MEASURING AND MODELING THE EFFECT OF PCB BIOAVAILABILITY ON ACCUMULATION IN AQUATIC FOOD CHAINS

By

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ABSTRACT

Title of Document: MEASURING AND MODELING THE EFFECT OF PCB BIOAVAILABILITY ON ACCUMULATION IN AQUATIC FOODCHAINS

Hilda Fadaei Khoei, Ph.D., 2017

Directed By: Dr. Upal Ghosh
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The primary goal for remediation of sediments contaminated with polychlorinated biphenyls (PCBs) is the reduction of bioaccumulation in the aquatic food web, particularly in fish that is the source of exposure to top level predators and humans. While empirical results are available in the literature on bioavailability reductions after amendment of PCB-contaminated sediment with a strong sorbent like activated carbon (AC) or biochar, there is a lack of quantitative understanding on how reductions in sediment porewater and food concentrations impact accumulation in fish. Although passive sampling can measure freely dissolved concentrations accurately, there is a major gap in the utilization of fate and biouptake models that can use such measurements. . In addition, well-calibrated partitioning models based on accurate freely dissolved concentrations that can predict uptake by pelagic organisms are lacking. The primary objective of this research was to test the ability of frequently used bioaccumulation models to predict changes in fish uptake upon

amendment of AC sediment and use passive sampling inputs and additional studies to refine the predictions made by these bioaccumulation models.

Results from laboratory exposure studies with pelagic and benthic feeding fish indicate that by incorporating changes in porewater and overlying freely dissolved PCB concentrations in kinetic bioaccumulation models and by taking into account changes in food concentration it is possible to predict effectiveness of sediment remediation in reducing PCB uptake in fish. Assimilation efficiency of PCBs in the sediment were independently measured in a separate study and incorporated into the model. The modified model led to reasonable estimations of PCB uptake in the benthic feeding fish and was capable of predicting the dominant exposure pathways in the benthic and pelagic feeding fish as a result of their different feeding behaviour. Additionally, passive sampling measurements were linked to PCB accumulation in algae and zooplankton and resulted in refined models. Lastly, several scenarios were simulated to show the potential of a linked fate and biouptake model to capture the effect of different inputs.

This research presents a robust modeling framework that is able to predict uptake in fish after *in situ* remediation that alters bioavailability of PCBs in sediments with implications for risk assessment and management.

Dedication

To My Family

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I would like to thank my advisor, Dr. Upal Ghosh for all of his mentorship and guidance throughout my doctoral studies. His patience, knowledge, incredible insight into different subjects, and support have been invaluable for me and for my growth as a researcher, and were instrumental in my being able to conduct this research properly.

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I worked with several researchers during my doctoral program at UMBC and I would like to thank them all – those who were in transition to their next career step when I joined Ghosh's lab, those who shared a longer part of their UMBC experience with me, and those who joined when I was getting ready for my transition to the next step.

Many of these people helped me along the way and I learned a lot from each of them. This does not exclude my fellow graduate students at the Chemical, Biochemical, and Environmental Engineering Department. I would also like to extend my thanks to the department faculty and the staff at the Technology Research Center.

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Chapter 1: Introduction

Polychlorinated Biphenyls (PCBs): Legacy Contaminants of Concern

Polychlorinated biphenyls (PCBs) are synthetic organic chemicals that were commercially produced in the Unites States from the 1930s to the 1970s for industrial applications. The backbone of the chemical structure is a biphenyl molecule, consisting of two hexagonal rings of carbon atoms connected by a carbon-carbon bond. PCBs have between 1 and 10 chlorine atoms substituting for hydrogen atoms on the biphenyl rings. Based on different number and positions of the chlorine atoms, 209 congeners can be formed (NRC, 2001).

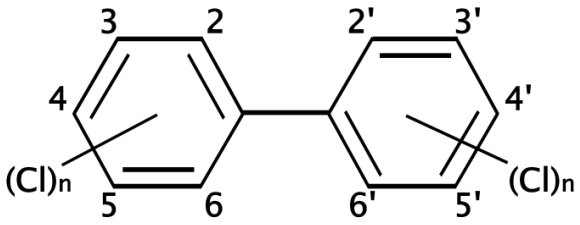

Figure 1.1. PCB structure

Due to low reactivity and high chemical stability, PCBs were used widely as hydraulic fluids, pump oils and insulating fluids in electrical transformers and capacitors (NRC, 2001). PCBs were also used as adhesives, dyes, inks, surface coatings, and flame retardants (Tiedje et al., 1993). These carefully selected properties led to long-term persistence of PCBs in the environment (Sinkkonen and Paasivirta, 2000). The widespread occurrence of PCBs and their potential adverse effects on the environment led to a ban on all uses of PCBs in 1979 by the U.S.

Environmental Protection Agency (U.S. EPA) and establishment of federal regulations on manufacture and disposal of these chemicals citing their persistent, bioaccumulative, and toxic nature (EPA, 1979).

As a result of past human activities, PCBs are ubiquitously found at high concentrations in marine and freshwater sediments (Petrović et al., 2001). Hudson River in New York, Commencement Bay in Washington, and New Bedford Harbor in Massachusetts are examples of sites listed on the National Priorities List (NRC, 2001).

When released to the water column, most of PCB molecules associate with the organic matter suspended in the water column due to their hydrophobicity (Luthy et al., 1997). The strong association between PCBs and organic matter typically leads to legacy accumulation in the impacted sediment beds. PCBs in polluted sediments can be taken up by pelagic or benthic organisms through two major pathways: absorption from water and ingestion of contaminated food and sediment (Arnot and Gobas, 2004b). Due to their hydrophobic nature, PCBs accumulate in the organism's lipid tissue (Ross, 2004). Bioaccumulation of PCBs leads to increasing body burdens of PCB for higher trophic level organisms, this phenomenon is known as biomagnification (McLeod et al., 2015).

The first adverse health effects of PCBs were recorded in the 1930s. PCBs have been shown to cause cancer in animals and have a number of effects on immune, nervous, and reproductive systems (Pieper, 2005). Epidemiological studies in humans provide evidence for carcinogenic effects of PCBs (Pieper, 2005). Bioaccumulation

of PCBs in aquatic and terrestrial food chains became recognized as a concern in the early 1960s (Walker, 1987), which led to several studies focused on understanding bioaccumulation processes and also remediation approaches that can reduce the risk posed by these chemicals to wildlife and humans. The US Environmental Protection Agency reports 0.02 and 0.002 ppm PCB concentrations in fish as action levels and tolerances for recreational and subsistence fishers, respectively (USEPA, 2000). To reduce exposure, many states have established consumption advisories to include large water bodies such as the Chesapeake Bay (MDE, 2014).

Passive Sampling

Accurate measurement of aqueous concentrations of hydrophobic organic compounds (HOCs) with conventional methods is challenging due to the association of HOCs with colloidal and dissolved organic matter. Conventional methods are also labor intensive and indicate only a one-time grab measurement (USEPA, 2012). Also, because HOCs are present in water at trace levels, large volumes of water need to be collected for direct measurement (Vrana et al., 2005). To address this challenge, passive sampling techniques have been developed as an innovative approach to measure HOC concentrations in the aqueous phase. Passive samplers are essentially pieces of organic polymers, including polyethylene (PE) and polyoxymethylene (POM) sheets and polydimethylsiloxane (PDMS)-coated solid phase micro-extraction (SPME) fibers. As shown in Figure 1.2, passive samplers operate in three regimes: kinetic, intermediate, and near equilibrium (Mayer et al., 2003). Sampling under the kinetic scenario applies at relatively short sampling times and targets a time-specific concentration that must be corrected to the equilibrium condition (Lydy et al., 2014).

Sampling under the near equilibrium regime applies at relatively long sampling times and requires polymer-water partition constants to deduce C_{medium} from $C_{sampler}$ (Mayer et al., 2014; Mayer et al., 2000).

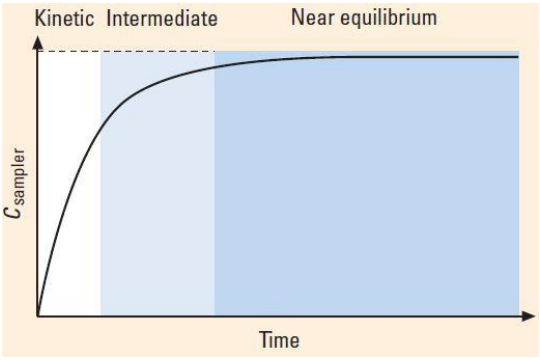

Figure 1.2. Generalized uptake profile for a passive sampling device (Mayer et al., 2003).

Sampling under the near equilibrium condition is preferred. However, mass transfer rates in sediment porewaters are slow and it takes a long time for equilibrium to occur between the samplers and aqueous phase (Booij et al., 1998). To address this issue, Booij et al. (2002) proposed spiking passive samplers with known amounts of HOC compounds, called performance reference compounds (PRCs), which do not ubiquitously exist in the environment. Since both adsorption and desorption, in samplers like PE, are governed by the same mass transfer processes, PRCs can be used to correct for non-equilibrium (Booij et al., 1998).

Currently passive samplers are used in surface waters (Booij et al., 2003; Fernandez et al., 2014), sediments (Booij et al., 2003; Fernandez et al., 2009), and

even for determination of contaminant loading into wastewater treatment plants (Harman et al., 2011). Deployment of passive samplers provides a time-averaged response. Additionally, passive sampling is a more cost effective method of measuring freely dissolved concentration of PCBs and passive sampler-based information can be used to better understand contaminant concentrations that result in real exposures and risks at Superfund sites (EPA, 2012). USEPA accepts the use of passive samplers as a reliable and accurate tool for measuring freely dissolved aqueous concentrations. In 2012, the USEPA published a set of guidelines for using passive samplers to monitor dissolved HOCs being released from sediment contamination (EPA, 2012). In addition, practical guidance documents have been developed to provide users of passive sampling with information on the various aspects of passive samplers, including laboratory, field, and analytical procedures involved in the application of the technology to evaluate contaminated sediments (Ghosh et al., 2014).

Activated Carbon Amendment to Reduce Bioavailability

Recent findings indicate that the freely dissolved concentration of PCBs in porewater is the driving force for transport to the water column and bioaccumulation in the food chain. Porewater PCBs can be attenuated by the presence of natural or anthropogenic black carbon and the binding of these chemicals to carbon particles can reduce the bioavailability to organisms (Luthy et al., 1997; NRC, 2003; Reichenberg and Mayer, 2006). Based on this emerging understanding of PCB bioavailability in sediments, amendment of contaminated sediment with sorbent activated carbon (AC) has gained attention in recent years as a nonremoval, *in situ* remediation technology.

AC amendment has been demonstrated to reduce porewater concentration of PCBs and reduce biouptake by deposit and filter feeders (Cho et al., 2009; Ghosh et al., 2011; Sun and Ghosh, 2007; Zimmerman et al., 2004). Successful laboratory and pilot-scale studies described in Ghosh et al. (2011) have led to an emerging acceptance of this new technology for sediment remediation as described in a recent U.S.EPA directive on *in situ* amendments (EPA, 2013b) and U.S.EPA proposed remedial action for the Superfund site in Housatonic River (EPA, 2014b).

The State of Bioaccumulation Models

The current practice in remedial investigations at PCB-contaminated sediment sites relies on empirical or literature-based partition constants to calculate porewater concentrations from bulk sediment concentrations (e.g., Upper Hudson River (Anchor QEA, 2010); Housatonic River (EPA, 2004); Grasse River (Alcoa, 2010b)). However, partition constants are notoriously unreliable and easily vary by an order of magnitude or more. The uncertainty of partition constants is magnified when sediments are amended with AC or other strong sorbents in an effort to reduce porewater concentrations and bioavailability. The uncertainty in partition constants prevents models from employing accurate descriptions of the processes affecting contaminant flux from porewater to the overlying water column and contaminant accumulation in the aquatic organisms. Bioaccumulation models are available that can predict uptake of hydrophobic organics in fish through water and food. These models are based on calibrated uptake rate constants, and site-specific values of chemical concentrations in water, in sediment, and in prey items (Arnot and Gobas, 2004b; Connolly, 1991). These models have been generally effective in predicting

uptake in large contaminated systems and have been used to forecast contamination levels achievable through natural attenuation and a combination of natural attenuation and removal or capping remediation approaches (Miller et al., 2011). However, the capability of these bioaccumulation models to predict changes after *in situ* sediment amendment is questionable and there are key uncertainties that need to be addressed especially when bioavailability in sediments is altered. The primary mechanism of *in situ* treatment with sorbents is the alteration of partitioning in sediments. Thus, accurate prediction of *in situ* treatment effectiveness requires proper measurement of the freely dissolved concentration in the sediment porewater and surface water and use of those measures in adequately calibrated bioaccumulation models. Furthermore, the current bioaccumulation models that have been applied to natural water systems are not suitable for benthivorous fish that resuspend (Scheffer et al., 2003) and ingest considerable amounts of sediments when feeding (Tolonen et al., 2000). Therefore, it is necessary to investigate changes in PCB uptake through sediment ingestion when total PCB concentration in the sediment remains constant but bioavailability is altered. Moermond et al. (2004) estimated the PCB assimilation rate from sediment (product of assimilation efficiency (AE) and ingestion rate) for carp from the dry to wet weight ratio of sediment and the food ingestion rate constant. However, their study focused on a natural lake system that did not explore changes that happen after bioavailability manipulation in sediment. Gaillard et al. (2014) examined the relative bioavailability of untreated PCB-impacted sediments with 0.3% black carbon compared with the bioavailability of PCBs carried by canola oil to carp but did not measure AE of sediment-bound PCBs.

Ingestion of contaminated food is an important uptake pathway that is taken into account by the commonly used PCB bioaccumulation models. Bioaccumulation factor (BAF)- K_{OW} correlations have been reported in the literature to estimate the PCB body burden in small organisms, such as algae and zooplankton (Borgå et al., 2005; Fisk et al., 2001; Hoekstra et al., 2002), which serve as food to the pelagic food web. However, most of these studies measured PCB water concentrations with XAD columns, which tend to overestimate the freely dissolved PCB concentration. Along with freely dissolved concentrations, XAD column measurements also include PCBs associated with dissolved organic carbon (DOC). However, a few of the aforementioned studies have adjusted for DOC based on expected sorption to DOC (Borgå et al., 2005). In addition, most of these reported BAF values are based on measurements in grab biota samples that are collected from the field, which can include suspended solids that can lead to overestimation of PCB levels.

Refining and Validating Bioaccumulation Models

One way to improve the predictions made by the bioaccumulation models is to use freely dissolved PCB concentrations, measured directly and accurately, as inputs to more refined models. If freely-dissolved concentrations are measured directly with techniques such as passive sampling, instead of being estimated from bulk sediment concentrations, when used as input to the bioaccumulation model can incorporate bioavailability changes in sediment PCBs. By focusing on the exposure, pathways to fish it may be possible to perform timely assessments of a remedy progress and mechanistically explain observed changes. Previous work by Werner et al. (2009) showed that sediment porewater PCB data can be used to predict uptake by

freshwater and marine benthic organisms. Partitioning of HOCs to passive sampling devices has proven to be a robust method for measuring freely dissolved concentrations in sediment porewater (Ghosh et al., 2014; Jonker and Koelmans, 2001; Lohmann, 2011; Mayer et al., 2003). Furthermore, more accurate partitioning models that can predict uptake by pelagic organisms, i.e. algae and zooplankton that serve as food to fish, can be developed by using passive sampler measurements for estimating aqueous concentration of PCBs. With a validated modified model for bioaccumulation in fish, which also includes the sediment ingestion pathway, timely assessments can be performed to monitor a remedy's progress upon engineering intervention like AC amendment.

Knowledge Gaps and Research Motivation

Ecological and human health impacts of bioaccumulative contaminants like PCBs are primarily manifested through accumulation of the compounds in higher trophic level organisms like fish that are consumed by humans and top predators in the ecosystem. Beneficial impacts of a remediation technology on fish are also easier to communicate to larger audiences and stakeholder groups. However, changes in fish are slow to manifest as a consequence of a remedial action and often one has to wait for several years to observe such change. To make timely assessments of remediation progress, one alternative is to perform appropriate measurements that indicate changes in key pathways of exposure to fish. Although some advances have been made recently to assess porewater concentrations using passive sampling techniques, which respond more rapidly to a remedial action, relationship of such measures to accumulation in fish has not been demonstrated. Also, there is a major gap in the

development and utilization of bioaccumulation models that can use passive sampling measurements and quantitatively link those measurements to uptake pathways and predict eventual changes in fish concentrations. By the use of innovative passive sampling approach, the partitioning constants that have been reported in the literature for the organisms at lower trophic level i.e. algae and zooplankton can be modified and improved. Once obtained, these modified BAF values will provide a more accurate estimation of PCB levels in the fish diet, which is one of the input parameters of bioaccumulation models.

Research Objectives

The overall objective of this dissertation research is to use refined sampling methods to assess PCB uptake pathways in fish, algae and zooplankton, improve biouptake model parameters for fish, and enhance our ability to predict changes in PCB biouptake in fish, especially after implementing a sediment remedy to reduce PCB availability to pore water. Specific knowledge gaps and associated research objectives are as follows:

1. There is a lack of quantitative information on how reductions in sediment porewater concentrations and reduced uptake at the base of the food chain impact the uptake in fish. While much work has been done on benthic invertebrates (McLeod et al., 2008; McLeod et al., 2007; Millward et al., 2005; Sun and Ghosh, 2007; Tomaszewski et al., 2007), the effect of sorbent amendment on pelagic invertebrates is not known. Therefore, if the previously reported BAF-K_{OW} models, which did not use passive sampling techniques to quantify aqueous concentrations, get revised, they can serve as a predictive tool to estimate uptake by algae and zooplankton either prior

to or after sediment AC amendment. Being able to track changes that will occur in the benthic and pelagic food web pathways upon amendment of a site with AC is key to our understanding of how treatment reduces biouptake in fish. Therefore, a key question to answer is: *How can passive sampling improve the prediction of PCB uptake in algae and zooplankton?*

2. Several researchers have devoted effort towards the development and improvement of food chain models. While these models have been generally effective in predicting uptake in large contaminated systems, the ability to predict changes after implementation of engineered remediation schemes is questionable and there are key uncertainties that need to be addressed when bioavailability in sediments is altered. For example, the frequently-used Arnot and Gobas (2004b) bioaccumulation model does not account for incidental sediment ingestion by fish. Based on my initial work, assimilation efficiency of sediment-bound PCBs has been identified as one of the parameters that needs to be accurately characterized to estimate uptake through sediment ingestion, especially for benthic feeding fish. However, the sediment assimilation efficiency values that have been reported in the literature are for benthic invertebrates. Also, previous studies on fish have focused on measuring fish assimilation efficiency from PCB-contaminated food (Burreau et al., 1997; Fisk et al., 1998; Gobas et al., 1993; Niimi and Oliver, 1983; Stapleton et al., 2004) and not PCBs in contaminated sediment. This gap leads to the following research question: *What is the assimilation efficiency of sediment-bound PCBs in fish and how does it change after AC amendment?*

3. Since ongoing PCB sources can affect the success of active remediation techniques as well as the extent of natural recovery, there is a need for combining fate and transport models, which can capture the effect of external PCB loads (Connolly, Rhea et al. 1999, SERDP 2012), with bioaccumulation models. Once validated, such models can also be used as a reliable means of back-calculating the AC amendment dose required to achieve a desired endpoint in recovery of fish tissue PCB levels. With all the above, the third research question to answer is: *How can an appropriately calibrated bioaccumulation model be coupled with a fate and transport model to evaluate effects of ongoing PCB inputs on fish recovery after remedy?*

Outline of the Dissertation and Contributions

Objectives 1 through 3 are addressed in chapters 2, 3, 4, 5, and 6, each written as a stand-alone manuscripts that have either been published or are in the process of submission to a peer-reviewed journal. These objectives were addressed through a series of laboratory aquaria experiments and mathematical modeling.

Chapter 2 provides my initial work exploring how PCB sorption in sediments affected exposure pathways and bioaccumulation in fish. The effectiveness of existing bioaccumulation models in predicting changes in PCB bioaccumulation in fish after *in situ* treatment of sediment with AC was evaluated. The first experiment was performed using zebrafish as the laboratory test species. The modeling effort of this work utilized passive sampling data as input to the bioaccumulation model. The experimental work was conducted at the Institute of Marine and Environmental Technology (IMET) facility with help from Dr. Allen Place's team. The team was responsible for maintaining the fish, sampling the fish and preparing the fish samples

for analysis. My contributions to the work included preparation of the experiment material, sample analysis, data interpretation, performing the model predictions, and writing the manuscript which was published in *Environmental Science and Technology* in 2015.

PCB accumulation in fish is influenced by many factors, such as bioavailability, growth, foraging behavior, movement, as well as PCB concentrations in water, in sediment, and in prey items. The second study, presented in **Chapter 3**, aimed at investigating how pelagic and benthic feeding fish respond to AC treatment by using mummichog (*Fundulus heteroclitius*) and catfish (*Corydoras aeneus*) in laboratory aquaria experiments. PCB exposure through contaminated food was introduced as an exposure pathway in this experiment, creating a more complex exposure compared to the first fish experiment. The results indicated the importance of accurately calibrating the sediment ingestion pathway for benthic feeding fish. The experimental work was conducted at the IMET facility and our collaborators at IMET were responsible for maintaining the fish, sampling the fish as well as preparing the fish samples for analysis. My contributions to the work included preparation of the experiment material, sample analysis, data interpretation, and writing the manuscript which is intended to be submitted for publication.

As part of the modeling work in Chapter 3, significant data gaps were identified which breache the integrity of bioaccumulation models to predict uptake through the sediment ingestion pathway. For example, there are no empirical data on how sediment remediation with AC impacts uptake in a fish through sediment

ingestion (especially for benthic-feeding fish). Therefore, research on dietary assimilation efficiencies (AEs) measured for PCBs in fish that were fed four experimental diets was undertaken and is reported in **Chapter 4**. Diets consisted of PCB-spiked earthworms, untreated sediment mixed with earthworms, AC-treated sediment mixed with earthworms, and AC mixed with earthworms. Fish exposure studies were conducted at the IMET facility by our IMET collaborators. I was responsible for the experiment design and material preparation. I interpreted the results and wrote the manuscript that has been published in *Environmental Toxicology and Chemistry*.

Fish exposures in Chapters 2 and 3 used well-characterized food as inputs to the fish. However, in a real field situation, the bioaccumulation model will need to accurately predict the concentrations of natural food items like algae and zooplankton for the pelagic feeding fish. The objective of **Chapter 5** is to utilize passive sampling techniques to refine measurement of aqueous PCBs, aiming at improving BAF-K_{OW} correlations for algae and zooplankton through laboratory exposure studies. I was responsible for designing and conducting the experimental work presented. I interpreted the results and wrote the manuscript which is intended to be submitted to *Environmental Toxicology and Chemistry*.

To investigate how ongoing PCB sources will exert control over the success of active remediation efforts in terms of fish recovery at a site, first the capability of existing bioaccumulation models to predict changes observed when PCB bioavailability in sediment is reduced was tested. In **Chapter 6**, several simulations were conducted using a fate model and the modified bioaccumulation model

developed from this research to evaluate the recovery of fish under different scenarios. The simulation results highlight the potential of the bioaccumulation model to be used as a scenario-testing tool and to be applied for solving engineering challenges.

Chapter 7 summarizes the contributions of this research to risk assessment and remediation efforts in terms of predicting efficacy of different remedial alternatives on the recovery of aquatic species and informing a decision on the dose of amendment that is needed to achieve target levels in fish tissue.

Chapter 2: Effect of PCB Bioavailability Changes in Sediments on Bioaccumulation in Fish

Hilda Fadaei, Aaron Watson, Allen Place, John Connolly, and Upal Ghosh
Environmental Science and Technology, Vol. 49, No. 20, pp. 12405–12413, 2015

Introduction

Polychlorinated biphenyls (PCBs) in polluted sediments can be taken up by pelagic or benthic organisms through two major pathways: absorption from water and ingestion of contaminated food and sediment (Arnot and Gobas, 2004b). Recent findings indicate that the freely dissolved concentration of PCBs in porewater is the driving force for transport to the water column and bioaccumulation in benthic organisms. Porewater PCBs can be attenuated by the presence of natural or anthropogenic black carbon (BC) and the strong binding of these chemicals to BC can reduce the bioavailability to benthic organisms (Luthy et al., 1997; NRC, 2003; Reichenberg and Mayer, 2006). Based on this emerging understanding of PCB bioavailability in sediments, amendment of contaminated sediment with sorbent activated carbon (AC) has gained attention in recent years as an *in situ* remediation technology. AC amendment has been demonstrated to reduce porewater concentration of PCBs and reduce biouptake by deposit and filter feeders (Cho et al., 2009; Ghosh et al., 2011; Sun and Ghosh, 2007). Successful laboratory and pilot-scale studies (Ghosh et al., 2011) have led to an emerging consideration of this new technology for sediment remediation as described in a recent USEPA directive on *in situ* amendments (EPA, 2013) and U.S.EPA proposed remedial action for the Superfund site in Housatonic River (EPA, 2014a). While there is general agreement that sorbent amendments reduce bioavailability of PCBs to the food chain, there is a lack of

quantitative understanding on how reductions in sediment porewater concentrations and reduced uptake at the base of the food chain impact accumulation in fish.

Food chain models are available that can be used to predict uptake of PCBs in a range of aquatic animals. However, there is limited knowledge of the ability of food chain models to predict PCB levels in fish after AC-treatment of the sediment either in laboratory or field settings. A common practice in remedial investigations at PCB contaminated sediment sites involves using biota-sediment accumulation factors (BSAFs) to calculate contaminant concentrations in benthic invertebrates from bulk sediment and empirical or literature-based partition constants to calculate porewater concentrations from bulk sediment concentrations (e.g., Upper Hudson River (Anchor QEA, 2010); Housatonic River (EPA, 2004); Grasse River (Alcoa, 2010b)). However, BSAFs and partition constants are notoriously unreliable and have a wide range of variability (Cornelissen et al., 2005; Lohmann et al., 2005). This uncertainty is accommodated by adjusting other model parameters as necessary to calibrate the model to contaminant concentrations measured in the water column and fish. The uncertainty of BSAFs and partition constants is magnified when sediments are amended with AC or other strong sorbents in an effort to reduce porewater concentrations and bioavailability. If accurate freely dissolved porewater and overlying water concentrations of PCBs can be measured directly, or computed, and used as inputs in bioaccumulation models, changes in biouptake resulting from sorbent amendment may be predicted more reliably. Experimental validation of this approach for predicting changes in PCB uptake by fish can lead to credible models that allow quick assessment of remediation progress by monitoring the critical

exposure pathways to fish i.e. food ingestion, porewater, and overlying water. Passive sampling can be a robust method for measuring freely dissolved concentrations in water, especially for strongly hydrophobic compounds like PCBs (Lohmann, 2011; Mayer et al., 2003). Previous work by Werner et al. (2010) showed that sediment porewater PCB data can be used to predict uptake by freshwater and marine benthic organisms.

A recent study by Kupryianchyk et al. (2013) investigated the effect of different AC treatments on reducing bioavailability to fish as well as the potential side effects of the treatment. The results showed reductions in PCB uptake by macroinvertebrates and fish in systems treated with either granular or powdered AC, with greater uptake reduction in the latter case. That study, however, did not attempt to explain the observations using a mechanistic biouptake model that can be used to link bioavailability changes in sediment to reduction of uptake in fish.

In the present study, we report results of a laboratory aquarium study where we evaluated the effect of *in situ* treatment of sediment with AC on PCB accumulation in fish. The objectives of this study were to evaluate whether previously reported results of PCB bioavailability reduction in benthic invertebrates is also observed in fish and to test existing approaches of modeling PCB uptake in fish to predict changes observed when the sediment is treated with AC. A passive sampling approach was used to directly measure freely dissolved PCBs in porewater and surface water. Ultimately, a sensitivity analysis was performed to serve as a guide for identifying the crucial parameters of the model that need to be measured accurately to reduce uncertainty in the model predictions.

Materials and Methods

Sediment Source

The laboratory exposure study was performed using three types of sediment: clean sediment, PCB-impacted sediment, and PCB impacted sediment treated with AC in the lab. The clean sediment was obtained from the Rhode River (RR) in MD, USA. PCB impacted sediment was obtained from near-shore area outside of the activated carbon treatment areas of Grasse River (GR), NY (Beckingham et al., 2013). Coal-based fine granular activated carbon (Carbsorb 75-300 μm; Calgon Carbon) was added to sediments at a target dose of 4.5% by dry weight.

Test Organisms

Zebrafish (*Danio rerio*, 8-12 week old juveniles) was used as model species to understand uptake and was cultivated in-house at the Institute of Marine and Environmental Technology. Fish were fed with fish-meal free, low PCB, plant protein based food flakes at 3.5 percent of their body weight per day, which was adequate to maintain the fish at average growth.

Measurement of Aqueous Concentration

76 μm-thick polyoxymethylene (POM) passive samplers were pre-cleaned via an ultrasonic extraction using 50% acetone in hexane, air-dried under a fume hood for 12 hours (Hale et al., 2010), and cut into strips with mass ~ 0.5 g. Aqueous PCB concentration was calculated from PCB concentration in the sampler based on K_{POM} values reported by Hawthorne et al. (2009).

Aquarium Setup

Four liters of sediment was added to triplicate 38-L glass covered fish tanks and allowed to settle and consolidate for a few days in static water. The amount of sediment was estimated based on sediment height in the aquaria and surface area of the tanks. Tanks were arranged in a parallel flow configuration and fed with recirculating, dechlorinated tap water at a recirculation rate of 8 gal/d (Figure 2.1). Passive samplers were introduced in the water column and in sediment in each aquarium and 10 individuals of zebrafish were added to each tank. The chemical composition of the water (pH, conductivity, and alkalinity), ammonia and nitrite levels were monitored throughout the experiment. pH and conductivity were measured using a Horiba U-22 multiparameter probe. Alkalinity, ammonia, and nitrate were measured with water quality test kits (Hach Co.). Each aquarium was equipped with a heater to maintain the water temperature uniformly at 28 °C, the optimal growth temperature for zebrafish, in all tanks. Tanks were equipped with air stones to maintain adequate oxygen level in the water. A photo period of 14 hours of light and 10 hours of darkness was maintained in the laboratory. The water drained from the tanks was collected in two separate sumps. An activated charcoal bag was placed in each sump to adsorb PCBs released from the tanks and prevent cross contamination by recirculating water.

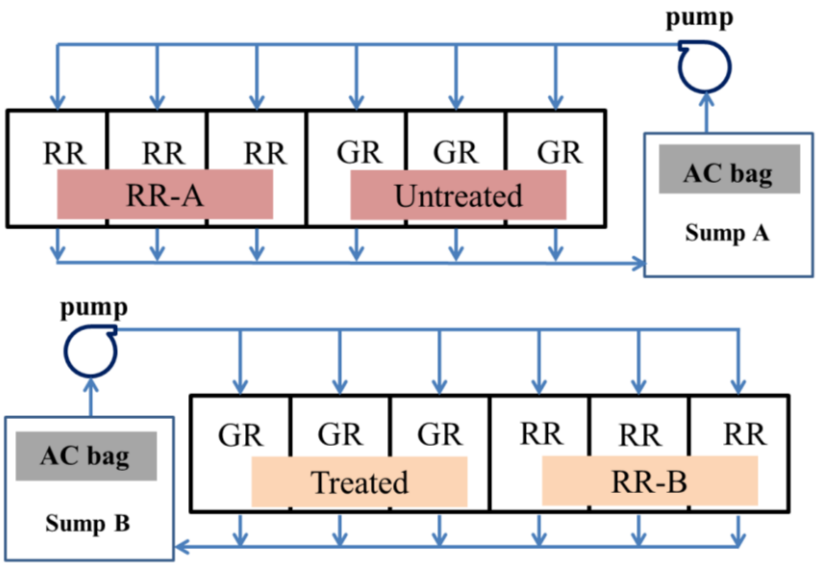

Figure 2.1. Aquaria setup to study the uptake of PCBs in fish. RR: clean Rhode River sediment; GR untreated: PCB impacted sediment from Grasse River; GR treated: PCB impacted sediment from Grasse River mixed with 4.5% AC in the laboratory.

Sampling and Analysis

Following 45-day and 90-day exposures, passive samplers were removed from the tanks, rinsed with deionized water and wiped dry. Sediment samples were collected from the tanks at the start of the experiment. Sediment and passive samplers were extracted in hexane/acetone (1:1, v/v), cleaned up, and analyzed for PCB congeners in a gas chromatograph with electron capture detection as described in Beckingham and Ghosh (2011). Five fish were sampled at the end of each time interval, sacrificed using dry ice, and were lyophilized and frozen until analysis. Fish tissue was ground with anhydrous sodium sulfate and extracted with hexane and acetone mixture (1:1, v/v) following method SW846 3550C. The lipids were removed by treating with concentrated sulfuric acid. Further cleanup was performed by treating the extract with activated copper and passing through a 3% deactivated florisil and

acidified silica gel column. The eluate was concentrated by nitrogen evaporation and analyzed for PCB congeners as described above. Lipid content in zebrafish tissue was measured in separate samples in triplicate using the gravimetric method described by Harvey et al. (1987).

Total Organic Carbon (TOC), Black Carbon (BC) and Activated Carbon (AC) Analyses

TOC was determined by thermal combustion method on a Shimadzu TOC analyzer with a solids sample module (TOC-5000A and SSM-5000A). BC and AC contents of the sediment were measured by wet chemical oxidation pretreatment (Grossman and Ghosh, 2009).

Observed Sediment-Water Partitioning Constant (K_d) Calculation

Measured PCB concentration in the sediment (ng/kg) and freely dissolved porewater PCB concentration measured with passive sampling (ng/L), were used to calculate K_d from equation 1:

$$K_d = \frac{C_S}{C_W} \quad (1)$$

Modeling Approach

PCB concentration in sediment porewater

The effect of AC on aqueous partitioning was predicted by modeling sorption to organic carbon (OC), native BC, and applied AC. Sorption to native BC was assumed to be linear (Werner et al., 2010) and sorption to AC was described by a Freundlich isotherm. The first modeling effort ignored the role of the native black carbon pool in partitioning of PCBs (equations 2 and 3):

$$K_d = f_{OC}\, K_{OC} \quad (Untreated) \qquad (2)$$

$$K_d = f_{OC}\, K_{OC} + f_{AC} K_f {C_w}^{n-1}\, (Treated) \qquad (3)$$

In the second approach, the black carbon pool was included (equations 4 and 5):

$$K_d = (f_{OC} - f_{BC})\, K_{OC} + f_{BC} K_{BC} \qquad (Untreated) \qquad (4)$$

$$K_d = (f_{OC} - f_{BC})\, K_{OC} + f_{BC} K_{BC} + f_{AC} K_f {C_w}^{n-1} \qquad (Treated) \qquad (5)$$

where C_W is the porewater concentration (ng/L), f_{OC}, f_{BC}, and f_{AC} are the fractions of OC, native BC, and AC in sediments, K_{OC} and K_{BC} are water-sorbent distribution constants for OC and BC, respectively, with units of (L/kg sorbent). K_d in equations 2 to 5 was defined as the ratio of measured PCB concentration in the sediment to unknown porewater concentration of PCB. C_W values that satisfy equations 2 to 5 were calculated. Modeled K_d was calculated from the predicted C_W (ng/L) and measured C_S (ng/kg) values.

K_{OC} (L/kg OC) values for PCB congeners were estimated using equation 6 (Werner et al., 2010). To use this empirical correlation, the octanol-water partition constant (K_{OW} (-)) was obtained from Hawker and Connell (1988).

$$\log(K_{OC}) = 0.74\, \log(K_{OW}) + 0.15 \qquad (6)$$

As reported by Werner et al. (2010), native black carbon adsorption of PCBs is linear below the microgram/L concentration range. K_{BC} (L/kg BC) was estimated using the following correlation with K_{OW} (Werner et al., 2010):

$$\log(K_{BC}) = 0.91\ \log(K_{OW}) + 1.37 \qquad (7)$$

n and K_f values used in our modeling approach were obtained from Gomez-Eyles et al. (2013), where the same coal-based fine granular activated carbon was used in the absence of sediment. Since natural organic matter in the sediment environment attenuates adsorption of PCBs to AC, a reduction factor of 16 was applied to the obtained K_f values (Werner et al., 2006).

PCB concentration in fish

Two approaches were taken in this study to estimate the PCB residue in fish. The first was the steady-state approach assuming thermodynamic equilibrium between water and fish lipid. K_{lipid} (L/kg lipid), the lipid-water equilibrium partitioning constant of PCBs, was used as a simplistic model to predict C_{lipid} (µg/kg lipid), using $C_{W,O}$ (µg/L). The overlying water concentrations used as inputs to both equilibrium and kinetic models were measured by passive sampling. K_{OW} (L/kg octanol) can be used as a surrogate to quantify chemical partitioning between the overlying water and the lipid fraction (Werner et al., 2010).

$$C_{lipid} = K_{lipid}\, C_{W,O} \qquad (8)$$

The second approach was the kinetic approach. The two frequently used bioaccumulation models ((Arnot and Gobas, 2004b) and (Connolly, 1991)) were used to generate predictions, and were compared to the measured data. Environmental properties (including measured freely dissolved PCB concentrations in the overlying water), chemical properties of PCBs, and biological characteristics of the fish were incorporated into the kinetic model and input parameters were calculated

independently (see Appendix I for a more detailed discussion of the two models). To ensure that the model is representative of experiment conditions, the following initial assumptions were made to obtain equation 9: (1) sediment porewater contribution to the respiratory exchange of PCBs was assumed to be zero; (2) dietary uptake was zero (PCB-free food); and (3) PCB loss via metabolism was negligible.

$$\frac{dM_B}{dt} = W_B k_1 m_O C_{W,O} - (k_2 + k_e) M_B \qquad (9)$$

As described by Arnot and Gobas (2004b), M_B is the mass (g) of PCB in the fish, dM_B/dt is the net flux of PCB being absorbed or depurated by fish at any point in time t (d), W_B is the wet weight of the fish (kg) at time t, k_1 is the gill uptake rate constant (L/kg.d), m_o is the fraction of the respiratory ventilation that involves overlying water (which equals 1 in this case), $C_{W,O}$ is the freely dissolved PCB concentration in the overlying water measured by passive sampling (g/L), k_2 is the gill elimination rate constant (d^{-1}), and k_e is the fecal egestion rate constant (d^{-1}).

Since concentrations in the overlying water increased over time, a linear interpolation between measured values from 0 to 45 and 45 to 90 days was used to define overlying water concentration (Figure S1).

$$\frac{dM_B}{dt} = W_B k_1 C_{W,O@t} - (k_2 + k_e) M_B \qquad (10)$$

Integration of equation 10 yields:

$$M_B = \frac{W_B k_1}{(k_2 + k_e)} \left(C_{W,O@t} - \frac{a}{(k_2 + k_e)} \right) + A e^{-(k_2 + k_e)t} \qquad (11)$$

Where a is the rate of change of aqueous concentration and A is the constant of integration obtained by fitting equation 11 to the initial conditions.

PCB concentrations in fish were predicted by solving for the mass of PCB in the fish at 45 and 90 days and converted to lipid normalized concentration using equation 12:

$$C_{lipid} = \frac{M_B}{W_B L_f} \qquad (12)$$

Where L_f is the lipid content of the fish (kg lipid/kg wet weight). For more information on the model parameters and detailed calculations of the rate constants, see Appendix I.

The sensitivity of the model output to changes in each input parameter is described as:

$$S = \frac{\frac{\Delta O}{O}}{\frac{\Delta I}{I}} \qquad (13)$$

Where ΔO is the change in the output (O) due to the change (ΔI) in the input variable (I). The sensitivity of the kinetic model output to dissolved oxygen concentration, overlying water concentration, fish wet weight, and fish lipid fraction was calculated for congeners with log (K_{OW}) values ranging from 5 to 7. Each input parameter was increased and decreased by 10% while maintaining other parameters constant.

Results and Discussion

Sediment Characteristics

TOC content in Rhode River was measured as 3.9±0.06% by dry weight and PCB concentration was determined to be below the level of detection (0.01 μg/g dry wt.). Total PCB concentration in the Grasse River sediment was measured as 0.67 μg/g dry wt. and averaged 2.2±0.06% for TOC content. Sediment PCB data at a congener level is shown in Table S1.

Aqueous PCB Concentrations

Total porewater dissolved PCB concentration in GR sediment was reduced from 631 (±23) to 1.3 (±0.2) ng/L, 99% reduction, in 90 days after amendment with AC (Figure 2.2, Table S4). The reduction in porewater concentration of AC-amended field sediments was previously reported to be in the range of 70-99% for hydrophobic organic chemicals (Ghosh et al., 2011). Total PCB concentration in overlying water 90 days after AC amendment was reduced from 184 (±15) to 7.6 (±2.5) ng/L (a 96% reduction) and was close to that seen in the clean RR sediment tanks (7.8 (±0.5) ng/L). In the untreated GR sediment tanks, porewater PCB concentrations were 3 to 7 fold higher than the overlying water concentrations, indicating sediment as the PCB source to the water column during the course of the experiment. Dichloro, and trichlorobiphenyls showed the highest flux from untreated GR sediment into the overlying water (Table S3). This concentration gradient was reversed in the AC-treated GR sediment tanks (Table S4) leading to a flux back into the sediment, indicating that AC-treated sediment acts as a sink (Table S3) as also reported in field observations by Beckingham and Ghosh (2013).

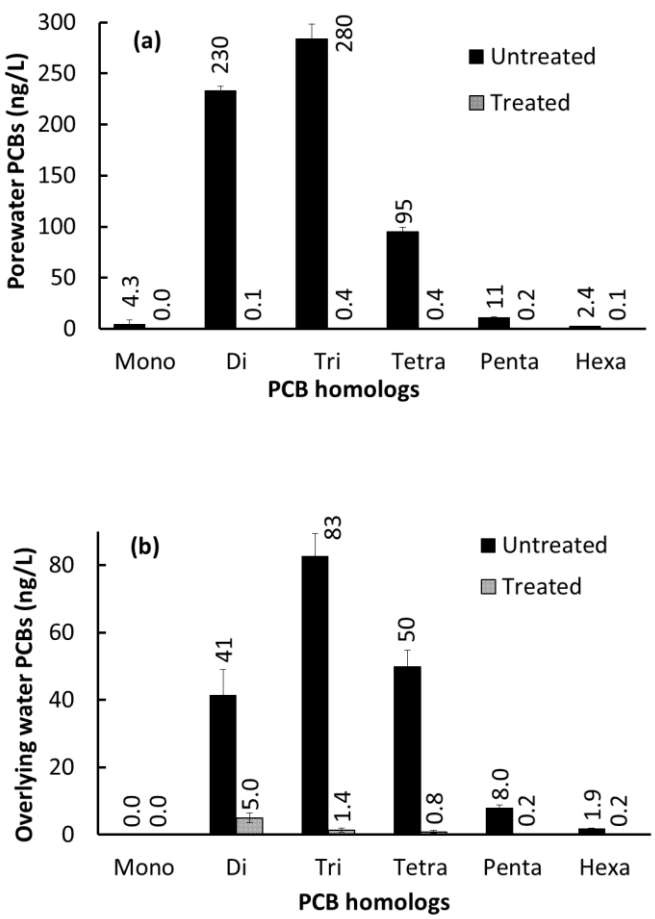

Figure 2.2. Freely dissolved PCB concentration in (a) sediment porewater and (b) overlying water of untreated and treated Grasse River sediments after 90 days. Error bars represent standard error.

Comparison of 45-day and 90-day results (588 (±16) and 631(±23) ng/L) shows that porewater concentrations in the untreated GR tanks were close to equilibrium after 45 days (t test, α=0.05). The overlying water concentration, however, increased from 96 ±(12) to 184 (±15) ng/L from 45 to 90 days likely due to continued sorption and gradual saturation of the sorptive surfaces with time (pipes, sump, and charcoal bag) (Table S4). Porewater PCB concentration in control RR sediments was low and similar to that in the AC-treated GR sediment. As illustrated

in Figure 2.1, control RR tanks received the same overlying water recirculation as the GR sediment tanks they were adjacent to. PCB data at a congener level is shown in Tables S1 and S2 for porewater and overlying water.

Although effort was made to avoid cross contamination between the GR and RR tanks by placing an activated charcoal bag in each sump, PCBs in the effluent recycle were not totally removed by bagged AC and therefore the recycled water carried some of the overlying water PCBs between tanks. This was not discovered until the sample analysis was completed and results were interpreted. This was mainly an issue between the untreated GR tanks and the RR control tanks adjacent to them (Table S4). However, the resulting elevated PCB concentration in the recirculated overlying water does not impact the study because overlying water concentrations were measured directly by passive sampling and in most contaminated field sites, ongoing inputs to overlying water is a reality. In the treated GR tanks, the porewater PCB concentration also remained similar in 45 and 90 days (t test, α=0.05) and was in the range of 1-2 ng/L. However, the overlying water PCB concentrations in the treated GR tanks increased from 3.5 ±0.7 to 7.6 ±2.5 ng/L (mostly contributed by dichlorobiphenyls; see SI) and were similar to the adjacent control tanks.

Partitioning constants (K_d) for untreated and treated GR sediments were predicted with sorption models for 21 dominant congeners in water, representing di, tri, tetra, and pentachlorobiphenyls (Figure 2.3). The observed K_d values for untreated GR sediment (based on 90-day porewater values) fell within the range predicted by K_d models with and without including BC. Observed K_d values for the treated GR sediment were nearly 2 orders of magnitude higher than untreated GR sediment,

demonstrating the efficacy of AC amendment in enhancing sorption capacity of the sediment and reducing aqueous PCB concentrations. There was some scatter in the observed K_d values for the treated GR sediment partially due to the uncertainty of measurements approaching analytical detection limits. For the untreated sediment, the model based on sorption to natural organic matter (equation 2), underestimated sorption (solid red line) while equation 4, which accounts for additional sorption to BC, overestimated sorption to untreated GR sediment (dashed red line). Depending on the model used (equation 2 vs. 4) the predicted porewater concentrations can vary by one order of magnitude, highlighting the previously discussed uncertainty associated with standard partition constants for estimating porewater concentrations. PCB sorption in the treated sediment is dominated by sorption to AC. Therefore, including or not including the BC pool in the sorption model (equations 3 and 5) did not make a difference in the results for the treated sediment. Since discrete values of n and K_f were used to calculate the K_d values, the results are shown in discrete gray symbols and not in a smooth line. The sorption models overestimated K_d for treated GR sediment likely due to uncertainty in estimating actual sorption capacity of the AC in the sediment matrix.

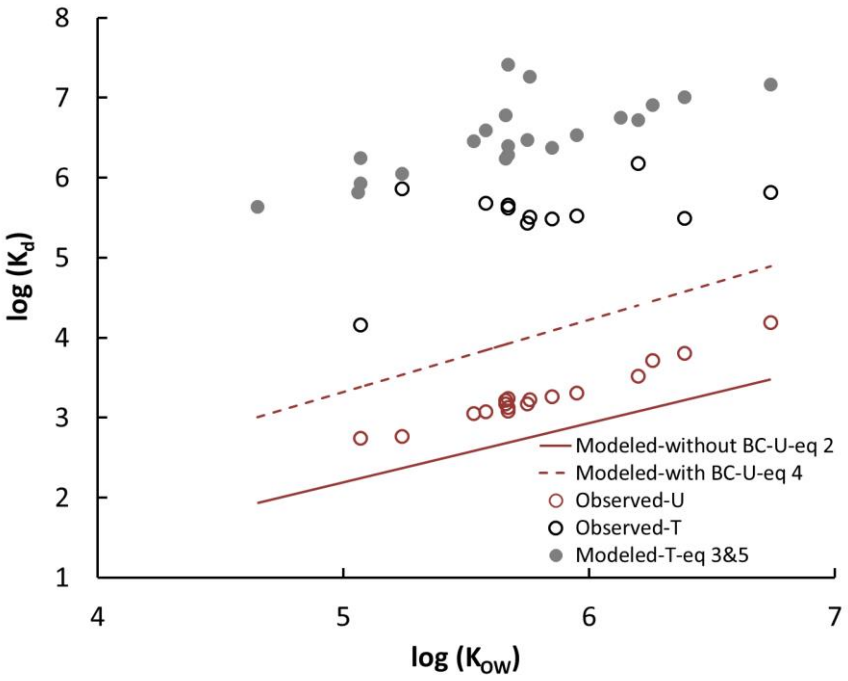

Figure 2.3. Observed and predicted K_d values versus K_{OW} for untreated (U) and treated (T) Grasse River sediments after 90 days. The red lines and the gray closed symbols represent the predicted values obtained from the partitioning models.

Bioaccumulation in Fish

The lipid content of the zebrafish based on wet weight was measured as 5.5±0.5%. PCB concentration in zebrafish exposed to untreated and treated GR sediments as well as control RR sediments are compared in Figure 2.4. The total PCB concentration in fish lipids was 27 ±1.3 µg/g in untreated GR sediment tanks and 3.5 ±0.3 µg/g in treated GR sediment tanks after 90 days exposure (87% reduction). Kupryianchyk et al. (2013) reported a 95% reduction in PCB uptake by Golden Orfe fish after 6 months of exposure to sediment treated with powdered AC and only 45% reduction in the same fish with granular AC (0.425-1.7 mm). Observed reduction in fish lipid PCBs in our study is consistent with our use of an intermediate particle size AC (75-300 µm) and shorter exposure period of 3 months. Fish PCB concentrations

in control RR sediment tanks were in the range of what was measured for the fish in treated GR sediment tanks (1.8 ±0.6 to 7.4 ±2.8). As discussed above, the elevated PCB levels in the fish from the control tanks is likely due to a combination of trace PCB levels in the RR sediment and a result of ongoing inputs from the overlying water of the adjacent tanks containing GR sediment. PCB results in the fish at a congener level are shown in Tables S1 and S2. The change in fish concentrations over time is shown in Figure S5. The variation between PCB levels in the fish at day 45 and day 90 shows that PCB concentrations may not have reached equilibrium in the fish. Plots of log (BCF) vs. log (K_{OW}) for fish exposed to untreated sediment are shown in Figure S6. The slopes of the line fitted to the observed data from 45 and 90 days were close to unity and an intercept close to but less than zero indicating near octanol-like partitioning in the lipids. The observed BCF values for untreated GR sediment fell within the range predicted by modeled values based on Di Toro et al. (2000) and Gobas (1993).

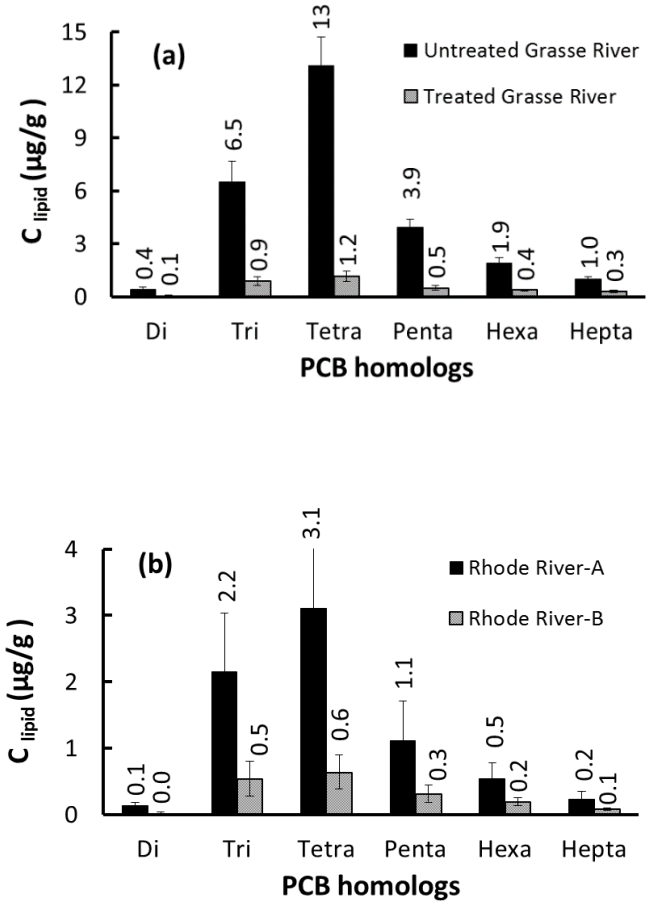

Figure 2.4. PCB concentration in zebrafish exposed to (a) untreated and treated Grasse River sediments and (b) Rhode River sediment for 90 days. Rhode River-A represents data from tanks adjacent to untreated Grasse River sediments and Rhode River-B represents data from tanks adjacent to the treated Grasse River sediments (see Figure 2.1). Error bars represent standard error.

Equilibrium Model

Overlying water concentrations measured by passive samplers were incorporated in the equilibrium model (assuming $K_{lipid} = K_{OW}$) to predict PCB residues in fish for 34 dominant congeners (equation 8; Figure 2.5a). Since fish were mainly in contact with the water column, predictions were based on the overlying water concentrations. The big reduction in uptake by fish after treatment with AC was

captured well by the model. There was a reasonable agreement between observed and predicted PCB concentrations in zebrafish exposed to the treated GR sediment. However, prediction of uptake for fish exposed to untreated GR sediment was higher than observed. This could be either due to overestimation of K_{lipid} values (assumed to be K_{OW}) or non-equilibrium conditions.

Kinetic Model

Overlying water concentrations were used to predict uptake of the same 34 congeners used for the equilibrium model. Treatment trends were predicted well by the Arnot and Gobas (2004b) kinetic model (equation 11; Figure 2.5b) and the root mean squared error was smaller than the values for the equilibrium model (Table S5). The predicted total PCBs for the fish exposed to untreated GR sediment exceeded the observed values by a factor of 2 (ranged from 0.1-8 for individual congeners). However, for the fish exposed to treated GR sediment the predicted total PCBs were lower than the observed values by a factor of 2 (ranged from 0.3-15 for individual congeners). It is important to recognize that the model parameters were not fit to the experimental results but obtained from existing literature. The use of empirical correlations for estimating the model parameters, such as uptake efficiency and filtration rate (equations 2 and 3 in the Appendix I), is one possible reason for the discrepancy between the observed and predicted values. These empirical correlations in the literature were approximated based on observations over a range of fish species, which leads to variations for individual species. Further, a generic fish fecal egestion rate constant was used (equation 5 in the Appendix I) which likely does not capture species-specific differences. Overall, the kinetic model resulted in better

predictions than the equilibrium model because it accounted for the time variable nature of uptake and loss processes (Figure S7).

