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Exploring Bioavailability of Hydrophobic Organic Contaminants in Sediments

A Dissertation submitted in partial satisfaction
of the requirements for the degree of

Doctor of Philosophy

in

Environmental Sciences

by

Fang Jia

June 2014

Dissertation Committee:

Dr. Jay Gan, Chairperson

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Dr. Daniel Schlenk

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The Dissertation of Fang Jia is approved:

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ABSTRACT OF THE DISSERTATION

Exploring Bioavailability of Hydrophobic Organic Contaminants in Sediments

by

Fang Jia

Doctor of Philosophy, Graduate Program in Environmental Sciences
University of California, Riverside, June 2014
Dr. Jay Gan, Chairperson

Due to high affinity for organic carbon phase, hydrophobic organic contaminants (HOCs) preferentially deposit in bed sediments in surface aquatic systems. Consequently, many contemporary sediment contaminants are HOCs, including DDTs, PCBs, and PBDEs. However, their accumulation potential and toxicity to benthic organisms in sediments are regulated by bioavailability, rather than bulk chemical concentrations. The overall purpose of the current project was to develop and apply chemically-based methods to explore bioavailability of HOCs in sediments, and help improve the assessment of their potential ecotoxicological risks and sometimes human health effects in the environment.

A solid phase microextraction (SPME) method using disposable polydimethylsiloxane (PDMS) fibers was developed for measuring the phase distribution of flame retardant PBDEs in sediments. Results showed that PBDEs were predominantly sorbed to the sediment phase, with freely dissolved concentration (C_{free}) only accounted for < 0.012% of the total chemical mass and < 0.43% of the dissolved mass. Addition of

black carbon further reduced bioavailability (or C_{free}) of HOCs as indicated by the matrix-SPME method. At 1% amendment rate in a sediment with low organic carbon (0.12%) content, C_{free} of selected PBDEs was reduced by 47.5–78.0%, 47.3–77.5%, and 94.1–98.3% with biochar, charcoal, and activated carbon, respectively. To overcome the shortcomings of current measurement methods, an isotope dilution method (IDM) was developed and applied for bioavailability prediction of legacy HOCs (e.g., DDT and its metabolites, PCBs) in historically-contaminated sediments from the Palos Verdes Superfund site. The IDM-based accessible concentration was shown to correlate closely with tissue residues in the exposed marine benthic polychaete *Neanthes arenaceodentata* ($R^2=0.84\text{--}0.94$). Bioavailability measurements from the SPME, IDM and Tenax methods were compared in amendment-based remediation. After normalizing over the unamended sediments, significant linear correlations ($R^2 > 0.90$, $p < 0.01$, slopes = 1.00–1.09) were found between these methods, suggesting they are interchangeable or complementary for evaluating remediation efficiency or progress.

Overall, the bioavailability estimation methods or their specific applications developed from this project will improve understanding environmental fate of HOCs and their potential toxicity to such organisms as the sediment-dwelling invertebrates. The developed methods may be readily adoptable for other HOCs as well as other matrices (e.g., soil).

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Chapter 1 Introduction

1.1. Bioavailability Concept

Due to high affinity for organic carbon particles, hydrophobic organic contaminants (HOCs) preferentially deposit in soil or sediment in the environment, where they are sequestered by geosorbents and as a result distributed in heterogeneous regions in the solid phase (Luthy et al., 1997). Use of the bulk chemical concentration in soil/sediment may not convey the actual risk, because the total concentration could substantially over-express the real availability of HOCs to organisms (Ehlers and Luthy, 2003). Thus, measuring bioavailability and applying it as an integral endpoint will be essential for improving risk assessment and guiding remediation practices.

Bioavailability is generally referred to as the extent to which molecular targets within organisms interact with chemicals (Ehlers and Luthy, 2003; Semple et al., 2004). In soil/sediment, many physical, chemical, and biological interactions affect the fraction of chemicals that may ultimately pass through the cellular membrane of an organism to elicit an ecotoxicological effect (National Research Council, 2002). There are two complementary concepts of bioavailability, i.e., chemical activity or the freely dissolved concentration, and bioaccessibility (Reichenberg and Mayer, 2006). Conceptually, in a soil/sediment environment, a chemical must be in the freely dissolved form (C_{free}) to be available to cross a cell membrane where the chemical may elicit toxic effects, be metabolized or accumulated. This is true even if the soil/sediment is ingested, as desorption (into gut fluid) must precede bioaccumulation. When the C_{free} is depleted through biouptake (or other disruptions, including remediation), it is then replenished via

desorption of the sorbed chemical from the accessible pool. Therefore, bioavailability is reflected in both C_{free} and accessibility (Cui et al., 2013b). The C_{free} describes the potential for a chemical to undergo spontaneous processes, such as diffusion and partitioning (Reichenberg and Mayer, 2006). At equilibrium, chemical activity is essentially the same in each matrix compartment. Therefore, bioaccumulation may be estimated by using a partitioning coefficient between liquid phase and biota (e.g., bioconcentration factor, BCF). Accessibility quantifies the actual amount of a chemical that is or may become available for bioaccumulation within a given time and under given conditions (Reichenberg and Mayer, 2006).

1.2. Bioavailability Measurement

Bioassays are the most direct ways to measure the bioavailability of HOCs. Although representing the ultimate validation of bioavailability, however, bioassays are usually expensive, time-consuming and species specific. Consequently, researchers have pursued the development of chemically-based methods, or biomimetic methods, for bioavailability estimation (Cui et al., 2013b; Reichenberg and Mayer, 2006). Based on the two endpoints of bioavailability (i.e., C_{free} and accessibility), there are generally two measurement methods, i.e., partial extraction and equilibrium sampling. The partial extraction techniques, such as mild solvent extraction, cyclodextrin extraction and Tenax-aided extraction, are commonly used to quantify the labile or reversibly sorbed chemical fraction in the matrices (e.g., sediment) to approximate bioaccessibility (Cornelissen et al., 2001; Kelsey et al., 1997; Reid et al., 2000). Various equilibrium or passive samplers, including semipermeable membrane devices (SPMDs), polyethylene devices (PEDs),

polyoxymethylene (POM), and solid phase microextraction (SPME), have been used to derive C_{free} by applying the equilibrium partitioning theory (EqP) (Fernandez et al., 2009; Hawthorne et al., 2011; Hawthorne et al., 2009; Huckins et al., 1993; Poerschmann et al., 1997).

1.2.1. Partial Extraction Methods

1.2.1.1. Mild Solvent Extraction

In mild extraction, a variety of “soft” solvent (e.g., *n*-butanol, methanol, ethyl acetate or even water) are used to assess the readily extractable fraction as an approximation of the bioavailable concentration (Kelsey et al., 1997; Khan et al., 2012; Tang and Alexander, 1999). Bioaccumulation or biodegradation of HOCs was found to be better predicted by the mild solvent extraction than the conventional exhaustive extraction in soil or sediment. For example, a significant linear correlation was observed between the amounts of pyrene degraded by bacteria and those extracted by *n*-butanol in soils (Liste and Alexander, 2002). The genotoxicity of the mutagenic polycyclic aromatic hydrocarbons (PAHs; e.g., 9-phylanthracene) was found to be positively correlated ($R = 0.69 - 0.87$) with their amounts extractable by *n*-butanol in soils (Alexander and Alexander, 2000). However, these correlations appear to be contingent on the solvent types and the extraction conditions used (e.g., temperature, agitation speed, extraction time). For example, mineralization of atrazine in aged soils was predicted well by its concentration extracted by methanol-water at the ratio of 1:1 under static conditions, and accumulation of atrazine to earthworm was predicted well with the concentration extracted by methanol-water at the ratio of 9:1 under static conditions, whereas the

concentrations obtained by other solvents (*n*-butanol, ethanol, hexane and methanol) or extraction under agitated conditions did not correspond closely with the endpoints measured by bioassays (Kelsey et al., 1997). Biodegradation and bioaccumulation of phenanthrene were predicted well only from its concentrations extracted by *n*-butanol (Kelsey et al., 1997; Liste and Alexander, 2002). Another study further showed that the extracted amounts of PAHs varied with different solvent mixtures (e.g., *iso*-propanol or ethanol with water), different ratios of mixture (5-100%), and different extraction durations (1 h to 7 d); only extraction with 70% ethanol-water solution over 1 d produced a good correlation between the extracted concentration and biodegradation of PAHs with a correlation slope close to 1:1 (Lei et al., 2006).

1.2.1.2. Cyclodextrin (CD) Extraction

Cyclodextrin is a group of cyclic oligosaccharides with a hydrophilic shell and a torus-shaped hydrophobic cavity that can readily form inclusion complexes with HOCs. Cyclodextrin was firstly investigated as a non-exhaustive extraction reagent to predict the microbial degradation potentials of HOCs in soil by Reid et al. (2000). Hydroxypropyl- β -cyclodextrin (HPCD), a six-glucose molecule, is the most used type of CD for bioavailability measurement. The concentrations of PAHs from HPCD extraction were well correlated (1:1) with the mineralization of individual PAHs in spiked samples (Reid et al., 2000) and mixture of PAHs in field samples (Stokes et al., 2005). A significant linear correlation was observed between the extractability of pesticides by HPCD and their bioaccumulation into earthworms (Hartnik et al., 2008). The extraction efficiency of HPCD is influenced by the difference between the extraction capacity of HPCD and the

sorption capacity of the soil/sediment sample under consideration. In order to capture all available HOCs, HPCD should have a much greater affinity for HOCs than that of soil/sediment. As HPCD encapsulates both hydrophobic and hydrophilic compounds in a sample, saturation of HPCD by the target contaminants should be avoided. On the other hand, the extraction efficiency of HPCD decreases with the molecular weight (or size) of HOCs. For example, the extraction efficiency of HPCD for pyrene ($35.4 \pm 4.8\%$) and benzo[α]pyrene ($14.1 \pm 2.8\%$) were much lower than that of phenanthrene ($71.8 \pm 6.3\%$) (Reid et al., 2000). This observation suggests that HOCs with large molecular weights need other types of CDs with larger hydrophobic cavities for complex formation (Hartnik et al., 2008; Liu et al., 2013) to avoid underestimation.

1.2.1.3. Tenax-aided Desorption

Tenax is a hydrophobic resin and can trap the desorbed HOCs from a soil or sediment sample and keep the aqueous phase free of HOCs as a way to facilitate the desorption process (Cornelissen et al., 1998). The desorption kinetics are then fitted to a two- or three-phase compartment model, which allows the estimation of the relative distribution of sorbed-HOCs with different desorption rates (i.e., rapid, slow and very slow desorption fractions) (Cornelissen et al., 2001; Cornelissen et al., 1997). The rapid desorption fraction of HOCs estimated by Tenax was found to be well correlated with the microbial degradation or bioaccumulation of PAHs (Cornelissen et al., 1998; You et al., 2006), dichlorodiphenyltrichloroethane (DDT; Morrison et al., 2000; Tang et al., 1999), polychlorinated biphenyls (PCBs), and pyrethroids (Kukkonen et al., 2004; You et al., 2006). However, sequential Tenax extraction is tedious and time-consuming (generally >

300 h for completing a Tenax-aided desorption experiment), which limits the broad applicability of this method for bioavailability prediction. As an alternative, a single-time-interval Tenax desorption (e.g., 6 h, F_{6h}) has been tested for estimation of the rapid desorption fraction (F_{rapid}). Studies comparing the single- and serial desorption schemes often showed under- or overestimations. However, a good agreement of F_{6h} with C_{free} of pyrethroids suggested a difference between F_{6h} and F_{rapid} (Yang et al., 2008). Another study showed that microbial degradation of PAHs with >5 rings was poorly correlated with F_{rapid} by Tenax (Cornelissen et al., 1998).

1.2.2. Passive Samplers

1.2.2.1. Types of Passive Samplers

Passive samplers are widely used to measure freely dissolved concentrations of HOCs in the aqueous phase (C_{free}), which expresses the potential for the chemicals to undergo partitioning or diffusion processes (Reichenberg and Mayer, 2006). Based on the EqP theory, at equilibrium, the concentration of HOC in one compartment is proportional to that in another, which is related by a partition constant between the two compartments. The measured C_{free} of HOCs has been successfully linked to bioaccumulation (Gomez-Eyles et al., 2012; Van der Wal et al., 2004; You et al., 2006) and toxicity (Fagervold et al., 2010; Greenberg et al., 2014) of nonpolar and polar compounds. Several types of passive samplers have been commonly used for measuring C_{free} , including PEDs, POM, SPME, among others. Since these samplers are made of different sorbent phases, they are used for the measurement of compounds with different polarities. Both PED and SPME with polydimethylsiloxane (PDMS) coating have been used on relatively nonpolar

compounds, while POM has been shown to have improved sensitivity for polar compounds (Allan et al., 2012; Jia et al., 2012; Oen et al., 2011; Tomaszewski and Luthy, 2008).

1.2.2.2. Measurement of C_{free} Using Passive Samplers

The uptake of HOCs to a passive sampler follows one-compartment rise to maximum kinetics:

$$C_{PSM,t} = C_{PSM,eq} \times (1 - e^{-k_e t}) \quad (1)$$

where $C_{PSM,t}$ ($\mu\text{g/L}$) and $C_{PSM,eq}$ ($\mu\text{g/L}$) are the amounts of HOCs absorbed on the passive sampler at time t (h) and at equilibrium, respectively; k_e (h^{-1}) is the elimination rate of HOCs from the passive sampler to the sample matrix. Figure 1.1 shows a typical sampling kinetic curve for passive samplers. The estimation of C_{free} through passive samplers is generally categorized into three ways, depending on the deployment time, i.e., linear, equilibrium, and kinetic sampling (Ouyang and Pawliszyn, 2008). For short-time sampling, when less than 50% of the equilibrium level is attained on the sampler ($t < t_{50}$), the amount of chemical extracted by the sampler follows a linear relationship with the sampling time (Arthur et al., 1992; Kataoka, 2002). For example, in the case of SPME, the short-time sampling is usually carried out using the injector-type SPME assembly, where sampling interval, agitation speed, and temperature must be precisely controlled. The C_{free} in the sample is quantified through external calibration (Wang et al., 2011).

