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Application of A Spatially Explicit Food Web Bioaccumulation Model to Predict PCB Exposure Sources For Sport Fish in the Detroit River

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APPLICATION OF A SPATIALLY EXPLICIT FOOD WEB BIOACCUMULATION
MODEL TO PREDICT PCB EXPOSURE SOURCES FOR SPORT FISH IN THE
DETROIT RIVER

by

Jingyuan Li

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DECLARATION OF CO-AUTHORSHIP AND PREVIOUS PUBLICATION

I. Co-Authorship Declaration

I hereby certify that this thesis incorporates material that is a result of joint research under the supervision of Dr. Ken Drouillard. Chapter 2 contains material from an article titled "Characterizing PCB Exposure Pathways from Sediment and Water in Aquatic Life Using a Food Web Bioaccumulation Model" which has published in *Integr Environ Assess Manag*. This article was co-authored by Li, J., McPhedran, K., Szalińska, E., Mcleod, A., Bhavsar, S., Bohr, J., Grgicak-Mannion, A., Drouillard, K. The main ideas and data analysis were generated by myself. The contributions of co-authors were through guidance with data collection and revising manuscript drafts.

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II. Declaration of Previous Publication

This thesis includes one original paper that has been previously submitted for publication in peer reviewed journals, as follows:

Thesis Chapter	Publication title/full citation	Publication status
Chapter 2	Li, J., McPhedran, K., Szalińska, E., Mcleod, A., Bhavsar, S., Bohr, J., Grgicak-Mannion, A., Drouillard, K. Characterizing PCB Exposure	In Press

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ABSTRACT

This thesis applied and validated a bioenergetic-based, steady-state food web bioaccumulation model to predict polychlorinated biphenyl (PCB) exposures in benthic invertebrates and sport fish of the Detroit River, a Great Lakes "area of concern" (AOC). First, it examined how model performance is influenced by modification of the proportion of overlying water and sediment porewater respired by benthic invertebrates. The results showed that PCB bioaccumulation measurements are significantly affected by variation in pollutant uptake and elimination routes via the overlying water, which in turn are affected by the degree of disequilibrium of PCBs between sediments and water. The second study evaluated how spatial movements of sport fish impact chemical exposures in the Detroit River. Multiple simulations were performed across different spatial boundaries encompassing the entire Detroit River. Model predictions were compared against 1152 empirical fish sample records that comprised 19 sport fish species. The study demonstrated that a 2-nation model which divided the river lengthwise into Canadian and US jurisdictions as two independent model zones, provided the best global fit for the majority of sport fish data. However, these improvements were not equally observed across species. Outlier species, which had poor prediction by the 2-nation model were separately evaluated to determine if alternate spatial scales provided better predictive accuracy. Finally, the model was calibrated for poorly performing species, which allowed cross-zone exposure. The calibrated model, subsequently, was used to predict jurisdiction sport fish consumption advisories and compared with official advisories issued in Ontario and Michigan for the Detroit River. The study demonstrated the importance of accounting for specific ecological factors, such as fish movement, to improve PCB bioaccumulation prediction, especially in highly heterogeneous water systems.

DEDICATION

To Emma and Maxwell

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CHAPTER 1

GENERAL INTRODUCTION

1.1 Introduction

The Great Lakes encompasses a uniquely productive ecosystem that plays an important role in the regional economy. It also facilitates access to and the enjoyment of environmental amenities, such as beaches, estuaries, fisheries, and cultural resources. However, contamination from legacy deposition in the sediment and run-off deposition in water have adversely affected human health and various ecosystems (Environment Canada 2017). These issues have received considerable publicity. In response to concerns regarding environmental degradation, the International Joint Commission through the Canada-U.S. Great Lakes Water Quality Agreement (GLWQA) called for the development and implementation of a remedial action plan (RAC) to restore ecosystem health in 43 Great Lakes "areas of concern" (AOCs) (IJC 2017).

The source control of contaminants and remediation activities are seemingly straightforward actions that promote environmental recovery in AOCs and mitigate impairments to the Great Lakes. However, given increasing pressure on government funds, the high costs of engineering remediation projects, and a desire to increase the level of local support, the biological response to these solutions must be carefully evaluated, and solutions should be ecologically and economically acceptable to diverse groups of stakeholders (Zarull et al. 1999). In this context, potential regulatory and remediation actions could benefit from rigorous ecological assessment to understand the actual or potential risks of contaminants and evaluate the associated uncertainties associated with the environmental fate, transport, and bioaccumulation of chemicals (Arnot et al. 2006). Field observations, laboratory experiments and mathematical modeling have been used to evaluate and quantify the regulators of exposure to contaminants in aquatic biota, and such analyses are essential parts of ecological assessments (Chapman and Anderson 2005). Field-based analysis is generally costly but extremely useful in characterizing site-specific chemicals and the spatial, temporal, and ecological factors that govern bioaccumulation. Laboratory experiments use standardized exposure techniques to investigate microscale issues in well-controlled lab environment and to establish environmental quality standards and guidelines (Van Geest et al. 2011). Such experiments may focus on assessments of different stages of contamination and restoration. Compared to these assessment methods, mathematic modeling utilizes theoretical knowledge of the bioaccumulation process to determine

the interactions and processes that govern bioaccumulation. These factors are often too complicated to be observed during field observations or experiments (Aral 2012) and enable simulation contrasts to be performed for hypothetical remedial activities as decision support tools for various remedial options. This thesis focuses on bioaccumulation model calibration and model validation in a complex riverine environment. Each term in the model is assessed to determine the sources of variation, and model predictions are compared using an extensive and independent validation data set to address the sources of variation at both the interindividual and interspecific levels of sport fish contamination in the Detroit River AOC.

One model that is relevant to such a study addresses the accumulation of persistent organic pollutants (POPs) in aquatic systems. Over the past 40 years, the study of POP bioaccumulation models has progressed to include numerous processes that govern chemical partitioning and bioavailability in water and sediments, as well as complex food web interactions (examples of comprehensive reviews: Mackay and Fraser 2000, Gobas and Morrison 2000, Barber 2003). Although bioaccumulation models have gained general scientific and regulatory acceptance as reliable tools for quantifying the bioaccumulation phenomenon, critical challenges remain. Most models treat contamination sources as one compartment in the environmental system, assume that all types of aquatic organisms equally utilize waterbodies and apply average concentrations of chemicals to describe the contamination exposure of the entire food web (Gustavson et al. 2011). This assumption fails to reflect the critical role of space in food web dynamics. More importantly, previously contained areas of high contamination (such as sediments), may spatially spread to the biota in adjacent areas as a result of the movement of organisms. This process may cause biased predictions in spatially non-explicit bioaccumulation models.

This thesis advances the literature by improving the model-based estimation of chemical bioaccumulation considering the spatially connected feeding interactions among various species in the food web. The analysis will focus on one class of POP: polychlorinated biphenyl (PCB). PCBs are one of eight chemicals of mutual concern identified by Canada and the United States under Annex 3 of the 2012 amended GLWQA. Despite being banned for more than 40 years, these chemicals still predominantly contribute to Beneficial Use Impairments (BUI), such as fish consumption advisories, in the Great Lake AOCs. This study will assess the significance, magnitude, and relative importance of several driving factors, such as the spatial movement of

organisms and spatial heterogeneity of pollutants, in estimating PCB concentrations in organisms. The research goal is to improve knowledge regarding the effects of spatial feeding interactions and the associated relationships with the exposure gradients of environmental contamination to support environmental management actions and provide a quantitative expression of exposure and risk in mobile sport fish species.

The modeling approaches that quantify POP bioaccumulation processes include (1) equilibrium partitioning-based models that utilize established correlations that exist between laboratory- and field-measured chemical concentrations in organism and those in the exposure media to predict bioaccumulation using endpoints, such as bioconcentration factor (BCF), bioaccumulation factor (BAF), bio-sediment accumulation factor (BSAF), and biomagnification factor (BMF) assessments (Neely et al. 1974, Veith et al. 1979, Meylan et al. 1999), and (2) mass balance models that realistically formulate contaminant partitioning, transport, and emission processes across different phase boundaries. (Thomann and Connolly 1984, Thomann 1989, Gobas 1993, Campfens and Mackay 1997, Morrison et al. 1997, Arnot and Gobas 2004). Equilibrium-based models have exhibited high accuracy in predictions involving moderately hydrophobic chemical (i.e., log Kow <5) concentrations in biota or when water is assumed to be the predominant exposure route (Di Toro et al. 1991). However, such models often poorly perform in empirical assessments of highly hydrophobic chemicals (i.e., log Kow >6) and when applied to field data sets related to such chemicals. This poor performance is further complicated when organisms are exposed to both overlying and pore waters with different chemical fugacities (DeBruyn and Gobas 2004).

Since they were first established, mass balance bioaccumulation models and their parameters have undergone various modifications in predictive algorithms and have been applied in various areas for bioaccumulation assessment. Such models utilize the concept of fugacity (Campfens and Mackay 1997, Clark et al. 1990, Gobas et al. 1988) and species-specific toxicokinetics (Gobas et al. 1993, Morrison et al. 1997, Arnot and Gobas 2004) to determine how biotic chemical exposure occurs. These methods have progressed from those based on simple generic food chains (Thomann and Connolly 1984) to those based on complex food web models that incorporate multiple feeding interactions (Gobas 1993, Morrison et al. 1997). In addition to estimating bioaccumulation and the environmental fate of PCBs (Gobas and Arnot 2010; Gobas and Wilconckson 2003), models have also been used to identify the sources of

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variability in contaminant concentrations in aquatic biota (McLeod et al. 2015). This capability is important from an ecological perspective, as well as for quantifying hazards and conducting risk assessments of bioaccumulating chemicals (Morrison et al. 2002).

This study applies a compartment-based, food web-based, non-equilibrium, steady state kinetic model that was previously developed by Arnot and Gobas (2004), who synthesized algorithms from several previously published food web models. This model has since been utilized and modified further to describe POP bioaccumulation in individual populations (Selck et al. 2012). Based on steady state conditions, the model assumes that the uptake and elimination of chemicals are balanced over the entire life cycle of the animal, and the prediction represents the final concentration in the organism. Although there is growing recognition that bioaccumulation is significantly influenced by seasonal temperature-related metabolic rates, age- and season-related growth rates, and weight loss, which are assumed to be constant in a steady state model (Mcleod et al. 2016), current non-steady state bioaccumulation models are only able to track the evolution of POP compounds in a single fish species as a function of time throughout the life span of the species (McLeod et al. 2016, Foekema et al. 2012; Ng and Gray 2009; Sijm et al. 1992). Yet, non-steady state processes have not been incorporated into a food web model to interpret bioaccumulation in a complex and highly detailed food web.

The objectives of this study are as follows: (1) assess the relative contribution and effect of spatial heterogeneity of contaminated water and sediment in a river system to PCB exposures in lower and upper trophic level organisms; (2) examine the potential effects of uncertainties in physiological and ecological model parameters based on estimates of PCB concentrations in organisms; and (3) test the effect of fish foraging range on a food web bioaccumulation model in predicting PCB concentrations. Based on these objectives, two primary hypotheses are described below.

In the second chapter, I examined how the proportion of overlying water relative to the sediment porewater respired by benthic invertebrates impacts bioaccumulation model predictions and accuracy. Previous publications of the steady state food web bioaccumulation model have recommended application of different proportions of respired water (overlying vs porewater) without extensive justification to the values applied or evaluation of the effect of change in this model parameter on model output and accuracy (Arnot and Gobas 1994; Selck et al. 2012). First I compared the model performance to predict PCB concentrations in benthic invertebrates using

two recommended respiration proportions and contrasted these estimates against empirically derived biota-sediment accumulation regressions (BSARs). Model accuracy was evaluated by comparing predictions in matched benthic invertebrate and sediment PCB contamination data sets generated across multiple locations in the Detroit River. Second, I contrasted the model accuracy to predict sport fish PCB concentrations between simulations adopting each recommended respiration proportion. As an addition reference to the two simulations above, the benthic invertebrate sub-model was replaced with the BSAR prediction algorithm to contrast simulation performances. Specific hypotheses addressed in Chapter 2 include the following:

Hypothesis 2.1	BSARs that include both PCB contamination in water and sediment will have higher accuracy than BSARs that only consider sediment PCB concentration.
Hypothesis 2.2	Models using a 95%: 5% overlying water/pore water respiration ratio for benthic invertebrates will predict lower PCB concentrations in benthic invertebrates and fish compared to those that adopt a 50% :50% overlying water/pore water ratio.
Hypothesis 2.3	The calibrated BSAR model will produce the most accurate PCB predictions in benthic invertebrates followed by the models using 50:50 overlying water/pore water ratio and 95:5 overlying water/pore water ratio.
Hypothesis 2.4	The hybrid BSAR sub-model will produce the most accurate PCB predictions in sport fish followed by the models using 50:50 overlying water/pore water ratio and 95:5 overlying water/pore water ratio.

In third chapter, I applied and validated a steady-state food web bioaccumulation model to predict PCB exposures in sport fish of the Detroit River, where sediment and water of the river were found to exhibit high spatial variations. The previously contained areas of high contamination may have spread to adjacent food webs as a result of fish movements. This process may cause biased predictions in single-compartment bioaccumulation models. I executed multiple simulations and contrasted the results against a total of 1152 validation fish sample

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records that comprised 19 sport fish species at different spatial scales (river-wide, 2 nations, 4 zones and 6 zones) to uncover how the spatial heterogeneity of contamination and species-specific movements contribute to variations in fish exposures. Specific hypotheses addressed in Chapter 3 included the following:

Hypothesis 3.1 The simulations using a different spatial scale (e.g., river-wide, 2-nation, 4-zone and 6-zone simulations) provides inconsistent global prediction of PCB concentrations in sport fish.

Hypothesis 3.2 Individual species of fish exhibit different spatially integrated exposures necessitating different spatial boundaries in model simulations to predict species-specific chemical exposures. The sport fish species are predicted with different accuracies in the selected best global simulation model.

Hypothesis 3.3 The calibrated model, which allowed cross-zone exposure by accounting for fish movement can improve PCB bioaccumulation prediction and provide the most consistent prediction of sport fish consumption advisories issued by Ontario and Michigan for the Detroit River AOC.

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CHAPTER 2

CHARACTERIZING PCB EXPOSURE PATHWAYS FROM SEDIMENT AND WATER IN

AQUATIC LIFE USING A FOOD WEB BIOACCUMULATION MODEL

2.1 Introduction

Food web bioaccumulation models are commonly used in risk assessments of persistent

organic pollutants (POPs) to establish cause-effect linkages between sediment and water

contamination and fish contamination (Arnot and Gobas 2004; Kashian et al. 2014). These

models are also used as decision support tools to assess planned contaminated sediment

mitigation efforts (Gobas and Arnot 2010), source abatement strategies (Morrison et al. 2002)

and as screening tools to assess food web biomagnification (Gobas and Morrison 2000). In

aquatic ecosystems, POPs become strongly associated with organic phases and settle to

sediments, where they may be lost through deep burial, or incorporated into the food web via

benthic-pelagic coupling (Thomann et al. 1992). Benthic-pelagic coupling becomes the most

pronounced as an entry point for contaminants into the food web following reductions in point

sources of water pollution such as wastewater discharges, resulting in sediments reverting from a

sink to a source (Larsson 1985). The ability to model POPs bioaccumulation in benthic

invertebrates with accuracy is therefore important to establish cause-effect linkages between

spatial patterns of sediment contamination and POPs concentrations in fish.

The Arnot and Gobas (2004) food web bioaccumulation model is commonly used to

predict POPs bioaccumulation patterns (Gobas and Arnot 2010; Figueiredo et al. 2014; Gobas

and Wilcockson 2003), and to characterize sources of variability in contaminant concentrations

in aquatic biota (Selck et al. 2012; McLeod et al. 2015). The model uses parameters specific to

the Great Lakes and chemical concentrations in sediments and water as its main inputs to predict

steady-state concentrations in simulated food web components, including benthic invertebrates

and fish, as its output. One attribute of this model, especially as it applies to benthic

invertebrates, is that it considers exposure and chemical losses to sediments and porewater as

well as to/from overlying water (Morrison et al. 1996; Arnot and Gobas 2004). This approach

differs from many conventional bioaccumulation studies, such as biota-sediment accumulation

factor (BSAF) frameworks (Burkhard et al. 2012; Judd et al. 2014), biomimetic/bioavailability

assessments (Trimble et al. 2008; Lydy et al. 2015), and refined models of sediment

bioavailability based on multiphase absorbents in sediments (Moermond et al. 2005, Hauck et al. 2007). The conventional bioaccumulation studies often ascribe most or all of the chemical exposure of invertebrates to the sediments they inhabit. Given that the Arnot and Gobas (2004) model is so commonly used in POPs risk assessments and as a decision support tool, there is a need to rigorously validate its predictions across many sites and food web components. Many of the validation studies performed on this model have focused on the global fit of model predictions to empirically measured POPs concentrations in organisms occupying different trophic positions and across different sets of chemicals (e.g., individual polychlorinated biphenyls (PCB) congeners) that vary in chemical hydrophobicity (Morrison et al. 1997, 1999, 2002; Kashian et al. 2010). Given the importance of benthic invertebrates as the chief vector transferring sediment-associated POPs to fish, there is a need to specifically validate the model predictions for this group of organisms included in its simulations. Morrison et al. (1996), developed the original benthic invertebrate sub-model that was subsequently adopted within the Arnot and Gobas (2004) framework and tested it against field data collected from four benthic invertebrate species but applied the model validation to only one location. Due to the strong dependence of the model on the ratio of the chemical potential (i.e., the fugacity ratio) in sediment and overlying water, it is important to demonstrate the model's applicability to benthic invertebrates collected from different locations where the sediment/water fugacity ratio varies.

A second issue concerns the adoption of recommended model settings (i.e., parameter values), which vary across different published applications of the model, but have been optimized under specific calibration exercises and, when changed, can have unintended impacts on model behavior and model output interpretation. One such change noted between the model descriptions by Arnot and Gobas (2004) and Selck et al. (2012) is related to the recommended parameter for the fraction of overlying water versus the porewater respired by benthic invertebrates. Variations in this parameter directly affects the model's sensitivity to water and sediment inputs, altering the overall importance of benthic-pelagic coupling and the relative contributions of sediments and water to fish body burdens at higher trophic levels. Arnot and Gobas (2004) recommended a value of 5% respired porewater and 95% respired overlying water, reasoning that porewater is likely to be anoxic and that benthos must ventilate a larger fraction of overlying water to satisfy their oxygen demands. In contrast, Selck et al. (2012) argued that the ventilation of burrows could vary considerably among different benthic invertebrates and may

depend on an organism's tolerance to anoxic conditions. They applied a respired fraction of 50% overlying water and 50% porewater in their model application for burrowing benthic invertebrates.

In the present study, we use a dataset consisting of paired benthos/sediment samples collected from 33 sampling stations distributed throughout the Detroit River in Ontario, Canada, and Michigan, US, and zone-specific water concentration estimates compiled for the system. A set of biota-sediment accumulation regressions (BSARs) were used to empirically evaluate whether PCB bioaccumulation in benthic invertebrates depends on both overlying water and sediment PCB concentrations or is mostly related to sediment exposure. Next, the Arnot and Gobas (2004) food web bioaccumulation model was compared between simulations using the overlying water/porewater respiration ratios for benthic invertebrates recommended by the authors and Selck et al. (2012) to determine which algorithm showed higher accuracy in the prediction of spatially explicit benthic invertebrate PCB concentrations. These two algorithms were also compared against empirically calibrated BSAR predictions. The two food web simulations and a hybrid BSARs/fish bioaccumulation model were then compared with respect to their ability to predict PCB bioaccumulation in Detroit River fish species. Finally, the implications of the different model simulations were compared with respect to potential management actions (i.e., whether to focus on remediating sediment or water PCB concentrations).

2.2 Methods

Biota sediment accumulation regressions (BSARs)

Biota-sediment accumulation regression (BSAR) models have been proposed as an alternative to the use of conventional biota-sediment accumulation factors (BSAFs), which assume equilibrium partitioning of hydrophobic organic compounds between biota and sediments and a constant capacity of sediment organic matter (Burkhard et al. 2009; Judd et al. 2014). BSARs provide site-specific calibration based on the linear relationship between the lipid-equivalent chemical concentration in the organism and the organic carbon-normalized concentration in sediments with the following general form:

(Eq. 1) $$C_{org(leq)} = \beta_{sed} \cdot C_{sed(oc)} + \beta_0$$

where $C_{org(leq)}$ and $C_{sed(oc)}$ are the lipid-equivalent chemical concentrations in the organism (ng·g^{-1} lipid equivalents) and the organic carbon-normalized concentration in the sediments (ng·g^{-1} organic carbon, OC); β_{sed} is the regression coefficient that specifies the mean bioavailability of sediment-associated chemical across sites (g OC·g^{-1} lipid equivalents); and β_0, if significant and positive, accounts for additional chemical exposure sources averaged across sites that are not accounted for by bulk sediment concentrations. For the present study, and to maintain consistency with the food web bioaccumulation model, the lipid-equivalent concentration in the animal is used as an alternative to lipid normalized concentrations to account for additional partition capacity of non-lipid organic matter (NLOM) in the animal. It is estimated according to the following equation:

(Eq. 2) $$C_{org(leq)} = \frac{C_{org}}{P_{org,lipid} + P_{org,NLOM} \times \varphi_{NLOM}}$$

where C_{org} is the wet weight chemical concentration in the organism (ng·g^{-1}); $P_{org,lipid}$ is the proportion of neutral lipids in the organism; $P_{org,NLOM}$ is the proportion of NLOM in the organism and estimated as the proportion of lean dry weight in the animal (dry weight minus lipid weight); and φ_{NLOM} is the NLOM partitioning equivalent in the organism relative to n-octanol. A summary of the model input parameters, their definitions and values or algorithms are provided in Table A1.

Eq. 1 can be applied to explore site-specific factors explaining chemical bioavailability to benthic organisms. In its basic form, Eq. 1 can be collapsed into a calibrated BSAF model by forcing the regression intercept to zero. In this case, β_{sed} becomes equivalent to the mean empirical BSAF determined across sampling locations:

(Eq. 3) $$C_{org(leq)} = \beta_{sed} \cdot C_{sed(oc)}$$

Alternatively, Eq. 1 can be expanded to include site-specific sediment and overlying water contamination as chemical sources:

(Eq. 4) $\qquad C_{org(leq)} = \beta_{sed} \cdot C_{sed(oc)} + \beta_w \cdot C_w + \beta_0$

where C_w is the dissolved chemical concentration in the overlying water (ng·mL^{-1}) and β_w is a coefficient related to chemical bioavailability from water (mL water ·g^{-1} lipid equivalents). The application of linear regressions to solve for Eq. 1, 3 and 4 is appropriate when $C_{org(leq)}$, $C_{sed(oc)}$ and C_w values are normally distributed. Alternatively, transformation of the above model inputs may be necessary to meet the assumptions of linear regression analysis.