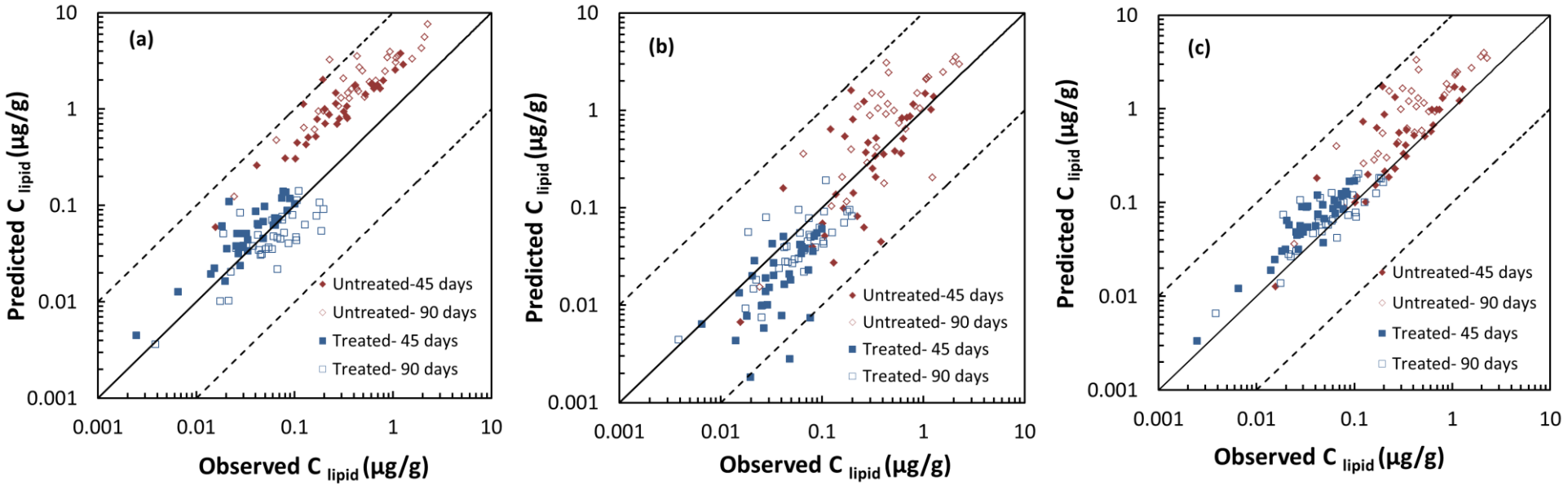

Figure 2.5. Observed and predicted PCB concentrations in zebrafish using the (a) equilibrium model (b) Arnot and Gobas bioaccumulation model without ingestion, and (c) Arnot and Gobas bioaccumulation model with ingestion. Closed symbols refer to 45 days results and open symbols refer to 90 days.

The sensitivity of the kinetic model output (C_{lipid}) with respect to each parameter was tested for conditions in the untreated GR tanks after 90 days (Figure S8). A positive sensitivity value indicates a direct relationship between the input parameter and the output and a negative value indicates an inverse relationship. Sensitivities to the positive and negative changes were identical for overlying water concentration ($C_{W,O}$) and similar for all congeners. However, the trends deviated for dissolved oxygen concentration (DO), fish wet weight (W_B) and lipid fraction (L_f) due to the non-linear change of model output with respect to these parameters (DO and L_f appear in the rate constants of the model). For the lower chlorinated PCBs (log (K_{OW}) less than 6), the model was most sensitive to $C_{W,O}$. For log (K_{OW}) larger than 6, the model was most sensitive to L_f, and DO and W_B. For all congeners DO concentration was inversely related to the uptake as high DO reduced ventilation rate. However, this effect was less pronounced for the lower chlorinated PCBs, likely due to the faster exchange kinetics of these compounds. In contrast, for the higher chlorinated PCBs with slower mass transfer, oxygen concentration was a rate limiting factor in fish uptake. Overall, the sensitivity of the model to W_B was lower compared to other three parameters over a large range of K_{OW}. The low sensitivity to changes in W_B was also reported for Thomann and Gobas models (Gobas, 1993; Thomann et al., 1992).

Generally, the kinetic model over-predicted the uptake of the low K_{OW} compounds and under-predicted the uptake of the high K_{OW} compounds (see Figure S9). There are a few possible explanations to this observation: 1) uncertainties in measuring aqueous concentrations and estimating fish ventilation rates, 2) model

parameters have dependencies on K_{OW} that may not be accurate, 3) some higher chlorinated PCBs may be coming from ingestion of sediment and/or food that picked up PCBs in the aquaria. To address the issue of ingestion exposure, equation 9 was modified by the addition of incidental ingestion of food/sediment. Exposure through ingestion was calibrated (separately for the untreated and treated GR sediment) by accounting for the observed uptake of the dominant heptachlorobiphenyl PCB-180 that could not be explained by uptake solely from water (Details in the Appendix I). Overall, including the ingestion exposure increased predicted uptake in fish, especially for the high K_{OW} compounds (Figure 2.5c). Including ingestion pathway affected the predictions for treated sediment more due to the fact that water concentrations were lower in the treated GR tanks, causing ingestion of PCBs to play a significant role in uptake. The relative contribution from the ingestion pathway to overall PCB uptake increased with increasing PCB hydrophobicity due to lower solubility and thus lower exposure of the heavier PCBs through water (Figure S10). Gill uptake followed the opposite trend as respiration was the dominant exposure pathway for the more water soluble PCBs. Although net uptake was greatly reduced after sediment treatment, the percent contribution from the ingestion pathway to the total PCB uptake in fish was 17% and 69% for untreated and treated sediment, respectively. This is due to lower aqueous PCB concentrations and thus gill uptake becoming a less significant pathway (congener-specific contributions are shown in Figure S10). Assuming that the fish exposed to untreated and treated GR sediment had the same ingestion rates, the ratio of assimilation efficiencies of untreated to

treated sediment-bound PCBs was calculated to be 2, indicating a reduction in assimilation efficiency of PCBs in the sediment upon amendment with AC.

Arnot and Gobas (2004b) and Connolly (1991) models were similar in terms of performance with root mean squared error values being close to each other. It should be emphasized that the predicted values generated by both models were in good agreement with the observed values (Figures 5b and S11) despite the fact that these models were not calibrated to the data. This highlights the broad applicability of such bioaccumulation models to a wide variety of environmental and biological conditions. The kinetics of uptake were modeled for congeners from tri to hexa groups, assuming constant water concentrations (Figure S12). Both models predict faster equilibrium times for lower chlorinated congeners than the higher ones due to higher mass transfer rates. Overall, the Arnot and Gobas model predicts shorter equilibration times due to faster exchange kinetics estimated by this model.

Percent Reduction in Aqueous PCBs and Bioaccumulation

Observed percent reductions in porewater, overlying water, and fish concentrations 90 days after amendment with AC are shown in Figure 2.6. For porewater, overlying water, and fish the effect of the treatment after 90 days was most pronounced on congeners with log (K_{OW}) less than 7. This is explained by faster mass transfer kinetics from sediment to AC for lower chlorinated compared to the higher chlorinated PCBs and greater bioavailability of these compounds. Porewater and overlying water showed similar reductions over the log (K_{OW}) range because overlying water concentration is controlled by the flux from sediment and therefore reductions in porewater concentrations translate to reductions in overlying water. It is

noteworthy that the observed reduction in fish was less than reductions observed in the overlying water, likely due to the concentrations in fish having not reached equilibrium in 90 days. To confirm this hypothesis, long-term simulations were conducted with the kinetic model for 120,150,180 and 210 days of exposure. The predictions for the 180 and 210-day exposures were not statistically different. Therefore, the 210-day results are shown in Figure 2.6. The predicted reduction in fish at equilibrium (green triangles) matched with reductions in porewater and overlying water. Thus, in the long-term in the field, the percent reductions observed in the porewater and water column are expected to be reflected in reductions in fish (in the absence of other ongoing inputs to the system).

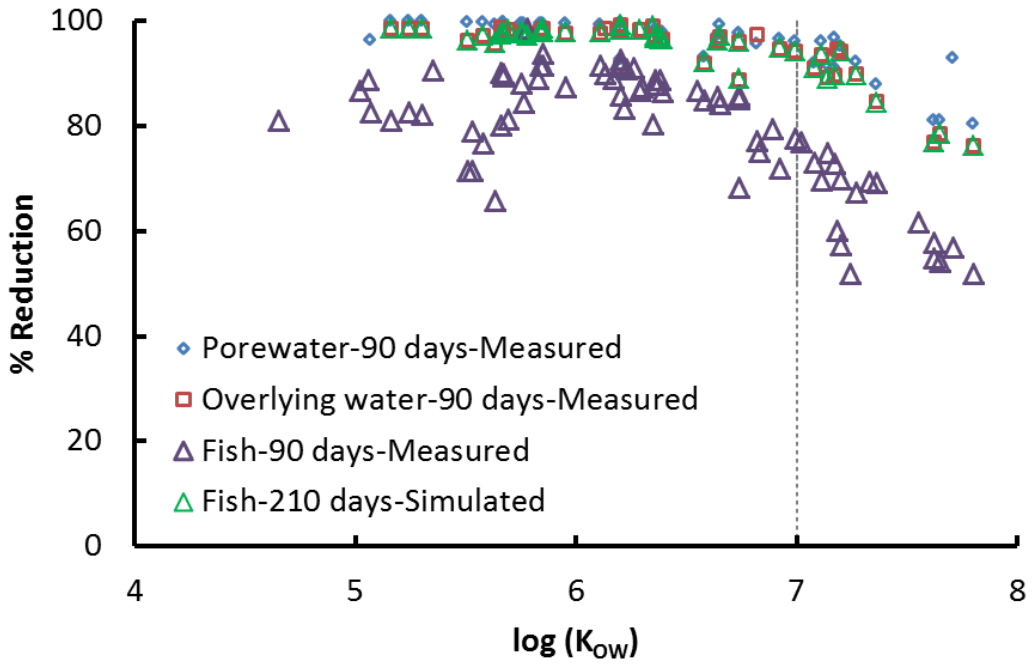

Figure 2.6. Percent reduction in water and fish concentrations after AC amendment.

Implications of This Research

While numerous studies in the past have demonstrated that PCB accumulation in benthic organisms can be reduced by amending with strong sorbents that attenuate sediment porewater concentrations, there is a lack of data on how fish respond to bioavailability changes in sediment. Results presented here confirm that indeed bioavailability changes in sediment are reflected in uptake in fish, primarily through reductions in PCB flux from sediments. In this work, we explain those observations also through direct measurement of freely dissolved porewater and overlying water concentrations and modeling uptake pathways to fish to mechanistically explain the experimental results. The research also addresses a key challenge in monitoring effectiveness of *in situ* remedies by demonstrating that by targeting assessment of exposure pathways to fish and measuring freely dissolved concentrations in overlying water using passive sampling, we can make reasonable assessments of long-term recovery of PCB residues in fish. However, it is noteworthy that these direct measurements will not replace freely dissolved concentrations computed from fate and transport models when long-term predictions are needed. Bioaccumulation models can be linked to fate and transport models which rely on robust partitioning estimates and include contributions from ongoing inputs in the field. Once linked, this combination can capture the effect of ongoing external PCB loads (Connolly et al., 1999; SERDP, 2012) and predict PCB concentrations in fish tissue over time. After validation, such models can also be used as a reliable means of back-calculating the AC amendment dose required to achieve a desired endpoint in recovery of fish tissue PCB levels.

Acknowledgements

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Chapter 3: Effect of Sediment AC Amendment on Pelagic and Benthic PCB Exposures to Fish

Hilda Fadaei, Aaron Watson, Allen Place, John Connolly, and Upal Ghosh

Introduction

In situ amendment of activated carbon (AC) is increasingly considered a remedial technology for sediments impacted with hydrophobic organic chemicals such as polychlorinated biphenyls (PCBs) (EPA, 2013a, 2014a; Rakowska et al., 2012). However, quantitative understanding of how contaminant bioavailability reductions and reduced uptake at the base of the food chain impact uptake by fish still remains a challenge. PCB accumulation in fish is influenced by many factors such as bioavailability, growth, foraging behavior, movement, as well as PCB concentrations in water, in sediment, and in prey items. Previously developed bioaccumulation models can be used in steady-state or dynamic mode to predict fish uptake in natural water systems (Arnot and Gobas, 2004b; Connolly, 1991). However, AC amendment can alter uptake through different pathways and therefore it is crucial to validate the ability of bioaccumulation models to predict these changes. Chemical activity, which can be assessed by passive sampler methods, can be used as a surrogate measure of PCB bioavailability in sediments (Lydy et al., 2014). Advances in passive sampling techniques and development of comprehensive guidelines on the use of passive samplers (Ghosh et al., 2014) have made the polymers reliable tools for measurement of bioavailability. Hence, validation of the use of such measures as input to bioaccumulation models is a next reasonable step. Parkerton and Connolly (2013) have emphasized the importance of conducting passive sampling measurements prior

to and after site remediation as well as the role these measurements can play in calibrating bioaccumulation models. Bioaccumulation models that capture the effect of bioavailability changes can be applied to evaluate the time-varying nature of bioaccumulation processes at different trophic levels after *in situ* treatment. Furthermore, such bioaccumulation models, if linked to fate and transport models, can track the effect of ongoing PCB sources on fish recovery. Once validated, combination of these models can be used to inform a decision on amendment dose required to achieve a desired endpoint in fish tissue or predict fish PCB bioaccumulation trajectories after *in situ* remediation of a PCB-contaminated site.

Kupryianchyk et al. (2013) showed reduction in fish PCB uptake upon addition of granular and powdered AC to sediment but did not link the observed results to modeling predictions. Our previous work (Fadaei et al., 2015) showed decreased uptake in zebrafish after AC amendment of the sediment and was the first study to show through quantitative modeling that predicted bioaccumulation in fish reflects bioavailability changes that were tracked by passive sampling. However, in the study by Fadaei et al. (2015), uptake in fish occurred mainly through absorption from water and exposure to PCBs through food uptake and incidental ingestion of sediment. In addition, the ingestion pathway was calibrated by fitting the model to the observed PCB value of heptachlorobiphenyl PCB-180 in zebrafish. Therefore, the present study was designed to: (a) incorporate PCB uptake through food and quantify changes that occur in this route after sediment AC amendment, (b) study how differently pelagic and benthic feeding fish respond to treatment when uptake occurs through all routes of exposure, (c) improve the calibration of the previously modified

bioaccumulation model by Fadaei et al. (2015) for ingestion of sediment-bound PCBs using independently measured assimilation efficiency of sediment-PCB matrix in the gut, and (d) determine whether freely dissolved concentration of PCBs in porewater and overlying water, obtained from passive sampling, when used as input to the bioaccumulation model can lead to accurate predictions of accumulation in the two different fish species. Results from this work can provide insight into the factors controlling short-term response to treatment when evaluating success of *in situ* amendment in targeted fish receptors with different foraging/swimming behavior. Such bioaccumulation model calibrated for sediment ingestion pathway together with site-specific values of chemical concentrations in water, sediment, and prey items can lead to more precise predictions of trajectory in various fish species including the benthic-feeding fish.

Materials and Methods

Sediment Source

The laboratory exposure study was performed using: clean sand, PCB-impacted sediment, and PCB impacted sediment treated with AC in the field. Sediments were collected from Grasse River (GR), NY by surface ponar grabs. Freshly deposited sediment was sampled along with AC treated sediment from this site. In 2006, granular activated carbon (particle size: 75-300 μm) was added to sediments at a target dose of 2.5% d.w. (+ 0.5x safety factor) (Beckingham and Ghosh, 2011). The treated sediment used for this experiment was collected from the area where activated carbon slurry was mixed (using an enclosed tilling device) into

the sediment. The sampling of untreated and AC-treated sediments occurred 6 years after the AC application.

Test Organisms

Mummichog (*Fundulus heteroclitius*) and cory catfish (*Corydoras aeneus*) were used as model species to study uptake. The mummichogs were cultivated at Delaware State University and the cory catfish were purchased from a local aquarium store. Fish were fed with benthic worms at 1.5 percent of their body weight per day, which was adequate to maintain the fish at average growth.

Food Preparation

Benthic worms (*Lumbriculus variegatus*) were purchased from Aquatic Research Organisms Inc. to be used as food for fish. Due to the different foraging behavior of the fish species, it was expected that the ingestion rate would be different between the two fish. Therefore, the food was labeled with decachlorobiphenyl (PCB 209) which is found at negligible levels in the Grasse River sediment (0.0003 μg/g d.w.). As a result, the uptake of PCB 209 through sediment ingestion can be ignored and uptake can be assumed to occur solely though the food. Three types of food were used in this experiment: PCB-free worms, worms exposed to untreated sediments, and worms exposed to treated sediments. After exposure of the worms to untreated and treated GR sediments for 30 days, worms were collected and allowed to depurate for 6 hours and then freeze-dried to be used for feeding the fish. Untreated GR sediment was labeled with PCB 209 prior to worm exposure. The desired volume of PCB 209 in hexane was dissolved in 10 mL of acetone, mixed well and added to the wet sediment intermittently (1 mL at a time). Sediment was shaken between each

spiking step. The sediment slurry was mixed on a rotator for 24 hours. Subsequently, sediment was left uncapped under a fume hood for 5 to 6 hours to let the acetone evaporate prior to the addition of worms to the sediment. Worms exposed to treated sediment and the PCB-free worms were spiked directly with PCB 209 after being freeze-dried. The desired volume of PCB 209 in hexane was dissolved in about 30 mL of acetone and was sprayed on the worms with a thin-layer chromatography spray bottle. Worms were mixed during this process to assure even distribution of PCB 209 on the food. To remove residual solvents used in spiking, worms were freeze-dried again after evaporation of the acetone. PCB levels (including PCB 209) were measured in the worms before beginning the experiment. Two feeding modes were used in this study: food was delivered to the surface of the water for the mummichogs and to ensure sufficient delivery of food to catfish, a tube was used to funnel food close to the sediment.

Measurement of Aqueous Concentration

76 µm-thick polyoxymethylene (POM) passive samplers were pre-cleaned via an ultrasonic extraction using 50% acetone in hexane, air-dried under a fume hood for12 hours (Hale et al., 2010). Aqueous PCB concentration was calculated from PCB concentration in the sampler based on K_{POM} values reported by (Hawthorne et al., 2009). To evaluate the state of the equilibrium between the passive sampler and freely dissolved PCBs in the water, Performance Reference Compounds (PRCs) were used. Desired volumes of PCB 29, 69, 155, and 192 in hexane were spiked into two batches of 80:20 (v:v) methanol/water solution. Amount of PRCs to be added to an incubation system with known number of samplers of specific mass and known solvent volume

was calculated from the equation in (Booij et al., 2002). POM strips were introduced to the jars after gentle mixing of the solutions. The jars were placed on an orbital shaker (30 rpm) for 4 days. Samplers were retrieved and wiped with Kimwipes. A few strips from each batch were analysed to determine the initial concentration in the samplers. The other strips were stored in the dark at 4℃ until use in experiment.

Aquarium Set Up

Four replicated sets of tanks were used in the present study: Two sets of tanks containing clean sand, a set containing PCB-impacted sediment, and a set containing PCB-impacted sediment treated with AC in the field. Sediments were homogenized in the laboratory before placement in the tanks. Each set contained three replicates (see Figure S1). Four liters of sediment was added to triplicate 38-L glass covered fish tanks and allowed to settle and consolidate for a few days in static water. The amount of sediment was estimated based on sediment height in the aquaria and surface area of the tanks. PRC-loaded passive samplers were introduced in the water column and in sediment in each aquarium (two strips in each phase, Figure 3.1). To obtain the vertical PCB concentration profile, the passive samplers were placed vertically in the sediment by the use of a T-shaped structure made from stainless steel mesh (see Figure S2). Three individuals of each fish species were added to each tank. Fish in one set of the sand tanks were fed PCB-free food and fish in the other set were fed benthic worms exposed to untreated sediment. The fish in the untreated and treated tanks were fed with worms that were exposed to untreated or treated sediments prior to the experiment, respectively. Water was maintained at static condition. The chemical composition of the water (pH, conductivity, and alkalinity), ammonia and

nitrite levels were monitored throughout the experiment. pH and conductivity were measured using a Horiba U-22 multiparameter probe. Alkalinity, ammonia, and nitrate were measured with water quality test kits (Hach Co.). When ammonia or nitrite levels exceeded the protective limit for fish, water was drained and tanks were refilled with fresh dechlorinated tap water (2-3 times per week and ~25% exchange each time). Each aquarium was equipped with a heater to maintain the water temperature uniformly at 28°C, the optimal growth temperature for the fish, in all tanks. Tanks were equipped with bubblers to maintain adequate oxygen concentrations in the water. A photo period of 14 hours of light and 10 hours of darkness was maintained in the laboratory.

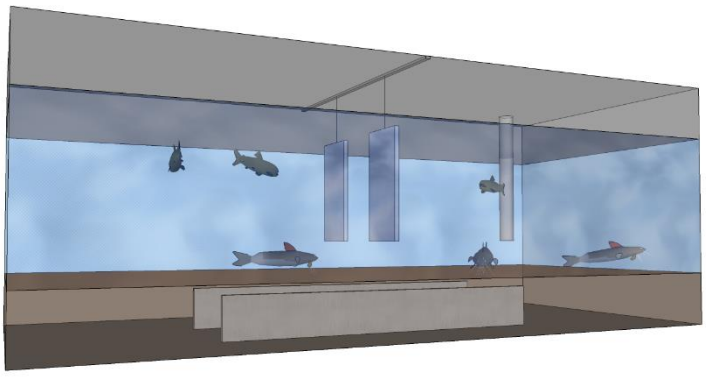


Figure 3.1. Components in each aquarium

Sampling and Analysis

Following 45-day and 90-day exposures, passive samplers were removed from the tanks, rinsed with deionized water and wiped dry. After 90 days of exposure, mummichog and catfish were depurated for gut clearance, sampled, sacrificed using dry ice, and were lyophilized and frozen until analysis. Fish tissue samples were

collected before exposure to PCBs to measure initial levels in the fish. Sediment samples were collected from the tanks at the start and end of the experiment. Sediment and passive samplers were extracted in hexane/acetone (1:1, v/v), cleaned up, and analyzed for PCB congeners in a gas chromatograph with electron capture detection as described in (Beckingham and Ghosh, 2011). Fish from each tank were pooled together, ground with anhydrous sodium sulfate and extracted with hexane and acetone mixture (1:1, v/v) following method SW846 3550C. The lipids were removed by treating with concentrated sulfuric acid. Further cleanup was performed by treating the extract with activated copper and passing through a 3% deactivated florisil and acidified silica gel column. The eluate was concentrated by nitrogen evaporation and analyzed for PCB congeners as described above. PCB analysis of the worm tissue was similar to fish tissue except that EPA 3630C method (silica gel cleanup) was used for cleanup. Lipid content in worm tissue was measured in triplicate using a colorimetric method as explained in Van Handel (1985). Separate samples were used to determine lipid content in mummichog and catfish tissue gravimetrically (Harvey et al., 1987).

Total Organic Carbon (TOC), Black Carbon (BC) and Activated Carbon (AC) Analyses

TOC was determined by thermal combustion method on a Shimadzu TOC analyzer with a solids sample module (TOC-5000A and SSM-5000A). BC and AC contents of the sediment were measured by wet chemical oxidation pretreatment (Grossman and Ghosh, 2009).

Correction for Non-Equilibrium Using PRCs

The PRC correction method is based on the assumption of the first order exchange kinetics, using molar volume adjustment (Huckins et al., 2006, P 223). The exchange rate constant for PRC congener uptake (k_e) was obtained from equation (1) (Oen et al., 2011):

$$k_e = -\frac{ln\left(\frac{C_{PRC,f}}{C_{PRC,i}}\right)}{t} \qquad (1)$$

Where t is the deployment time (d), $C_{PRC,i}$ and $C_{PRC,f}$ are the initial and final PRC concentration in the sampler, respectively.

The sampling rate (R_S), which is the apparent water volume extracted per unit time by the sampler, was calculated for PRC congener from equation (2) (Tomaszewski and Luthy, 2008):

$$R_S = k_e K_{POMW} M_{POM} \qquad (2)$$

where K_{POMW} is the POM-water partition constant and M_{POM} is the mass of POM.

The sampling rate by PRC loss from the POM samplers was used to obtain the sampling rate for other PCBs based on the empirical correlation below (Huckins et al., 2006, P 223):

$$R_S = R_{S,PRC}\left(\frac{V_{m,PRC}}{V_m}\right)^{0.39} \qquad (3)$$

where V_m and $V_{m,PRC}$ are the molar volume for the target PCB and PRC congeners, respectively. The sampling rate for the target PCB congeners was used to back-calculate k_e for that congener from equation (2) and obtain aqueous concentration of that compound (C_W) based on the first-order exchange kinetics (Oen et al., 2011):

$$C_{POM} = K_{POMW} C_W [1 - exp(-k_e t)] \qquad (4)$$

PCB Bioaccumulation Factor (BAF) for Fish

To calculate PCB buildup in fish, the bioaccumulation factor was calculated as follows:

$$BAF = \frac{C_{fish}}{C_{water}} \qquad (5)$$

where C_{fish} is the PCB concentration in the fish lipid (µg/kg lipid) and C_{water} is the PCB concentration in the water (µg/L), which was calculated from the PCB concentration in the passive sampler. Overlying water concentrations were used for both mummichog and catfish when calculating BAF.

Modeling Approach

PCB concentration in fish

The equilibrium and kinetic approaches were taken to estimate the PCB residue in fish. For the equilibrium approach, K_{lipid} (L/kg lipid), the lipid-water equilibrium partition constant of PCBs, was used as a simplistic model to predict C_{lipid} (µg/kg lipid), using $C_{W,O}$ (µg/L). The overlying water concentrations used as inputs to equilibrium model were measured by passive sampler. K_{OW} (L/kg octanol) can be used as a surrogate to quantify chemical partitioning between the overlying water and the lipid fraction (Werner et al., 2010).

$$C_{lipid} = K_{lipid}\, C_{W,O} \qquad (6)$$

The Connolly bioaccumulation model (Connolly, 1991) was used in kinetic mode to generate predictions of PCB body burden in fish after 90 days. Input parameters (i.e. environmental properties, PCB chemical properties and biological characteristics) were calculated independently (see Appendix II for a more detailed discussion of the model). The following assumptions were made to obtain equation 7: (1) porewater and overlying water PCBs play a 20% and 80% role in the respiratory exchange in the catfish, respectively (m_P = 0.2 and m_O = 0.8), (2) overlying water PCBs play a 100% role in the respiratory exchange in the mummichog (m_P = 0 and m_O = 1), (3) fish weight changes with time but lipid content remains constant, and (4) loss via biotransformation is negligible for both fish. As described by Connolly (1991), C_B is the concentration (µg/g wet) of PCB in the fish, dC_B/dt represents the accumulation of PCB by fish at any point in time t (d), k_u is the rate constant for PCB uptake across the gill (L/g wet/d), m_P is the fraction of the respiratory ventilation that involves porewater, m_O is the fraction of the respiratory ventilation that involves overlying water, $C_{W,P}$ and $C_{W,O}$ are the freely dissolved PCB concentration in the porewater and overlying water (µg/L), respectively, α_{ij} is the efficiency at which ingested chemical from prey j is assimilated by species i (unitless), G_{Dij} is the ingestion or consumption rate of species i on species j (g wet prey/g wet/ d), C_j is the concentration of PCB in species j (µg/g wet), k is the rate constant for excretion (d^{-1}), and G is the growth rate of fish (g wet/g wet/d) . It is assumed that for most organic chemicals, gill is the major site of depuration. Representation of contribution from porewater and overlying water to the respiratory uptake of PCBs in equation 7 was

taken from the Arnot and Gobas (2004b) model.

$$\frac{dC_B}{dt} = [k_u\,(m_P\,C_{W,P} + m_O\,C_{W,O}) + \sum_{j=1}^{n} \alpha_{ij}\; G_{D_{ij}}\,C_j] - (k+G)C_B \qquad (7)$$

To address PCB uptake through ingestion of sediment particles, equation 7 was modified by the addition of incidental sediment ingestion as an exposure pathway (McLeod et al., 2008), resulting in:

$$\frac{dC_B}{dt} = [k_u\,(m_P\,C_{W,P} + m_O\,C_{W,O}) + \alpha\,G_D\,C_{worm} + IR\,\beta\,C_S] - (k+G)C_B \qquad (8)$$

where IR is the sediment ingestion rate of the fish (g/g wet/d), β is the assimilation efficiency of the sediment-bound PCB (unitless) and C_S is the PCB concentration in the ingested sediment (µg/g).

Since there was not a statistically significant change in aqueous concentrations between 45 and 90 days results, values measured by the passive samplers after 90 days were used for $C_{W,P}$ and $C_{W,O}$. β values were obtained for different PCB congeners from a correlation derived in another study conducted by the authors which measured assimilation efficiency of sediment-bound PCBs in diets containing untreated and treated sediment (not published). α values were obtained from Connolly (1991). The ingestion rate for mummichog was found to be higher than catfish by an average factor of 1.8±0.06 for all four sets of tanks (Table S4). For detailed description of how decachlorobiphenyl was used to calculate G_D and more information on the calculation of the model parameters, see Appendix II. Integration of equation 8 yields:

$$C_B = \frac{k_u\,(m_P\,C_{W,P} + m_O\,C_{W,O}) + \alpha\,G_D\,C_{worm} + IR\,\beta\,C_S}{(k+G)}\left(1 - e^{-(k+G)t}\right) + Ae^{-(k+G)t} \quad (9)$$

Where A is the constant of integration obtained by fitting equation 9 to the initial conditions. C_B was converted to lipid normalized concentrations using equation (10):

$$C_{lipid} = \frac{C_B}{L_f} \quad (10)$$

Where L_F is the lipid content of the fish (g lipid/g wet weight).

Results and Discussion

Sediment Characteristics

Total PCB concentrations in the GR sediment were measured as 1.6 µg/g d.w. Due to minimal water exchange, PCB concentration in the sediment did not change significantly (t test, α=0.05) between the start and the end of experiment (Figure S3). Wet chemical oxidation of the treated and untreated sediment samples resulted in 2.8 ± 1.4% AC and 0.15 ± 0.05% BC, respectively. Since new sediment deposition was sampled along with treated sediment, AC level was relatively lower than the values observed in surface grabs collected during 2007 to 2009 (AC doses varied spatially, ranging from 0.24% to 16.9% over the monitoring period) (Beckingham et al., 2013; Beckingham and Ghosh, 2011).

Aqueous PCB Concentrations

Total porewater dissolved PCB concentration in GR sediment was reduced from 116 (±39) to 4.2 (±1.2) ng/L, 96% reduction, in 90 days after amendment with

AC (Figure 3.2a, Table S2). Total PCB concentration in overlying water 90 days after AC amendment was reduced from 44 (±18) to 4.3 (±1.2) ng/L (a 90% reduction). Since these tanks were run in static mode, PCBs in porewater and overlying water were coming close to equilibrium except for di and tri-chlorinated PCBs which were present at lower concentrations in the overlying water compared to porewater. Since the tanks were not fully covered, di and tri groups were likely lost from the overlying water through volatilization or through aerobic degradation in the water column. Porewater concentrations at different depths of the sediment were not statistically different since the sediments collected from the field were homogenized in the lab before being transferred to the tanks (data not shown). The homolog distribution was consistent with the previously reported dominance of lower chlorinated PCBs in GR sediments (Beckingham and Ghosh, 2011). Overlying water concentration in the sand tanks which received PCB-free food (Sand I) was low and represented sum of background PCBs and potential PCB losses from the fish consuming clean worms containing PCBs at background levels (Table S2, Figure S4). As shown in Figure S4, overlying water PCB concentration, corrected for non-equilibrium conditions, was elevated in the sand tanks which received PCB-contaminated food (Sand II) compared to overlying water in Sand I tanks (significant difference, t test, α=0.05). Desorption of PCBs from the uneaten food as well as PCB excretion from the fish are likely the contributing factors to this rise (see page S9 of Appendix II). The net result of PCB input to the overlying water and PCB loss due to water exchange in the tanks led to continuous accumulation of PCBs in the overlying water (Figure S5b). Total porewater PCBs were measured as 6.3 ng/L in Sand II tanks after 90 days, indicating

the ability of the PCBs to diffuse from the overlying water into the sand matrix to absorb some of the PCBs from the overlying water due to its diffusive properties (Table S2, Figure S7). Sand II tanks also experienced an increase in porewater concentration from 45 to 90 days due to the increase in PCB input to overlying water. Overall, the changes in PCB porewater and overlying water concentration with time were not statistically significant for untreated and treated tanks (t test, α=0.05, Figures S6 and S8).

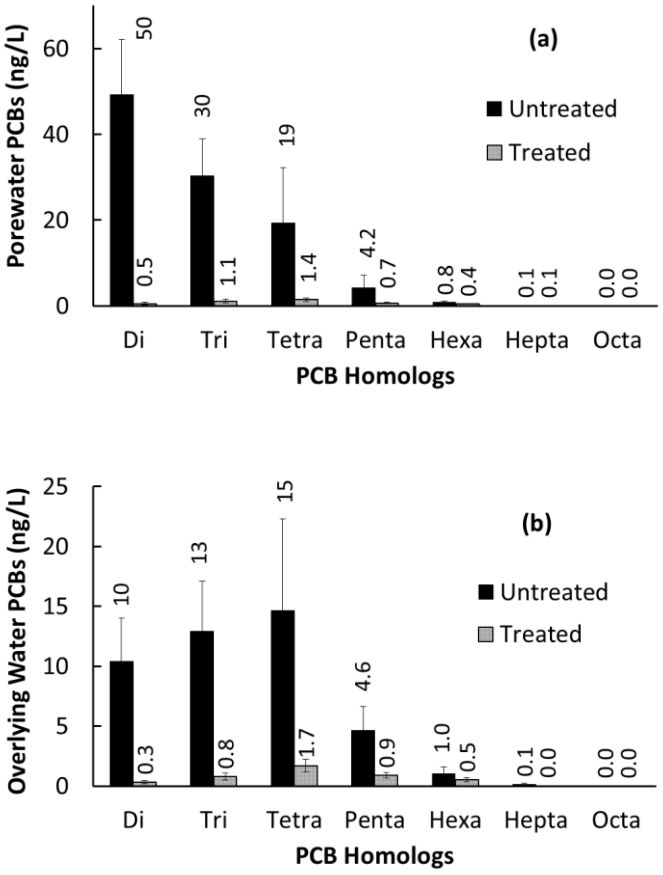


Figure 3.2. PCB concentration in (a) sediment porewater and (b) overlying water of untreated and treated Grasse River sediments after 90 days. Error bars represent standard error.

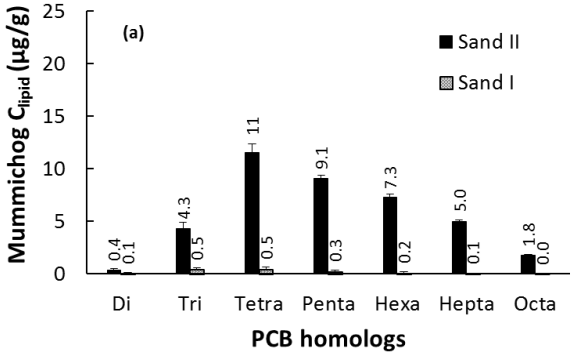
As mentioned above, the presented aqueous concentrations were corrected for sampler non-equilibrium using PRCs. PRC loss was higher in the overlying water passive samplers than the porewater samplers in all four types of tanks (Figures S9 and S10) as a result of enhanced mass transfer in the overlying water due to the fish movement. PRC loss for overlying water and porewater samplers in all tanks followed a reverse relationship with log K_{OW} due to slower mass transfer of the heavier congeners. PRC loss was not significantly different among tanks.

Bioaccumulation in Organisms

The worms that were used as food contained 2% lipid based on wet weight. The total PCB concentration in worm lipids was 69±4.5 µg/g lipid in untreated GR sediment tanks and 21 ±2.3 µg/g lipid in treated GR sediment tanks after 30 days exposure (70% reduction in total PCBs, Figures S11 and S12). The observed reduction was less than the values reported by (Beckingham and Ghosh, 2011) followed by the 14-day exposure of worms in the laboratory to field-treated GR sediment (collected 3 years after AC application) and untreated GR sediment (89-98%). It should be highlighted that the PCB concentration in the untreated sediment that was used for the worm exposure in this study was 3 µg/g d.w., which was higher than the treated sediment concentration (1.8 µg/g d.w.), and hence resulting in measuring higher reduction in worm uptake. This difference can be due to lower extraction efficiency in the treated sediment as Beckingham et al. (2013) observed a reduced extraction efficiency of PCBs by about 50% from sediment treated with 5% AC. The 2012 surface sediment sampling was conducted using ponar grab sampling and hence, newly deposited sediment was collected, leading to dilution of AC in the

surface sediments in the treated areas. A detailed analysis of sediment cores from 2016 confirms a deposition rate of 1.5 cm/year in Grasse River (data not shown).

The lipid content of the mummmichog and catfish based on wet weight was measured as 7.7±0.92% and 7.4±0.91%, respectively. PCB concentrations in the fish in the untreated and treated GR tanks as well as sand are compared in Figure 3.3. Reported residual PCBs in fish were corrected for background levels. The total PCB concentration in mummichog lipids was 66 ±4.1 µg/g lipid in untreated GR sediment tanks and 18 ±0.7 µg/g lipid in treated GR sediment tanks after 90 days exposure (73% reduction). For catfish, total PCB concentration in untreated and treated GR tanks were 18 ±5.5 and 13 ±2.3 µg/g lipid, respectively (27% reduction). Mummichog in both untreated and treated tanks had higher PCB body burden which can be a kinetic effect as a result of higher ventilation and feeding rate of the mummichogs (see Table S2).



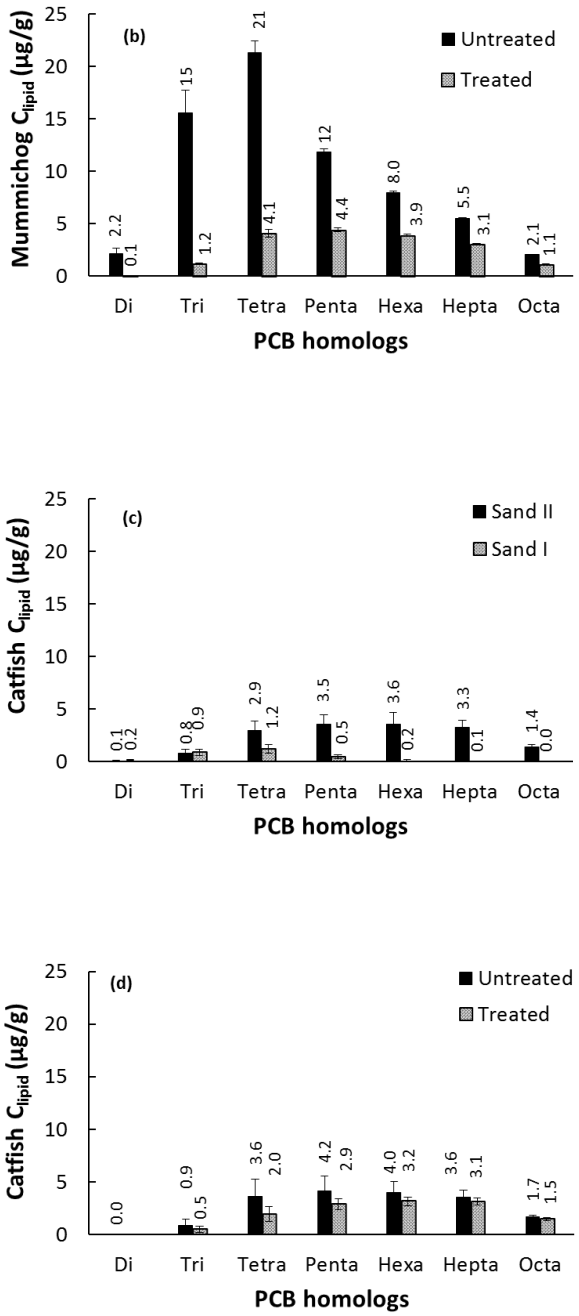


Figure 3.3. PCB concentration in mummichog and catfish sampled from the four different tanks after 90 days. Error bars represent standard error. Fish in Sand I tanks were fed with PCB-free worms, fish in Sand II and Untreated tanks were fed with worms exposed to untreated sediments, and fish in Treated tanks were fed with worms exposed to treated sediments.

It should be noted that di and tri-chlorinated PCBs did not accumulate in catfish likely due to biotransformation of the lower chlorinated PCBs by catfish. Ability of catfish to metabolize PCBs has been previously reported in the literature i.e. the induction of monooxygenase activity in the presence of Aroclor 1254 (Hill et al., 1976) and tetrachlorobiphenyl (Doi et al., 2000). The percent reduction in catfish was lower than mummichog, suggesting that slower kinetics along with metabolism might be leading to lower observed reductions in catfish. Concentration dependent metabolism rates may have resulted in pronounced metabolism rates in the catfish for exposure to untreated sediment and therefore reduced the apparent treatment effectiveness. Fish PCB concentrations in Sand II tanks for both species were between fish concentrations in the treated and untreated tanks. Catfish and mummichog in Sand II tanks had lower body burden than the fish exposed to untreated sediment because they were fed the same food but did not get exposed to dissolved PCBs through flux from the sediment and intake of sediment particles. Reduction in both fish species is still lower than the observed reduction (87%) for total PCBs in the aforementioned study by the authors (Fadaei et al., 2015) that exposed zebrafish to untreated and lab-treated GR sediment for 90 days. The lower AC content of the sediment used in this study (2.8%) compared to the Grasse River sediment used in the earlier work (4.5% AC) can account for the observed difference. In addition, the extent of equilibrium between fish and overlying water is unknown in both studies and once the fish reach equilibrium these reductions are likely to change. Existence of non-equilibrium condition between the fish and water is further supported by the evidence of growth in mummichog (Table S3). According to Table

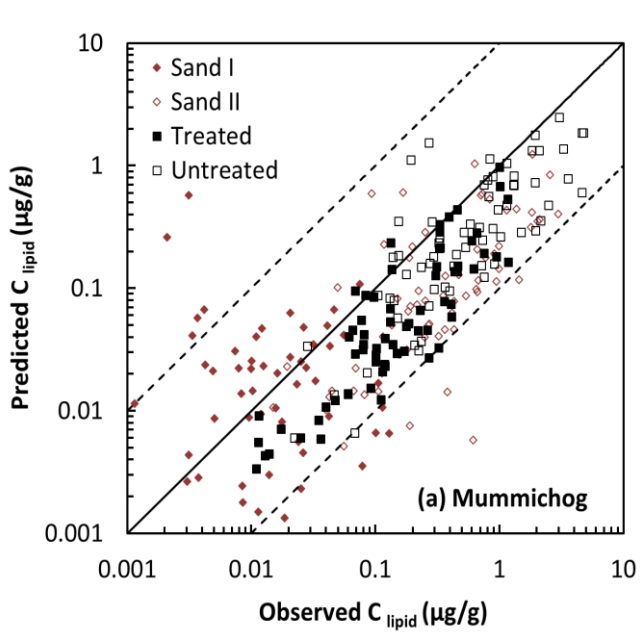
S3, growth was more significant for the mummichog due to higher ingestion rate of this species than catfish (discussed in the kinetic model section). Fish weight changes in untreated and treated tanks were similar for both mummichog and catfish.

Plots of log (BAF) against log (K_{OW}) for both fish exposed to untreated and treated sediment are shown in Figure S13 for both fish. The slopes of the lines fitted to the observed data were close to unity, indicating near octanol-like partitioning in the lipids. The observed BAF values for untreated and treated tanks were about an order of magnitude higher than predictions using (Di Toro et al., 2000) correlation.

Equilibrium Model

Overlying water concentrations measured by passive samplers were incorporated in the equilibrium model (assuming $K_{lipid} = K_{OW}$) to predict PCB residues in mummichog and catfish for 75 congeners (Figure 3.4). It is noteworthy that predictions for catfish were also based on overlying water concentrations and porewater was not considered as a contributing factor to PCB uptake. The reduction in uptake by fish after treatment with AC was captured well by the model. Observed values in catfish were reasonably close to predicted values by the equilibrium model (root mean squared error (RMSE) values were calculated as 0.51 and 0.17 for catfish exposed to untreated and treated sediment, respectively). The equilibrium models under-predicted PCB body burden for most of the congeners in mummichog (RMSE values were calculated as 1.0 and 0.23 for mummichog exposed to untreated and treated sediment, respectively). The discrepancies between the observed and predicted values by the equilibrium model for both fish species can be partly due to the simplistic assumption that lipid phase in the fish acts similar to octanol in terms of

partitioning behavior. Additionally, the observed discrepancy can be attributed to nonequilibrium conditions. The ratio of predicted to observed values were plotted against log K_{OW} to see if any significant pattern is observed for prediction accuracy over a range of hydrophobicity (Figures S14 and S15). No significant trend was observed between the over- or under-predictions and the PCB hydrophobicity for both fish species from Sand I, untreated, and treated tanks. Since it is not clear if the fish reached equilibrium in 90 days of exposure, a kinetic model based on the study by Connolly 1991 was also used to predict uptake in the short-term lab exposure.



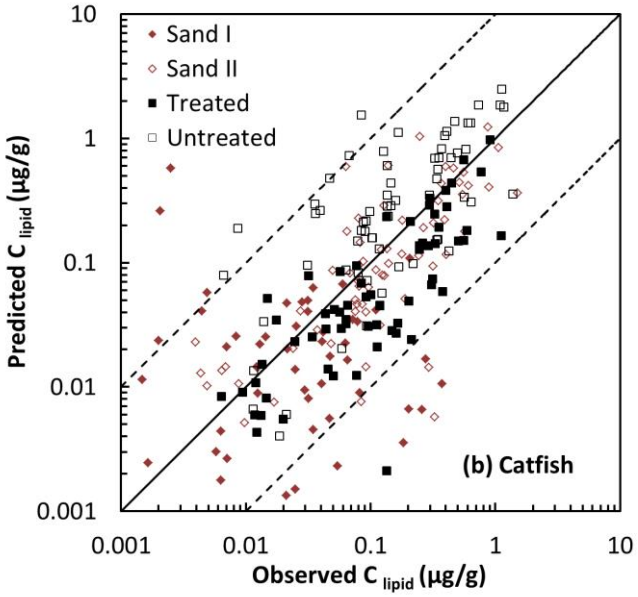


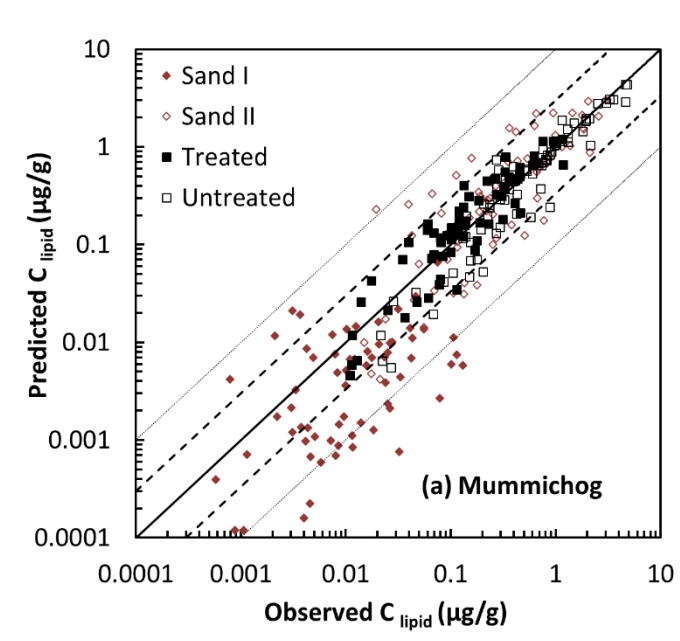
Figure 3.4. Observed vs predicted PCB concentrations in (a) mummichog and (b) catfish after 90 days using the equilibrium model. The dashed lines represent 10 times the values of the 1:1 line.

Kinetic Model

Overlying water and porewater concentrations were used to predict uptake of the same 75 congeners used for the equilibrium model. Sediment ingestion was included in the model as a pathway due to observed uptake of the dominant heptachlorobiphenyl PCB-180 in both fish species that could not be explained by uptake solely from water (Figures S17 and S18). In the process of model calibration for sediment ingestion rate, it was found that catfish had higher sediment ingestion rate (IR) than mummichog (0.03 versus 0.01 kg dry sed/ kg wet weight.d) which is not surprising since catfish are bottom feeders. Calculation of food ingestion rate (G_D) using the PCB-209-labeled food showed that mummichog in all tanks had higher G_D than catfish (Table S4), which is consistent with the higher percent change in weight in mummichog. However, since both species were kept in the same tank, an

experimental artefact may have impacted the calculated ingestion rates for the two fish based on the measured PCB-209 levels in the tissue. Due to its swimming and foraging behavior catfish could have ingested some of the feces egested by mummichog or feces egested by themselves that settled on the surface sediment. Therefore, the PCB-209 levels in catfish from different tanks may not solely reflect food ingestion but also ingestion of feces. Treatment trends for mummichog were predicted well by the Connolly (1991) kinetic model (equation 9; Figure 3.5a) and the RMSE values were smaller than the values for the equilibrium model (Table S5). Predicted total PCBs for the mummichog exposed to untreated GR sediment were comparable to the observed values (ranged from 0.2-2.6 for individual congeners) and exceeded the observed values by a factor of 1.2 for the fish exposed to treated sediment (ranged from 0.3-2.8 for individual congeners). This factor was 1.2 and 0.4 for Sand II and Sand I tanks, respectively, for total PCBs. Overall, the kinetic model was reasonably accurate in predicting PCB residue in mummichog. The discrepancy between predicted and observed values for mummichog in sand I tanks was likely due to the lower concentration in the water and fish from these tanks, thus the measurements were more susceptible to analytical error. For catfish, the Connolly kinetic model predictions did not improve significantly over the predictions made by the equilibrium model (Table S5) and the kinetic model over-predicted uptake for most of the lower-chlorinated PCB congeners (Figure 3.5b). Predicted total PCBs for the catfish exposed to untreated GR sediment were 3.5 times higher than the observed values (ranged from 0.3-67 for individual congeners) and exceeded the observed values by a factor of 1.9 for the fish exposed to treated sediment (ranged from 0.3-23

for individual congeners). This factor was 2.7 and 0.4 for Sand II and Sand I tanks, respectively, for total PCBs. Assuming that the hypothesis made about ingestion of feces by catfish is valid, the true food ingestion rate by catfish should be lower than that incorporated into the model, leading to lower uptake predictions than the current estimations and mitigating the overprediction bias in the predictions. Another modification which can possibly improve the kinetic model predictions for the catfish would be to incorporate biotransformation rate constant in the model as a loss process. Although there is a body of literature reporting metabolism of PCB congeners in fish (Arnot et al., 2008a; Arnot et al., 2008b; Tang et al., 2017), biotransformation was not included in the catfish model due to lack of existence of species-specific rate constants.



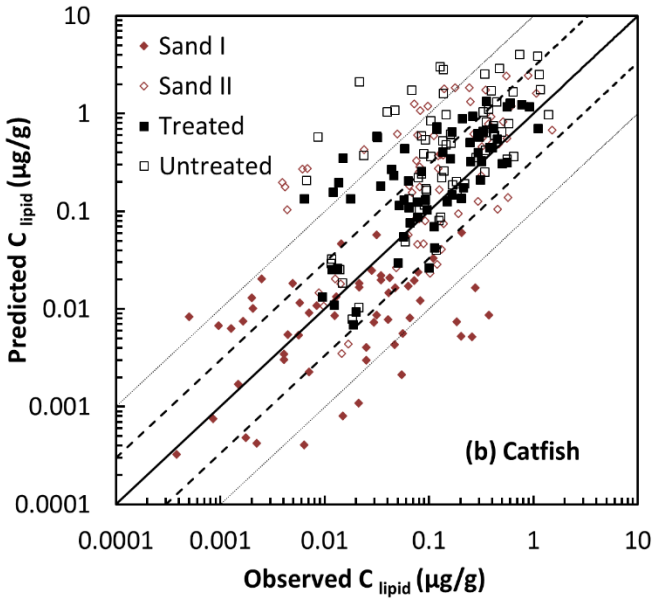


Figure 3.5. Observed vs predicted PCB concentrations in (a) mummichog and (b) catfish after 90 days using the Connolly kinetic model which accounts for uptake through sediment ingestion. The dashed lines represent 3 and 10 times the values of the 1:1 line.

Overall, the modified kinetic model (equation 8) took into account the time variable nature of uptake and loss processes and resulted in better predictions than the equilibrium model. It is important to recognize that such reasonable predictions are attributed to the use of species-specific respiration rate, and use of food and sediment ingestion rates that were derived from measured values in each fish instead of using empirical correlations from the literature. The only two parameters that were obtained from less case-specific sources were the assimilation efficiency of PCBs in food (α) and assimilation efficiency of sediment-bound PCBs (β). However, it is difficult to provide a quantitative discussion on the importance of accurate measurement of these input parameters before conducting an uncertainty analysis. The relative contribution from the ingestion pathway to overall PCB uptake increased

with increasing PCB hydrophobicity for both fish (Figures 6 and S19). This was due to lower solubility and thus lower exposure of the heavier PCBs through water. Gill uptake followed the opposite trend with hydrophobicity as respiration was the dominant exposure pathway for the more water soluble PCBs. PCB uptake for both fish in all three sets of tanks was dominated by food uptake followed by sediment ingestion for both fish species in the treated tanks and gill uptake for both fish species in the untreated tanks. Although net uptake was greatly reduced after sediment treatment, the percent contribution from the ingestion pathway to the total PCB uptake in mummichog was 4% and 17% for untreated and treated sediment, respectively (Figure 3.6). The corresponding values for catfish were 24 % and 43 %, respectively (Figure S19). This is due to lower aqueous PCB concentrations in the treated tanks and thus gill uptake becoming a less significant pathway. Seeing higher contribution from sediment ingestion pathway to the catfish uptake was expected due to the foraging behavior of this species.