When the deployment time falls into the equilibrium regime ($t > t_{95}$ or more than 95% of the equilibrium level has been attained), the amount of HOCs enriched on the

sampler reaches a partitioning equilibrium between the sorbent of the passive sampler and the sampled matrix (e.g., overlying- or pore-water of a sediment sample). In the equilibrium regime, the effect of other variables, such as matrix interference, may be discounted (Mayer et al., 2000). The fundamental principle of equilibrium sampling is to measure the concentration of HOCs in the passive sampler at phase equilibrium ($C_{PSM,eq}$, $\mu\text{g/L}$) and then use a sampler-to-water partition coefficient ($K_{PSM,s}$) to derive C_{free} ($\mu\text{g/L}$) (Mayer et al., 2000):

$$C_{free} = \frac{C_{PSM,eq}}{K_{PSM,s}} \quad (2)$$

When the sampler deployment time t is between the linear and equilibrium regimes ($t_{50} < t < t_{95}$), C_{free} may be estimated through the kinetic sampling model:

$$C_{free} = \frac{C_{PSM(t)}}{(1 - e^{-k_e t}) \times K_{PSM,s}} \quad (3)$$

The kinetic sampling uses shortened sampling time (Bao et al., 2013; Cui et al., 2013a), which helps minimize sampler surface fouling and increases the feasibility of using passive samplers under field conditions (Tomaszewski and Luthy, 2008). Further, k_e may be estimated by characterizing the elimination rate of a preloaded performance reference compound (PRC) from the same sampler. Therefore, under the kinetic regime, C_{free} may be estimated according to the following equation:

$$C_{free} = \frac{C_{PSM(t)}}{\left(1 - \frac{C_{PSM,PRC(t)}}{C_{PSM,PRC(0)}}\right) \times K_{PSM,s}} \quad (4)$$

where $C_{\text{PSM, PRC}}(0)$ and $C_{\text{PSM, PRC}}(t)$ are the concentrations of the PRC on the passive sampler at time 0 and t , respectively. The PRC-calibration has been employed in passive samplers like PEDs (Tomaszewski and Luthy, 2008) and recently SPME (Fernandez et al., 2014). The use of PRC calibration significantly shortens the sampling time, and makes the deployment time under field conditions a less stringent requirement.

1.3. Factors Affecting Bioavailability in Sediment/Soil

Upon deposition into sediment or soil, HOCs interact with geosorbents with different affinities, causing the sorbed HOCs to desorb at different rates. The properties of both sediment/soil and HOCs affect desorption or bioavailability of the sorbed HOCs. The properties include the organic carbon (OC) content, black carbon (BC) content, texture, clay content and microporosity of the sediment (or soil), and molecular properties of HOCs (e.g., hydrophobicity) (Alexander and Alexander, 2000). In addition, the contact time may also have an impact on the distribution and bioavailability of HOCs (Alexander, 2000), a phenomenon commonly referred as “aging”.

1.3.1. Sediment/Soil Properties

1.3.1.1. Organic Matter

The organic matter (OM) of a sediment or soil may include both the amorphous and “glassy” organic matter phases and the relative composition of these different OM affects the distribution and bioavailability of HOCs. Sorption of HOCs to sediment or soil is thus comprised of absorption into the “rubbery” amorphous organic carbon and more extensive adsorption onto the glassy carbon such as black carbon (Xing and Pignatello, 1997), as shown in the following equation (Accardi-Dey and Gschwend, 2002):

$$C_s = f_{oc}K_{oc}C_w + f_{BC}K_{BC}C_w^{n_{BC}} \quad (5)$$

where C_s ($\mu\text{g}/\text{kg}$) is the overall concentration of HOCs sorbed to the sediment or soil, C_w ($\mu\text{g}/\text{L}$) is the dissolved concentration of HOCs, f_{oc} and f_{BC} are the OC and BC contents, respectively, K_{oc} is the linear amorphous OC-water partition coefficient, K_{BC} is the Freundlich sorption coefficient for BC, and n_{BC} is the Freundlich nonlinearity constant for the sorption to BC. Adsorption to amorphous OC is considered a dissolution process, which may be regarded as linear. However, adsorption to BC is non-linear, and it may exceed the adsorption to amorphous OC by 10 – 100 times for some PAHs (Cornelissen et al., 2005). Therefore, the extensive adsorption to BC sequesters more HOCs in comparison to adsorption to amorphous OC. Under this circumstance, the bioavailable fractions of the sorbed HOCs are greatly reduced. Various BCs have been added to sediment/soil to sequester HOCs as a remediation option, with the purpose of reducing the available fraction of HOCs for biodegradation or bioaccumulation (Ghosh et al., 2011).

1.3.1.2. Sediment/Soil Texture

In addition to organic carbon, the texture of a sediment or soil may also influence the bioavailability of the sorbed HOCs. However, distribution of HOCs in different particle sizes of sediment is mainly driven by organic carbon in the sediment (Ghosh et al., 2000; Oen et al., 2006). By examining the distribution of PAHs in different fractions of field sediments, Ghosh et al. (2000) found that the lighter coal/wood-derived particle fractions (contributing 5% of the total mass) contained 62% of PAHs, while the heavier and dense mineral fractions (contributing 95% of the total weight) contained only 38% of

PAHs. The decreased bioavailability of PAHs was attributed to the strong binding of these chemicals to the organic carbon fractions (Ghosh et al., 2001). Cui et al. (2011) examined the distribution fractions of pyrene in different particle sizes of sediment samples and also found that the distribution of pyrene had a close correlation with OC ($R^2=0.99$, $p < 0.01$) and BC contents ($R^2 = 0.84$, $p < 0.05$). Studies on desorption of HOCs from different particle fractions revealed that slow release of HOCs to aqueous phase was due to the pronounced gradual desorption rate from the organic particle fractions, as compared to that from the mineral fractions (Ghosh et al., 2001). Correspondingly, PAHs in the mineral fractions (75%) degraded microbially much more rapidly than in the organic fraction (0%) (Ghosh et al., 2003). Mehler et al. (2011) found that the bioavailable concentration (C_{free}) of HOCs was higher in coarse sediment fractions than in the fine particle fractions, which may be due to a higher organic carbon content in the fine particles. Therefore, investigation into the distribution of HOCs in different particle size fractions may improve the understanding of factors regulating the bioavailability of HOCs in sediment/soil.

1.3.2. HOC Properties

The properties of HOCs, e.g., hydrophobicity or $\log K_{ow}$, also affect the interaction of HOCs with geosorbents in sediment/soil and subsequently, contaminant bioavailability. Hydrophobicity indicates the affinity of HOCs to solid particles, e.g., sediment or soil particles. Generally HOCs with a large K_{ow} tend to be sequestered more strongly in the solid phase and have stronger interactions with the geosorbents. The strong binding suppresses desorption of HOCs from the matrix to the aqueous phase,

which influences the potential for bioaccumulation or biodegradation. A strong linear correlation was observed between the hydrophobicity of PCBs and their affinity to the lipid of freshwater oligochaete ($\log K_{\text{lipid}}$) in field sediment for PCBs with $\log K_{\text{ow}}$ up to 7, suggesting higher accumulation potency of PCBs with higher $\log K_{\text{ow}}$ values in the test organisms (Burkhard et al., 2013). However, PCBs possessing very large K_{ow} values may have a low bioavailability, likely due to exclusion of large molecules in the uptake and transport processes. Studies showed that the relationship between the hydrophobicity and bioaccumulation potential of PCBs is parabolic with a peak at $\log K_{\text{ow}}$ around 7 (Lamoureux and Brownawell, 1999). A similar effect of hydrophobicity on bioavailability was also observed for polybrominated diphenyl ethers (PBDEs). The desorption rate of PBDEs decreased with the increase of the number of substituted bromine atoms (Br) or hydrophobicity of these chemicals, suggesting the potential entrapping of the highly hydrophobic congeners into the porous organic matter and relatively lower bioavailability in the sediment (Liu et al., 2011). A similar parabolic curve with a turning point at $\log K_{\text{ow}}$ approximately 7 – 8 was also observed between the $\log K_{\text{ow}}$ of PBDE congeners and their affinities to a polyethylene sampler (Bao et al., 2011), suggesting that the accumulation of PBDEs in a polyethylene sampler may be similar to that in the lipids of biota.

1.3.3. Contact Time

Contact time is another factor influencing interactions between HOCs and geosorbents and hence bioavailability. As HOCs persist in sediment or soil, they will gradually become less available for bioaccumulation or biodegradation, a phenomenon

commonly termed “aging”. Previous studies showed that after many years from the initial deposition, even if HOCs were still in the sediment or soil, they became substantially less accessible to the indigenous microbes and the biodegradability of HOCs decreased significantly as aging was prolonged (Hatzinger and Alexander, 1995). Morrison et al. (2000) reported that after 49 yr of aging, only 30%, 12%, and 34% of DDT, DDE and DDD were available for bioaccumulation into earthworms. Nyholm et al. (2010) found that the bioaccumulation of brominated flame retardants (BFRs) by earthworm also decreased as the residues were aged in the soil samples.

1.4. Research Objectives and Hypotheses

The overall goal of this project was to develop and apply chemically-based bioavailability methods to better understand the environmental fate and ecotoxicological risks of HOCs in sediment, including PBDEs, DDT and DDT metabolites, and PCBs.

There were four hypothesis-driven specific objectives:

Objective 1: Develop SPME-based bioavailability methods for measuring C_{free} of PBDE congeners in sediment to understand their phase distribution in the sediment-water system.

Hypothesis 1: Owing to their ubiquity and persistence in sediment, the environmental fate and ecological risks of PBDEs are of great concern. As PBDEs are highly hydrophobic with $\log K_{\text{ow}} > 6$ for most congeners, it may be hypothesized that PBDEs have a strong affinity to the sediment organic matter and dissolved organic matter, and that only a small fraction of PBDEs in a sediment sample is in the freely dissolved form, which translates

to limited bioaccumulation or toxicity that is best predicted through the measured bioavailability.

Objective 2: Develop a matrix-SPME method to evaluate sequestration efficiencies of different types of black carbons for PBDE congeners in the sediment environment.

Hypothesis 2: Black carbons generally have high sequestration capacity for HOCs and they are often used as sediment amendments to mitigate or immobilize HOCs such as PAHs, PCBs, and chlorinated pesticides. It may be hypothesized that black carbons are able to effectively immobilize PBDEs, and that the sequestration efficacy depends on the types of black carbons as well as the sediment properties and characteristics of individual PBDE congeners.

Objective 3: Develop a new chemical method for bioavailability measurement and apply the developed method for prediction of bioavailability of recalcitrant HOCs in historically-contaminated sediments.

Hypothesis 3: The isotope dilution concept has been extensively applied in evaluating bioavailability of metals in soils or sediments. Although HOCs are structurally different from metals, they behave like some metals in that they are stable and have a high affinity for sediment and dissolved organic matters. Therefore, it may be hypothesized that the isotope dilution theory may be similarly applied to the estimation of bioavailability of HOCs in sediment or soil samples. The isotope dilution method is simple and may be widely used to improve our understanding of bioavailability of recalcitrant HOCs in field

samples, including historically contaminated sediments that may have drastically reduced bioavailability due to factors such as aging.

Objective 4: Compare the performance of different bioavailability estimation methods.

Hypothesis 4: Various chemically-based methods have been used for bioavailability estimation, including SPME, Tenax-aided desorption, and isotope dilution method (IDM). It may be hypothesized that although these methods operate on different principles and they provide different values, there may be coherent relationships (e.g., linear correlation) among these methods, allowing the interchangeable or complementary use of these methods for bioavailability evaluation.

References

- Accardi-Dey, A., Gschwend, P.M., 2002. Assessing the combined roles of natural organic matter and black carbon as sorbents in sediments. *Environmental Science & Technology* 36, 21-29.
- Alexander, M., 2000. Aging, bioavailability, and overestimation of risk from environmental pollutants. *Environmental Science & Technology* 34, 4259-4265.
- Alexander, R.R., Alexander, M., 2000. Bioavailability of genotoxic compounds in soils. *Environmental Science & Technology* 34, 1589-1593.
- Allan, I.J., Ruus, A., Schaanning, M.T., Macrae, K.J., Naes, K., 2012. Measuring nonpolar organic contaminant partitioning in three Norwegian sediments using polyethylene passive samplers. *Science of the Total Environment* 423, 125-131.
- Arthur, C.L., Killam, L.M., Buchholz, K.D., Pawliszyn, J., Berg, J.R., 1992. Automation and optimization of solid-phase microextraction. *Analytical Chemistry* 64, 1960-1966.
- Bao, L.-J., You, J., Zeng, E.Y., 2011. Sorption of PBDE in low-density polyethylene film: Implications for bioavailability of BDE-209. *Environmental Toxicology and Chemistry* 30, 1731-1738.
- Bao, L.J., Jia, F., Crago, J., Zeng, E.Y., Schlenk, D., Gan, J., 2013. Assessing bioavailability of DDT and metabolites in marine sediments using solid-phase microextraction with performance reference compounds. *Environmental Toxicology and Chemistry* 32, 1946-1953.

- Burkhard, L.P., Mount, D.R., Highland, T.L., Hockett, J.R., Norberg-King, T., Billa, N., Hawthorne, S.B., Miller, D.J., Grabanski, C.B., 2013. Evaluation of PCB bioaccumulation by *Lumbriculus variegatus* in field-collected sediments. *Environmental Toxicology and Chemistry* 32, 1495-1503.
- Cornelissen, G., Gustafsson, O., Bucheli, T.D., Jonker, M.T.O., Koelmans, A.A., Van Noort, P.C.M., 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* 39, 6881-6895.
- Cornelissen, G., Rigterink, H., Ferdinandy, M.M.A., Van Noort, P.C.M., 1998. Rapidly desorbing fractions of PAHs in contaminated sediments as a predictor of the extent of bioremediation. *Environmental Science & Technology* 32, 966-970.
- Cornelissen, G., Rigterink, H., ten Hulscher, D.E.M., Vrind, B.A., van Noort, P.C.M., 2001. A simple Tenax (R) extraction method to determine the availability of sediment-sorbed organic compounds. *Environmental Toxicology and Chemistry* 20, 706-711.
- Cornelissen, G., vanNoort, P.C.M., Govers, H.A.J., 1997. Desorption kinetics of chlorobenzenes, polycyclic aromatic hydrocarbons, and polychlorinated biphenyls: Sediment extraction with Tenax(R) and effects of contact time and solute hydrophobicity. *Environmental Toxicology and Chemistry* 16, 1351-1357.

- Cui, X., Bao, L., Gan, J., 2013a. Solid-phase microextraction (SPME) with stable isotope calibration for measuring bioavailability of hydrophobic organic contaminants. *Environmental Science & Technology* 47, 9833-9840.
- Cui, X., Hunter, W., Yang, Y., Chen, Y., Gan, J., 2011. Biodegradation of pyrene in sand, silt and clay fractions of sediment. *Biodegradation* 22, 297-307.
- Cui, X., Mayer, P., Gan, J., Cui, X.Y., 2013b. Methods to assess bioavailability of hydrophobic organic contaminants: principles, operations, and limitations. *Environmental Pollution* 172.
- Ehlers, L.J., Luthy, R.G., 2003. Contaminant bioavailability in soil and sediment. *Environmental Science & Technology* 37, 295A-302A.
- Fagervold, S., Chai, Y., Davis, J., Wilken, M., Cornelissen, G., Ghosh, U., 2010. Bioaccumulation of polychlorinated dibenzo-p-dioxins/dibenzofurans in *E. fetida* from floodplain soils and the effect of activated carbon amendment. *Environmental Science & Technology*, 5546-5552.
- Fernandez, L.A., Lao, W., Maruya, K.A., Burgess, R.M., 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* 48, 3925-3934.
- Fernandez, L.A., Macfarlane, J.K., Tcaciuc, A.P., Gschwend, P.M., 2009. Measurement of freely dissolved PAH concentrations in sediment beds using passive sampling with low-density polyethylene strips. *Environmental Science & Technology* 43, 1430-1436.