Process-based food web bioaccumulation model

In contrast to BSARs, which are calibrated based on site-specific data, the food web bioaccumulation model is a process-based model developed for hydrophobic organic compounds and solved for multiple species of organisms inhabiting a site (Arnot and Gobas 2004). The main model parameters are not calibrated based on site-specific information, other than the main model inputs, which include the mean annual water temperature, geometric mean of water and sediment chemical concentrations within the food web zone of interest, organism whole body lipid contents (and dorsal muscle lipid contents for fish), organism NLOM contents (and dorsal muscle NLOM contents for fish) and species-specific feeding relationships as specified by the diet matrix. The food web bioaccumulation model is fully described by Arnot and Gobas (2004) and McLeod et al. (2015). For brevity, only the main equations used in this model are outlined below. The equation predicting steady-state concentrations in a given organism is as follows:

(Eq. 5) $\qquad C_{org} = \dfrac{G_{diet} \cdot \Sigma_{i=1}^{n} \left(P_{diet(i)} \cdot E_{diet} \cdot C_{diet(i)} + P_{sed} \cdot E_{sed} \cdot C_{sed(OC)} \right) + G_v \cdot E_w \cdot \left(C_{(p,w)} \cdot P_{(p,w)} + C_{(o,w)} \cdot P_{(o,w)} \right)}{\dfrac{E_w \cdot G_v}{K_{BW}} + \dfrac{E_{f(bio)} \cdot G_{f(bio)}}{K_{BF(bio)}} + \dfrac{E_{f(sed)} \cdot G_{f(sed)}}{K_{BF(sed)}} + G_{gro}}$

where C_{org}, $C_{diet(i)}$, $C_{sed(OC)}$, $C_{(p,w)}$, and $C_{(o,w)}$ are the chemical concentrations in the organism (ng·g^{-1} wet weight), the ingested biological dietary items of diet type (i) in units of ng·g^{-1} wet weight in food, the ingested sediment (ng·g^{-1} OC), porewater (ng·mL^{-1}), and the overlying water (ng·mL^{-1}), respectively. The terms G_{diet}, G_v, $G_{f(bio)}$, $G_{f(sed)}$, and G_{gro} refer to the organism's feeding rate (g food·g^{-1}BW·d^{-1}), gill ventilation rate (mL·g^{-1} BW·d^{-1}), fecal egestion rate of unassimilated biological dietary items (g feces$_{(bio)}$·g^{-1} BW·d^{-1}), fecal egestion rate of

unassimilated sediment (g feces$_{(sed)}$·g^{-1} BW·d^{-1}) and animal growth rate (d^{-1}), respectively. The unitless terms E_{diet}, E_{sed}, $E_{f(bio)}$, $E_{f(sed)}$ and E_w represent the chemical assimilation efficiency from ingested food, chemical assimilation efficiency from ingested sediment, chemical transfer efficiency from animal to feces for biological ingested dietary items, the transfer efficiency from animal feces for unassimilated sediment present in feces and the chemical transfer efficiency between the organism and its gills, respectively. The terms $P_{diet(i)}$, P_{sed}, $P_{(o,w)}$, and $P_{(p,w)}$ refer to the proportion of a given item (i) to the total diet of the animal, the proportion of sediment present in the total diet of the animal, or the proportion of overlying water and pore water to the total respired water in each species in the simulation, respectively. The terms K$_{BW}$, K$_{BF(bio)}$ and K$_{BF(sed)}$ refer to the organism/water partitioning coefficient (mL·g^{-1} BW), the organism/feces partitioning coefficient (g feces·g^{-1} BW) for feces generated from biological ingested food items, and the organism/feces partitioning coefficient (g feces·g^{-1} BW) for unassimilated sediment present in the feces of the animal.

Eq. 5 provides the capability to treat ingested sediments differently from ingested biological items that may be present in an animal's food, as specified by the feeding matrix used in the model, and to consider different fractions of respired water, consisting of either pore water or overlying waters. The algorithms describing the model parameter estimates for ingested biological dietary items (E$_{diet}$, G$_{f(bio)i}$, E$_{f(bio)i}$, and K$_{BF(bio)i}$) are described in detail by Arnot and Gobas (2004) and McLeod et al. (2015). However, these previous studies were less explicit in describing how estimates of these parameters are obtained for ingested sediments and are therefore outlined in detail below.

The term E_{sed} is generally considered to be less efficient than E_{diet}. For simplicity, the model assumes that chemical assimilation from ingested sediments is lower than from ingested biological items by a factor of 4 and is predicted based on congener-specific hydrophobicity. Using the equation specifying E_{diet} in Arnot and Gobas (2004), E_{sed} is given by the following equation:

(Eq. 6) $\qquad E_{sed} = \dfrac{E_{diet}}{4} = \dfrac{1}{(3.0 \times 10^{-7} \cdot K_{OW} + 2.0) \cdot 4}$

The term K_{ow} refers to each PCB congener's octanol/water partition coefficient. The amount of unassimilated sediment in feces ($G_{f,sed}$) following the ingestion of sediments is handled according to the equation below:

$$\text{(Eq. 7)} \qquad G_{f,sed} = P_{sed} \times [(1 - AE_{OC,sed}) \times P_{OC} + (1 - AE_{IM,sed}) \times P_{IM}]$$

where $AE_{OC,sed}$ is the dietary assimilation efficiency of OC ingested with sediments, and $AE_{IM,sed}$ is the assimilation efficiency of inorganic matter (IM) ingested with sediments; P_{OC} and P_{IM} represent the proportions of organic matter and IM in ingested sediments by weight, respectively. In the model simulations, only OC is considered to be digestible and assimilated. We assume OC and IM to be the only sediment components; thus the sum of P_{OC} and P_{IM} is equal to one. $K_{BF(sed)}$ is described below.

$$\text{(Eq. 8)} \qquad K_{BF(sed)} = \frac{(1 - AE_{OC,sed}) \cdot P_{OC} \cdot \varphi_{OC} \cdot K_{OW} + (1 - AE_{IM,sed}) \cdot P_{IM} \cdot \varphi_{IM} \cdot K_{OW}}{P_{org,lipid} \cdot K_{OW} + P_{org,NLOM} \cdot \varphi_{NLOM} \cdot K_{OW} + P_{org,wat}}$$

where φ_{OC}, φ_{IM}, and φ_{NLOM} are the partitioning capacities of unassimilated sediment OC, unassimilated sediment IM present in feces, and NLOM in the organism relative to n-octanol. For the present simulations, values of 0.35 (Seth et al. 1999), 0, and 0.05 (Debruyn and Gobas 2007) were applied for φ_{OC}, φ_{IM}, and φ_{NLOM}, respectively. Eq. 8 does not consider the small partitioning capacity associated with unassimilated water ingested with sediments because the dry weight and OC-normalized sediment concentrations are used as model inputs.

Sediment/water fugacity ratios were used to determine the equilibrium status of pollutants between the overlying water and bottom sediment to provide interpretative values regarding water and sediment sources to food web components. A sediment/water fugacity ratio equal to 1 indicates equilibrium; values greater than 1 indicate that sediments are a potential source of PCBs in water; and values less than 1 imply that sediments are a net PCB sink. Sediment/water fugacity ratios were calculated as follows:

$$\text{(Eq. 9)} \qquad \frac{f_{sed}}{f_w} = \frac{C_{sed(dry)}}{C_w} \cdot \frac{1}{(P_{OC} \cdot \varphi_{OC} \cdot K_{OW} + P_{IM} \cdot \varphi_{IM} \cdot K_{OW}) \cdot \rho_{sed}}$$

where $C_{sed(dry)}$ is the concentrations in sediment (ng·g^{-1} dry weight), and ρ_{sed} is the bulk density of sediments, estimated to be 1.2 g·mL^{-1} (McLeod et al. 2015). Porewater PCB concentrations (ng·mL^{-1}) were calculated by the model according to the equilibrium partitioning algorithm recommended by Arnot and Gobas (2004) and modified to include the IM content as follows:

$$\text{(Eq. 10)} \qquad C_{(p.w)} = \frac{C_{sed(dry)}}{(P_{OC} \cdot \varphi_{OC} \cdot K_{OW} + P_{IM} \cdot \varphi_{IM} \cdot K_{OW})}$$

Study area

The model input and validation data were obtained from the Detroit River, an International Joint Commission-Designated Great Lakes Area of Concern (AOC). The Detroit River is divided by the international border between Canada and the US into stretches located in the province of Ontario and the state of Michigan, respectively. PCB contamination in sediments and water have been intensively characterized for this system, and there are large spatial gradients between the US and Canadian jurisdictions (Drouillard 2010; Szalinska et al. 2013). The inputs of PCB contamination are from multiple sources such as local contaminants from historical industries, contaminated brownfield sites, sewage treatment plants, sewer overflows, and urban runoff (Drouillard et al. 2006). PCBs are a major cause of fish consumption advisories issued for the Detroit River (Kashian et al. 2010; OMOECC 2017) and have been the target of sediment cleanup activities in the system (Heidke et al. 2003).

Data

For the model simulations predicting congener-specific PCB concentrations in benthic invertebrates and fish, the recommended parameter values and the diet/feeding matrix previously developed for the Detroit River by McLeod et al. (2015) was used, in addition to updated PCB concentrations from sediment and water described by Drouillard (2010) and Szalinska et al. (2013). The simulations involved similar model inputs and parameters, except for the two overlying/porewater water respiration fractions being compared. The congener-specific PCB concentrations in water used in the zone- and site-specific simulations were obtained from

Drouillard et al. (2010) and compiled to obtain geometric mean PCB concentrations in overlying water for each zone generated for the year 2002. A total of 174 individual water samples that were obtained from the water column 1 m below the river water surface at 29 stations were used in this study (Drouillard et al. 2016). The congener-specific PCB concentrations in sediments used in the zone-wide simulations were obtained from Szalinska et al. (2013). The Detroit River was divided into six food web zones (upstream, midstream and downstream zones in both the US and Canada), and the model used the geometric mean concentrations of each PCB congener in water and surface sediments from each zone as model inputs (Figure 2.1). The six zones exhibit significant differences in sediment and water contaminants because large islands and shipping channels complicate the flow patterns and separate the previous and ongoing sources of PCBs from the US and Canadian sides of the river (Drouillard et al. 2006, Drouillard et al. 2013).

For benthic invertebrate validations, samples of sediments and matched biota were collected in a separate survey completed in July of 2008 (n=33 stations). The stations were selected using a stratified random design, employing river segments representative of the modeling zones. Ten petite Ponar grab samples were collected at each site and pooled in a large plastic tray. The sediments were manually stirred and a subsample was removed and placed in a glass jar for PCB analysis. The remaining sediments were sieved through a 2-mm bucket sieve at each location. All visible live benthic invertebrates were removed from the sieve, placed in a jar with overlying water and stored in a cooler for transport to the laboratory. The organisms were allowed to depurate their gut contents for 8 to 12 h and then manually sorted, blot dried and frozen for chemical analysis. For stations with a high benthic invertebrate biomass, the organisms were pooled into samples by type of species; for stations with a low biomass, the samples were pooled by including all organisms as a mixed-sample pool. PCB concentrations were determined in 57 pooled samples of benthic species, including mayflies (n=14 samples), zebra mussels (n=12 samples), chironomids (n=7), oligochaetes (n=2), amphipods (n=1), leeches (n=1), mussels (n=1) and mixed benthic pools (n=19). These samples were distributed across 25 sample stations.

The extraction and rinsing of PCBs from sediments was performed following the methods of Drouillard et al. (2006). The PCBs in benthic invertebrates were extracted as per Daley et al. (2009). The cleaned samples were analyzed using an Agilent 5890 gas chromatograph equipped with a ^{63}Ni micro-electron capture detector (GC-ECD), a 7673A auto-

sampler and a 30 m x 0.25 mm x 0.1 µm DB-5 column. The samples were analyzed in batches of 6 samples; each batch included a method blank, a reference sample (NIST SRM 1944 for sediments or an in-house Detroit River carp reference for benthos) and a diluted certified standard (Quebec Ministry of Environment Congener Mix; Accustandard, New Haven, CT, US). The samples were analyzed for the following PCB congeners (IUPAC #): 31/28, 44, 49, 52, 70, 74, 87, 95, 99, 101, 105/132, 110, 118, 138, 149, 153, 156/171, 158, 170, 180, 183, 187, 194, 195/208, 199, and 206. The detection limits for PCBs ranged from 0.01 to 0.2 ng·g^{-1} dry weight in sediments and from 0.03 to 0.08 ng·g^{-1} wet weight in benthic invertebrates. There were 3.0% and 14.8% non-detects in sediment and paired benthos tissue concentration, respectively. Only the paired detected sediment and benthos tissue concentrations were included in the analysis.

The surrogate recovery standard (1,3,5-tribromobenzene) spiked into samples prior to extraction yielded average±standard error values of 70.0±2.9% and 71.3±2.7% in sediments and benthic invertebrates, respectively. The recovery was higher for PCB-30 (84.3±3.0%) due to the lower volatility of this recovery standard and most PCBs of interest. The reference samples exhibited PCB concentrations within two standard deviations of certified or in-house database values and were in compliance with the quality assurance/quality control procedures used in the Canadian Association for Laboratory Accreditation Inc. (CALA)-accredited Organic Analytical Laboratory of the Great Lakes Institute for Environmental Research (GLIER), University of Windsor, Windsor, ON, Canada. Neutral lipids in benthic invertebrates were determined gravimetrically based on a subsample of the solvent extracts used for PCB analysis (Drouillard et al. 2004). Organic carbon was measured based on loss on ignition as described by Drouillard et al. (2006).

Fish PCB concentrations employed for food web validation were obtained from an in-house GLIER database of dorsal muscle samples. These samples were analyzed in fish for congener-specific PCBs by the GLIER Organic Analysis Laboratories (OAL) and were collected from the Detroit River between 1998 and 2016. The validations also incorporated data from the Ontario Ministry of Environment and Climate Change (OMECC) Fish Contaminant Monitoring Program and the Michigan Department of Environmental Quality (MDEQ) sport fish database. Fish data from the OMECC database were available from 1998 to 2008, and fish data from the MDEQ database were available from 1998 to 2015. The combined fish validation database provided a total of 1237 sample records that comprised 23 fish species (including 18 sport fish

species) collected from locations across all six river sections. Only the PCB concentrations from the dorsal muscle of sport fish were available from the government monitoring programs. The fish PCB concentrations were converted to lipid equivalents using Eq. 2, for comparison with the model outputs. The congener-specific simulation results were then summed across all model congeners to generate a sum PCB concentration for comparison with the validation results. The methods used for the processing of fish fillet samples vary between agencies, MDEQ uses a skin-on sample fillet, while OMECC uses a skin-off sample fillet for contaminant residue analysis (Kashian et al. 2010). However, the lipid-equivalent correction is expected to eliminate differences in fillet sample-processing methods. A summary of the observed total PCBs in each fish species and the corresponding lipid contents is provided in Table A2.

Model evaluation and validation

Empirical BSARs (Eq. 1, 3 and 4) were fit through multiple linear regressions. Model selection was based on an evaluation of three criteria: (1) whether the slope was significantly different than zero, (2) the coefficient of determination (R^2) from the linear regressions, and (3) consideration of the magnitude of Akaike's information criterion (AIC) and Bayesian information criteria (BIC) generated for each model fit (Burnham and Anderson 2002). Compared with AIC, BIC imposes a greater penalty for the additional parameters added to the model. The model with the combined features of a high R^2 and low AIC/BIC was selected as the best BSAR. All evaluation factors are estimated using SAS statistic analysis software.

Food web bioaccumulation model simulations were performed on a site-specific basis or a zone-wide basis depending on which validation dataset was employed for comparison with the simulation results. Site-specific simulations were contrasted with matched sediment and benthos samples to validate model accuracy for benthic invertebrates. In this case, the sediment concentration from a given sampling location was used as the model input, and the model-predicted benthic invertebrates concentrations were compared with the observed benthic invertebrate concentrations for the same site. Zone-wide simulations were conducted by dividing the Detroit River into six zones (Figure 2.1) and using the geometric mean concentration of each PCB congener in water and surface sediments from each zone as model inputs. The zone-wide simulations were contrasted against the fish validation database and were compared with the predicted lipid-equivalent concentrations in fish from a given zone that best corresponded to the

collection location of the fish sample. Since site-specific water concentrations of PCBs were not available, the closest matching zone-wide water concentration was employed as the water input during site-specific simulations. Zone-wide validation of fish concentrations were also applied by replacing the benthic invertebrate sub-model with the benthic invertebrate concentrations estimated using the best-fit BSAR model. This approach represents a hybrid between the empirically calibrated BSAR model and the process-based food web bioaccumulation model applied to fish and zooplankton. In addition to R^2 and AICs/BICs, two statistics recommended in previous studies (USEPA 2009, Bennett et al. 2013, von Stackelberg et al. 2002) were applied to validate the model estimation including the relative percent different:

$$\text{(Eq. 11)} \qquad RPD = (\sum_1^n \frac{(C_{org(p)} - C_{org(o)})}{(C_{org(p)} - C_{org(o)})/2})/n \cdot 100\%$$

and the root mean square error:

$$\text{(Eq. 12)} \qquad RMSE = \sqrt{\frac{\sum_1^n (C_{org(p)} - C_{org(o)})^2}{n}}$$

where $C_{org(p)}$ refers to the predicted chemical concentrations in the organism, $C_{org(o)}$ refers to the observed chemical concentrations in the organism, n refers to the number of observations. The calculated metrics (AIC/BIC, RPD, and RMSE) closest to zero indicate better model performance.

2.3 Results

Empirical observations

Figure 2.1 shows the spatial patterns of the sum PCB concentrations in sediments, water, and benthic invertebrates. Overall, there was a general correspondence between the spatial patterns of contamination observed in the contamination sources (sediments and water) and biota, although greater variation was apparent in the benthic invertebrates data than in the sediment and water data. The PCB concentrations on the US side of the river were significantly higher than in the sampled Canadian waters ($C_{org(leq)}$: $F_{1,55}=6.83$, $p<0.01$, ANOVA; $C_{sed(oc)}$: $F_{1,55}=7.2$, $p<0.01$, ANOVA). There were also significant differences in the sum PCB concentrations in different river sections ($C_{org(leq)}$: $F_{5,51}=4.52$, $p<0.01$, ANOVA; $C_{sed(oc)}$: $F_{5,51}=6.35$, $p<0.01$, ANOVA). A similar spatial pattern of sum PCB concentrations was found in the water samples (C_w: $F_{1, 192}=101.85$, $p<0.01$, ANOVA; C_w: $F_{5, 188}=22.11$, $p<0.01$, ANOVA).

BSAR evaluation

The fit of the BSAR regression models applied to log-transformed and nontransformed $C_{org(leq)}$, $C_{sed(oc)}$, and C_w are presented in Table 2.1. Given that the intercept of Eq. 1 was statistically significant (β_0=0.97, p<0.05), Eq. 3 (BSAF model) was rejected. $C_{org(leq)}$, $C_{sed(oc)}$, and C_w were log transformed to satisfy normality assumptions of linear regression (Royston 1992).

The estimated coefficient for $log(C_{sed})$ was positive and statistically significant for both Eqs. 2a and 4a (Eq. 2a: β_{sed}=0.45, p<0.05; Eq. 4a: β_{sed}=0.41, p<0.05). The estimated coefficient for C_w in Eq. 4a was also statistically significant (β_w=0.13, p<0.05), indicating that dissolved PCB concentrations in water are significant contributors to PCB exposure in benthic invertebrates. Concerning the multicollinearity issue between $C_{sed(oc)}$ and C_w, no strong correlation was found between the two contamination sources (corr[$C_{sed(oc)}$, C_w]=0.34,). The different magnitudes of coefficients between $C_{sed(oc)}$ and C_w in Eq. 4a (β_{sed}>β_w) suggests that the sediment is a stronger factor affecting PCB bioaccumulation than water. In Eq. 2a, β_0 represents exposure sources averaged across sites without accounting for sediment contamination, whereas it represents factors that are not otherwise controlled by sediment and water contamination in Eq. 4a. The estimate of the intercept term (β_0) exhibits a positive, statistically significant sign in both Eq. 2a and Eq. 4a.

Food web bioaccumulation model validation (benthic invertebrates)

Next, both the BSAR (Eq. 2a and 4a in Table 2.1) and the process-based food web bioaccumulation model simulations (contrasted between the 95/5% and 50/50% overlying/pore water respiration fractions) were compared for their abilities to predict PCB concentrations in benthic invertebrates at each location of benthos collection. Model accuracy was evaluated by applying goodness of fit tests to log-transformed predicted-versus-observed sum PCB concentrations (Figure 2.1) and across individual PCB congeners (Table 2.2) for each benthic invertebrate sample from the individual sampling locations. Because only five of the 26 field-observed PCB congener concentrations differed significantly between taxa obtained from the same location (Kruskal-Wallis test, p<0.05), the validation results for different invertebrate taxa groups were treated similarly in validation trials.

Overall, compared with the process-based food web bioaccumulation model estimations, the BSAR estimated tissue PCB concentrations had a stronger fit relative to the expected 1:1 relationship, except for sites with low benthos contamination, where the BSARs tended to underpredict PCBs in benthic invertebrates. BSAR Eq. 2a had an overall mean model bias (predicted/observed PCB concentration ± standard deviation) of 2.17±3.72, and 83% and 65% of the model predictions were within a factor of 4 and 2, respectively, from field measurements. For BSAR Eq. 4a, the overall mean model bias decreased to 1.89±2.99, and 86% and 68% of the predictions were within a factor of 4 and 2, respectively, from field measurements. For the process-based food web bioaccumulation model, 80% of the model predictions were within a factor of 4 of field measurements, regardless of the assumptions about the overlying water respiration fraction in benthic invertebrates. This level of performance is consistent with previous studies regarding the model's predictive accuracy (Kashian et al. 2010). For model simulations that assumed a larger overlying water fraction ($P_{(o,w)} = 95\%$), the overall mean model bias was 3.02±2.67, and 51% of the samples had predicted PCB concentrations within a factor of 2 of observed concentrations. For model simulations that assumed a smaller overlying water fraction ($P_{(o,w)} = 50\%$), the mean model bias reduced to 2.67±1.86, and the percentage of predicted sum PCB concentrations within a factor of 2 of observed sum PCB concentrations increased to 53%.

A linear regression was performed between log-predicted and log-observed PCB concentrations across individual congeners for each of the four simulations being contrasted, and the resultant equations and regression statistics are summarized in Table 2.2. All four simulations had regression slopes significantly different from zero ($p<0.05$, ANOVA). The F-test showed that the slopes were significantly different from one ($P_{(o,w)} = 95\%$: $F_{1, 832}=139.75$, $p<0.05$; $P_{(o,w)} = 50\%$: $F_{1,831}=147.33$, $p<0.05$; BSAR Eq. 2a: $F_{1,807}=46.59$, $p<0.05$; BSAR Eq. 4a: $F_{1,796}=44.22$, $p<0.05$; Wald test). The R^2 values ranged from 0.37 to 0.43 across simulations, with the highest fit ascribed to BSAR Eq. 4a, closely followed by the $P_{(o,w)} = 50\%$ simulation. Comparing the regression results for the food web bioaccumulation model with $P_{(o,w)} = 95\%$ and $P_{(o,w)} = 50\%$, the simulation using $P_{(o,w)} = 50\%$ had better goodness of fit regression characteristics for R^2, lower AIC/BIC and lower RMSE. Compared with the BSAR results, the process-based model simulations was close to equivalent in performance.

Next, simulation results obtained using different models ($BSAR_{(Csed\ only)}$, $BSAR_{(Csed+Cw)}$, $P_{(o,w)}$ =95%, and 50%) were contrasted with the fish contamination database (Figure 2.3). For the hybrid BSAR/food web models, tissue concentrations in benthos were predicted by Eq. 2a and 4a while Eq. 5 was applied to estimate PCB accumulation in fish. The results from the hybrid BSAR/food web models underestimated fish contaminant concentration (Figure 2.3). The overall mean model bias was 3.14±5.1 and 2.58±3.9, 38% and 42% of the predicted PCB concentrations were within a factor of 2 of the observed PCB concentrations for $BSAR_{(Csed\ only)}$ and $BSAR_{(Csed+Cw)}$, respectively. For the model with $P_{(o,w)} = 95\%$, the overall mean model bias was 3.15±4.2, and 38% of the predicted sum PCB concentrations were within a factor of 2 of the observed sum PCB concentrations. This result is consistent with a previous study conducted in the Detroit River (Kashian et al. 2010). For $P_{(p,w)} = 50\%$, the overall mean model bias decreased to 2.58±3.5, and the percentage of the predicted sum PCB concentrations within a factor of 2 of observed concentrations increased to 42%, which was similar to the $BSAR_{(Csed+Cw)}$ model.