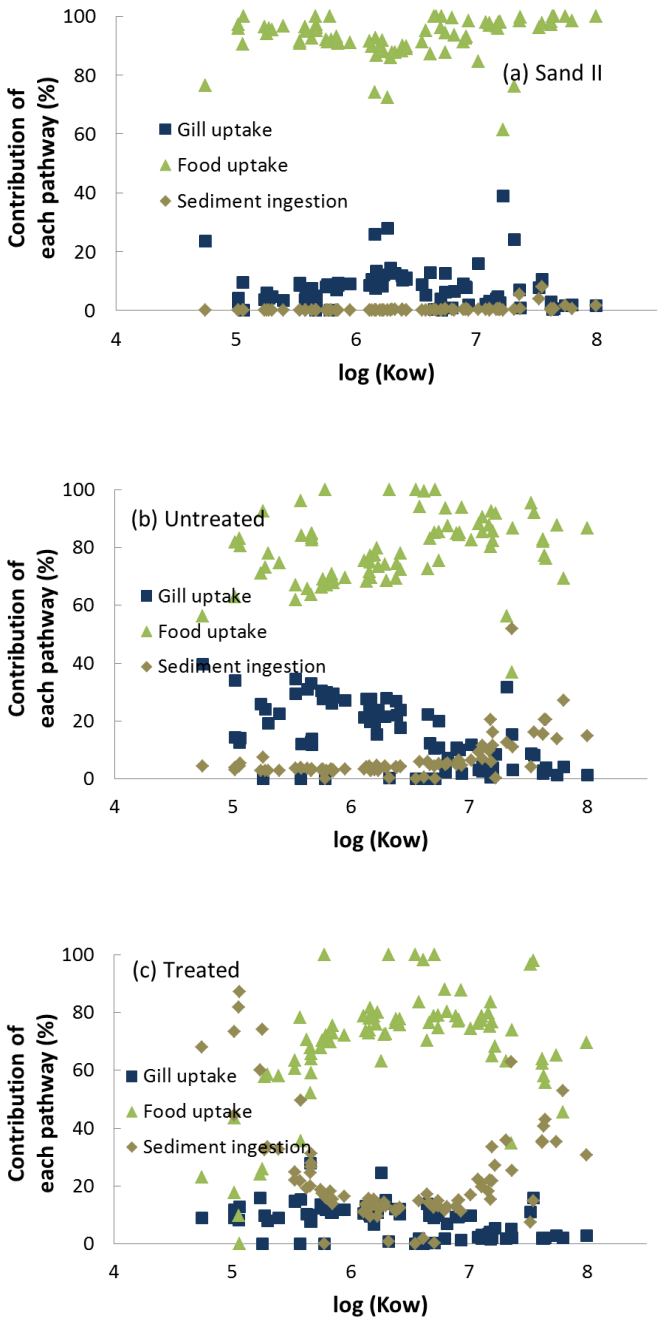


Figure 3.6. The relationship between modeled contributions of gill and food uptake, as well as sediment ingestion to the body burden and K_{ow} of PCB congeners in mummichog exposed to (a) Sand II, (b) untreated, and (c) treated sediment.

Percent Reduction in Aqueous PCBs and Bioaccumulation

Observed percent reductions in porewater, overlying water, and both fish concentrations 90 days after amendment with AC are shown in Figure 3.7. For porewater, overlying water, and fish the effect of the treatment after 90 days was most pronounced on congeners with log (K_{OW}) less than 6. This is explained by faster mass transfer kinetics from sediment to AC for lower chlorinated compared to the higher chlorinated PCBs and greater bioavailability of these compounds. Porewater and overlying water did not show similar reductions over the log (K_{OW}) range. It is noteworthy that the observed reduction in mummichog and catfish were close to but not exactly the same as reductions observed in the overlying water and porewater, respectively, likely due to the concentrations in fish having not reached equilibrium in 90 days. Furthermore, since the food was not in equilibrium with the overlying water or porewater, the reductions in fish body burden for both species are not expected to reach exactly that of the overlying water or porewater. Long-term simulations were conducted with the kinetic model for 1000 days of exposure (Figure 3.7). The predicted reduction in mummichog at 1000 days after the treatment (green triangles) were slightly lower than the observed reductions at 90 days. The predicted reduction in catfish at 1000 days (green triangles) were higher than the observed reductions at 90 days (27% observed reduction versus 49% predicted reduction for total PCBs), suggesting the effect of slower kinetics in the observed response of catfish to treatment. If the hypothesis that ingestion of feces can act as another exposure route for catfish is considered valid and a lower value is used for the ingestion rate of catfish, the predicted reductions will be increased. Furthermore, if the assumption of

the 20% role of porewater in the respiratory ventilation of catfish is changed to a higher value, the predicted reductions will be increased.

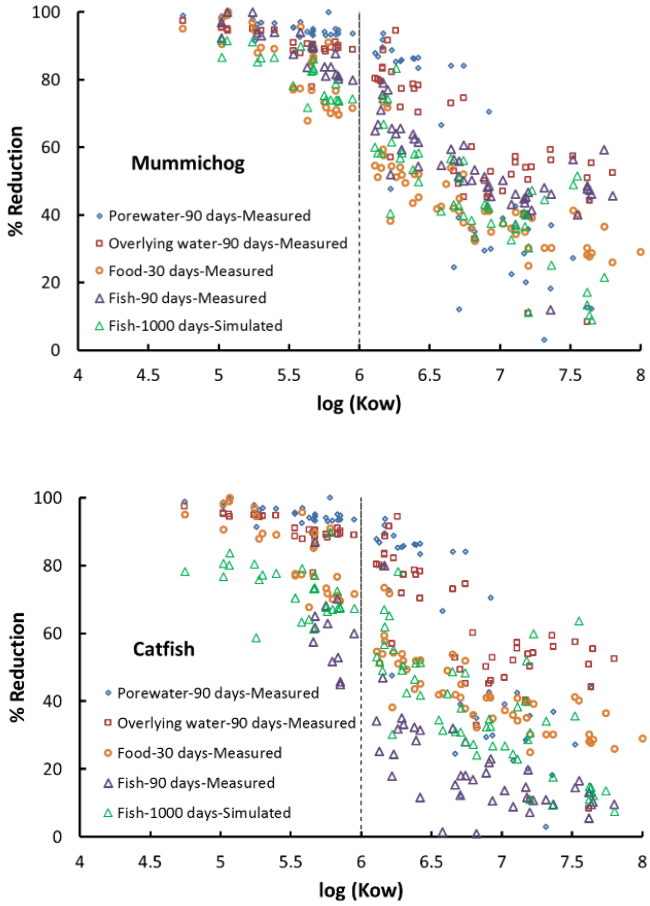


Figure 3.7. Percent reduction in water, food, and fish concentrations after AC amendment.

Since the observed difference between the body burden of the fish in untreated tanks and Sand II tanks can represent sum of uptake from water and sediment ingestion, the ability of the bioaccumulation model to predict this term was tested. The predictions were within an order of magnitude from the observed values with

some consistent over-prediction bias for the case of mummichog species (Figure S20).

Implications of This Research

Results from this work show that PCB bioavailability changes in sediment are reflected in uptake by fish, primarily through reductions in flux from sediments and reduced bioaccumulation by benthic organisms. The use of sediments that were treated in the field in 2006 facilitates long-term effectiveness monitoring of AC amendment and provides evidence that AC in the sediment has been diluted due to deposition of new sediment. The modeled uptake through each pathway reiterates the importance of food intake to PCB bioaccumulation, especially the more hydrophobic congeners, by both fish. Depending on the swimming behavior of the fish, either gill uptake or sediment ingestion is the second key pathway for uptake, so fish with different foraging behavior respond differently to sediment amendment with AC. In the case of catfish and mummichog, different exchange rates and biology can lead to the fish which exhibits faster kinetics i.e. mummichog, to reflect changes in bioavailability much faster than catfish. Other researchers have tried to improve the predictions with the bioaccumulation models by including sediment ingestion as an exposure pathway (Moermond et al., 2004; van Beusekom et al., 2006) but have not used independently measured assimilation efficiency for sediment-bound PCBs as input to their models. The modified bioaccumulation model that was used in this study is the first to quantify this pathway through direct measurement of assimilation efficiency of sediment-bound PCBs. However, since sediment ingestion rate was obtained by fitting the model to the observed data, more data when sediment

ingestion rate is calculated independently is needed to validate the modified bioaccumulation model. Overall, the kinetic bioaccumulation model can predict uptake in fish using freely dissolved porewater and overlying water concentrations obtained from passive sampling as well as concentrations in food and sediment. The reasonable predictions made by the kinetic model demonstrates the capability of such a model to be linked with fate and transport models and used as a tool to predict achievable reductions in pelagic and benthic-feeding fish residing in a water body in the presence of all PCB exposure pathways after addition of a known dose of carbonaceous material to the sediment.

Chapter 4: Assimilation Efficiency of Sediment-Bound PCBs Ingested by Fish Impacted by Strong Sorption

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Introduction

Bioaccumulation models are available that can predict uptake of hydrophobic organics, such as polychlorinated biphenyls (PCBs) through water and food. These models are based on calibrated uptake rate constants, and site-specific values of chemical concentrations in water, sediment, and prey items (Arnot and Gobas, 2004b; Connolly, 1991). While these models have been generally effective in predicting uptake in large contaminated systems, the ability to predict changes after engineering alterations in sediments is questionable and there are key uncertainties that need to be addressed especially when bioavailability in sediments is altered. For instance, one factor that plays an important role in the PCB dietary uptake, mainly for the more hydrophobic congeners, is the efficiency with which fish assimilate chemicals from dietary sources, which can change after sediment amendment. Dietary sources not only include prey items but can contain matrices other than food, such as sediment particles. Others in the scientific community have theorized that PCBs sorbed to activated carbon (AC) particles can be available for uptake in fish after ingestion (Weber, 2005). Sediment ingestion is critically important for benthivorous fish, since they resuspend (Scheffer et al., 2003) and ingest considerable amounts of sediments when feeding (Tolonen et al., 2000). Therefore, it is necessary to investigate changes in PCB uptake through sediment ingestion when total PCB concentration in the sediment remains constant but bioavailability is altered. (Gaillard et al., 2014)

compared the relative bioavailability of PCB-impacted sediments containing 0.3% native black carbon with the bioavailability of PCBs carried by canola oil to carp but did not measure assimilation efficiency (AE) of sediment-bound PCBs. The findings of this study revealed that PCBs sorbed to sediment were as available as PCBs in canola oil at three tested concentrations. The authors suggested that the experiment should be repeated with sediment of various ages and black carbon content to evaluate how sediment properties can affect PCB bioavailability. In our previous work (Fadaei et al., 2015) exposure through ingestion was calibrated (separately for the untreated and treated sediment) by accounting for the observed uptake of the dominant heptachlorobiphenyl PCB-180 that could not be explained by uptake solely from water and PCB-free food. Assuming that the fish exposed to untreated and treated sediment had the same ingestion rates, the ratio of AEs of untreated to treated sediment-bound PCBs was calculated to be 2. These findings led to exploring changes that occur in AE of PCBs after AC amendment of sediment. However, frequently used bioaccumulation models such as the Arnot and Gobas (2004b) model allow the incidental sediment ingestion by fish to be included as part of the diet and apply the assimilation efficiency values for biotic diets to sediments. Not using characterized assimilation efficiency values for the PCBs bound to the sediment implies that these models may be less suitable for bottom-feeding fish. To address this gap, literature studies have included sediment ingestion as an exposure pathway (Moermond et al., 2004; van Beusekom et al., 2006). In our previous work (Fadaei et al., 2015) we showed that while AC amendment reduced uptake in fish, a substantial portion of the remaining uptake came from the sediment ingestion pathway (69%

contribution from this pathway to the total fish PCB uptake exposed to the treated sediment). However, it should be noted that these values were obtained from fitting the model to the observed data and not from independent measures of ingestion rate and assimilation efficiency. Moermond et al. (2004) modeled the PCB assimilation rate from sediment for carp based on observations that benthivorous fish ingest as much sediment as invertebrate food and estimating the lumped product of AE and ingestion rate from empirical correlations. Furthermore, their study focused on a natural lake system that did not explore changes that happen after bioavailability manipulation in sediment. Given the importance of incidental sediment ingestion as an uptake pathway, it is important to define sediment ingestion rate and AE terms independently, and as accurately as possible. Several methods, such as gravimetric analysis of fish gut contents and a mass balance tracer approach, have been proposed to measure sediment ingestion rate (Doyle et al., 2011). While numerous laboratory studies have measured PCB AE of contaminated food in fish (Burreau et al., 1997; Fisk et al., 1998; Gobas et al., 1993; Niimi and Oliver, 1983; Stapleton et al., 2004) (Table 4.1), no study to our knowledge has assessed AE of PCBs associated with contaminated sediment in fish. Since deposit feeding invertebrates feed on sediment and detritus at high feeding rates to obtain required nutrients for energy budgets and survival (Arnot and Gobas, 2004b), PCB uptake through sediment ingestion for these organisms has been widely studied. Therefore, most of the AE values for sediment ingestion that exist in the literature are for aquatic invertebrates. Researchers have reported AE values ranging from 15 to 75% for tetra- to hexachlorobiphenyl compounds in spiked sediments fed to amphipods, oligochaetes, clams, and mussels

(McLeod et al., 2004b; Sun et al., 2009; Wang and Fisher, 1999) (Table 4.1). McLeod et al. investigated the bioavailability to clams (*Macoma balthica*) via PCB-spiked diets which included different carbonaceous particles (McLeod et al., 2004b). Their findings are the only AE values for activated carbon reported in the literature.

The present study was designed to investigate the effect of sorption on fish dietary AE of PCBs in sediments. Dietary AE of PCBs in different dietary matrices, including worms, worms mixed with sediment, worms mixed with AC-treated sediment and worms mixed with AC was measured 24 hours after feeding. Understanding how the AE of particle-associated PCBs changes after AC amendment will help characterize PCB uptake by fish through the sediment ingestion pathway more accurately and quantify how uptake through this pathway changes upon addition of activated carbon to sediments.

Table 4.1. Reported assimilation efficiency values for fish and invertebrates

Organism	Food	Compound [a]	AE [b] %	Reference
Fish				
Juvenile carp	frozen bloodworm blended with cod liver oil containing PCBs	tetra, hexa, hepta-CB	40	Stapleton et al. (2004)
Rainbow trout	commercial fish food + PCBs dissolved in hexane and mixed with capelin fish oil (gavaged)	di to deca-CB	75 (average)	Niimi and Oliver (1983)
Juvenile rainbow trout	commercial fish food + PCBs dissolved in hexane	PCBs	31-49	Fisk et al. (1998)
Pike	rainbow trout injected with PCBs dissolved in rainbow trout lipid	tri to hexa-CB	44-71	Burreau et al. (1997)
Goldfish	commercial fish food + PCBs dissolved in petroleum ether	tetra, hexa, octa, deca-CB	26-53	Gobas et al. (1993)
Amphipod				
Diporeia sp	sediment	HCBP	46-58	Kukkonen and Landrum (1995)
			36-52	Kukkonen and Landrum (1995)
Oligochaete				
Limnodrilus hoffmeisteri	sediment	HCBP	15–37	Klump et al. (1987)
Lumbriculus variegatus	sediment	PCBs	10-36	Sun et al. (2009)
Clam				
Macoma balthica	wood particles	TCBP	75	McLeod et al. (2004a)
Macoma balthica	activated carbon	TCBP	Less than 2	McLeod et al. (2004a)
Zebra mussel				
Dreissena polymorpha	sediment	HCBP	30	Bruner et al. (1994); Gossiaux et al. (1998)

[a] HCBP = hexachlorobiphenyl; TCBP = tetrachlorobiphenyl.
[b] AE = assimilation efficiency

Materials and Methods

Food Preparation

Four types of diets were used in the present study: PCB-spiked worms (W), clean worms mixed with untreated spiked sediment (U), clean worms mixed with treated spiked sediment (T), and clean worms mixed with PCB-spiked AC particles (AC). Lyophilized earthworms (*Lumbricus terrestris*) were used as clean food and Rhode River sediment, a fine grained silty sediment which had a measured PCB concentration below the level of detection (0.01 μg/g dry wt.), was used as the clean sediment matrix. Coal-based powdered activated carbon (≤ 44μm; Calgon Carbon) was used as an amendment to the sediment. A PCB congener mixture standard from Ultra Scientific (RPC-EPA2-1), which contains 16 PCB congeners spanning a wide range of log K_{OW} values, was used to spike the food. For PCB-spiked food, a specific volume of the PCB standard solution in acetone was added to lyophilized earthworms, completely covering them. After the earthworm mixture was shaken for 12 hours, the solvent was evaporated under a nitrogen stream. For the other three diets, the spiking procedure used by McLeod et al. (2004b) was followed, that is, specific volumes of the PCB standard in acetone were added to glass vials containing dichloromethane and evaporated to dryness by gentle hand swirling, leaving the compounds adhered to the inside walls of the vials. Clean Rhode River sediment was ground up with a mortar and pestle to be used as untreated sediment or mixed with AC to make the treated sediment. Untreated sediment, treated sediment (sediment +5% AC), and AC particles were added to separate vials as suspensions in 5 ml deionized water. Spike vials were sealed with Teflon septa and mixed on a rotator for

21 days. Once air-dried, 20% sediment (including AC mass for treated sediment) or AC particles and 80% clean worms by weight as well as the spiked earthworms were shaped into 2 mm pellets using carboxymethyl cellulose and water solution (additional 2.5% carboxymethyl cellulose by dry weight food) (see Figure S1 in the Appendix III). The optimal 20 to 80% mass distribution was chosen based on test studies conducted prior to the main experiment that used pellets containing different amounts of sediment for feeding the fish. Higher percentage of sediment or AC caused the fish to avoid the pellets or the pellets to fall apart too soon. An initial mass of PCBs in the food pellets was measured before the start of the experiment.

Test Organisms and Feeding Procedure

Mummichogs (*Fundulus heteroclitius*) were spawned at Delaware State University and the fertilized eggs were transported to the Institute of Marine and Environmental Technology (Baltimore, MD, USA) where they hatched and were raised until they reached adult size weight (~ 20 g wet). The fish used in this experiment comprised males and females and were similar in size to minimize effects of size and age on PCB uptake. The fish were acclimated to their new diet a week prior to beginning the experiment by being fed with pellets composed of 20% sediment or AC particles and 80% clean worms by weight. Subsequently, the fish were fed pre-weighed and equal amount of food three times during 7 hours, based on a feeding rate of 1.5% (mass dry food/mass wet fish body weight) per day, and sampled after a 17-hour fasting period. The pellets sank to the bottom of each tank and were consumed shortly after being offered to fish, with the exception of the AC pellets, for which less than 5% of the AC particles remained uneaten due to the pellets

breaking apart (the 5% was determined visually). Feces at the bottom of the tanks were siphoned out frequently throughout the feeding period to avoid introducing more PCBs to the fish through ingestion of feces. It should be noted that feces were not analyzed for PCBs in the present study. This study was carried out in accordance with the guidelines of the International Animal Care and Use Committee of the University of Maryland Medical School (IACUC protocol #1015008).

Aquarium Set Up

Four sets of tanks (triplicate tanks for each set) were used for the four types of food (see Figure S2). Each tank contained 8 L of synthetic seawater (as grams per liter: NaCl, 21.998; MgCl, 6.89; CaCl, 1.26; KCl, 0.66; SrCl, 0.015; LiCl, 0.01; $NaSO_4$, 2.53; $MgSO_4$, 1.87; $NaBO_4$, 0.04; $NaMoO_4$, 0.00001; $NaCO_3$, 0.06; $NaHCO_4$, 0.23) diluted with dechlorinated tap water to a salinity of 15 psu, and one individual mummichog. There was an even distribution of male and female fish for each of the four sets of tanks (Table S1). Fish were maintained under static conditions and the chemical composition of the water (pH, conductivity, and alkalinity), ammonia and nitrite levels were monitored throughout the experiment. pH and conductivity were measured using a Horiba U-22 multiparameter probe. Alkalinity, ammonia, and nitrate were measured with water quality test kits (Hach Co.). Each tank was equipped with a heater to maintain the water temperature uniformly at 28°C, the optimal growth temperature for fish, in all tanks. Tanks were equipped with air stones to maintain adequate oxygen level in the water. A 14:10-hr light:dark photoperiod was maintained in the laboratory.

Sampling and PCB Analysis

Fish from all tanks were sampled 24 hours after feeding started, sacrificed using dry ice, and the digestive tract from the stomach to the anus, which will be referred to as the gut in this manuscript, was removed from the fish by dissection. Gut contents were purged manually and preserved for PCB analysis. The gut and the rest of the body (referred to as fish tissue in this manuscript) were each lyophilized and frozen until analysis. Separate fish tissue and gut samples were used to determine background PCB levels in the fish prior to exposure. Fish from each tank were analyzed individually. Fish tissue samples were ground with anhydrous sodium sulfate and extracted with a hexane:acetone mixture (1:1, v/v) following method SW846 3550C. Prior to extraction, surrogate recovery standards (PCB BZ#14 and 65) were added to assess processing efficiency. Percent surrogate recovery in all analyzed samples was within the criteria of 100 ± 30%. The lipids were removed by treating with concentrated sulfuric acid. Further cleanup was performed by treating the extract with activated copper and passing through a 3% deactivated florisil and acidified silica gel column. The eluate was concentrated by nitrogen evaporation and analyzed for PCB congeners as described in Fadaei et al. (2015), using PCB BZ#30 and 204 as internal standards. A quality control plan was implemented to ensure that the chemical analyses performed were accurate (Fadaei et al., 2015). PCB analysis of the food pellets, gut tissue and gut content samples were similar to fish tissue except that EPA 3630C method (silica gel cleanup) was used for cleanup.

Data Analysis

The assimilation efficiency (AE) was calculated from equation 1 as described in the dietary exposure test section (equation A7.7, Appendix 7) of the Organisation for Economic Co-operation and Development Guidelines for Testing of Chemicals (OECD, 2011):

$$\mathrm{AE} = \frac{\text{PCB body burden in fish}}{\text{mass of PCBs that was ingested by the fish}} \qquad (1)$$

The following assumptions were made to use equation 1: (1) Losses from the fish during the experiment are insignificant, i.e. depuration and PCB loss via respiration and fecal egestion are negligible, (2) biotransformation of PCBs is minimal, and (3) the sampling occurs at the linear portion of the uptake curve, i.e. days 1 to 3 in a typical exposure (OECD, 2011).

Since the uneaten AC particles were siphoned out and no uneaten food was observed in the case of the other three pellets, dissolution of PCBs associated with food into the water was minimized. Therefore, the ratio measured in the present study represents direct AE as this was only exposure through food and did not include aquatic exposure.

Partition constants (K_d) for three of the diets were predicted by modeling sorption to organic carbon (OC) and applied AC.

$$K_d = f_{OC}\, K_{OC} \quad (U\ diet) \qquad (2)$$

$$K_d = f_{OC}\, K_{OC} + f_{AC} K_{AC} \quad (T\ and\ AC\ diets) \qquad (3)$$

where f_{OC} and f_{AC} are the fractions of OC and AC in sediments, K_{OC} and K_{AC} are water-sorbent distribution constants for OC and AC, respectively with unit of (L/kg sorbent). Total organic carbon and black carbon content in untreated Rhode River sediment were measured as 3.9±0.06% and 0.2±0.01% by dry weight (Average ± S.E.), respectively. AC content in the solids portion of the T and AC diets were 5% and 100%, respectively.

K_{OC} (L/kg OC) values for PCB congeners were estimated using equation 4 (Werner et al., 2010). To use this empirical correlation the octanol-water partitioning constant (K_{OW} (-)) was obtained from Hawker and Connell (1988).

$$\log(K_{OC}) = 0.74\ \log(K_{OW}) + 0.15 \qquad (4)$$

Sorption to AC was described by a Freundlich isotherm, assuming n=1 for all PCB congeners because the n values reported by (Gomez-Eyles et al., 2013) were close to 1 for most of the PCB congeners. K_{AC} values for different congeners were obtained from published isotherm study results by Gomez-Eyles et al. (2013) using coal-based AC. K_{AC} was calculated from the mean of the ratios of sediment to aqueous PCBs at different concentrations (Table S2).

Partition constant between particle and octanol (K_{po}) was calculated as:

$$K_{po} = \frac{K_d}{K_{ow}} \qquad (5)$$

where K_{ow} is the partition constant between octanol and water as reported in Hawker and Connell (1998).

Results and Discussion

Fish Weights and PCBs in Food

The average weight of the fish in different tanks was 16±0.73 g (Average ± S.E.) (Table S1). The total PCB concentration was 1.0 and 1.2 µg/g dry weight for W and T diets (not significantly different, p=0.09, ANOVA); 0.3 and 4.1 µg/g dry weight for U and AC diets, respectively (see Table S3 for congener specific concentrations in all the four diets). For the AC diet, AC was spiked with higher PCB levels due to anticipated reduced AE and to allow accumulation of detectable levels of PCBs in the fish. The final total PCB mass that measured in W and U diets after the spiking procedure was half of what was spiked, suggesting that a portion of the added PCBs were lost through the spiking procedure. This residual was reduced to one-fifth for the T and AC diets, likely due to lower extraction efficiency of PCBs in the presence of AC. The actual measured PCB masses in the food were used for AE calculations and may provide a conservative estimate of AE for T and AC where extraction efficiency was poor.

AE for Worm Diet

Figure 4.1a shows the results of PCB analyses in the food, fish tissue, gut tissue, and gut content for the PCB-spiked worms (W) diet. Reported residual PCBs in fish tissue and gut tissue were corrected for background levels. The majority of the adsorbed PCBs were assimilated in the fish tissue after 24 hours. Gut tissue PCBs

contributed on average 11% of the total PCB body burden for fish that fed on W diet. The results also indicate that the post-feeding 17 hour fasting/purging period was sufficient to eliminate most of the unabsorbed PCBs through gut contents.

AE-K_{OW} Relationship

In the case of the W diet, AEs of PCBs show an initial increase (strong correlation with log K_{OW}, p=0.007 < 0.05, Pearson's test) up to a log K_{OW} value of 6.5 followed by a decrease (strong correlation with log K_{OW}, p=0.006 < 0.05, Pearson's test) with increasing log K_{ow} (Figure 4.1b). Such bell-shaped response of AE with respect to K_{ow} of compounds has been observed before such as in the data for rainbow trout (Fisk et al., 1998) also shown in Figure 4.1b. Previous work by Gobas et al. (Arnot and Gobas, 2004a; Gobas et al., 1988) reviewed empirical measurements of AE in the literature and concluded that dietary AE is initially independent of log K_{OW} and starts decreasing at log K_{OW} of 6 for a range of hydrophobic organic chemicals due to reduced bioavailability and steric hindrance in crossing biological membranes. The predicted values by the Gobas et al. (1988) and Lo et al. (2015) models were plotted in Figure 4.1b. In these non-linear models AE (α) is presented as $\alpha = (2 + 3 \times 10^{-7} \times K_{OW})^{-1}$ and $\alpha = (1.9 + 5.6 \times 10^{-9} \times K_{OW})^{-1}$, respectively. Gobas at al. model predictions were statistically different ($1\text{-}R^2 = 0.93$) than absolute values of AE for the W diet. The predicted values by the Gobas model were derived by fitting a non-linear correlation to empirical data from various fish species that may not have the capability to predict variations in fish species, feeding rate, diet type and quality, as well as food concentration. Using the relationship derived from one species and size

(rainbow trout) by Lo et al. led to improved predictions ($1\text{-}R^2 = 0.51$) compared to the relationship derived for multiple species and sizes by Gobas et al.

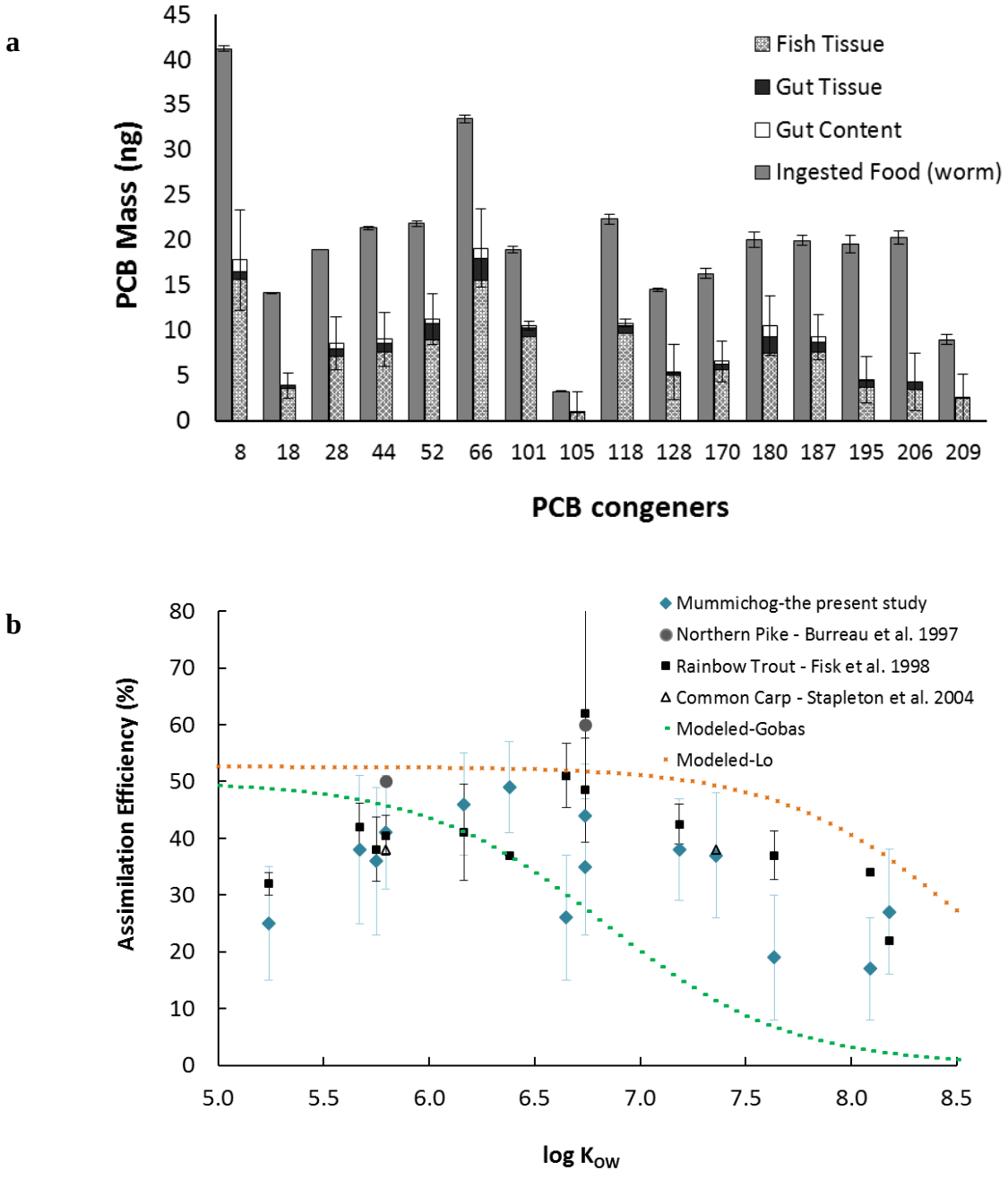


Figure 4.1. (a) Mass of PCBs in the W (worm) diet, fish tissue, gut tissue, and gut content, and (b) assimilation efficiency of different PCBs in the W diet as a function of log K_{OW} and their comparison with literature values. The lines in Figure 1b represent the AE-log K_{OW} correlations developed by Gobas et al. (1988) and Lo et al. (2015). Error bars represent standard error.

Comparison of Observed AE for Worm Diet with Literature Values

AE of different PCBs in the W diet was mostly similar to the values reported in the literature for fish (Burreau et al., 1997; Fisk et al., 1998; Stapleton et al., 2004) (Figure 4.1b, see also Table 4.1 for other literature values). Arnot and Gobas 2004b reported that the empirical AE observations are highly variable in fish ranging between 0 and 90%. They attributed the variance in measured AE to the differences in composition and sorption capacity of dietary matrices (e.g., organic carbon and soot carbon content), and differences in how various species process food in the gut. The above factors explain the discrepancy between the Gobas AE model and reported values in the literature (including the results from the present study). The three cited studies in the literature used rainbow trout, commercial fish food, and frozen bloodworm as the food matrix, respectively. It should be highlighted that results from the present study reflect true AE measured at a shorter time while values reported in the cited studies are net AE values measured at longer exposure times. The observed difference is also attributed to use of fish from different species (which leads to differences in gut morphology and food digestion processes) (Arnot and Gobas, 2004b), age, and size (Barber, 2008; Fisk et al., 1998). In addition, different food lipid content and composition (Dabrowska et al., 1999; Gobas et al., 1993), food digestibility (Gobas et al., 1999), fish feeding rate (Clark and Mackay, 1991), and the method used to deliver PCBs to the animal food (Nichols et al., 2001) can result in variations in AE among studies. In the W diet, average AE of the 16 congeners and AE of hexachlorobiphenyl were 34 and 35%, respectively, which compare well with

the PCB AE values reported for members of amphipod, oligochaete, and zebra mussel group (Tables S4 and 1).

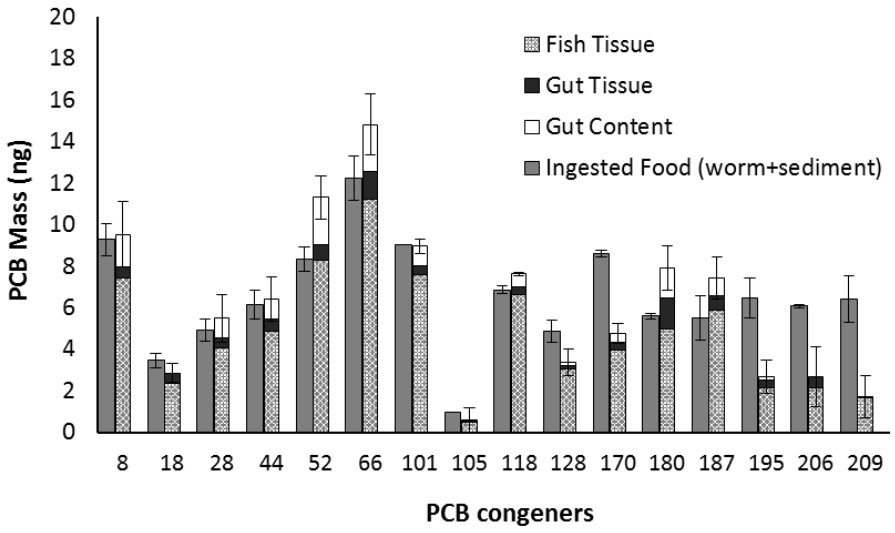
AE for Sediment and AC Diets

Consistency of the AE results of PCBs in food discussed in the previous section with literature values confirmed the accuracy of the experiment design and the analytical method of the present study to measure AE. This section discusses the AE of PCBs associated with the sediment and carbon phases in matrices that composed of PCB-free worm and PCB-spiked solids.

Figure 4.2 shows the results of PCB analyses in the food, fish tissue, gut tissue, and gut content for the three diets that contained a non-food portion: clean worms mixed with untreated spiked sediment (U), clean worms mixed with treated spiked sediment (T), and clean worms mixed with PCB-spiked AC particles (AC). Reported residual PCBs in fish tissue and gut tissue were corrected for background levels. Figures 4.2a through 4.2c indicate that the majority of the adsorbed PCBs were assimilated in the fish tissue after 24 hours with little residue in the gut tissue. Also, purging was effective in minimizing residual PCBs in the gut. Gut tissue PCBs contributed on average 10 and 13% of the total PCB body burden for fish that fed on U and AC diets, respectively, and higher levels were observed with T diet (23%). Gut tissue contributed to body burden of lower chlorinated congeners more in the T and AC diets versus the U diet. As the gut tissue is the medium through which PCBs are being transported from the gut contents into the fish, one would expect to see higher concentration in the gut tissue than the rest of the organism. In addition, it is possible that some of the fine AC remains stuck within the gut. It was presumed that any PCBs

not measured in the tissue, gut and gut content was lost through fecal and gill elimination. In order to support the assumption that PCB loss through the gills did not interfere with the AE calculation, a kinetic bioaccumulation model (Connolly, 1991) was used to quantitate the maximum PCB loss through the gills in the 24 hour exposure and depuration period (see Equations 2 to 4 in Appendix III). The loss of total PCBs through the gills was less than 1% of the total PCB ingested by the fish (see Table S5 for congener level losses through the gills).

a



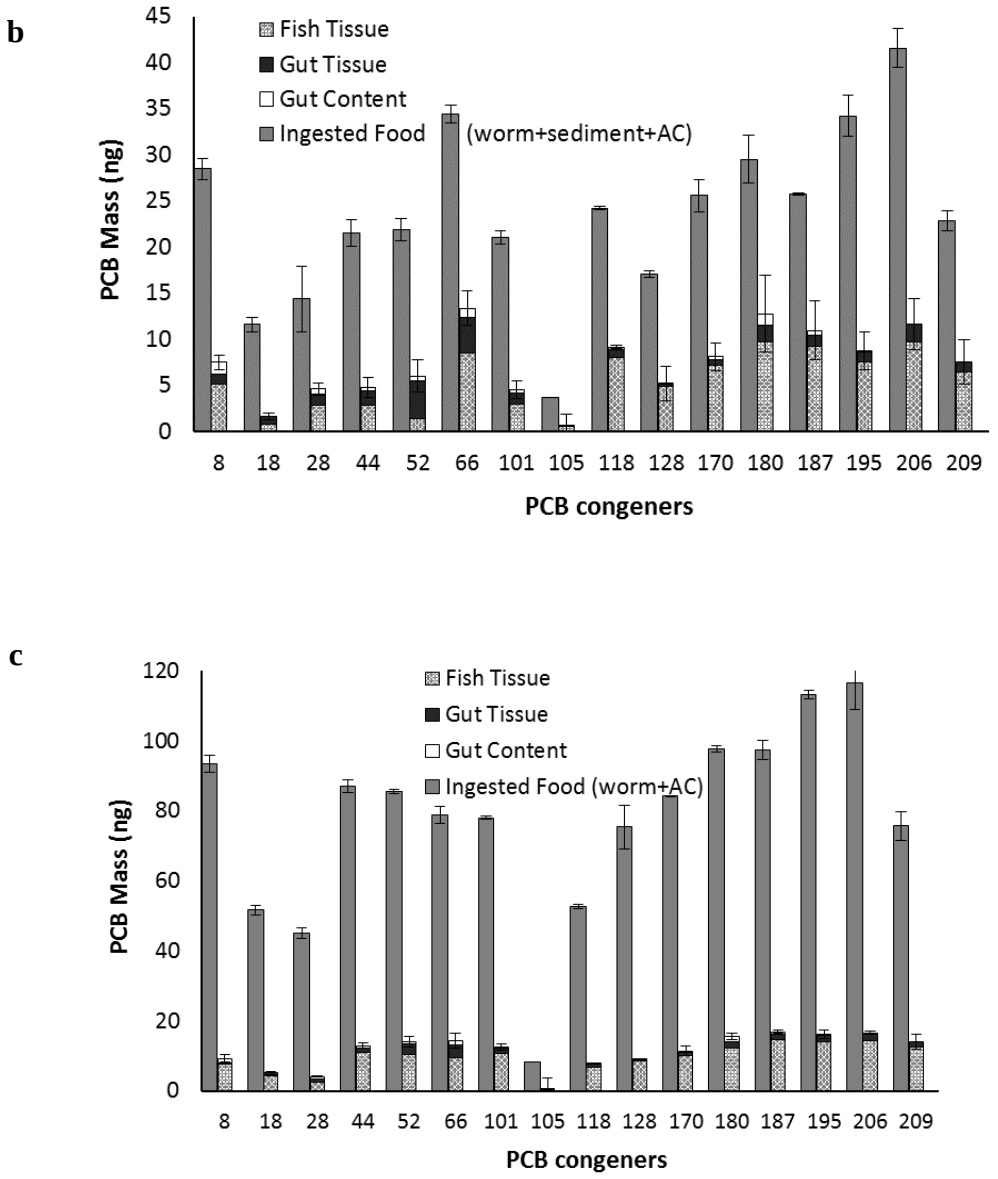


Figure 4.2. Mass of PCBs in the food, fish tissue, gut tissue, and gut content for the (a) U (worm + sediment), (b) T (worm + sediment + AC), and (c) AC (worm + AC) diets. Error bars represent standard error.

AE Comparison among Diets And Comparison With Literature Values

AE of sediment-bound PCBs was reduced by 31 to 93% for different congeners upon amendment of sediment with AC (Figures 4.3a and 4.3b, Table S4).

The reduction in bioavailability to fish due to the addition of AC to the diet was more pronounced for the lower chlorinated PCBs, likely due to the faster mass transfer kinetics of these spiked compounds to the AC particles (Werner et al., 2006). The ratio of directly measured AEs of untreated to treated sediment-bound PCBs was found to be 2 for the majority of the PCB congeners used in the present study (Table S4). This ratio is identical to the value calculated independently in Fadaei et. al. (2015) for the ratio of the product of ingestion rate and AE for fish exposed for 90 days to untreated and treated sediment.

The sediment-bound PCBs in U diet were more bioavailable to fish than those in the W diet (Figure 4.3a and 4.1b). This suggests that PCBs bound to untreated sediment were not resistant to gut fluids. Hypothetically, this could be due to longer residence time of the PCBs in the gut in the presence of untreated sediment as time required to digest and pass the meal can differ. Further investigations may be required to better understand the relationship between food quality, gut passage time, and AE. Unfortunately, feces were not quantitatively collected in the present study, preventing diet digestion efficiency calculations across the diet treatments. Gaillard et al. (2014) compared differences between PCB bioavailability in sediment and food matrices. Three diets spiked with increasing masses of PCBs in canola oil and three diets contaminated via increasing masses of PCBs in sediment were fed to carp over an exposure period of 15 days. Gaillard et al. (2014) measured the relative bioavailability by comparing the slopes of the fish PCB concentration plotted against diet PCB concentration for sediment and oil-based diets. The results demonstrated that the sediment-bound PCBs were as bioavailable as those spiked into canola oil

and fed to carp in standard diet (the aforementioned study also used 21% sediment by dry weight in one of their PCB contaminated diets and the sediment contained 3.4% organic carbon). DiPinto and Coull (1997) observed that uptake of Aroclor 1254 by juvenile fish *L. xanthurus* was five times higher from contaminated sediments than contaminated prey. In an identically designed feeding experiment, DiPinto (1996) found similar response by juvenile *L. xanthurus* for the organophosphate pesticide azinphosmethyl (uptake was eight times higher from contaminated sediments than from contaminated prey).

In the case of the AC diet, the presence of AC resulted in strong adsorption of PCBs to the diet matrix and hence reduced AE of all the PCB congeners including the lower chlorinated ones which had much higher AE values than the higher chlorinated PCBs in the W and U diets (Figure 4.3c). AC diet showed the lowest AE values and this was not surprising, given the strong sorption of PCBs to activated carbon. However, the observed uneaten food (<5%) in the tanks that received AC diet implies that the calculated AE values were likely underestimated for this diet as the fish did not ingest all the PCBs administered to the food. A comparison of AE between Figures 4.1b and 4.3c suggests that reduced bioavailability of the PCBs in the AC diet affects the extractability of the PCBs in the gut and therefore reduces the efficiency with which fish assimilate PCBs from the AC-food matrix (29 to 86% reduction in AE for different congeners when comparing AC to food only). Since AC pellets were initially spiked with 3.9 times higher sum PCBs than the W pellets (Figures 4.1a and 4.2c), concentration effects can lead to a more conservative estimate of AE for the AC diet. This is mainly because of the nonlinearity of PCB sorption to AC which can

result in weaker sorption at higher concentrations (Cornelissen et al., 2005) and therefore better extraction of the PCBs in the gut. While the calculated AE from the present study was 12±1% for PCB 52 in the AC diet ($C_{PCB\ 52\ in\ food}$ = 0.3 µg/g), Mcleod et al. (2004b) reported AE of less than 2% in clam *Macoma balthica* for the same congener spiked into fine-mesh activated carbon (coal-based, 50 * 200) ($C_{PCB\ 52\ in\ food}$ = 800 µg/g). Mcleod et al. (2004b) observed lower values, likely due to the use of 100% AC in the diet as opposed to use of 20% AC by dry weight food in the present study. Furthermore, different digestion mechanisms of the fish compared to that of clam can be a contributing factor to this difference.

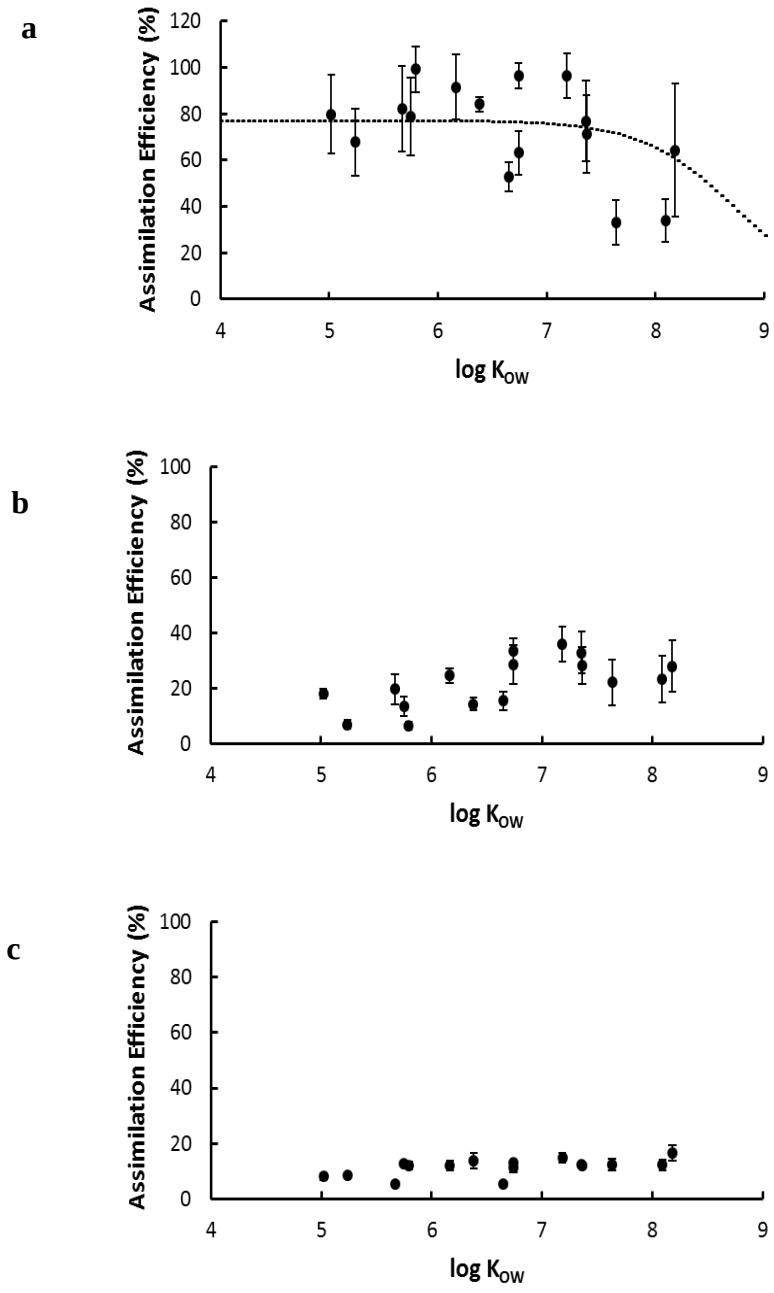


Figure 4.3. Assimilation efficiency as a function of log K_{OW} for the (a) U (worm + sediment), (b) T (worm + sediment + AC), and (c) AC (worm + AC) diets. Error bars represent standard error.

AE-K_{OW} and AE-K_d Relationships

A trend similar to Figure 4.1b was observed for the AEs of PCBs in U diet (Figure 4.3a) with an inflection point around log K_{OW}=7. Fitting the non-linear model to the data in Figure 4.3a resulted in: $AE = (1.3 + 2.4 \times 10^{-9} \times K_{OW})^{-1}$. For the T diet (Figure 4.3b), the statistical analysis did not determine a strong correlation between AE on log K_{OW} ($p=0.08 > 0.05$, Pearson's test). There was no clear relationship between PCB AE values for the AC diet and log K_{OW} (Figure 4.3c). In Figure 4.3, assimilation efficiency values of PCBs were related only to the compounds' hydrophobicity, while sediment geochemistry also plays some role in PCB bioavailability and hence the fish dietary uptake through sediment ingestion. Therefore, AE was plotted against estimated log K_d of U, T, and AC diets for all congeners (Figure 4.4) and individual congeners (Figures 4.5 and S3). As seen in Figure 4.4, there is a strong general trend of decreasing AE with increasing PCB partitioning into the ingested solids as the PCBs are becoming more associated with non-digestible carbon and are not being released through digestion. There is some scatter among the individual congeners in each solid category which is not explained by compound K_d alone (Figure 4.4a). Compound structure and ability to be absorbed in the gut after being released from the solid matrix is not captured by compound K_{OW} alone. The scatter is not reduced significantly when the AE is plotted against the log K_{po} (Figure 4.4b, K_{po} is defined in Equation 5 as partitioning between particle and octanol).

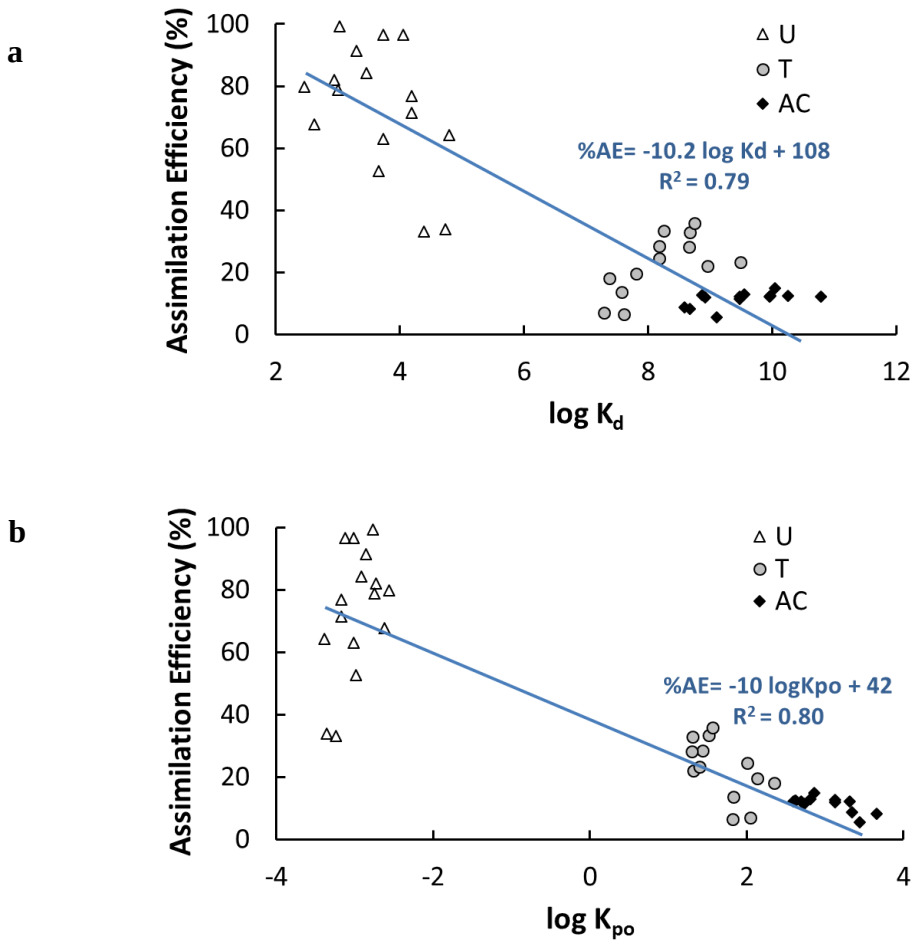


Figure 4.4. Assimilation efficiency of U (worm + sediment), T (worm + sediment + AC), and AC (worm + AC) diets as a function of (a) log K_d and (b) log K_{po}.

AE-log K_d plots for individual congeners (Figure 4.5) showed a strong relationship across different diets. R^2 values improved as the degree of chlorination increased. This could be due to an experimental artefact, which could lead to underestimation of the true AE values for the lower chlorinated PCBs because of their faster rate of depuration compared to the larger PCBs (Fisk et al., 1998). These relationships emphasize how the PCB bioavailability in the fish gut is impacted by the geosorbent type.