- Ghosh, U., Gillette, J.S., Luthy, R.G., Zare, R.N., 2000. Microscale location, characterization, and association of polycyclic aromatic hydrocarbons on harbor sediment particles. *Environmental Science & Technology* 34, 1729-1736.
- Ghosh, U., Luthy, R.G., Cornelissen, G., Werner, D., Menzie, C.A., 2011. In-situ sorbent amendments: A new direction in contaminated sediment management. *Environmental Science & Technology* 45, 1163-1168.
- Ghosh, U., Talley, J.W., Luthy, R.G., 2001. Particle-scale investigation of PAH desorption kinetics and thermodynamics from sediment. *Environmental Science & Technology* 35, 3468-3475.
- Ghosh, U., Zimmerman, J.R., Luthy, R.G., 2003. PCB and PAH speciation among particle types in contaminated harbor sediments and effects on PAH bioavailability. *Environmental Science & Technology* 37, 2209-2217.
- Gomez-Eyles, J.L., Jonker, M.T.O., Hodson, M.E., Collins, C.D., 2012. Passive samplers provide a better prediction of PAH bioaccumulation in earthworms and plant roots than exhaustive, mild solvent, and cyclodextrin extractions. *Environmental Science & Technology* 46, 962-969.
- Greenberg, M.S., Chapman, P.M., Allan, I.J., Anderson, K.A., Apitz, S.E., Beegan, C., Bridges, T.S., Brown, S.S., Cargill, J.G.t., McCulloch, M.C., Menzie, C.A., Shine, J.P., Parkerton, T.F., 2014. Passive sampling methods for contaminated sediments: Risk assessment and management. *Integrated environmental assessment and management* 10, 224-236.

- Hartnik, T., Jensen, J., Hermens, J.L.M., 2008. Nonexhaustive beta-cyclodextrin extraction as a chemical tool to estimate bioavailability of hydrophobic pesticides for earthworms. *Environmental Science & Technology* 42, 8419-8425.
- Hatzinger, P.B., Alexander, M., 1995. Effect of aging of chemicals in soil on their biodegradability and extractability. *Environmental Science & Technology* 29, 537-545.
- Hawthorne, S.B., Jonker, M.T.O., van der Heijden, S.A., Grabanski, C.B., Azzolina, N.A., Miller, D.J., 2011. Measuring picogram per liter concentrations of freely dissolved parent and alkyl PAHs (PAH-34), using passive sampling with polyoxymethylene. *Analytical Chemistry* 83, 6754-6761.
- Hawthorne, S.B., Miller, D.J., Grabanski, C.B., 2009. Measuring low picogram per liter concentrations of freely dissolved polychlorinated biphenyls in sediment pore water using passive sampling with polyoxymethylene. *Analytical Chemistry* 81, 9472-9480.
- Huckins, J.N., Manuweera, G.K., Petty, J.D., Mackay, D., Lebo, J.A., 1993. Lipid-containing semipermeable-membrane devices for monitoring organic contaminants in water. *Environmental Science & Technology* 27, 2489-2496.
- Jia, F., Cui, X.Y., Wang, W., Delgado-Moreno, L., Gan, J., 2012. Using disposable solid-phase microextraction (SPME) to determine the freely dissolved concentration of polybrominated diphenyl ethers (PBDEs) in sediments. *Environmental Pollution* 167, 34-40.

- Kataoka, H., 2002. Automated sample preparation using in-tube solid-phase microextraction and its application - a review. *Analytical and Bioanalytical Chemistry* 373, 31-45.
- Kelsey, J.W., Kottler, B.D., Alexander, M., 1997. Selective chemical extractants to predict bioavailability of soil-aged organic chemicals. *Environmental Science & Technology* 31, 214-217.
- Khan, M.I., Cheema, S.A., Shen, C., Zhang, C., Tang, X., Shi, J., Chen, X., Park, J., Chen, Y., 2012. Assessment of phenanthrene bioavailability in aged and unaged soils by mild extraction. *Environmental Monitoring and Assessment* 184, 549-559.
- Kukkonen, J.V.K., Landrum, P.F., Mitra, S., Gossiaux, D.C., Gunnarsson, J., Weston, D., 2004. The role of desorption for describing the bioavailability of select polycyclic aromatic hydrocarbon and polychlorinated biphenyl congeners for seven laboratory-spiked sediments. *Environmental Toxicology and Chemistry* 23, 1842-1851.
- Lamoureux, E.M., Brownawell, B.J., 1999. Chemical and biological availability of sediment-sorbed hydrophobic organic contaminants. *Environmental Toxicology and Chemistry* 18, 1733-1741.
- Lei, L., Bagchi, R., Khodadoust, A.P., Suidan, M.T., Tabak, H.H., 2006. Bioavailability prediction of polycyclic aromatic hydrocarbons in field-contaminated sediment by mild extractions. *Journal of Environmental Engineering* 132, 384-391.

- Liste, H.H., Alexander, M., 2002. Butanol extraction to predict bioavailability of PAHs in soil. *Chemosphere* 46, 1011-1017.
- Liu, H., Cai, X., Chen, J., 2013. Mathematical model for cyclodextrin alteration of bioavailability of organic pollutants. *Environmental Science & Technology* 47, 5835-5842.
- Liu, M., Tian, S., Chen, P., Zhu, L., 2011. Predicting the bioavailability of sediment-associated polybrominated diphenyl ethers using a 45-d sequential Tenax extraction. *Chemosphere* 85, 424-431.
- Luthy, R.G., Aiken, G.R., Brusseau, M.L., Cunningham, S.D., Gschwend, P.M., Pignatello, J.J., Reinhard, M., Traina, S.J., Weber, W.J., Westall, J.C., 1997. Sequestration of hydrophobic organic contaminants by geosorbents. *Environmental Science & Technology* 31, 3341-3347.
- Mayer, P., Vaes, W.H.J., Wijnker, F., Legierse, K., Kraaij, R.H., Tolls, J., Hermens, J.L.M., 2000. Sensing dissolved sediment porewater concentrations of persistent and bioaccumulative pollutants using disposable solid-phase microextraction fibers. *Environmental Science & Technology* 34, 5177-5183.
- Mehler, W.T., Li, H.Z., Pang, J.X., Sun, B.Q., Lydy, M.J., You, J., 2011. Bioavailability of hydrophobic organic contaminants in sediment with different particle-size distributions. *Archives of Environmental Contamination and Toxicology* 61, 74-82.

- Morrison, D.E., Robertson, B.K., Alexander, M., 2000. Bioavailability to earthworms of aged DDT, DDE, DDD, and dieldrin in soil. *Environmental Science & Technology* 34, 709-713.
- Nyholm, J.R., Asamoah, R.K., van der Wal, L., Danielsson, C., Andersson, P.L., 2010. Accumulation of polybrominated diphenyl ethers, hexabromobenzene, and 1,2-dibromo-4-(1,2-dibromoethyl)cyclohexane in earthworm (*Eisenia fetida*). Effects of soil type and aging. *Environmental Science & Technology* 44, 9189-9194.
- Oen, A.M.P., Cornelissen, G., Breedveld, G.D., 2006. Relation between PAH and black carbon contents in size fractions of Norwegian harbor sediments. *Environmental Pollution* 141, 370-380.
- Oen, A.M.P., Janssen, E.M.L., Cornelissen, G., Breedveld, G.D., Eek, E., Luthy, R.G., 2011. In Situ measurement of PCB pore water concentration profiles in activated carbon-amended sediment using passive samplers. *Environmental Science & Technology* 45, 4053-4059.
- Ouyang, G., Pawliszyn, J., 2008. A critical review in calibration methods for solid-phase microextraction. *Analytica Chimica Acta* 627, 184-197.
- Ouyang, G., Vuckovic, D., Pawliszyn, J., 2011. Nondestructive sampling of living systems using in vivo solid-phase microextraction. *Chemical Reviews* 111, 2784-2814.
- Poerschmann, J., Zhang, Z.Y., Kopinke, F.D., Pawliszyn, J., 1997. Solid phase microextraction for determining the distribution of chemicals in aqueous matrices. *Analytical Chemistry* 69, 597-600.

- Reichenberg, F., Mayer, P., 2006. Two complementary sides of bioavailability: Accessibility and chemical activity of organic contaminants in sediments and soils. *Environmental Toxicology and Chemistry* 25, 1239-1245.
- Reid, B.J., Stokes, J.D., Jones, K.C., Semple, K.T., 2000. Nonexhaustive cyclodextrin-based extraction technique for the evaluation of PAH bioavailability. *Environmental Science & Technology* 34, 3174-3179.
- National Research Council, 2002. Bioavailability of contaminants in soils and sediments: processes, tools, and applications. National Academies Press, Washington, D.C.
- Semple, K.T., Doick, K.J., Jones, K.C., Burauel, P., Craven, A., Harms, H., 2004. Defining bioavailability and bioaccessibility of contaminated soil and sediment is complicated. *Environmental Science & Technology* 38, 228A-231A.
- Stokes, J.D., Wilkinson, A., Reid, B.J., Jones, K.C., Semple, K.T., 2005. Prediction of polycyclic aromatic hydrocarbon biodegradation in contaminated soils using an aqueous hydroxypropyl-beta-cyclodextrin extraction technique. *Environmental Toxicology and Chemistry* 24, 1325-1330.
- Tang, J., Alexander, M., 1999. Mild extractability and bioavailability of polycyclic aromatic hydrocarbons in soil. *Environmental Toxicology and Chemistry* 18, 2711-2714.
- Tang, J.X., Robertson, B.K., Alexander, M., 1999. Chemical-extraction methods to estimate bioavailability of DDT, DDE, and DDD in soil. *Environmental Science & Technology* 33, 4346-4351.

- Tomaszewski, J.E., Luthy, R.G., 2008. Field deployment of polyethylene devices to measure PCB concentrations in pore water of contaminated sediment. *Environmental Science & Technology* 42, 6086-6091.
- Van der Wal, L., Jager, T., Fleuren, R., Barendregt, A., Sinnige, T.L., Van Gestel, C.A.M., Hermens, J.L.M., 2004. Solid-phase microextraction to predict bioavailability and accumulation of organic micropollutants in terrestrial organisms after exposure to a field-contaminated soil. *Environmental Science & Technology* 38, 4842-4848.
- Wang, W., Delgado-Moreno, L., Ye, Q.F., Gan, J., 2011. Improved measurements of partition coefficients for polybrominated diphenyl ethers. *Environmental Science & Technology* 45, 1521-1527.
- Xing, B.S., Pignatello, J.J., 1997. Dual-mode sorption of low-polarity compounds in glassy poly(vinyl chloride) and soil organic matter. *Environmental Science & Technology* 31, 792-799.
- Yang, Y., Hunter, W., Tao, S., Gan, J., 2008. Relationships between desorption intervals and availability of sediment-associated hydrophobic contaminants. *Environmental Science & Technology* 42, 8446-8451.
- You, J., Landrum, P.F., Lydy, M.J., 2006. Comparison of chemical approaches for assessing bioavailability of sediment-associated contaminants. *Environmental Science & Technology* 40, 6348-6353.

Figures

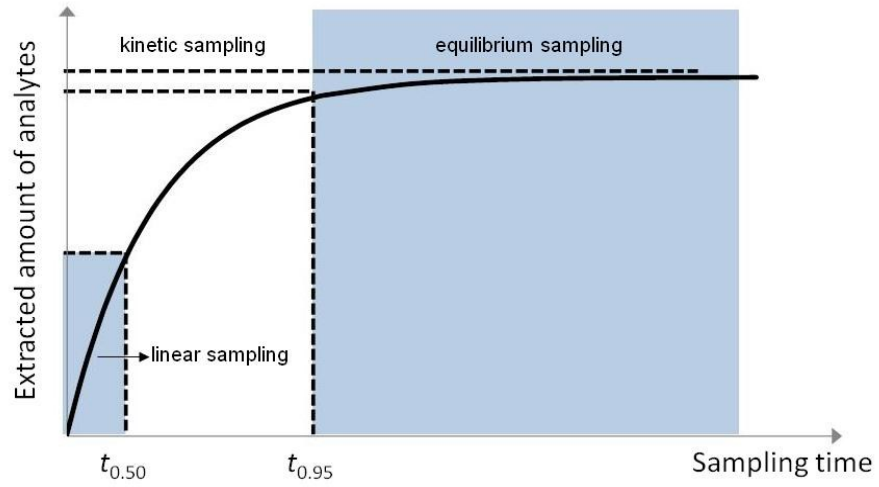


Figure 1.1. Typical sampling profile of passive samplers for hydrophobic organic contaminants (HOCs) (Modified from Ouyang et al., 2011)

Chapter 2 Using Disposable Solid-Phase Microextraction Method to Determine the Freely Dissolved Concentration of Polybrominated Diphenyl Ethers (PBDEs) in Sediment

2.1. Introduction

Polybrominated diphenyl ethers (PBDEs) are a class of highly hydrophobic organic contaminants (HOCs, $\log K_{ow} > 6$ for most congeners) that have been widely used as flame retardant additives in numerous commercial products (Birnbaum and Staskal, 2004; Rahman et al., 2001). PBDEs have been shown to persist in the environment (Andrade et al., 2010) and also to have significant bioaccumulation potential (Ciparis and Hale, 2005; Nyholm et al., 2010). In addition, recent toxicity data suggested PBDEs as potential disruptors to thyroid hormone balance (Darnerud, 2008; Hamers et al., 2006; Legler and Brouwer, 2003; McDonald, 2002), and probable carcinogens (Zhang et al., 2008). These properties dictate that the environmental fate and effects of PBDEs must be thoroughly characterized (Muresan et al., 2010; Yu et al., 2011; Zhang et al., 2011).

