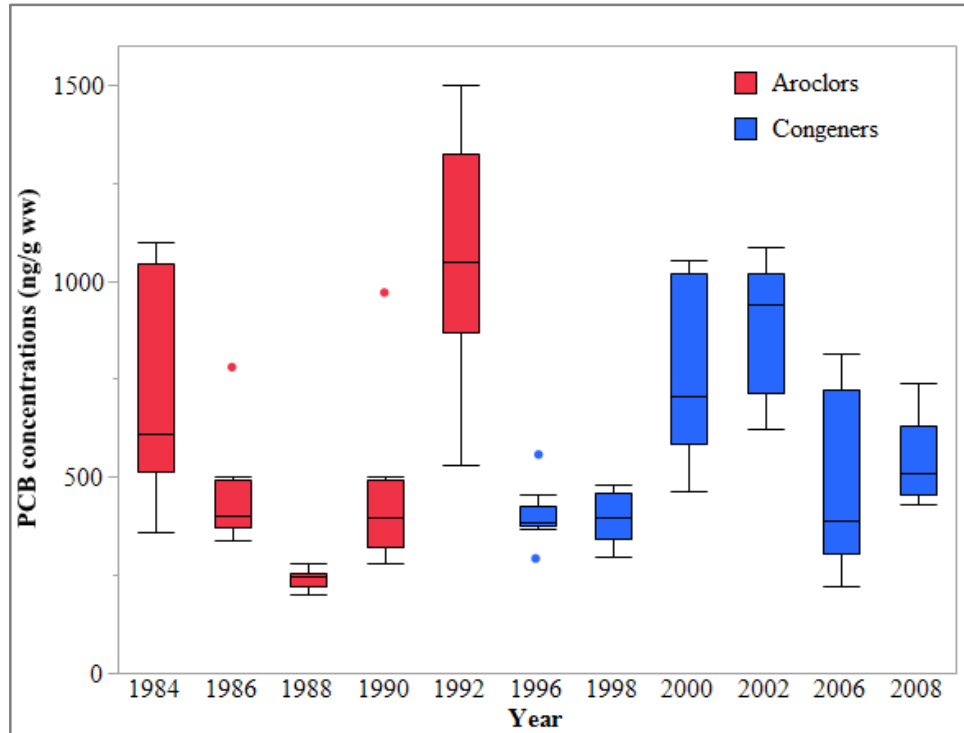
Figure B-15. Total PCB concentrations in whole lake trout from Apostle Islands (U.S. EPA, 1984-2008). The Aroclor method was used prior to 1996 and the congener method was applied since 1996 data. The horizontal line within the box represents the median while the whiskers represent the 5th percentile and 95th percentile, respectively.