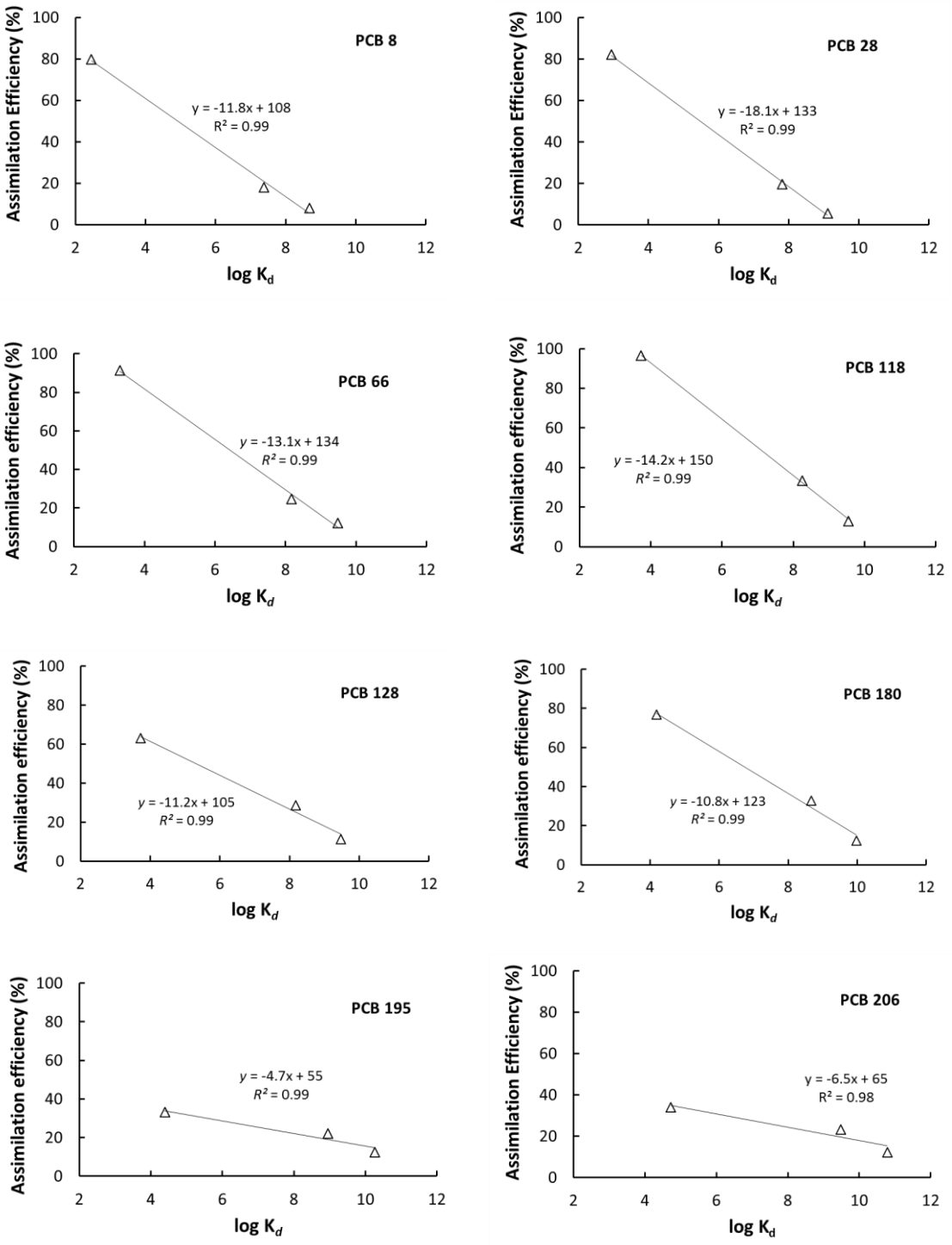


Figure 4.5. AE-log K_d plots for representative congeners from each homolog group. Partition constants (K_d) were calculated as $K_d = f_{OC} K_{OC}$ for U (worm + sediment) diet and as $K_d = f_{OC} K_{OC} + f_{AC} K_{AC}$ for T (worm + sediment + AC) and AC (worm + AC) diets. Remaining congener plots are shown in Supplemental Figure S3.

Change in PCB Uptake Prediction Using Measured AE for Sediments

Three hypothetical scenarios were simulated to evaluate how the measured AE for sediments impact prediction of PCB uptake in benthivorous fish. The PCB uptake through sediment ingestion pathway was estimated based on different AE values for the different scenarios. For the three scenarios, in order to predict uptake through ingestion of treated sediment, the AE for sediment treated with 5% AC was chosen to be: (1) the same as food (the AE results found for the W diet), (2) 100 % AE for all the PCB congeners, and (3) same as AE results for the T diet obtained from the present study. Predictions of PCB body burden were generated and limited to the congeners used in the present study, assuming that a 0.9 kg catfish was in contact with the sediment concentration of 1.6 μg/g d.w for 180 days. The modified version of the Connolly bioaccumulation model (Connolly, 1991) (Equation 5 in Appendix III), which included gill uptake, ingestion of PCB contaminated food and sediment as the uptake pathways, was used. The model assumption was that the fish fed on benthic worms (*Lumbriculus variegatus*) with incidental sediment ingestion. The concentration in the food was estimated from laboratory measured porewater concentrations of treated sediment. It was assumed that catfish ingest as much sediment as invertebrate food. The simulation was also repeated for sediment ingestion rates of 50, 20 and 10% of the food ingestion rate. See Appendix III for a more detailed discussion of the model. Table 4.2 summarizes the simulation results for the different scenarios and shows that using our independently measured AE for sediment PCBs as an input to the model leads to a prediction of PCB uptake in fish at 6 μg/g lipid. If we did not have access to the AE values reported from the present

study and would assume that AE values for sediment-bound PCBs are either the same as PCBs in the food or 100% for all the congeners, we then would overestimate the total PCB uptake in fish at 10 and 24 µg/g lipid, respectively (see row 1 in Table 4.2). As the sediment ingestion rate decreased, not only the uptake predictions for the fish in all the three scenarios decreased, but also the difference between predicted values from scenario 1 and 3 decreased. This is mainly due to the smaller contribution of sediment ingestion to uptake as the sediment ingestion rate is reduced.

Table 4.2. Results of total PCB uptake predictions for catfish exposed to sediment for 180 days based on different choices of AE values for the sediment ingestion pathway and sediment ingestion rate. W and T represent PCB-spiked worms and clean worms mixed with treated spiked sediment, respectively.

	Choice of AE values for sediment		
	Measured AE for W diet	100% AE for all congeners	Measured AE for T diet
Choice of sediment ingestion rate	Total concentration in lipid (µg/g)		
1.0 x G_D	10	24	5.5
0.5 x G_D	5.5	13	3.5
0.2 x G_D	2.8	5.6	1.9
0.1 x G_D	1.9	3.3	1.4

G_D is the food ingestion rate

Implications of This Research

Fish are exposed to PCBs from both particulate and dissolved phases. Few efforts have been made to modify the traditional bioaccumulation models by addition of a term for uptake through ingestion of sediment-associated PCBs. In this regard, measurement of AE of sediment-bound PCBs and estimating contaminant bioavailability in the gut is critical. The previously developed non-linear model

(Gobas et al., 1988) does not account for effects of geochemistry in matrices other than food and is therefore not suitable for estimating AE of PCBs associated with sediment particles. The present study takes a first step towards improving the predictions made by bioaccumulation models after AC amendment of PCB-impacted sediments by looking at the differences in the uptake efficiency of PCBs in food versus sediment with and without AC amendment. Our results indicated that PCBs in the AC-amended sediment are 31 to 93% less available for uptake through the gastrointestinal tract of mummichog. Untreated sediment PCBs were assimilated more efficiently than PCBs in the worms. Reduced uptake from the T diet showed the effect of enhanced sportive properties of sediment on PCB accumulation through ingestion and addresses the issue raised by Gaillard et al. (2014) that effect of black carbon contents on bioavailability of sediment-bound PCBs should be further investigated. Our simulation results for a specific case of catfish exposure showed that assuming AE for sediment and food are the same one can overestimate uptake from AC-amended sediments by 31 to 82% (depending on the sediment ingestion rate chosen). The AE values reported in the present study, which are the first report of AE for sediment ingestion by fish, can support the development of bioaccumulation models to evaluate the contribution of sediment ingestion to PCB bioaccumulation in fish in contaminated systems before and after application of carbonaceous material to the sediments. These modified bioaccumulation models can provide a more accurate tool for risk assessment and forecasting the success of different remedial alternatives based on the recovery of fish, the primary risk driver for PCB exposure, in an aquatic ecosystem.

Acknowledgements

We would like to thank the National Institute of Environment and Health Sciences, Superfund Research Program for financial support (Grant # R01ES020941).

Chapter 5: Improving PCB Bioaccumulation Factors for Algae and Zooplankton Using Passive Samplers

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Introduction

Accumulation of PCBs in the aquatic and terrestrial food chain can pose a major risk to human health and wildlife due to bioaccumulative and toxic properties of these compounds. PCB bioaccumulation models can be used in the equilibrium or kinetic mode to predict uptake in higher trophic level organisms like fish. Predictions from bioaccumulation models can ultimately support improved risk assessment, short or long-term evaluation of remedy effectiveness, and inform management decisions. PCB accumulation by fish is controlled by two main uptake pathways: ingestion of contaminated food and uptake from water through the gills, both of which are driven by freely dissolved PCBs which are readily available for diffusive uptake through the biological membranes of fish and by organisms that serve as food to fish. Depending on the foraging and swimming behavior of the fish, exchange through the gills can occur from overlying water, porewater, or both. Furthermore, PCBs in the fish diet are indirectly related to overlying and porewater concentration as the lower trophic level organisms at the base of pelagic and benthic food chains are in equilibrium with these phases, respectively. PCB intake through ingestion of food contribute to 99% of the PCB residue in Lake Michigan trout fish according to (Thomann and Connolly, 1984) and by 60 to 99% as found through a modeling effort that we have performed for catfish exposure to untreated sediment (data presented in Chapter 5). Therefore, measurement of PCB body burden in the food is a very critical input to the model. Given the important role of aqueous freely dissolved concentrations in dictating the

bioaccumulation in the benthic invertebrates, algae, and zooplankton, numerous studies in the literature have focused on measuring bioaccumulation factors (BAF) for these small organisms. BAF can be related to the octanol-water partition constant (K_{OW}) as it is correlated with the potential for a chemical to bioaccumulate in organisms at steady state. The theoretical basis behind this relationship is that hydrophobic compounds accumulate primarily in organism lipids and that lipids behave similar to octanol, and partitioning in lipids can be correlated to K_{OW}. Therefore, several studies in the literature have reported BAF and K_{OW} correlations, aiming to serve as a predictive model of PCB uptake by these organisms. The efforts in the literature that attempted to develop such correlations for algae have shown an initial increase in BAF with K_{OW} followed by a decline in BAF for the higher chlorinated PCBs when plotted against K_{OW} (Sijm et al., 1995; Swackhamer and Skoglund, 1993). Stange and Swackhamer (1994) speculated that three possible factors contribute to this phenomenon: (a) slow partitioning into the algal phase which delays equilibrium, (b) the more hydrophobic PCBs may partition to dissolved organic carbon in the medium, making them less available for partitioning to algae, and (c) highly chlorinated PCBs experience restricted membrane permeability. Sijm et al. (1995) showed that the linear relationship between BAF and hydrophobicity is disturbed due to inability of centrifugation technique to separate organic matter excreted by the algae from the aqueous phase. This is mainly an issue for the higher chlorinated PCBs which have a high affinity to dissolved organic carbon (DOC). The reported BAF - K_{OW} correlations for zooplankton were developed based on water PCB measurements with XAD columns which tend to overestimate the freely dissolved

PCB concentration (Borgå et al., 2005; Fisk et al., 2001; Hoekstra et al., 2002). Along with the freely dissolved concentration, XAD columns measurements also include PCBs associated with DOC that are incorrectly measured as freely dissolved PCBs. However, a few of the aforementioned studies have adjusted for DOC (Borgå et al., 2005). In addition, most of these reported BAF values are based on measurements in grab biota samples that are collected from the field. These samples can include suspended solids that can lead to overestimation of PCB levels.

To circumvent the weaknesses of the biota partitioning models and due to the inadequacy to describe partitioning under active growth conditions, Arnot and Gobas (2004b) suggested use of a kinetic model for predicting PCB uptake in zooplankton. However, allometric gill ventilation and the bioenergetics relationship for zooplankton feeding rate were obtained from empirical relationships for fish (Arnot and Gobas, 2004a). These correlations are not very strong as they were developed based on observations in a range of species and therefore cannot provide the most accurate estimation of uptake for zooplankton.

In the present study, we performed laboratory exposure experiments to accurately measure PCB BAF values for algae and zooplankton. We used a passive dosing technique to maintain an environmentally-relevant low freely dissolved concentration exposure to the organisms. By performing the exposure in the laboratory, the sampling artefact associated with the presence of particle-associated PCBs in the biota samples can be avoided. The BAF-K_{OW} correlations developed from this work can facilitate tracking the changes that will occur at the base of the pelagic food web under natural conditions or upon remedy implementation and therefore

quantitatively assess how a remedy reduces PCB biouptake through the food ingestion in fish.

Materials and Methods

Test Chemicals and Materials

A PCB congener mixture standard from Ultra Scientific (RPC-EPA2-1), which contains 16 PCB congeners spanning log K_{OW} range of 5 to 8, was used to spike the polyethylene (PE) and the food for zooplankton. The following PCB congeners were selected: 8, 18, 28, 44, 52, 66, 101,105,118, 128,170,180,187,195, 206, and 209. One gram of 25 micron-thick PE was used as partitioning donors in the passive dosing procedure.

Test Organisms and Culture Renewal

Freshwater green algae (*Selenastrum capricornutum*) and freshwater Daphnid (*Daphnia magna*) were chosen due to their ubiquitous use in exposure studies and being common freshwater organisms. Algae, Daphnid, and YTC Daphnid feed mixture were purchased from Aquatic BioSystems (Fort Collins, CO). Algae and YTC were kept at 4 °C until use. *Daphnia* culture was gently poured into 2 L beaker and aerated.

Moderately hard reconstituted water, 80 to 100 mg $CaCO_3$/L, was aerated for at least 24 hours, and 500 mL of the water was transferred to 1 mL beakers to start new cultures (see the Appendix IV for the water constituents). The purpose of the aeration was to dissolve the added chemicals and stabilize the medium. Cultures were maintained at 26 ±1 °C under a 16:8 h light-dark cycle. Gentle aeration was provided.

Ten adult *Daphnia* were placed in every beaker and were fed with 3 mL of algae mix and 1 mL of YTC starter every other day (0.3 mL algae, 0.1 mL YTC per live adult *Daphnia*). Water in culture chambers was changed every other day. All neonates and dropped carapaces were removed daily. The adults' third brood neonates were used for the main experiments.

Test Exposure Study

Prior to the main exposure experiment, test studies were conducted to find the optimal number of days during which ten individual *Daphnia* could be cultured in the selected volume of moderately hard reconstituted water. Day ten was found to be the cutoff because *Daphnia* started to look lethargic and rotate around themselves shortly after that. This could be due to long duration of exposure to PCBs at the specific concentrations applied or not being able to provide the stress-free environment for the *Daphnia* as they grew larger in size.

Experimental Design

To establish and maintain constant exposure, an equilibrium partitioning approach from a loaded polymer, known as passive dosing approach, was used. To dose the algae with PCBs, appropriate mass of PE, impregnated with PCBs, were added to the glass vials containing algae cells and media (the impregnation approach is explained below and in Supplemental Figure S1a). The ratio of the mass of PCBs in the algal cells to the mass of PCBs in the PE strip was calculated to ensure that algae was not depleting the passive sampler. Algae cultures were kept in the 4 °C refrigerator and were taken out for manual shaking several times during the day. Due to the small size of algal cells, two days of contact with the PCB-dosed PE was

expected to be long enough for equilibrium to occur. PCB concentration in the algae media was kept similar to PCB level in the *Daphnia* media in order to avoid biodilution when feeding the *Daphnia* with the algae. After two days, pieces of the PE sheets and aliquots of algae cells were sampled for PCB analysis. Cultures were centrifuged for 20 minutes at 7000 rpm, the supernatant was decanted and the algal cells were extracted in hexane/acetone (1:1, v/v), cleaned up, and analyzed for PCB congeners in a gas chromatograph with electron capture detection as described in (Beckingham and Ghosh, 2011). In this case, the PE sheets served as a source for PCBs and were used as a passive sampler that could help measure PCB levels in the water since the PE comes to equilibrium with the water. The importance of keeping the chemical concentrations in the water constant during bioaccumulation tests was highlighted by (Arnot and Gobas, 2006) which was satisfied by the use of PCB-loaded polymers in this experiment.

To prepare the PCB-dosed water appropriate for *Daphnia* growth, an appropriate mass of impregnated PE sheets was added to the moderately hard water which was poured into a glass carboy (Figure S1b). In order to expedite the transfer of PCBs to the media, the carboy was placed on a magnetic stirrer and the media was mixed for about two weeks prior to the experiment while the carboy mouth was covered with a stopper wrapped in aluminium foil.

The experimental setup consisted of nine replicates and three controls. The *Daphnia* was held in 1-L glass beakers filled with 500 mL of PCB-dosed moderately hard reconstituted water, 80 to 100 mg $CaCO_3$/L. To provide a buffer and maintain the desired freely dissolved concentration, 24 mg of the PE strips placed previously in

the carboy were cut and added to each beaker (Figure S1c). Cultures were maintained under the same temperature and photoperiod that was used for the culture renewal. Ten adult *Daphnia* were placed in every beaker and gentle aeration was provided. These organisms were the third brood neonates from the new cultures started in the lab that grew into adult size. The feeding volume and frequency were kept the same as what was used for the culture renewal except that the PCB-dosed algae was used to feed the *Daphnia*. Water in culture chambers was changed every other day. A ten-day exposure period was chosen based on the findings of the test exposure study that was discussed above. Following the exposure, *Daphnia* from every three beakers were pooled together as one sample to obtain enough mass for detecting PCBs, leading to three replicates. PE sheets were retrieved from each beaker and analysed for PCBs to obtain water concentrations. *Daphnia* collected from the controls were pooled together as one sample for background level measurement.

Impregnation Approach for Loading the Polymers

Prior to use, PE strips were cleaned by soaking twice, for 24 h, in acetone, followed by soaking twice, for 24 h, in hexane. Desired volumes of PCB compounds in acetone were spiked into a batch of 80:20 (v:v) methanol:water solution. Amount of PCBs to be added to an incubation system with known number of PE strips of specific mass and known solvent volume was calculated from the equation in Booij et al. (2002) PE strips were introduced to the impregnation jar once the spiked PCBs were mixed into the solution. The jar was placed on an orbital shaker (30 rpm) and samplers were equilibrated for two weeks. After that, the samplers were withdrawn

and submerged in DI water overnight to remove any residual methanol from the samplers.

PCB Analysis

PE strips were extracted in hexane, cleaned up, and analyzed for PCB congeners (Perron et al., 2009; Tomaszewski and Luthy, 2008). Algae and zooplankton samples were ground with anhydrous sodium sulfate and extracted with a hexane and acetone mixture (1:1, v/v) following method SW846 3550C. Cleanup was performed by passing the extract through a 3% deactivated silica gel column (EPA method 3630C). The eluate was concentrated by nitrogen evaporation and analyzed for PCB congeners using gas chromatograph with electron capture detection as described in (Beckingham and Ghosh, 2011).

Calculation of Aqueous Concentration

Aqueous PCB concentration was calculated from PCB concentration in the PE sampler based on PE-water partition constant (K_{PE}) values reported by Smedes et al. (2009a).

Data Analysis

PCB concentration in the biota and water were used to calculate BAF from equation below:

$$BAF = \frac{C_{lipid}\ (\frac{\mu g}{kg\ lipid})}{C_W\ (\frac{\mu g}{L})} \qquad (1)$$

Where C_{lipid} is the lipid-normalized PCB concentration in algae or zooplankton and C_W is the freely dissolved concentration of PCBs in the water, measured with PE polymer.

As mentioned above, the commonly used bioaccumulation model by Arnot and Gobas 2004b suggests a kinetic modeling approach for uptake prediction in algae and zooplankton in order to address growth effects in the model. The growth rate constant (k_G) appears in the model at steady state (Arnot and Gobas, 2004b). Arnot and Gobas model was used to make predictions of BAF values as follows. A simplified version of the model is shown in equation 2, see the Appendix IV for a more detailed discussion of the kinetic model.

$$\frac{dM_B}{dt} = W_B\, k_1\, m_O\, C_{W,O} + W_B\, k_D\, C_D - (k_2 + k_E + k_M)\, M_B \qquad (2)$$

As described by Arnot and Gobas, M_B is the mass (g) of PCB in the organism, dM_B/dt is the net flux of PCB being absorbed or depurated by the organism at any point in time t (d), W_B is the wet weight of the organism (kg) at time t, k_1 is the gill uptake rate constant (L/kg d), m_o is the fraction of the ventilation that involves overlying water (which equals 1 in this case), $C_{W,O}$ is the freely dissolved PCB concentration in the overlying water measured by passive sampling (g/L), k_D is the clearance rate constant (kg/kg d) for chemical uptake via ingestion of food and water, C_D is the concentration of chemical (g/kg) in food, and k_2 is the elimination rate constant via the respiratory area (d^{-1}), k_E is the rate constant for chemical elimination via excretion into egested feces (d^{-1}), and k_M is the rate constant for metabolic transformation of the chemical (d^{-1}).

For algae k_D is zero, and k_E is insignificant. Since PCB metabolism by algae and zooplankton can be neglected, k_M was not taken into account as an excretion pathway for either organism. The overlying water concentration ($C_{W,O}$) was calculated from PCB concentration in the sampler based on K_{PE} values reported by Smedes et al. (2009b). PCB concentrations in algae and zooplankton were predicted by solving for the mass of PCB at 2 and 10 days, respectively, from equation 3 and converted to lipid normalized concentration using equation 4:

$$M_B = \frac{W_B k_1 C_{W,O} + W_B k_D C_D}{(k_2 + k_E)} (1 - e^{-(k_2+k_E)t}) + Ae^{-(k_2+k_E)t} \qquad (3)$$

$$C_{lipid} = \frac{M_B}{W_B L_B} \qquad (4)$$

Where L_B is the lipid content of the biota (kg lipid/kg wet weight). L_B was chosen as 1.5 and 3% for algae and zooplankton, respectively (EFED-USEPA, 2009).

Additionally, the EPA's KABAM model (EFED-USEPA 2009) suggests the following calculation for obtaining BAF for algae and zooplankton, which also relies on kinetic parameters to get C_B (PCB concentration in the biota on a wet weight basis) at steady state and then uses total water concentration ($C_{W,T}$) and a factor to get the freely dissolved concentration. The kinetic rate constants used in the KABAM model were estimated based on what is discussed in the Arnot and Gobas 2004b (see the Appendix IV).

$$C_B = \frac{k_1 \emptyset C_{WT,O} + k_D C_D}{k_2 + k_E + k_G + k_M} \qquad (5)$$

$$BAF = \frac{\frac{C_B}{L_B}}{\emptyset\ C_{WT,O}} \qquad (6)$$

For algae, k_D is zero, and k_E is considered to be insignificant. k_G, and k_M can be neglected for algae and zooplankton for the same reasons discussed above. When calculating C_B and BAF from equation 5 and 6, the term $\phi\ C_{WT,O}$ was substituted with water concentrations calculated from passive sampling data.

Results and Discussion

The observed results for both organisms were compared to estimations made by both of the kinetic models discussed above to check the consistency of our results with the frequently used models. However, since we are proposing that accurate BAF values can be derived by using passive sampling/dosing techniques, we also compared the algae and zooplankton calculated BAF values from this study to literature results in order to show the improvements that can be made to these correlations using the polymers for dosing and measurement.

Algae log BAF- log K_{OW}

PCBs generally accumulate in the lipid phase of the algae. Therefore, BAF that was calculated from the measured PCB concentrations in the algae and the aqueous phase, was correlated with a surrogate measure of PCB partitioning into lipids, K_{OW} (K_{OW} was obtained from Hawker and Connell (1988). The developed BAF-K_{OW} correlation and the correlation reported by Swackhamer and Skoglund, 1993, as well as the predictions made by the Arnot and Gobas (2004b) and EPA's KABAM (2009) models, discussed in Data Analysis Section, are shown in Figure 5.1.

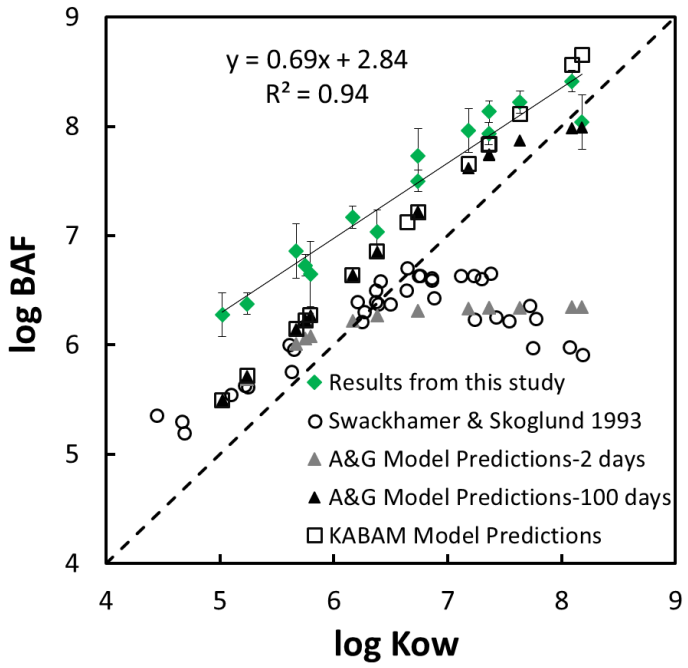

Figure 5.1. Observed log BAF- log K_{OW} correlation for algae from this study compared to the correlation from the literature and independently calculated BAFs from algae concentration predictions using Arnot & Gobas (2004b) and KABAM (2009) bioaccumulation models.

The literature values reported by Swackhamer and Skoglund (1993) are based on a three day laboratory exposure study with *Scenedesmus*. Swackhamer and Skoglund (1993) did not filter the water samples used in their study and DOC was likely present in the water samples after centrifugation. The authors corrected for the DOC, but the correction was possibly not adequate, leading to association of the higher chlorinated PCBs with the DOC phase. We suspect that this experimental artefact resulted in the overestimation of the freely dissolved PCBs in the water phase, and hence underestimation of BAFs for the higher chlorinated PCBs. The impact of DOC-associated PCBs in skewing the aqueous measurements was simulated in Appendix IV. In contrast, the decline in BAF values was not observed in

the results from our study as a result of accurate estimation of freely dissolved concentrations using passive samplers, even for the strongly hydrophobic compounds. Although different algae species were used in the two studies, it is unlikely that the extent of PCB bioaccumulation differs significantly between the two species, especially after normalization to lipids. Active growth has been stated in the literature as a contributing factor to non-equilibrium conditions of the algae partitioning due to increase in biomass. Therefore, it should be emphasized that this correlation cannot be extrapolated to conditions where algal population growth rate is high. BAF values calculated based on algae concentration predictions using KABAM model were close to, but lower than the observed BAF values for algae. The KABAM model, as noted above, relies on kinetic rate constants, which were obtained from correlations reported by Arnot and Gobas, to estimate PCB concentration at the steady state. As previously stated, the algal uptake and loss rate constants were obtained empirically using phytoplankton, algae and cyanobacteria data. Therefore, there will be some uncertainty associated with the KABAM model predictions. For the same reason, the BAF values calculated from Arnot and Gobas model predictions for a two-day exposure were about 1 to 2.5 orders of magnitude lower than our observed results and were also lower than the BAFs estimated from KABAM model predictions which provides a more accurate representation of equilibrium condition. We think that a two-day exposure is sufficient for the PCBs in the algae to reach equilibrium with the PCBs in the water due to the small size of these organisms. Predicting log BAF values that are lower than the observed results reinforces the conjecture that the Arnot and Gobas model is not capable of accurately predicting the kinetics of uptake. The

simulation results for a long exposure (100 days) indicated that the BAFs predicted by the Arnot and Gobas model became closer to the observed results and matched tightly with the equilibrium values (KABAM model predictions). The simulation results suggest that if the kinetic model is run for a longer time it can predict the final equilibrium values.

Algae log BAF- log $K_{\text{veg-oil}}$

In Figure 5.1 K_{OW} was used as a surrogate for partitioning of PCBs into the lipid phase of algae. In order to make the correlation more accurate, log BAF values were plotted against log $K_{\text{veg-oil}}$ (Figure 5.2). Due to the presence of sugar groups in algal lipids, their structure is more similar to higher plant lipids than animal lipids and hence $K_{\text{veg-oil}}$ was used as a surrogate for $K_{\text{algae-lipid}}$. $K_{\text{veg-oil}}$ represents the ratio of PCB concentration in the vegetable oil to that of water, which is similar to the ratio that BAF represents.

For most of the congeners used in this study $K_{\text{veg-oil}}$ values were obtained from Gilbert et al. (2016). Gilbert et al. used partitioning constant of organochlorine compounds from lipids into polydimethylsiloxane from the literature (Jahnke et al., 2008) to calculate K_{lipid}. Jahnke et al. selected lipids from different trophic levels such as vegetable oil, fish oil and seal oil to derive K_{lipid} values ($K_{\text{veg-oil}}$ in this case). For congeners used in this study for which $K_{\text{veg-oil}}$ values were not reported by Jahnke et al., the average of the values reported for other congeners with the same chlorination level was used for $K_{\text{veg-oil}}$.

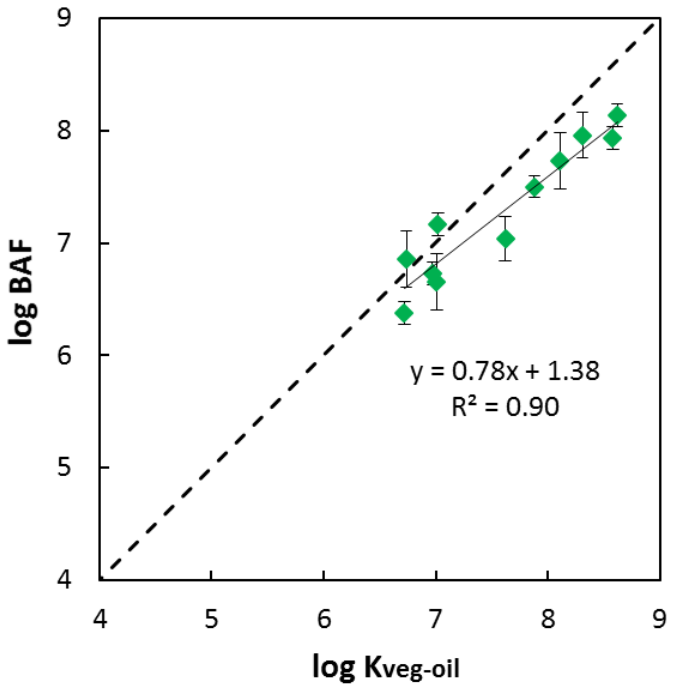

Figure 5.2. Observed log BAF-log $K_{veg\text{-}oil}$ correlation for algae from this study. $K_{veg\text{-}oil}$ values were obtained from Gilbert et al. (2016).

The observed BAF values aligned closer to $K_{veg\text{-}oil}$ values compared to the K_{OW} values in Figure 5.1. The slope of the fitted line to the log BAF- log K_{lipid} data was closer to unity and the intercept was smaller than that of log BAF- log K_{OW} fitted line. These results suggest that lipid is the main storage site for PCBs in algae and that algae lipids are similar to vegetable oil.

Zooplankton log BAF- log K_{OW}

The log BAF measured for *Daphnia* in the present study is plotted against log K_{OW} in Figure 5.3 along with a correlation reported in the literature for zooplankton (Hoeskstra et al. 2002), and predictions made by the Arnot and Gobas 2004 and EPA's KABAM 2009 models, (discussed in Data Analysis Section).

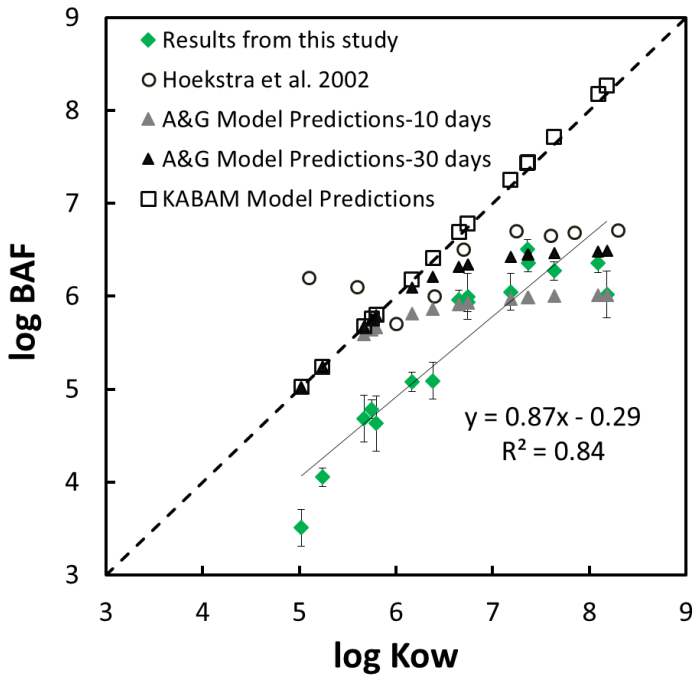

Figure 5.3. Observed log BAF-log K_{OW} correlation for zooplankton from this study compared to the correlation from the literature and independently calculated BAFs from zooplankton concentration predictions using Arnot & Gobas and KABAM bioaccumulation models.

The literature values do not correlate well with K_{OW} while results from this study using passive samplers led to tighter log BAF- log K_{OW} correlation (R-square = 0.84). BAF values calculated based on zooplankton concentration predictions using KABAM model were about one order of magnitude higher than the observed BAF values for zooplankton and aligned with the 1:1 line. It appears that the KABAM model is calibrated to result in a BAF value at equilibrium that is nearly identical to compound K_{OW}. The difference between observed and modeled results originates partly from the uncertainty in estimating the KABAM model parameters which was also discussed for the case of algae. Similarly, the kinetic rate constants were obtained from Arnot and Gobas (2004b), which uses empirical correlations obtained

from fish data to obtain the gill ventilation and feeding rates of zooplankton (Arnot and Gobas, 2004a). The Arnot and Gobas model predictions for the 10-day exposure led to BAF values that were close to the observed results in the log K_{OW} range of 6.5 to 8 and were smaller than those obtained by the KABAM model. When the exposure time was increased to 30 days, the calculated BAFs from the Arnot and Gobas model were within an order of magnitude from the observed results and get close to the KABAM model predictions. The discrepancy between the 30-day simulations and the observed results can be attributed to the inaccuracy of the kinetic parameters to predict observed BAF values for zooplankton accurately, or non-equilibrium conditions in the observed results, or a combination of both. According to the simulation results after a long exposure, the BAFs predicted by the Arnot and Gobas model approach equilibrium (KABAM model predictions).

Conclusion

Bioaccumulation factors for PCBs in small benthic and pelagic organisms can be calculated based on the ratio of lipid normalized biota concentrations to the aqueous concentrations. The more accurate the measurement of these two terms, the more accurate the calculated BAF will be. Consequently, more accurate BAF- K_{OW} correlations can be derived and hence, the estimations obtained from such correlations will be more realistic. In this regard, passive sampling can be used to improve the aqueous concentration measurements and to improve the developed correlations for benthic organisms as well as smaller pelagic organisms such as algae and zooplankton which have been the focus of this study. Properly characterized BAF will enable better predictions of treatment efficacy based on changes in overlying

concentration. Given the critical role that phytoplankton and zooplankton play in the pelagic food chain, results from this work can refine the predictions of uptake in fish generated by the kinetic bioaccumulation models which rely on PCB levels in the diet as well as the water. The ingested food has a larger contribution to PCB uptake in fish, especially for the higher chlorinated PCBs which are more lipophilic. Therefore, any error in estimating PCB levels in the food can propagate into the model output and lead to uncertainty in the results. Although the derived BAF- K_{OW} correlations using passive sampling were improved compared to the selected studies from the literature, uptake predictions with the frequently used bioaccumulation models at short and long exposure times suggested using a kinetic model for estimation of PCB bioaccumulation in algae and zooplankton. Therefore, future work will focus on fitting the correlations that are used in the Arnot and Gobas model to the observed data from this work to further increase the accuracy of the model rate constants and hence the model outcome. This study is part of a larger effort by the authors aiming at developing a robust modeling framework which relies on improved set of parameters for biouptake modeling using freely dissolved concentrations and can be used for predicting recovery of aquatic species after *in situ* treatment with carbonaceous material.

Chapter 6: Effect of Ongoing PCB Sources on Fish Recovery

Hilda Fadaei and Upal Ghosh

Introduction

Aquatic environments continue to receive inputs of organic pollutants such as polychlorinated biphenyls (PCBs) from current and historical industrial sources. Remedial action at contaminated sites focuses on mitigating risks to entire ecosystems and to human health by reducing or eliminating exposure pathways (NRC, 2003; USEPA, 2004). Before additional cleanup steps can be effective, source control - the degradation of contaminated soils and sediments - should be completed in order to limit the reintroduction of PCBs into the remediated areas. Due to the impact of non-point sources on the success of active remediation techniques as well as the extent of natural recovery, it is crucial to assess ongoing PCB sources.

Mechanistic fate and transport models that can assess the rate of recovery in the absence of active remediation of sediments (i.e., natural recovery) and can predict the effect of additional external sources have been developed (Connolly et al., 2000). These mechanistic models have been used at several sites, including the lower Fox River, Green Bay, the Pawtuxet River, the James River, and the Lower Hudson River (Connolly et al., 2000). However, these models are not based on accurately measured freely dissolved concentrations and are not developed to target *in situ* treatments where pollutant bioavailability is altered.

Passive sampling devices, which have been recently developed to accurately measure freely dissolved concentrations of hydrophobic compounds (Booij et al.,

2003; Friedman et al., 2009; Verweij et al., 2004), can be used to assess the sources of dissolved PCBs in water (Dang et al., 2013). However, there is a major gap in the development and utilization of fate and biouptake models that can use passive sampling measurements and predict the impact of ongoing inputs in the context of an *in situ* remedy. There is a need for developing a framework that can quantitatively link passive sampling measurements to uptake pathways and predict eventual changes in fish concentrations. Therefore, this chapter aims at combining a fate and transport model with a bioaccumulation model to capture effects of ongoing PCB input on fish recovery with and without active remediation efforts. This chapter addresses the last research question: *"How can an appropriately calibrated bioaccumulation model be used in conjunction with fate and transport models to evaluate effects of ongoing PCB inputs on fish recovery after remedy?"*

The bioaccumulation modeling efforts described in Chapters 2, 4, and 5, tie passive sampling measurements of freely dissolved concentrations of PCBs in water to uptake in the pelagic and benthic food webs. Accurate calibration of food chain models that can respond to changes in bioavailability of PCBs is key to our understanding of how treatment reduces biouptake in fish in natural environments. Since freely dissolved concentrations can be used as measures of bioavailability, the use of passive sampling inputs to food chain models in this work further improved the accuracy with which water exposure, pelagic exposure, and benthic exposure pathways to fish can be predicted. However, the progression of freely dissolved concentrations at the site after implementation of a remedy can be impacted by the nature and extent of ongoing inputs of contaminants.

Here I evaluated the impact of ongoing inputs on recovery at a hypothetical sediment site by using a simple material balance model to predict changes in sediment and freely dissolved concentrations over time and feeding those inputs to a bioaccumulation model to predict changes in PCB concentration in fish over time for different field scenarios. The scenarios tested included:

(1) The site is untreated and receives ongoing sediment deposition load with a PCB concentration same as bed sediments. The sediment deposition rate was assumed to be 1.5 cm/y as determined for Grasse River, NY;

(2) Natural recovery, in which no amendment is added to the sediments and the site has no ongoing sources. The new depositing sediment was assumed to be clean;

(3) Natural recovery, in which no amendment is added to the sediments and the site has ongoing sources of PCBs. The source is basically the PCBs associated with the depositing sediment which enter the river section through the upstream input. The depositing sediment was assumed to have 25% of the sediment PCB concentration;

(4) Uniform activated carbon amendment, in which all sediments in the study site are treated with equal dosing of activated carbon and the site has no ongoing sources of PCBs. In this case, fish are assumed to reside entirely within the treated study area; and

(5) Uniform activated carbon amendment, in which all sediments in the study site are treated with equal dosing of activated carbon and the site has ongoing sources of PCBs. The source is basically the PCBs associated with the

depositing sediment which enter the river section through the upstream input. The depositing sediment was assumed to have 25% of the sediment PCB concentration. In this case, fish are assumed to reside entirely within the treated study area.

Each scenario is discussed in details in the Description of Scenarios Section below.

Modeling Approach

Using the well calibrated bioaccumulation model developed through efforts discussed in the previous chapters, the effect of ongoing sources on the recovery of fish was evaluated using scenarios that rely on knowledge of various inputs in the field. The modified bioaccumulation model is not capable of capturing the effect of ongoing PCB sources on fish recovery without being linked to a PCB fate model. Therefore, results from the PCB fate model was used as porewater and overlying water concentration inputs to the bioaccumulation model. PCB transport and fate was simulated in the lower Grasse River, New York. Mass balances were constructed for a sediment control volume (C.V.) with a surface area of 1 m^2 and depth of 5 cm and a water column control volume with a surface area of 1 m^2 and depth of 1 m.

PCB and AC Fate Models

The PCB fate model was developed based on the modeling approach taken by Connolly et al. (2000). PCBs are present in three forms in a river: dissolved organic matter (DOM)-associated PCBs, particulate-associated PCBs and the freely dissolved form. The particle-associated component dominates in terms of mass budgets in sediments, and the freely dissolved component is key to understanding

thermodynamic partitioning between phases. Thus, the PCB fraction associated with the DOM component is small in terms of the mass budget and was neglected in the model.

Sediment PCB and AC Mass Balances

Figure 6.1a shows a schematic of the PCB fate and transport model for the sediment bed of a typical river. The processes that were neglected for simplifying the simulation of the above scenarios are crossed out in Figure 6.1a.

The following assumptions were applied to construct a mass balance for PCB 101 in the sediment bed:

(1) An active bioturbation was assumed such that it can be assumed that the sediment bed is completely mixed at every time step, i.e. freshly deposited sediment gets mixed with the whole sediment in the C.V.;
(2) Groundwater advection, dispersion, and biodegradation were neglected due to their insignificant contribution of PCBs;
(3) Settling and burial rates were assumed to be equal, i.e. sediment compaction is negligible;
(4) New depositing sediment has the same organic carbon content as the bed sediments;
(5) Resuspension of sediment into the water column was neglected;
(6) PCB exchange between the sediment bed and water column through diffusion was not taken into account in the sediment bed mass balance;

(7) Since the freely dissolved fraction is negligible for PCBs, especially for a pentachlorobiphenyl (PCB 101), only particulate PCBs were accounted for in the sediment bed mass balance; and

(8) It was assumed that PCBs in the sediment carbon pool were in instant equilibrium with porewater PCBs.

Figure 6.1b shows the simplified diagram of the processes incorporated into the sediment bed PCB and AC mass balances to reflect the above assumptions. Transport of sediment PCBs due to the processes shown in Figure 6.1b is explained by the equations below:

$$M_{dep} = C_{P,W}\, w_s\, A\, \Delta t \qquad (1)$$

$$M_{bur\,[i]} = C_{P,bed\,[i-1]}\, w_b\, A\, \Delta t \qquad (2)$$

$$M_{t\,[i]} = M_{t\,[i-1]} + M_{dep} - M_{bur\,[i-1]} \qquad (3)$$

where $C_{P,W}$ is particulate-associated PCB concentration in the water column (M L^{-3}), w_s is sediment particle settling velocity (L T^{-1}), A is surface area of the C.V. (L^2), Δt is time step (T), $C_{P,bed}$ is particulate-associated PCB concentration in the sediment bed (M L^{-3}), and w_b is velocity due to net deposition (L T^{-1}). A=1 m^2 and Δt=1 day, $C_{P,bed,0}$ [M L^{-3}] was calculated by $C_{P,bed,0}$ [M M^{-1}] × ρ_{dry} [M L^{-3}]. Where $C_{P,bed,0}$ =0.018×10^{-6} kg/kg dry from previous measurements (Chapter 3) and ρ_{dry} = 307 kg/m^3 (Avnimelech et al., 2001). w_s = w_b = 1.5 cm/yr (based on analysis of sediment cores from 2016). Equation 3 was solved for a time horizon of 0 to 5 years with Δt=1 day. The mass present in the C.V., the mass

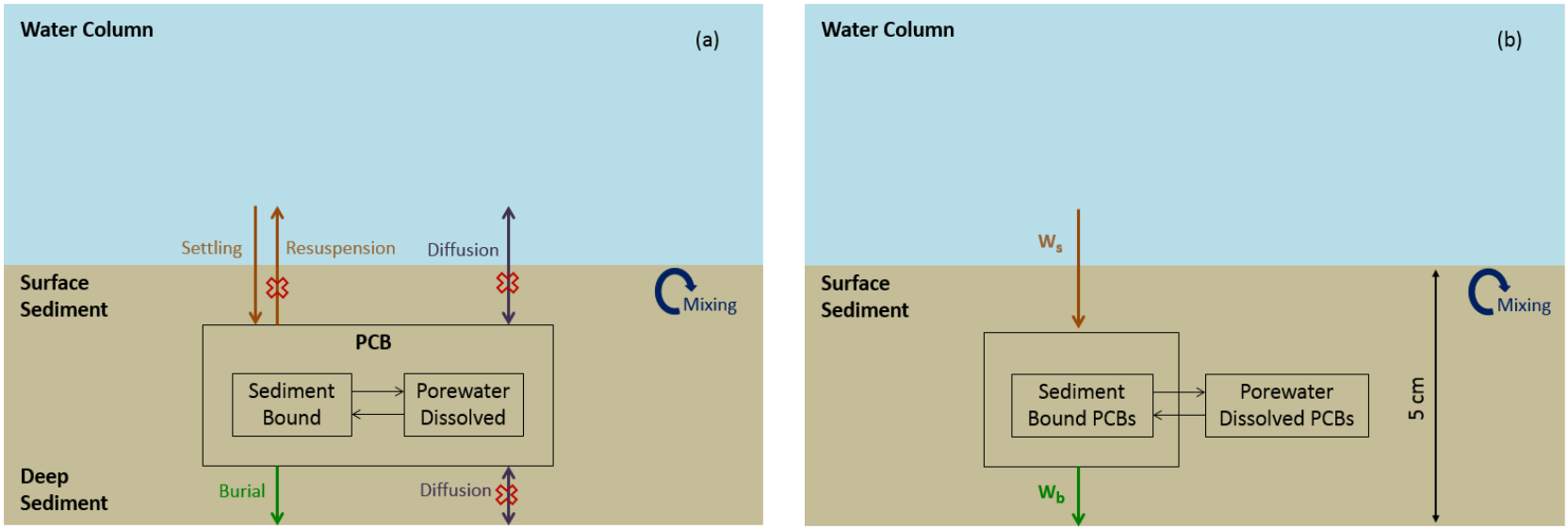

Figure 6.1. Inputs and outputs of the PCB fate and transport model for the sediment bed of (a) a typical river (b) the 1-m^2 control volume defined for the purpose of this study.

leaving the C.V. through burial at every time point, and the fixed amount of mass entering the C.V. through deposition was used to calculate mass for the following time point.

Equations below explain the transport of AC particles in the sediment due to the processes shown in Figure 6.1b:

$$M_{dep} = C_{AC,W}\, w_s\, A\, \Delta t \qquad (4)$$

$$M_{bur\,[i]} = C_{AC,bed\,[i-1]}\, w_b\, A\, \Delta t \qquad (5)$$

$$M_{t\,[i]} = M_{t\,[i-1]} + M_{dep} - M_{bur\,[i-1]} \qquad (6)$$

where $C_{AC,W}$ is AC concentration in the water column (M L^{-3}), w_s is sediment particle settling velocity (L T^{-1}), A is surface area of the C.V. (L^2), Δt is time step (T), $C_{AC,bed}$ is AC concentration in the sediment bed (M L^{-3}), and w_b is velocity due to net deposition (L T^{-1}). $C_{AC,W}$ equals zero and hence the AC mass entering the C.V. through deposition was zero for all five scenarios. A=1 m^2 and Δt=1 day, $C_{AC,bed,0}$ [M L^{-3}] was calculated by $f_{AC,bed,0}$ [M M^{-1}] × ρ_{dry} [M L^{-3}], where $f_{AC,bed,0}$ =0.05 (for the AC-treated scenarios) and ρ_{dry} = 307 kg/m^3. w_s = w_b = 1.5 cm/yr (based on analysis of sediment cores from 2016). Equation 6 was solved for the time horizon of 0 to 5 years with Δt=1 day. Similar to the PCB mass balance, the mass present in the C.V., the mass leaving the C.V. through burial at every time point, and the fixed amount of mass entering the C.V. through deposition was used to calculate the AC mass for the following time point.

Knowing the mass of AC in the C.V. at every time point from the AC mass balance equations, the partitioning constant (K_d) was calculated for each scenario. Sediment PCB mass at every time point obtained from PCB mass balance was converted to PCB concentration using the volume. These concentrations were converted to freely dissolved PCB concentrations in the porewater using K_d.

Water Column PCB Mass Balance

Figure 6.2a shows a schematic of the PCB fate and transport model for the water column of a typical river. The processes that were neglected for simplifying the simulation of the above scenarios are crossed out in Figure 6.2a. The following assumptions were applied to construct a mass balance for PCB 101 in the water column:

(1) The PCB ongoing input to the water column was assumed to be in the form of suspended sediments. The freely dissolved PCB concentrations in the water column were obtained from partition constant (see equation 12); and

(2) Only freely dissolved PCBs were accounted for in the water column mass balance for PCB 101.

Additional assumptions that were made for each scenario will be discussed in the following sections.

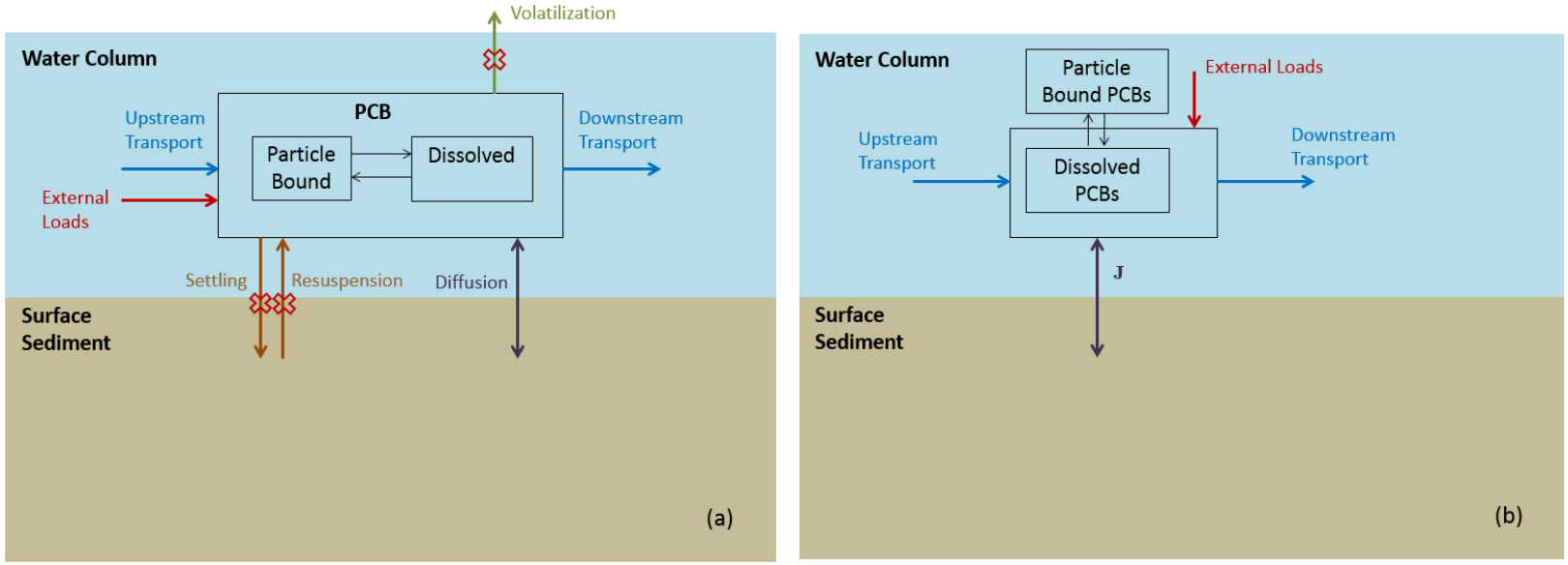

Figure 6.2. Inputs and outputs of the PCB fate and transport model for the water column of (a) a typical river (b) the 1-m^2 control volume defined for the purpose of this study.

Figure 6.2b shows the simplified diagram of the processes incorporated into the water column PCB mass balance to reflect the above assumptions. A chemostatic? model was used to predict the concentration of the overlying water PCBs in the C.V. The mass balance equation for the freely dissolved PCBs in the water column is:

$$Q_{input}\ C_{D,W,input}\ + A\ k\ \left(C_{D,bed\ porewater} - C_{D,W}\right) = Q_{output}\ C_{D,W} \quad (7)$$

where Q is volumetric flow rate ($L^3\ T^{-1}$), $C_{D,W,input}$ is freely dissolved PCB concentration in the water column entering the C.V. ($M\ L^{-3}$), $C_{D,bed\ porewater}$ is freely dissolved PCB concentration in the porewater ($M\ L^{-3}$), $C_{D,W}$ is water column freely dissolved PCB concentration in the C.V. or leaving the C.V. ($M\ L^{-3}$), A is surface area of the C.V. (L^2), and k is sediment-water mass transfer coefficient ($L\ T^{-1}$).

Q for the C.V. was obtained as 0.3 m^3/d by multiplying the water velocity of 1 ft/d (0.3 m/d) as reported in Alcoa (2010a) for Grasse River by the cross section of 1 m^2 (1-m water depth by 1-m river width). It was assumed that $Q_{input} = Q_{output}$, as there were no sources or sinks of water. Due to the assumption that the water column C.V. is fully mixed, water column concentration inside the C.V. was the same as the concentration leaving the C.V. ($C_{D,W,output} = C_{D,W,inside\ C.V.} = C_{D,W}$). The value used for $C_{D,W,input}$ in every scenario is discussed under each scenario description. Porewater concentrations were obtained from sediment mass balance models (equations 1 through 6), A=1 m^2, and k = 0.03 m/d (Alcoa, 2001). Equation 7 was solved for $C_{D,W}$.