The bed sediment is a primary sink for PBDEs in the environment (Mai et al., 2005; Nylund et al., 1992; Renner, 2000). Most studies to date on PBDEs have considered the bulk sediment chemical concentration as the indicator of contamination. Because of their strong hydrophobicity, PBDEs are expected to interact strongly with sediment organic matter, leading to low concentrations in the sediment porewater (Jeong et al., 2008). While in the sediment porewater, as demonstrated for many other HOCs, PBDEs are expected to sorb to dissolved organic carbon (DOC) (Delgado-Moreno et al., 2010; ter Laak et al., 2009), rendering the freely dissolved concentration (C_{free}) even

lower. A number of studies have shown that C_{free} in sediments provides a better prediction for bioavailability of HOCs than their bulk sediment concentration (Hunter et al., 2008; Hunter et al., 2009; Ramos et al., 1998; Reichenberg and Mayer, 2006). To estimate C_{free} , methods based on the use of solid phase microextraction (SPME) have been developed for a range of HOCs (Bondarenko and Gan, 2009; Pawliszyn et al., 1997; Poerschmann et al., 1997; Wang et al., 2011), including pyrethroids (Bondarenko et al., 2006; Delgado-Moreno et al., 2010; Hunter et al., 2008), PAHs (Potter and Pawliszyn, 1994), and PCBs (Oen et al., 2011; Yang et al., 1998; Yang et al., 2006). However, so far only a few limited SPME applications have been reported for PBDEs. In a recent study, Wang et al. (2011) used an injector-type SPME to evaluate sorption of selected PBDE congeners to sediments and showed that the use of SPME resulted in improved K_d (or K_{oc}) measurements due to selective detection of C_{free} . However, injector-type SPME is not suitable for many sampling scenarios because long equilibrium time is needed for strongly hydrophobic compounds such as PBDEs. As a variation of SPME, disposable SPME fibers, such as polydimethylsiloxane (PDMS) fibers, have been shown to be highly compatible with bench scale bioassays (Hunter et al., 2009) and adaptable for in-situ sampling (Mayer et al., 2000b), offering matrix-calibrated measurement of C_{free} (Jahnke and Mayer, 2010; Mayer et al., 2000b).

In this study, we developed a SPME method for PBDEs using disposable PDMS fibers. Three most frequently detected PBDE congeners, BDE 47, 99, and 153, were used as the model PBDEs to evaluate the fiber uptake kinetics and derive the PDMS-to-water partition coefficient (K_{PDMS}). The developed SPME method was compared against the

conventional solvent extraction approach in characterizing phase distribution of PBDEs in different sediments.

2.2. Materials and Methods

2.2.1. Chemicals, Sediments, and PDMS Fiber.

Standards of 2,2',4,4'-tetrabromodiphenyl ether (BDE 47), 2,2',4,4',5-pentabromodiphenyl ether (BDE 99), and 2,2',4,4',5,5'-hexabromodiphenyl ether (BDE 153) in isooctane (50 µg/mL) were purchased from AccuStandard (New Haven, CT). External surrogate decachlorobiphenyl (PCB 209) was purchased from Fisher Scientific (Pittsburgh, PA). All other solvents and chemicals used in the present study were of analytical or gas chromatography (GC) grade.

Three sediments with no detectable PBDE levels were used, including San Diego Creek sediment (SD, Orange County, CA), Salinas Potrero sediment (SP, Santa Rosa, CA), and Jordan Lake Reservoir sediment (JL, Chatham County, NC). All sediments were wet-sieved through a 2-mm mesh and stored at 4 °C before use. The sediment OC content was measured by combustion on a nitrogen-carbon analyzer (Thermo Finnigan, Woods Hole, MA) after the inorganic carbon was removed with 1 M HCl. The selected properties of the sediments are shown in Table 2.1.

SPME fibers (430-µm diameter) coated with 35 µm PDMS were purchased from Polymicro Technologies (Phoenix, AZ). The volume of PDMS polymer coating per length was 51.1 µL/m. The PDMS fibers were pre-cleaned by Soxhlet extraction with ethyl acetate for 72 h and cut into 1-cm pieces with a razor blade before use.

2.2.2. Partition Coefficient (K_{PDMS}) Measurement

The PDMS-to-water partition coefficient (K_{PDMS}) is an essential parameter for deriving C_{free} (Hunter et al., 2009; Mayer et al., 2000b; Pawliszyn et al., 1997; Poerschmann et al., 1997). To obtain K_{PDMS} , 4 L of ultrapure water was spiked with BDE 47, 99, and 153 standards at different levels (5, 2, and 0.5 $\mu\text{g/L}$, respectively) using their stock solutions made in acetone while keeping the final acetone concentration in the amended water at less than 0.01% (v/v). After thorough mixing, 100-mL aliquots of the mixture were dispensed into 125-mL glass jars. Two pieces of pre-cleaned 1-cm PDMS fibers were then introduced into each jar. The jars were closed with Teflon-faced caps, wrapped in aluminum foil, and agitated on a horizontal shaker at 120 rpm. At pre-determined intervals, individual jars were removed and analyzed for PBDEs in both the water and on the PDMS fiber over a 33-d period.

The concentration of PBDEs on the PDMS fiber (C_{PDMS}) was analyzed following a simple solvent extraction procedure. The fibers were first wiped dry with paper towel and placed into 350- μL autosampler vial inserts, to which 200 μL of hexane was added. The vials were sonicated for 10 min in a Fisher Scientific IS30H ultrasound bath, from which an aliquot was directly injected into the GC inlet for analysis. This simplified procedure gave a recovery of 97 - 113% for the selected PBDE congeners in preliminary experiments. The concentration of PBDEs in water (equivalent to C_{free} in the absence of a sorbent phase) was obtained through liquid-liquid extraction (LLE) by mixing 50 mL of the sample with 50 mL of methylene chloride for 1 min. The same extraction procedure was repeated for a total of three times and the combined extract was passed through 20 g

anhydrous sodium sulfate held by Whatman No. 41 filter paper (Whatman, Maidstone, UK) into a 250-mL round-bottom flask. The extract was condensed at 35 °C to <10 mL on a vacuumed Rotavapor RE 121 (Buchi, Flawil, St. Gallen, Switzerland), and was further concentrated to near dryness under N₂. The residue was reconstituted in 1.0 mL of hexane and transferred to an autosampler vial for analysis on GC-MS. Preliminary experiments showed a recovery of 89.0-125.3% for the LLE method. The C_{PDMS} and C_{free} measured at the steady state were used for calculating K_{PDMS} values:

$$K_{\text{PDMS}} = \frac{C_{\text{PDMS}}}{C_{\text{free}}} \quad (1)$$

2.2.3. PBDE Uptake Kinetics Experiment

The kinetics for PBDEs to accumulate into the PDMS fiber from a sediment porewater sample was investigated to find the time for C_{PDMS} to reach an apparent equilibrium. To generate sediment porewater, 250 g (dry weight equivalent) of sediment were added with 250 mL water containing 0.2% NaN₃ and mixed for 5 d at 120 rpm on a mechanical shaker. After equilibration, the sediment slurry was centrifuged at 3,000 rpm (SORVALL GSA rotor) for 30 min, and the overlying water was filtered through polycarbonate membranes (0.45 μm pore diameter) to remove suspended particles. The DOC level of sediment porewater samples was analyzed on an Apollo 9000 total OC analyzer (Tekmar-Dohrmann, Mason, OH). The UV absorbance value of DOM at the wavelength of 254 nm was measured on a Varian Cary 50 UV-visible spectrophotometer (Varian Co., U.S.).

The derived porewater (about 250 mL) was then spiked with 250 μ L of PBDE mixture (1 mg/L) in acetone and mixed at 15 rpm for 24 h. Upon equilibrium, one piece of 1-cm long PDMS fiber was introduced to an aliquot of porewater (10 mL) and agitated on a horizontal shaker at 120 rpm. The fibers were removed at different intervals up to 12 d for analysis of C_{PDMS} . The retrieved PDMS fibers were wiped with paper towel, extracted and analyzed as described above.

The time for PBDE accumulation to reach an apparent steady state on the PDMS fibers was estimated by fitting C_{PDMS} to a one-compartment rise to maximum equation:

$$C_{\text{PDMS},t} = C_{\text{PDMS,eq}} \times (1 - e^{-kt}) \quad (2)$$

where $C_{\text{PDMS},t}$ (mg/L) is the PBDE concentration on PDMS fiber at time t (d), $C_{\text{PDMS,eq}}$ is the PBDE concentration on PDMS fiber at equilibrium, and k (d^{-1}) is the uptake rate constant.

2.2.4. PBDE Phase Distribution Characterization

The developed SPME method was used to evaluate PBDE distribution among the different phases in a sediment-water binary system. To spike sediments with PBDEs, a mixture of PBDE standards in acetone was applied to 10 g of coarse silica sand in a 1.9-L wide mouth jar. After the carrier solvent was evaporated in the fume hood, 250 g (dry weight equivalent) of wet sediment were added and mixed thoroughly with a stainless steel spatula. All spiked sediments were equilibrated at 120 rpm on a mechanical shaker for 7 d. Preliminary experiments showed that mixing for 7 d resulted in uniform chemical distribution in the sediments. Sub-samples (20 g dry weight) of the homogenized sediments and 20 mL of water were transferred to a 250-mL polyethylene centrifuge

bottle and mixed for 5 d at 120 rpm on a mechanical shaker. After the 5-d equilibration, the sediment slurry was centrifuged at 3,000 rpm (SORVALL GSA rotor) for 30 min to separate the solid and water phases. The derived porewater was filtered through polycarbonate membranes (0.45 μm pore diameter) and subjected to the following analyses.

An aliquot (10 mL) of the porewater sample was used for measuring C_{free} by equilibrating the porewater sample with one PDMS fiber (1 cm) for 5 d at 120 rpm. A second aliquot (5 mL) of the porewater was analyzed for DOC level. The remaining porewater (5 mL) was analyzed for the total PBDE concentration (C_w) by LLE using hexane (ter Laak et al., 2008). Briefly, the porewater sample (5 mL) was mixed with 5 mL of hexane in a 20-mL glass vial at 120 rpm for 2 h and then placed in a freezer (-21°C). After the water was frozen, the hexane phase was decanted and recovered. The hexane extract was then concentrated and reconstituted in 200 μL of hexane before analysis on GC-MS. The recoveries of this LLE method were 85.6 - 114.4% for the selected PBDE congeners.

The sediment phase was extracted for three consecutive times by mixing the sediment (2 g dry weight) with 50 mL of methylene chloride: acetone (1:1, v/v) in the ultrasound bath for 20 min for three consecutive times. The extracts were combined and passed through a Whatman No. 41 filter paper filled with 20 g of anhydrous sodium sulfate. The filtrate was concentrated and recovered in 10 mL of hexane, an aliquot of which was analyzed. Preliminary experiments showed that the above sediment extraction method gave recoveries ranging from 90.0 to 129.5%.

2.2.5. Chromatographic Analysis of PBDEs

The quantitative analysis of PBDEs was carried out on an Agilent 6890 GC coupled with an Agilent 5973 mass spectrometer (Agilent, Santa Clara, CA). A DB-5MS capillary column (30 m × 0.25 mm × 0.25 μm) (J&W Scientific, Folsom, CA) was used for the separation. An aliquot of 2 μL was injected in the splitless mode. The initial oven temperature was 100 °C, which was held for 1 min and then ramped at 10 °C/min to a final temperature of 300 °C (held for 5 min). Helium was used as the carrier gas at a flow rate of 1.0 mL/min. External calibration standards were prepared in hexane and analyzed under the same conditions on the same day of sample analysis. The mass spectrometer was operated in electron ionization mode at 70 eV in the selected ion monitoring (SIM) mode. Mass fragments monitored were m/z 326, 484 and 486 for BDE 47, m/z 404, 406, 564 and 566 for BDE 99, m/z 482, 484, 486 and 643 for BDE 153, and m/z 496, 498 and 500 for PCB 209.

2.2.6. Quality Assurance and Quality Control (QA/QC)

All treatments included three replicates. Ultrapure water was used as control blanks for DOC and UV absorbance analysis. Significance between different treatments was tested using paired *t* test with SPSS 15.0 (SPSS, Chicago, IL).

2.3. Results and Discussion

2.3.1. PDMS-to-Water Partition Coefficient (K_{PDMS})

The coefficient K_{PDMS} is essential for deriving C_{free} of HOCs when using PDMS fibers. In measuring K_{PDMS} , PBDEs in water may be lost due to sorption to the walls of the glass container. To overcome this potential artifact, both PDMS fiber and water were

concurrently analyzed. There was a clear increasing trend for all PBDEs in their accumulation into the PDMS fiber (Figure 2.1a) and depleting trend for the bathing water (Figure 2.1b). However, the time to reach an apparent steady state varied greatly among the different PBDE congeners, ranging from 8.3 d for BDE 47 to 32.8 d for BDE 153 (data not shown). The average $\log K_{\text{PDMS}}$ calculated at the steady state was 5.51 (5.46 – 5.55) for BDE 47, 5.53 (5.47 – 5.58) for BDE 99, and 5.76 (5.68 – 5.83) for BDE 153. The relatively large K_{PDMS} values suggested a strong affinity of the selected PBDEs for the PDMS polymer. From Mayer et al. (2000a), hydrophobicity of HOCs was the dominant factor governing their partitioning between PDMS and water phase. From the reported K_{ow} values, BDE 153 ($\log K_{\text{ow}} = 7.90$) is more hydrophobic than BDE 99 ($\log K_{\text{ow}} = 7.32$), which is more hydrophobic than BDE 47 ($\log K_{\text{ow}} = 6.81$), correlating generally with the degree of bromination (Braekevelt et al., 2003). Therefore, the derived K_{PDMS} coincided closely with K_{ow} or the degree of Br substitution of PBDE congeners.

There are few experimentally measured K_{PDMS} values for PBDEs in the literature. Ter Laak et al. (2008) estimated the $\log K_{\text{PDMS}}$ values by equilibrating the preloaded fibers (114.5 μm thickness of glass core and 30 μm thickness of PDMS coating) with 38 mL of water phase for as long as 37 days, and the average $\log K_{\text{PDMS}}$ values were 5.91, 6.35, and 6.47 for BDE 47, 99, and 153, respectively. These values were consistently larger than those observed in the current study. Variations in K_{PDMS} values have been seen for other HOCs as well and have been attributed to differences in cross-linking of the coating phase among PDMS fibers from different manufacturers. Also, using a large solution-to-fiber ratio to maintain negligible depletion of HOCs by the fiber was found to

minimize errors in obtaining K_{PDMS} values (Difilippo and Eganhouse, 2010; Gorecki and Pawliszyn, 1997).

2.3.2. Uptake Kinetics in Sediment Porewater

The uptake kinetics of PBDE congeners in sediment porewater samples under agitated conditions is shown in Figure 2.2. The time for attaining 90% of equilibrium ($t_{0.9}$) was estimated using Equation 2. In general, an apparent equilibrium was reached within 5 d for most of the treatments (Figure 2.2).

The uptake kinetics of PBDEs appeared to depend on the physicochemical properties of both the PBDE congener and sediment. In the same porewater, the uptake rate consistently followed a trend of BDE 47 > BDE 99 ~ BDE 153, where BDE 47 was always the first one to reach the apparent equilibrium (Figure 2.2). For example, in the JL sediment porewater, BDE 47 reached an apparent equilibrium in 1.85 d, whereas $t_{0.9}$ was 2.37 d for BDE 99 and 2.53 d for BDE 153. Nonpolar or monopolar compounds with higher polarizability present a higher dispersive interaction potential with the hydrophobic surface provided by DOM (Schwarzenbach et al., 2003). Therefore, the mass transfer rate of PBDE congeners with higher polarizability may be lowered due to the stability of the PBDE-DOM complex enhanced by the dispersive interaction. Wang et al. (2008) calculated the polarizability for PBDEs and for the congeners considered in this study, their mean molecular polarizability values (α) are 29.51, 32.43, and 35.74 for BDE 47, 99, and 153, respectively. The non-specific interactions between BDE 47 and DOM may thus be weaker than the other congeners, leading to its relatively faster

transport through the boundary layer than BDE 99 or BDE 153, and consequently faster uptake kinetics on the PBDE fiber.