Next, goodness of fit tests of log-predicted versus log-observed PCB congener concentrations were performed and compared to fish (Table 2.3). For all four models, the estimated slopes were significantly different from zero ($p<0.05$, ANOVA), and the F-tests indicated that the slopes were significantly different from one at the 5% level ($P_{(o,w)} = 95\%$: $F_{1, 17450}=1872.72$, $p<0.05$; $P_{(o,w)} = 50\%$: $F_{1,17450}=6.38$, $p<0.05$; $BSAR_{(Csed\ only)}$: $F_{1,17450}=424.97$, $p<0.05$; $BSAR_{(Csed+Cw)}$: $F_{1,17450}=3465.38$, $p<0.05$; Wald test).

Focusing on the food web bioaccumulation model, the model assuming $P_{(o,w)} = 50\%$ showed better prediction of PCB concentrations in fish samples, as demonstrated by steeper slopes with higher explanatory power. For the $P_{(o,w)} = 95\%$ model, the regression explained 23.2% of the variation in the empirical data. For the $P_{(p,w)} = 50\%$ model, 24.4% of the variation of the empirical data was explained. While the $P_{(o,w)} = 95\%$ model produced a better RPD result, the $P_{(p,w)} = 50\%$ model consistently emerged as showing higher accuracy; compared with the values presented by the other models. The $P_{(p,w)} = 50\%$ model presented lower AIC/BIC values of 39,882/39,966 and relatively lower RMSE of 1243.6. In this case, the process-based method ($P_{(p,w)} = 50\%$ model) performed better than the hybrid

BSAR/bioaccumulation model across a number of model performance measures on both an absolute basis (Figure 2.3) and a relative basis (Table 2.3).

Primary sources of PCB body burdens in benthic invertebrate and fish

We evaluated the primary source of PCB body burden in biota between various river sections. Because of the failure of BSAR$_{(Csed\ only)}$ to account for water sources, we only compared the results from BSAR$_{(Csed+Cw)}$ and two exposure scenarios of the food web bioaccumulation model. In the simulation, first sediment-derived and then water-derived chemicals were hypothetically set to zero and compared with the baseline simulation including water and sediment contamination. The difference in biota PCB concentrations estimated between the simulations was then used to estimate the percentage of the body burden of PCBs in benthos and fish derived from water or sediment (Figure 2.4).

There were significant differences in the estimated percentages of the benthos body burden originating from sediments in different river sections (for BSAR$_{(Csed+Cw)}$, benthos: $F_{5,150}$=8.20, p<0.05 ANOVA; $P_{(o,w)}$ = 95%, benthos: $F_{5,150}$=32.65, p<0.05 ANOVA; for $P_{(o,w)}$ =50%, benthos: $F_{5,150}$=9.01, p<0.05, ANOVA). In BSAR$_{(Csed+Cw)}$, sediment was the primary source across all river sections for benthos, and the percentages of the sediment-derived body burden estimated by this model were significantly higher than those estimated by both food web bioaccumulation models in the corresponding river reaches (p<0.05 ANOVA). For the food web models (95% versus 50%), $P_{(o,w)}$ = 95% implied that benthos derived a large proportion (>50%) of their PCB burden from water. In contrast, model runs assuming $P_{(o,w)}$ = 50% showed that the biota derived more than half of their contaminant body burden from the sediment in most river locations, except in the US upstream and Canadian downstream reaches. Consistent observations between model simulations were observed for fish, with significant differences in the estimated percentages of fish PCB body burden originating from sediments in different sections of the river (for BSAR$_{(Csed+Cw)}$, fish: $F_{5,150}$=8.24, p<0.05 ANOVA; for $P_{(o,w)}$ = 95%, fish: $F_{5,150}$=12.38, p<0.05, ANOVA; for $P_{(o,w)}$ =50%, fish: $F_{5,150}$=14.36, p<0.05, ANOVA). However, the sediment-derived body burden was lower in fish than in benthos because fish are exposed only to sediment-derived contaminants through food web transfer and consumption of benthic components of the food web. The estimated percentages of sediment-derived PCB body burden in fish from BSAR$_{(Csed+Cw)}$ were also significantly higher than those obtained from both

food web bioaccumulation models (p<0.05 ANOVA). The empirical BSAR/food web hybrid model estimated that more than half of the average contaminant body burden was derived from sediments, with the exception of the Canadian downstream and the US upper stream. The food web bioaccumulation model estimated that less than half of the average contaminant body burden was derived from sediments under both exposure scenarios, with the exception of the middle stream and the US downstream reaches according to the $P_{(o,w)} = 50\%$ model.

Difference in the percentages of PCB body burdens in biota between the two exposure scenarios in the food web bioaccumulation model are related to sediment-water disequilibrium conditions within the system. The equilibrium status of PCB congeners between sediments and water can be evaluated based on the f_{sed}/f_w values of the six river sections (Figure 2.5). Among the PCB congeners, more than half (58%) exhibited f_{sed}/f_w values between 2 to 10 (mean=8.67±11.41) (See Figure A1. f_{sed}/f_w versus logK_{ow} for the 26 PCB congeners across the six river sections). Thus, PCBs in sediments tended to exceeded equilibrium concentrations in water throughout the Detroit River. However, the spatial distribution of f_{sed}/f_w values varied significantly in different sections of the river ($F_{5,640}$=14.76, p<0.05, ANOVA). The spatial pattern of f_{sed}/f_w was similar to the distribution of the percentages of PCB body burdens in benthic invertebrates and fish (Figure 2.4). These results indicate that (1) the extent of disequilibrium between the overlying water and sediments influences the predominant uptake route of PCBs, and (2) respiration of larger fractions of porewater by benthos contributes to higher trophic transfer of PCBs to fish.

The extent of sediment/water disequilibrium was greatest in the middle reach on the Canadian side of the border (p<0.05, Tukey's test). The high f_{sed}/f_w value observed in this area may occur because legacy sediment deposition zones, such as Turkey Creek in the middle Canadian river reach, are highly stable during disturbance events, and desorption processes are negligible. In the upper river reach, however, over one-third of the PCBs (39%) exhibited f_{sed}/f_w values less than one, possibly suggesting upstream water sources as a potentially important vector for contaminant entry. A comparison of f_{sed}/f_w values in the same river reach on the US and Canadian sides showed significant differences, except in the upstream of the river. In US waters, the f_{sed}/f_w values were significantly different (p<0.05, Tukey's test) between the three river reaches. In contrast, the f_{sed}/f_w values in the Canadian middle stream reaches were significantly higher than those in the upper and lower river reaches (p<0.05, Tukey's test). In

addition, the relationships between the degree of disequilibrium and K_{ow} values were not consistent across river strata. In the US upstream and middle stream of the river, f_{sed}/f_w values exhibited no relationship with K_{ow} values (p>0.05, ANOVA). In contrast, a declining trend in f_{sed}/f_w values with increasing chemical hydrophobicity was observed in all other sections of the river. The above pattern is opposite to what would be expected if kinetic limitations to desorption cause higher sediment loss of less hydrophobic PCBs to overlying waters and suggests instead larger sources of lower K_{ow} congeners relative to higher K_{ow} PCBs.

2.4 Discussion

The empirically calibrated BSAR(Csed+Cw) provided the strongest site-specific prediction of benthic invertebrate PCB concentrations among the different BSARs tested. The calibrated BSAR model also exhibited marginally better performance than the $P_{(o,w)} = 50\%$ process-based food web bioaccumulation model. The increased accuracy of BSAR(Csed+Cw) indicates that PCBs present within the overlying water are important for benthic invertebrate PCB bioaccumulation.

The conclusions from both the BSAR and process-based food web bioaccumulation models are consistent with the conclusion of Morrison et al. (1996), who indicated that PCB concentrations in water and sediment and the magnitude of the sediment/water fugacity ratio are all important for benthic invertebrate PCB bioaccumulation. Compared with the kinetics of chemical exchange between benthos and water, the chemical kinetics controlling chemical flux between benthos and sediments are considered slow ($G_{diet}E_{diet,sed} < G_v E_w$) (Morrison et al. 1996; Selck et al. 2012). The changing status of overlying water, as PCB source or PCB depuration media, dependent on f_{sed}/f_w cannot be predicted by any of the BSARs tested (Burkhard 2009).

Interestingly, our study obtained opposing results regarding the effectiveness of remediation strategies for reducing the contaminant burden of aquatic biota based on different model simulations. The two best-fitting models for fish (hybrid BSAR-food web model and the food web model assuming $P_{(o,w)} = 50\%$) suggest that sediment remediation is the best strategy of reducing fish contamination. Alternatively, the food web model assuming $P_{(o,w)} = 95\%$ implies that reducing PCB concentrations in overlying water would be the most effective clean-up strategy. Previously established algorithms provided different risk assessment outcomes, indicating that the interpretation of model output must be carefully evaluated prior to

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using these models as decision support tools. Our study demonstrated that PCB bioaccumulation is greatly affected by both the absolute level of PCBs in sediment and overlying water as well as the equilibrium status between water and sediments.

The estimated f_{sed}/f_w values demonstrated that contaminants bound to sediments were less important than overlying water to fish contaminant resides in the upstream and the Canadian lower reaches of the river compared to other food web zones. Further regulation of sewer overflows and urban surface runoff could be considered at these locations. Indeed, recent evaluation of a long-term biomonitoring data set at a site in the Canadian upstream reach indicated a significant declining trend in PCB water concentrations with time where the PCB half-life in water was 7 years (Drouillard et al. 2016). These improvements in water quality should translate into improved fish quality. In river reaches characterized by high f_{sed}/f_w values (e.g., the Canadian middle and US middle and downstream reaches), the estimates obtained using the hybrid BSAR/food web model and $P_{(o,w)} = 50\%$ benthos respiration both indicated that benthos and fish derived a large proportion of their PCB burden from PCBs in sediments. For these regions of the Detroit River, which also have the highest degree of sediment and fish contamination, sediment remediation actions should be the strongest priority.

Although water was demonstrated to be a significant PCB exposure pathway, the improvement to the model fit of BSAR$_{(Csed+Cw)}$ was admittedly small (3% improvement in R^2) compared to BSAR$_{(Csed)}$. One possible explanation is that the paired benthos-sediment-water PCB concentration input data were not available for the calibration of the site-specific model. The PCB concentrations in water were derived from an independent mussel biomonitoring database (Drouillard 2010) that was decoupled in space and time from the timing of sediment/benthos collections. Given the technical challenges of measuring dissolved water PCB concentrations and the general sparsity of such datasets available for model parameterization, previous food web bioaccumulation modeling studies commonly treat the water body as a single compartment and assume that the average chemical concentration represents the distribution of chemical concentrations to which the biota is exposed (Gobas et al. 1995, Gobas and Arnot 2010). We expect that a fully matched water, sediment and benthos data set would likely increase the accuracy of BSAR$_{(Csed+Cw)}$ over what was presently observed. In addition, our water concentration data may not sufficiently represent the water PCB bioavailable fraction to which benthos are exposed. The burrowing, ventilating, and feeding activities of benthic invertebrates

could result in increased bioavailability of contaminants in interstitial and pore waters and overlying waters closer to the sediment/water interface (Reynoldson 1987, Warren et al. 1998). Therefore, the position of water sample extraction requires further consideration.

The BSAR and process-based bioaccumulation models utilized in the present study also adopted a simplistic approach to sediment classification and compartmentalization. They attribute all chemical partitioning to OC. However, there is a rich and growing literature demonstrating varied partitioning capacities for POPs among different organic sediment fractions, including labile organic carbon and more refractory carbon components such as black carbon (BC) (Ghosh et al. 2003, Cornelissen and Gustaffsson 2005, Moermond et al. 2005, Koelmans et al. 2006). Due to its strong sorption efficiency, BC can reduce the bioavailability of PCBs for biota uptake and exposure (Janssen et al. 2010). Previous works had shown improved accuracy of model simulations for PCB bioaccumulation when considering BC (Hauck et al. 2007, Selck et al. 2012) However, accommodating a sediment BC fraction within the model would involve addition of parameters related to AE_{BC}, X_{BC}, and φ_{BC} in Eqs 7-10 commensurate with the equivalent model terms used for OC and IM. Similarly, an expanded BSAR could account for a separate BC coefficient compared to labile OC. Addition of BC to the BSAR and process-based food web models would generate lower benthos PCB concentration estimates and therefore improvement in model accuracy would only occur for sites and PCB congeners that were overestimated by the current model which was relatively common for benthos (Figure 2.2) but much less common for fish (Figure 2.3). Unfortunately, the BC contents of sediments were not available from paired sediment/benthos samples used in the present research and therefore a modified model accounting for BC-partitioning could not be evaluated. This underscores a need for inclusion of BC analysis in conventional sediment chemistry surveys.

A surprising result of the present research was that the hybrid BSAR/food web bioaccumulation model had lower accuracy than the $P_{(o,w)} = 50\%$ process-based food web bioaccumulation model when used to estimate fish PCB concentrations. This finding is related to the difference in scale of model application from site-specific to zone-specific model simulations. The variation in fish PCB concentrations explained by the hybrid and process-based models was considerably lower (by approximately half) than the variation explained for site-specific benthic invertebrate PCB concentrations. However, fish exhibit much wider spatial foraging movements and more complex dietary interactions than benthic invertebrates (McLeod

et al. 2015). The spatially heterogeneous nature of contaminants in the environment coupled with species specific differences in fish movements could significantly affect PCB exposures by fish. For the fish simulations, a number of simplifying assumptions were made. First, differences in model inputs of water and sediment PCB concentrations were limited to six spatial zones that were assumed to be homogenous with respect to chemical inputs and habitat characteristics. Second, we assumed that each model zone contained the same set of organisms, that organisms exhibited identical food web relationships and that all species movements were restricted by the spatial boundaries of each model zone. These assumptions are likely to be false in many cases and some species of fish are likely to move beyond individual food web zone boundaries. However, given that BSARs provided only a marginal improvement to the benthic invertebrate sub-model and generated poorer predictions in fish relative to the $P_{(o,w)} = 50\%$ food web bioaccumulation model, this implies that efforts to further improve and optimize the process-based food web bioaccumulation model would be better directed toward increasing the realism of fish ecology than increasing accuracy of benthic invertebrate exposures.

2.5 Conclusion

Many past studies have verified the applicability of the process-based food web bioaccumulation model for predicting PCB and POPs concentrations in different food web components across different freshwater systems (Morrison et al. 1996, 1997, 2002, Arnot and Gobas 2004). The present study isthe first to employ such detailed chemical data and to validate the model across different spatial scales using a comprehensive validation dataset consisting of more than 1200 benthos and fish samples. The process-based food web bioaccumulation model predicted PCB bioaccumulation in biota with comparable accuracy to the best fitting empirically calibrated BSAR model for benthos and a superior prediction for fish PCB contamination. Given that the BSAR model was calibrated with the same data set on which it was evaluated, whereas that process-based food web model remained independent, the similarity in model performance provides strong support for the general utility of the Arnot and Gobas food web bioaccumulation model as a decision support tool for PCB bioaccumulation. The study further showed that different benthic invertebrate contaminant exposure scenarios affect model accuracy and contribute to different interpretations about the best remediation approach used to address fish contamination.

The research indicates that different regions of the Detroit River necessitate different remedial actions in order to reduce PCB concentrations in fish. Three river reaches (middle and lower U.S. and middle Canadian) were predicted to be responsive to contaminated sediment removal, whereas the remaining reaches would respond more favorably to further reductions in water PCB contamination. However, given that the middle and lower U.S reaches are among the most highly contaminated areas of the river and fish are likely to move outside of the simulated food web zones, sediment clean-up activities in these zones could have benefits to fish PCB contamination both within and outside the contaminated reaches.

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Figure 2.1 Sites along the Detroit River where sediment and benthic invertebrate collection was conducted in 2008 and where water sample collection was conducted in 2002. Each sampling location may include one or more samples and species, depending on biomass availability.
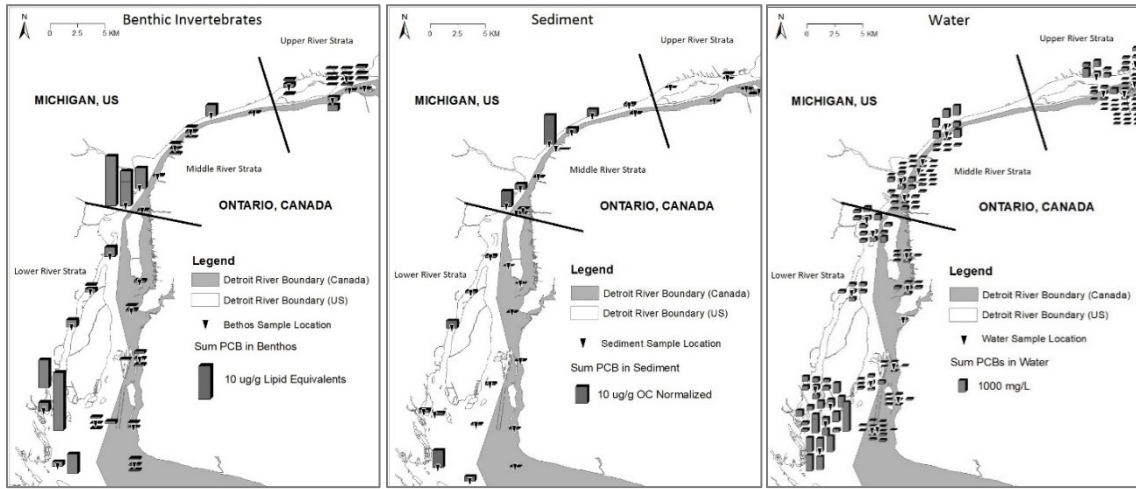
Figure 2.2 Observed versus predicted sum PCB concentrations in benthic invertebrates compared with a 1:1 fit line (diagonal dashed line). Left figure: filled triangles indicate the results estimated by $BSAR_{(Csed)}$; crosses indicate the results estimated by $BSAR_{(Csed+Cw)}$. Right figure: open circles indicate the results estimated by the food web bioaccumulation model assuming that $P_{(o,w)} = 95\%$; filled squares indicate the results assuming that $P_{(o,w)} = 50\%$.
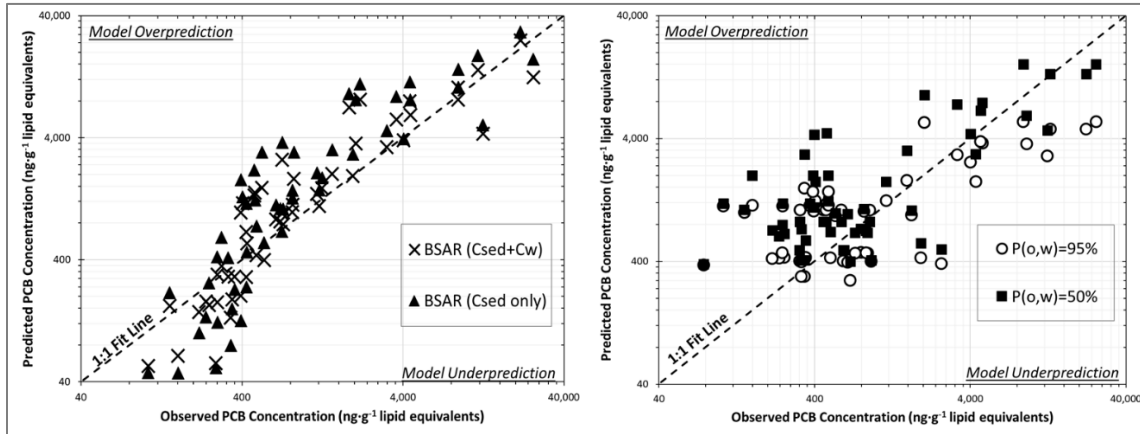
Figure 2.3 Observed versus predicted sum PCB concentrations in 23 fish species compared with a 1:1 fit line (diagonal dashed line). Left figure: filled triangles indicate the results estimated by BSAR$_{(Csed)}$; crosses indicate the results estimated by the BSAR$_{(Csed+Cw)}$. Right figure: open circles represent results estimated by the food web bioaccumulation model assuming that $P_{(o,w)} = 95\%$ for benthos; filled squares represent results estimated assuming that $P_{(o,w)} = 50\%$ for benthos.
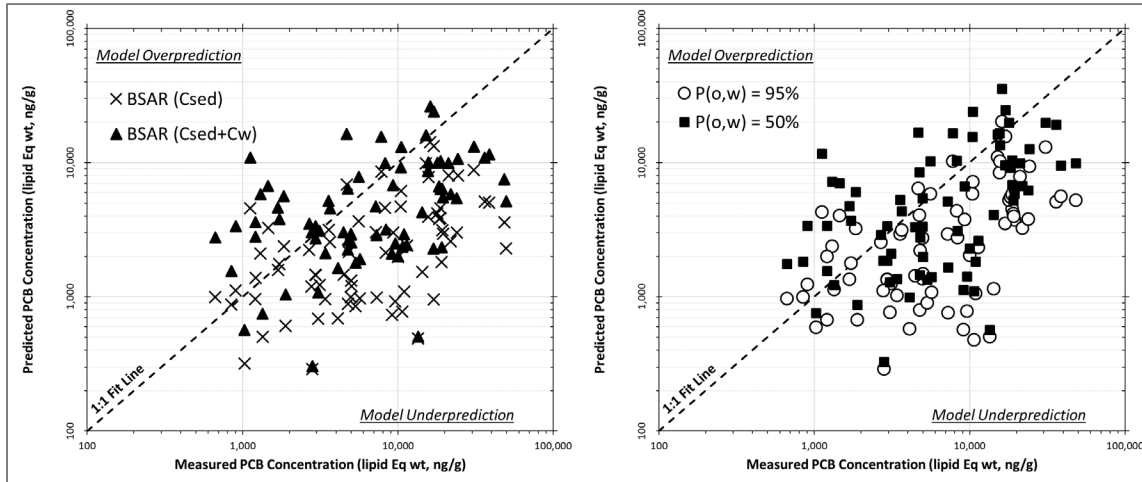
Figure 2.4 Percentages of the body burden of individual PCB congeners concentrations in benthic invertebrates (top plot) and fish species (bottom plot) derived directly and indirectly from exposure to sediment-derived contaminants. White bars represent results of the BSAR$_{(Csed+Cw)}$ model; black bars represent the model assuming that $P_{(o,w)} = 50\%$; hatched bars represent the model results based on the assumption that $P_{(o,w)} = 95\%$. Error bars indicate the standard deviations of the percentage values; the horizontal dashed line indicates a percentage of 50%.
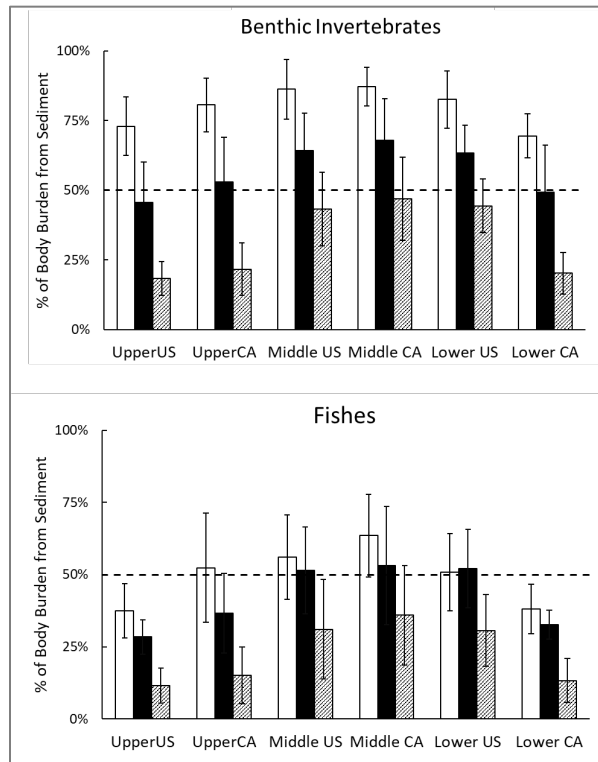
Figure 2.5 Sediment/water fugacity ratios of PCBs across the six river sections. The upper and lower boundaries of the boxes correspond to the 25th and 75th percentiles, respectively; the solid lines in the middle of the box indicate the median; and filled squares indicate the mean. Boxes labeled with the same letter are not significantly different at the 5% level ($p < 0.05$, Tukey's test).
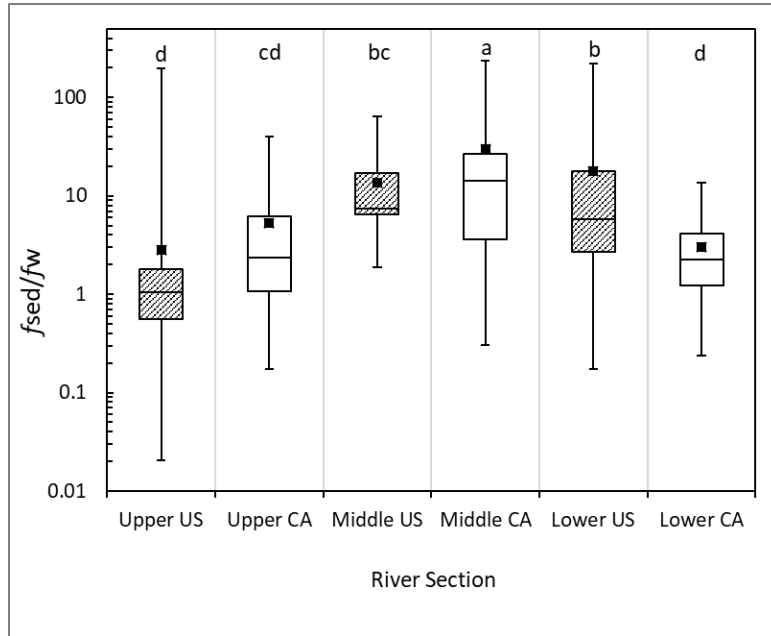
Table 2.1 Linear regression between the concentrations of individual PCB congeners in benthos tissue, sediment and water

	β_{sed}	β_w	β_0	R^2	RMSE	AIC	BIC	N
Log-transformed Linear Regression								
log-transformed Eq. 2 (Eq.2a): $log(C_{org}) = \beta_{sed} \cdot log(C_{sed}) + \beta_0$	0.45* (0.02)		0.97* (0.03)	0.40	0.43	907	917	808
log-transformed Eq. 4 (Eq. 4a): $log(C_{org}) = \beta_{sed} \cdot log(C_{sed}) + \beta_w \cdot log(C_w) + \beta_0$	0.41* (0.02)	0.13* (0.02)	0.55* (0.03)	0.43	0.42	872	886	797
Untransformed Linear Regression								
Eq. 2: $C_{org} = \beta_{sed} \cdot C_{sed} + \beta_0$	0.44* (0.03)		56.41* (7.05)	0.25	181.61	10701	10711	808
Eq. 4: $C_{org} = \beta_{sed} \cdot C_{sed} + \beta_w \cdot C_w + \beta_0$	0.44* (0.03)	-0.18 (0.33)	58.16* (7.75)	0.27	181.69	10703	10717	797

Note: a. Standard errors are given in parentheses.

b. * indicates that the estimation is significant at the 5% level.