Modified PCB Bioaccumulation Model

As described in the introduction, the modeling effort in the present chapter targeted simulating field scenarios that relied on a well calibrated bioaccumulation

model as described in Chapters 4 and 5 as well as knowledge of various inputs in the field. The modified model that was developed in Chapter 5 was used to report trajectories of catfish PCB concentrations under the five scenarios discussed in the Modeling Approach Section:

$$\frac{dC_B}{dt} = [k_u\,(m_P\,C_{W,P} + m_O\,C_{W,O}) + \sum_{j=1}^{n} \alpha_{ij}\; G_{D_{ij}}\,C_j] - (k+G)C_B \qquad (8)$$

C_B is the concentration (µg/g wet) of PCB in the fish, dC_B/dt represents the accumulation of PCB by fish at any point in time t (d), k_u is the rate constant for PCB uptake across the gill (L/g wet/d), m_P is the fraction of the respiratory ventilation that involves porewater, m_O is the fraction of the respiratory ventilation that involves overlying water, $C_{W,P}$ and $C_{W,O}$ are the freely dissolved PCB concentration in the porewater and overlying water (µg/L), respectively, α_{ij} is the efficiency at which ingested chemical from prey j is assimilated by species i (unitless), G_{Dij} is the ingestion or consumption rate of species i on species j (g wet prey/g wet/ d), C_j is the concentration of PCB in species j (µg/g wet), k is the rate constant for excretion (d^{-1}), and G is the growth rate of fish (g wet/g wet/d). It is assumed that for most organic chemicals gill is the major site of depuration.

To address PCB uptake through ingestion of sediment particles, equation 8 was modified by the addition of incidental sediment ingestion as an exposure pathway, (McLeod et al., 2008) resulting in:

$$\frac{dC_B}{dt} = [k_u\,(m_P\,C_{W,P} + m_O\,C_{W,O}) + \alpha\,G_D\,C_{worm} + IR\,\beta\,C_S] - (k+G)C_B \qquad (9)$$

Where IR is the sediment ingestion rate of the fish (g/g wet/d), β is the assimilation efficiency of the sediment-bound PCB (unitless) and C_S is the PCB concentration in the ingested sediment (µg/g).

As a simplistic assumption, temperature was assumed to be constant throughout the five-year modeling period. Lipid level and growth rate were assumed to remain constant in catfish. Benthic invertebrates and algae were considered as food for catfish (diet composed of 80% invertebrates and 20% algae). Equation 10 from Werner et al. (2010) was used to predict PCB values in the invertebrates at equilibrium.

$$\log(C_{lipid}) = 0.91\ \log(K_{OW}) + 0.5 + \log(C_{porewater}) \qquad (10)$$

Equation 11 was used to predict PCB values in the algae at equilibrium.

$$C_{lipid} = K_{lipid}\ C_{overlying\ water} \qquad (11)$$

Porewater and surface water concentrations were used to predict uptake through the gills (m_p=0.8 and m_o=0.2). These concentrations were obtained from the fate model results to predict changes in catfish PCB body burden over a five-year projection period.

Description of the Scenarios

The values used for constructing the mass balances for each scenario are shown in Table 6.1.

Scenario 1-Untreated Site

This scenario serves as a baseline for the PCB concentrations in the absence of natural recovery and active treatment processes. The new depositing sediment was assumed to have the same PCB concentration as the sediment, which was used in the input term to the sediment and water column PCB mass balances. The AC mass balance was not included in the fate model as the sediment bed contains no AC. The K_d term used to obtain the aqueous freely dissolved concentrations was defined as:

$$K_d = f_{OC} K_{OC} \quad (12)$$

Where f_{OC} is the fraction of organic carbon (OC) in sediment (TOC = 2.2±0.06% in Grasse River) and K_{OC} is the water-OC distribution constant (L/kg OC). The empirical correlation below was used to obtain K_{OC} (Hawker and Connell 1988).

$$\log(K_{OC}) = 0.74 \log(K_{OW}) + 0.15 \quad (13)$$

Scenario 2-Natural Recovery with No Ongoing Source

Natural recovery relies on deposition of new clean sediment. The AC mass balance was not included in the fate model as the sediment bed contains no AC. K_d was estimated from equation 12.

Table 6.1. Values used to construct the mass balances for the fate and transport of PCBs and AC. Subscripts 0 represent initial values. * The [M M^{-1}] concentrations included in this table were converted to [M L^{-3}] unit using the sediment bed bulk density (ρ_{bed}).

Scenario	$C_{P,W}$ (kg/ kg dry)*	$C_{P,bed,0}$ (kg/kg dry)*	$C_{AC,W}$ (kg/kg dry)*	$C_{AC,bed,0}$ (kg/kg dry)*	$C_{D,W,\ input}$ (kg/L)
Untreated Site - no AC - with ongoing source	0.018×10^{-6}	0.018×10^{-6}	N/A	N/A	0.018×10^{-6} / K_d
Natural Recovery -no AC - no ongoing source	0	0.018×10^{-6}	N/A	N/A	0
Natural Recovery -no AC - with ongoing source	$0.25\times0.018\times10^{-6}$	0.018×10^{-6}	N/A	N/A	$0.25\times0.018\times10^{-6}$ /K_d
Full Treatment with AC - no ongoing source	0	0.018×10^{-6}	0	0.05	0
Full Treatment with AC - with ongoing source	$0.25\times0.018\times10^{-6}$	0.018×10^{-6}	0	0.05	$0.25\times0.018\times10^{-6}$ /K_d

Scenario 3-Natural Recovery with Ongoing Source

The new depositing sediment was assumed to be clean. The source is basically the PCBs associated with the depositing sediment which enter the river section through the upstream input. The depositing sediment was assumed to have 25% of the sediment PCB concentration, which was used in the input term to the sediment and water column PCB mass balances. The AC mass balance was not included in the fate model as the sediment bed contains no AC. K_d was estimated from equation 12.

Scenario 4-Full Treatment of the Site with AC with No Ongoing Source

The new depositing sediment was assumed to be clean. A typical target dose of 5% AC was used as starting sediment AC content. The K_d term used to obtain the aqueous freely dissolved concentrations was defined as:

$$K_p = f_{OC} K_{OC} + f_{AC} K_{AC} \quad (14)$$

Where f_{OC} and f_{AC} are the fraction of OC and AC in sediment, K_{OC} and K_{AC} are the water-sorbent distribution constant for OC and AC (L/kg sorbent), respectively.

It was assumed that the new depositing sediment has the same organic carbon content as the sediment bed (TOC = 2.2±0.06% in Grasse River). Equation 13 was used to obtain K_{OC} and K_{AC} was obtained from published isotherm study results by Gomez-Eyles et al. 2013.

Scenario 5-Full Treatment of the Site with AC with Ongoing Source

While the sediments are the predominant source of PCBs to the water column, the upstream input can bring PCBs to the site which was considered as an external PCB load. The new depositing sediment was assumed to have 25% of the sediment PCB concentration, which was used in the input term to the sediment and water column PCB mass balances. The rest of the modeling process was the same as Scenario 4.

Results and Discussion

Simulation results are plotted in Figure 6.3 for changes in sediment, porewater, overlying water and catfish concentrations over the course of five years. PCB concentration remains constant for the untreated sediment scenario, which PCB input to the water column and sediment bed is present in the form of PCB-contaminated depositions. Sediment concentrations for the natural recovery scenario with no ongoing source overlap with the AC-treated sediment with no ongoing source concentrations. This is because the only difference between the latter scenarios is the addition of AC (see Table 1) which does not change the PCB levels in the sediment drastically. Since it was assumed that the newly depositing sediment contains no PCBs, a reducing trend in concentration is observed for these two scenarios. A similar trend was observed for the concentrations in the natural recovery and treated sediment scenarios which received an ongoing input, except that the reduction was less pronounced than the previous two scenarios which did not receive PCB inputs.

Porewater concentrations associated with the untreated sediment followed the same trend as the sediment concentration since the sediment received a constant source and no treatment was taken into account. Porewater concentrations reduced

over time during natural recovery as more clean sediment deposited and diluted the PCBs. Comparison of porewater concentrations for the untreated and natural recovery with ongoing source scenarios after five years showed a 58% reduction. In the case of the untreated and natural recovery with no source scenarios, the reduction was 77% after five years. Porewater concentrations for the AC-treated scenario with no ongoing source reduced significantly compared to the latter scenarios (99.8% reduction at the end of Year 5 compared to untreated scenario concentrations at Year 5). This reduction was increased from 77% to 99.6% at Year 5 for the AC-treated scenario with an ongoing source. The ongoing source affected the success of the AC remedy as porewater concentrations started increasing.

Since overlying water concentrations are dictated by the flux from the sediment as well as any ongoing inputs, the three scenarios that took into account the ongoing source, i.e. untreated scenario, natural recovery, and treated scenarios with AC with ongoing sources had the highest overlying water levels, followed by the natural recovery case and AC-treated scenario with no source. The difference between the purple and green lines, as well as orange and blue lines is more in the overlying water than in the porewater because the source directly translates to overlying water concentrations. Porewater and overlying water PCB levels were identical for the untreated scenario. Porewater PCB levels were an order of magnitude higher than overlying water for the natural recovery and AC-treated with no source scenarios. Similar difference was observed in Grasse River through previous measurement of PCB concentrations in porewater and overlying water in Beckingham and Ghosh (2013). The ratio of porewater to overlying water concentrations was

calculated as 0.02 for the AC-treated with a PCB source, indicating that sediment served as a sink for PCB in this case.

As expected, catfish exposed to the untreated sediment and the associated porewater and overlying water had the highest concentration compared to the catfish in the four other scenarios. Comparison of the blue and orange lines, as well as the purple and green lines indicates that presence of ongoing sources negatively impacts the recovery of catfish mainly due to increasing overlying water and porewater concentration through the deposition process. Fish response to natural recovery was slower than response to AC treatment. Percent reduction in catfish at the end of Year 5 was 63 for natural recovery with ongoing source, 83 for natural recovery without ongoing source, 90 for AC-treated sediment with ongoing source, and 99 for AC-treated sediment without ongoing source.

Conclusion

The simulation results for the scenarios presented in this chapter indicated that the refined bioaccumulation model when used in combination with a fate model can predict the effect of ongoing PCB inputs on recovery of fish through natural recovery and sediment AC amendment. The effect of ongoing PCB input on long-term fish recovery was captured well by this modeling framework. In other words, the developed framework can inform the effectiveness of natural recovery processes or the success of a remedy such as sediment AC amendment in the presence and absence of ongoing sources. This modeling framework needs to be refined by using more realistic assumptions and must be verified in the field through post-hoc analysis of data from a site undergoing remediation.

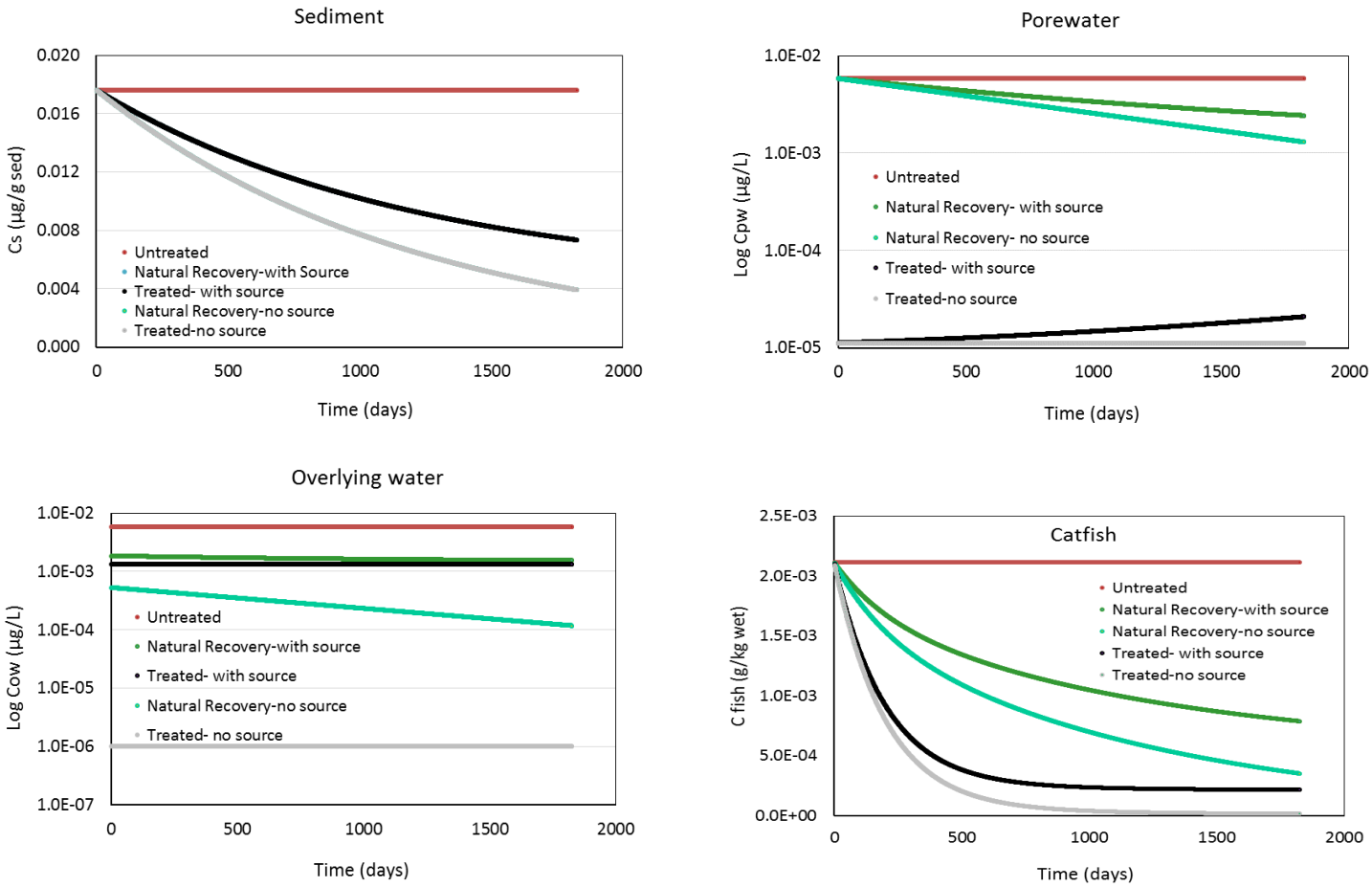

Figure 6.3. Simulation results for sediment, porewater, overlying water, and fish concentrations changes under the five scenarios during a five-year period. Results were generated by running linked fate and bioaccumulation models.

Chapter 7: Research Summary and Recommendations

Conclusions toward Motivating Research Questions

This research addresses the persistent and widespread problem of contamination of the aquatic food web by legacy toxic pollutants such as polychlorinated biphenyls (PCBs). Novel approaches of in-place management of polluted sediments, such as amendment with activated carbon, is gradually being advanced to the field through pilot and full-scale projects. While several studies have shown effectiveness of such treatments in reducing the bioavailability of PCBs in benthic organisms, there is limited experimental or modeling assessment of how bioavailability changes in sediments impact bioaccumulation in fish. In my doctoral research, I aimed to fill these gaps by characterizing the bioaccumulation models for their application to cases where the contaminated sediment is amended with AC. This research uses novel methods of measuring freely dissolved concentrations i.e. passive sampling and utilizes these measures to improve the predictions of PCB uptake by different aquatic organisms. Insights and conclusions were drawn toward the three motivating questions of this research as follows.

1. *How can passive sampling improve the prediction of PCB uptake in algae and zooplankton?*

Given the important role of PCBs in the food in fish bioaccumulation, the last experimental part of this research, presented in Chapter 5, focused on improving partitioning models that can predict uptake by small pelagic organisms. BAF-K_{OW} correlations for algae and zooplankton were derived based on passive sampling

measurements. These revised predictive correlations can capture the effect of bioavailability changes in the sediment on uptake by pelagic organisms and subsequently on bioaccumulation in fish.

2. *What is the assimilation efficiency of sediment-bound PCBs in fish and how does it change after AC amendment?*

Impact of the bioavailability of ingested PCBs in the gut was assessed through laboratory aquarium experiments using different dietary matrices, including PCB spiked sediment with and without AC amendment as well as AC particles spiked with PCBs. Results presented in Chapter 4 demonstrated that enhanced sportive properties of sediment reduces uptake in fish through the sediment ingestion pathway. Fish that were fed the PCB-spiked untreated sediment and those fed AC particles exhibited the highest and lowest AEs over a wide K_{OW} range, respectively. AEs of sediment-bound PCBs were significantly reduced (31 to 93% reduction for different congeners) upon amendment with AC. These results help improve the predictions of PCB bioaccumulation in fish, especially for the benthivorous species, in contaminated systems before and after application of AC to the sediments.

3. *How can an appropriately calibrated bioaccumulation model be used in conjunction with fate and transport models to evaluate effects of ongoing PCB inputs on fish recovery after remedy?*

Results in Chapter 2 confirmed that indeed bioavailability changes in sediment are reflected in uptake in fish through reductions in PCB flux from sediments. The amendment also reduced the PCB uptake in fish by 87% after 90 days

of exposure. Freely dissolved PCBs in porewater and overlying water measured by passive sampling were reduced by more than 95% upon amendment with 4.5% fine granular AC. These observations were also explained through passive sampling measurement of freely dissolved porewater and overlying water concentrations and modeling uptake pathways to fish to mechanistically explain the experimental results. Predicted uptake using the kinetic model was generally within a factor of two for total PCBs measured in fish. Results presented in this chapter demonstrated that by assessment of exposure pathways to fish and measuring freely dissolved concentrations in sediment porewater and overlying water, we can make reasonable assessments of long-term recovery of PCB residues in fish.

The study presented in Chapter 3 incorporated food ingestion pathway in the fish exposure study aiming at explaining the bioaccumulation reduction in fish through reductions in flux from sediments and reduced bioaccumulation by benthic organisms. Freely dissolved porewater and overlying water concentrations in this study were also obtained from passive sampling. This is the first use of field-treated sediment with AC after 6 years that confirmed the effectiveness of AC amendment and reported that AC has been stable in the field. AC treatment resulted in 96% reduction in total PCB concentration in porewater and 90% reduction in overlying water. Uptake of PCBs in worms exposed to treated sediment was decreased by 70% compared to worms exposed to untreated sediments. Overall, the uptake of PCBs was much higher in the mummichog than in the catfish likely due to different respiration rates, which affected the kinetics of PCB uptake. After 90 days of exposure, both fish showed reduced uptake of PCBs in tanks with sediment treated with AC (27 and 73%

for catfish and mummichog, respectively). Bioaccumulation modeling in kinetic mode resulted in more accurate predictions than when in equilibrium mode. The kinetic model which included the sediment ingestion pathway, estimated more contribution from this route to total PCB uptake by catfish. Food intake was found to be the dominant uptake pathway for both mummichog and catfish, especially for the more hydrophobic congeners. Depending on the swimming behavior, fish responded differently to sediment amendment with AC. Therefore, gill uptake and sediment ingestion were the second key uptake pathways for mummichog and catfish, respectively. Results presented in this chapter also showed that by independently measuring the assimilation efficiency for sediment-bound PCBs and including the sediment ingestion pathway in the kinetic bioaccumulation model, reasonable predictions can be made.

The simulation results for the scenarios presented in Chapter 6 indicated that the refined bioaccumulation model when used in combination with a fate model can predict the effect of ongoing PCB inputs on recovery of fish after sediment AC amendment and therefore inform the success of the remedy. Following five years of exposure, percent reduction in catfish was 83, 90, and 99 for natural recovery, AC-treated sediment with ongoing source, and without ongoing source, respectively.

Implications of Research

This research is focused on the environmental fate, biological uptake, and novel management of a persistent legacy pollutant that is widespread in the natural food chain. We believe that the findings will be of interest to the scientific and engineering community interested in understanding the transfer of sediment pollutants into the aquatic food web and solving remediation challenges associated with legacy pollutants in sediments.

The developed modeling effort: (i) will provide a robust framework for predicting efficacy of different remedial alternatives on the recovery of aquatic species over an extended period of time, (ii) can be used as a scenario-testing tool which can inform a decision on the dose of amendment that is needed to reduce uptake in the food chain to a target level, and (iii) can be used to establish water quality criteria based on desired PCB levels in fish. The last aspect can be helpful in guiding regulatory agencies in the recent effort to develop total maximum daily loads for bioaccumulative pollutants like PCBs.

Recommendations for Future Work

The research in this dissertation showed the ability of bioaccumulation models to predict reduction in uptake by fish as a result of reduced flux of contaminants from porewater to the overlying water. However, there is a lack of a structured framework to evaluate the effectiveness in the food chain up to fish, especially in the context of ongoing inputs in a natural water body. If passive samplers are used at a site to measure the overlying water concentration, ongoing inputs will be taken into account through the passive sampling measurements. Future work can focus on relaxing some

of the simplifying assumptions made when applying the bioaccumulation model and the fate and transport model. Once, more realistic assumptions are made, the modeling framework developed from this work can be validated by investigating its ability to predict the long-term recovery of fish in some of the major Superfund sites, such as Hudson River by comparing the model output with the collected data. Furthermore, the spatial scale of the modeling can be extended to incorporate changes along the length of a river section. Further investigation on why catfish behaves differently than mummichog is needed and it is important to test if other bottom feeding fish, e.g. carp, behave similarly to catfish in terms of PCB biotransformation.

Appendix I: Supporting Information for Chapter 2

The effect of PCB bioavailability changes in sediments on bioaccumulation in fish

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The supplementary section contains 5 tables and 12 figures and a total of 29 pages, including title page.

I. List of Figures

II. List of Tables

Bioaccumulation models

1. (Arnot and Gobas, 2004b)

1.1. Assumptions

In order to ensure that the model is representative of experiment conditions, the following modifications were applied:

1) Exchange kinetics were relatively slow (unsteady state condition).
2) Sediment porewater did not contribute to the respiratory ventilation.
3) Since the food was PCB-free, dietary uptake was zero.
4) PCB metabolism by fish was considered to be insignificant.
5) Temperature was assumed to be constant throughout the experiment (28 °C).

1.2. Rate constant calculations

Gill uptake rate constant (k_1):

$$k_1 = E_W G_V / W_B \qquad (1)$$

Where E_W is the uptake efficiency (unitless), G_V is the filtration rate (L/day) and W_B is the wet weight of the fish (kg).

$$E_W = (1.85 + 155/K_{OW})^{-1} \qquad (2)$$

The empirical correlation below was used to estimate the filtration rate for fish.

$$G_V = 1400\ W_B^{0.65} / DO \qquad (3)$$

Where DO is the dissolved oxygen concentration in the water (mg O_2/L). DO was defined at 28°C as 7.81 mg/L.

Gill elimination rate constant (k_2):

$$k_2 = k_1 / (L_f K_{OW}) \qquad (4)$$

Where L_f is the lipid content of the fish (kg lipid/kg wet weight).

Fecal egestion rate constant (k_e):

Fecal egestion rate was estimated from dietary uptake rate constant:

$k_e=0.25\ k_D$ (5)

Dietary uptake rate constant (k_D) was described using the following equation:

$k_D = E_D G_D / W_B$ (6)

Where E_D is the dietary uptake efficiency of PCB via the gastro-intestinal tract (unitless), G_D is the ingestion rate of the organism (kg/day) and W_B is the wet weight of the fish (kg).

The following two-phase resistance model was used to estimate E_D for fish:

$E_D = (3.0*1^{-7} K_{OW} +2.0)^{-1}$ (7)

3.5 percent of fish body weight per day, assuming each zebrafish weighed 1 g, resulted in feeding rate of $3.5*10^{-5}$ (kg/day).
3.6

2. (Connolly, 1991)

2.1. Assumptions

The same assumptions mentioned under section 1.1 are valid for this model.
The simplified form of Connolly's model after applying the above assumptions is shown below where C_B is the concentration of PCB in the fish (µg/g(w)), where g(w) is grams of wet weight; k_u is the rate constant for PCB uptake across the gill (L/g(w)/d), $C_{W,O}$ is the freely dissolved PCB concentration in the overlying water (µg/L), k is the rate constant for excretion of PCBs (d^{-1}). It is assumed that for most organic chemicals gill is the major site of depuration.

$dC_B/dt = k_u C_{W,O} - kC_B$ (8)

Since concentrations in the overlying water increased over time, a linear interpolation between measured values from 0 to 45 and 45 to 90 days was used to define overlying water concentration (Figure S1). The integration of equation 8 yields:

$$C_B = \frac{k_u}{k}\left(C_{W,O@t} - \frac{a}{k}\right) + Ae^{-kt} \qquad (9)$$

Where a is the rate of change of aqueous concentration and A is the constant of integration.

2.2. Rate constant calculations

Gill uptake rate constant (k_u):

$k_{u=}\ \varepsilon r/C_{O2}$ (10)

Where ε is the ratio of mass transfer rates of PCBs to O_2. This ratio can be set to 1 as at the higher K_{OW} levels, the model is insensitive to this parameter. r is the respiration rate of the fish (in units of g of O_2/g(w)/d) and C_{O2} is the oxygen concentration of the water (g of O_2/L) .
r was obtained as 6.5 µmol/g(w)/h from (Barrionuevo and Burggren, 1999). C_{O2} was assumed to be at saturation (7.81 mg/L at T=28°C).

Excretion rate constant (k):

$k = k_u / (L_f K_{OW})$ (11)

Where L_f is the lipid content of the fish (kg lipid/kg wet weight).

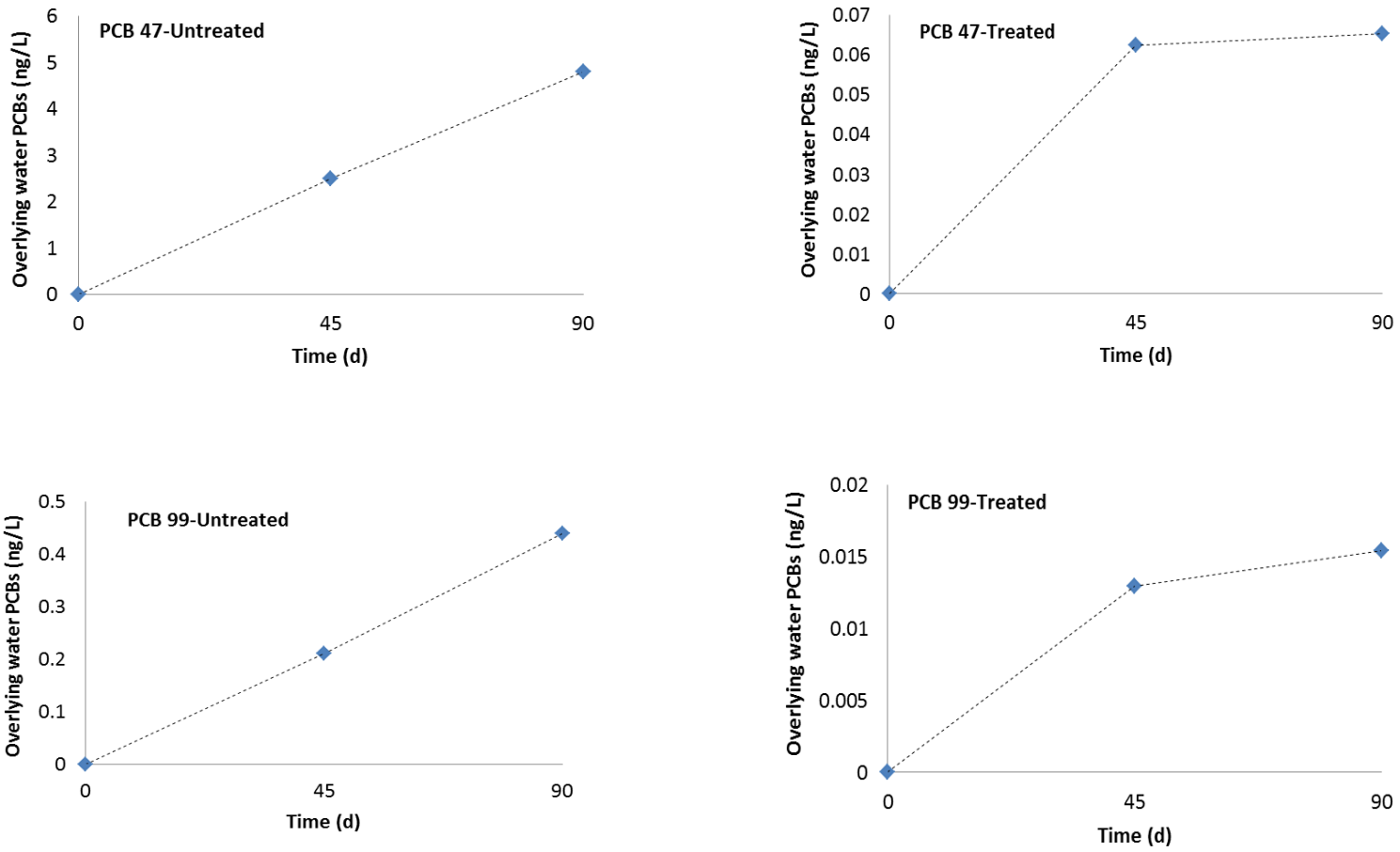


Figure S1. Example of linear interpolation between measured values from 0 to 45 and 45 to 90 days for PCB 47 and PCB 99 to define overlying water concentration as input to bioaccumulation model. Concentration in the water from 0 to 45 and 45 to 90 days was expressed as $C_{W,O@t}$= at+b, where a is the slope and b is the intercept.

Table S1. PCB concentration in sediment (initial), overlying water, porewater, and fish (after 45 days) for different congeners

PCB compound	Sediment (µg/g dw)	Overlying water (ng/L)		Porewater (ng/L)		Fish (µg/g lipid)	
		Untreated	Treated	Untreated	Treated	Untreated	Treated
(4+10)	0.04	11	0	144	0	0.06	0.03
(7+9)	0.002	0.16	0.26	4.6	0.08	0	0
(6)	0.01	0.69	0	14	0	0.01	0
(8+5)	0.06	5.1	0	106	0	0.08	0.03
(19)	0.01	2.7	0	18	0	0.03	0.001
(12+13)	0.001	0	0	0.7	0	0	0
(18)	0.02	5.7	0.19	28	0.09	0.20	0.03
(15+17)	0.04	10	0.32	48	0.10	0.19	0.04
(24+27)	0.01	2.0	0	10	0	0.07	0.004
(16+32)	0.04	10	0.35	55	0.21	0.26	0.03
(26)	0.01	1.7	0.05	5.9	0	0.29	0.03
(25)	0.01	0.70	0	2.2	0	0.11	0.01
(31)	0.03	5.4	0.22	18	0.11	1.1	0.10
(28)	0.02	4.2	0.19	13	0.09	0.80	0.08
(21+33+53)	0.02	2.4	0.19	12	0.11	0.17	0.06
(51)	0.004	0.61	0.05	1.6	0.05	0.04	0.02
(22)	0.01	2.1	0.17	8.3	0	0.34	0.06
(45)	0.004	0.88	0	2.6	0	0.09	0.01
(46)	0.002	0.43	0	1.2	0	0.02	0.01
(52+43)	0.03	4.2	0.17	10	0.13	1.3	0.09
(49)	0.02	2.5	0.10	5.6	0.08	0.70	0.06
(47)	0.02	2.5	0.06	5.0	0.06	0.62	0.03
(48)	0.002	0.14	0.02	0.8	0.01	0.39	0.01

(44)	0.02	2.9	0.13	6.6	0.08	0.74	0.07
(37)	0.01	1.1	0.01	2.5	0.01	0.18	0.02
42	0.01	1.2	0.06	2.7	0.03	0.27	0.03
(41+71)	0.01	2.3	0.07	5.2	0	0.12	0.02
(64)	0.01	0.93	0.04	2.1	0.02	0.34	0.03
(40)	0.005	0.93	0	2.0	0	0.14	0.02
(100)	0.001	0.09	0	0.16	0	0.04	0
(63)	0.001	0.13	0	0.23	0	0.07	0.01
(74)	0.01	0.59	0.02	1.1	0	0.32	0.03
(70+76)	0.01	0.90	0.04	1.7	0.02	0.53	0.04
(66 + 95)	0.02	2.4	0.09	4.4	0.05	1.2	0.08
(91)	0.01	0.41	0	0.70	0	0.17	0.02
(56+60)	0.01	1.3	0.05	2.3	0.04	0.64	0.05
(92+84+89)	0.01	0.77	0.02	1.4	0.03	0.41	0.03
(101)	0.01	0.45	0.04	0.69	0.03	0.34	0.05
(99)	0.004	0.21	0.01	0.33	0.01	0.16	0.03
(83)	0.001	0.09	0	0.14	0	0.05	0.004
(97)	0.002	0.16	0.01	0.23	0	0.10	0.01
(81+87)	0.01	0.31	0.02	0.48	0.01	0.20	0.03
(85)	0.003	0.17	0	0.25	0	0.10	0.01
(136)	0.002	0.10	0	0.16	0	0.05	0.01
(77+110)	0.02	0.79	0.05	1.2	0.04	0.61	0.07
(82 + 151)	0.005	0.32	0.07	0.46	0.08	0.14	0.02
(135+144+147+124)	0.004	0.10	0.004	0.15	0	0.11	0.02
(107)	0.001	0.04	0	0.04	0	0.05	0.01
(123+149)	0.01	0.35	0.2	0.48	0.2	0.21	0.04
(118)	0.01	0.16	0.02	0.21	0.01	0.22	0.04
(134)	0.001	0.10	0.07	0.13	0.07	0.02	0.004

(114+131)	0.001	0.0	0	0.06	0	0.06	0
(146)	0.003	0.0	0	0.05	0	0.04	0.02
(153)	0.004	0.05	0.01	0.07	0.005	0.13	0.05
(132)	0.003	0.08	0.02	0.11	0.01	0.08	0.02
(105)	0.0004	0.01	0.001	0.02	0.0005	0.02	0.002
(141)	0.002	0.03	0	0.04	0	0.04	0.01
(137+176+130)	0.001	0.01	0	0.02	0	0.02	0.01
(163+138)	0.01	0.12	0.01	0.16	0.01	0.26	0.08
(158)	0.001	0.01	0	0.02	0	0.03	0.01
(178+129)	0.003	0.02	0.005	0.03	0.01	0.06	0.02
(175)	0.0004	0	0.0003	0	0.0003	0.01	0.001
(187+182)	0.01	0.03	0.01	0.05	0.01	0.10	0.04
(183)	0.002	0.01	0.001	0.01	0	0.03	0.01
(128)	0.001	0.02	0	0.02	0	0.03	0.01
(185)	0.0002	0.001	0	0.003	0	0.001	0
(174)	0.002	0.01	0.001	0.02	0	0.04	0.02
(177)	0.003	0.02	0.003	0.03	0.004	0.06	0.02
(202+171+156)	0.001	0.002	0	0.004	0	0.01	0.01
(157+200)	0.001	0.002	0.0002	0.004	0.0004	0.01	0.01
(172 + 197)	0.001	0.01	0	0.01	0	0.03	0.01
(180)	0.01	0.03	0.01	0.04	0.01	0.11	0.05
(193)	0.001	0	0	0.002	0	0	0
(191)	0	0.001	0	0	0	0.01	0.01
(199)	0.0003	0	0	0	0	0.005	0.003
(170+190)	0.002	0.01	0.001	0.02	0	0.04	0.02
(198)	0	0	0	0	0	0.003	0.002
(201)	0.003	0.01	0.004	0.01	0.005	0.06	0.04
(203+196)	0.003	0.01	0.002	0.01	0.004	0.08	0.05

(208+195)	0.001	0.002	0	0.003	0	0.02	0.01
(207)	0	0	0	0	0	0	0.001
(194)	0.002	0.003	0.001	0.005	0.002	0.04	0.02
(205)	0.000	0	0	0	0	0	0
(206)	0.001	0	0	0.001	0	0.01	0.01
(209)	0	0	0	0	0	0.002	0.002

Table S2. PCB concentration in overlying water, porewater, and fish (after 90 days) for different congeners

PCB compound	**Overlying water (ng/L)**		**Porewater (ng/L)**		**Fish (µg/g lipid)**	
	Untreated	Treated	Untreated	Treated	Untreated	Treated
(4+10)	24	4.84	136	0	0.09	0.02
(7+9)	0.48	0.15	3.8	0.14	0.01	0
(6)	2.0	0	11	0	0.05	0.01
(8+5)	15	0	82	0	0.25	0.04
(19)	5.0	0	22	0	0.04	0.005
(12+13)	0.2	0	0.7	0	0	0
(18)	9.4	0.13	34	0.03	0.38	0.07
(15+17)	18	0.26	62	0.07	0.43	0.08
(24+27)	3.4	0	12	0	0.11	0.01
(16+32)	19	0.28	70	0.12	0.45	0.09
(26)	2.9	0.08	8.3	0	0.52	0.05
(25)	1.2	0	3.2	0	0.21	0.02
(31)	9.1	0.20	26	0.08	2.0	0.20
(28)	7.1	0.17	19	0.05	1.6	0.17
(21+33+53)	4.0	0.15	16	0.05	0.36	0.10
(51)	1.1	0.05	2.5	0.02	0.07	0.02

(22)	4.0	0.11	12	0.03	0.45	0.10
(45)	1.5	0	3.7	0	0.10	0.02
(46)	0.8	0	1.8	0	0.03	0.01
(52+43)	8.1	0.16	16	0.10	2.1	0.18
(49)	5.0	0.11	9.7	0.07	1.1	0.10
(47)	4.8	0.07	9.4	0.06	1.1	0.07
(48)	0.6	0.02	0.56	0	1.2	0.02
(44)	5.4	0.11	11	0.06	1.1	0.13
(37)	2.1	0	4.1	0	0.44	0.05
42	2.3	0.05	4.4	0.02	0.30	0.05
(41+71)	4.3	0.07	8.3	0	0.31	0.06
(64)	1.8	0.04	3.5	0.02	0.43	0.05
(40)	1.8	0.02	3.3	0	0.11	0.02
(100)	0.18	0	0.29	0	0.06	0.01
(63)	0.26	0	0.42	0	0.11	0.01
(74)	1.2	0.02	2.0	0.004	0.58	0.04
(70+76)	1.6	0.03	2.4	0.01	0.83	0.07
(66 + 95)	4.8	0.03	7.7	0.04	2.27	0.19
(91)	0.8	0.01	1.3	0	0.26	0.03
(56+60)	2.6	0.06	4.2	0.03	0.88	0.07
(92+84+89)	1.5	0.01	2.4	0.02	0.23	0.04
(101)	0.83	0.03	1.0	0.03	0.67	0.07
(99)	0.44	0.02	0.61	0.01	0.28	0.04
(83)	0.20	0	0.26	0	0.08	0.01
(97)	0.31	0.01	0.42	0	0.16	0.02
(81+87)	0.64	0.02	0.85	0.02	0.35	0.04
(85)	0.34	0.01	0.45	0	0.17	0.02
(136)	0.21	0	0.28	0	0.07	0.01

(77+110)	1.7	0.05	2.4	0.04	0.93	0.11
(82 + 151)	0.60	0.05	0.80	0.06	0.20	0.03
(135+144+147+124)	0.22	0.01	0.27	0.01	0.18	0.03
(107)	0.09	0	0.10	0	0.09	0.01
(123+149)	0.45	0.05	0.58	0	0.38	0.06
(118)	0.32	0.01	0.41	0.01	0.41	0.06
(134)	0.11	0.06	0.15	0.06	0.04	0.01
(114+131)	0.10	0	0.13	0	0.09	0
(146)	0.08	0	0.10	0	0.12	0.03
(153)	0.11	0.01	0.14	0.005	0.22	0.06
(132)	0.17	0.01	0.21	0.01	0.12	0.02
(105)	0.03	0.001	0.04	0.0002	0.02	0.004
(141)	0.06	0.002	0.08	0.003	0.06	0.01
(137+176+130)	0.03	0	0.04	0	0.04	0.01
(163+138)	0.26	0.01	0.31	0.01	0.49	0.11
(158)	0.03	0	0.03	0	0.06	0.01
(178+129)	0.05	0.01	0.07	0.01	0.10	0.03
(175)	0.01	0	0.01	0.0002	0.01	0
(187+182)	0.07	0.01	0.09	0.01	0.18	0.05
(183)	0.03	0.001	0.03	0.002	0.06	0.02
(128)	0.04	0	0.05	0	0.04	0.01
(185)	0.005	0	0.01	0	0.005	0
(174)	0.03	0.002	0.04	0.001	0.08	0.02
(177)	0.05	0.005	0.06	0.01	0.10	0.03
(202+171+156)	0.01	0	0.01	0	0.01	0.01
(157+200)	0.01	0.0003	0.01	0	0.02	0.01
(172 + 197)	0.01	0	0.02	0	0.05	0.02
(180)	0.06	0.01	0.08	0.01	0.24	0.07

(193)	0	0	0	0	0.02	0
(191)	0	0	0.002	0	0.02	0.01
(199)	0.004	0	0.005	0	0.01	0.01
(170+190)	0.02	0.003	0.03	0.003	0.09	0.03
(198)	0	0	0.0004	0	0.01	0.003
(201)	0.02	0.01	0.03	0.01	0.13	0.06
(203+196)	0.02	0.005	0.03	0.01	0.16	0.07
(208+195)	0.005	0	0.01	0.0004	0.03	0.01
(207)	0	0	0	0	0.001	0
(194)	0.01	0.002	0.01	0.002	0.07	0.03
(205)	0	0	0	0	0.001	0
(206)	0.001	0	0.002	0	0.03	0.02
(209)	0	0	0	0	0.002	0.003

Flux calculation

Equation below was used to calculate the magnitude of the flux between two types of sediment and the overlying water based on concentrations on days 45 and 90. C_{PW} and C_{OW} are in units of μg m^{-3} and k_f of m d^{-1} and flux in units of μg m^{-2} d^{-1}.

$J = k_{GR} (C_{PW} – C_{OW})$ (12)

Since the mesocosms had relatively low flow, 2 cm d^{-1} was obtained from field studies in Grasse River in fall and winter as the mass transfer rate coefficient (Alcoa, 2001). This value is close to the 0.35 to 1.51 cm d^{-1} range reported from microcosm studies with Grasse River under low-flow conditions (Ortiz et al., 2004).

Degree of chlorination	**J (μg m^{-2} d^{-1})**			
	Untreated GR sediment		**Treated GR sediment**	
	45 days	90 days	45 days	90 days
Mono	0.71	0.09	ND	ND
Di	5.05	3.84	ND	-0.10
Tri	3.40	4.03	-0.02	-0.02
Tetra	0.63	0.90	-0.01	-0.01
Total PCBs	**9.79**	**8.85**	**-0.03**	**-0.12**

Table S3. Flux from water into the sediment.

Total PCB concentrations in porewater, overlying water and fish

	Rhode River (control)		Grasse River	
	B Adjacent to treated GR	A Adjacent to untreated GR	Treated	Untreated
Total PCB concentrations after 45 days of exposure				
Porewater (ng/L)	1.9 ± 0.7	1.8 ± 0.5	1.9 ± 0.3	588 ± 16
Overlying water (ng/L)	3.0 ± 0.4	5.9 ± 1.3	3.5 ± 0.7	96 ± 12
Fish (µg/g lipid)	3.2 ± 1.1	2.3 ± 0.2	2.1 ± 0.2	16 ± 3.2
Total PCB concentrations after 90 days of exposure				
Porewater (ng/L)	4.0 ± 2.0	1.0 ± 0.1	1.3 ± 0.2	631 ± 23
Overlying water (ng/L)	7.8 ± 0.5	23.3 ± 4.5	7.6 ± 2.5	184 ± 15
Fish (µg/g lipid)	1.8 ± 0.6	7.4 ± 2.8	3.5 ± 0.3	27 ± 1.3

Table S4. Summary of total PCB concentrations in porewater, overlying water and fish after 45 and 90 days of exposure to Rhode River, untreated and treated Grasse River sediments.

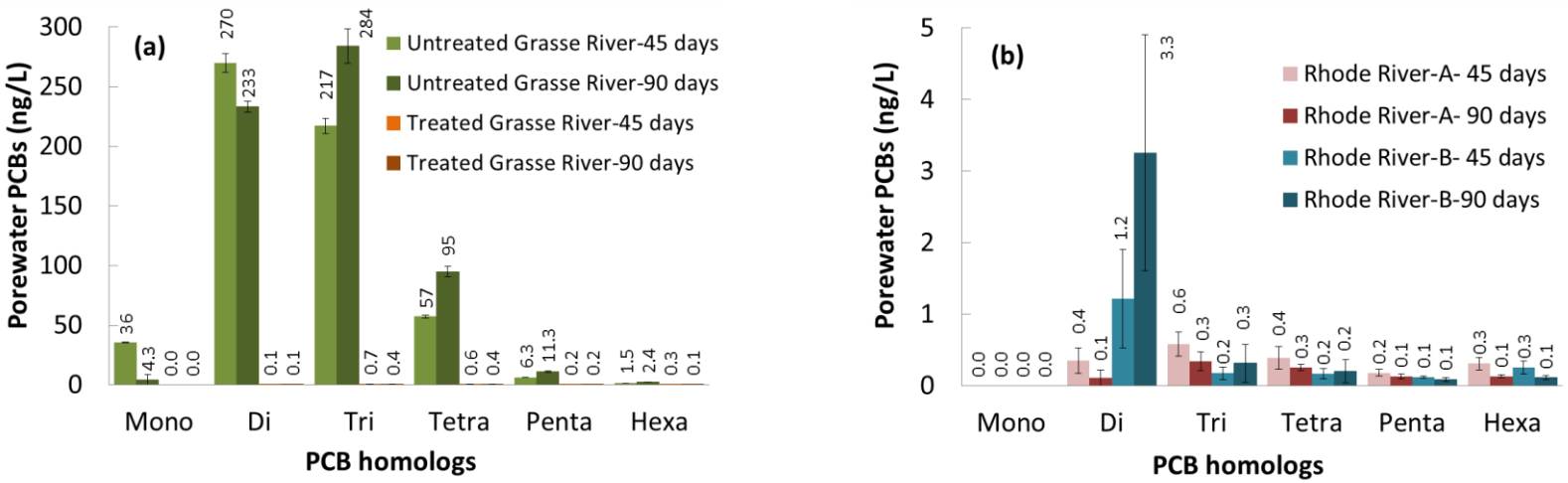


Figure S2. Porewater concentrations in (a) untreated and treated Grasse River sediments and (b) Rhode River sediment after 45 and 90 days. Error bars represent standard error.

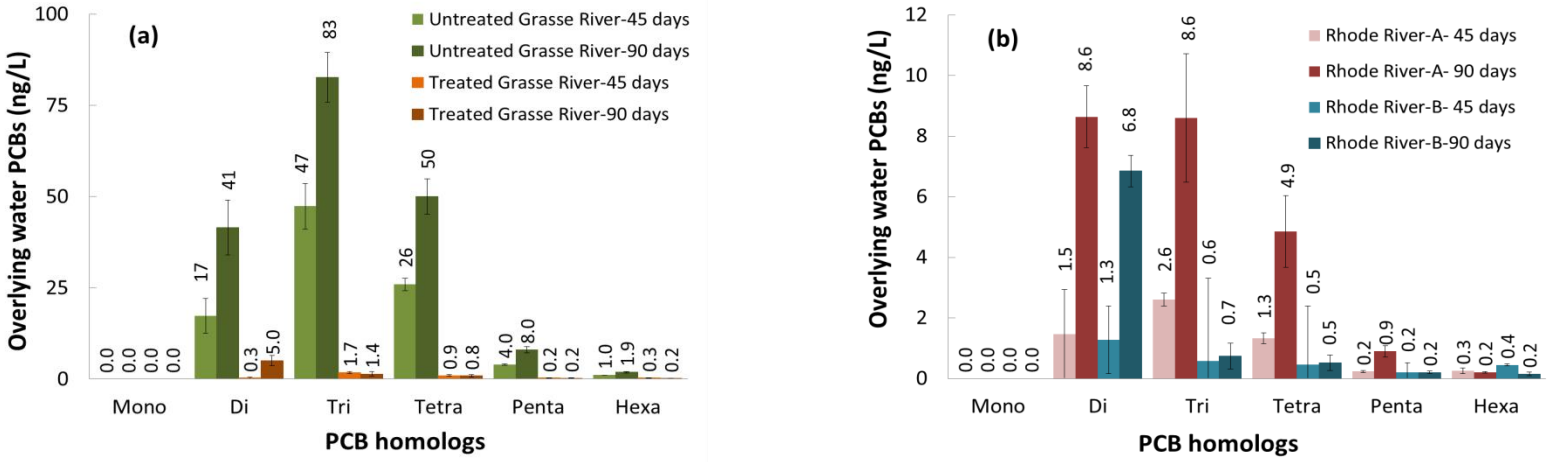


Figure S3. Overlying water concentrations in (a) untreated and treated Grasse River sediments and (b) Rhode River sediment after 45 and 90 days. Error bars represent standard error.

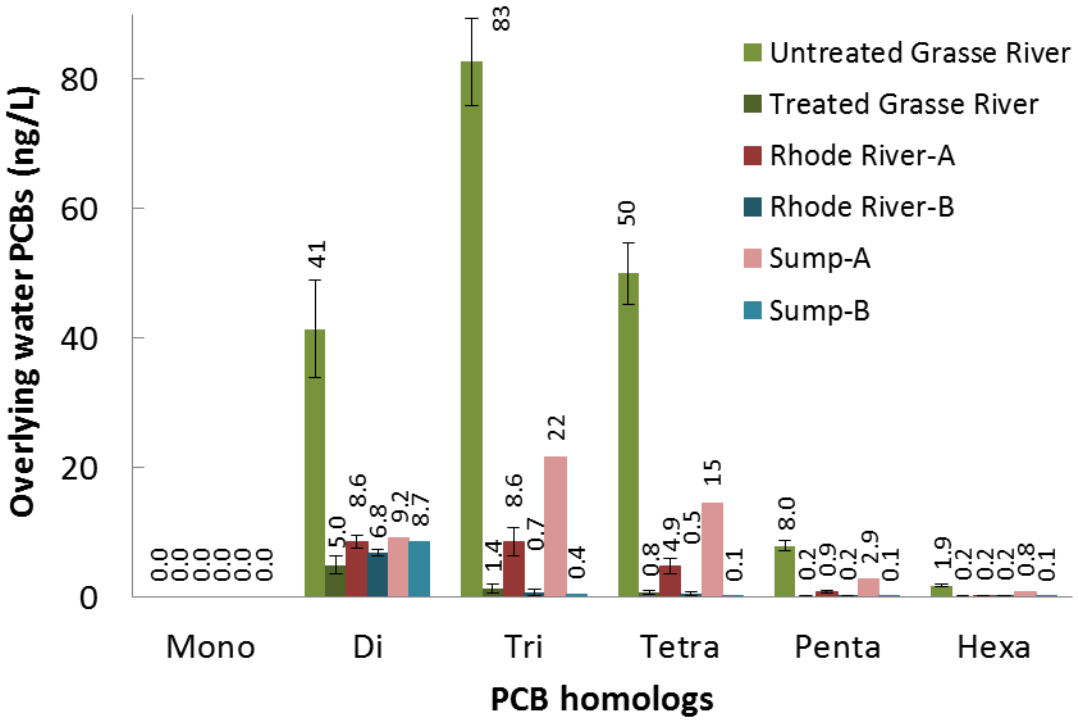


Figure S4. PCB concentration in overlying water after 90 days. Error bars represent standard error.
Rhode River-A represents data from tanks adjacent to untreated Grasse River sediments and Rhode River-B represents results from tanks adjacent to the treated Grasse River sediments. Sump-A and Sump-B are shown in Figure 1.

Cross-transfer of PCBs from Grasse River tanks to Rhode River tanks

Cross contamination between the GR and RR tanks due to ineffective removal of PCBs from the effluent recycle may have also caused PCB deposition in the sump and recirculation line during the early stages of the experimental setup. Elevated concentrations of aqueous PCBs, primarily coeluting congeners PCB-4/PCB-10, was observed in the sump connected to these tanks (see Figure S4). These two dichloro-PCBs are known products of microbial dechlorination(Kjellerup et al., 2014) and may have been formed from PCBs collected in the recirculation sump and AC bag. The resulting elevated PCB concentration in the recirculated overlying water does not impact the study because the water concentrations were measured and in most contaminated field sites, ongoing inputs to overlying water is a reality.

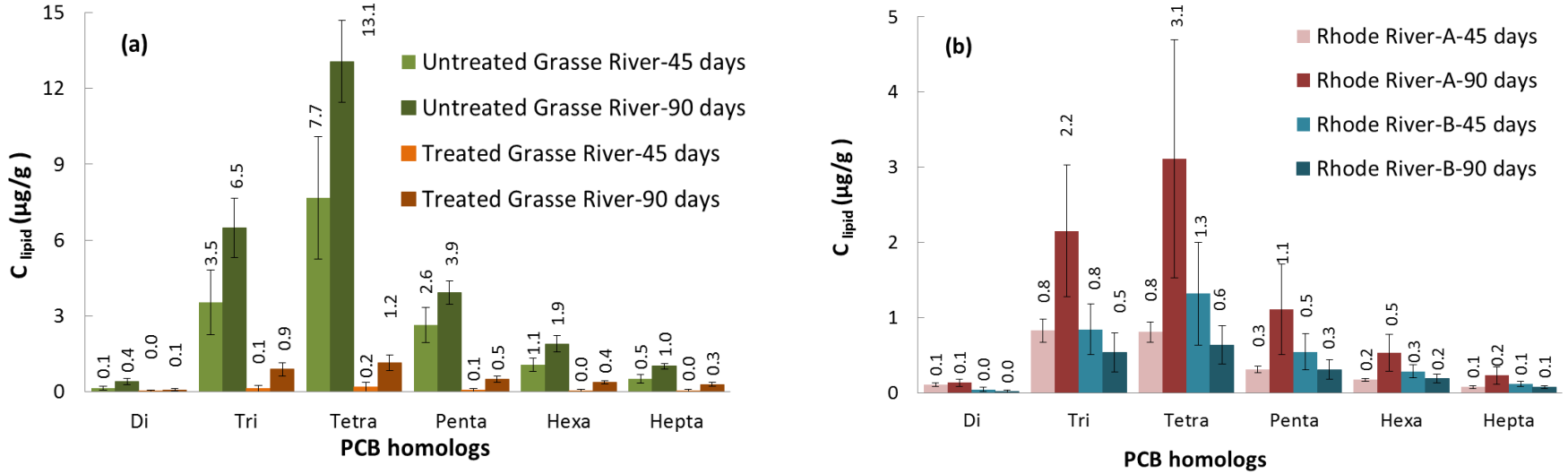


Figure S5. PCB concentrations in fish exposed to (a) untreated and
treated Grasse River sediments and (b) Rhode River sediment for 45 and 90 days. Error bars represent standard error.