The source of DOC also affected $t_{0.9}$. Following 5 d mixing, all three PBDE congeners reached an apparent steady state in the JL porewater. However, in the SD porewater, only BDE 47 appeared to have reached an apparent equilibrium, while BDE 99 and 153 reached only 86.3% and 88.6% of their equilibrium levels, respectively. Since DOC levels were similar for JL (34.9 mg/L) and SD (32.6 mg/L) sediments, the difference in PBDE uptake kinetics may be attributed to the different properties of DOC. The UV absorbance at 254 nm has been shown to correlate with aromatic carbon content of a DOC solution (Weishaar et al., 2003). Among the three sediments used in this study, the estimated aromaticity as given by $SUVA_{254}$ increased in the order $JL < SP < SD$. Therefore, DOM in the JL porewater may have a lower aromaticity, resulting in weaker affinity between DOM and PBDEs or enhanced PBDE transport across the boundary layer due to the increased lability of the DOM-PBDE complex. The difference in DOM aromaticity may also have influenced PBDE uptake in the SP porewater that had the highest DOC level (62.9 ± 0.2 mg/L) but intermediate $SUVA_{254}$ (Table 2.1).

When the partition of PBDEs into the PDMS phase reached equilibrium, C_{free} of PBDEs in the bathing aqueous phase may be estimated from C_{PDMS} using the previously derived K_{PDMS} (Table 2.2). Under the experimental conditions, the fraction of PBDEs partitioned into the PDMS fiber at equilibrium was 5.1 – 6.5% for SD, 3.1 – 3.7% for SP, and 13.7 – 14.5% for JL porewater, generally meeting the prerequisite for non-depletive sampling of SPME (Difilippo and Eganhouse, 2010). The estimated C_{free} consistently

followed the order of BDE 47 > BDE 99 > BDE 153 in the same porewater sample. This trend was apparently related to the hydrophobicity of the individual PBDE congeners. There were also significant differences in C_{free} among different sediment porewater samples. For BDE 47, the mean C_{free} was 10.7 ng/L in the JL porewater, but only 4.2 ng/L in the SD porewater or 2.5 ng/L in the SP porewater. Similar differences were also observed for the other two congeners. As discussed above, this trend was attributable to the combined effect of both the DOC level and properties.

2.3.3. Phase Distribution of PBDEs in Sediments

Phase distribution of PBDEs in the sediment-water binary system at equilibrium was further evaluated using the developed SPME method (Table 2.3). The majority of PBDEs were found to be sorbed on the solid phase, accounting for $96.20 \pm 0.60\%$ to $99.80 \pm 0.17\%$ for BDE 47, $96.46 \pm 1.00\%$ to $99.87 \pm 0.14\%$ for BDE 99, and $96.58 \pm 0.78\%$ to $99.91 \pm 0.09\%$ for BDE 153. Among the three sediments, the sediment-sorbed fraction was consistently the smallest for the JL sediment and the largest for the SP sediment. For the SD and SP sediments, the sediment-sorbed fraction exceeded 99% for all three PBDE congeners. The relatively weak sorption to the JL sediment may be attributed to its low sediment OC content, validating that OC acts as the main sorbent in sediments for PBDEs (Accardi-Dey and Gschwend, 2002; Agarwal and Bucheli, 2011; Sun et al., 2010). In the same sediment, the sediment-sorbed fraction was generally larger for BDE 153 than for BDE 47 or BDE 99. The fraction of PBDEs in the porewater was consistently small as compared to the sediment-sorbed fraction. With the exception of the JL sediment, the fraction in the whole porewater was always <1% of the total PBDE

recovered from the sediment slurry. The freely dissolved fraction, in relation to the whole sediment sample, was even smaller, accounting for <0.012% of the total chemical mass.

Due to the presence of DOM in the sediment porewater, C_{free} was much smaller than C_w . The relative distribution of PBDEs between the truly dissolved phase and DOC was calculated from the difference between C_w and C_{free} (Table 2.3). The fraction of the truly dissolved form (f_{free}) was only 0.31 – 0.43% of C_w for BDE 47. The relative composition decreased to 0.24 – 0.28% for BDE 99, and only 0.02 – 0.10% for BDE 153. Therefore, in all sediment samples, C_{free} only accounted for < 0.43 % of C_w of the porewater, suggesting a predominant association of PBDEs with DOM in the sediment porewater. In a previous study where a batch equilibration setup was used for measuring K_d , Wang et al (2011) showed that C_{free} accounted for 21.8 – 60.6% of C_w for BDE 47, and 16.6 – 74.9% for BDE 99. The much larger C_{free} fraction in that study was the result of low DOC levels (2.54 – 7.01 mg/L) in the aqueous phase due to the use of a very small solid-to-solution ratio (1:50, w:w). The DOC levels observed in this study were comparable to those found in sediment porewater samples (Gao et al., 1998; Mitra et al., 1999) and therefore, the fraction of C_{free} seen in this study may be more representative of realistic phase distribution of PBDEs in sediments.

2.3.4. PBDE Partition Coefficients

The sediment-to-water partition coefficient K_d is traditionally calculated as the ratio of C_s over C_w . As shown in earlier studies, the ability of PDMS fibers to selectively detect C_{free} may be used to improve the estimation of K_d or K_{oc} . The partition coefficients K_d and hence K_{oc} were calculated using both C_w and C_{free} in this study (Table 2.4). For

the same sediment-PBDE congener combination, K_d values obtained by the SPME method was 217 – 321-fold that derived with the conventional LLE method for BDE 47, 310 – 422-fold that for BDE 99, and 993 – 4032-fold that for BDE 153. Underestimation in K_d for PBDEs was previously reported when the conventional batch equilibration method was used (Wang et al., 2011). However, the magnitude of underestimation was substantially greater in this study as compared to Wang et al. (2011). The discrepancy again may be attributed to the use of different solid-to-solution ratios and the resulting different DOC levels in the aqueous phase.

After OC normalization, the average log K_{oc} values were 6.32 – 6.54 for BDE 47, 6.56 – 6.91 for BDE 99, and 7.08 – 7.54 for BDE 153 (Table 2.5). The ranges of the derived log K_{oc} values were similar to those found in Wang et al. (2011) (5.76 – 6.45 for BDE 47, 6.18 – 6.94 for BDE 99, and 6.17 – 7.31 for BDE 153). Barrington et al. (2002) reported that log K_{oc} for soot carbon was 7.43 ± 0.08 for BDE 47 and as high as 8.11 ± 0.06 for BDE 99, suggesting that the properties of sediment OC, such as black carbon content, may also affect the sorption affinity of PBDEs to sediments.

The separate analyses of C_w and C_{free} also afforded the calculation of K_{DOC} , which is otherwise difficult to obtain experimentally. The K_{DOC} was calculated as:

$$K_{DOC} = \frac{C_w - C_{free}}{C_{free} [DOC]} \quad (3)$$

The estimated log K_{DOC} values were between 6.57 – 6.96 for BDE 47, 6.80 – 7.11 for BDE 99, and 7.28 – 8.09 for BDE 153 (Table 2.5). The derived K_{DOC} values were generally similar to the K_{oc} values for the same sediment. Among the three sediments, the

K_{DOC} values for SD were consistently larger than those for SP and JL sediments (Table 2.5), suggesting that the source or properties of sediment DOC (e.g., aromaticity) may also affect the sorption of PBDEs to DOC (Uhle et al., 1999).

The partition coefficients K_{oc} and K_{DOC} are expected to govern both environmental processes and potential bioavailability of PBDEs. While sorption to sediment OC decreases the overall porewater concentration of PBDEs, association with DOC may increase their presence in the sediment porewater and thus contribute to enhanced mobility of PBDEs in surface streams or during surface runoff. Results from this study showed that K_{oc} and K_{DOC} for the same PBDE congeners were generally similar, implying that the partitioning of PBDEs into sediment porewater would depend closely on the sediment OC content and the actual DOC level in the porewater. The porewater DOC level is in turn related closely to the stability of sediment aggregates (Delgado-Moreno et al., 2010). For instance, even though the JL sediment had the lowest sediment OC content (0.24%), its porewater contained a similar level of DOC to that of the SD sediment (Table 2.1). Therefore, it may be expected that PBDEs are more susceptible to offsite transport and dispersion in a system with sediments similar to the JL sediment. In addition, DOM was also shown to enhance the leaching of PBDEs under landfills (Kim et al., 2006; Osako et al., 2004), which is an important route for PBDEs to enter the environment (Darnerud et al., 2001).

2.4. Conclusion

Results from this study suggested that C_{free} and hence bioavailability of PBDEs in the bed sediment may be influenced by both the specific PBDE congener and the

sediment. In general, C_{free} may be expected to decrease as the degree of bromination increases. Therefore, highly brominated PBDEs are less bioavailable to small benthic invertebrates than the less brominated congeners. Low sediment OC content, as seen with the JL sediment in this study, may lead to high C_{free} for the same PBDE congeners, suggesting increased bioavailability to benthic organisms. For instance, assuming that bioavailability is directly proportional to C_{free} , the potential aquatic toxicity or bioaccumulation of BDE 47, 99, or 153 would be 1.3 – 10.5 greater in the JL sediment than in the SD or SP sediment. Therefore, the phase distribution of PBDEs or their bioavailability in the sediment environment will be site-specific, depending closely on the properties of sediment organic carbon. In addition, although not considered in this study, contact time in sediment is also known to affect HOC phase distribution and C_{free} (Welsh et al., 2009). These uncertainties together make the prediction of the biological effects of PBDEs from the commonly measured bulk sediment concentrations very difficult, if possible at all. As demonstrated in this study, the use of disposable SPME fibers may be a simple and inexpensive alternative to the conventional measurement, lending critical bioavailability information that is valuable for understanding the actual bioavailability or ecotoxicological effects from PBDE contamination.

References

- Accardi-Dey, A., Gschwend, P.M., 2002. Assessing the combined roles of natural organic matter and black carbon as sorbents in sediments. *Environmental Science & Technology* 36, 21-29.
- Agarwal, T., Bucheli, T.D., 2011. Is black carbon a better predictor of polycyclic aromatic hydrocarbon distribution in soils than total organic carbon? *Environmental Pollution* 159, 64-70.
- Andrade, N.A., McConnell, L.L., Torrents, A., Ramirez, M., 2010. Persistence of polybrominated diphenyl ethers in agricultural soils after biosolids applications. *Journal of Agricultural and Food Chemistry* 58, 3077-3084.
- Barring, H., Bucheli, T.D., Broman, D., Gustasson, O., 2002. Soot-water distribution coefficients for polychlorinated dibenzo-p-dioxins, polychlorinated dibenzofurans and polybrominated diphenylethers determined with the soot cosolvency-column method. *Chemosphere* 49, 515-523.
- Birnbaum, L.S., Staskal, D.F., 2004. Brominated flame retardants: Cause for concern? *Environmental Health Perspectives* 112, 9-17.
- Bondarenko, S., Gan, J., 2009. Simultaneous measurement of free and total concentrations of hydrophobic compounds. *Environmental Science & Technology* 43, 3772-3777.
- Bondarenko, S., Putt, A., Kavanaugh, S., Poletika, N., Gan, J.Y., 2006. Time dependence of phase distribution of pyrethroid insecticides in sediment. *Environmental Toxicology and Chemistry* 25, 3148-3154.

- Braekevelt, E., Tittlemier, S., Tomy, G., 2003. Direct measurement of octanol-water partition coefficients of some environmentally relevant brominated diphenyl ether congeners. *Chemosphere*, 563-567.
- Ciparis, S., Hale, R., 2005. Bioavailability of polybrominated diphenyl ether flame retardants in biosolids and spiked sediment to the aquatic oligochaete, *Lumbriculus variegatus*. *Environmental Toxicology and Chemistry*, 916-925.
- Darnerud, P.O., 2008. Brominated flame retardants as possible endocrine disrupters. *International Journal of Andrology* 31, 152-160.
- Darnerud, P.O., Eriksen, G.S., Johannesson, T., Larsen, P.B., Viluksela, M., 2001. Polybrominated diphenyl ethers: Occurrence, dietary exposure, and toxicology. *Environmental Health Perspectives* 109, 49-68.
- Delgado-Moreno, L., Wu, L., Gan, J., 2010. Effect of dissolved organic carbon on sorption of pyrethroids to sediments. *Environmental Science & Technology* 44, 8473-8478.
- Difilippo, E.L., Eganhouse, R.P., 2010. Assessment of PDMS-water partition coefficients: Implications for passive environmental sampling of hydrophobic organic compounds. *Environmental Science & Technology* 44, 6917-6925.
- Gao, J.P., Maguhn, J., Spitzauer, P., Kettrup, A., 1998. Distribution of polycyclic aromatic hydrocarbons (PAHs) in pore water and sediment of a small aquatic ecosystem. *International Journal of Environmental Analytical Chemistry* 69, 227-242.

- Gorecki, T., Pawliszyn, J., 1997. Effect of sample volume on quantitative analysis by solid-phase microextraction .1. Theoretical considerations. *Analyst* 122, 1079-1086.
- Hamers, T., Kamstra, J.H., Sonneveld, E., Murk, A.J., Kester, M.H.A., Andersson, P.L., Legler, J., Brouwer, A., 2006. In vitro profiling of the endocrine-disrupting potency of brominated flame retardants. *Toxicological Sciences* 92, 157-173.
- Hunter, W., Xu, Y.P., Spurlock, F., Gan, J., 2008. Using disposable polydimethylsiloxane fibers to assess the bioavailability of permethrin in sediment. *Environmental Toxicology and Chemistry* 27, 568-575.
- Hunter, W., Yang, Y., Reichenberg, F., Mayer, P., Gan, J., 2009. Measuring pyrethroids in sediment pore water using matrix-solid phase microextraction. *Environmental Toxicology and Chemistry*, 36-43.
- Jahnke, A., Mayer, P., 2010. Do complex matrices modify the sorptive properties of polydimethylsiloxane (PDMS) for non-polar organic chemicals? *Journal of Chromatography A* 1217, 4765-4770.
- Jeong, S., Wander, M.M., Kleineidam, S., Grathwohl, P., Ligouis, B., Werth, C.J., 2008. The role of condensed carbonaceous materials on the sorption of hydrophobic organic contaminants in subsurface sediments. *Environmental Science & Technology* 42, 1458-1464.
- Kim, Y.J., Osako, M., Sakai, S.I., 2006. Leaching characteristics of polybrominated diphenyl ethers (PBDEs) from flame-retardant plastics. *Chemosphere* 65, 506-513.