Table 2.2 Linear regression and performance matrix between predicted and observed PCB congeners in benthos samples from individual sampling locations

Model	Est. intercept (SE)	Est. slope (SE)	R^2	AIC	BIC	RMSE	RPD	N
$P_{(o,w)}$=95%	0.70* (0.05)	0.54* (0.02)	0.37	233	242	305.5	-20.8%	833
$P_{(o,w)}$=50%	0.63* (0.05)	0.67* (0.03)	0.42	230	240	300.0	-19.5%	833
BSAR$_{(Csed\ only)}$	1.03* (0.03)	0.41* (0.03)	0.41	224	233	296.7	-14.1%	808
BSAR$_{(Csed+Cw)}$	1.00* (0.03)	0.43* (0.02)	0.43	212	222	287.8	-14.0%	797

Note: a. Estimated intercept/slope, R^2, and AIC/BIC were calculated from linear regression between log-predicted and log-observed PCB congeners in benthos. RMSE and RPD were calculated using untransformed predicted and observed PCB congeners in benthos.

b. Standard errors are given in parentheses

c. * indicates that the estimation is significant at the 5% level.

Table 2.3 Linear regression and performance matrix between predicted and observed PCB congeners in individual fish samples

Model	Est. Intercept (S.E.)	Est. Slope (S.E.)	R^2	AIC	BIC	RMSE	RPD	N
$P_{(o,w)}$=95%	3.87* (0.02)	0.21* (0.004)	0.23	40, 350	40,598	1254.9	-12.4%	17,451
$P_{(o,w)}$=50%	4.32* (0.02)	0.23* (0.004)	0.24	39, 882	39,966	1243.6	-17.1%	17,451
BSAR$_{(Csed\ only)}$	4.42* (0.02)	0.17* (0.003)	0.19	42,572	42,588	1255.2	-16.9%	17,451
BSAR$_{(Csed+Cw)}$	3.86* (0.02)	0.20* (0.003)	0.18	42,436	42,451	1262.6	-22.4%	17,451

Note:a. Estimated intercept/slope, R^2, and AIC/BIC were calculated from linear regression between log-predicted and log-observed PCB congeners in benthos. RMSE and RPD were calculated using untransformed predicted and observed PCB congeners in benthos.

b. Standard errors are given in parentheses

c. * indicates that the estimation is significant at the 5% level.

CHAPTER 3

USE OF A SPATIALLY EXPLICIT FOOD WEB BIOACCUMULATION MODEL TO
UNCOVER ECOLOGICAL AND PHYSIOLOGICAL DRIVERS OF PCB
BIOACCUMULATION RISK IN DETROIT RIVER SPORT FISH

3.1 Introduction

Despite being banned for more than 40 years, polychlorinated biphenyls (PCBs) still
contribute to beneficial use impairments (BUIs), such as fish consumption advisories, which
continue to be issued by regulatory agencies across several Laurentian Great Lakes "Areas of
Concern" (AOCs) (Gandhi et al. 2016). Following removal of identified point sources,
contaminated sediments often become a focus for further remediation activities of these priority
chemicals of concern (Hartig et al. 2018). However, the ability to forecast clean-up action
benefits on fish consumption advisories remains challenging due to the temporal and spatial
integration of PCBs by fish as well as the complexity of physiological and ecological factors that
contribute to species- and individual-specific differences in chemical bioaccumulation in sport
fish (Gustavson et al. 2011). The matter becomes even more complex in AOCs that exhibit
pronounced heterogeneity in water and sediment contamination such as the case for the Detroit
River AOC (Drouillard et al. 2006; McLeod et al. 2015). Bioaccumulation modeling enables
quantitative analysis of the relationships between chemical concentrations and body burden of
toxic chemicals in aquatic organisms, which can be directly linked to forecasting ecological
benefits from sediment remediation projects. Since they were first established, the predictive
algorithms of mass balance bioaccumulation models and their parameters have undergone
various modifications, and these models have been applied for bioaccumulation assessments in
various areas. Bioaccumulation models of this type are most widely applied to hydrophobic
organic compounds and utilize chemical partitioning relationships between environmental and
biotic phases (Campfens and Mackay 1997, Clark et al. 1990, Gobas et al. 1988) and species-
specific toxicokinetics (Gobas 1993, Morrison et al. 1997, Arnot and Gobas 2004) to determine
how organisms are exposed to bioaccumulative chemicals of concern. The models have
progressed from those based on simple generic food chains (Thomann and Connolly 1984) to
those involving complex food web models that incorporate multiple feeding interactions (Gobas
1993, Morrison et al. 1997). These models have been used to estimate bioaccumulation and the

environmental fate of persistent organic pollutants (POPs) including PCBs (Gobas and Arnot 2010; Figueiredo et al. 2014; Gobas and Wilconckson 2003) and to identify the sources of variability in contaminant concentrations in aquatic biota (McLeod et al. 2015). These capabilities are important from an ecological perspective as well as for quantifying hazards and conducting risk assessments for bioaccumulating chemicals (Morrison et al. 2002).

Previous research on bioaccumulation models provided important insights into and evidence of major factors that influence chemical accumulation in organisms. However, most studies assumed that all simulated aquatic organisms utilize a given waterbody equally and apply system-wide average chemical concentrations in water and sediments to describe POPs exposures (Gustavson et al., 2011). These studies often failed to acknowledge that varied foraging strategies and movement patterns exhibited by species may lead to significantly different chemical exposures within the same waterbody (Linkov et al. 2002, Melwani et al. 2007). Additionally, spatial variation in diets can have great effects on feeding patterns (Little et al. 1998, Morton et al. 1987, Prochazka 1998), which could significantly influence the contaminant exposure gradients experienced by different aquatic organisms living in the same waterbody. As such, most previous applications of bioaccumulation models have not considered the spatial heterogeneity of contaminants in the environment, the spatial component of feeding interactions, or the variability in foraging behaviors among species (Kashian et al. 2010).

Mcleod et al. (2015) used a modified Arnot and Gobas bioaccumulation model to demonstrate the uncertainty of the trophic magnification factors (TMFs) for PCBs due to a combination of fish migration and spatial heterogeneity of contamination. The authors found that fish movement caused an underprediction of TMFs in areas of relatively high contamination, whereas TMFs were overpredicted in less contaminated areas. Under Arnot and Gobas's (2004) framework, Kim et al. (2016) developed a multicompartment model that considered fish migration based on a two-dimensional chemical concentration gradient. The findings suggested that model designs that ignore contaminant concentration heterogeneity and fish migration may result in systematically biased TMF values.

von Stackelberg et al. (2017) incorporated a spatial random-walk exposure submodel into a food web bioaccumulation modeling framework to estimate chemical body burdens in fish (e.g. FishRand spatially explicit model). The spatial submodel was generated using GIS-based interpolated sediment and water concentrations associated with the probability of fish exposure

to contamination sources based on species-specific foraging ranges, habitat sizes, and attraction to particular areas of contaminated sites (Linkov et al. 2002). The above authors showed that the spatially explicit approach performed consistently better than nonspatial methods. While such an approach provides a strong enhancement to model simulations, there are often gaps in our understanding of ecological profiling (i.e., what constitutes habitat attractors for each simulated species) coupled with the limited availability of high-resolution information on habitat layers and differences in chemical contamination within each habitat type. Furthermore, validation data sets used in the above studies have tended to be relatively small with emphasis placed on validating model predictions across different species but often having few replicates available for the given species.

In the present study, we applied a modified version of the Arnot and Gobas food web bioaccumulation model to simulate PCB concentrations in sport fish of the Detroit River AOC (Li et al. In Press). The model was applied across multiple simulations, with each simulation using a different a spatial scale (e.g., river-wide, 2-nation, 4-zone and 6-zone simulations) that collectively encompassed the full geographic boundary of the AOC. We then contrasted predictions from each simulation against a comprehensive fish validation dataset consisting of 1152 sample records from 19 sport fish species in order to select the best global simulation that generated the highest accuracy across all fish. Next, individual fish species were evaluated for deviation against the predictive accuracy of the global model and evaluated separately to determine whether they could be better predicted using calibrated model simulations by either incorporating a cross-zone contamination exposure factor or using a different spatial scale model. This iterative process enabled species-specific foraging ranges to be assigned based on empirical information rather than pre-assigning it as a model assumption. Finally, we contrast our calibrated predictions of fish consumption advisories against those issued by regulatory agencies in Ontario and Michigan to determine the accuracy of our model to forecast this beneficial use impairment in the Detroit River.

3.2 Methods

Food web bioaccumulation model

The formulation of the food web bioaccumulation model that was utilized in the present study was fully described by Arnot and Gobas (2004) and McLeod et al. (2015) with modification as described in Li et al. (In Press). For brevity, only the main equations and associated modification are outlined below. A summary of the model input parameters, their definitions and values or algorithms are provided in Table A1 in the Appendix. The model provides steady-state concentration estimates for each organism included in the simulation using model inputs of water and sediment contamination for a given contaminant. The basic equation used to predict steady-state concentrations in an organism is as follows:

(eq. 1)
$$C_{org} = \frac{G_{diet} \cdot E_{diet} \cdot \Sigma(P_{diet} \cdot C_{diet}) + G_v \cdot E_w \cdot (C_{(p,w)} \cdot P_{(p,w)} + C_{(o,w)} \cdot P_{(o,w)})}{\frac{E_w \cdot G_v}{K_{BW}} + E_{diet} \cdot \Sigma\left(G_f \cdot \frac{P_{f,lipid} \cdot K_{ow} + P_{f,NLOM} \cdot K_{ow} \cdot \varphi_{NLOM} + P_{f,w}}{K_{BW}}\right) + G_{gro}}$$

where C_{org}, C_{diet}, $C_{(p,w)}$, and $C_{(o,w)}$ are the chemical concentrations in the organism (ng/g wet weight), ingested diet items (ng/g, including sediment ng·g⁻¹organic carbon (OC) ($C_{sed(oc)}$) as a potential item), porewater (ng·m/L), and overlying water (ng·m/L), respectively. The terms G_{diet}, G_v, G_f and G_{gro} are the organism's feeding rate (g food/g ·BW/d), gill ventilation rate (mL/g·BW/d), fecal egestion rate (g feces·/g ·BW/d), and growth rate (/d), respectively. The terms E_{diet} and E_w represent the organism's chemical absorption efficiency from food and water, respectively. The terms P_{diet}, $P_{(o,w)}$ and $P_{(p,w)}$ refer to the proportion of a given food item (food, overlying water, and porewater, respectively) in the diet of a species. The terms $P_{f,lipid}$, $P_{f,NLOM}$ and $P_{f,w}$ represent the proportion of lipids, nonlipid organic matter (NLOM), and water in feces from a given dietary item, respectively. The term φ_{NLOM} is the NLOM partitioning equivalent in the organism compared to octanol. The terms K_{ow} and K_{BW} refer to each PCB congener's octanol/water partitioning coefficient and biota-water partitioning coefficient, respectively.

One modification to eq. 1 involves altering the fecal egestion rate of ingested sediment ($G_{f,sed}$) to consider the individual effect of chemical distribution between OC and inorganic matter (IM), as follows:

(eq. 2)
$$G_{f,sed} = P_{sed} \times [(1 - AE_{OC,sed}) \times X_{OC} + (1 - AE_{IM,sed}) \times X_{IM}]$$

where p_{sed} is the proportion of sediment in the diet. $AE_{OC,sed}$ and $AE_{IM,sed}$ are the dietary assimilation efficiencies of OC and IM in sediments, respectively. Only OC is assumed to be partially digestible and assimilated ($AE_{OC,sed}$=30%; $AE_{IM,sed}$=0). X_{OC} and X_{IM} represent the fractions by weight of OC and IM in sediments, respectively. We consider OC and IM to be the only dietary components from the sediment. Hence, the sum of X_{OC} and X_{IM} equals one. Next, the elimination of chemicals from the sediment through feces (the term enclosed in parentheses in the denominator in eq. 1) can be modeled based on the relative partitioning capacities of the different components of the sediment as follows: $E_{diet,sed} \cdot G_{f,sed}(P_{f,OC} \cdot \varphi_{OC} \cdot K_{ow} + P_{f,IM} \cdot \varphi_{IM} \cdot K_{ow})/K_{BW}$. The term $E_{diet,sed}$ represents the organism's chemical absorption efficiency from sediment, which is assumed to be fourfold lower than the assimilation efficiency from its diet ($E_{diet,sed} = E_{diet}/4$). The terms φ_{OC} and φ_{IM} refer to the partitioning capacities of OC and IM in sediments relative to octanol, respectively. $P_{f,OC}$ and $P_{f,IM}$ are the proportions of OC and IM in feces from sediments, respectively.

C_{org} can be converted to a lipid equivalent concentration ($C_{org(leq)}$) as follows:

$$\text{(eq. 3)} \qquad C_{org(leq)} = \frac{C_{org}}{P_{org,lipid} + P_{org,NLOM} \times \varphi_{NLOM}}$$

where $P_{org,lipid}$ and $P_{org,NLOM}$ refer to the proportions of lipids and NLOM, respectively, in benthos. Lipid equivalent PCB concentrations normalized for the differences in the animal partitioning capacity due to the differences in the lipid and NLOM contents will vary across species and within a species based on the tissue type. The PCB concentration in fish dorsal muscle is estimated using the following equation:

$$\text{(eq. 4)} \qquad C_{org(dorsal)} = \frac{C_{org(leq)} \times P_{dorsal,lipid}}{100}$$

where $P_{dorsal,lipid}$ is the fish dorsal muscle lipid content. Estimated $C_{org(dorsal)}$ values are necessary to compare the model-predicted PCB concentrations with the guidelines of fish consumption advisories regarding edible filets.

The food web bioaccumulation model is formulated and mathematically implemented through a system of dynamic models developed in a Microsoft Excel data sheet. First, a deterministic model is used to provide an estimate of the geometric mean PCB concentration in fish, and all input model parameters are held constant. Second, Oracle Crystal Ball (Goldman 2002) is used to execute Monte-Carlo-based probabilistic calculations. The Monte Carlo simulations were applied in many previous studies on food web bioaccumulation models that estimated the PCB concentration distribution based on the uncertainty surrounding the model parameters (Gobas 1993; von Stackelberg et al., 2002; Selck et al., 2012; McLeod et al., 2015). Using the Monte Carlo interface, the model is run for a total of 10,000 iterations. During each iteration, one random number for each model input is chosen from the defined statistical distribution, and the output of the congener-specific PCB concentration in each sport fish species is saved. The overall model validation was evaluated by examining the means and 95% confidence intervals of the model output trials across all simulation iterations. The statistical distribution of model inputs is described in detail in Table A1.

Study area

The present study system is the Detroit River, North America, which was designated as a Great Lakes AOC in 1986 due to the severely degraded status of its ecosystem, resulting in a series of BUIs, many of which were tied to organic pollutants present in sediment and water. PCBs are a major cause of fish consumption advisories issued for the Detroit River (Kashian et al. 2014; OMECP 2017) and have been the target of sediment cleanup activities in the system (Heidke et al. 2002). The river is a highly industrialized waterway that connects Lake St. Clair with Lake Erie. The river is channelized by fast-flowing shipping channels, and many islands separating US and Canadian sources of pollution along the river. The water and sediment concentrations have been intensively sampled across various spatial and temporal scales, which provides important input parameters for the model simulation (Drouillard 2013; Szalinska et al. 2013). Other general input parameters that will be used to characterize the Detroit River food web were obtained from the literature (Morrison et al. 1997, Arnot and Gobas 2004, Kashian et al. 2010, Selck et al. 2012, Mcleod et al. 2015).

Data

The simulations were the same for all model inputs and parameters except for the zone-specific PCB concentrations in sediment and water. Congener-specific PCB concentrations of water used in the simulations were obtained from Drouillard et al. (2013) and compiled to produce the geometric PCB overlying water concentration for each zone generated during the year 2002. The congener-specific PCB concentrations in sediments used in the simulations were obtained from Szalinska et al. (2013). The samples were analyzed for the following PCB congeners (IUPAC #): 31/28, 44, 49, 52, 70, 74, 87, 95, 99, 101, 105/132, 110, 118, 138, 149, 153, 156/171, 158, 170, 180, 183, 187, 194, 195/208, 199, and 206. Only a common set of congeners detected in water and sediment were included in the analysis. PCB congeners with undetected concentrations were assigned a value of zero when summed across all congeners to generate a total PCB concentration.

Fish PCB concentrations used for the food web validation were obtained from an in-house Great Lakes Institute for Environmental Research (GLIER) database of dorsal muscle samples. These samples were analyzed for congener-specific PCBs in fish by the GLIER Organic Analysis Laboratories (OAL) and were collected from the Detroit River between 1998 and 2016. The validations also incorporated data from the Ontario Ministry of Environment, Conservation and Parks (OMECP) Fish Contaminant Monitoring Program and the Michigan Department of Environmental Quality (MDEQ) sport fish database. Fish data from the OMECP database were available from 1998 to 2010, and fish data from the MDEQ database were available from 1998 to 2015. The agency datasets provided only sum PCB concentrations rather than congener-specific PCBs. The combined fish validation database provided a total of 1152 records that comprised 19 sport fish species that are most commonly caught in the Detroit River with capture location information.

The methods used to process the fish filet samples vary among agencies. MDEQ often uses a skin-on sample filet (except for bullhead, channel catfish, muskellunge, pike, carp, and freshwater drum), while OMECP uses a skin-off sample filet for contaminant residue analysis. While the skin contains a portion of lipids that could result in high PCB concentrations compared to skin-off filets, the lipid percentage in dorsal muscle ($P_{dorsal,lipid}$ in eq. 4.) cannot be used to distinguish skin-on from skin-off samples due to a lack of empirical species-specific data. Instead, a combined estimation of lipid contents was utilized as the model input. The $P_{dorsal,lipid}$ values for each sport fish species in the Detroit River are summarized in Table A3.

Model validation and application

Both the deterministic model and uncertainty models were run for four multicompartment simulations in which food webs were discretely compartmentalized into a set of spatial zones (e.g., river-wide, 2 nations, 4 zones and 6 zones) that collectively encompassed the entire Detroit River for a given simulation (Figure 3.1). The river-wide model treats the Detroit River as a single zone and assumes that different fish species equally utilize the waterbody and applies river-wide average concentrations of congeners in water and sediment to describe contamination exposure. The 2-nation model divides the river lengthwise into Canadian and US jurisdictions as two independent model zones. The 2-nation model is consistent with the current practice of Ontario and Michigan applying independent fish consumption advisories within their own jurisdictional waters along the Detroit River but effectively assumes that fish do not cross between the two jurisdictions. Additionally, the Detroit Rivers is considered highly channelized river system, approximately 68 million metric tons of commercial cargo is shipped on the river annually (Bennion and Manny, 2011). From an ecological point of view, associated fish community is highly sensitive to anthropogenic, nonperiodic disturbances (Hondorp et al. 2014). It is anticipated that fish tend to avoid navigational shipping channel which limit their movement into the other side of the river (Boase et al. 2011, Manny and Kenaga 1991). Similar to the 2-nation model, the zones in the 4-zone model were delineated by the political boundaries but further subdivided into upstream and downstream reaches using a transect specified by the upstream boundary of Fighting Island for each respective country. The division of the river into upstream and downstream reaches is consistent with Ontario's approach to fish consumption advisory calculation that divides the Canadian portion of the river into upstream and downstream boundaries to produce separate sets of fish advisory information for each river section. However, this practice differs from Michigan which provides a single set of fish consumption advice information for the entire US side of the Detroit River. The 6-zone model further divides the upstream portions of the 4-zone model into upstream and middle-stream zones using the island of Belle Isle to demarcate the upper and middle reaches. From an ecological point of view the section of Detroit River spanning the middle reach of the six-zone model is considered highly channelized, lacking any islands and almost entirely composed of navigational shipping channel except for the very near shore. It is anticipated that fish which avoid cooler, fast flowing waters are likely to avoid the channelized portion of this reach.

For each model simulation, the geometric mean concentration of each PCB congener in the water and surface sediments from each zone were used as deterministic model inputs, whereas the arithmetic mean concentration and its standard deviation of each PCB congener from each zone were used as uncertainty model inputs. The results of each simulation were then contrasted against the fish validation dataset to select the best global simulation model from across the 4 simulations. Model selection was based on an evaluation of (1) the coefficient of determination (R^2) from the linear regressions between the predicted PCB concentration and the field-observed PCB concentration (All evaluation factors are estimated using SAS statistic analysis software.) and (2) the geometric mean of the model bias (predicted/observed PCB concentration) for 26 PCB congeners in all sport fish species for which empirical data were available. The model with the combined features of a high R^2 and low model bias was selected as the best global model. Four simulations were considered for validation, including PCB lipid equivalent concentrations ($C_{org(leq)}$) and wet weight PCB dorsal concentrations ($C_{org(dorsal)}$), from both the deterministic models and uncertainty models.