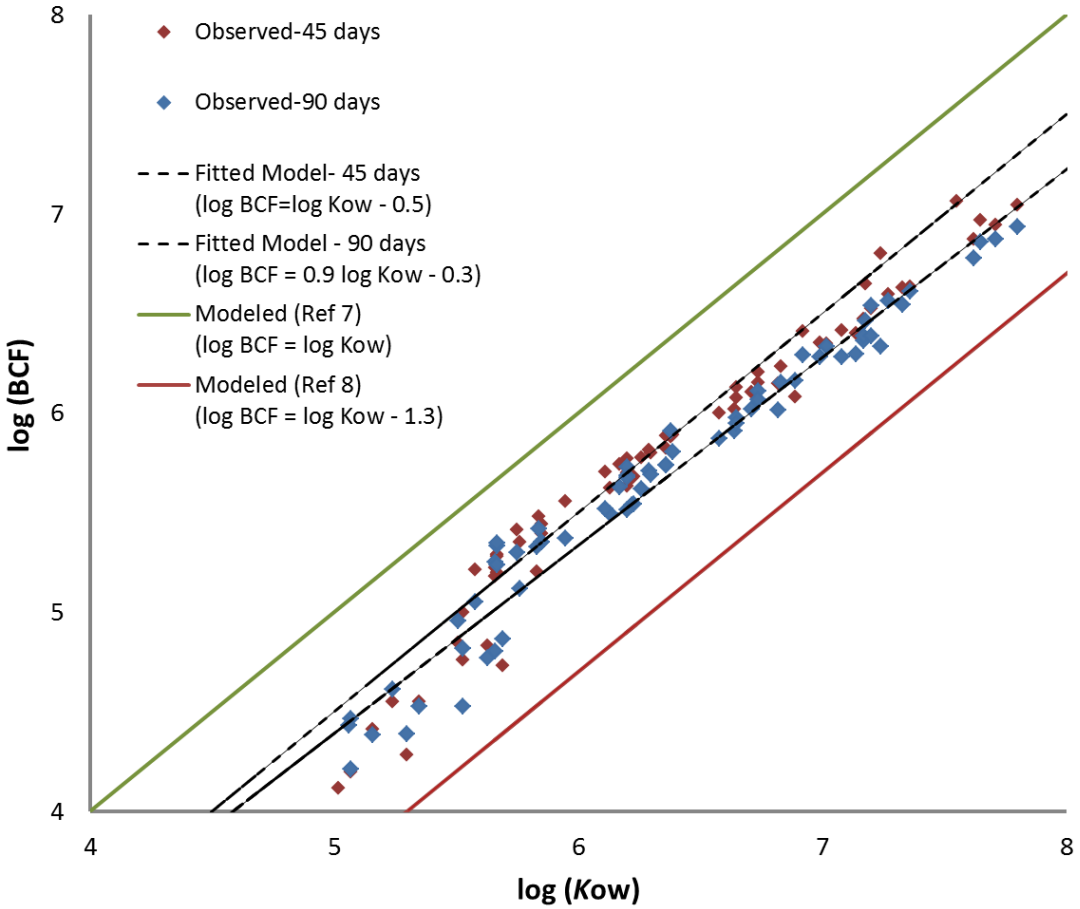


Figure S6. Observed log (BCF) values vs. log (K_{OW}) for fish exposed to untreated sediment.
log (BCF) values are calculated based on overlying water concentrations. Modeled BCF values were obtained from Gobas (Gobas, 1993) and Di Toro et al.(Di Toro et al., 2000)

	Unreated-45 days	Unreated-90 days	Treated-45 days	Treated-90 days
RMSE Equilibrium Model	0.97	1.96	0.03	0.04
RMSE Kinetic Model	0.36	0.88	0.03	0.05

Table S5. Root mean squared error (RMSE) values for the two models.

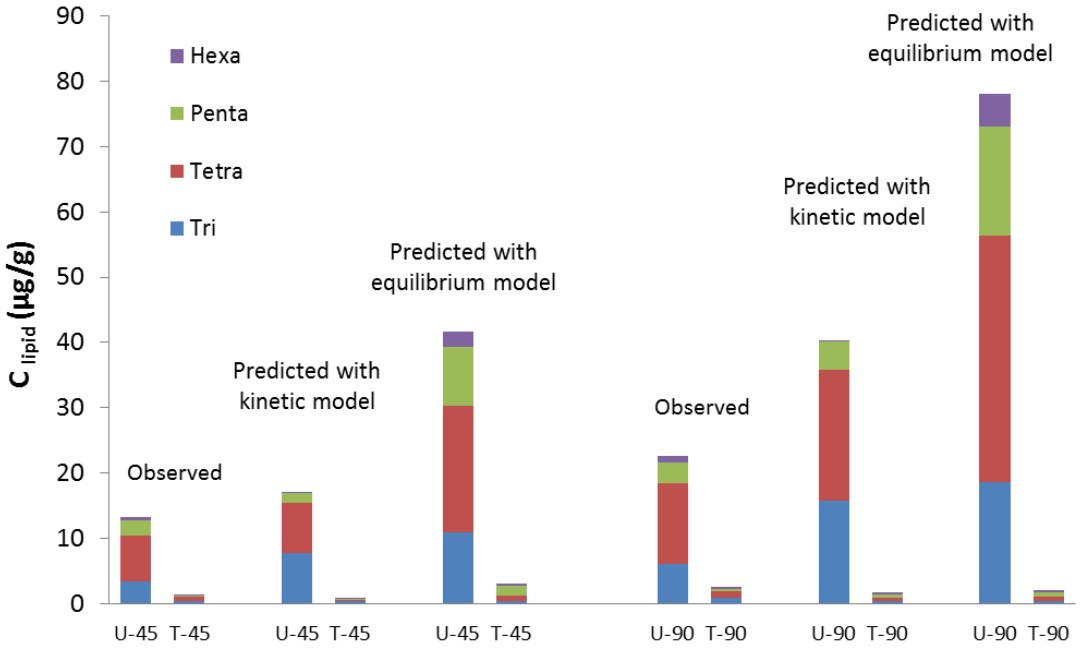


Figure S7. Predicted and observed PCB concentrations in zebrafish after 45 and 90 days. Predictions are based on the overlying water concentrations using the equilibrium and the kinetic (Arnot and Gobas) models. U and T relate to fish exposed to untreated and treated sediment, respectively.

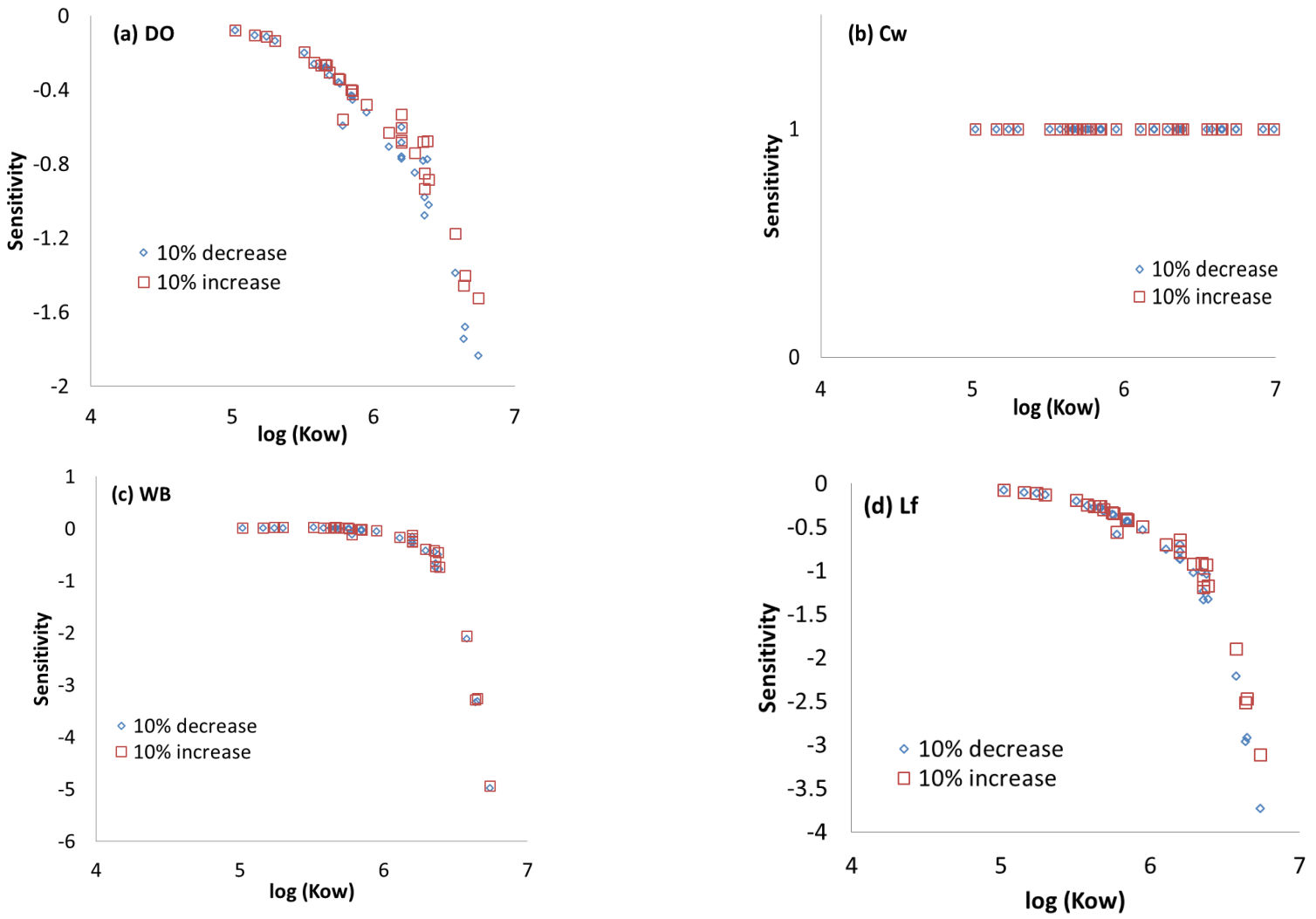


Figure S8. Sensitivity analysis. Blue symbols indicate a 10% decrease in the parameter value; red points represent a 10% increase. Figures represent model sensitivity to changes in (a) dissolved oxygen concentration, (b) overlying water concentration, (c) fish wet weight, and (d) fish lipid fraction.

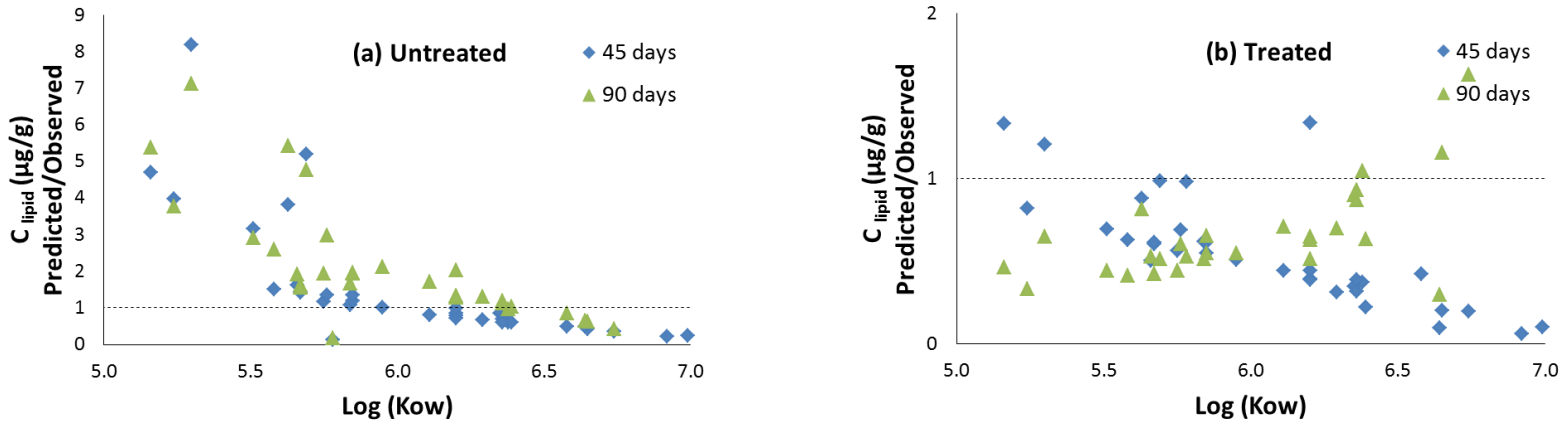


Figure S9. Ratio of predicted to observed PCB concentrations in zebrafish plotted against K_{ow} for different PCB congeners after 45 and 90 days. The predictions are based on Arnot and Gobas model for fish exposed to (a) untreated and (b) treated sediment.

Modified bioaccumulation model

The Arnot and Gobas bioaccumulation model was modified by addition of the term $IR.\alpha.C_S$ to account for the incidental sediment ingestion by fish (McLeod et al., 2008).

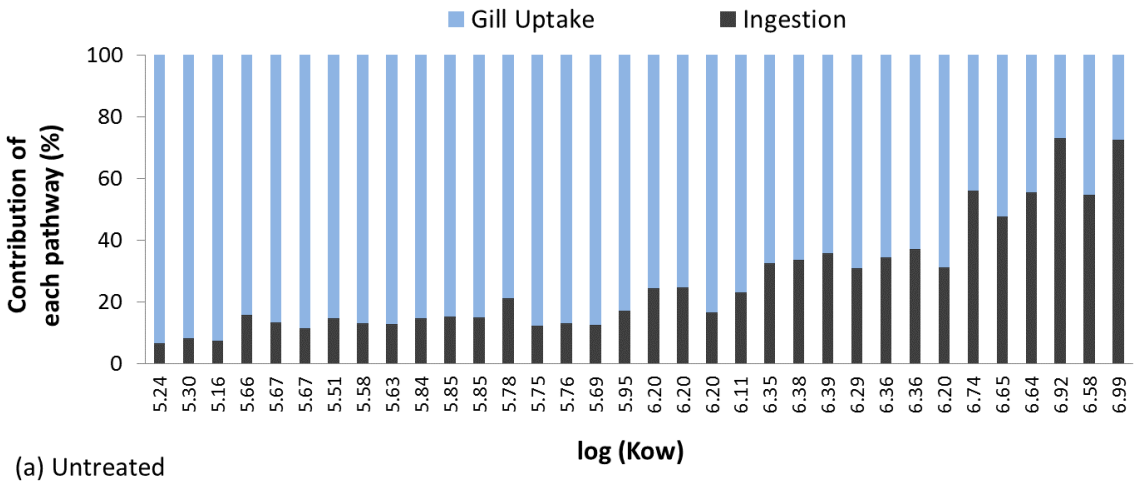
$$dM_B/dt = W_B\,(k_1\,C_{W,O}+IR.\alpha.C_S)-(k_2 + k_e)M_B \qquad (13)$$

Where IR is the sediment ingestion rate of the fish (kg/kg wet weight.d), α is the assimilation efficiency of the sediment-bound PCB (unitless) and C_S is the PCB concentration in the ingested sediment (g/kg).

Since concentrations in the overlying water increased over time, a linear interpolation between measured values from 0 to 45 and 45 to 90 days was used to define overlying water concentration (Figure S1). The integration of equation 13 yields:

$$M_B = \frac{W_B k_1}{(k_2+k_e)}\left(C_{W,0@t} - \frac{a}{(k_2+k_e)}\right) + Ae^{-(k_2+k_e)t} + \frac{IR\alpha W_B C_S}{(k_2+k_e)} \qquad (14)$$

(IR.α) was calculated from equation 14 using the measured body burden of a heptachlorobiphenyl (PCB-180) in fish as well as known values of the gill uptake and excretion parameters. The corresponding body burden was used for exposure to treated and untreated sediments. The uptake through sediment ingestion pathway was estimated by letting (IR.α) remain constant and using the corresponding measured Cs for the remaining congeners.



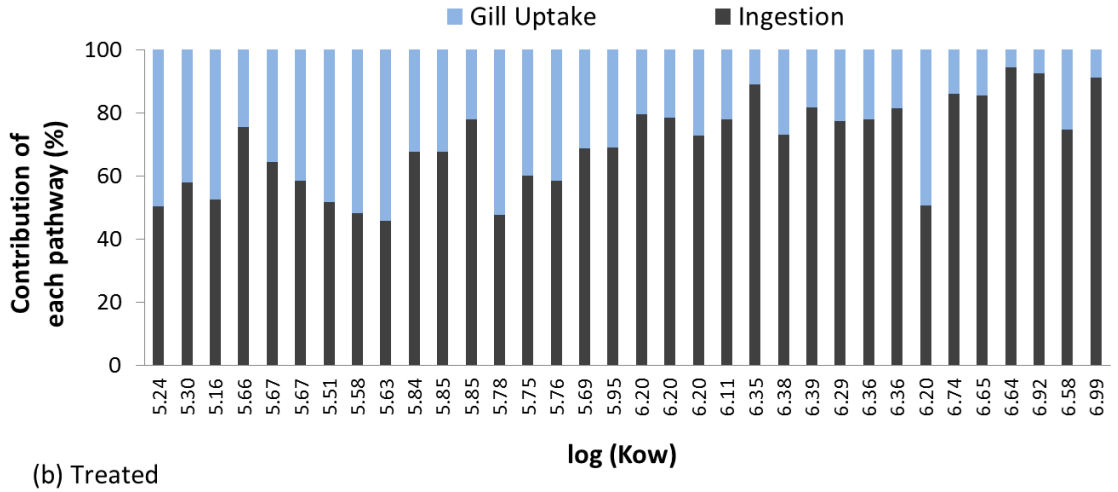


Figure S10. The relationship between modeled contributions of gill uptake and sediment ingestion to the body burden and K_{ow} of PCB congeners in fish exposed to (a) untreated and (b) treated sediment.

Predictions with Connolly Bioaccumulation Model

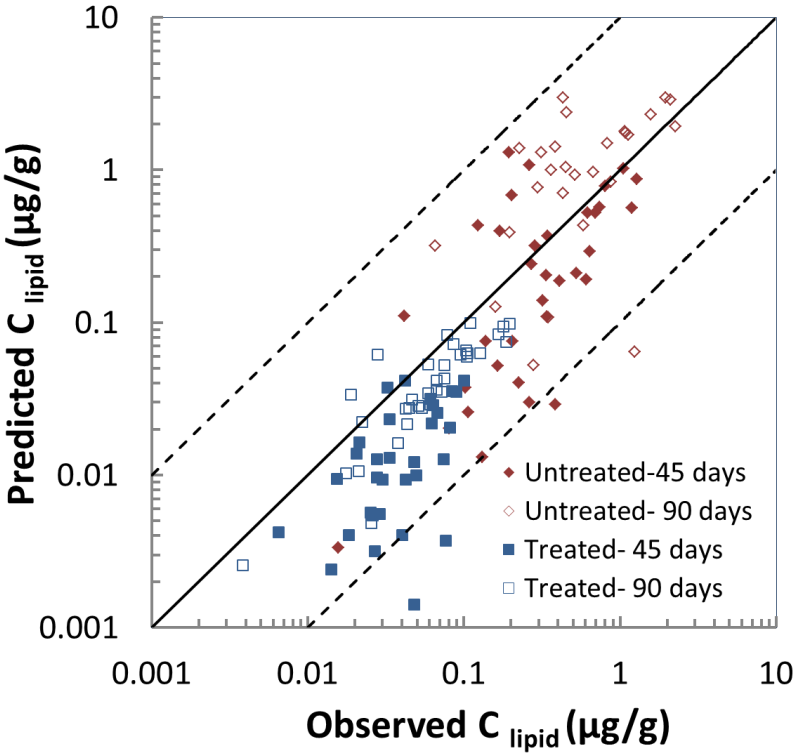


Figure S11. Observed and predicted PCB concentrations in zebrafish using Connolly bioaccumulation model. Closed symbols refer to 45 days results and open symbols refer to 90 days.

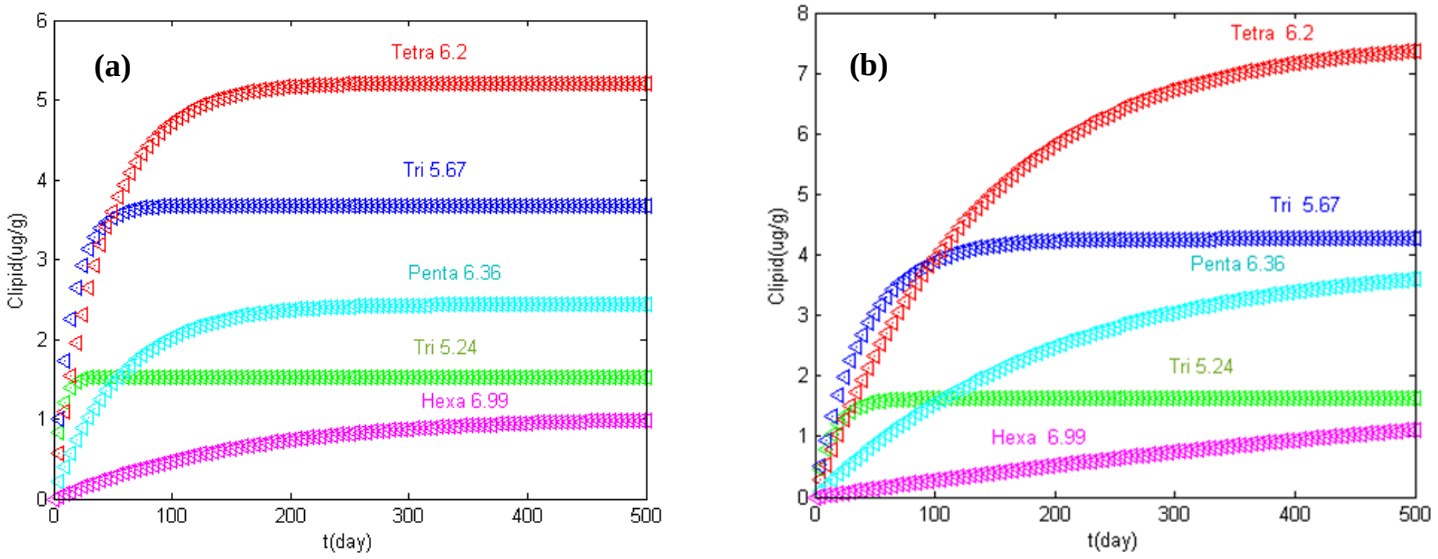


Figure S12. Comparison of kinetics of uptake between (a) Arnot and Gobas and (b) Connolly models.

Appendix II: Supporting Information for Chapter 3

Effect of Sediment AC Amendment on Pelagic and Benthic PCB Exposures to Fish

Hilda Fadaei[1], Aaron Watson[2], Allen Place[3], John Connolly[4], and Upal Ghosh[1*]

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[4]Anchor QEA, LLC, 123 Tice Boulevard, Suite 205, Woodcliff Lake, New Jersey 07677, United States

The supplementary section contains 5 tables and 23 figures and a total of 22 pages, including title page.

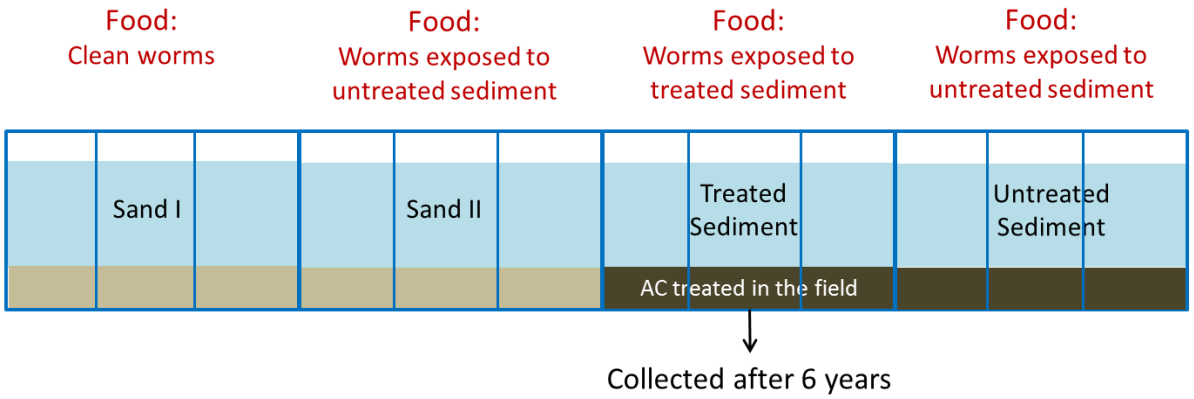


Figure S1. Series of aquaria setup to study the uptake of PCBs in fish.

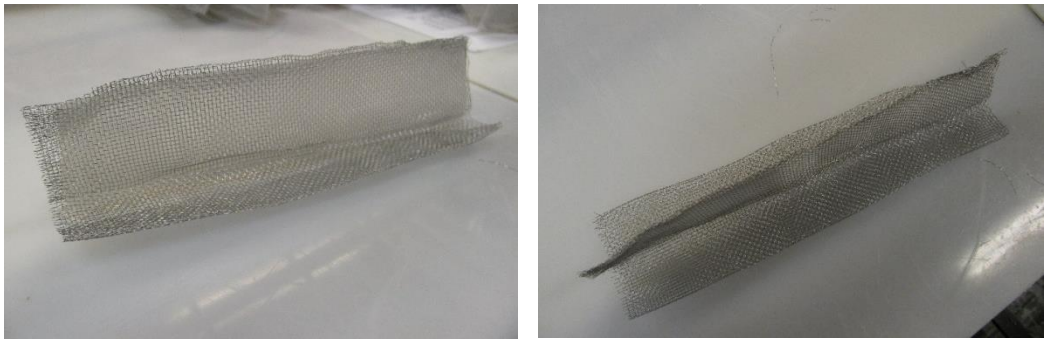


Figure S2. T-shaped stainless steel mesh structure used for holding the passove samples vertically in the sediment.

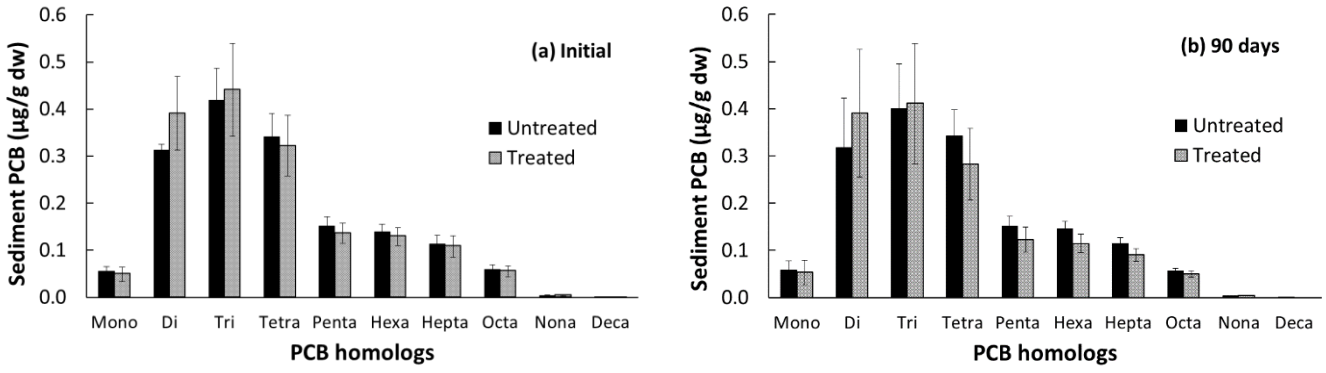


Figure S3. Sediment PCB concentrations at the beginning and the end of experiment. Error bars represent standard error.

Table S1. PCB concentration in sediment, overlying water, porewater, and fish for different congeners after 90 days

PCB compound	Sediment (µg/g dw)		Overlying water (ng/L)				Porewater (ng/L)				Fish (µg/g lipid)							
											Mummichog				Catfish			
	Untreated	Treated	Sand I	Sand II	Untreated	Treated	Sand I	Sand II	Untreated	Treated	Sand I	Sand II	Untreated	Treated	Sand I	Sand II	Untreated	Treated
(4+10)	0.14	0.20	3.3	3.1	7.2	0.2		0.85	33	0.34								
(7+9)	0.002	0.002			0.03	0.002			0.26	0.001								
(6)	0.02	0.02	0.1	0.2	0.30	0.01		0.28	2.0	0.02	0.01	0.02	0.21		0.02	0.007		
(8+5)	0.15	0.16		0.4	2.8	0.13		0.14	14	0.18	0.09	0.37	1.9	0.06	0.17	0.09	0.04	
(19)	0.03	0.04	0.01	0.1	1.8	0.08		0.48	4.5	0.11	0.02	0.07	0.45	0.03	0.04	0.03	0.03	0.03
(12+13)	0.002	0.002	0.03	0.01				0.06	0.05	0.004	0.001							
(18)	0.01	0.02	0.01	0.06	0.6	0.03			1.2	0.03	0.01	0.04	0.36		0.02	0.01	0.01	
(15+17)	0.10	0.11	0.04	0.52	4.2	0.24		0.02	8.6	0.31	0.10	0.65	3.6	0.22	0.21	0.14	0.13	0.12
(24+27)	0.03	0.03	0.01	0.12	1.1	0.06		0.26	2.4	0.08	0.03	0.16	1.0	0.06	0.06	0.04	0.04	0.05
(16+32)	0.09	0.09	0.03	0.59	3.0	0.16		0.05	7.6	0.23	0.13	1.4	4.6	0.32	0.26	0.18	0.14	0.17
(26)	0.03	0.03	0.02	0.14	0.6	0.06		0.20	1.4	0.09	0.04	0.42	1.5	0.15	0.12	0.13	0.17	0.09
(25)	0.01	0.01	0.003	0.04	0.20	0.02		0.09	0.46	0.03	0.01	0.11	0.39	0.04	0.04	0.03	0.04	0.02
(31)	0.05	0.05	0.01	0.24	1.0	0.10		0.03	2.1	0.12	0.08	0.95	2.5	0.26	0.21	0.27	0.36	0.14
(28)	0.02	0.01	0.002	0.10	0.34	0.03		0.13	0.64	0.03	0.03	0.43	0.91	0.09	0.08	0.10	0.13	0.04
(21+33+53)	0.02	0.02	0.01	0.09				0.05	1.01	0.07	0.00							
(51)	0.01	0.01	0.02	0.10	0.58	0.05		0.06	0.94	0.06	0.02	0.32	0.73	0.12	0.05	0.04	0.05	0.04
(22)	0.01	0.01	0.005	0.04	0.10	0.01		0.05	0.23	0.01	0.01	0.08	0.24	0.02	0.02	0.02	0.01	
(45)	0.005	0.005	0.01	0.04	0.23	0.02		0.01	0.39	0.02	0.003	0.04	0.14	0.02	0.01	0.01	0.01	0.001
(46)	0.003	0.002		0.02	0.11	0.01		0.003	0.25	0.01								
(52+43)	0.06	0.05	0.03	0.57	3.0	0.31		0.42	4.0	0.26	0.11	2.0	4.6	0.76	0.30	0.57	0.76	0.38
(49)	0.04	0.03	0.15	0.45	1.9	0.20		0.29	3.2	0.17	0.08	1.8	3.3	0.62	0.21	0.36	0.48	0.27
(47)	0.05	0.04	0.02	0.57	2.6	0.26		0.36	3.3	0.21	0.12	3.0	4.8	0.95	0.38	0.90	1.1	0.60
(48)								0.26	0.002									
(44)	0.02	0.02	0.01	0.15	0.85	0.09			1.1	0.06	0.02	0.54	1.1	0.19	0.05	0.05	0.05	0.02
(37)	0.02	0.01	0.03	0.13	0.65	0.06		0.29	0.92	0.05	0.01	0.35	0.97	0.12	0.05	0.12	0.15	0.05
42	0.01	0.01	0.02	0.09	0.38	0.04		0.06	0.49	0.03	0.01	0.27	0.53	0.10	0.04	0.08	0.10	0.04
(41+71)	0.03	0.02	0.05	0.21	1.1	0.11		0.17	1.5	0.10	0.03	0.99	1.9	0.36	0.07	0.08	0.07	0.03
(64)	0.01	0.01	0.01	0.09	0.35	0.04		0.03	0.44	0.03	0.02	0.43	0.69	0.14	0.05	0.14	0.17	0.07
(40)	0.01	0.01			0.36	0.08		0.12	0.12	0.12	0.01				0.004	0.01		
(100)	0.003	0.002	0.01	0.04	0.11	0.02		0.04	0.13	0.01	0.01	0.22	0.29	0.10	0.03	0.08	0.08	0.06
(63)	0.004	0.003	0.02	0.06	0.17	0.02			0.18	0.01	0.01	0.22	0.33	0.07	0.03	0.08	0.10	0.04
(74)	0.01	0.00	0.01	0.08	0.18	0.02			0.06	0.02	0.02	0.37	0.52	0.12	0.04	0.14	0.16	0.23
(70+76)	0.005	0.004	0.002	0.04	0.14	0.02		0.05	0.12	0.01	0.02	0.18	0.33	0.08	0.02	0.10	0.11	0.04
(66 + 95)	0.05	0.04	0.01	0.40	1.5	0.25		0.02	1.8	0.19								
(91)	0.02	0.01	0.01	0.14	0.51	0.10		0.01	0.62	0.08	0.02	0.91	1.3	0.44	0.07	0.27	0.33	0.25
(56+60)	0.02	0.01	0.02	0.17	0.54	0.11		0.20	0.59	0.07	0.03	0.99	1.3	0.46	0.08	0.41	0.46	0.31
(92+84+89)	0.03	0.02	0.05	0.73	0.74	0.15		0.07	0.70	0.14	0.06	0.64	1.2	0.34	0.12	0.30	0.45	0.26
(101)	0.02	0.01	0.01	0.18	0.55	0.12		0.10	0.58	0.08	0.05	1.4	1.8	0.66	0.10	0.54	0.62	0.43
(99)	0.01	0.006	0.01	0.08	0.23	0.05		0.16	0.25	0.03	0.02	0.67	0.82	0.31	0.06	0.34	0.37	0.27

Table S1. PCB concentration in sediment, overlying water, porewater, and fish for different congeners after 90 days

PCB compound	Sediment (µg/g dw)		Overlying water (ng/L)				Porewater (ng/L)				Fish (µg/g lipid)							
											Mummichog				Catfish			
(83)	0.004	0.003	0.03	0.10	0.84	0.05	Zero	0.08	0.12	0.02	0.004	0.19	0.27	0.10	0.01	0.07	0.09	0.06
(97)	0.003	0.003	0.01	0.04	0.08	0.02		0.05	0.10	0.01	0.01	0.15	0.24	0.08	0.01	0.07	0.08	0.06
(81+87)	0.002	0.003	0.01	0.04				0.06		0.01								
(85)	0.004	0.003	0.01	0.04	0.12	0.03		0.01	0.10	0.01	0.01	0.25	0.33	0.13	0.02	0.14	0.15	0.10
(136)	0.01	0.006	0.01	0.04	0.10	0.04		0.01	0.06	0.03	0.005	0.19	0.28	0.13	0.01	0.09	0.11	0.09
(77+110)	0.04	0.03	0.02	0.32	0.94	0.20		0.02	1.1	0.14	0.06	2.6	3.0	1.2	0.14	1.10	1.16	0.80
(82 + 151)	0.02	0.01	0.02	0.17	0.31	0.09		0.03	0.35	0.06	0.02	1.2	1.3	0.60	0.05	0.38	0.38	0.34
(135+144+147+124)	0.02	0.01	0.01	0.001	0.15	0.07		0.15	0.08	0.06	0.01	0.62	0.76	0.33	0.04	0.33	0.36	0.30
(107)								0.07	0.01	0.01	0.01	0.24	0.43	0.19	0.01		0.19	0.15
(123+149)	0.03	0.02	0.003	0.08	0.26	0.13		0.03	0.18	0.11	0.04	1.8	2.1	1.0	0.06	0.63	0.65	0.57
(118)	0.01	0.01	0.01	0.11	0.21	0.05			0.22	0.03	0.03	0.74	0.84	0.33	0.05	0.42	0.43	0.32
(134)			0.005	0.02				0.09	0.01	0.01								
(114+131)	0.001	0.0004	0.01	0.05				0.03	0.005	0.005	0.01	0.20				0.18	0.19	0.00
(146)	0.01	0.009	0.01	0.07	0.10	0.05		0.02	0.06	0.04	0.02	0.71	0.81	0.39	0.04	0.48	0.51	0.42
(153)	0.01	0.01	0.003	0.06	0.10	0.05		0.02	0.13	0.04	0.03	0.84	0.89	0.47	0.06	0.61	0.63	0.49
(132)	0.01	0.009	0.01	0.03		0.01		0.04	0.05	0.02	0.01	0.47	0.60	0.27	0.02	0.14	0.17	0.17
(105)	0.0004	0.0003			0.01	0.002		0.03	0.01	0.001	0.001	0.02	0.03	0.01	0.002	0.02	0.01	0.01
(141)	0.01	0.009		0.04	0.05	0.04		0.03	0.04	0.03	0.004	0.25	0.29	0.13	0.01	0.13	0.14	0.14
(137+176+130)	0.004	0.003	0.001	0.001	0.005	0.002		0.00003	0.002	0.002	0.005	0.19	0.23	0.11	0.01	0.08	0.09	0.08
(163+138)	0.04	0.03	0.01	0.15	0.22	0.12		0.01	0.16	0.09	0.05	1.9	1.9	1.0	0.09	0.93	1.2	0.96
(158)	0.002	0.002	0.004	0.02	0.02	0.01		0.01	0.01	0.01	0.004	0.12	0.14	0.07	0.01	0.08	0.09	0.08
(178+129)	0.01	0.01	0.001	0.01	0.01	0.01		0.003	0.01	0.01	0.01	0.68	0.76	0.41	0.02	0.41	0.43	0.39
(175)	0.002	0.001	0.001	0.002	0.001	0.001		0.0001	0.001	0.0004	0.001	0.07	0.09	0.05	0.003	0.05	0.06	0.05
(187+182)	0.03	0.02	0.0003	0.02	0.02	0.01		0.001	0.01	0.01	0.03	2.1	2.2	1.2	0.06	1.5	1.4	1.1
(183)	0.01	0.005	0.001	0.00	0.01	0.003			0.002	0.002	0.01	0.27	0.30	0.18	0.01	0.20	0.23	0.21
(128)	0.002	0.001	0.001	0.01	0.02	0.01		0.06	0.01	0.01	0.01	0.12	0.13	0.07	0.01	0.08	0.09	0.07
(185)	0.001	0.001	0.001	0.001	0.001	0.0005		0.0002	0.0003	0.0004	0.001	0.04	0.05	0.03	0.0004	0.01	0.01	0.01
(174)	0.01	0.004	0.0001	0.003	0.01	0.002		0.0001	0.002	0.001	0.01	0.25	0.27	0.17	0.002	0.10	0.10	0.10
(177)	0.02	0.01	0.0002	0.01	0.01	0.01		0.00001	0.01	0.005	0.01	0.67	0.72	0.41	0.01	0.33	0.35	0.32
(202+171+156)	0.004	0.002		0.002		0.001		0.0001	0.003	0.0002	0.01	0.18	0.20	0.12	0.01	0.12	0.13	0.11
(157+200)	0.003	0.002	0.02	0.04	0.005	0.002		0.02		0.001	0.002	0.09	0.10	0.06	0.003	0.06	0.06	0.06
(172 + 197)	0.01	0.004	0.03	0.03	0.05	0.001			0.05	0.04	0.004	0.17	0.19	0.10	0.01	0.14	0.17	0.15
(180)	0.02	0.02	0.00002	0.001	0.02	0.01		0.001	0.01	0.01	0.01	0.11	0.16	0.14	0.01	0.10	0.31	0.34
(193)			0.003	0.003	0.004	0.002		0.01	0.001	0.001		0.05	0.18	0.08		0.09	0.12	0.10
(191)	0.0003	0.00001	0.0001	0.0003		0.0001		0.00004	0.001	0.0001	0.0005	0.02	0.02	0.01	0.004	0.02	0.02	0.02
(199)	0.001	0.001		0.0003	0.0004	0.0004		0.001	0.0004	0.0002	0.0004	0.06	0.07	0.04		0.01	0.01	0.01
(170+190)	0.01	0.01		0.001	0.01	0.003		0.00003	0.004	0.003	0.01	0.38	0.43	0.23	0.01	0.30	0.35	0.32
(198)	0.0005	0.0004	0.00003	0.0002	0.0001	0.0001		0.00001	0.0001	0.0001		0.02	0.02	0.01	0.0007	0.02	0.02	0.02
(201)	0.02	0.02		0.004	0.01	0.004		0.0002	0.004	0.003	0.01	0.77	0.89	0.46	0.01	0.58	0.65	0.56
(203+196)	0.02	0.02			0.01	0.003			0.004	0.003	0.01	0.51	0.58	0.31	0.01	0.46	0.57	0.51
(208+195)	0.004	0.004			0.001	0.001		0.0002	0.001	0.001	0.001	0.13	0.15	0.08	0.001	0.10	0.12	0.11

Table S1. PCB concentration in sediment, overlying water, porewater, and fish for different congeners after 90 days

PCB compound	Sediment (µg/g dw)		Overlying water (ng/L)				Porewater (ng/L)				Fish (µg/g lipid)							
											Mummichog				Catfish			
(207)	0.0004	0.0003				0.0001		0.0001	0.00003	0.0001	0.001	0.02	0.03	0.01	0.003	0.01	0.02	0.02
(194)	0.01	0.01	0.001	0.001	0.003	0.001		0.00003	0.001	0.001	0.004	0.14	0.15	0.08	0.01	0.14	0.19	0.18
(205)	0.0004	0.0003				0.0001			0.0001	0.0001								
(206)	0.004	0.003									0.0003	0.04	0.04	0.02	0.001	0.06	0.08	0.07
(209)	0.0002	0.0002									0.27	0.91	1.0	0.24	0.23	0.70	0.62	0.19
Total	**1.5**	**1.5**	**4.3**	**12**	**44**	**4.3**	**0.0**	**6.3**	**104**	**4.2**	**2**	**41**	**68**	**18**	**4**	**17**	**19**	**14**

	Sand (control)		Grasse River	
	Sand I-clean food	Sand II-untreated food	Treated	Untreated
Total PCB concentrations after 45 days of exposure				
Porewater (ng/L)	N.D.	1.5 ± 0.4	5.1 ± 1.5	137 ± 32
Overlying water (ng/L)	0.5 ± 0.4	5.2 ± 1.2	5.6 ± 1.6	36 ± 9.8
Total PCB concentrations after 90 days of exposure				
Porewater (ng/L)	N.D.	6.3 ± 1.5	4.2 ± 1.2	116 ± 39
Overlying water (ng/L)	1.0 ± 0.2	8.6 ± 2.1	4.3 ± 1.2	44 ± 18
Catfish (µg/g lipid)	2.7 ± 1.1	16 ± 4.2	13 ± 2.3	18 ± 5.5
Mummichog (µg/g lipid)	1.5 ± 0.5	39 ± 2.2	18 ± 0.7	66 ± 4.1

Table S2. Summary of total PCB concentrations in porewater, overlying water and fish after 45 and 90 days of feeding and exposure to sand untreated and treated Grasse River sediments.

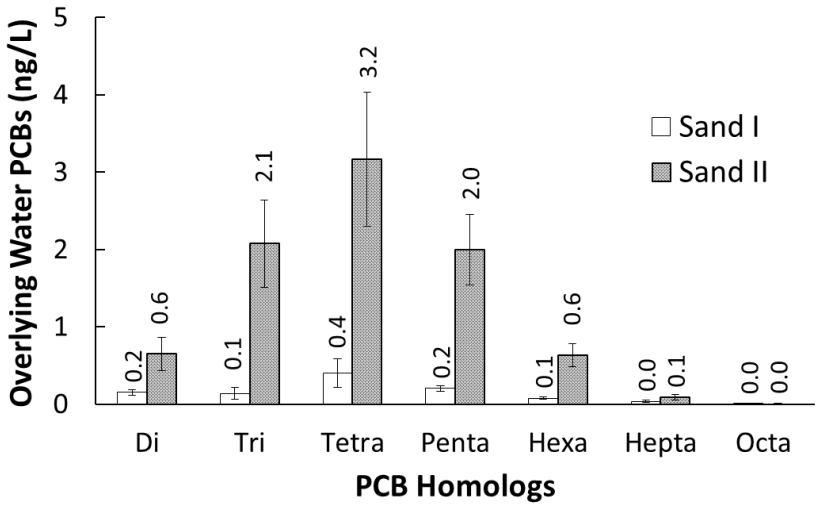


Figure S4. Overlying water concentrations in Sand I and Sand II tanks after 90 days. Error bars represent standard error.

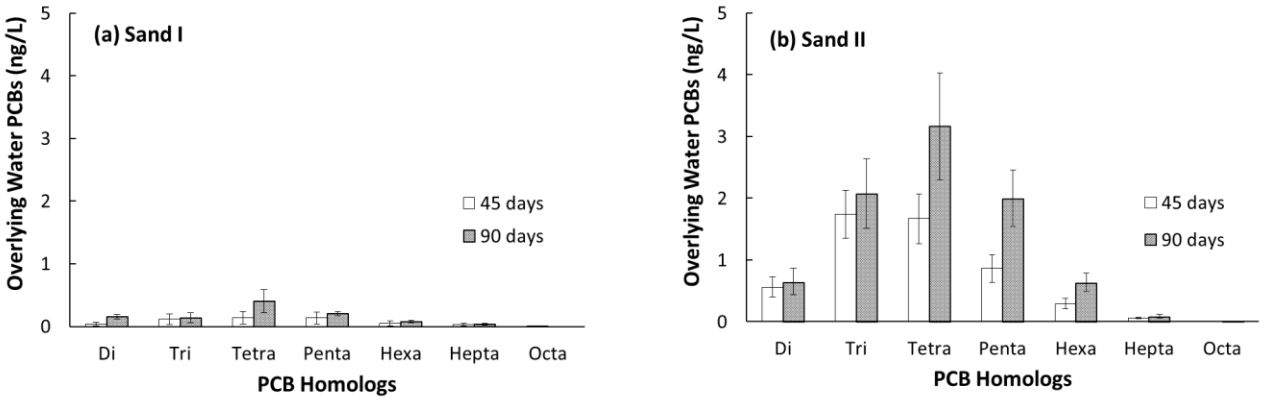


Figure S5. Overlying water concentrations in (a) Sand I and (b) Sand II after 45 and 90 days. Error bars represent standard error.

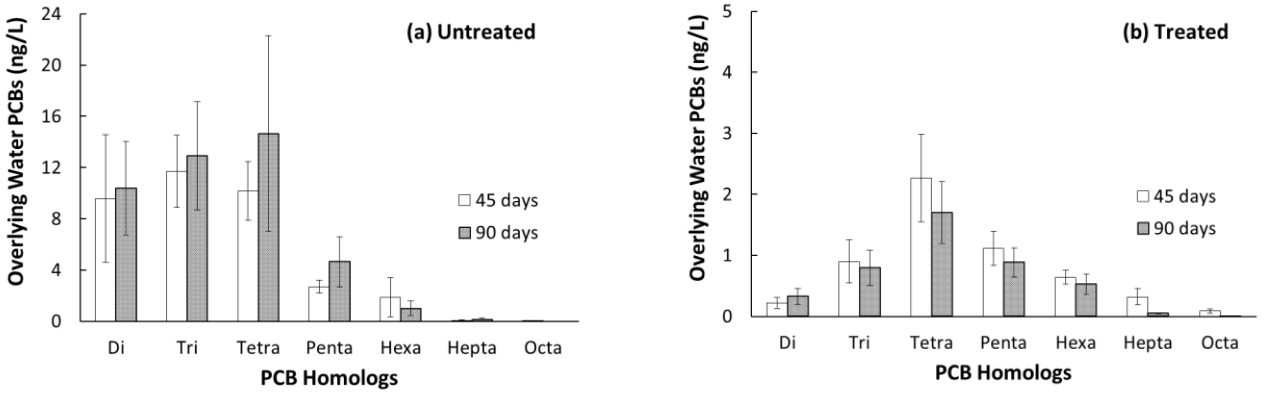


Figure S6. Overlying water concentrations in (a) untreated and (b) treated Grasse River sediments after 45 and 90 days. Error bars represent standard error.

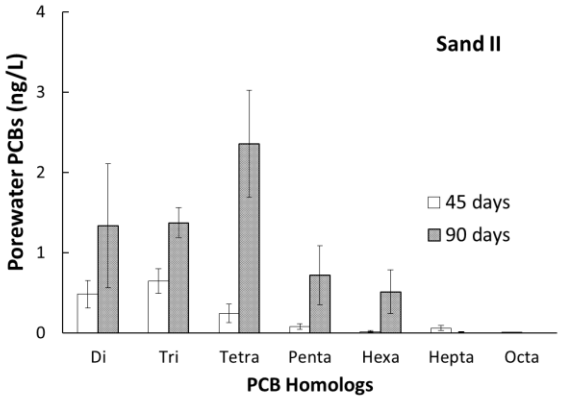


Figure S7. Porewater concentrations in Sand II tanks after 45 and 90 days. Error bars represent standard error.

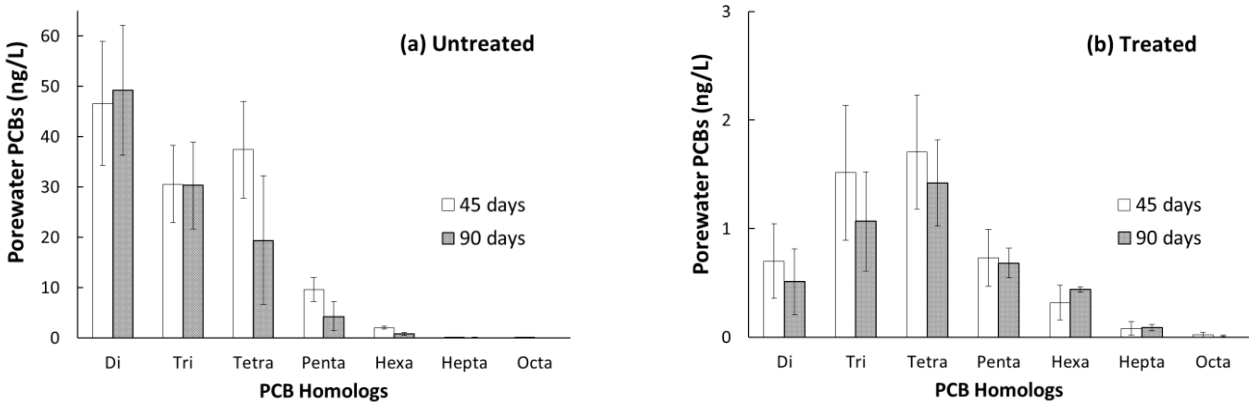


Figure S8. Porewater concentrations in (a) untreated and (b) treated Grasse River sediments after 45 and 90 days. Error bars represent standard error.

Calculating PCB excretion from the fish to the overlying water in the Sand II tanks

Tanks were refilled with fresh water (2-3 times per week and ~25% exchange each time). Therefore, it was assumed that on day 83 all the PCBs in the water were flushed out. PCB mass that was excreted from each fish species to the water was calculated from equation below, knowing the excretion rate constant and body burden of each fish at every time point from t=83 d to t=90 d.

$$M_{PCB} = \left[\left(\sum_{i=83}^{90}(k+G)*C_{B,i}\right)*n*W_B\right]_{catfish} + \left[\left(\sum_{i=83}^{90}(k+G)*C_{B,i}\right)*n*W_B\right]_{mummichog} \qquad (1)$$

Where (k+G) is the PCB excretion rate constant for the fish, $C_{B,i}$ is the PCB body burden in the fish at each time point i, n is the number of fish in each tank (n=3) and W_B is the wet weigh of each fish individual. For information on how k and G were obtained look at Connolly bioacumulation paramters section of this document.
PCB mass in the overlying water at t=90 d was calculated from the measured concnetration in the overlying water ($C_{W,O}$) and the volume of each tank (30 L).

$$M_{PCB} = C_{W,O} * V \qquad (2)$$

Ratio of PCB mass excreted from both fish to the mass in water varied from 0.3 to 51 for different PCB congeners.