- Legler, J., Brouwer, A., 2003. Are brominated flame retardants endocrine disruptors? *Environment International* 29, 879-885.
- Mai, B.X., Chen, S.J., Luo, X.J., Chen, L.G., Yang, Q.S., Sheng, G.Y., Peng, P.G., Fu, J.M., Zeng, E.Y., 2005. Distribution of polybrominated diphenyl ethers in sediments of the Pearl River Delta and adjacent South China Sea. *Environmental Science & Technology* 39, 3521-3527.
- Mayer, P., Vaes, W.H.J., Hermens, J.L.M., 2000a. Absorption of hydrophobic compounds into the poly(dimethylsiloxane) coating of solid-phase microextraction fibers: High partition coefficients and fluorescence microscopy images. *Analytical Chemistry* 72, 459-464.
- Mayer, P., Vaes, W.H.J., Wijnker, F., Legierse, K., Kraaij, R.H., Tolls, J., Hermens, J.L.M., 2000b. Sensing dissolved sediment porewater concentrations of persistent and bioaccumulative pollutants using disposable solid-phase microextraction fibers. *Environmental Science & Technology* 34, 5177-5183.
- McDonald, T.A., 2002. A perspective on the potential health risks of PBDEs. *Chemosphere* 46, 745-755.
- Mitra, S., Dickhut, R.M., Kuehl, S.A., Kimbrough, K.L., 1999. Polycyclic aromatic hydrocarbon (PAH) source, sediment deposition patterns, and particle geochemistry as factors influencing PAH distribution coefficients in sediments of the Elizabeth River, VA, USA. *Marine Chemistry* 66, 113-127.

- Muresan, B., Lorgeoux, C., Gasperi, J., Moilleron, R., 2010. Fate and spatial variations of polybrominated diphenyl ethers in the deposition within a heavily urbanized area: Case of Paris (France). *Water Science and Technology* 62, 822-828.
- Nyholm, J.R., Asamoah, R.K., van der Wal, L., Danielsson, C., Andersson, P.L., 2010. Accumulation of polybrominated diphenyl ethers, hexabromobenzene, and 1,2-dibromo-4-(1,2-dibromoethyl)cyclohexane in earthworm (*Eisenia fetida*). Effects of soil type and aging. *Environmental Science & Technology* 44, 9189-9194.
- Nylund, K., Asplund, L., Jansson, B., Jonsson, P., Litzen, K., Sellstrom, U., 1992. Analysis of some polyhalogenated organic pollutants in sediment and sewage-sludge. *Chemosphere* 24, 1721-1730.
- Oen, A.M.P., Janssen, E.M.L., Cornelissen, G., Breedveld, G.D., Eek, E., Luthy, R.G., 2011. In situ measurement of PCB pore water concentration profiles in activated carbon-amended sediment using passive samplers. *Environmental Science & Technology* 45, 4053-4059.
- Osako, M., Kim, Y.J., Sakai, S.I., 2004. Leaching of brominated flame retardants in leachate from landfills in Japan. *Chemosphere* 57, 1571-1579.
- Pawliszyn, J., Pawliszyn, B., Pawliszyn, M., 1997. Solid phase microextraction (SPME). *The Chemical Educator* 2, 1-7.
- Poerschmann, J., Zhang, Z.Y., Kopinke, F.D., Pawliszyn, J., 1997. Solid phase microextraction for determining the distribution of chemicals in aqueous matrices. *Analytical Chemistry* 69, 597-600.

- Potter, D.W., Pawliszyn, J., 1994. Rapid-determination of polyaromatic hydrocarbons and polychlorinated-biphenyls in water using solid-phase microextraction and GCMS. *Environmental Science & Technology* 28, 298-305.
- Rahman, F., Langford, K.H., Scrimshaw, M.D., Lester, J.N., 2001. Polybrominated diphenyl ether (PBDE) flame retardants. *Science of the Total Environment* 275, 1-17.
- Ramos, E.U., Meijer, S.N., Vaes, W.H.J., Verhaar, H.J.M., Hermens, J.L.M., 1998. Using solid-phase microextraction to determine partition coefficients to humic acids and bioavailable concentrations of hydrophobic chemicals. *Environmental Science & Technology* 32, 3430-3435.
- Reichenberg, F., Mayer, P., 2006. Two complementary sides of bioavailability: Accessibility and chemical activity of organic contaminants in sediments and soils. *Environmental Toxicology and Chemistry* 25, 1239-1245.
- Renner, R., 2000. Increasing levels of flame retardants found in North American environment. *Environmental Science & Technology* 34, 452A-453A.
- Schwarzenbach, R.P., Gschwend, P.M., Imboden, D.M., 2003. *Environmental Organic Chemistry*. John Wiley & Sons, Inc., Hoboken, NJ, USA.
- Sun, K., Gao, B., Zhang, Z.Y., Zhang, G.X., Liu, X.T., Zhao, Y., Xing, B.S., 2010. Sorption of endocrine disrupting chemicals by condensed organic matter in soils and sediments. *Chemosphere* 80, 709-715.
- ter Laak, T.L., Busser, F.J.M., Hermens, J.L.M., 2008. Poly(dimethylsiloxane) as passive sampler material for hydrophobic chemicals: Effect of chemical properties and

- sampler characteristics on partitioning and equilibration times. *Analytical Chemistry* 80, 3859-3866.
- ter Laak, T.L., ter Bekke, M.A., Hermens, J.L.M., 2009. Dissolved organic matter enhances transport of PAHs to aquatic organisms. *Environmental Science & Technology* 43, 7212-7217.
- Uhle, M.E., Chin, Y.P., Aiken, G.R., McKnight, D.M., 1999. Binding of polychlorinated biphenyls to aquatic humic substances: The role of substrate and sorbate properties on partitioning. *Environmental Science & Technology* 33, 2715-2718.
- Wang, W., Delgado-Moreno, L., Ye, Q.F., Gan, J., 2011. Improved measurements of partition coefficients for polybrominated diphenyl ethers. *Environmental Science & Technology* 45, 1521-1527.
- Wang, Z.Y., Zeng, X.L., Zhai, Z.C., 2008. Prediction of supercooled liquid vapor pressures and n-octanol/air partition coefficients for polybrominated diphenyl ethers by means of molecular descriptors from DFT method. *Science of the Total Environment* 389, 296-305.
- Weishaar, J.L., Aiken, G.R., Bergamaschi, B.A., Fram, M.S., Fujii, R., Mopper, K., 2003. Evaluation of specific ultraviolet absorbance as an indicator of the chemical composition and reactivity of dissolved organic carbon. *Environmental Science & Technology* 37, 4702-4708.
- Welsh, G., Mueller, K., Soman, R., Vonderheide, A., Shann, J., 2009. Accessibility of polybrominated diphenyl ether congeners in aging soil. *Journal of Environmental Monitoring* 11, 1658-1663.

- Yang, Y., Miller, D.J., Hawthorne, S.B., 1998. Solid-phase microextraction of polychlorinated biphenyls. *Journal of Chromatography A* 800, 257-266.
- Yang, Z.Y., Zeng, E.Y., Xia, H., Wang, J.Z., Mai, B.X., Maruya, K.A., 2006. Application of a static solid-phase microextraction procedure combined with liquid-liquid extraction to determine poly(dimethyl)siloxane-water partition coefficients for selected polychlorinated biphenyls. *Journal of Chromatography A* 1116, 240-247.
- Yu, Z.Q., Zheng, K.W., Ren, G.F., Wang, D.C., Ma, S.T., Peng, P.A., Wu, M.H., Sheng, G.Y., Fu, J.M., 2011. Identification of monochloro-nonabromodiphenyl ethers in the air and soil samples from South China. *Environmental Science & Technology* 45, 2619-2625.
- Zhang, X.M., Diamond, M.L., Robson, M., Harrad, S., 2011. Sources, emissions, and fate of polybrominated diphenyl ethers and polychlorinated biphenyls indoors in Toronto, Canada. *Environmental Science & Technology* 45, 3268-3274.
- Zhang, Y., Guo, G.L., Han, X., Zhu, C., Kilfoy, B.A., Zhu, Y., Boyle, P., Zheng, T., 2008. Do polybrominated diphenyl ethers (PBDEs) increase the risk of thyroid cancer? *Biosci Hypotheses* 1, 195-199.

Tables

Table 2.1. Selected properties of sediments and sediment porewater used in the study

Sediment ^a	OC (% dry weight) ^b	Particle Distribution			DOC (mg/L) ^c	SUVA ₂₅₄ (L mgC ⁻¹ m ⁻¹) ^d
		sand %	silt %	clay %		
SD	1.4	41	37	22	32.6 ± 1.6	3.32
SP	2.5	8	78	14	62.9 ± 0.2	1.44
JL	0.24	78	17	5	34.9 ± 0.1	0.13

^aSD = San Diego Creek sediment, Orange County, CA; SP = Salinas Potrero sediment, Santa Rosa, CA; JL = Jordan Lake Reservoir sediment, Chatham County, NC.

^bOC = organic carbon content in the bulk sediment.

^cDOC = dissolved organic carbon content in the sediment porewater.

^dSUVA₂₅₄ = UV absorbance at 254 nm divided by the dissolved organic carbon concentration.

Table 2.2. Freely dissolved concentration (C_{free}) of PBDEs (ng/L) in sediment porewater

	SP ^a sediment	SD sediment	JL sediment
BDE 47	2.46 ± 0.07	4.17 ± 0.11	10.66 ± 0.05
BDE 99	2.36 ± 0.10	3.89 ± 0.11	10.00 ± 0.06
BDE 153	1.15 ± 0.06	1.97 ± 0.03	5.57 ± 0.17

^aSP = Salinas Potrero sediment, Santa Rosa, CA; SD = San Diego Creek sediment, Orange County, CA; JL = Jordan Lake Reservoir sediment, Chatham County, NC.

Table 2.3. Phase distribution of PBDEs at equilibrium based on the recovered chemical mass

	<u>Whole Sediment</u>			<u>Sediment Porewater</u>	
	Sediment %	Water %	Free ‰	DOC %	Free %
BDE 47					
SD ^a	99.35 ± 0.57	0.97 ± 0.14	0.35 ± 0.05	99.66 ± 0.02	0.34 ± 0.02
SP	99.80 ± 0.17	0.29 ± 0.02	0.14 ± 0.03	99.57 ± 0.10	0.43 ± 0.10
JL	96.20 ± 0.60	3.79 ± 0.60	1.17 ± 0.13	99.69 ± 0.03	0.31 ± 0.03
BDE 99					
SD	99.18 ± 0.06	0.82 ± 0.06	0.20 ± 0.02	99.76 ± 0.02	0.24 ± 0.02
SP	99.87 ± 0.14	0.19 ± 0.12	0.05 ± 0.01	99.72 ± 0.17	0.28 ± 0.17
JL	96.46 ± 1.00	3.53 ± 1.00	0.81 ± 0.12	99.76 ± 0.05	0.24 ± 0.05
BDE 153					
SD	99.07 ± 0.04	0.93 ± 0.04	0.02 ± 0.00	99.98 ± 0.00	0.02 ± 0.00
SP	99.91 ± 0.09	0.13 ± 0.06	0.01 ± 0.00	99.91 ± 0.04	0.09 ± 0.04
JL	96.58 ± 0.78	3.42 ± 0.78	0.34 ± 0.05	99.90 ± 0.01	0.10 ± 0.01

^aSD = San Diego Creek sediment, Orange County, CA; SP = Salinas Potrero sediment, Santa Rosa, CA; JL = Jordan Lake Reservoir sediment, Chatham County, NC.

Table 2.4. Sediment-water partition coefficient (K_d) of PBDEs in sediments measured by liquid-liquid extraction (LLE) or solid phase microextraction (SPME)

	SD ^a sediment	SP sediment	JL sediment
BDE 47 ($\times 1000$)			
LLE	0.10 \pm 0.01	0.34 \pm 0.02	0.03 \pm 0.00
SPME	29.52 \pm 4.51	73.69 \pm 14.50	8.29 \pm 1.04
BDE 99 ($\times 1000$)			
LLE	0.12 \pm 0.01	0.67 \pm 0.43	0.03 \pm 0.01
SPME	51.07 \pm 5.78	207.39 \pm 51.68	12.15 \pm 1.94
BDE 153 ($\times 1000$)			
LLE	0.11 \pm 0.00	0.85 \pm 0.40	0.03 \pm 0.01
SPME	429.51 \pm 50.14	882.57 \pm 162.98	29.24 \pm 4.85

^aSD = San Diego Creek sediment, Orange County, CA; SP = Salinas Potrero sediment, Santa Rosa, CA; JL = Jordan Lake Reservoir sediment, Chatham County, NC.

Table 2.5. Organic-carbon normalized sediment-water partition coefficient (K_{oc}) and dissolved organic carbon and water partition coefficient (K_{DOC})

	SD ^a sediment		SP sediment		JL sediment	
	Log K_{oc}	Log K_{DOC}	Log K_{oc}	Log K_{DOC}	Log K_{oc}	Log K_{DOC}
BDE 47	6.32 ± 0.06	6.96 ± 0.02	6.46 ± 0.08	6.57 ± 0.10	6.54 ± 0.05	6.96 ± 0.04
BDE 99	6.56 ± 0.05	7.11 ± 0.04	6.91 ± 0.12	6.80 ± 0.29	6.70 ± 0.07	7.09 ± 0.10
BDE 153	7.48 ± 0.05	8.09 ± 0.03	7.54 ± 0.08	7.28 ± 0.19	7.08 ± 0.07	7.46 ± 0.07

^aSD = San Diego Creek sediment, Orange County, CA; SP = Salinas Potrero sediment, Santa Rosa, CA; JL = Jordan Lake Reservoir sediment, Chatham County, NC.

Figures

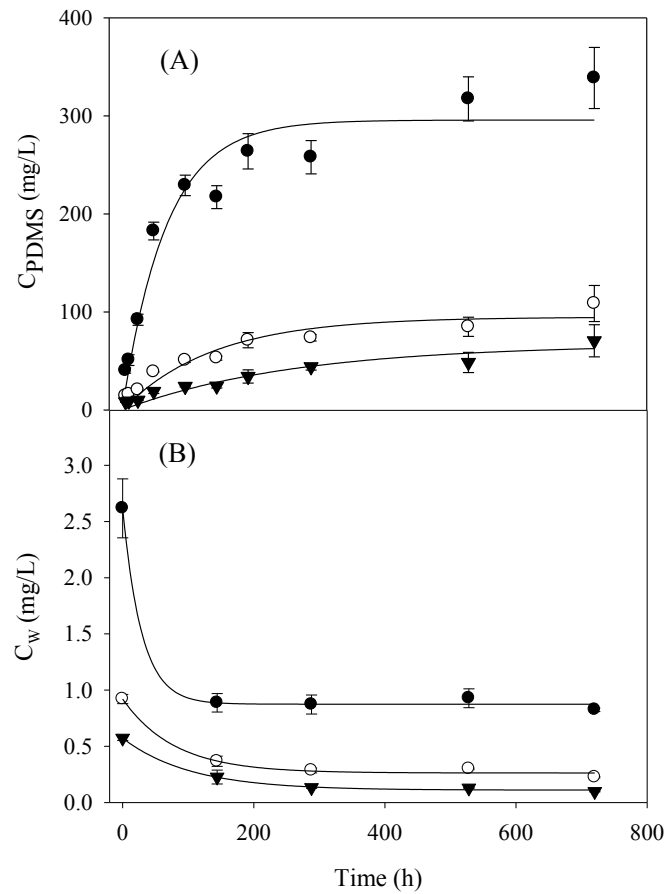


Figure 2.1. (A) Accumulation of BDE 47 (black circle), BDE 99 (white circle), and BDE 153 (black triangle) into the PDMS fibers and (B) depletion of PBDEs from the water phase.