After the determination of the global model selection, each fish species was evaluated separately to designate species which were adequately predicted by the model and those which were poorly predicted. When the geometric mean of empirical measurement in a given species was within a factor of 2 of the global model prediction, it was considered adequately predicted by the models (USEPA 2000, von Stackelberg et al. 2002). Fish species that were over- or under-predicted by more than a factor of 2 were designated as poorly predicted. Additional model evaluation was subsequently performed for the poorly predicted species. This involved (1) re-evaluation if an alternative spatial scale simulation provided an adequate, within a factor of 2, prediction for each poorly predicted species; and (2) establish a species-specific adjustment factor to estimate the weight of exposure necessarily to bring the poorly predicted species into compliance with the 2-fold prediction criteria. The latter entails semi-calibration of the model and essentially estimates how much exposure a given fish species needs in its home zone relative to an adjacent zone in order to provide model predictions with equivalent accuracy as the non-calibrated strongly predicted species.

Finally, the best global fit model and semi-calibrated model were compared and applied to estimate the level of fish consumption advice to specify the number of recommended fish meals per month of particular species consistent with existing sport fish consumption advice

information. The cumulative frequency distributions of PCB concentrations in fish were estimated using the probabilistic model. The estimated PCB concentrations from 10,000 iterative simulation trials were then categorized into bins bounded by the sum PCB concentration threshold trigger levels used to establish the restrictive meal limits. The model-predicted advisory in each model zone was estimated based on the minimum trigger level category whose cumulative frequency distribution of estimation exceeded the 75% quantile of the 10,000 iterative estimations. This frequency spectrum method prevents biases due to an incorrect assumption of the distribution of the estimated concentrations (Kashian et al. 2010).

3.3 Results

Empirical observations

A summary of the field-observed sum PCB concentrations in each sport fish species, the number of fish samples, and the sources of information is provided in Table 3.1. Overall, the empirical observations provide evidence for differences in sum PCB concentrations across different reaches of the Detroit River for all fish species. Both the wet weight and lipid equivalent sum PCB concentrations in the fish captured on the US side of the river were significantly higher than those in the fish sampled from Canadian waters ($C_{org(leq)}$: $F_{1,1150}=34.84$, $p<0.01$, ANOVA; $C_{org(dorsal)}$: $F_{1,1150}=201.65$, $p<0.01$, ANOVA). There were also significant differences in the sum PCB concentrations in the fish captured from the six different reaches of the river ($C_{org(leq)}$: $F_{5,1146}=8.68$, $p<0.01$, ANOVA; $C_{org(dorsal)}$: $F_{5,1146}=52.65$, $p<0.01$, ANOVA). Moreover, there were significant differences in the sum PCB concentrations across the 19 sport fish species ($C_{org(leq)}$: $F_{18,1133}=7.92$, $p<0.01$, ANOVA; $C_{org(dorsal)}$: $F_{18,1133}=29.26$, $p<0.01$, ANOVA). Despite the relatively large number of observations of PCB concentrations in Detroit River sportfish, there were data gaps with respect to fish sample locations and the availability of replicates at different river reaches. There were fewer fish samples from the middle river reaches than the upper and lower river reaches. No empirical data were available on the US side of the river for black crappie, gizzard shad, and muskellunge.

As a steady-state model (eq. 1), the simulation results do not provide size- and age-specific PCB concentration predictions. Concerning the empirical PCB concentrations correlated with fish size (Gewurtz et al., 2001), linear regressions between the logarithm of the observed sum PCB concentration (both in wet weight and on a lipid equivalent basis) and the logarithm of

fish length were performed for each sport fish species for all locations and captured years (Table A4). Three out of the 19 sport fish species (including walleye, white bass, and white perch) showed a statistically significant relationship between the sum PCB concentration and length (p<0.05). Among these three species, the lengths of walleye and white perch spatially varied among the six river reaches (p<0.05 ANOVA). Therefore, the size range selection method (Bhavsar et al. 2007, Gewurtz et al. 2010) was adopted to limit the impact of size. The constrained size ranges were 34-60, 25-37, and 21-49 cm for walleye, white bass, and white perch, respectively.

Next, previous studies showed evidence of a temporal trend in PCB concentrations in fishes in the Great Lakes (Gewurtz et al., 2010; Sadraddini et al., 2011; Chang et al., 2012). Five and six out of the 19 sport fish species showed significantly different sum PCB concentrations in wet weight and on a lipid equivalent basis among the sample years, respectively (p<0.05, ANOVA) (Table A5). The Mann-Kendall test with Sen's method was performed to determine the consistency in the temporal trend (Gibert 1987). Three species, including bowfin, bullhead, and gar pike, showed consistent temporal trends at the 5% level. Because the spatial variation in the sample year for bowfin was not statistically significant among the six river reaches (Table A5), and bullhead and longnose gar accounted for only 7% of the total empirical observations, we decided to combine the empirical data from different years for the subsequent analysis.

Model validation

The model validation was performed with zone-specific predictions in each simulation and contrasted with empirical PCB concentrations in fish that were captured from the same model zone. The ratio of the predicted to measured PCB concentrations follows a lognormal distribution (Shapiro-Wilk normality test, p > 0.05). Therefore, the model biases across the models of different zones were compared using the geometric mean instead of the arithmetic mean. In general, the uncertainty models were found to produce estimations that were consistent with the estimations from the deterministic models in terms of R^2 of the linear regression between the estimated log PCB concentrations against log measured PCB concentrations in fish, but with much smaller 95% confidence intervals of the model bias (Figure A2). This difference could be caused by the complexity of the simulation using 17 parameters that were allowed to vary, which also influenced the 7 submodels in the uncertainty simulations. In addition, the

performance level of the model using 26 individual PCB congeners was consistent with the performance of the model using the sum PCB concentrations, with slightly higher R^2 and lower model bias (Table A6). Hence, we focus on our description of the validation using the sum PCB concentration resulting from uncertainty models.

Figure 3.2 shows a peak in the goodness-of-fit test and a dip in the mean model bias for the 2-nation model for both wet weight concentration and lipid equivalent concentration. This figure indicates that the 2-nation simulation provided the best global simulation among different simulation series predictions. The 2-nation model still tended to overestimate the individual fish concentrations as a whole but to a lesser extent than the other models, with the mean model bias values of all simulations (Figure 3.2 a and b) within a factor of 2. The river-wide scale simulation resulted in the poorest fitted model validation with the lowest R^2 and highest variation in the model bias (e.g., largest 95% confidence interval). The R^2 increased by approximately 10% from the river-wide model to the other multizone models in all simulations. While the 6-zone model produced validations that had a better goodness of fit than the river-wide scale simulation (R^2 increased by 9.2% to 12.4%), it tended to generate the largest overestimation (the mean model bias increased by 1.14 to 1.41 compared to river-wide model).

In general, the wet weight concentration and lipid equivalent concentration generated consistent trends, while the model that used the wet weight concentration performed better than the model that used the lipid equivalent concentration, as evidenced by an increased R^2 and decreased model bias when the same zone-specific predictions were compared. The relatively good performance of the model that utilized the wet weight concentration could be attributed to the application of field-observed species-specific lipid contents in dorsal muscle samples as the model input. This result could also be caused by the incorrect model input of the whole-body lipid content for estimating PCB concentrations on a lipid equivalent basis. The determination of the whole-body lipid content requires information from whole body homogenates which is less empirically robust compared to dorsal muscle lipid contents. All subsequent model validations are reported on a wet-weight basis.

Figure 3.3 contrasts simulation results obtained using the 2-nation uncertainty model against the fish contamination database. Overall, the predicted sum PCB concentrations were significantly correlated with the observed sum PCB concentrations ($p<0.05$; ANOVA). A total of 54.4% of the individual observed concentrations were underpredicted (e.g., below the 1:1 fit

line) by the model, with 45.6% of the observations being overpredicted (e.g., above the 1:1 fit line). As indicated by the dashed lines in Figure 3.3, a majority of the model predictions (63.7%) were within a factor of 4 of the observed concentrations. A total of 34.5% of the model predictions were observed to be within a factor of 2 of the individual observations. This level of performance is consistent with that in previous studies regarding the predictive success of the model (Kashian et al. 2010). The fish samples were separated into the national food web modeling zones (Figure 3.3 a and b), and the estimated slopes of the linear regression of the log-predicted versus log-observed sum PCB concentrations were significantly different from zero for both zones (p<0.05, ANOVA). The F-test indicated that the results were significantly different from one at the 5% level (fish caught in US water: $F_{1, 615}$=52.78, p<0.05; fish caught in Canadian water: $F_{1,553}$=61.92, p<0.05; Wald test). Overall, the PCB concentrations in fish from the US food web modeling zones were predicted to achieve PCB concentrations that were 2.0- to 5.3-fold higher than concentrations estimated in the same species on the Canadian side of the river. The simulation tended to overestimate the sum PCB concentrations for US-caught fish, as evidenced by the 2.68 mean of model bias, whereas the model produced more accurate concentrations with slight underestimation for the Canadian-caught fishes, as evidenced by the 0.95 mean of model bias.

Next, the species-specific validations of the 2-nation simulations are further scrutinized. Seven species were accurately predicted by the 2-nation model on both the US and Canadian sides of the river (i.e., the species measured concentrations were within a factor of 2 error of the model predictions). These included carp, freshwater drum, gizzard shad, largemouth bass, muskellunge, sunfish, and yellow perch. Validation data were only partially available for gizzard shad and muskellunge which had empirical measurements on only the Canadian side of the river. The species that fell outside the factor of 2 boundaries were then compared to the results from other zoning model simulations. Two classes of fish species were considered to be inadequately predicted by the 2-nation model simulation. The first class of poorly predicted fish species was underpredicted on the Canadian side and/or overpredicted on the US side by the bioaccumulation model. These included black crappie, channel catfish, gar pike, redhorse sucker, rock bass, smallmouth bass, white bass, white perch, and walleye. Compared to the 2-nation model, the river-wide model exhibited improved performance with a greatly lower model bias of 0.9-1.3 for black crappie, channel catfish, white bass, and white perch (Table 3.2), whereas the 4-

zone model showed an improvement over the 2-nation model for redhorse sucker (mean of model bias reduced to 0.9 from 2.2). Although the 2-nation model performed poorly for gar pike, rock bass, smallmouth bass, and walleye, the degree of model bias was considerably lower than that in other zone models. For gar pike and walleye, the river-wide model exhibited slightly improved prediction versus the 4-zone and 6-zone models (mean model bias reduced from 3.9 to 3.0 for gar pike and from 2.7 to 2.4 for walleye); however, it still provided a relatively poorer fit based on the factor of 2 accuracy criteria. Rock bass and smallmouth bass were overestimated in river-wide and all other finer zone models compared to 2-nation model (mean model bias is from 2.5 to 3.9 for rock bass and from 3.3 to 3.8 for smallmouth bass.

The second class of poorly predicted fish species includes bowfin, bullhead, and northern pike. The 2-nation model greatly overestimated the PCB concentrations on both the Canadian and US sides of the model zone, as did all other models. While the 2-nation model still provided the most accurate prediction for these fishes, its average model bias estimated from 5.4- to 7.5-fold higher predicted concentrations relative to measured concentrations. Given the similar magnitude of overestimation between the Canadian and US zone simulations from the 2-nation model (Figure 3.3), the model bias of the PCB residues in US-caught fish may be caused by movements to the less-contaminated and more vegetated Canadian waters, assuming that the same Canadian-caught species that forage and are exposed to highly contaminated US water would only increase the error associated with model predictions.

Model calibration

Two model calibrations were performed to attempt to improve the accuracy of the model. First, a species-specific-scale calibration used the most accurate estimates from the other zoning models to substitute for the species that fell outside the factor of 2 boundaries from the 2-nation model. Given that the 2-nation model estimates were still relatively more accurate than those of the other zone models for some of poorer predicted fish species, only black crappie, channel catfish, white bass, white perch, and redhorse sucker were calibrated in the species-specific-scale model simulation. Second, a 2-nation blended model incorporated species-specific adjustment factors to correct for the biased tendency toward overestimations or underestimations for the poorly predicted fishes. For the first class of poorly predicted fish species, the underestimation of fish on the Canadian side of the river and the overestimation of fish on the US side of the river

demonstrated that Canadian fish that swim into US waters are likely to increase their exposure to the high degree of sediment PCB contamination on the US side of the Detroit River, and vice visa for US fish. Table 3.3 provides an estimation of the percentages of contamination exposure in the Canadian and US zones from additional simulations that applied weighted-average PCB concentrations in sediment and water inputs in the 2-nation model zones to improve the prediction within the 2-fold error margin. The adjustment factors were defined toward a conservative correction factor, and the minimum exposure percentages in the other side of the river were applied to the calibrated simulation.

For the species for which the 2-nation model was underestimated in Canadian water (including black crappie, redhorse sucker, rock bass, white bass, white perch), the magnitudes of underestimations were similar across all five fish species (average model biases were from 0.2 to 0.3). Minimum proportions of 17.5% to 34.5% of US contamination exposure were necessary to improve the model predictions to within the acceptable margins. For the species that were overestimated in US water, rock bass exhibited the greatest overprediction by 6-fold. Minimum contamination exposures in Canadian waters on the order of 91-100% were needed to achieve a satisfactory fit. For the other four fish species (including channel catfish, gar pike, smallmouth bass, and walleye) with similar overestimations (mean model biases were 2.3-3.5), minimum proportions of 10% to 30% of Canadian contamination exposure were necessary to generate model predictions within acceptable error margins. Next, for the second class of poorly predicted fish species that were consistently overestimated by the 2-nation model (including bowfin, bullhead, and northern pike), we assumed US-caught fish exposure to be 99% accounted for by Canadian contamination and 1% by US contamination and Canadian-caught fish exposure to be 100% accounted for by Canadian contamination. Finally, in cases where the species was accurately predicted by the 2-nation model on both the US and Canadian sides of the river, the adjustment factor equaled one, which indicated an absence of cross-nation contamination exposure.

The 2-nation blended model and species-specific-scale model simulations were compared for their abilities to predict PCB concentrations in fish tissue at both the river-wide scale and within each model zone (Table 3.4). Overall, compared with the results of the uncalibrated 2-nation model, both calibrated models provided more accurate predictions of PCB concentrations relative to the field-measured PCB concentrations. However, this improvement was not

consistent across different model zones. The species-specific-scale model had a lower overall model bias of 1.36 ± 3.88 compared to that of the uncalibrated model (1.42 ± 3.19), and 53.2% of the predictions were within a factor of 2 from the individual field measurement (compared to 34.5% in the original 2-nation model). However, the species-specific-scale model had a greater mean of model bias than the uncalibrated model in the Canadian model zone, while both biases were still within a 2-fold margin. The 2-nation blended model had best fit among the three models, with the lowest overall mean model bias (1.21 ± 3.05) and highest percentage of within-factor-two predictions (68.4%). The R^2 values of linear regression between log-predicted and log-observed PCB concentrations ranged from 42% to 54% across calibrated simulations, with the best fit achieved by the blended model.

Application of calibrated model to predict fish consumption advice

Finally, the original 2-nation, 2-nation blended, and species-specific-scale models were applied to generate fish consumption advice and to compare these recommendations to the current fish consumption advisories issued by Michigan and Ontario. In the Detroit River AOC, OMECP issues the advisory for the fish in Canadian waters, and the Michigan Department of Health and Human Services (MDHHS) issues the advisory for the fish in US waters. For both advisories, multiple contaminants (e.g., Hg, PCBs, dioxin) are designated as contributors to the most stringent meal recommendation limits (OMECP 2017; MDHHS 2016). While OMECP has more stringent trigger values of PCB concentrations for the "Do Not Eat" category than MDHHS (844 ng/g vs. 2700 ng/g), MDHHS is more conservative when defining the trigger values for the PCB concentrations for other meal categories (Table A7). Because the present study focuses on only PCB contamination, we estimate meal categories assuming that PCBs cause the most stringent advisory benchmarks. While fish length is not considered by the food web bioaccumulation model, the published meal recommendation limits span the different fish length categories. Our model input of species-specific body weight in the food web bioaccumulation model is calculated using empirical observations. Additionally, fish body weight was correlated with length (ANOVA $p<0.05$). As such, we estimated the meal-per-month recommendations with an assumption of the level of accumulation based on the average fish length in the empirical observations.

Figure 3.4 shows the simulated number of fish meals per month of particular species that are acceptable to eat for the general public contrasted with current fish consumption advisories (completed output is shown in Table 3.5). Overall, the original 2-nation model and two calibrated models provided similar results for recommended fish meals per month. On the Canadian side of the river, in both calibrated models, 18 out of 19 fish species were within one advice category difference compared to OMECP advisories, which was slightly better than the uncalibrated 2-nation model (17 out of 19). On the US side of the river, the uncalibrated 2-nation model and calibrated 2-nation blended model resulted in 12 out of 17 fish species within a one advice category difference compared to MDHHS advisories, whereas the species-specific-scale model resulted in 11 fish species that were within one meal advice difference. The number of fish meals per month estimated by the uncalibrated 2-nation model accurately matched the published advisory for five fish species on the Canadian side of the river (e.g., black crappie, sunfish, bowfin, bullhead, and yellow perch), and six fish species on the US side of the river (e.g., carp, channel catfish, freshwater drum, gizzard shad, sucker, and walleye). While the calibrated models significantly improved the accuracy in estimation of PCB concentration in fish tissue, these improvements were not evenly translated to better accuracies in fish consumption advice. In the Canadian model zone, sucker, rock bass, and white bass were effectively calibrated by the blended model and the estimations of channel catfish and white bass were significantly improved by the species-specific-scale model. However, in the US model zone, only rock bass were effectively calibrated to a better fit by the blended model, while the species-specific-scale model resulted a poorer fit for redhorse sucker.

Comparing the best calibrated model (2-nation blended model) with the uncalibrated 2-nation model revealed that the cross-nation exposure calibration improved the estimation from less restrictive advisories in the Canadian-zone model to a relatively more consistent estimation with OMECP published advisories. For the original 2-nation model, nine out of the 19 fish species (i.e., 47%) for the general public and 11 out of the 19 fish species (i.e., 58%) for the sensitive population were underpredicted (i.e., less restrictive advice) to be greater than one meal limit category (Table A8). For the blended model, the percentage of underprediction reduced to 37% for the general public and remained unchanged for the sensitive population (i.e., 58%). As channel catfish, freshwater drum, gar pike, gizzard shad, and white perch are listed as no-consumption fish for the sensitive population by the Ontario advisories, both models added carp

and muskellunge into the "Do Not Eat" category but provided less restrictive advice for gizzard shad and white perch. In the US model zone, MDHHS published advisories are unavailable for bowfin and gar pike; thus, the original 2-nation model tended to issue more restrictive advisories, while the advice provided by blended model can be considered generally less conservative. For the original 2-nation model, seven out of the 17 fish species (i.e., 41%) for the general public were overpredicted (i.e., more restrictive advice) to be greater than one meal limit category. In contrast, the advice for 24% of fish species provided by the 2-nation blended model was more restrictive than the MDHHS fish consumption advisory. These results affirm that the exposure of fish to the cross-zone contamination likely generated more restrictive advisories on the Canadian side of the river and less restrictive advisories on the US side of the river.

3.4 Discussion

This study demonstrates that the 2-nation model provided the most accurate uncalibrated prediction of fish contamination among the tested multi-compartment models. However, these improvements were not equally observed across species, which is supported by previous studies. The contamination levels of seven species were accurately predicted by the 2-nation model (including carp, freshwater drum, gizzard shad, largemouth bass, muskellunge, sunfish, and yellow perch); sunfish was classified as less mobile fishes with limited home ranges. Empirical studies have shown that sunfish (bluegill and pumpkinseed) have home ranges of less than one ha (Gunning and Shoop 1963; Paukert et al. 2004). Klinard et al. (2017) revealed site fidelity of sunfish to the shallow littoral flats on either side of the shipping channel of Detroit River and a lack of cross-channel movements. The comparison of the 6-zone uncertainty model to the 2-nation model indicated that the model bias decreased from 1.7 to 1.1 with narrower 95% confidence intervals (Table 3.2). The 2-nation model predictions are consistent with 4-zone model for gizzard shad (model bias is 0.8 for 2-naiton model and 1.1 for 4-zone model). The feeding physiology and behavior likely contribute to these patterns. Gizzard shad exhibits less mobile omnivorous pump-filter feeding habits, consuming zooplankton, phytoplankton and detritus (Schaus et al. 2002; Sampson et al. 2009; Yako et al. 1996,) in proximity to the shoreline and in deposition areas.

For common carp, the river-wide, 2-nation, and 4-zone models showed similar model performances and were all more accurate than the 6-zone model. This result may be attributed to

the uncertainty regarding the movement of carp. Some studies showed relatively sedentary habits and a homing ability with a home range of less than 500 m (Reynolds 1983; Crook 2004; Brown et al. 2001). However, Koehn and Nicol (1998) showed that carp is a highly mobile species that could swim upstream and downstream and cover distances of more than 100 km per month.

The movement behavior along the shoreline for largemouth bass and yellow perch results in a best fit of the 2-nation model simulation (Table 3.2). Largemouth bass swims as far as 3 km from their home ranges during the spawning season (Diana et al. 1990). Adult largemouth bass primarily utilize the area near the shoreline and feed near vegetated areas in the shallow reach of the water column that increase pretty density as well as improve the probability of encountering prey (Winter 1977, Crowder and Cooper 1979, Stuber et al. 1982, Hanson et al. 2007). Yellow perch exhibit similar patterns; while this species can move from 30 to 60 km away from the original tagging locations (Marsden et al. 1993), its movement is often close and parallel to the shoreline (Kelso 1976, Radabaugh et al. 2010), and mainly consuming a mix of pelagic and benthic invertebrates (von Stackelberg et al. 2017).

Freshwater drum and muskellunge were classified as highly mobile species. Both species are able to travel more than 150 km (Funk 1957, Curry 2007); however, the performance of the river-wide model was slightly poorer than that of the 2-nation model for these two species. One possible explanation for this difference is that the diets of freshwater drum are primarily composed of sediment and benthic invertebrates (Wahl et al. 1988, Russell et al. 1999), which are often more plentiful close to the vegetated shorelines of the river. Adult muskellunge often remain in the vicinity of the original capture sites, thus implying restricted home range tendencies (Crossman, 1956; Muir and Sweet 1964; Miles 1978; Brewer 1980). There are no field-measured data for muskellunge on the US side of the river, and therefore, using the river-wide average PCB concentration as input in the river-wide model may not be representative of the true contamination exposure.

Next, the improvement by the 2-nation blended model highlighted the importance of incorporating species-specific fish movement as a function of the way in which sediment exposure concentrations are quantified. Among the fish species that were underpredicted on the Canadian side and overpredicted on the US side by the bioaccumulation model (including black crappie, channel catfish, gar pike, rock bass, redhorse sucker, smallmouth bass, white bass, white perch, and walleye), black crappie, channel catfish, white bass, and walleye are classified as

active and highly mobile fishes (Burger et al. 2001, Butler and Wahl 2011, Pflieger 1975, Wang et al. 2007), which are more likely to reflect integrated exposure resulting in a homogenization of differences in exposure to contamination from the US and Canadian sides. Except black crappie (field observation data were only available in the lower Canadian river, n=5), the other three species had a fairly evenly distributed number of samples across the model zones. Compared to the 2-nation model, the blended model as well as the river-wide model exhibited improved performance with a greatly lower model bias of 0.9-1.3 for these species. White bass was underestimated by the 2-nation model in the Canadian water zone and well predicted in the US water zone (Figure 3.3). Forty percent of the diet matrix of white bass is assumed to be plankton (McLeod et al. 2015). In US zones, there are also notably higher sum PCB concentrations in sediments in proximity to the shoreline and in deposition areas (e.g., lower reaches of Trenton Channel and near Celeron Island), which indirectly can influence phytoplankton growth and nutrient concentrations. If fish spend a larger fraction of their time in these areas of the river, then the Canadian zone sum PCB concentration estimates may underestimate the actual PCB concentrations in diet experienced by fish.

Channel catfish has omnivorous habits, and its diet in the Detroit River is primarily based on benthos and small fishes, which are often more available near the shallow shoreline areas. Therefore, it was expected that the 2-nation model would provide fairly good estimations on both sides of the river zone, and the improvement achieved by the 2-nation blended model and river-wide model could be caused by incorporating cross-zone exposure. For walleye, however, the river-wide model provided a relatively poorer fit than the 2-nation model, with a higher bias (mean of model bias increased from 1.7 to 2.6). Additionally, the 2-nation model performed better in the Canadian zone (mean of model bias of 0.8) than in the US zone (mean of model bias of 3.5). As such, the 2-nation model was considered to be the most susceptible to model bias as a consequence of walleye movements in and out of the model zones possibly extending beyond the Detroit River system.