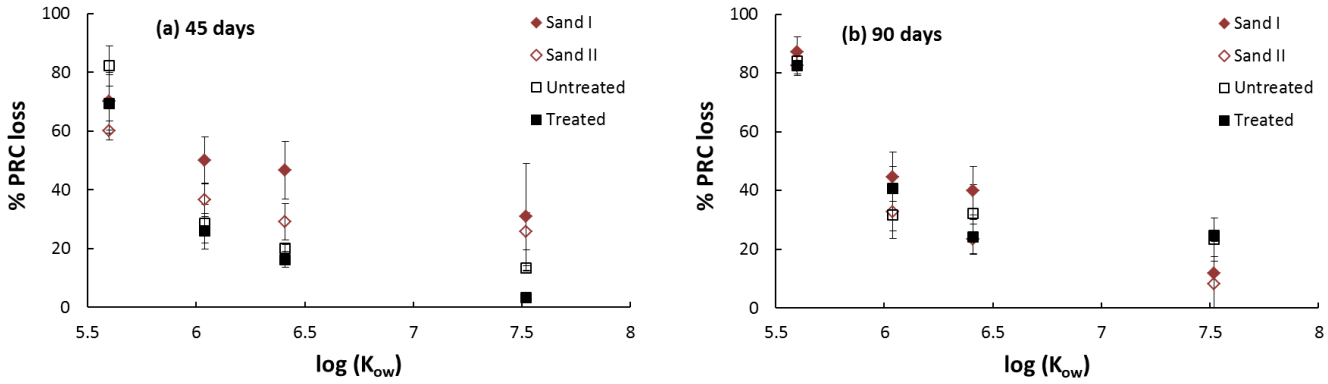


Figure S9. PRC loss in the overlying passive samplers plotted against K_{OW} after (a) 45 and (b) 90 days.

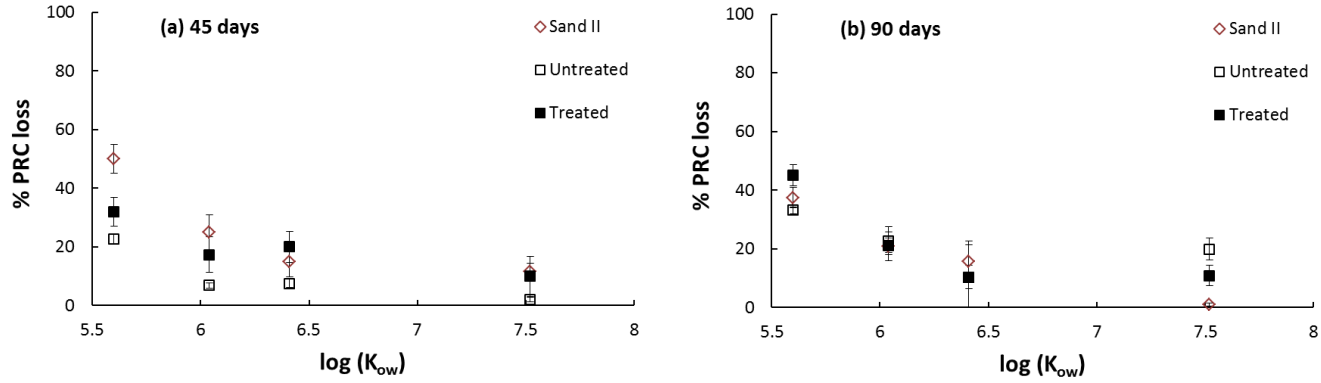


Figure S10. PRC loss in the porewater passive samplers plotted against K_{OW} after (a) 45 and (b) 90 days.

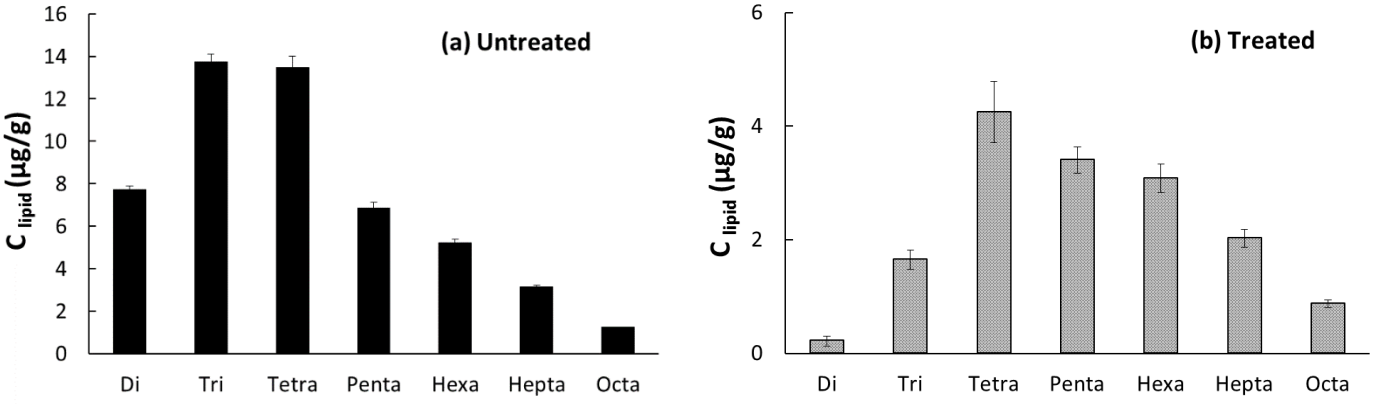


Figure S11. PCB concentration in *Lumbriculus* sampled after 30-day exposures to untreated and treated sediments. Error bars represent standard error.

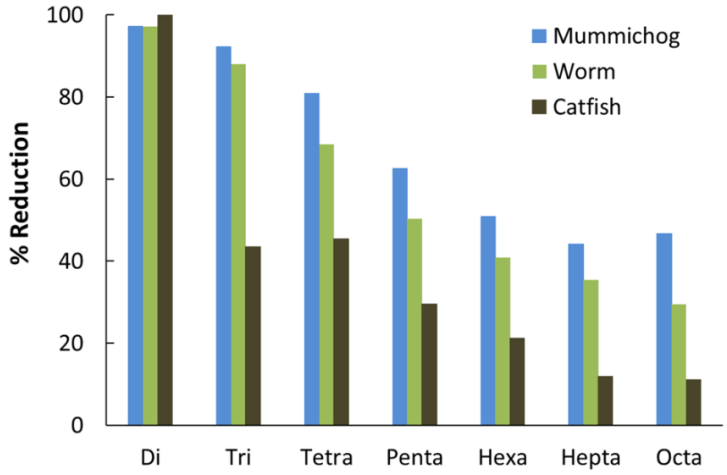


Figure S12. Percent PCB reduction in *Lumbriculus* after 30 days and in the two fish species after 90 days of exposure to treated sediment, respectively.

Tank	% Change	
	Catfish	Mummichog
Sand I	-4.9±10	84±17
Sand II	-1.0±8.0	70±19
Treated	14±4.0	52±19
Untreated	14±4.0	48±8.0

Table S3. Percent change in weight over 90 days.

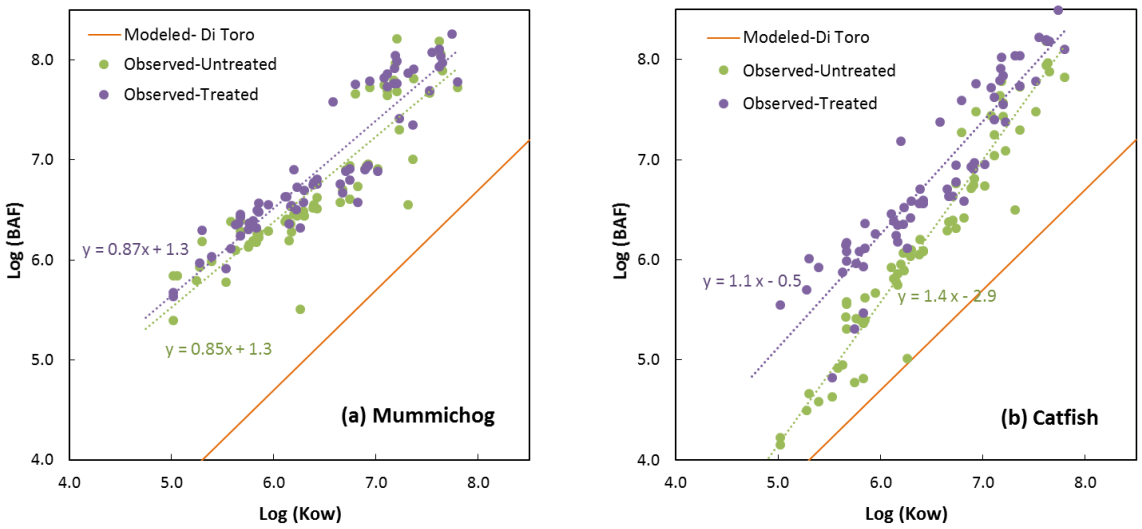


Figure S13. Observed log BAF- log K_{OW} correlation for (a)mummichog and (b) catfish. Modeled BAF values were obtained from Di Toro et al. (log BAF=Log K_{OW} -1.3).

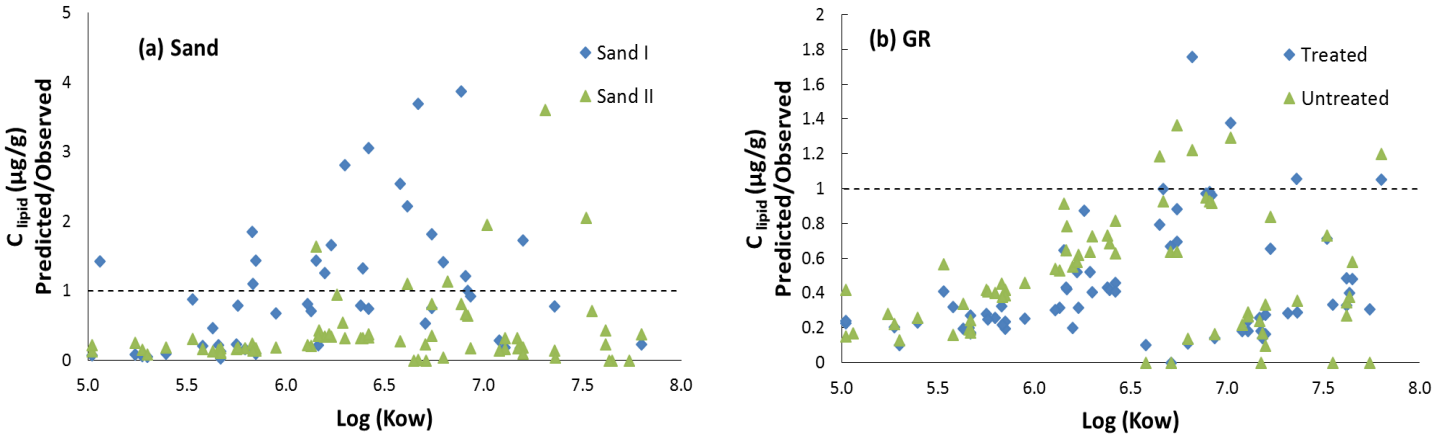


Figure S14. Ratio of predicted to observed PCB concentrations in mummichog plotted against K_{OW} for different PCB congeners in fish exposed to (a) sand and (b) GR sediments.The predictions are based on equilibrium partitioning of PCBs between fish lipid and water.

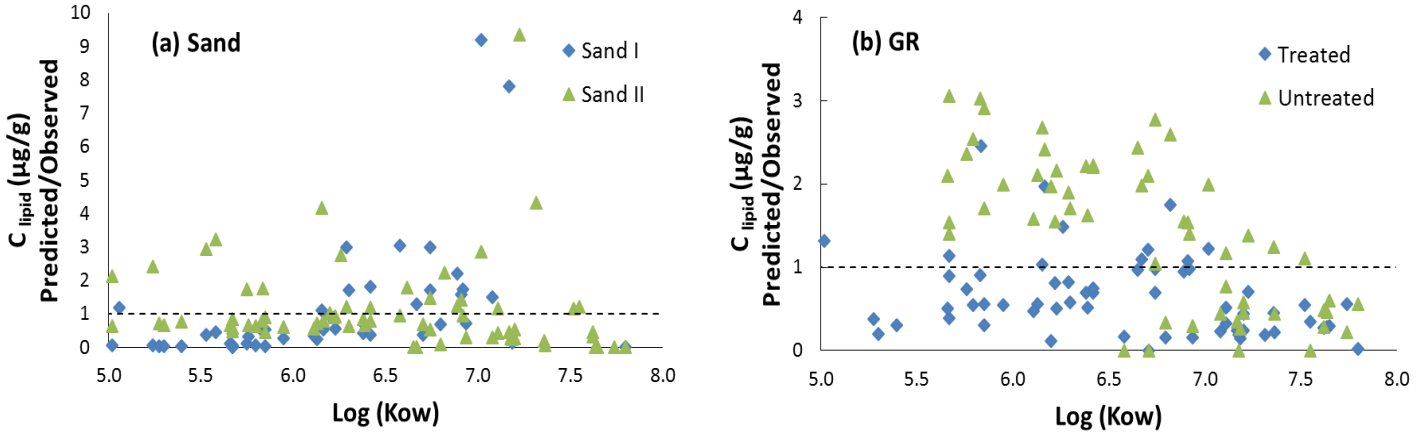


Figure S15. Ratio of predicted to observed PCB concentrations in catfish plotted against K_{OW} for different PCB congeners in fish exposed to (a) sand and (b) GR sediments.The predictions are based on equilibrium partitioning of PCBs between fish lipid and water.

Connolly(Connolly, 1991) bioaccumulation model parameters

Gill uptake rate constant (k_u):

$$k_{u=} \varepsilon r/C_{O2} \qquad (3)$$

Where ε is the ratio of mass transfer rates of PCBs to O_2. This ratio can be set to 1 as at the higher K_{OW} levels, the model is insensitive to this parameter. r is the respiration rate of the fish (in units of g of O_2/g(w)/d) and C_{O2} is the oxygen concentration of the water (g of O_2/L) .

Mummichog
r was obtained as 198 ml O_2/kg(w)/h from Kidder et al.(Kidder et al., 2006) (using Figure 5 and individual fish wet weight of 2 g). This oxygen consumption rate was converted to mg O_2/kg(w)/h unit assuming O_2 density of 1.43 mg/ml. C_{O2} was assumed to be at saturation (7.81 mg/L at T=28°C).

Catfish
$V_{O2[rest]}$ for the tropical species at 25°C was in the range 3.4 to 4.4 mg O_2 h^{-1} (average: 3.9 mg O_2 h^{-1}) for a 50 g weight fish. r was scaled to body mass to the 0.75 power resulting in r=0.21 mg O_2 h^{-1} g^{-1}. C_{O2} was assumed to be at saturation (7.81 mg/L at T=28°C).

Assimilation efficiency of PCBs in food (*α*):

The assimilation efficiency values were obtained from Table II of the Connolly paper.(Connolly, 1991)

Food ingestion rate (G_D):

In order to determine whether one fish species got more food than the other species in the same tank, observed body burden of decachlorobiphenyl (PCB 209) was used. Since PCB 209 is found at low levels in the Grasse River sediment, the uptake of this congener through sediment ingestion can be ignored. PCB 209 contribution to total PCB mass in fish through gill uptake (PCB 209 can desorb from food to the water) was determined by the bioaccumulation model and was found to be negligible over the course of the experiment. Therefore, PCB 209 uptake can be assumed to occur solely though the food.

$$C_B = \frac{IR\ \alpha\ C_D}{(k + k_G)}[1 - \exp(-(k + G) * t)] \qquad (4)$$

$$7.9 \times 10^{-5} = \frac{IR \times\ 0.1\ \times 9.9 \times 10^{-5}}{0.005}[1 - \exp(-(0.005) * 90)] \qquad (5)$$

Table S4 shows the calculated ratio of the food ingestion rate of the mummichog to catfish in each tank.

Tank	Ingestion Rate (G_D) Ratio (mummichog/catfish)
Sand I	1.8
Sand II	1.8
Treated	1.7
Untreated	2.0

Table S4. Ratio of the calculated ingestion rate of mummichog to catfish.

Assimilation efficiency of sediment-bound PCBs (β):

These values were obtained from a correlation developed from results from a recent study by the authors (not published) which looked into changes in assimilation efficiency of PCBs associated with different sediment matrices that composed of naturally occurring black carbon or added as an amendment to the sediment at different doses.

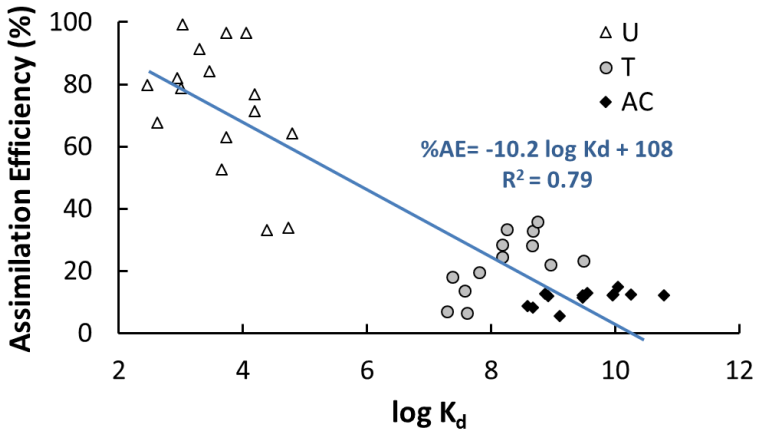


Figure S16. Assimilation efficiency of U, T, and AC diets as a function of log K_d. Triangles, circles and diamonds represent data for fish that fed on U, T, and AC diets, respectively.

Sediment ingestion rate (IR):

IR for every tank was calculated from equation 6 using the measured body burden of a heptachlorobiphenyl (PCB-180) in fish, corresponding β, C_S as well as known values of the gill uptake, dietary uptake and excretion parameters. The corresponding body burden, β, and sediment concentrations were used for exposure to Sand II, treated and untreated sediments.

$$C_B = \frac{k_u\,(m_P\,C_{W,P} + m_O\,C_{W,O}) + \alpha\,G_D\,C_{worm} + IR\,\beta\,C_S}{(k+G)}\left(1 - e^{-(k+G)t}\right) \qquad (6)$$

The uptake through sediment ingestion pathway was estimated by letting IR remain constant and using the corresponding β and measured Cs for the remaining congeners.

Excretion rate constant (k):

$$k = k_u / (L_F K_{OW}) \qquad (7)$$

Where L_F is the lipid content of the fish (kg lipid/kg wet weight).

Growth rate (G):

Initial and final weight of the fish, as well as exposure duration (Δt=90 days) were used to calculate the growth rate from equation below:

$$\ln W_{@t=90} - \ln W_{@t=0} = G\ (\Delta t) \qquad (8)$$

	Sand I	Sand II	Treated	Untreated
	RMSE-Equilibrium Model			
catfish	0.11	0.23	0.17	0.51
mummichog	0.09	0.63	0.23	1.0
	RMSE-Kinetic Model-including sediment ingestion			
catfish	0.07	0.63	0.31	1.0
mummichog	0.04	0.46	0.17	0.53

Table S5. Root mean squared error (RMSE) values for model predictions.

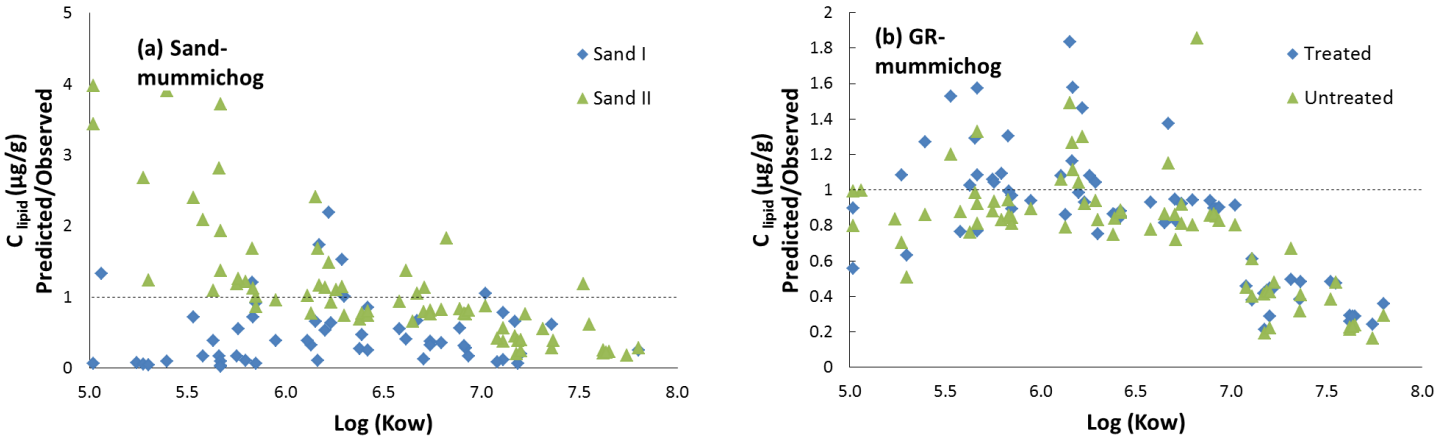


Figure S17. Ratio of predicted to observed PCB concentrations in mummichog plotted against K_{OW} for different PCB congeners in fish exposed to (a) sand and (b) GR sediments.The predictions are based on Connolly model which does not account for sediment ingestion.

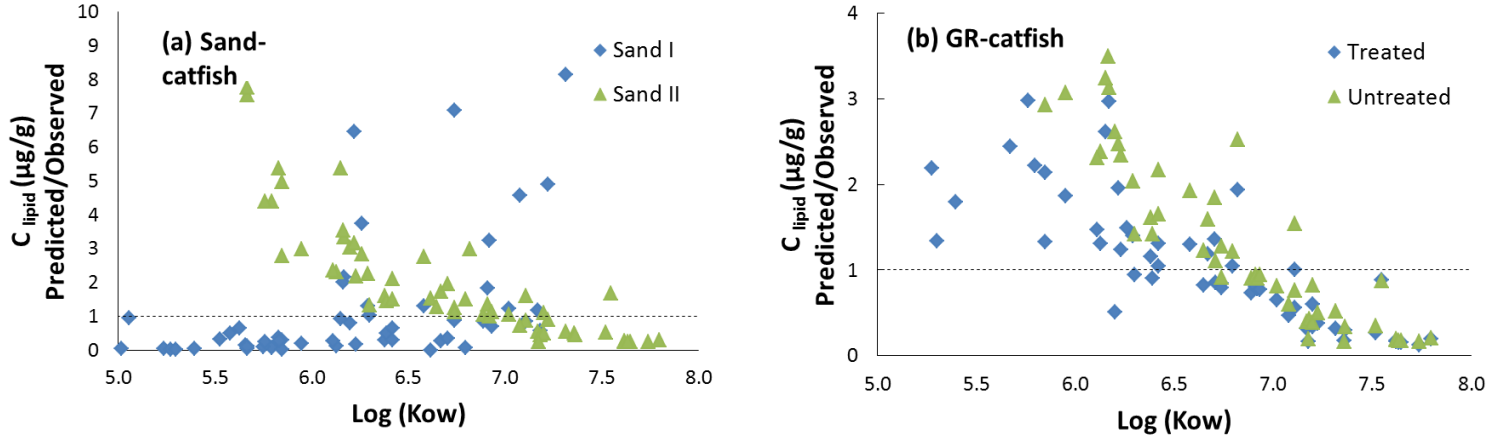


Figure S18. Ratio of predicted to observed PCB concentrations in catfish plotted against K_{OW} for different PCB congeners in fish exposed to (a) sand and (b) GR sediments.The predictions are based on Connolly model which does not account for sediment ingestion.

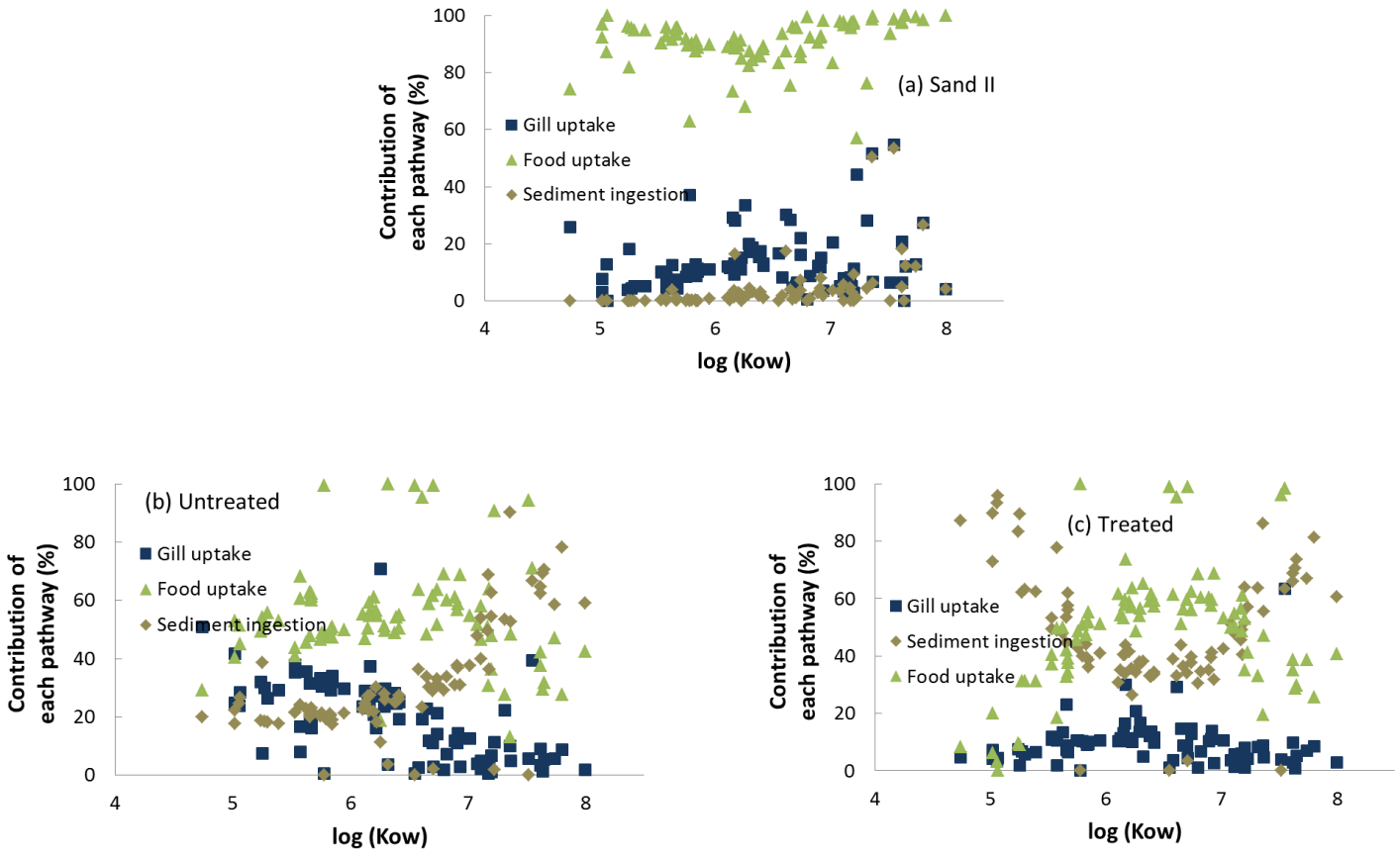
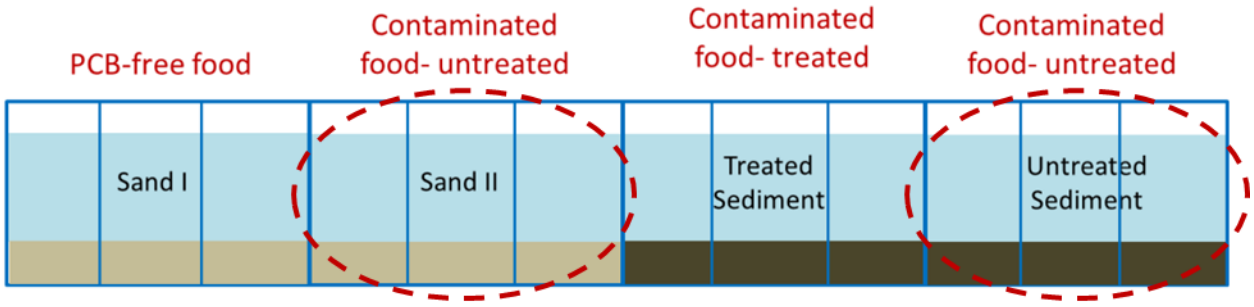


Figure S19. The relationship between modeled contributions of gill and food uptake, as well as sediment ingestion to the body burden and K_{ow} of PCB congeners in catfish exposed to (a) Sand II, (b) untreated, and (c) treated sediment.

Comparison of modeled and observed PCB uptake from water by the two fish

The difference between observed body burdens of the fish in the two sets of tanks that are shown below represents uptake through water only. The obtained results were compared to modeled PCB uptake from water in the untreated tanks.



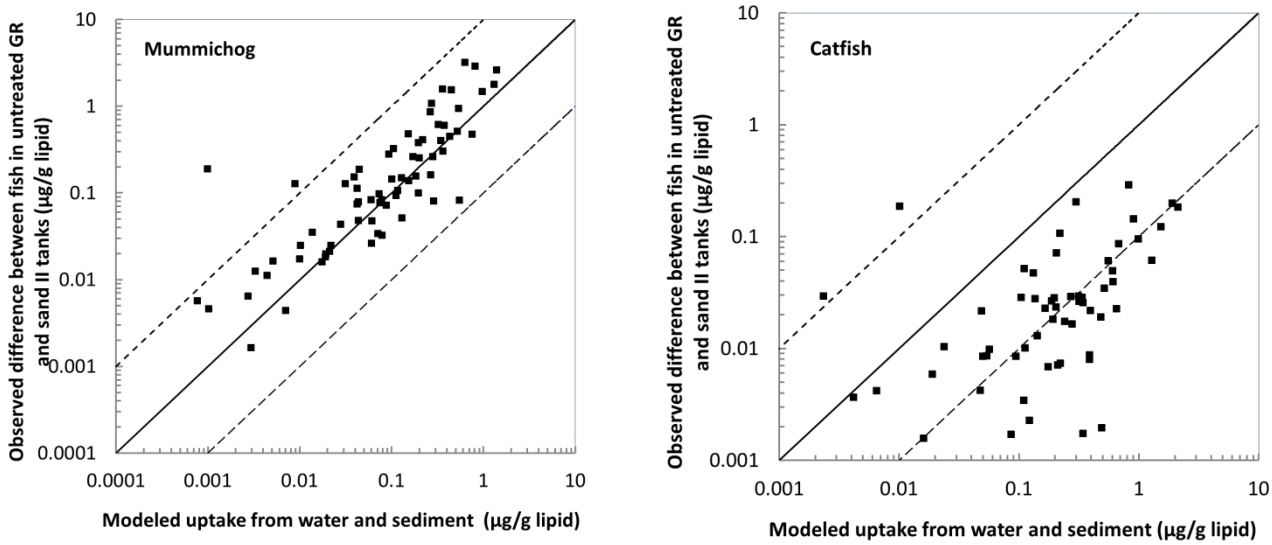


Figure S20. Comparison of the modeled and observed PCB uptake from water by the two fish.

Appendix III: Supporting Information for Chapter 4

Assimilation Efficiency of Sediment-Bound PCBs Ingested by Fish Impacted by Strong Sorption

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The supplementary section contains 5 tables and 3 figures and a total of 13 pages, including title page.

I. List of Figures

II. List of Tables

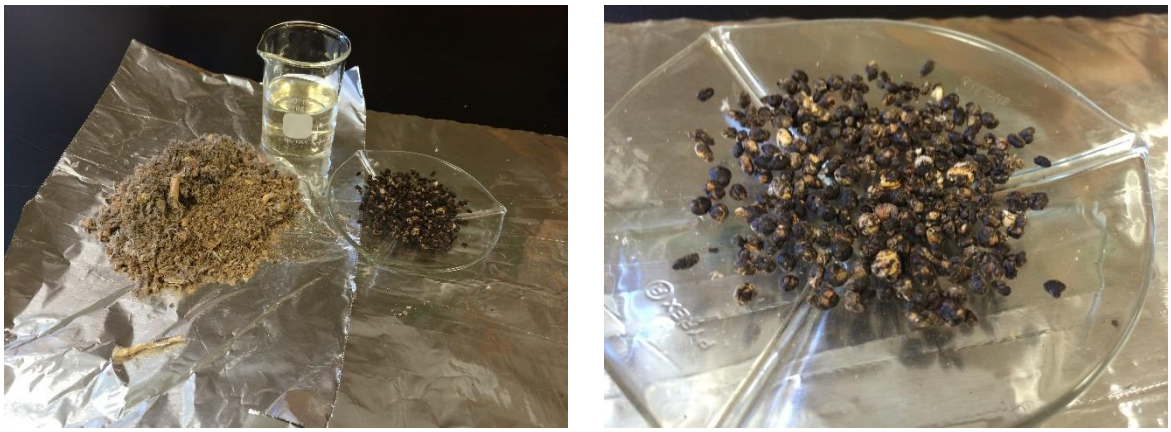


Figure S1. Lyophilized earthworms, carboxymethyl cellulose and pellets of food.

Figure S2. Aquarium set up and four types of food for each tank.

Table S1. Fish body weights and gender

Tank	Wet weight (g)	Sex	Tank	Wet weight (g)	Sex
Worm (W)			**AC**		
1	14.7	M	1	14.5	F
2	18.3	F	2	16.6	M
3	16.5	M	3	14.1	M
Untreated sediment (U)			**Treated sediment (T)**		
1	18.9	F	1	15.4	F
2	17.9	M	2	15	M
3	10.6	M	3	19.8	M

Table S2. Log K_{AC} values obtained from Gomez-Eyles et al. 2013

	log K_{AC}
2,4'-dichlorobiphenyl (BZ # 8)	8.7
2,2',5-trichlorobiphenyl (BZ # 18)	8.6
2,4,4'-trichlorobiphenyl (BZ # 28)	9.1
2,2',3,5'-tetrachlorobiphenyl (BZ # 44)	8.9
2,2',5,5'-tetrachlorobiphenyl (BZ # 52)	8.9
2,3',4,4'-tetrachlorobiphenyl (BZ # 66)	9.5
2,2',4,5,5'-pentachlorobiphenyl (BZ # 101)	9.5
2,3,3',4,4'-pentachlorobiphenyl (BZ # 105)	9.5
2,3',4,4',5-pentachlorobiphenyl (BZ # 118)	9.6
2,2',3,3',4,4'-hexachlorobiphenyl (BZ # 128)	9.5
2,2',3,3',4,4',5-heptachlorobiphenyl (BZ # 170)	10
2,2',3,4,4',5,5'-heptachlorobiphenyl (BZ # 180)	10
2,2',3,4',5,5',6-heptachlorobiphenyl (BZ # 187)	10
2,2',3,3',4,4',5,6-octachlorobiphenyl (BZ # 195)	10.3
2,2',3,3',4,4',5,5',6-nonachlorobiphenyl (BZ # 206)	10.8
decachlorobiphenyl (BZ # 209)	10.8

Table S3. Congener specific PCB concentration in different diets

		W	U	T	AC
	log Kow	**C_{food} (µg/g food)**			
2,4'-dichlorobiphenyl (BZ # 8)	5.0	0.1	0.03	0.09	0.3
2,2',5-trichlorobiphenyl (BZ # 18)	5.2	0.05	0.01	0.04	0.2
2,4,4'-trichlorobiphenyl (BZ # 28)	5.7	0.06	0.02	0.05	0.1
2,2',3,5'-tetrachlorobiphenyl (BZ # 44)	5.8	0.07	0.02	0.07	0.3
2,2',5,5'-tetrachlorobiphenyl (BZ # 52)	5.8	0.07	0.03	0.07	0.3
2,3',4,4'-tetrachlorobiphenyl (BZ # 66)	6.2	0.1	0.04	0.1	0.3
2,2',4,5,5'-pentachlorobiphenyl (BZ # 101)	6.4	0.06	0.03	0.07	0.3
2,3,3',4,4'-pentachlorobiphenyl (BZ # 105)	6.7	0.01	0.00	0.01	0.0
2,3',4,4',5-pentachlorobiphenyl (BZ # 118)	6.7	0.07	0.02	0.08	0.2
2,2',3,3',4,4'-hexachlorobiphenyl (BZ # 128)	6.7	0.05	0.02	0.06	0.2
2,2',3,3',4,4',5-heptachlorobiphenyl (BZ # 170)	7.4	0.05	0.02	0.08	0.3
2,2',3,4,4',5,5'-heptachlorobiphenyl (BZ # 180)	7.4	0.07	0.02	0.1	0.3
2,2',3,4',5,5',6-heptachlorobiphenyl (BZ # 187)	7.2	0.07	0.02	0.08	0.3
2,2',3,3',4,4',5,6-octachlorobiphenyl (BZ # 195)	7.6	0.06	0.02	0.1	0.4
2,2',3,3',4,4',5,5',6-nonachlorobiphenyl (BZ # 206)	8.1	0.07	0.02	0.1	0.4
decachlorobiphenyl (BZ # 209)	8.2	0.03	0.01	0.08	0.2
Total		**1.0**	**0.3**	**1.2**	**4.1**

Table S4. Congener specific data for PCB AEs among different diet

		W	U	T	AC
	log Kow	**Assimilation Efficiency**			
2,4'-dichlorobiphenyl (BZ # 8)	5.0	38±13	80±17	18±2	8±1
2,2',5-trichlorobiphenyl (BZ # 18)	5.2	25±10	68±14	7±2	9±1
2,4,4'-trichlorobiphenyl (BZ # 28)	5.7	38±13	82±18	20±6	5±0.2
2,2',3,5'-tetrachlorobiphenyl (BZ # 44)	5.8	36±13	79±17	14±4	13±1
2,2',5,5'-tetrachlorobiphenyl (BZ # 52)	5.8	41±10	99±10	6±1	12±1
2,3',4,4'-tetrachlorobiphenyl (BZ # 66)	6.2	46±9	91±14	25±3	12±2
2,2',4,5,5'-pentachlorobiphenyl (BZ # 101)	6.4	49±8	84±3	14±2	14±3
2,3,3',4,4'-pentachlorobiphenyl (BZ # 105)	6.7	26±11	53±6	16±3	6±0.2
2,3',4,4',5-pentachlorobiphenyl (BZ # 118)	6.7	44±9	96±5	33±5	13±0.2
2,2',3,3',4,4'-hexachlorobiphenyl (BZ # 128)	6.7	35±12	63±10	29±7	11±2
2,2',3,3',4,4',5-heptachlorobiphenyl (BZ # 170)	7.4	35±12	71±17	28±7	12±1
2,2',3,4,4',5,5'-heptachlorobiphenyl (BZ # 180)	7.4	37±11	77±17	33±8	12±0.4
2,2',3,4',5,5',6-heptachlorobiphenyl (BZ # 187)	7.2	38±9	96±10	36±6	15±2
2,2',3,3',4,4',5,6-octachlorobiphenyl (BZ # 195)	7.6	19±11	33±10	22±8	12±2
2,2',3,3',4,4',5,5',6-nonachlorobiphenyl (BZ # 206)	8.1	17±9	34±9	23±8	12±2
decachlorobiphenyl (BZ # 209)	8.2	27±11	64±29	28±9	17±3
Average of AE values for each diet		**34**	**73**	**22**	**11**

Bioaccumulation Model (Connolly, 1991)

$$\frac{dC_B}{dt} = \left[k_u \left(m_P\, C_{W,P} + m_O\, C_{W,O}\right) + \alpha\, G_D\, C_{worm} + IR\, \beta\, C_S\right] - (k + k_e + G) C_B \qquad (1)$$

The following assumptions were made to obtain equation 1: (1) fish weight changes with time but lipid content remains constant and (2) loss via metabolism is negligible. As described by (Connolly, 1991), C_B is the concentration (µg/g wet) of PCB in the fish, dC_B/dt represents the accumulation of PCB by fish at any point in time t (d), k_u is the rate constant for PCB uptake across the gill (L/g wet/d), m_p is the fraction of the respiratory ventilation that involves porewater, m_o is the fraction of the respiratory ventilation that involves overlying water (m_p=0.2, m_o=0.8), $C_{W,P}$ and $C_{W,O}$ are the freely dissolved PCB concentration in the porewater and overlying water (µg/L), respectively, α is the efficiency at which ingested chemical from food assimilated by the fish (unitless), G_D is the ingestion or consumption rate of food (g wet food/g wet/ d), C_{worm} is the concentration of PCB in the food (µg/g wet), IR is the sediment ingestion rate of the fish (g/g wet/d), β is the assimilation efficiency of the sediment-bound PCB (unitless) and C_S is the PCB concentration in the ingested sediment (µg/g), k is the rate constant for gill elimination (d^{-1}), k_e is the fecal egestion rate constant for fecal egestion (d^{-1}), and G is the growth rate of fish (g wet/g wet/d) . It is assumed that for most organic chemicals gill is the major site of depuration. Representation of contribution from porewater and overlying water to the respiratory uptake of PCBs in equation 1 was taken from the (Arnot and Gobas, 2004b) model. k and ke terms are lumped together as one excretion term in Connolly model but they are represented separately here similar to Arnot and Gobas 2004 model.

- **Modeling PCB loss through the gills for mummichog**

Gill elimination rate constant (k) was calculated from equation 2.

$$k = k_u / (L_F\, K_{OW}) \qquad (2)$$

where L_F is the lipid content of the fish (kg lipid/kg wet weight) and k_u is the gill uptake rate constant. L_F for mummichog was measured as 7.7% and k_u was calculated from equation 3.

$$k_{u=}\ \varepsilon r / C_{O_2} \qquad (3)$$

where ε is the ratio of mass transfer rates of PCBs to O_2. This ratio can be set to 1 as at the higher K_{OW} levels, the model is insensitive to this parameter. r is the respiration rate of the fish (in units of g of O_2/g(w)/d) and C_{O_2} is the oxygen concentration of the water (g of O_2/L). r was obtained as 78 ml O_2/kg(w)/h from Kidder et al. (using Figure 5 and individual fish wet weight of 17 g). This oxygen consumption rate was converted to mg O_2/kg(w)/h unit assuming O_2 density of 1.43 mg/ml. C_{O_2} was assumed to be at saturation (7.81 mg/L at T=28°C).

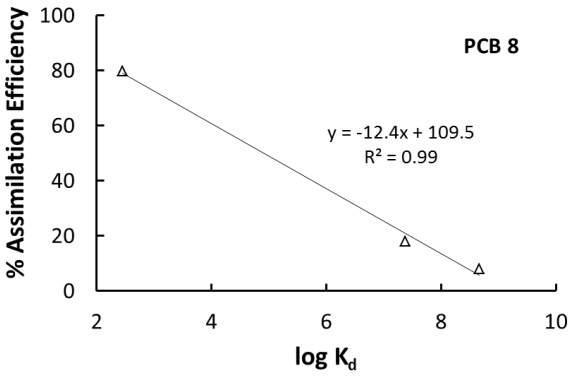
PCB mass loss through the gills can be calculated from:

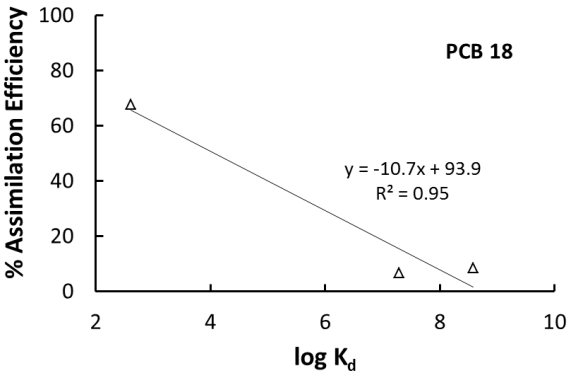
$$PCB\ mass\ loss\ through\ the\ gills = C_B \times W_B \times k \times t \quad (4)$$

where W_B is the mummichog wet weight (g) and t is the exposure duration (1 day).

Table S5. Congener specific ratio of PCB loss through the gills to the PCB ingested by the fish in different diets

	W	**U**	**T**	**AC**
	$\frac{\text{Mass PCB lost through the gills}}{\text{Mass PCB ingested by the fish}}(\%)$			
2,4'-dichlorobiphenyl (BZ # 8)	0.70	0.66	0.15	0.07
2,2',5-trichlorobiphenyl (BZ # 18)	0.63	0.34	0.03	0.04
2,4,4'-trichlorobiphenyl (BZ # 28)	0.69	1.38	0.48	0.14
2,2',3,5'-tetrachlorobiphenyl (BZ # 44)	0.43	0.64	0.18	0.05
2,2',5,5'-tetrachlorobiphenyl (BZ # 52)	0.60	0.91	0.32	0.09
2,3',4,4'-tetrachlorobiphenyl (BZ # 66)	0.38	0.67	0.25	0.10
2,2',4,5,5'-pentachlorobiphenyl (BZ # 101)	0.27	0.40	0.17	0.05
2,3,3',4,4'-pentachlorobiphenyl (BZ # 105)	0.05	0.08	0.02	0.01
2,3',4,4',5-pentachlorobiphenyl (BZ # 118)	0.11	0.23	0.07	0.03
2,2',3,3',4,4'-hexachlorobiphenyl (BZ # 128)	0.06	0.10	0.03	0.01
2,2',3,3',4,4',5-heptachlorobiphenyl (BZ # 170)	0.02	0.02	0.01	0.002
2,2',3,4,4',5,5'-heptachlorobiphenyl (BZ # 180)	0.02	0.05	0.01	0.003
2,2',3,4',5,5',6-heptachlorobiphenyl (BZ # 187)	0.03	0.09	0.02	0.01
2,2',3,3',4,4',5,6-octachlorobiphenyl (BZ # 195)	0.003	0.002	0.001	0.000
2,2',3,3',4,4',5,5',6-nonachlorobiphenyl (BZ # 206)	0.001	0.001	0.000	0.000
decachlorobiphenyl (BZ # 209)	0.001	0.001	0.000	0.000
$\frac{\sum \text{Mass PCB lost through the gills}}{\sum \text{Mass PCB ingested by the fish}}(\%)$	**0.42**	**0.39**	**0.10**	**0.03**


PCB 8
y = -12.4x + 109.5
R² = 0.99
% Assimilation Efficiency
log K_d


PCB 18
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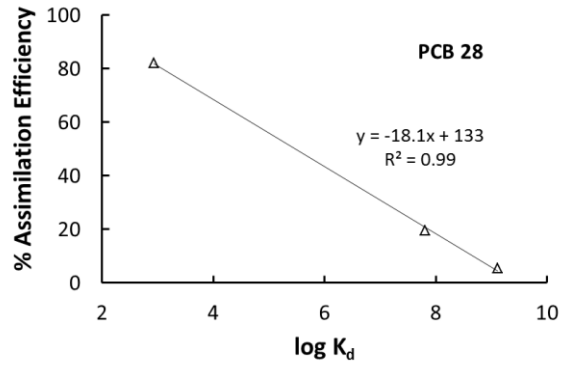
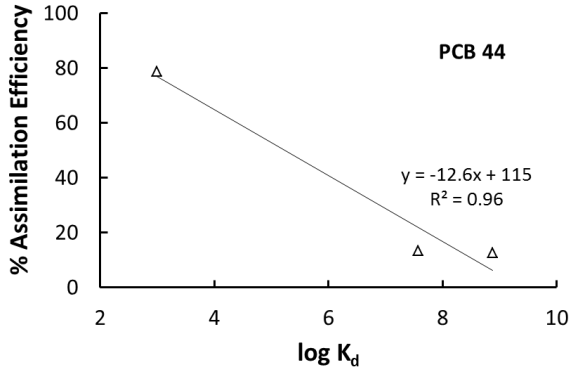
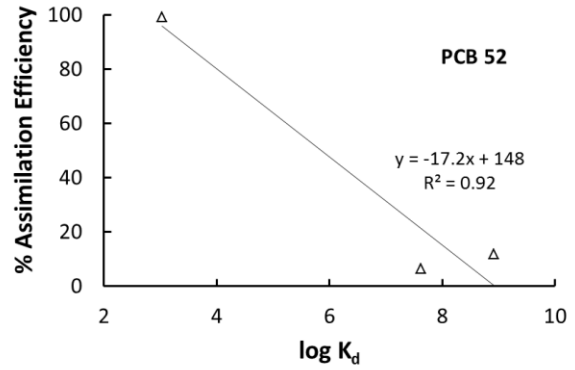
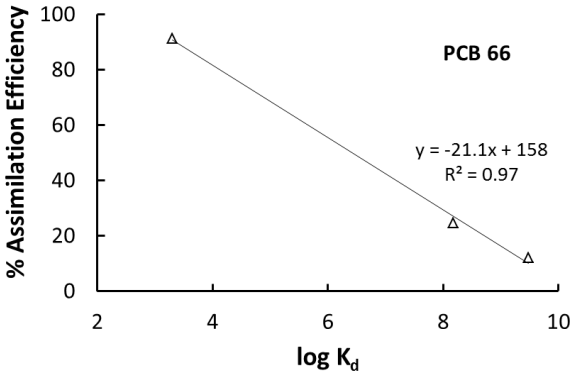
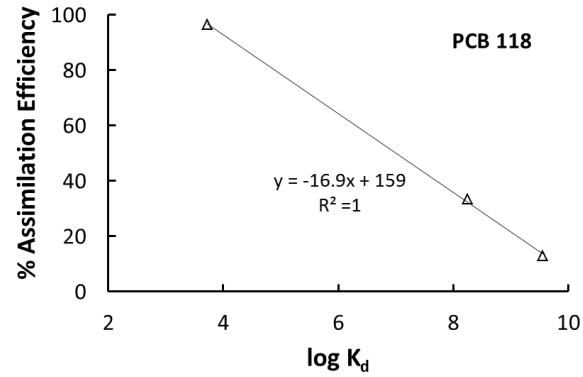
R² = 0.95
% Assimilation Efficiency
log K_d

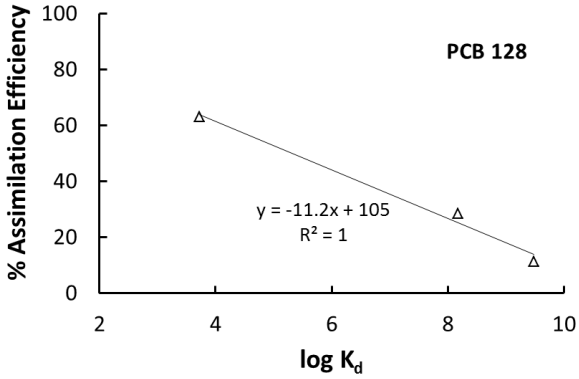

PCB 28
y = -18.1x + 133
R² = 0.99
% Assimilation Efficiency
log K_d


PCB 44
y = -12.6x + 115
R² = 0.96
% Assimilation Efficiency
log K_d


PCB 52
y = -17.2x + 148
R² = 0.92
% Assimilation Efficiency
log K_d


PCB 66
y = -21.1x + 158
R² = 0.97
% Assimilation Efficiency
log K_d


PCB 118
y = -16.9x + 159
R² =1
% Assimilation Efficiency
log K_d


PCB 128
y = -11.2x + 105
R² = 1
% Assimilation Efficiency
log K_d

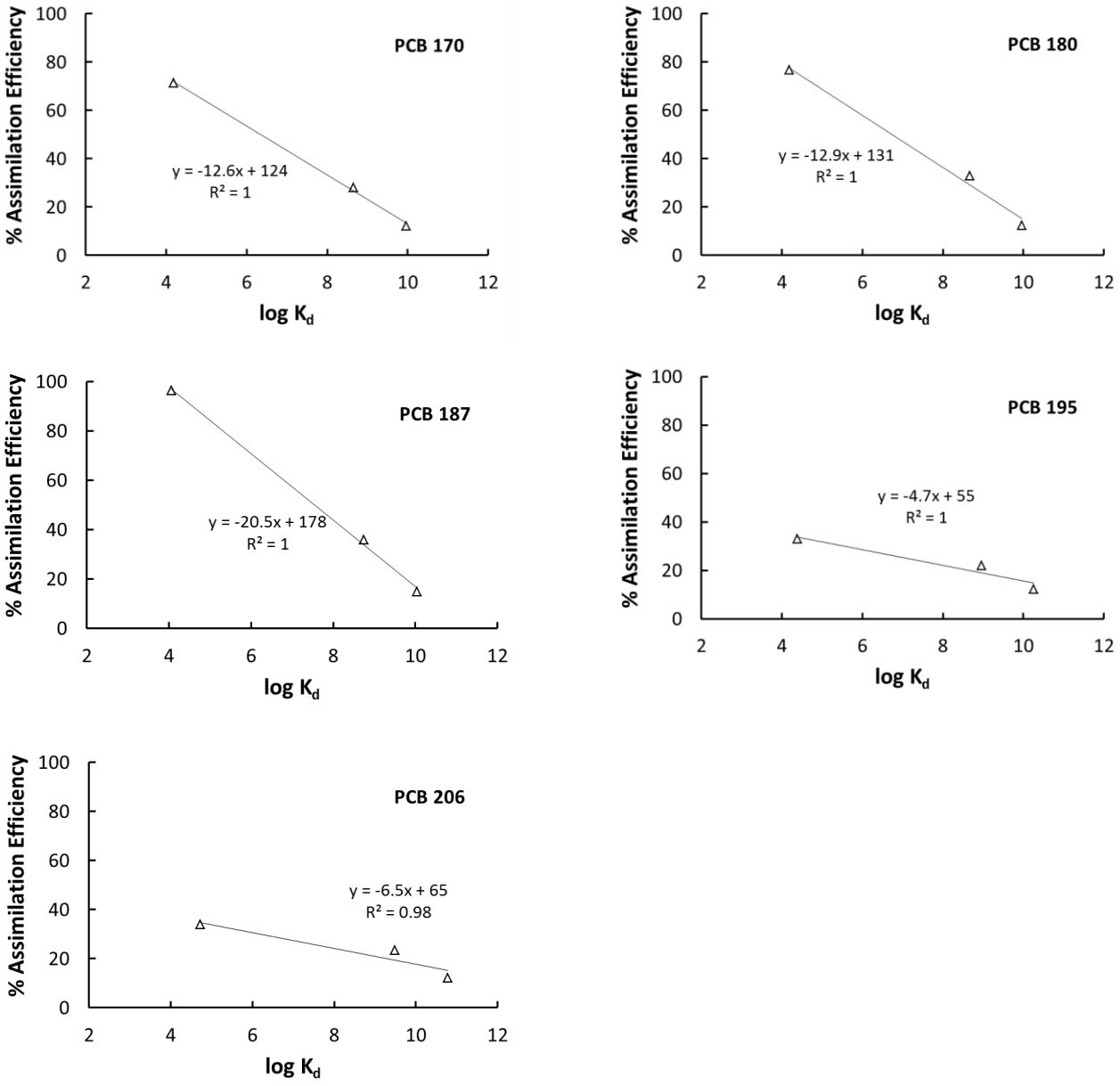


Figure S3. Assimilation efficiency of U, T, and AC diets as a function of log K_d for individual congeners.