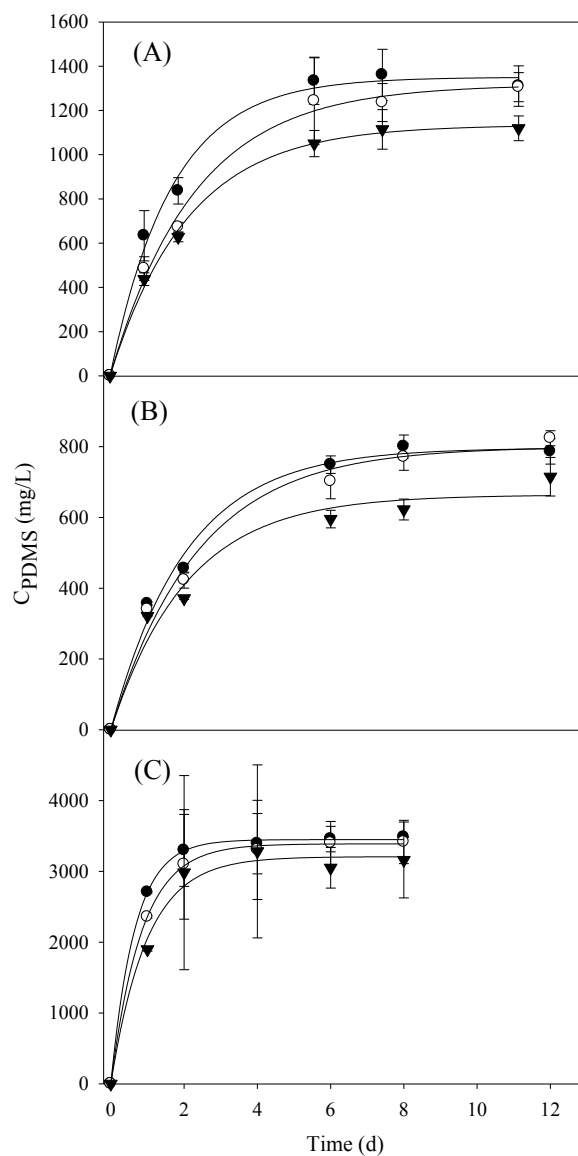


Figure 2.2. Uptake kinetics of BDE 47 (black circle), BDE 99 (white circle), and BDE 153 (black triangle) by PDMS fibers in agitated porewater samples derived from (A) San Diego Creek sediment (SD), (B) Salinas Potrero sediment (SP), and (C) Jordan Lake Reservoir sediment (JL).

Chapter 3 Comparing Black Carbon Types in Sequestering Polybrominated Diphenyl Ethers (PBDEs) in Sediments

3.1. Introduction

Polybrominated diphenyl ethers (PBDEs) are a group of hydrophobic brominated flame retardants used widely in a variety of consumer products ranging from automobile accessories, plastics, textiles, furnishing foams, to electronic appliances to prevent the development of fire (Eguchi et al., 2011; Rahman et al., 2001). There have been primarily three commercial formulations of PBDEs in use, i.e., penta-, octa-, and deca-BDE, among which penta-BDE has attracted more attention because of its dominant global consumption and relatively higher ecological toxicities as compared to the more highly brominated PBDEs (La Guardia et al., 2006). Many PBDE congeners resulting from the penta-BDE formulations have been frequently found in both environmental compartments (Hale et al., 2003; Nylund et al., 1992) and humans (Meironyte et al., 1999; Toms et al., 2009).

Congeners contained in the penta-BDE products are highly hydrophobic with $\log K_{ow} > 6$ for most congeners, and thus they are mainly associated with the bed sediment in the environment (Lacorte et al., 2003; Mai et al., 2005). As demonstrated previously for many other hydrophobic organic contaminants (HOCs, e.g., PCBs, PAHs), the bulk sediment concentration is often a poor indicator of the potential bioavailability of PBDEs to benthic organisms due to their strong interactions with the organic matter phase (Cui et al., 2013; Jia et al., 2012; Liu et al., 2011). Rather, the freely dissolved concentration (C_{free}), which may be measured using passive samplers such as solid phase

microextraction (SPME), has been shown to correlate closely with the bioavailability of HOCs (Oleszczuk et al., 2012). On the other hand, a large number of studies have shown that black carbon (BC) may enhance the sorption or sequestration of HOCs in sediment (Accardi-Dey and Gschwend, 2002; Jeong et al., 2008; Jonker and Koelmans, 2002; Millward et al., 2005; Pignatello et al., 2006; Yang et al., 2009a,b). BC has been used as a remediation option at contaminated sites to sequester HOCs in the bed sediment and reduce their flux to the water column (Beckingham and Ghosh, 2011; Chai et al., 2012; Oen et al., 2012; Werner et al., 2010). However, BC materials vary greatly in their origin and physicochemical properties (e.g., surface area, microporosity) (Chai et al., 2012; Choi et al., 2013; Rakowska et al., 2012), and little is known about their differences in sequestering sediment PBDEs (Barring et al., 2002).

In this study, we developed a matrix-SPME method by using disposable polydimethylsiloxane (PDMS) fibers to measure C_{free} of common penta-BDE congeners in sediments, and then evaluated three different types of BC, i.e., biochar, charcoal, and activated carbon, in their effects on C_{free} in sediments. Findings from this study may be used for optimizing the selection of BC materials in mitigating PBDE contamination in sediments.

3.2. Materials and Methods

3.2.1. Chemicals and PDMS Fiber

Standards of 2,2',4,4'-tetrabromodiphenyl ether (BDE 47), 2,2',3,4,4'-pentabromodiphenyl ether (BDE 85), 2,2',4,4',5-pentabromodiphenyl ether (BDE 99), 2,2',4,4',6-pentabromodiphenyl ether (BDE 100), 2,2',4,4',5,5'-hexabromodiphenyl

ether (BDE 153), and 2,2',4,4',5,6'-hexabromodiphenyl ether (BDE 154) in isooctane (50 µg/mL) were purchased from AccuStandard (New Haven, CT). External surrogate decachlorobiphenyl (PCB 209) was purchased from Fisher Scientific (Pittsburgh, PA). All other solvents and chemicals used in the present study were of analytical or gas chromatography (GC) grade.

Thin fiber (430-µm diameter) coated with 35 µm PDMS was purchased from Polymicro Technologies (Phoenix, AZ). The volume of PDMS polymer coating per length was 51.1 µL/m. The PDMS fibers was pre-cleaned by Soxhlet extraction with ethyl acetate for 72 h and cut into 1-cm pieces with a razor blade before use (Yang et al., 2009c).

3.2.2. Sediments and Black Carbon Materials

Two sediments with no detectable PBDE residues were used, including San Diego Creek sediment (SD, Orange County, CA) and Jordan Lake Reservoir sediment (JL, Chatham County, NC). All sediments were wet-sieved through a 2-mm mesh and stored at 4 °C before use. The sediment OC contents were measured by combustion on a nitrogen-carbon analyzer (Thermo Finnigan, Woods Hole, MA) after removing the inorganic carbon with 1 M HCl. BC content was determined by first combusting in a muffle furnace at 375 °C for 24h, digesting with HCl (1 M), and then analyzing on the elemental analyzer (Gustafsson et al., 1997). The measured OC and BC contents were 0.87% and 0.11% for the SD sediment, and 0.12% and below detection limit for the JL sediment, respectively.

Three different BCs, including activated carbon, charcoal, and biochar were selected based on their different source materials, combustion methods, and wide availability and application. The activated carbon was purchased from Calgon Carbon (Pittsburg, PA). The charcoal was derived from the combustion of macrocarpa in New Zealand at 400 °C. The biochar sample was produced by incomplete combustion of pine chips at 400 °C. All BC materials were ground in a mortar, passed through a No.100 mesh (0.149 mm pore size), and stored at room temperature before use. The OC content of the BC materials was analyzed as mentioned above. The specific surface areas (SSA) and microporosity were determined by Brunauer-Emmett-Teller (BET) nitrogen isotherms using an ASAP-2010 Surface Area Analyzer (Micromeritics, Norcross, GA). The properties of biochar, charcoal, and activated carbon are shown in Table 3.1.

3.2.3. Partition Coefficient (K_{PDMS}) Measurement

When SPME is used for measuring C_{free} , the fiber-water partition coefficient (K_{PDMS}) is critical to interpret the concentration on PDMS fiber (C_{PDMS}). For a certain type of SPME and HOC, the K_{PDMS} is constant at a given temperature. Therefore, the K_{PDMS} for all six PBDE congeners were determined using a single concentration with a previous method (Jia et al., 2012). Briefly, 1.5 L of ultrapure water was spiked with BDE 47, 85, 99, 100, 153, and 154 standards at around 0.5 µg/L using stock solutions made in acetone, while keeping the final acetone concentration in the spiked water at less than 0.1% (v/v). After thorough mixing, 100-mL aliquots of the mixture were dispensed into 125-mL glass jars. One piece of pre-cleaned 1-cm PDMS fiber was placed in each jar. The jars were closed with aluminum foil-lined caps, and agitated on a horizontal shaker

at 120 rpm. A previous study showed that PBDE congeners needed 33 d to reach partition equilibrium between the PDMS fiber and the water phase (Jia et al., 2012). In this study, all jars were shaken for 40 d and then removed for analysis of PBDE concentrations both in the aqueous phase and on the PDMS fiber.

The concentration of PBDEs in water (equivalent to C_{free}) was measured after liquid-liquid extraction (LLE) by mixing 50 mL of the water sample with 50 mL methylene chloride for 1 min in a glass separatory funnel. An aliquot (10 μL) of PCB 209 was added as a recovery surrogate before the extraction. The same extraction procedure was repeated for a total of three times and the combined extract was passed through 20 g anhydrous sodium sulfate into a 250-mL round-bottom flask. The extract was condensed at 35 °C to <10 mL on a vacuumed Rotavapor RE 121 (Buchi, Flawil, St. Gallen, Switzerland), and was further dried under N_2 . The residue was reconstituted in 0.5 mL hexane and transferred to an autosampler vial for analysis on GC-MS. The recoveries of the LLE method were 85.6 – 114.4% for the selected PBDE congeners. The C_{PDMS} was analyzed following a simple solvent extraction procedure. The fibers were first wiped dry with paper towel and transferred into 350- μL glass vial inserts housed in 2-mL autosampler vials, to which 200 μL of hexane was added. The vials were sonicated for 10 min in a Fisher Scientific IS30H ultrasound water bath, from which an aliquot was injected directly for analysis. This procedure gave a recovery of 97 – 113% for the selected PBDE congeners. The C_{PDMS} ($\mu\text{g/L}$) and C_{free} ($\mu\text{g/L}$) at the steady state were used for calculating K_{PDMS} :

$$K_{\text{PDMS}} = \frac{C_{\text{PDMS}}}{C_{\text{free}}} \quad (1)$$

3.2.4. PBDE Uptake Kinetics Experiments

The sediments were spiked with selected PBDE congeners and equilibrated before use for evaluating the uptake kinetics of PBDEs into the PDMS fiber imbedded in the sediment matrix. The PBDE stock solution in acetone was first applied to 10 g of silica sand in a 1.9-L wide mouth jar. The sand was passed through a 0.149-mm mesh before use. After the carrier solvent was removed in the fume hood, 250 g (dry weight equivalent) of sediment was added and mixed thoroughly with a stainless steel spatula. The spiked sediments (around 0.5 mg/kg) were mixed at 120 rpm on a shaker for 7 d. A previous study showed that 7 d was adequate for the spiked chemicals to reach uniform distribution and phase equilibrium in sediment for selected PBDEs (Cui et al., 2011; Jia et al., 2012).

The spiked sediments were used for measuring PBDE uptake kinetics under either mixing or static conditions. Two different sediment-water ratios were used. For the mixing treatment, 2 g (dry weight) of sediment was mixed in a 20-mL glass scintillation vial with 3 mL 0.2% NaN₃ solution. One piece of pre-cleaned SPME fiber (1 cm) was added to each vial. Closed sample vials were mixed on a horizontal shaker at low speed (120 rpm), and three replicate vials were removed at different time intervals up to 28 d. Fibers were extracted and analyzed as described above. The low sediment-water ratio would enhance homogenization and shorten the time to reach equilibrium. For the static treatment, sediment (150 g dry weight) was placed in a 300-mL wide mouth jar. The

sediments were covered with 2 cm water containing 0.2% NaN₃ to mimic field conditions. In order to minimize disturbance to the sediment during sampling, PDMS fibers (1 cm) were tied to a thin polyester thread and pushed into the sediment bed. Sampling continued till 83 d for the static experiment.

3.2.5. Black Carbon Amendment Experiments

To compare the BC materials for their effectiveness in decreasing C_{free} of PBDEs in sediments, the JL and SD sediments were amended with activated carbon, charcoal, or biochar before they were used for the fiber exposure. The sediments were spiked with each PBDE congener at 100 µg/kg and equilibrated for 7 d as described above, and then mixed with activated carbon, charcoal, or biochar at 0 (unamended control), 0.5, 1.0, 1.5, 3.0, and 6.0% based on the sediment dry weight. The BC-amended sediments were mixed for 7 d at 120 rpm to generate PBDE-contaminated sediment samples. An aliquot of the amended sediment (1.0 g, dry weight), one piece of 1-cm PDMS fiber, and 1.5 mL water were placed in a 20-mL glass vial for measuring C_{free} of PBDEs as described above. After 7 d of mixing, the PDMS fibers were retrieved, extracted and analyzed.

3.2.6. Chemical Analysis

The quantitative analysis of PBDEs was carried out on an Agilent 6890 GC coupled with an Agilent 5973 mass spectrometer (Agilent, Santa Clara, CA) or Agilent 6890 GC coupled with electron capture detector (ECD). The instrument conditions for the GC-MS analysis may be found elsewhere (Jia et al., 2012). For the GC-ECD analysis, a DB-5MS capillary column (30 m × 0.25 mm × 0.25 µm) (J&W Scientific, Folsom, CA) was used for separation. A 1-µL aliquot was injected in the inlet at 250 °C and in the

pulsed splitless mode at 50 psi. The oven temperature was initiated at 80 °C for 1 min, then ramped at 20 °C/min to a temperature of 280 °C and held for 5 min, and finally ramped at 2 °C/min to 300 °C and held for 2 min. Helium was used as the carrier gas at a flow rate of 1.0 mL/min. The ECD detector was held at 300 °C and N₂ was used as the makeup gas. External calibration standards were prepared in hexane and analyzed under the same conditions on the same day of sample analysis.