For longnose gar, which exhibits site fidelity with broad but extensive spawning migration (Sakaris et al. 2003, Johnson and Noltie 1996), the 2-nation model provided the best fit, while the contamination level was largely overestimated in all other models. The simulation result from the 2-nation model suggested that US caught longnose gar may originate from the Canadian side of the river. The accuracy of the 2-nation model was high on the Canadian side of

the river (mean of model bias of 1.0), and the simulated result of sum PCB concentration in longnose gar by the 2-nation model on the Canadian side of the model zone (146.06 ng/g) was within a factor-2 margin of the field-measured sum PCB concentration on the US side of the Detroit River (273.49 ng/g). Longnose gar prefers habitats with complex macrophytes (Landsman et al. 2011), which are most plentiful on the downstream Canadian side of river, which is characterized by less pullulation and lower turbidity. Lastly, redhorse sucker, rock bass, white perch, and smallmouth bass are classified as sedentary and display site fidelity (Fajen 1962, Funk 1957, Gerber and Haynes 1988, McGrath and Austin 2009). However, only redhorse sucker showed an improvement when the 4-zone model was applied instead of the 2-nation model (mean of model bias reduced to 0.9 from 2.2). The finer-zoned models performed poorly in the other three species in comparison to the 2-nation model. In contrast, the 2-nation blended model was able to significantly improve the accuracy of the prediction for all four fish species (Table 3.3), which demonstrated the possibility of cross-zone exposure.

Finally, for bowfin, bullhead, and northern pike, the 2-nation model greatly overestimated the PCB concentrations on both the Canadian and US sides of the model zone, as did all other models (Table 3.2). Bowfin is considered a high-site-fidelity species but with substantial movement postspawning (Midwood et al. 2018). This species has a preference for shallow and heavily vegetated habitats (Scott and Crossman 1998). The measured data for bowfin reflected only seven fish samples (n=3 in US water and n=4 in Canadian water) and therefore may not be representative of the species' sum PCB concentration in each water zone. However, the estimated fish advice for bowfin in Canadian water closely matched the published OMECP advisory.

Bullhead has linear home ranges of 0.5-2 km and high seasonal variation in movement, especially during the spawning season (Sakaris et al. 2005). Northern pike is a sit-and-wait predator (Webb and Skadsen 1980) with a home range of approximately 100 m in diameter and prefers shallow vegetated areas (Diana et al. 1977; Cook and Bergersen 1988). While both fishes were generally classified as stationary, the 4-zone and 6-zone models unexpectedly overestimated the PCB concentrations compared to the 2-nation simulations for these fishes. Given the similar magnitude of overestimation between the Canadian and US zone simulations, the model bias of the PCB residues in US-caught fish may be caused by movements to the less-contaminated and more vegetative-covered Canadian waters, assuming that the same Canadian-

caught species that forage and are exposed to highly contaminated US water would only increase the error associated with model predictions. Thus, the conclusion concerning mobility patterns is considered unassigned, although the weight of the evidence from previous research on fish movement suggests that these three fish species are considered less mobile fishes, and multizone models would provide more accurate predictions than river-wide models.

One important application of the model is to provide predicted advice information for sport fish species not presently included in the official advisory information. Due to lacking empirical data, for Detroit River specifically, fish advice information was not available for bowfin, longnose gar, and muskellunge in Canadian jurisdiction. Model predicted Ontario advisories for these species ranged from 8 meal-per-month for general public (bowfine) to no-consumption for sensitive populations (longnose gar and muskellunge). The advice information in US jurisdiction was not available for black crappie, sunfish, bowfin, longnose gar, gizzard shad, muskellunge, northern pike, and white perch. Model predicted Michigan advisories for these species ranged from 0.5 to 2 meal-per-month (black crappie, sunfish, bowfine, northern pike, and which perch) to limited meals (longnose gar, gizzard shad, and muskellunge). While our results suggest that taking into account the movement ecology of these species significantly improve predictions (R^2 from the linear regressions between the predicted PCB concentration and the field-observed PCB concentration increased from 22% to 39%; mean of model bias reduced from 1.88 to 1.31), the fish advice estimates ended up being comparable between calibrated and non-calibrated models (Table S7). Therefore, movements and model zoning resolution may not be the only factors contributing to model inaccuracy. For example, the complex macrophyte communities were demonstrated as an important factor in determining fish distribution (Lapointe 2007) but were not considered in the present study. While the higher PCB concentrations in sediments in proximity to the shoreline and in deposition areas that may support high macrophyte growth, the high turbidity and runoff in some areas can reduce the abundance of submersed macrophytes on the US side of the Detroit River (Schloesser and Manny 2007). Additionally, the distribution of river fish is associated with depth, current velocity, slope, and cover (Fladung et al. 2003). Lastly, location specific feeding matrix and size- and age-related non-steady-state bioaccumulation of PCBs could also contribute to additional error propagation.

3.5 Conclusions

The present study contributes to improved understanding of factors that impact bioaccumulation by considering the spatial connectivity of pollution in sediment, water, and feeding systems. The uncalibrated 2-nation model, which constrains the contamination exposure within the river portion of each country, provided a fairly good fit to both empirical data and published fish consumption advice generated for the Detroit River. It verified the applicability of the process-based food web bioaccumulation model for predicting POPs concentrations in different food web components across different freshwater systems. Furthermore, the model calibration which allowed the cross-zone exposure demonstrated the importance of accounting for specific ecological factors, such as fish movement, to improve PCB bioaccumulation predictions, especially in highly heterogeneous water systems. In areas with low contamination, the possible foraging of fish in neighboring highly contaminated areas can cause underprediction of PCB concentrations. The reverse is also true, as the PCB concentrations in fish in highly contaminated areas will be miscalculated due to the exposure to less-contaminated adjacent areas of the water bodies. Such information is critical to be justified in bioaccumulation models in order to improve their accuracy of prediction when applied to predict advice information for sport fish species not presently included in official consumption advisories. Moreover, despite notable efforts to remove contaminated sediments from the AOC, restrictions on fish consumption advisories continue to be issued for the system necessitating consideration of additional remedial actions within the system. Additional model simulations considering fish movements within prospective clean-up areas and the implications of sediment remediation to future fish consumption advisories will benefit stakeholders to help prioritize remediation targets and justify the costs of these activities.

Figure 3.1. Model zoning and sites along the Detroit River where fishes were captured. Each sampling location may include one or more samples and species.
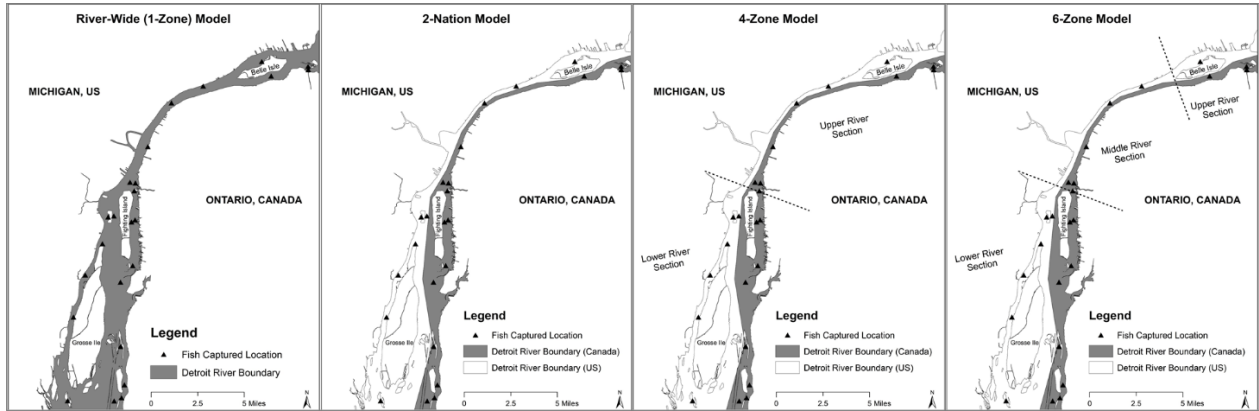
Figure 3.2 Comparison of model performance. Symbols of filled squares represent the R^2 for the linear regression between the logarithmic-transformed estimated PCB concentrations against the logarithmic-transformed observed PCB concentrations in fish samples; symbols of filled circles represent the geometric mean of model bias. Error bars represent the 95% confidence interval for the model bias. Panel a shows the validation result from the uncertainty model using the sum PCB concentration in wet weight (ng/g wet wt.); panel b shows the validation result from the uncertainty model using the sum PCB lipid equivalent concentrations (ng/g lipid eq.).
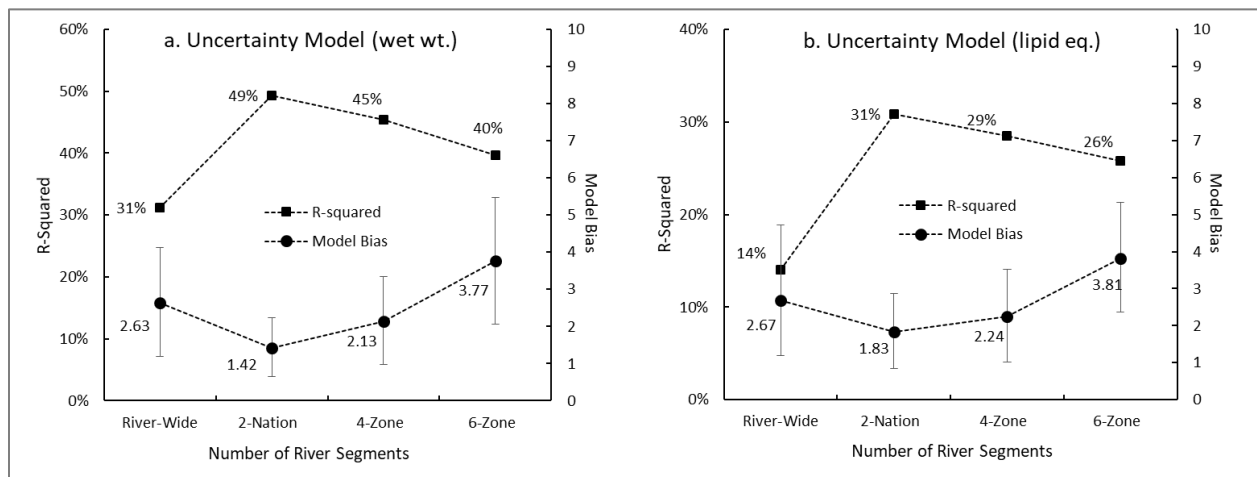
Figure 3.3 Predicted versus observed sum PCB wet-weight concentrations (ng/g) in fish species compared with a 1:1 fit line (solid diagonal line), 2-fold model bias margin (diagonal dash-dotted line), and 4-fold model bias margin (diagonal dashed line) using 2-nation simulation. a. The filled squares represent the results for the fish species on the Canadian side of the Detroit River. b. The filled circles indicate the results for the fish species on the US side of the Detroit River. Error bars are 95% confident intervals around the geometric mean concentration for observed data and model predictions.
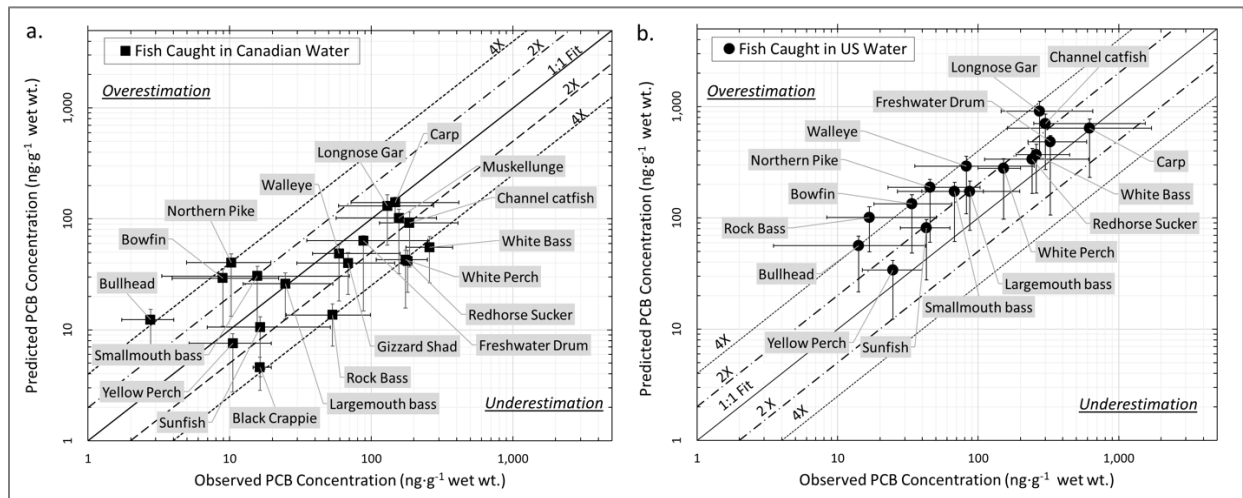
Figure 3.4 Published fish consumption advice in the Detroit River versus 2-nation model-predicted, 2-nation blended model-predicted, and species-specific-scale model-predicted fish consumption advisories compared with a 1:1 fit line (dash diagonal line). a. The results for the comparison between OMECP advisory and estimated advisory on the Canadian side of the Detroit River. b. The results for the comparison between MDHHS advisory and estimated advisory on the US side of the Detroit River. (Note that the fish meals per month may be the same for different species and are therefore overlapped in the figure below. Only the species that were calibrated to different trigger levels compared to the results from the original 2-nation model are labeled).
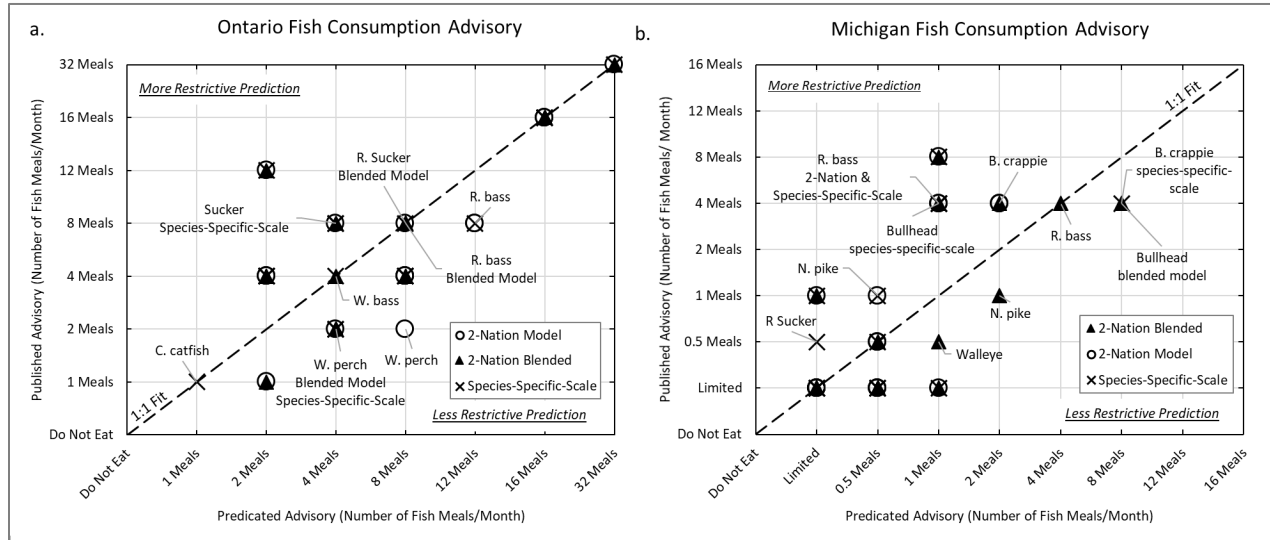
Table 3.1 Field-observed sum PCB concentrations (mean ± SD ng/g wet weight) in sport fish from government fish advisory programs and GLIER surveys (1998-2016)

	Upper US	Upper CA	Mid US	Mid CA	Lower US	Lower CA
Black Crappie						16.7 ±4.2
						(5, GLI)
Sunfish	86.4 ±52.3	8.3 ±4.9		29.8 ± 18.0		41.5 ±21.8
(Bluegill, Pumpkinseed)	(2, GLI)	(7, GLI)		(2, GLI)		(4, GLI)
Bowfin	38.6 ±24.2	3.9 ±0				20.7±4.3
	(3, GLI)	(2, GLI)				(2, GLI)
Bullhead	10.0 ±12.0	4.2 ±3.8			51.3 ±48.4	4.5 ±6.5
(Brown, Black)	(10, MDQ)	(22, GLI)			(13, GLI, MDQ)	(14, GLI)
Common Carp	1519.2 ±1742.9	94.9 ±78.2	2956 ±1820.5	1089 ±1145.0	2215.7 ±1683.7	187.1 ± 212.9
	(16, GLI, MDQ)	(4, GLI)	(24, MDQ, MDR)	(10, MOE)	(162, GLI,MDQ,MDR)	(22, GLI, MOE)
Channel catfish	73.0 ±143.0			728 ±732.7	1395.1 ±1105.0	14.4 ±0
	(4, MDQ)			(5, MOE)	(13, MDQ)	(2, GLI)
Freshwater Drum		127.2 ±199.5	413.9 ±242.6	78.6 ±75.1		180.4 ±206.7
		(18, MDQ)	(10, MDQ, MDR)	(13, MOE)		(21, MOE)
Longnose Gar	339.9 ±243.6	178.0 ±129.4		374.2 ±282.2		140.2 ±121.2
	(6, GLI)	(14, GLI)		(8, GLI)		(16, GLI)
Gizzard Shad		80.2 ±95.1				110.7 ±78.7
		(6, GLI)				(13, GLI)
Largemouth bass	740.9 ±1490.9	42.4 ±13.9			104.8 ±75.6	31.4 ±28.2
	(5, MDQ)	(5, MOE)			(11, GLI, MDQ)	(12, GLI, MOE)
Muskellunge		1056.3 ±558.9				155.0 ± 96.8
		(2, GLI)				(10, GLI)
Northern Pike	47.0 ±48.5	10.5 ±8.5			87.4 ± 37.8	29.4 ± 12.5
	(10, MDQ)	(18, GLI)			(10, MDQ)	(2, GLI)
Rock Bass	15.0 ±18.5	10.4 ±9.6		51.4 ±36.4	43.2 ±28.2	69 ± 21.7
	(12, MDQ)	(2, GLI)		(5, MOE)	(16, GLI, MDQ)	(5, OME)
Redhorse Sucker		180.3	338.8 ± 276.3			
		(1, GLI)	(10, MDQ, MDR)			
Smallmouth bass	72.6 ± 45.1	46.36 ±62.2			158.9 ±221.3	49.5 ±84.6
	(10, MDQ)	(13, GLI)			(12, GLI, MDQ)	(6, GLI)
Walleye		70.5 ±109.3		163.1 ±196.9	234.9 ±297.1	61.3 ±62.1
		(6, GLI)		(28, MOE)	(141, GLI, MDQ, MDR)	(23, GLI, MOE)
White Bass	192.5 ±101.6			310 ±180.9	371.5 ± 203.9	304.1 ± 247.8
	(6, MDQ)			(82, MOE)	(13,GLI, MDQ)	(51, GLI, MOE)
White Perch	160 ±54.78	182.8 ±90		230 ±74.0		284.3 ± 216.5
	(5, MDQ)	(5, GLI)		(6, MOE)		(26, GLI, MOE)
Yellow Perch		11.5 ±9.1	27.6 ±17.0		36.3 ±41.2	17.9 ±6.1
		(26, GLI)	(10, MDQ, MDR)		(25,GLI, MDQ)	(14, GLI)

Note: acronyms for the agencies are Great Lakes Institute for Environmental Research (GLI); Michigan Department of Environmental Quality (MDQ); Michigan Department of Natural Resources (MRD); Ontario Ministry of Environment and Climate Change (OME)

Table 3.2 Mean of model bias (predicted sum PCB/observed sum PCB) with its 95% confidence interval of uncertainty model simulations for different zones

Fish Species	# obs	Model Bias (95% Confident Interval)			
		River Wide	*2-Nation*	*4-Zone*	*6-Zone*
Black Crappie	5	1.3	0.4	0.6	0.6
		(1.07 - 1.79)	(0.36 - 0.62)	(0.53 - 0.91)	(0.42 - 0.73)
Sunfish	16	3.1	1.7	1.3	1.1
(Bluegill, Pumpkinseed)		(1.84 - 5.53)	(0.89 - 3.39)	(0.67 - 2.46)	(0.75 - 1.68)
Bowfin	7	8.7	5.4	8.3	8.0
		(3.31 - 23.08)	(2.45 - 10.99)	(3.59 - 17.07)	(3.9 - 15.8)
Bullhead	59	14.0	7.5	10.4	11.7
(Brown, Black bullhead)		(10.24 - 19.01)	(4.29 - 16.98)	(4.46 - 24.07)	(9.3 - 14.7)
Carp	218	1.1	1.0	1.2	1.6
		(0.76 - 1.47)	(0.74 - 1.35)	(0.92 - 1.65)	(1.23 - 2.19)
Channel catfish	24	1.3	1.7	2.3	2.9
		(0.61 - 3.88)	(0.47 - 4.90)	(0.81 - 6.72)	(1.13 - 7.34)
Freshwater Drum	64	2.0	1.2	2.4	4.5
		(0.94 - 2.67)	(0.68 - 2.31)	(1.15 - 3.07)	(1.57 - 6.01)
Longnose Gar	38	3.0	1.7	3.4	3.9
		(1.62 - 7.17)	(1.20- 4.26)	(1.18 - 6.18)	(2.87 - 5.49)
Gizzard Shad	19	2.6	0.8	1.1	1.3
		(1.27 - 6.72)	(0.42 - 2.22)	(0.51- 3.01)	(0.95 - 3.63)
Largemouth bass	33	2.4	1.7	2.2	2.7
		(1.49 - 7.19)	(0.39 - 4.58)	(0.55 - 6.23)	(0.92 - 6.63)
Muskellunge	12	2.7	0.8	1.2	1.7
		(0.89 - 5.34)	(0.51 - 1.69)	(0.43 - 2.37)	(0.57 - 3.32)
Northern Pike	40	8.7	6.2	8.9	9.5
		(5.85 - 13.03)	(2.79 - 15.70)	(4.03 - 12.44)	(6.1 - 12.8)
Redhorse Sucker	11	5.5	2.2	0.9	1.8
		(1.6 - 12.7)	(0.88 - 3.1)	(0.42 - 1.75)	(0.99 - 3.33)
Rock Bass	40	2.9	2.0	2.5	3.6
		(1.70 - 4.89)	(1.15 - 3.33)	(1.70 - 3.79)	(2.20 - 5.77)
Smallmouth bass	41	3.3	2.4	3.3	3.8
		(1.28 - 4.93)	(1.60 - 3.68)	(2.24 - 5.14)	(2.52 - 5.75)
Walleye	116	2.4	1.7	2.6	2.7
		(1.81 - 3.26)	(0.43 - 2.27)	(1.96 - 3.47)	(0.90 - 3.65)
White Bass	152	0.9	0.7	0.4	0.5
		(0.70 - 1.24)	(0.58 - 1.14)	(0.25 - 0.69)	(0.34 - 0.95)
White Perch	42	1.1	0.4	0.5	0.6
		(0.76 - 1.47)	(0.24 - 0.61)	(0.25 - 0.77)	(0.41 - 0.84)
Yellow Perch	95	2.6	1.5	1.9	2.0
		(1.45 -3.12)	(0.87 - 2.61)	(1.15 -2.17)	(1.15 - 3.11)

Table 3.3 Estimated weighted average proportion of exposures to Canadian and US contaminants in selected fish species necessary to generate a prediction by the 2-nation model simulation to be within a factor of 2-fold error of the model predictions.