- **Improved predictions of PCB uptake in catfish using the modified bioaccumulation model**

Detailed discussion of the model can be found on page S6. Integration of equation 1 and including the uptake and loss pathways related to the catfish exposure scenario yields:

$$C_B = \frac{k_u\,(m_P\,C_{W,P} + m_O\,C_{W,O}) + \alpha\,G_D\,C_{worm} + IR\,\beta\,C_S}{(k+G)}\left(1 - e^{-(k+G)t}\right) + Ae^{-(k+G)t} \quad (5)$$

where A is the constant of integration obtained by fitting equation 5 to the initial conditions. For estimation of k_u from equation 3, catfish-specific respiration rate (r) was used.

Catfish

$V_{O2[rest]}$ for the tropical species at 25°C was in the range 3.4 to 4.4 mg O_2 h^{-1} (average: 3.9 mg O_2 h^{-1}) for a 50 g weight fish. r was scaled to body mass (900 g) to the 0.75 power resulting in r=0.04 mg O_2 h^{-1} g^{-1}. C_{O2} was assumed to be at saturation (7.81 mg/L at T=28°C).

α was obtained from the measured AE values for the food (W diet) and β values were assumed to be :

(1) the same as food (the AE results found for the W diet)
(2) 100 % for all the PCB congeners
(3) the same as the results for T diet

for the different scenarios. Ingestion rate of food by fish was calculated as (Arnot and Gobas 2004):

$$G_D = 0.022\ W_B^{0.85} \exp(0.06\,T)/W_B \quad (6)$$

where W_B is the catfish wet weight (kg) and T is the water temperature (°C). The division by W_B is to report the G_D value in kg food/kg fish/d unit and does not exist in the original equation reported by Arnot and Gobas 2004 since their bioaccumulation model was based on PCB mass and not concentration.

Equation 7 from Werner et al. 2010 was used to predict PCB values in the worms at equilibrium. Corresponding porewater concentrations (corrected for non-equilibrium) were obtained from passive sampler measurement in the same sediment (Cs = 1.6 µg/g d.w).

$$\log(C_{lipid}) = 0.91 \cdot \log(K_{OW}) + 0.50 + \log(C_{aq}) \quad (7)$$

Appendix IV: Supporting Information for Chapter 5

Improving PCB Bioaccumulation Factors for Algae and Zooplankton Using Passive Samplers

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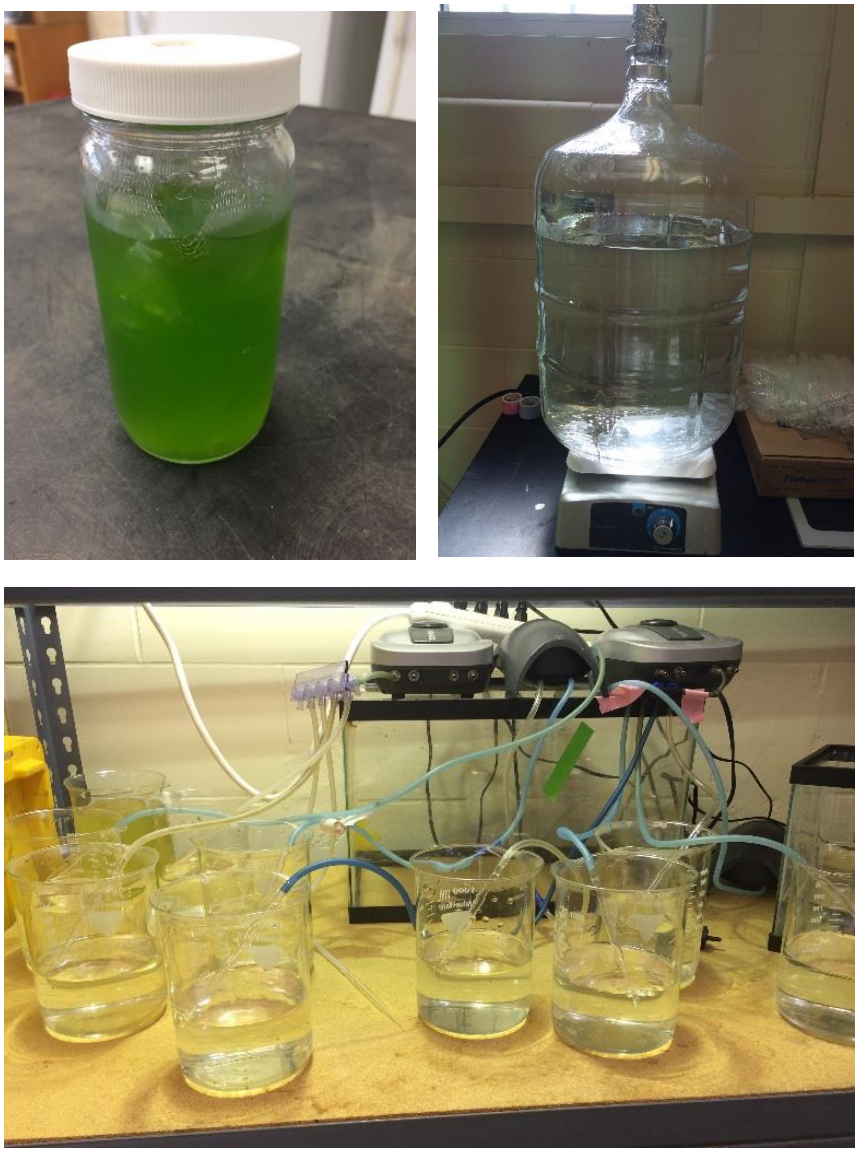


Figure S1- (a) Glass vials containing algae cells, media, and PCB-impregnated polymer, (b) glass carboy containing, *Daphnia* media, and PCB-impregnated polymer, (c) replicate *Daphnia* exposure beakers.

PCBs partition among the aqueous and different solid phases according to the following equilibrium distribution:

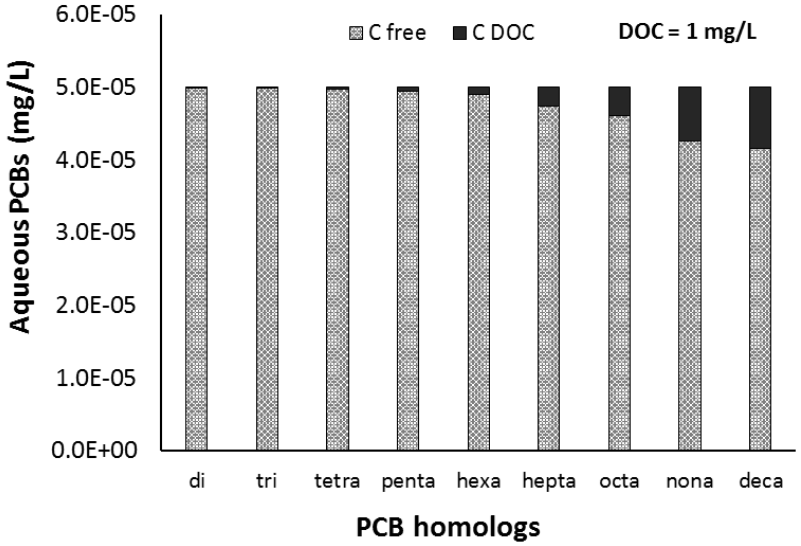
$$C_{total} = C_{free} + DOC\ K_{DOC}\ C_{free} + POC\ K_{POC}\ C_{free} \qquad (1)$$

The POC associated PCBs were neglected in this calculation.

$$C_{total} = C_{free}\ (1 + DOC\ K_{DOC}) \qquad (2)$$

$$C_{free} = \frac{C_{total}}{(1 + DOC\ K_{DOC})} \qquad (3)$$

A typical total surface water concentration of 50 ng/L was assumed. Varying DOC levels of 1, 10, and 50 mg/L, which are typical values for the surface water, were used to simulate the contribution of DOC-associated PCBs to total PCBs in the water. K_{DOC} partitioning values for PCBs were obtained from reported correlation by Burkhard (2000) for naturally occurring DOC ($\log K_{DOC} = 0.71 \times \log K_{OW} - 0.5$). C_{DOC} was calculated by subtraction of C_{free} from C_{total}. C_{DOC} and C_{free} values for different PCB homolog groups are shown in the following Figure S2 for the three DOC levels.



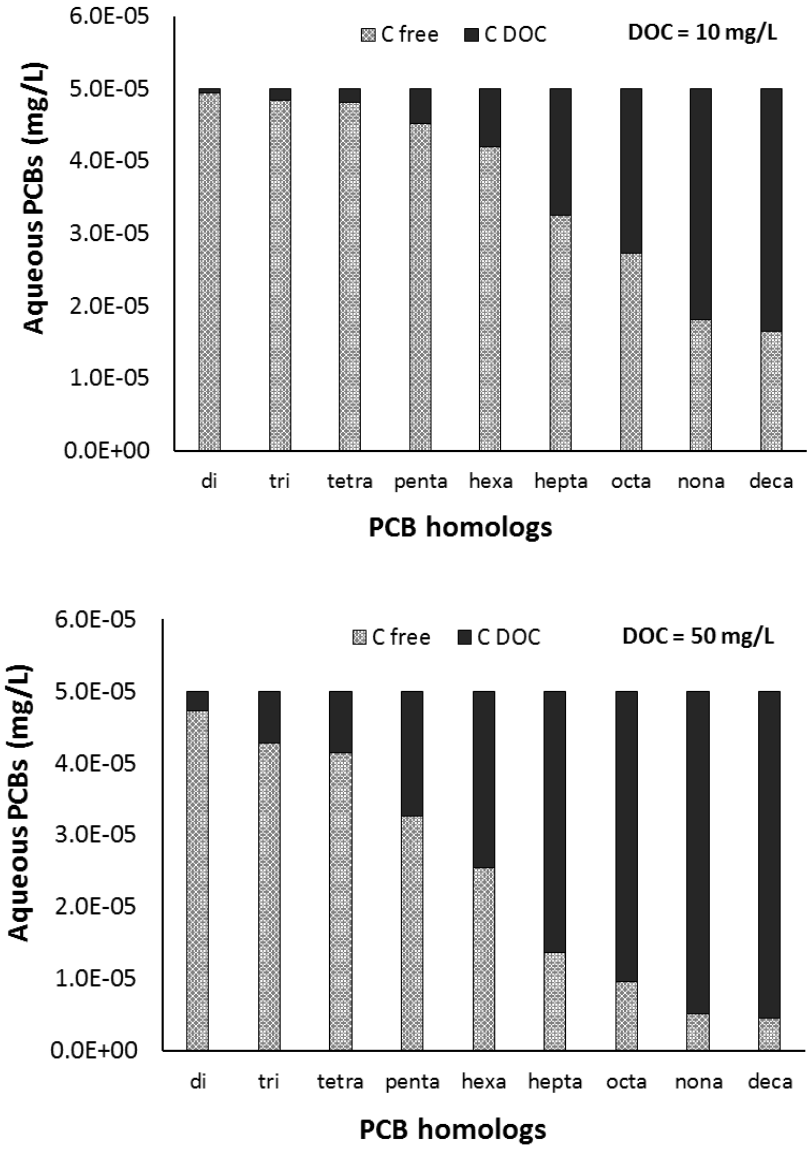


Figure S2- Contribution from DOC-associated PCBs to total PCBs at different DOC levels.

For environmentally relevant surface water concentrations of PCBs, percent PCBs associated with DOC were in the range of 0.1 to 17, 1 to 67, and 5 to 91 for 1, 10, and 50 mg/L DOC in water, respectively. The highest DOC-associated PCBs were observed for the case of DOC=50 mg/L. Effect of DOC presence is more pronounced for the more hydrophobic congeners as these heavier compounds have higher affinity to the organic phase. These simulation results suggest that if one was to use the traditional methods of measuring PCBs in the aqueous phase, which do not always provide an efficient removal of the DOC phase and the associated PCBs, the freely dissolved measurements can be skewed and erroneous due to the DOC-associated PCBs in the above ranges.

Standard, Synthetic, Moderately Hard Freshwater

To prepare 20 L of standard, synthetic, moderately hard, reconstituted water, the reagent grade chemicals were used as follows:

A properly cleaned glass carboy was used, 19 L of deionized water was placed in the carboy, 1.20 g of MgSO4, 1.92 g NaHCO3, and 0.080g KCl was added to the carboy. Water was aerated overnight. 1 L of deionized water was placed in a separate flask and 1.20 g of CaSO4C2 H2O was added to the water. The water was stirred on magnetic stirrer until calcium sulfate was dissolved, and was then added to the 19 L above, and mixed well. The measured pH, hardness and alkalinity are listed in Table S1.

Reagent Added (mg/L)				Approximate Final Water Quality		
$NaHCO_3$	$CaSO_4.2H2O$	$MgSO_4$	KCl	pH	Hardness (mg $CaCo_3$/L)	Alkalinity
96	60	60	4.0	7.4-7.8	80-100	57-64

Table S1- Approximate water quality of the moderately hard water

Arnot and Gobas (2004b) Bioaccumulation Model

A simplified version of the Arnot and Gobas model is shown below. As described by Arnot and Gobas, M_B is the mass (g) of PCB in the organism, dM_B/dt is the net flux of PCB being absorbed or depurated by the organism at any point in time t (d), W_B is the wet weight of the organism (kg) at time t, k_1 is the gill uptake rate constant (L/kg.d), m_o is the fraction of the ventilation that involves overlying water (which equals 1 in this case), $C_{W,O}$ is the freely dissolved PCB concentration in the overlying water measured by passive sampling (g/L), k_D is the clearance rate constant (kg/kg.d) for chemical uptake via ingestion of food and water, C_D is the concentration of chemical (g/kg) in food, and k_2 is the elimination rate constant via the respiratory area (d^{-1}), k_E is the rate constant for chemical elimination via excretion into egested feces (d^{-1}), and k_M is the rate constant for metabolic transformation of the chemical (d^{-1}).

$$\frac{dM_B}{dt} = W_B\, k_1\, m_O\, C_{W,O} + W_B\, k_D\, C_D - (k_2 + k_E + k_M)M_B \qquad (4)$$

Integration of equation 4, neglecting k_M, yields:

$$M_B = \frac{W_B k_1\, C_{W,O} + W_B\, k_D\, C_D}{(k_2 + k_E)}\,(1 - e^{-(k_2+k_E)t}) + Ae^{-(k_2+k_E)t} \qquad (5)$$

Where A is the constant of integration obtained by fitting equation 5 to the initial conditions.

For algae, k_D is zero, and k_E is considered to be insignificant. The overlying water concentration ($C_{W,O}$) was obtained from PCBs measured in PE polymer. Concentration in the food for zooplankton (C_D) was calculated based on the KABAM model prediction of algae uptake at steady state (EFED-USEPA, 2009). PCB concentrations in algae and zooplankton were predicted by solving for the mass of PCB at 2 and 10 days, respectively and converted to lipid normalized concentration using equation 6:

$$C_{lipid} = \frac{M_B}{W_B L_B} \qquad (6)$$

Where L_B is the lipid content of the biota (kg lipid/kg wet weight).

Algae Kinetic Parameters

For algae, a biphasic relationship was used for k_1 and k_2 based on a water-organic carbon two-phase resistance model:

$$k_1 = (A_P + ((B_P / K_{OW}))^{-1} \qquad (7)$$

where A_P and B_P are constants (with units of time) describing the resistance to PCB uptake through respectively the aqueous and organic phases of the algae. Constant B_P (default value = 5.5 [± 3.7]) is derived by calibration to empirical k_2 values from various phytoplankton, algae and cyanobacteria species over a range of K_{OW} using data in described in Koelmans et al. [1993, 1995, 1999]. Constant A_P (default value = 6.0 [± 2.0] $.10^{-5}$) is derived from calibration to phytoplankton field BCF data from the Great Lakes (Oliver and Niimi, 1988; Swackhamer and Skoglund, 1993).

The elimination rate constant k_2 (d^{-1}) is closely related to k_1 as both k_1 and k_2 involve the same processes of water ventilation and membrane permeation:

$$k_2 = k_1/K_{BW} \qquad (8)$$

Where K_{BW} (L/kg wet weight) is the biota-water partition constant. The partitioning of PCBs between algae and water is believed to occur into the lipids, non-lipid organic matter (e.g. proteins and carbohydrates) and water. Each of these media has their own capacity to sorb and "store" PCB congeners. Hence, for every PCB congener in algae we define an organism-water partition constant, K_{BW}, on a wet weight basis (ww) as:

$$K_{BW} = k_1 / k_2 = v_{LB} \cdot K_{OW} + v_{NB} \cdot \beta \cdot K_{OW} + v_{WB} \qquad (9)$$

where v_{LB} is the lipid fraction (kg lipid/kg organism ww), v_{NB} is the non-lipid organic matter (NLOM) fraction (kg NLOM/kg organism ww) and v_{WB} is the water content (kg water/kg organism ww) of the organism (v_{LB} = 0.015, v_{NB} = 0.085, and v_{WB} =0.9). β is a proportionality constant expressing the sorption capacity of NLOM to that of octanol. Based on previous work (Gobas et al., 1999), a value of approximately 0.035 ± 0.004 was chosen. This implies that the

sorption affinity of NLOM for PCBs is approximately 3.5% that of octanol. While the sorption affinity of NLOM is low compared to that of lipid, it can play an important role in controlling the partitioning of organic chemicals in organisms that have low lipid contents (e.g. phytoplankton, algae, certain invertebrates).

For the calculation of the algae-water partition constant (K_{PW}) NLOM fraction in equation 6 is replaced by the non-lipid organic carbon fraction (kg NLOC/kg organism ww) (Skoglund and Swackhamer, 1999) with a proportionality constant of 0.35 as:

$$K_{PW} = v_{LP} \cdot K_{OW} + v_{NP} \cdot 0.35 \cdot K_{OW} + v_{WP} \qquad (10)$$

<u>Zooplankton Kinetic Parameters</u>

Uptake rate constant (k_1):

$$k_1 = E_W G_V / W_B \qquad (11)$$

Where E_W is the uptake efficiency (unitless), G_V is the filtration rate (L/day) and W_B is the wet weight of the *Daphnia* (kg).

$$E_W = (1.85 + 155/K_{OW})^{-1} \qquad (12)$$

The empirical correlation below was used to estimate the filtration rate for *Daphnia*.

$$G_V = 1400\ W_B^{0.65} / DO \qquad (13)$$

Where DO is the dissolved oxygen concentration in the water (mg O_2/L). DO was defined at 26°C as 8.1 mg/L.

Elimination rate constant (k_2):

$$k_2 = k_1 / (L_z K_{OW}) \qquad (14)$$

Where L_z is the lipid content of the zooplankton (kg lipid/kg wet weight).

Dietary uptake rate constant (k_D):

Dietary uptake rate constant (k_D) was described using the following equation:

$$k_D = E_D G_D / W_B \qquad (15)$$

Where E_D is the dietary uptake efficiency of PCB via the gastro-intestinal tract (unitless), G_D is the ingestion rate of the organism (kg/day) and WB is the wet weight of *Daphnia* (kg).

The following two-phase resistance model was used to estimate E_D for *Daphnia*:

$E_D = (3.0*10^{-7} K_{OW} +2.0)^{-1}$ (16)

G_D, the food ingestion rate (kg algae/ kg *daphni*.d) was estimated based on the 3 mL of algae that was added to each beaker every other day (1.5 mL algae per day), wet weight of each algal cell (10^{-11} g/cell, (Hu, 2014)), cell count (cells/mL) provided by the supplier (Aquatic BioSystems), and the weight of the *Daphnia*.

Fecal egestion rate constant (k_E):

Fecal egestion rate was estimated from dietary uptake rate constant:

$k_E=0.25\ k_D$ (17)

Bibliography

Alcoa, 2001, Comprehensive Characterization of the Lower Grasse River, Volume 1 – Main Report.

Amended April 2001. Available online at: http://www.thegrasseriver.com/Env_Mon_DataSumRpts.htm.

Alcoa, 2010a, Draft Analysis of alternatives report, Grasse River study area,Massena, New York.

Alcoa, 2010b, Modeling PCB Fate in the Lower Grasse River, Appendix A of the Lower Grasse River Analysis of Alternatives Report, submitted to USEPA Region 2.

Anchor QEA, 2010, The Upper Hudson River PCB Modeling System, Hudson River PCBs Superfund Site, Prepared for General Electric Corporation.

Arnot, J., and F. Gobas, 2004a, A food web bioaccumulation model for organic chemicals in aquatic ecosystems - SETAC Supplemental Data Archive S.3.

Arnot, J. A., and F. A. P. C. Gobas, 2004b, A food web bioaccumulation model for organic chemicals in aquatic ecosystems: Environmental Toxicology and Chemistry, v. 23, p. 2343-2355.

Arnot, J. A., and F. A. P. C. Gobas, 2006, A review of bioconcentration factor (BCF) and bioaccumulation factor (BAF) assessments for organic chemicals in aquatic organisms: Environmental Reviews, v. 14, p. 257-297.

Arnot, J. A., D. Mackay, and M. Bonnell, 2008a, Estimating metabolic biotransformation rates in fish from laboratory data: Environmental Toxicology and Chemistry, v. 27, p. 341-351.

Arnot, J. A., D. Mackay, T. F. Parkerton, and M. Bonnell, 2008b, A database of fish biotransformation rates for organic chemicals: Environmental Toxicology and Chemistry, v. 27, p. 2263-2270.

Avnimelech, Y., G. Ritvo, L. E. Meijer, and M. Kochba, 2001, Water content, organic carbon and dry bulk

density in flooded sediments: Aquacultural Engineering, v. 25, p. 25–33

Barber, M. C., 2008, Dietary uptake models used for modeling the bioaccumulation of organic contaminants in fish: Environmental Toxicology and Chemistry, v. 27, p. 755-777.

Barrionuevo, W. R., and W. W. Burggren, 1999, O2 consumption and heart rate in developing zebrafish (Danio rerio): influence of temperature and ambient O2: American Journal of Physiology - Regulatory, Integrative and Comparative Physiology, v. 276, p. R505-R513.

Beckingham, B., D. Buys, H. Vandewalker, and U. Ghosh, 2013, Observations of limited secondary effects to benthic invertebrates and macrophytes with activated carbon amendment in river sediments: Environmental Toxicology and Chemistry, v. 32, p. 1504-1515.

Beckingham, B., and U. Ghosh, 2011, Field-Scale Reduction of PCB Bioavailability with Activated Carbon Amendment to River Sediments: Environmental Science & Technology, v. 45, p. 10567-10574.

Beckingham, B., and U. Ghosh, 2013, Polyoxymethylene passive samplers to monitor changes in bioavailability and flux of PCBs after activated carbon amendment to sediment in the field: Chemosphere, v. 91, p. 1401-1407.

Booij, K., J. R. Hoedemaker, and J. F. Bakker, 2003, Dissolved PCBs, PAHs, and HCB in Pore Waters and Overlying Waters of Contaminated Harbor Sediments: Environmental Science & Technology, v. 37, p. 4213-4220.

Booij, K., H. M. Sleiderink, and F. Smedes, 1998, Calibrating the uptake kinetics of semipermeable membrane devices using exposure standards: Environmental Toxicology and Chemistry, v. 17, p. 1236-1245.

Booij, K., F. Smedes, and E. M. van Weerlee, 2002, Spiking of performance reference compounds in low density polyethylene and silicone passive water samplers: Chemosphere, v. 46, p. 1157-1161.

Borgå, K., A. T. Fisk, B. Hargrave, P. F. Hoekstra, D. Swackhamer, and D. C. G. Muir, 2005, Bioaccumulation Factors for PCBs Revisited: Environmental Science & Technology, v. 39, p. 4523-4532.

Bruner, K. A., S. W. Fisher, and P. F. Landrum, 1994, The Role of the Zebra Mussel, Dreissena polymorpha, In Contaminant Cycling: II. Zebra Mussel Contaminant Accumulation from Algae and Suspended Particles, and Transfer to the Benthic Invertebrate, Gammarus fasciatus: Journal of Great Lakes Research, v. 20, p. 735-750.

Burreau, S., J. Axelman, D. Broman, and E. Jakobsson, 1997, Dietary uptake in pike (Esox lucius) of some polychlorinated biphenyls, polychlorinated naphthalenes and polybrominated diphenyl ethers administered in natural diet: Environmental Toxicology and Chemistry, v. 16, p. 2508-2513.

Cho, Y.-M., U. Ghosh, A. J. Kennedy, A. Grossman, G. Ray, J. E. Tomaszewski, D. W. Smithenry, T. S. Bridges, and R. G. Luthy, 2009, Field Application of Activated Carbon Amendment for In-Situ Stabilization of Polychlorinated Biphenyls in Marine Sediment: Environmental Science & Technology, v. 43, p. 3815-3823.

Clark, K. E., and D. Mackay, 1991, Dietary uptake and biomagnification of four chlorinated hydrocarbons by guppies: Environmental Toxicology and Chemistry, v. 10, p. 1205-1217.

Connolly, J., J. Rhea, and J. Benaman, 1999, Effective decision-making models for evaluating sediment management options, Quantitative Environmental Analysis,LLC.

Connolly, J. P., 1991, Application of a food chain model to polychlorinated biphenyl contamination of the lobster and winter flounder food chains in New Bedford Harbor: Environmental Science & Technology, v. 25, p. 760-770.

Connolly, J. P., H. A. Zahakos, J. Benaman, C. K. Ziegler, J. R. Rhea, and K. Russell, 2000, A Model of PCB Fate in the Upper Hudson River: Environmental Science & Technology, v. 34, p. 4076-4087.

Cornelissen, G., Ö. Gustafsson, T. D. Bucheli, M. T. O. Jonker, A. A. Koelmans, and P. C. M. van Noort, 2005, Extensive Sorption of Organic Compounds to Black Carbon, Coal, and Kerogen in Sediments and Soils: Mechanisms and Consequences for Distribution, Bioaccumulation, and Biodegradation: Environmental Science & Technology, v. 39, p. 6881-6895.

Dabrowska, H., S. W. Fisher, K. Dabrowski, and A. E. Staubus, 1999, Dietary uptake efficiency of 2,2ĭ,4,4ĭ,5,5ĭ-hexachlorobiphenyl in yellow perch and rainbow trout: Role of dietary and body lipids: Environmental Toxicology and Chemistry, v. 18, p. 938-945.

Dang, V. D., D. M. Walters, and C. M. Lee, 2013, Assessing ongoing sources of dissolved-phase polychlorinated biphenyls in a contaminated stream: Environmental Toxicology and Chemistry, v. 32, p. 535-540.

Di Toro, D. M., J. A. McGrath, and D. J. Hansen, 2000, Technical basis for narcotic chemicals and polycyclic aromatic hydrocarbon criteria. I. Water and tissue: Environmental Toxicology and Chemistry, v. 19, p. 1951-1970.

DiPinto, L. M., 1996, Trophic Transfer of a Sediment-Associated Organophosphate Pesticide from Meiobenthos to Bottom Feeding Fish: Archives of environmental contamination and toxicology, v. 30, p. 459-466.

DiPinto, L. M., and B. C. Coull, 1997, Trophic transfer of sediment-associated polychlorinated biphenyls from meiobenthos to bottom-feeding fish: Environmental Toxicology and Chemistry, v. 16, p. 2568-2575.

Doi, A. M., Z. Lou, E. Holmes, C. Li, C. S. Venugopal, M. O. James, and K. M. Kleinow, 2000, Effect of micelle fatty acid composition and 3,4,3', 4'-tetrachlorobiphenyl (TCB) exposure on intestinal [(14)C]-TCB bioavailability and biotransformation in channel catfish in situ preparations: Toxicological sciences : an official journal of the Society of Toxicology, v. 55, p. 85-96.

Doyle, J. R., A. M. Al-Ansari, R. L. Gendron, P. A. White, and J. M. Blais, 2011, A method to estimate sediment ingestion by fish: Aquatic Toxicology, v. 103, p. 121-127.

EFED-USEPA, 2009, User's Guide and Technical Documentation, KABAM version 1.0 (Kow (based) Aquatic Bioaccumulation Model), Environmental Fate and Effects Division.

EPA, 1979, Polychlorinated Biphenyls 1929-1979: Final Report.

EPA, 2004, Model Calibration: Modeling Study of PCB Contamination in the Housatonic River, Region 1 Report.

EPA, 2012, Guidelines for Using Passive Samplers to Monitor Organic Contaminants at Superfund Sediment Sites, *in* O. o. S. R. a. T. I. a. O. o. R. a. Development, ed., United States, p. 32.

EPA, **2013a**, Use of Amendments for In Situ Remediation at Superfund Sediment Sites, Office of Superfund Remediation and Technology Innovation.

EPA, 2013b, Use of Amendments for In Situ Remediation at Superfund Sediment Sites Use of Amendments for In Situ Remediation at Superfund Sediment Sites, Office of Superfund Remediation and Technology Innovation.

EPA, **2014a**, Statement of Basis for EPA's Proposed Remedial Action for the Housatonic River "Rest of River", Region 1 Report.

EPA, 2014b, Statement of Basis for EPA's Proposed Remedial Action for the Housatonic River "Rest of River" Statement of Basis for EPA's Proposed Remedial Action for the Housatonic River "Rest of River", Region 1 Report.

EPA, **2013**2013, Use of Amendments for In Situ Remediation at Superfund Sediment Sites, Office of Superfund Remediation and Technology Innovation.

Fadaei, H., A. Watson, A. Place, J. Connolly, and U. Ghosh, 2015, Effect of PCB Bioavailability Changes in Sediments on Bioaccumulation in Fish: Environmental Science & Technology, v. 49, p. 12405-12413.

Fernandez, L. A., C. F. Harvey, and P. M. Gschwend, 2009, Using Performance Reference Compounds in Polyethylene Passive Samplers to Deduce Sediment Porewater Concentrations for Numerous Target Chemicals: Environmental Science & Technology, v. 43, p. 8888-8894.

Fernandez, L. A., W. Lao, K. A. Maruya, and R. M. Burgess, 2014, Calculating the Diffusive Flux of Persistent Organic Pollutants between Sediments and the Water Column on the Palos Verdes Shelf Superfund Site Using Polymeric Passive Samplers: Environmental Science & Technology, v. 48, p. 3925-3934.

Fisk, A. T., R. J. Norstrom, C. D. Cymbalisty, and D. C. G. Muir, 1998, Dietary accumulation and depuration of hydrophobic organochlorines: Bioaccumulation parameters and their relationship with the octanol/water partition coefficient: Environmental Toxicology and Chemistry, v. 17, p. 951-961.

Fisk, A. T., G. A. Stern, K. A. Hobson, W. J. Strachan, M. D. Loewen, and R. J. Norstrom, 2001, Persistent Organic Pollutants (POPs) in a Small, Herbivorous, Arctic Marine Zooplankton (Calanus hyperboreus): Trends from April to July and the Influence of Lipids and Trophic Transfer: Marine Pollution Bulletin, v. 43, p. 93-101.

Friedman, C. L., R. M. Burgess, M. M. Perron, M. G. Cantwell, K. T. Ho, and R. Lohmann, 2009, Comparing Polychaete and Polyethylene Uptake to Assess Sediment Resuspension Effects on PCB Bioavailability: Environmental Science & Technology, v. 43, p. 2865-2870.

Gaillard, J., D. Banas, M. Thomas, A. Fournier, and C. Feidt, 2014, Bioavailability and bioaccumulation of sediment-bound polychlorinated biphenyls to carp: Environmental Toxicology and Chemistry, v. 33, p. 1324-1330.

Ghosh, U., S. Kane Driscoll, R. M. Burgess, M. T. O. Jonker, D. Reible, F. Gobas, Y. Choi, S. E. Apitz, K. A. Maruya, W. R. Gala, M. Mortimer, and C. Beegan, 2014, Passive sampling methods for contaminated sediments: Practical guidance for selection, calibration, and implementation: Integrated Environmental Assessment and Management, v. 10, p. 210-223.

Ghosh, U., R. G. Luthy, G. Cornelissen, D. Werner, and C. A. Menzie, 2011, In-situ Sorbent Amendments: A New Direction in Contaminated Sediment Management: Environmental Science & Technology, v. 45, p. 1163-1168.

Gilbert, D., G. Witt, F. Smedes, and P. Mayer, 2016, Polymers as Reference Partitioning Phase: Polymer Calibration for an Analytically Operational Approach To Quantify Multimedia Phase Partitioning: Analytical Chemistry, v. 88, p. 5818-5826.

Gobas, F. A. P. C., 1993, A model for predicting the bioaccumulation of hydrophobic organic chemicals in aquatic food-webs: application to Lake Ontario, v. 69, p. 1–17.

Gobas, F. A. P. C., J. R. McCorquodale, and G. D. Haffner, 1993, Intestinal absorption and biomagnification of organochlorines: Environmental Toxicology and Chemistry, v. 12, p. 567-576.

Gobas, F. A. P. C., D. C. G. Muir, and D. Mackay, 1988, Dynamics of dietary bioaccumulation and faecal elimination of hydrophobic organic chemicals in fish: Chemosphere, v. 17, p. 943-962.

Gobas, F. A. P. C., J. B. Wilcockson, R. W. Russell, and G. D. Haffner, 1999, Mechanism of Biomagnification in Fish under Laboratory and Field Conditions: Environmental Science & Technology, v. 33, p. 133-141.

Gomez-Eyles, J. L., C. Yupanqui, B. Beckingham, G. Riedel, C. Gilmour, and U. Ghosh, 2013, Evaluation of Biochars and Activated Carbons for In Situ Remediation Of Sediments Impacted With Organics, Mercury, And Methylmercury: Environmental Science & Technology, v. 47, p. 13721-13729.

Gossiaux, D. C., P. F. Landrum, and S. W. Fisher, 1998, The assimilation of contaminants from suspended sediment and algae by the zebra mussel, Dreissena polymorpha: Chemosphere, v. 36, p. 3181-3197.

Grossman, A., and U. Ghosh, 2009, Measurement of activated carbon and other black carbons in sediments: Chemosphere, v. 75, p. 469-475.

Hale, S. E., S. Kwon, U. Ghosh, and D. Werner, 2010, Polychlorinated Biphenyl Sorption to Activated Carbon and the Attenuation Caused by Sediment: Global NEST Journal, v. 12, p. 318-326.

Harman, C., M. Reid, and K. V. Thomas, 2011, In Situ Calibration of a Passive Sampling Device for Selected Illicit Drugs and Their Metabolites in Wastewater, And Subsequent Year-Long Assessment of Community Drug Usage: Environmental Science & Technology, v. 45, p. 5676-5682.

Harvey, H. R., G. Eglinton, S. C. M. O'Hara, and E. D. S. Corner, 1987, Biotransformation and assimilation of dietary lipids by Calanus feeding on a dinoflagellate: Geochimica et Cosmochimica Acta, v. 51, p. 3031-3040.

Hawker, D. W., and D. W. Connell, 1988, Octanol-water partition coefficients of polychlorinated biphenyl congeners: Environmental Science & Technology, v. 22, p. 382-387.

Hawthorne, S. B., D. J. Miller, and C. B. Grabanski, 2009, Measuring Low Picogram Per Liter Concentrations of Freely Dissolved Polychlorinated Biphenyls in Sediment Pore Water Using Passive Sampling with Polyoxymethylene: Analytical Chemistry, v. 81, p. 9472-9480.

Hill, D. W., E. Hejtmancik, and B. J. Camp, 1976, Induction of hepatic microsomal enzymes by Aroclor® 1254 inIctalurus punctatus (channel catfish) - Springer, v. 16, p. 495-502.

Hoekstra, P. F., T. M. O'Hara, C. Teixeira, S. Backus, A. T. Fisk, and D. C. G. Muir, 2002, Spatial trends and bioaccumulation of organochlorine pollutants in marine zooplankton from the Alaskan and Canadian Arctic: Environmental Toxicology and Chemistry, v. 21, p. 575-583.

Hu, W., 2014, Dry Weight and Cell Density of Individual Algal and Cyanobacterial Cells for Algae Research and Development, University of Missouri-Columbia.

Huckins, J. N., J. D. Petty, and K. Booij, **2006**, P 223, Monitors of Organic Chemicals in the Environment Springer: New York, NY.

Jahnke, A., M. S. McLachlan, and P. Mayer, 2008, Equilibrium sampling: Partitioning of organochlorine compounds from lipids into polydimethylsiloxane: Chemosphere, v. 73, p. 1575-1581.

Jonker, M. T. O., and A. A. Koelmans, 2001, Polyoxymethylene Solid Phase Extraction as a Partitioning Method for Hydrophobic Organic Chemicals in Sediment and Soot: Environmental Science & Technology, v. 35, p. 3742-3748.

Kidder, G. W., C. W. Petersen, and R. L. Preston, 2006, Energetics of osmoregulation: I. oxygen consumption by Fundulus heteroclitus: Journal of Experimental Zoology Part A: Comparative Experimental Biology, v. 305A, p. 309-317.

Kjellerup, B. V., C. Naff, S. J. Edwards, U. Ghosh, J. E. Baker, and K. R. Sowers, 2014, Effects of activated carbon on reductive dechlorination of PCBs by organohalide respiring bacteria indigenous to sediments: Water Research, v. 52, p. 1-10.

Klump, J. V., J. R. Krezoski, M. E. Smith, and J. L. Kaster, 1987, Dual Tracer Studies of the Assimilation of an Organic Contaminant from Sediments by Deposit Feeding Oligochaetes: Canadian Journal of Fisheries and Aquatic Sciences, v. 44, p. 1574-1583.

Kukkonen, J., and P. F. Landrum, 1995, Measuring assimilation efficiencies for sediment-bound PAH and PCB congeners by benthic organisms: Aquatic Toxicology, v. 32, p. 75-92.

Kupryianchyk, D., M. I. Rakowska, I. Roessink, E. P. Reichman, J. T. C. Grotenhuis, and A. A. Koelmans, 2013, In situ Treatment with Activated Carbon Reduces Bioaccumulation in Aquatic Food Chains: Environmental Science & Technology, v. 47, p. 4563-4571.

Lo, J. C., D. A. Campbell, C. J. Kennedy, and F. A. P. C. Gobas, 2015, Somatic and gastrointestinal in vivo biotransformation rates of hydrophobic chemicals in fish: Environmental Toxicology and Chemistry, v. 34, p. 2282-2294.

Lohmann, R., 2011, Critical Review of Low-Density Polyethylene's Partitioning and Diffusion Coefficients for Trace Organic Contaminants and Implications for Its Use As a Passive Sampler: Environmental Science & Technology, v. 46, p. 606-618.

Lohmann, R., J. K. MacFarlane, and P. M. Gschwend, 2005, Importance of Black Carbon to Sorption of Native PAHs, PCBs, and PCDDs in Boston and New York Harbor Sediments: Environmental Science & Technology, v. 39, p. 141-148.

Luthy, R. G., G. R. Aiken, M. L. Brusseau, S. D. Cunningham, P. M. Gschwend, J. J. Pignatello, M. Reinhard, S. J. Traina, W. J. Weber, and J. C. Westall, 1997, Sequestration of Hydrophobic Organic Contaminants by Geosorbents: Environmental Science & Technology, v. 31, p. 3341-3347.

Lydy, M. J., P. F. Landrum, A. M. P. Oen, M. Allinson, F. Smedes, A. D. Harwood, H. Li, K. A. Maruya, and J. Liu, 2014, Passive sampling methods for contaminated sediments: State of the science for organic contaminants: Integrated Environmental Assessment and Management, v. 10, p. 167-178.

Mayer, P., T. F. Parkerton, R. G. Adams, J. G. Cargill, J. Gan, T. Gouin, P. M. Gschwend, S. B. Hawthorne, P. Helm, G. Witt, J. You, and B. I. Escher, 2014, Passive sampling methods for contaminated sediments: Scientific rationale supporting use of freely dissolved concentrations: Integrated Environmental Assessment and Management, v. 10, p. 197-209.

Mayer, P., J. Tolls, J. L. Hermens, and D. Mackay, 2003, Equilibrium sampling devices: Environmental Science & Technology, v. 37, p. 184A-191A.

Mayer, P., W. H. J. Vaes, and J. L. M. Hermens, 2000, Absorption of Hydrophobic Compounds into the Poly(dimethylsiloxane) Coating of Solid-Phase Microextraction Fibers: High Partition Coefficients and Fluorescence Microscopy Images: Analytical Chemistry, v. 72, p. 459-464.

McLeod, A. M., J. A. Arnot, K. Borgå, H. Selck, D. R. Kashian, A. Krause, G. Paterson, G. D. Haffner, and K. G. Drouillard, 2015, Quantifying uncertainty in the trophic magnification factor

related to spatial movements of organisms in a food web: Integrated Environmental Assessment and Management, v. 11, p. 306-318.

McLeod, P. B., S. N. Luoma, and R. G. Luthy, 2008, Biodynamic modeling of PCB uptake by Macoma balthica and Corbicula fluminea from sediment amended with activated carbon: Environ Sci Technol, v. 42, p. 484-90.

McLeod, P. B., M. J. van den Heuvel-Greve, R. M. Allen-King, S. N. Luoma, and R. G. Luthy, 2004a, Effects of Particulate Carbonaceous Matter on the Bioavailability of Benzo[a]pyrene and 2,2‘,5,5‘-Tetrachlorobiphenyl to the Clam, Macoma balthica: Environmental Science & Technology, v. 38, p. 4549-4556.

McLeod, P. B., M. J. van den Heuvel-Greve, R. M. Allen-King, S. N. Luoma, and R. G. Luthy, 2004b, Effects of Particulate Carbonaceous Matter on the Bioavailability of Benzo[a]pyrene and 2,2‘,5,5‘-Tetrachlorobiphenyl to the Clam, Macoma balthica: Environmental Science & Technology, v. 38, p. 4549-4556.

McLeod, P. B., M. J. van den Heuvel-Greve, S. N. Luoma, and R. G. Luthy, 2007, Biological uptake of polychlorinated biphenyls by Macoma balthica from sediment amended with activated carbon: Environmental Toxicology and Chemistry, v. 26, p. 980-987.

MDE, 2014, Maryland Fish Consumption Advisories, Baltimore, MD.

Miller, R., K. J. Farley, J. R. Wands, R. Santore, A. D. Redman, and N. B. Kim, 2011, Fate and Transport Modeling of Sediment Contaminants in the New York/New Jersey Harbor Estuary: Urban Habitats.

Millward, R. N., T. S. Bridges, U. Ghosh, J. R. Zimmerman, and R. G. Luthy, 2005, Addition of Activated Carbon to Sediments to Reduce PCB Bioaccumulation by a Polychaete (Neanthes arenaceodentata) and an Amphipod (Leptocheirus plumulosus): Environmental Science & Technology, v. 39, p. 2880-2887.

Moermond, C. T. A., F. C. J. M. Roozen, J. J. G. Zwolsman, and A. A. Koelmans, 2004, Uptake of Sediment-Bound Bioavailable Polychlorobiphenyls by Benthivorous Carp (Cyprinus carpio): Environmental Science & Technology, v. 38, p. 4503-4509.

Nichols, J. W., P. N. Fitzsimmons, F. W. Whiteman, D. W. Kuehl, B. C. Butterworth, and C. T. Jenson, 2001, Dietary uptake kinetics of 2,2',5,5'-tetrachlorobiphenyl in rainbow trout: Drug metabolism and disposition: the biological fate of chemicals, v. 29, p. 1013-1022.

Niimi, A. J., and B. G. Oliver, 1983, Biological Half-lives of Polychlorinated Biphenyl (PCB) Congeners in Whole Fish and Muscle of Rainbow Trout (Salmo gairdneri): Canadian Journal of Fisheries and Aquatic Sciences, v. 40, p. 1388-1394.

NRC, 2001, A risk-management strategy for PCB-contaminated sediments: Wahington, DC: National Academy Press.

NRC, 2003, Bioavailability of Contaminants in Soils and Sediments:Processes, Tools, and Applications: Washington, DC, The National Academies Press.

OECD, 2011, OECD Guidelines for Testing of Chemicals-305, Organisation for Economic Co-operation and Development.

Oen, A. M. P., E. M. L. Janssen, G. Cornelissen, G. D. Breedveld, E. Eek, and R. G. Luthy, 2011, In Situ Measurement of PCB Pore Water Concentration Profiles in Activated Carbon-Amended Sediment Using Passive Samplers: Environmental Science & Technology, v. 45, p. 4053-4059.

Oliver, B. G., and A. J. Niimi, 1988, Trophodynamic analysis of polychlorinated biphenyl congeners and other chlorinated hydrocarbons in the Lake Ontario ecosystem: Environmental Science & Technology, v. 22, p. 388-397.

Ortiz, E., R. Luthy, D. Dzombak, and J. Smith, 2004, Release of Polychlorinated Biphenyls from River Sediment to Water under Low-Flow Conditions: Laboratory Assessment: Journal of Environmental Engineering, v. 130, p. 126-135.

Parkerton, T. F., and J. P. Connolly, 2013, Modeling bioaccumulation in coupled pelagic-€ “benthic food chains: Past insights and future directions: Environmental Toxicology and Chemistry, v. 32, p. 1931-1934.

Perron, M. M., R. M. Burgess, K. T. Ho, M. C. Pelletier, C. L. Friedman, M. G. Cantwell, and J. P. Shine, 2009, Development and evaluation of reverse polyethylene samplers for marine phase ii whole-sediment toxicity identification evaluations: Environmental Toxicology and Chemistry, v. 28, p. 749-758.

Petrović, M., E. Eljarrat, M. J. López de Alda, and D. Barceló, 2001, Analysis and environmental levels of endocrine-disrupting compounds in freshwater sediments: TrAC Trends in Analytical Chemistry, v. 20, p. 637-648.

Pieper, D. H., 2005, Aerobic degradation of polychlorinated biphenyls: Applied microbiology and biotechnology, v. 67, p. 170-191.

Rakowska, M. I., D. Kupryianchyk, J. Harmsen, T. Grotenhuis, and A. A. Koelmans, 2012, In situ remediation of contaminated sediments using carbonaceous materials: Environmental Toxicology and Chemistry, v. 31, p. 693-704.

Reichenberg, F., and P. Mayer, 2006, Two complementary sides of bioavailability: Accessibility and chemical activity of organic contaminants in sediments and soils: Environmental Toxicology and Chemistry, v. 25, p. 1239-1245.

Ross, G., 2004, The public health implications of polychlorinated biphenyls (PCBs) in the environment: Ecotoxicology and Environmental Safety, v. 59, p. 275-291.

Scheffer, M., R. Portielje, and L. Zambrano, 2003, Fish facilitate wave resuspension of sediment: Limnology and Oceanography, v. 48, p. 1920-1926.

SERDP, 2012, Improved Understanding of the Impact of Ongoing, Low Level Contaminant Influx to Aquatic Sediment Site Restoration, Strategic Environmental Research and Development Program.

Sijm, D. T. H. M., J. Middelkoop, and K. Vrisekoop, 1995, Algal density dependent bioconcentration factors of hydrophobic chemicals: Chemosphere, v. 31, p. 4001-4012.

Sinkkonen, S., and J. Paasivirta, 2000, Degradation half-life times of PCDDs, PCDFs and PCBs for environmental fate modeling: Chemosphere, v. 40, p. 943-949.

Skoglund, R. S., and D. L. Swackhamer, 1999, Evidence for the Use of Organic Carbon as the Sorbing Matrix in the Modeling of PCB Accumulation in Phytoplankton: Environmental Science & Technology, v. 33, p. 1516-1519.

Smedes, F., R. W. Geertsma, T. v. d. Zande, and K. Booij, 2009a, Polymer−Water Partition Coefficients of Hydrophobic Compounds for Passive Sampling: Application of Cosolvent Models for Validation: Environmental Science & Technology, v. 43, p. 7047-7054.

Smedes, F., R. W. Geertsma, T. v. d. Zande, and K. Booij, 2009b, Polymer−Water Partition Coefficients of Hydrophobic Compounds for Passive Sampling: Application of Cosolvent Models for Validation: Environmental Science & Technology, v. 43, p. 7047-7054.

Stange, K., and D. L. Swackhamer, 1994, Factors affecting phytoplankton species-specific differences in accumulation of 40 polychlorinated biphenyls (PCBs): Environmental Toxicology and Chemistry, v. 13, p. 1849-1860.

Stapleton, H. M., R. J. Letcher, J. Li, and J. E. Baker, 2004, Dietary accumulation and metabolism of polybrominated diphenyl ethers by juvenile carp (Cyprinus carpio): Environmental Toxicology and Chemistry, v. 23, p. 1939-1946.

Sun, X., and U. Ghosh, 2007, PCB Bioavailability Control in Lumbriculus Variegatus through Different Modes of Activated Carbon Addition to Sediments: Environmental Science & Technology, v. 41, p. 4774-4780.

Sun, X., D. Werner, and U. Ghosh, 2009, Modeling PCB Mass Transfer and Bioaccumulation in a Freshwater Oligochaete Before and After Amendment of Sediment with Activated Carbon: Environmental Science & Technology, v. 43, p. 1115-1121.

Swackhamer, D. L., and R. S. Skoglund, 1993, Bioaccumulation of PCBs by algae: Kinetics versus equilibrium: Environmental Toxicology and Chemistry, v. 12, p. 831-838.

Tang, B., X.-J. Luo, Y.-H. Zeng, and B.-X. Mai, 2017, Tracing the Biotransformation of PCBs and PBDEs in Common Carp (Cyprinus carpio) Using Compound-Specific and Enantiomer-Specific Stable Carbon Isotope Analysis: Environmental Science & Technology, v. 51, p. 2705-2713.

Thomann, R. V., and J. P. Connolly, 1984, Model of PCB in the Lake Michigan lake trout food chain: Environmental Science & Technology, v. 18, p. 65-71.

Thomann, R. V., J. P. Connolly, and T. F. Parkerton, 1992, An equilibrium model of organic chemical accumulation in aquatic food webs with sediment interaction: Environmental Toxicology and Chemistry, v. 11, p. 615-629.

Tiedje, J. M., J. F. Quensen, J. Chee-Sanford, J. P. Schimel, and S. A. Boyd, 1993, Microbial reductive dechlorination of PCBs: Biodegradation, v. 4, p. 231-240.

Tolonen, K. T., J. Karjalainen, S. Staff, and M. Leppä, 2000, Individual and population-level food consumption by cyprinids and percids in a mesotrophic lake: Ecology of Freshwater Fish, v. 9, p. 153-162.

Tomaszewski, J. E., and R. G. Luthy, 2008, Field Deployment of Polyethylene Devices to Measure PCB Concentrations in Pore Water of Contaminated Sediment: Environmental Science & Technology, v. 42, p. 6086-6091.

Tomaszewski, J. E., D. Werner, and R. G. Luthy, 2007, Activated carbon amendment as a treatment for residual ddt in sediment from a superfund site in San Francisco Bay, Richmond, California, USA: Environmental Toxicology and Chemistry, v. 26, p. 2143-2150.

USEPA, **2000** *Guidance for Assessing Chemical Contaminant Data for Use in Fish Advisories, Volume 2, Risk Assessment and Fish Consumption Limits, Third Edition*

USEPA, 2004, The incidence and severity of sediment contamination in surface waters of the United States., National Sediment Quality Survey 2nd ed.

van Beusekom, O. C., E. Eljarrat, D. Barceló, and A. A. Koelmans, 2006, Dynamic modeling of food-chain accumulation of brominated flame retardants in fish from the Ebro River Basin, Spain: Environmental Toxicology and Chemistry, v. 25, p. 2553-2560.

Van Handel, E., 1985, Rapid determination of total lipids in mosquitoes: Journal of the American Mosquito Control Association, v. 1, p. 302-304.

Verweij, F., K. Booij, K. Satumalay, N. van der Molen, and R. van der Oost, 2004, Assessment of bioavailable PAH, PCB and OCP concentrations in water, using semipermeable membrane devices (SPMDs), sediments and caged carp: Chemosphere, v. 54, p. 1675-1689.

Vrana, B., I. J. Allan, R. Greenwood, G. A. Mills, E. Dominiak, K. Svensson, J. Knutsson, and G. Morrison, 2005, Passive sampling techniques for monitoring pollutants in water: TrAC Trends in Analytical Chemistry, v. 24, p. 845-868.

Walker, C. H., 1987, Kinetic models for predicting bioaccumulation of pollutants in ecosystems: Environmental Pollution, v. 44, p. 227-240.

Wang, W.-X., and N. S. Fisher, 1999, Assimilation efficiencies of chemical contaminants in aquatic invertebrates: A synthesis: Environmental Toxicology and Chemistry, v. 18, p. 2034-2045.

Weber, W. J., 2005, Comment on "Addition of Carbon Sorbents to Reduce PCB and PAH Bioavailability in Marine Sediments: Physicochemical Tests": Environmental Science & Technology, v. 39, p. 1197-1198.

Werner, D., U. Ghosh, and R. G. Luthy, 2006, Modeling Polychlorinated Biphenyl Mass Transfer after Amendment of Contaminated Sediment with Activated Carbon: Environmental Science & Technology, v. 40, p. 4211-4218.

Werner, D., S. E. Hale, U. Ghosh, and R. G. Luthy, 2009, Polychlorinated Biphenyl Sorption and Availability in Field-Contaminated Sediments†: Environmental Science & Technology, v. 44, p. 2809-2815.

Werner, D., S. E. Hale, U. Ghosh, and R. G. Luthy, 2010, Polychlorinated Biphenyl Sorption and Availability in Field-Contaminated Sediments: Environmental Science & Technology, v. 44, p. 2809-2815.

Zimmerman, J. R., U. Ghosh, R. N. Millward, T. S. Bridges, and R. G. Luthy, 2004, Addition of Carbon Sorbents to Reduce PCB and PAH Bioavailability in Marine Sediments: Physicochemical Tests: Environmental Science & Technology, v. 38, p. 5458-5464.