Canadian Caught Underestimated Fish	Original Model Bias	% Contamination of CA	% Contamination of US	Updated Model Bias	Contamination Adjustment Factor for CA Model Zone	Contamination Adjustment Factor for US Model Zone
Black Crappie	0.3	0 - 81.5%	18.5% - 100%	0.50 -1.31	81.5%	18.5%
Redhorse Sucker	0.2	0 - 66.0%	34.0% - 100%	0.50 - 1.10	66.0%	34.0%
Rock Bass	0.3	0 - 74.5%	25.5% - 100%	0.50 - 1.22	74.5%	25.5%
White Bass	0.2	0 - 65.5%	34.5% - 100%	0.50 - 1.01	65.5%	34.5%
White Perch	0.2	0 - 82.5%	17.5% - 100%	0.50 - 1.34	82.5%	17.5%
US Caught Overestimated Fish	**Original Model Bias**	**% Contamination of CA**	**% Contamination of US**	**Updated Model Bias**	**Contamination Adjustment Factor for CA Model Zone**	**Contamination Adjustment Factor for US Model Zone**
Channel Catfish	2.3	19.0% - 100%	0 - 81.0%	0.52 - 2.00	19.0%	81.0%
Longnose Gar	3.3	10.0% - 100%	0 - 90.0%	0.75 - 2.00	10.0%	90.0%
Rock Bass	6.0	91.0% - 100%	0 - 9.0%	1.58 - 2.00	91.0%	9.0%
Smallmouth Bass	2.5	25.5% - 100%	0 - 74.5%	0.59 - 2.00	25.5%	74.5%
Walleye	3.5	28.5% - 100%	0 - 71.5%	0.81 - 2.00	28.5%	71.5%
Consistently Overestimated Fish	**Original Model Bias in US Model Zone**	**% Contamination of CA**	**% Contamination of US**	**Updated Model Bias in US Model Zone**	**Contamination Adjustment Factor for CA Model Zone**	**Contamination Adjustment Factor for US Model Zone**
Bowfin	4.0	99%	1%	0.87	99%	1%
Bullhead	4.0	99%	1%	0.88	99%	1%
Northern Pike	4.1	99%	1%	0.89	99%	1%

Table 3.4 Comparison of 2-nation model, 2-nation blended model, and species-specific-scale model performance using sum PCB concentrations. Performance matrixes include coefficient of determination values (R^2) of the linear regression between logarithmic-transformed estimated PCB concentrations against observed PCB concentrations in fish samples and the geometric mean of model bias and 95% confidence interval for the bias.

	N	Num of Caliberated Obs	R^2	Model Bias	95% CI for Model Bias	
Canadian Model Zone						
2-Nation Original Model	629	0	36%	0.95	0.71	1.06
2-Nation Blended Model	629	195	46%	1.08	0.61	1.32
Species-Specific Scale Model	629	183	38%	1.23	1.02	1.82
US Model Zone						
2-Nation Original Model	411	0	40%	2.68	2.12	2.93
2-Nation Blended Model	411	168	45%	1.49	1.28	1.73
Species-Specific Scale Model	411	51	39%	2.19	1.75	3.39
Total						
2-Nation Original Model	1040	0	49%	1.42	0.97	2.30
2-Nation Blended Model	1040	363	54%	1.21	0.95	1.20
Species-Specific Scale Model	1040	234	49%	1.36	1.09	1.82

Table 3.5 The original 2-nation model-predicted fish consumption advisories and published fish consumption advice in the Detroit River, Lake Erie Western Basin, or Lake St. Clair. In the table, published advisories based on the Detroit River that were caused by PCBs are listed first. The species-specific advisories for other contaminants and/or statewide advisories were applied if the PCB-caused Detroit River advisories were not available.

Location	Species	Published Public pop (meal/month)	Published Sensitive pop (meal/month)	2nation original Predicted Public pop (meal/month)	2nation original Predicted Sensitive pop (meal/month)	2nation blended Predicted Public pop (meal/month)	2nation blended Predicted Sensitive pop (meal/month)
ON	Black Crappie[a]	32	12	32	32	32	32
ON	Sunfish[a]	16	4	16	16	16	16
ON	Bowfin[ab]	8	4	8	8	8	8
ON	Bullhead[a]	16	8	16	16	16	16
ON	Carp	4	4	2	Do Not Eat	2	Do Not Eat
ON	Channel Catfish	1	Do Not Eat	2	Do Not Eat	2	Do Not Eat
ON	Freshwater Drum	4	Do Not Eat	2	Do Not Eat	2	Do Not Eat
ON	Gar Pike[c]	4	Do Not Eat	2	Do Not Eat	2	Do Not Eat
ON	Gizzard Shad	2	Do Not Eat	4	4	4	4
ON	Largemouth Bass	8	4	4	4	4	4
ON	Muskellunge[ad]	12	4	2	Do Not Eat	2	Do Not Eat
ON	Northern Pike	4	4	8	8	8	8
ON	Sucker	8	8	12	12	8	8
ON	Rock Bass	8	4	12	12	8	8
ON	Smallmouth Bass	4	4	8	8	8	8
ON	Walleye	4	4	8	8	8	8
ON	White Bass	4	4	8	8	4	4
ON	White Perch	2	Do Not Eat	8	8	4	4
ON	Yellow Perch	16	4	16	16	16	16
MI	Black Crappie[a]	4	NA[e]	2	NA	2	NA
MI	Sunfish[a]	8	NA	1	NA	1	NA
MI	Bowfin	NA	NA	1	NA	8	NA
MI	Bullhead	4	NA	2	NA	8	NA
MI	Carp	Limited[f]	NA	Limited	NA	Limited	NA
MI	Channel Catfish	Limited	NA	Limited	NA	Limited	NA
MI	Freshwater Drum	Limited	NA	Limited	NA	Limited	NA
MI	Gar Pike	NA	NA	Limited	NA	Limited	NA
MI	Gizzard Shad	Limited	NA	Limited	NA	Limited	NA
MI	Largemouth Bass	Limited	NA	1	NA	1	NA
MI	Muskellunge[a]	1	NA	Limited	NA	Limited	NA
MI	Northern Pike[a]	1	NA	0.5	NA	2	NA
MI	Sucker	0.5	NA	0.5	NA	0.5	NA
MI	Rock Bass	4	NA	1	NA	4	NA
MI	Smallmouth Bass	Limited	NA	0.5	NA	0.5	NA
MI	Walleye	0.5	NA	0.5	NA	1	NA
MI	White Bass	Limited	NA	0.5	NA	0.5	NA
MI	White Perch	Limited	NA	0.5	NA	0.5	NA
MI	Yellow Perch	4	NA	1	NA	1	NA

Note:

[a], Published fish consumption advisory caused by non-PCB contamination (e.g., Hg or dioxin).

[b], OMECP advisory for bowfin is available for the Thames River near Lake St Clair.

[c], OMECP advisory for gar pike (longnose gar) is available for only the Grand River (below Dunnville Dam to Port Maitland).

[d], OMECP advisory for muskellunge is available for Lake St Clair.

[e], Michigan fish consumption advisory mainly focuses on the general public.

[f], Per Michigan fish consumption advisory, the sensitive population should avoid eating fish listed as "Limited"; the general public may safely eat one or two meals per year listed as "Limited".

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CHAPTER 4

GENERAL DISCUSSION

4.1 Discussion

This thesis advances the literature by improving model-based estimation of PCB bioaccumulation considering non-sedimentary routes of exposure by benthic invertebrate and the spatially connected feeding interactions among various fish species in a freshwater food web. Chapter II initially calibrated a process-based food web bioaccumulation model using paired benthos and sediment samples taken from the river to ensure realistic predictions at the base of the food web in the study area. The result demonstrated that PCB bioaccumulation measurements are significantly affected by variations in pollutant uptake and elimination routes via the overlying water, which in turn are affected by the degree of disequilibrium of PCBs between sediments and water. Chapter III demonstrated the importance of accounting for specific ecological factors, such as fish movement, in bioaccumulation models, especially in highly heterogeneous water systems. Such information is critical to be justified in bioaccumulation models in order to improve the accuracy of model prediction of consumption advice information for sport fish species and to provide a useful interactive product to be used by stakeholders to determine likely benefits of cleanup action in a contaminated water system.

The conventional bioaccumulation studies such as BSAF frameworks rest on the assumption that sediment exposure is the dominant exposure route of chemicals to benthic invertebrates without considering uptake from the overlying water. Compared with conventional bioaccumulation studies, the process-based food web bioaccumulation model also considers exposure and chemical losses to porewater as well as to/from overlying water (Morrison et al. 1997; Arnot and Gobas 2004). The process-based food web bioaccumulation model predicted PCB bioaccumulation in biota with comparable accuracy to the best fitting empirically calibrated BSAR model for benthos and a superior prediction for fish PCB contamination. Given that the BSAR model was trained with the same data set on which it was evaluated, whereas that process-based food web model remained independent, the similarity in model performance provides strong support that PCB concentrations in water and sediment and the magnitude of the sediment/water fugacity ratio are all important for benthic invertebrate PCB bioaccumulation.

Although water was demonstrated to be a significant PCB exposure pathway, the improvement to the model fit of $BSAR_{(Csed+Cw)}$ was admittedly small compared to $BSAR(_{Csed})$. One possible explanation is that the present study suffered from less complete data on water PCB concentrations than did the paired sediment inputs used for the site-specific model calibration. The PCB concentrations in water were derived from an independent mussel biomonitoring database (Drouillard 2010) that was decoupled in space and time from the timing of sediment/benthos collections. A fully matched water, sediment and benthos data set would likely increase the $BSAR_{(Csed+Cw)}$ performance over what was presently observed.

Both BSAR and process-based bioaccumulation models utilized in this thesis adopted a simplistic approach to sediment classification. The BSARs applied considered only a single sediment compartment consisting of organic carbon (OC) and assumed that all PCBs present in dry sediment were associated with this compartment. The process-based food web bioaccumulation model considered OC and inorganic matter (IM), but similar to the BSAR, attributed all chemical partitioning to OC. There is a growing literature demonstrating varied partitioning capacities for POPs among different organic sediment fractions, including labile organic carbon and more refractory carbon components such as black carbon (BC) (Ghosh et al. 2003, Cornelissen and Gustaffsson 2005, Moermond et al. 2005, Koelmans et al. 2006). One study of a BC-inclusive BSAF model demonstrated that, compared with the BSAF estimation without considering BC, model bias was reduced by a factor of 3 (Hauck et al. 2007). Selck et al. (2012) modified the Arnot and Gobas model to accommodate PCB partitioning to BC and concluded that the elevated partitioning of PCBs to BC and the proportion of BC in the sediment were among the most important processes driving variation in PCB accumulation in benthic invertebrates. These processes accounted for 60% and 67% of the total variation in PCB-153 concentrations in mayflies and polychaetes, respectively. Unfortunately, the BC contents of sediments were not available from paired sediment/benthos samples used in this thesis. This underscores a need for inclusion of BC analysis in conventional sediment chemistry surveys.

Four specific hypotheses were outlined and tested in Chapter 2 as outlined in Chapter 1. The test outcomes for each hypothesis are stated below:

Hypothesis 2.1   BSARs that include both PCB contamination in water and sediment will have higher accuracy than BSARs that only consider sediment PCB concentration.

Hypothesis 2.1 was accepted. Compared to BSAR$_{(Csed\ only)}$, BSAR$_{(Csed+Cw)}$ exhibited improved performance with overall mean model bias decreased from 2.17 to 1.89, and the R^2 of linear regression between log-predicted and log-observed PCB concentrations increased from 0.41 to 0.43.

Hypothesis 2.2   Models using a 95:5% overlying water/pore water respiration ratio for benthic invertebrates will predict lower PCB concentrations in benthic invertebrates and fish compared to those that adopt a 50:50 overlying water/pore water ratio.

Hypothesis 2.2 was accepted. For model simulations that assumed $P_{(o,w)} = 95\%$, 61% and 42% of the individual observed concentrations were underpredicted by the model for benthic invertebrates and fishes, respectively. For model simulations that assumed $P_{(o,w)} = 50\%$, these underpredictions reduced to 54 % and 35%.

Hypothesis 2.3   The calibrated BSAR model will produce the most accurate PCB predictions in benthic invertebrates followed by the models using 50:50 overlying water/pore water ratio and 95:5 overlying water/pore water ratio.

Hypothesis 2.3 was accepted. Overall, compared with the process-based food web bioaccumulation model estimations, the BSAR estimated tissue PCB concentrations had a stronger fit relative to the expected 1:1 relationship. BSAR$_{(Csed\ only)}$ had 83% of the model predictions were within a factor of 4 from field measurements. For BSAR$_{(Csed+Cw)}$, 86% of the predictions were within a factor of 4, from field measurements. For the process-based food web bioaccumulation model, 80% of the model predictions were within a factor of 4 of field

measurements, regardless of the assumptions about the overlying water respiration fraction in benthic invertebrates.

Hypothesis 2.4   The hybrid BSAR-food web bioaccumulation model will produce the most accurate PCB predictions in sport fish followed by the models using 50:50 overlying water/pore water ratio and 95:5 overlying water/pore water ratio.

Hypothesis 2.4 was rejected. The hybrid BSAR-food web bioaccumulation model had lower accuracy than both process-based food web bioaccumulation models ($P_{(o,w)}$=50% and $P_{(o,w)}$=95%). For the $P_{(o,w)}$=95% model, the regression explained 23.2% of the variation in the empirical data. For the $P_{(o,w)}$=50% model, the R^2 increased to 24.4%. For the hybrid BSAR-food web bioaccumulation model, the regression explained only 18.1% of the variation in the empirical data.

Chapter III highlighted the importance of incorporating species-specific fish movement as a function of the way in which sediment exposure concentrations are quantified in bioaccumulation measures. The fish species with short movement distances are exposed to the constant PCB concentration present in their small home ranges, while the more mobile predators are likely exposed to a large gradient of PCB concentrations and couple the pathways of PCB transfer. As a result, traditional single compartment model (river wide model) which assumes that different fish species equally utilize the waterbody generated the poorest model validation and tended to generate overestimation. The uncalibrated 2-nation model, which constrains the contamination exposure within the river portion of each country, provides the best global fit result. However, these improvements were not equally observed across species. That could be caused by cross-zone exposure. In areas with low contamination, the foraging of fish in neighboring highly contaminated areas can cause underprediction of PCB concentrations. The reverse is also true, as the PCB concentrations in fish in highly contaminated areas will be miscalculated due to the exposure to less-contaminated adjacent areas. Compared to the 2-nation model, the blended model as well as the river-wide model which allow for cross-zone exposure in some fish species exhibited improved performance for black crappie, channel catfish, white

bass, and walleye. These four fish species are classified as active and highly mobile fishes by previous studies (Burger et al. 2001, Butler and Wahl 2011, Pflieger 1975, Wang et al. 2007), which are more likely to reflect integrated exposure resulting in a homogenization of differences in exposure to contamination from the US and Canadian sides.

One important application of the process-based food web bioaccumulation model is to provide predicted advice information for sport fish species not presently included in the official advisory information. Due to lacking empirical data, Detroit River fish advice information was not available for bowfin, longnose gar, and muskellunge in Canadian jurisdiction, and was not available for black crappie, sunfish, bowfin, longnose gar, gizzard shad, muskellunge, northern pike, and white perch in US jurisdiction. While our results suggest that fish advice estimates for these species were comparable between calibrated and non-calibrated models, the estimated fish advisories by the best global fit model were less restrictive than the existing Ontario fish advisories in the Canadian portion of the river with low contamination levels. Moreover, the advisories were more restrictive than Michigan advisories in the US portion of the river with high contamination levels. As a result, taking into account the movement ecology of these species could significantly improve predictions.

The present model simulation also shows that fish movements and model zoning resolution are not the only factors contributing to model inaccuracy. For example, the complex macrophyte communities were demonstrated as an important factor in determining fish distribution (Lapointe 2005) but were not considered in the present study. While the higher PCB concentrations in sediments in proximity to the shoreline and in deposition areas that may support high macrophyte growth, the high turbidity and runoff in some areas can reduce the abundance of submersed macrophytes on the US side of the Detroit River (Schloesser and Manny 2007). Moreover, incorrect assumptions related to the feeding matrix and size- and age-related non-steady-state bioaccumulation of PCBs could also contribute to additional error propagation. A more detailed and thorough analysis of how incorporating environmental and ecological parameters and physiological characteristics into the appropriate model calibration will better reflect the heterogeneous environment that fish inhabit remains an important area for future research.

Three specific hypotheses were outlined and tested in Chapter 3 as outlined in Chapter 1 of this thesis. The test outcomes for each hypothesis are stated below:

Hypothesis 3.1 The simulations using different spatial scales (e.g., river-wide, 2-nation, 4-zone and 6-zone simulations) provides inconsistent global prediction of PCB concentrations in sport fish.

Hypothesis 3.1 was accepted. The 2-nation model provided the strongest global fit to empirical observations. The river-wide scale simulation resulted in the poorest fitted model validation with the lowest R^2 and highest variation in the model bias. The R^2 increased by approximately 10% from the river-wide model to the other multizone models in all simulations. While the 6-zone model produced validations that had a better goodness of fit than the river-wide scale simulation, it tended to generate the largest overestimation.

Hypothesis 3.2 Individual species of fish exhibit different spatially integrated exposures necessitating different spatial boundaries in model simulations to predict species-specific chemical exposures. The sport fish species are predicted with different accuracies in the selected best global simulation model.

Hypothesis 3.2 was accepted. Seven species were accurately predicted by best global simulation model (i.e. 2-nation model) on both the US and Canadian sides of the river. These included carp, freshwater drum, gizzard shad, largemouth bass, muskellunge, sunfish, and yellow perch. Compared to the 2-nation model, the river-wide model exhibited improved performance with a greatly lower model bias for black crappie, channel catfish, white bass, and white perch, whereas the 4-zone model showed an improvement over the 2-nation model for redhorse sucker.

Hypothesis 3.3 The calibrated model, which allowed cross-zone exposure by accounting for fish movement can improve PCB bioaccumulation prediction and provide the most consistent prediction of sport fish consumption advisories issued by Ontario and Michigan for the Detroit River AOC.

This hypothesis was accepted. The 2-nation blended model had a lower overall model bias of 1.21 ± 3.05 compared to that of the uncalibrated 2-nation model (1.42 ± 3.19), and 68.4% of the predictions were within a factor of 2 from the individual field measurement (compared to 34.5% in the uncalibrated 2-nation model). The R^2 values of linear regression between log-

predicted and log-observed PCB concentrations ranged from 42% to 54% across calibrated simulations, with the best fit achieved by the blended model. The number of fish meals per month estimated by the uncalibrated 2-nation model accurately matched the published advisory for five fish species on the Canadian side of the river (e.g., black crappie, sunfish, bowfin, bullhead, and yellow perch), and six fish species on the US side of the river (e.g., carp, channel catfish, freshwater drum, gizzard shad, sucker, and walleye). In the Canadian model zone, sucker, rock bass, and white bass were effectively calibrated by the blended model. In the US model zone, rock bass were effectively calibrated to a better fit by the blended model.

With a growing database accumulating on fish telemetry, future model applications should accommodate empirically derived foraging ranges and habitat affiliation rules. Once this information is accomplished for multiple sport fish species, the Detroit River AOC could be divided into habitat boundaries as opposed to simple areal boundaries used in this thesis. Habitat boundaries in future simulations could take into consideration water depth, current velocity, delineate wetland types and regions, sediment characteristics and benthic invertebrate biomass - habitat relationships. Subsequently, sediment PCB concentrations should be extrapolated to individual habitat boundaries identified above to generate new simulation sets that can be contrasted against the spatial scale boundaries adopted in this study.

With the objective of restoring and maintaining the Great Lakes ecosystem, natural resource managers are required to quantify the threats of toxic substances to human and ecosystem health and implement remedial actions to address these threats. These actions require science-based approaches and economic justification. Therefore, to provide a rationale for making sound environmental decisions, a consistent risk assessment approach is needed. The model should be applied to prospective U.S. EPA sediment remediation projects being planned for the Detroit River AOC. The model can be parameterized with existing sediment and water inputs and compared with different simulations that accommodate post-remediation sediment targets to estimate the potential benefits and priority of individual sediment clean-up actions. The simulation can also be performed to determine the relative importance of PCBs in water and sediments as contributors to fish bioaccumulation potentials and to make remediation priority suggestions about whether remedial actions performed within the jurisdiction are likely to have a positive effect on reducing the number or intensity of fish consumption restrictions issued.

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Table A1. List of model parameters and descriptions

Parameter	Description	Value	Distribution	Reference
Direct input term				
$AE_{lipid,\ benthos}$	Dietary assimilation efficiency for lipids in benthos	75%	Triangle Min=40% Max=80%	Arnot and Gobas 2004
$AE_{lipid,\ fish}$	Dietary assimilation efficiency for lipids in fishes	92%	Triangle Min=80% Max=100%	Gobas et al. 1999
$AE_{NLOM,\ benthos}$	Dietary assimilation efficiency for NLOM in benthos	75%	Triangle Min=40% Max=80%	Arnot and Gobas 2004
$AE_{NLOM,\ fish}$	Dietary assimilation efficiency for NLOM in fishes	60%	Triangle Min=40% Max=80%	Nichols et al. 2001
$AE_{oc,\ sediment}$	Dietary assimilation efficiency for OC in sediment	30%	Triangle Min=15% Max=35%	Based on professional judgement
$AE_{IM,\ sediment}$	Dietary assimilation efficiency for IM in sediment	0	Fixed Term	Based on professional judgement
AE_w	Dietary assimilation efficiency for water	25%±6.25%	Lognormal	Arnot and Gobas 2004
BW	Organism body weight	*	Lognormal	McLeod et al. 2015
C_w	Concentration of chemical in water	*	Lognormal	Drouillard et al. 2010
C_{sed}	Concentration of chemical in sediment	*	Lognormal	Szalinska et al. 2013
Kow	Octanol-water partitioning coefficient	*	Fixed term	Hansen et al. 1999
$P_{(p,w),\ benthos}$	Fraction of respired pore water by benthos	50%	Triangle Min=10% Max=70%	Selck et al. 2012
$P_{(o,w),\ fish}$	Fraction of respired overlying water by fishes	100%	Fixed Term	Arnot and Gobas 2004
P_{diet}	Proportion of dietary item	*	Lognormal	McLeod et al. 2015
$P_{org,\ lip}$	Proportion of lipid in the organism (or dietary item)	*	Lognormal	McLeod et al. 2015
$P_{org,\ w}$	Proportion of water in the organism (or dietary item)	*	Lognormal	McLeod et al. 2015
X_{OC}	Fraction of OC in sediment	2.9±3.0	Lognormal	Szalinska et al. 2013
T	Mean of water annual temperature	13±3.8 C^O	Normal	Morrison et al. 1997
ρ_{sed}	Density of sediment	1.2 g/mL	Fixed term	McLeod et al. 2015
φ_{NLOM}	NLOM partitioning equivalent in organism compared to octanol	0.05	Fixed term	Debruyn and Gobas 2007

Calculated term using direct input term and referenced equation			
CO_2	Concertation of oxygen in water	$= 0.24 \cdot T + 14.04 \cdot 0.9$	Arnot and Gobas 2004
$C_{(p,w)}$	Concentration of contaminant in pore water	$= C_{sed}/(X_{OC} \cdot K_{OC} \cdot \rho_{sed})$	Arnot and Gobas 2004
E_w	Chemical absorption efficiency from water	$= 1/(1.857 + 155/K_{ow})$	Arnot and Gobas 2004
E_d	Chemical absorption efficiency from food	$= 1/(0.00000003 \cdot K_{ow} + 2)$	Arnot and Gobas 2004
G_d	Organism feeding rate	$= 0.022 \cdot BW^{0.95} \cdot Exp(0.06 \cdot T)$	Arnot and Gobas 2004
G_v	Organism gill ventilation rate	$= 1400 \cdot BW^{0.65}/CO_2$	Arnot and Gobas 2004
G_{growth}	Organism growth rate	$= 0.0005 \cdot BW^{-0.2}$	Arnot and Gobas 2004
Koc	Organic carbon-water partitioning coefficient	$= 0.35 \cdot K_{ow}$	Seth et al. 1999
$P_{org, NLOM}$	Proportion of NLOM in the organism (or dietary item)	$= 100\% - P_{org,lip} - P_{org,w}$	McLeod et al. 2015
$P_{(o,w), benthos}$	Fraction of respired overlying water by benthos	$= 100\% - P_{(p,w),benthos}$	Selck et al. 2012

Note: * denotes that values are congener specific, site specific, or species specific and available in the referenced articles.

Table A2. Field measurements for mean of sum PCB concertation and fraction of lipid content in the fish and their standard deviations (SD) from government fish advisory programs and GLIER surveys (1998-2016)

Species	# of obs	Sum PCB (ng/g wet wt)	SD	Lipid (%)	SD
Black Crappie	5	16.70	4.18	0.25	0.11
Bluegill Sunfish	8	47.37	35.68	0.35	0.42
Bowfin	7	23.59	21.05	0.46	0.46
Brook Silversides	11	88.81	80.36	2.47	0.74
Bullhead	71	13.49	27.64	0.69	0.65
Carp	238	1973.01	1741.90	9.48	5.75
Channel catfish	24	920.69	1031.85	3.92	3.65
Emerald Shiner	8	229.89	80.37	2.47	0.91
Freshwater Drum	64	269.17	248.65	4.05	1.54
Gar Pike	38	203.35	187.56	1.94	1.65
Gizzard Shad	19	101.06	82.79	2.81	1.80
Largemouth bass	33	165.05	584.85	0.53	0.40
Muskellunge	12	305.24	398.90	1.04	1.27
Northern Pike	40	39.81	43.62	0.37	0.25
Redhorse Sucker	30	338.80	276.29	2.30	0.74
Rock Bass	40	37.34	30.79	0.33	0.17
Round Goby	5	26.25	21.44	1.82	0.80
Smallmouth bass	41	86.17	135.38	0.72	0.74
Spottail Shiner	61	122.91	145.68	4.15	2.73
Walleye	198	892.81	1250.16	4.02	3.37
White Bass	152	308.63	205.95	2.50	1.84
White Perch	37	261.79	188.74	2.65	3.04
Yellow Perch	95	24.05	25.39	0.41	0.41

Table A3. Mean and standard deviation of lipid percentages in sport fish dorsal muscle measured in GLIER and government fish advisory program from 1998-2016. Note: lipid content information is not available for some fish samples (*n=218*).

Fish Species	Skin-off			Skin-on			Combined		
	# of obs	Lipid	SD	# of obs	Lipid	SD	# of obs	Lipid	SD
Black Crappie	5	0.25	0.11				5	0.25	0.11
Bluegill	16	0.63	0.67				16	0.63	0.67
Bowfin	7	0.46	0.46				7	0.46	0.46
Bullhead	71	0.69	0.65				71	0.69	0.65
Common Carp	88	4.58	4.48	130	8.31	4.53	218	5.29	4.70
Channel catfish	19	3.92	3.65				19	3.92	3.65
Freshwater Drum	59	3.10	5.04				59	3.10	5.04
Gar Pike	46	2.09	1.71				46	1.94	1.65
Gizzard Shad	19	2.81	1.80				19	2.81	1.80
Largemouth bass	8	0.84	0.52	15	0.36	0.17	23	0.53	0.40
Muskellunge	12	1.04	1.27				12	1.04	1.27
Northern Pike	41	0.44	0.49				41	0.44	0.49
Redhorse Sucker	1	7.57		30	2.30	0.77	31	2.47	1.19
Rock Bass	5	0.59	0.19	33	0.41	0.29	38	0.44	0.28
Smallmouth bass	28	0.78	0.81	13	0.58	0.56	41	0.72	0.74
Walleye	37	0.80	1.03	120	1.55	1.09	157	1.31	1.25
White Bass	4	0.88	0.41	16	2.91	1.84	20	2.50	1.84
White Perch	16	2.43	2.53				16	2.43	2.53
Yellow Perch	45	0.62	0.51	50	0.22	0.12	95	0.41	0.41

Table A4. Summary of fish length range, linear regression and performance matrix between log-observed PCB concentration and log-length and test of the spatial variation in length.

Fish Species	Obs	Length (cm)	SD	PCB (wet wt.) vs. Length		PCB (lipid Eq) vs. Length		Variation in Length between 6 river strata
				Slope SE	P-Value	Slope SE	P-Value	ANOVA P-Value
Black Crappie	5	88.2	92.4	-0.06	0.602	-0.10	0.594	NA
				0.10		0.16		
Sunfish	16	29.4	33.3	-0.55	0.129	-0.57	0.126	0.364
(Bluegill, Pumpkinseed)				0.34		0.35		
Bowfin	7	76.4	202.8	-4.36	0.247	-0.51	0.336	0.300
				3.33		0.47		
Bullhead	47	29.2	3.0	0.46	0.827	0.28	0.884	**0.076**
(Brown, Black)				2.10		1.91		
Common Carp	238	75.0	98.3	0.16	0.656	0.18	0.570	0.268
				0.37		0.31		
Channel catfish	24	74.1	106.9	1.60	0.114	0.85	0.326	0.260
				0.97		0.85		
Freshwater Drum	64	41.5	7.0	0.67	0.486	2.21	0.093	0.374
				0.95		1.28		
Gar Pike	38	107.4	280.8	-0.30	0.099	1.00	0.236	**<0.01**
				6.27		0.68		
Gizzard Shad	19	55.9	57.5	0.52	0.403	0.08	0.777	0.302
				0.61		0.28		
Largemouth bass	33	33.9	6.9	0.30	0.775	1.25	0.261	**<0.01**
				1.03		1.09		
Muskellunge	12	118.1	266.5	2.71	0.375	0.44	0.259	0.774
				2.92		0.37		
Northern Pike	40	64.1	109.6	0.67	0.158	0.72	0.107	0.996
				0.28		0.44		
Rock Bass	40	20.3	3.0	1.16	0.373	0.18	0.885	**0.045**
				1.29		1.23		
Sucker	11	44.9	8.0	3.02	0.037	1.08	0.628	0.000
(White or Redhorse)				1.24		2.16		
Smallmouth bass	41	32.6	8.8	0.91	0.224	0.82	0.383	**0.021**
				0.74		0.93		
Walleye	**198**	**46.8**	**9.8**	**2.38**	**0.012**	**1.92**	**<0.01**	**<0.01**
				0.63		**0.55**		
White Bass	**157**	**31.4**	**3.9**	**1.06**	**<0.01**	**0.96**	**0.02**	0.346
				0.37		**0.41**		
White Perch	**44**	**35**	**40**	**5.48**	**<0.01**	**0.44**	**0.05**	0.702
				0.68		**0.22**		
Yellow Perch	75	40	62	-0.01	0.967	-0.09	0.551	0.098
				0.14		0.14		

Table A5. Tests of the temporal trends in the sum PCB concentrations in fishes. If there are significant differences in PCB concentrations between sample years (p<0.05, ANOVA), the Mann-Kendall test with Sen's method was performed to determine the consistency in the temporal trend (p<0.05 of Sen's slope).

	Log (PCB wet wt.) vs. Year	Log (PCB lipid eq) vs. Year	Log (PCB wet wt.) vs. Year		Log (PCB lipid eq) vs. Year		Variation in year of capture between 6 river strata
	ANOVA (P-value)	ANOVA (P-value)	Sen's slope	P-value	Sen's slope	P-value	ANOVA (P-value)
Black Crappie	0.19	0.13	-	-	-	-	NA
Sunfish (Bluegill, Pumpkinseed)	0.54	0.53	-	-	-	-	0.86
Bowfin	**<0.01**	**<0.01**	-0.48	**0.08**	-0.71	**0.08**	0.20
Bullhead (Brown, Black)	**<0.01**	**<0.01**	-0.23	**<0.01**	-0.27	**<0.01**	**<0.01**
Common Carp	0.65	0.87	-	-	-	-	0.34
Channel catfish	0.31	0.93	-	-	-	-	**<0.01**
Freshwater Drum	**0.03**	**0.02**	-0.23	0.27	-0.22	0.25	0.25
Gar Pike	**0.02**	**<0.01**	-0.23	**0.02**	-0.22	**0.02**	**<0.01**
Gizzard Shad	0.77	0.93	-	-	-	-	0.13
Largemouth bass	0.39	0.78	-	-	-	-	0.21
Muskellunge	0.16	0.35	-	-	-	-	0.98
Northern Pike	0.07	0.46	-	-	-	-	0.09
Rock Bass	0.25	**<0.01**	-0.24	0.14	-0.13	0.19	0.16
Sucker (White or Redhorse)	0.75	0.26	-	-	-	-	0.09
Smallmouth bass	0.55	0.42	-	-	-	-	**<0.01**
Walleye	0.21	0.11	-	-	-	-	**0.01**
White Bass	0.55	0.98	-	-	-	-	**<0.01**
White Perch	0.06	**<0.01**	-0.10	0.31	-0.28	0.42	0.787
Yellow Perch	**<0.01**	0.078	-0.24	0.14	-0.13	0.19	**<0.01**

Table A6. Comparison of deterministic and uncertainty model performance using PCB congener concentrations in both wet weight basis (ng/g wet weight) and lipid equivalent basis (ng/g lipid eq). Performance matrixes include coefficient of determination values (R^2) of the linear regression between logarithmic-transformed estimated PCB concentrations against observed PCB concentrations in fish samples and the geometric mean of model bias and 95% confidence interval for the bias.

	River Segment	R-squared	Model Bias	95% CI	95% CI	*N*
	River Wide	31.8%	2.5	1.4	3.1	11467
Deterministic Model	2-Nation	53.1%	0.8	0.5	1.1	11467
PCB Congener (wet wt.)	4-Zone	52.3%	1.2	0.7	1.5	11467
	6-Zone	42.9%	1.6	1.0	1.9	11467
	River Segment	R-squared	Model Bias	95% CI	95% CI	*N*
	River Wide	36.8%	2.4	1.6	3.0	11467
Uncertainty Model	2-Nation	52.3%	1.3	0.8	1.6	11467
PCB Congener (wet wt.)	4-Zone	52.7%	1.9	1.2	2.4	11467
	6-Zone	47.6%	3.4	2.2	4.3	11467
	River Segment	R-squared	Model Bias	95% CI	95% CI	*N*
	River Wide	10.0%	2.4	0.8	3.0	7800
Deterministic Model	2-Nation	32.7%	1.7	0.7	1.3	7800
PCB Congener (Lipid Eq)	4-Zone	27.7%	1.6	0.6	1.2	7800
	6-Zone	29.3%	2.9	0.9	1.7	7800
	River Segment	R-squared	Model Bias	95% CI	95% CI	*N*
	River Wide	10.2%	2.3	1.5	3.5	7800
Uncertainty Model	2-Nation	29.6%	1.5	1.1	2.3	7800
PCB Congener (Lipid Eq)	4-Zone	26.9%	2.2	1.3	2.8	7800
	6-Zone	22.9%	3.7	2.2	4.8	7800

Table A7. Sum PCB concentrations that trigger fish consumption advisory and meal categories as outlined in the advisories issued by the Province of Ontario and State of Michigan. Ontario advisories are defined separately for the general population and sensitive population (i.e., women of child-bearing age and children younger than 15 years old). Michigan has a unified advisory for all populations, while the sensitive population is advised to avoid eating fish listed as "limited" (general public is recommended to eat 1 or 2 times each year listed as "Limited").

Meals/Month	Ontario General Population (ng/g)	Ontario Sensitive Population (ng/g)	Michigan All Population (ng/g)
32	<26	<26	NA
16	26-53	26-53	<10
12	53-70	53-70	10-20
8	70-105	70-105	20-30
4	105-211	105-211	30-50
2	211-422	NA	50-110
1	422-844	NA	110-210
0.5	NA	NA	210-430
Limited	NA	NA	430-2700
Do Not Eat	>844	>211	>2700

Table A8. The model-predicted fish consumption advisories and published fish consumption advice.

Location	Species	Model input fish size (cm)	Published advisory fish size (cm)	Published Public pop (meal/month)	Published Sensitive pop (meal/month)	2nation original Predicted Public pop (meal/month)	2nation original Predicted Sensitive pop (meal/month)	2nation blended Predicted Public pop (meal/month)	2nation blended Predicted Sensitive pop (meal/month)	2nation specific scale Predicted Public pop (meal/month)	2nation specific scale Predicted Sensitive pop (meal/month)
ON	**Black Crappie**[a]	21 ± 4	20-25	32	12	32	32	32	32	32	32
ON	**Sunfish**[a]	19 ± 10	20-25	16	4	16	16	16	16	16	16
ON	**Bowfin**[ab]	57 ± 4	50-55	8	4	8	8	8	8	8	8
ON	**Bullhead**[a]	30 ± 3	25 30	16	8	16	16	16	16	16	16
ON	**Carp**	57 ± 11	55-60	4	4	2	Do Not Eat	2	Do Not Eat	2	Do Not Eat
ON	**Channel Catfish**	50 ± 6	45 50	1	Do Not Eat	2	Do Not Eat	2	Do Not Eat	1	Do Not Eat
ON	**Freshwater Drum**	41± 8	40 45	4	Do Not Eat	2	Do Not Eat	2	Do Not Eat	2	Do Not Eat
ON	**Gar Pike**[c]	72± 10	70-75	4	Do Not Eat	2	Do Not Eat	2	Do Not Eat	2	Do Not Eat
ON	**Gizzard Shad**	32± 10	40 45	2	Do Not Eat	4	4	4	4	4	4
ON	**Largemouth Bass**	37± 5	35 40	8	4	4	4	4	4	4	4
ON	**Muskellunge**[ad]	82 ± 10	>75	12	4	2	Do Not Eat	2	Do Not Eat	2	Do Not Eat
ON	**Northern Pike**	55 ± 11	60-65	4	4	8	8	8	8	8	8
ON	**Sucker**	41 ± 5	40-45	8	8	8	8	8	8	4	4
ON	**Rock Bass**	20 ± 4	20 25	8	4	12	12	8	8	12	12
ON	**Smallmouth Bass**	24 ± 5	25-30	4	4	8	8	8	8	8	8
ON	**Walleye**	44 ± 11	40-45	4	4	8	8	8	8	8	8
ON	**White Bass**	31 ± 4	30 35	4	4	4	4	4	4	4	4
ON	**White Perch**	22 ± 3	20 25	2	Do Not Eat	4	4	8	8	4	4
ON	**Yellow Perch**	19 ± 6	20 25	8	8	16	16	16	16	16	16
MI	**Black Crappie**[a]	21 ± 4	Any size	4	NA[e]	2	NA	2	NA	8	NA
MI	**Sunfish**[a]	14 ± 4	Any size	8	NA	1	NA	1	NA	1	NA
MI	**Bowfin**	52 ± 9	NA	NA	NA	1	NA	8	NA	1	NA
MI	**Bullhead**	28 ± 3	Any size	4	NA	1	NA	8	NA	1	NA
MI	**Carp**	58 ± 8	Any size	Limited[f]	NA	Limited	NA	Limited	NA	Limited	NA
MI	**Channel Catfish**	53 ± 7	Any size	Limited	NA	Limited	NA	Limited	NA	Limited	NA
MI	**Freshwater Drum**	44 ± 4	Any size	Limited	NA	Limited	NA	Limited	NA	Limited	NA
MI	**Gar Pike**	64± 10	NA	NA	NA	Limited	NA	Limited	NA	Limited	NA
MI	**Gizzard Shad**	32± 10	Any size	Limited	NA	Limited	NA	Limited	NA	Limited	NA
MI	**Largemouth Bass**	31± 8	Any size	Limited	NA	Limited	NA	Limited	NA	Limited	NA
MI	**Muskellunge**[a]	82 ± 10	Any size	1	NA	Limited	NA	Limited	NA	Limited	NA
MI	**Northern Pike**[a]	64 ± 8	Any size	1	NA	0.5	NA	2	NA	0.5	NA
MI	**Sucker**	43 ± 6	<43	0.5	NA	0.5	NA	0.5	NA	Limited	NA
MI	**Rock Bass**	20 ± 3	Any size	4	NA	Limited	NA	4	NA	Limited	NA
MI	**Smallmouth Bass**	33 ± 10	Any size	Limited	NA	0.5	NA	1	NA	0.5	NA
MI	**Walleye**	50 ± 8	Any size	0.5	NA	0.5	NA	1	NA	0.5	NA
MI	**White Bass**	33 ±3	Any size	Limited	NA	Limited	NA	Limited	NA	Limited	NA
MI	**White Perch**	22 ± 3	Any size	Limited	NA	Limited	NA	Limited	NA	Limited	NA
MI	**Yellow Perch**	20 ± 4	Any size	4	NA	1	NA	1	NA	1	NA

[a], Published fish consumption advisory caused by non-PCB contamination (e.g., Hg or dioxin).

[b], OMECP advisory for bowfin is available for the Thames River near Lake St Clair.

[c], OMECP advisory for gar pike (longnose gar) is available for only the Grand River (below Dunnville Dam to Port Maitland).

[d], OMECP advisory for muskellunge is available for Lake St Clair.

[e], Michigan fish consumption advisory mainly focuses on the general public.

[f], Per Michigan fish consumption advisory, the sensitive population should avoid eating fish listed as "Limited"; the general public may safely eat one or two meals per year listed as "Limited".

Figure A1. Sediment/water fugacity ratios of PCBs versus log K_{ow} for the 26 PCB congeners. (Legend of river reach with a * indicates a significantly negative relationship between fsed/fw and LogKow at the 5% level.
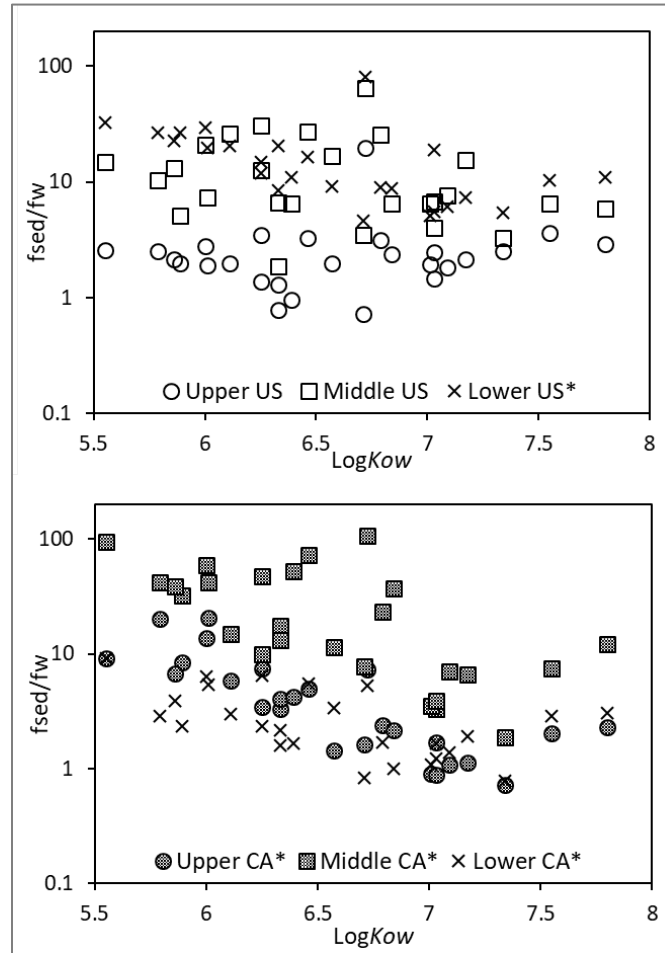
Figure A2. Comparison of deterministic and uncertainty model performance. Symbols of filled squares represent the R^2 for the linear regression between the logarithmic-transformed estimated PCB concentrations against the logarithmic-transformed observed PCB concentrations in fish samples; symbols of filled circles represent the geometric mean of model bias. Error bars represent the 95% confidence interval for the model bias. Panel a shows the validation result from the deterministic model using the sum PCB concentration in wet weight (ng/g wet weight); panel b shows the validation result from the uncertainty model using the sum PCB concentration in wet weight (ng/g wet weight); panel c shows the validation result from the deterministic model using the sum PCB lipid equivalent concentrations (ng/g lipid eq); panel d shows the validation result from the uncertainty model using the sum PCB lipid equivalent concentrations (ng/g lipid eq).
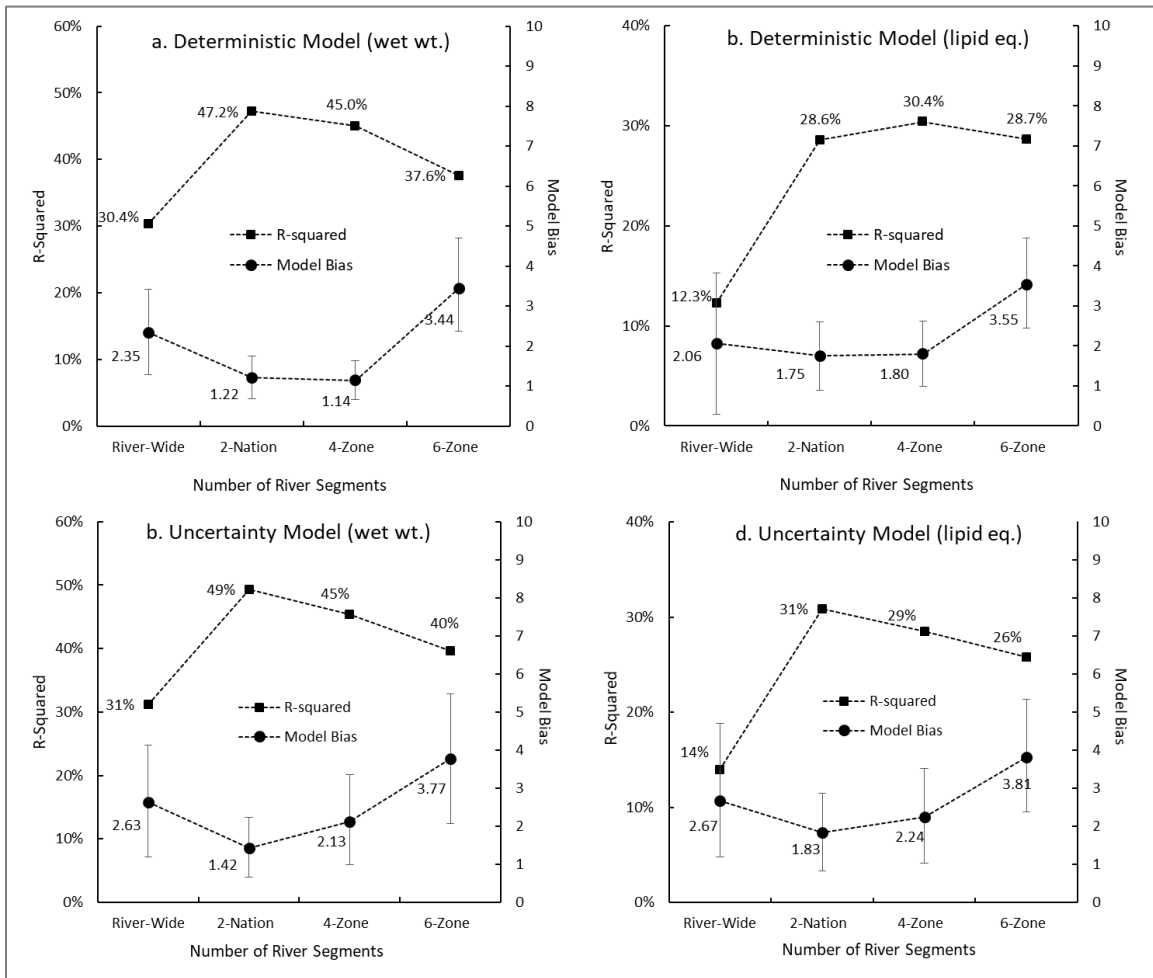
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