3.2.7. Quality Control and Data Analysis

Several quality control measures were used in the current study. The measurement of K_{PDMS} included six replicates and the standard deviations for each congener were within 0.9-1.8% of the average values. The measurement of PBDE concentrations on the PDMS fibers included three replicates and the standard deviations were within 0.01-16.3% of the average values. The calibration curve was prepared daily and was used only when the regression coefficient was 0.999 or greater. Significance between different treatments was tested using paired *t* test and one-way ANOVA with SPSS 15.0 (SPSS, Chicago, IL).

3.3. Results and Discussion

3.3.1. PDMS-Water Partition Coefficient (K_{PDMS})

The K_{PDMS} was measured under controlled conditions by dividing C_{PDMS} over C_{free} at equilibrium. The average log K_{PDMS} values for BDE 47, 85, 99, 100, 153, and 154 were 5.89, 6.24, 6.68, 6.45, 6.80, and 6.94, respectively. The large K_{PDMS} values suggested a strong affinity of PBDEs for the PDMS polymer (Table 3.2). The partition of PBDE congeners to PDMS polymer followed the same trend as their hydrophobicity or K_{ow} (Jia

et al., 2012). The log K_{ow} values were found to generally follow a linear relationship with the number of Br substitution in PBDEs but was also affected by the position of Br substitutions (Braekevelt et al., 2003). For instance, the derived K_{PDMS} values correlated well ($R^2 = 0.80$, $p < 0.05$) with the log K_{ow} values for the selected PBDEs reported by Braekevelt et al. (2003). The derived K_{PDMS} values were also in good agreement with those reported by ter Laak et al. (2008), where K_{PDMS} values were 5.91, 6.35, and 6.47 for BDE 47, 99, and 153, respectively.

3.3.2. Uptake Kinetics in Sediment

Figure 3.1 shows the uptake of three PBDE congeners from sediment into PDMS fiber under mixing conditions. Under static conditions, equilibrium was not reached even after 83 d (data not shown). In contrast, under mixing conditions, an apparent steady state in PBDE accumulation on the fiber was attained within 7 d for the selected congeners in all sediments. Therefore, 7 d of mixing was used as the time interval for the matrix-SPME method in the subsequent experiments.

The uptake kinetics depended on the physicochemical properties of both the PBDE congeners and the sediment. In the same sediment, the uptake rate consistently followed the order BDE 47 > BDE 99 > BDE 153 (Figure 3.1). For example, in the SD sediment, the time for attaining 95% of the equilibrium (t_{95}) was estimated to be 1.8 d for BDE 47, 4.0 d for BDE 99, and 4.2 d for BDE 153, respectively. This finding was consistent with our previous observation on the uptake of PBDEs from porewater samples (Jia et al., 2012), and may be attributed to the differences in molecular sizes or degrees of Br substitution (Wang et al., 2008). When PDMS fibers were used to sample

PCB congeners in water, the time to reach equilibrium increased from 4 d for PCB 1 to 16 d for PCB 209 (Yang et al., 2006), also suggesting the dependence of the uptake kinetics on molecular weights. Sediment types also affected the time to attain equilibrium on the fiber (Figure 3.1). Accumulation was consistently more rapid in the SD sediment than in the JL sediment for the same PBDE congener. For example, t_{95} values for BDE 99 in the SD and JL sediment were 4.0 d and 6.7 d, respectively. The differences between the sediments may be attributed to the different contents and properties of the dissolved organic matter (DOM) in the sediment porewater. The higher OC content in the SD sediment resulted in a higher DOM level in the sediment porewater, thus facilitating the partitioning equilibrium process of PBDEs to the PDMS fibers (ter Laak et al., 2009).

When the partition of PBDEs into PDMS reached equilibrium, C_{free} of PBDEs in the sediment porewater may be estimated from the derived K_{PDMS} over C_{PDMS} using Equation 1. The estimated C_{free} consistently followed the order of BDE 47 > BDE 99 > BDE 153 in the same sediment. For example, in the SD sediment, the average C_{free} was 15.2, 2.1, and 0.7 ng/L for BDE 47, 99, and 153, respectively, suggesting that adsorption to the sediment phase became more pronounced with highly brominated congeners. The C_{free} values differed significantly between the two sediments for the same congener. For example, C_{free} was 176.8 ± 8.6 , 27.9 ± 1.7 , and 5.5 ± 0.4 ng/L for BDE 47, 99, and 153 in the JL sediment, which were higher than the relative congeners in the SD sediment. The decrease in C_{free} in the SD sediment may be attributed to its relatively higher OC content (0.87% in the SD vs. 0.12% in the JL sediment) and BC content (0.11% in the SD vs. below detection limit in the JL sediment).

3.3.3. Differences among Black Carbon Types in Sequestering PBDEs

At equilibrium, sorption or sequestration of PBDEs by black carbon was reflected in the change their levels detected on the PDMS fiber (C_{PDMS}). In the JL sediment, C_{PDMS} decreased significantly with BC amendment, and the reduction varied among the types of black carbon (Figure 3.2). For example, when the JL sediment was amended with biochar at 0.5%, C_{PDMS} was reduced to 30.0 – 67.8% of the level in the unamended sediment. The effect of charcoal (29.7 – 63.5%) was similar to that of biochar (Figure 3.2). In comparison, much greater decreases in C_{PDMS} consistently occurred in the activated carbon-amended sediment (Figure 3.2). For instance, in the JL sediment containing 0.5% activated carbon, C_{PDMS} decreased to 1.8 – 8.1% of the level in the unamended treatment for the different congeners. On the average, addition of activated carbon at 1.0% resulted in C_{PDMS} decrease to 1.7 – 5.9 % of the control level for the selected BDE congeners, suggesting the much greater ability for activated carbon to sequester PBDEs in the sediment than the other black carbon materials.

As partitioning and micropore-filling (or adsorption) are the two dominant mechanisms for sorption of HOCs on organic sorbents (Kleineidam et al., 2002; Xia and Ball, 1999), it is likely that the OC content and microporosity contributed to the different sequestration efficiencies of the three different types of BC. In particular, the higher sequestration efficiency of activated carbon as compared to biochar or charcoal may be attributed to its microporosity (Table 3.1). The measured BET specific surface area of activated carbon was 19.7 times of biochar and 6.1 times of charcoal. Moreover, the estimated volume of micropores for activated carbon was 15.1 and 5.2 times of that of

biochar and charcoal, respectively (Table 3.1). Similar sorption patterns were previously observed for 1,2-dichlorobenzene, where sorption by activated carbon was 7.4-fold that of charcoal, coinciding with the differences in specific surface area (3.8-fold) and micropore volumes (4.4-fold) (Kleineidam et al., 2002). In the current study, charcoal showed similar inhibitory effect as biochar. However, it is well known that biochar produced from different feed materials or at different pyrolytic temperatures may have different sorption capacities. For instance, biochar showed increased sorption capacity for nitrobenzene with increased pyrolytic temperature from 100 to 700 °C (Chen et al., 2008).

Amending BC in the SD sediment was less effective at decreasing PBDE accumulation on the PDMS fiber than in the JL sediment (Figure 3.3). For example, when the SD sediment was amended with 0.5% biochar or charcoal, C_{PDMS} showed no significant decrease compared to the unamended sediment. When the amendment rate was increased, C_{PDMS} for all PBDEs generally decreased in the SD sediment. However, the amendment-induced decrease in C_{PDMS} was much smaller in the SD sediment than in the JL sediment amended at the same rate (Figures 3.2 and 3.3). When the activated carbon was added at 0.5% to the SD sediment, the accumulation onto the fiber was reduced to 67.8 – 94.6% of that in the unamended sediment, whereas it decreased to 1.8 – 8.1% of the unamended control for the JL sediment. The difference may be again due to the relatively high indigenous OC content in the SD sediment (Cui et al., 2011).

Among the different BDE congeners, the effect of BC on C_{PDMS} followed the order tetra BDEs > penta BDEs > hexa BDEs. For example, in the JL sediment amended

with 6% charcoal, the average accumulation on PDMS fiber decreased to 18.1, 23.1, and 27.0% for tetra BDEs, penta BDEs, and hexa BDEs, respectively. This observation was in agreement with studies on PCB congeners. In Sun and Ghosh (2008), with amendment of activated carbon at 0.5-fold of the indigenous total OC content, the aqueous concentrations of di- and tri- CBs decreased more than 90%, while the decreases were 35 – 57% for tetra- and penta- PCBs. Pore-filling was proposed as the primary mechanism for the sorption of HOCs onto natural organic matter (Ran et al., 2004; Xing et al., 1996). Thus molecular volume (MV) of the sorbate may affect the sorption capacity. The MV of BDE 47 ($770.68 \times 10^{-3}\text{nm}^3$) was smaller than BDE 85 ($856.13 \times 10^{-3}\text{nm}^3$) (Table 3.2), coinciding with the relatively higher sequestration of BDE 47. In addition, biochar and charcoal exhibited different selectivity for PBDE congeners from activated carbon. For instances, in the JL sediment, at lower amendment rates (0.5 and 1.0%), both biochar and charcoal suppressed C_{PDMS} of BDE 47 the most but BDE 153 and 154 the least. However, at higher amendment rates (3.0 and 6.0%), C_{PDMS} of BDE 100 was decreased the most while BDE 85 was decreased the least. Contrary to biochar and charcoal, activated carbon consistently suppressed C_{PDMS} of BDE 47 the most at all amendment levels. Micropore size distribution analysis revealed that the median pore width for activated carbon, biochar, and charcoal was 6.365, 19.004, and 18.900 Å, respectively. Therefore, with abundant smaller micropores, activated carbon likely provided more sorption sites for smaller molecules like BDE 47.

3.3.4. Effect of Black Carbon Amendment on C_{free}

By using the derived K_{PDMS} values, C_{free} of each BDE congener was estimated from C_{PDMS} for the various treatments. Table 3.3 shows C_{free} of each PBDE congener in the unamended sediments and sediments amended with 1% of biochar, charcoal, or activated carbon. In general, in the unamended sediments or biochar (or charcoal) amended treatments, C_{free} in the SD sediment was smaller than that in the JL sediment. For example, the mean C_{free} levels of BDE 99 were 0.58 ± 0.02 and 2.03 ± 0.06 ng/L in the unamended SD and JL sediments, respectively, and they decreased to 0.56 ± 0.01 and 0.63 ± 0.03 ng/L after amending with 1% biochar (Table 3.3). However, in sediments amended with activated carbon, C_{free} of each BDE congener was found to be higher in the SD sediment than that in the JL sediment (Table 3.3). For instance, C_{free} levels of BDE 85 were 1.76 ± 0.01 and 0.24 ± 0.01 ng/L in the SD and JL sediments with 1% activated carbon. This observation was consistent with the above findings that activated carbon reduced the accumulation of PBDEs on the PDMS fiber by a smaller degree in the SD sediment than in the JL sediment, and that the indigenous organic matter in the SD sediment may have masked some of the effect by the extraneous BC. In a previous study, higher OC contents in sediments were also shown to suppress the effect of BC on C_{free} and hence bioavailability of phenanthrene (Cui et al., 2011).

The observation that the decrease in C_{free} depended on both the types of sediment and carbon sorbent has practical implications. In low-OC sediments such as the JL sediment, PBDEs may be readily sequestered with a carbon sorbent. For example, C_{free} of BDE 47 in the unamended JL sediment was 13.84 ± 0.29 ng/L, but it was reduced to 2.54

± 0.01 , 2.50 ± 0.00 , and 0.23 ± 0.00 ng/L with 6% addition of biochar, charcoal, and activated carbon, respectively. Activated carbon evidently is much more efficient at reducing C_{free} of PBDEs than the other BC materials considered in this study, suggesting that a larger quantity of the less efficient biochar or charcoal may have to be used to achieve a similar reduction. In addition, for high-OC sediments such as the SD sediment, BC sorbents may need to be applied at much higher rates, or a more efficient sorbent such as activated carbon, must be used to achieve significant sequestration.

3.4. Conclusions

In this study, a matrix-SPME method was developed for measuring C_{free} of PBDEs in sediments and the method was further used to compare the efficiency of different BC materials in sequestering PBDEs by decreasing C_{free} . Findings from this study showed that although C_{free} of PBDEs was reduced by BC amendment, the reduction varied greatly among different types of BC, with activated carbon showing substantially much greater efficiency than biochar or charcoal. In addition, likely due to the different distributions of their micropores, activated carbon preferentially sequestered low brominated BDEs (e.g., BDE 47), while biochar or charcoal was shown to selectively sorb high brominated BDEs. Reduction of C_{free} by the same BC amendment also differed greatly between sediments, and a higher indigenous OC content appeared to suppress the effect of BC. On the other hand, the sequestration capacity of BC may change as a result of aging effect, as natural organic matter or colloids may either compete for the sorption site or block the micropores. Thus a further understanding of the effect of aging on the

sequestration of PBDEs and other HOCs by BC, and the dependence on BC types, is required before application for *in-situ* remediation of contaminated sediments.

References

- Accardi-Dey, A., Gschwend, P.M., 2002. Assessing the combined roles of natural organic matter and black carbon as sorbents in sediments. *Environmental Science & Technology* 36, 21-29.
- Barring, H., Bucheli, T.D., Broman, D., Gustasson, O., 2002. Soot-water distribution coefficients for polychlorinated dibenzo-p-dioxins, polychlorinated dibenzofurans and polybrominated diphenylethers determined with the soot cosolvency-column method. *Chemosphere* 49, 515-523.
- Beckingham, B., Ghosh, U., 2011. Field-scale reduction of PCB bioavailability with activated carbon amendment to river sediments. *Environmental Science & Technology* 45, 10567-10574.
- Braekvelt, E., Tittlemier, S., Tomy, G., 2003. Direct measurement of octanol-water partition coefficients of some environmentally relevant brominated diphenyl ether congeners. *Chemosphere* 51, 563-567.
- Chai, Y., Currie, R.J., Davis, J.W., Wilken, M., Martin, G.D., Fishman, V.N., Ghosh, U., 2012. Effectiveness of activated carbon and biochar in reducing the availability of polychlorinated dibenzo-p-dioxins/dibenzofurans in soils. *Environmental Science & Technology* 46, 1035-1043.
- Chen, B., Zhou, D., Zhu, L., 2008. Transitional adsorption and partition of nonpolar and polar aromatic contaminants by biochars of pine needles with different pyrolytic temperatures. *Environmental Science & Technology* 42, 5137-5143.

- Choi, Y., Cho, Y.-M., Gala, W.R., Luthy, R.G., 2013. Measurement and modeling of activated carbon performance for the sequestration of parent- and alkylated-polycyclic aromatic hydrocarbons in petroleum-impacted sediments. *Environmental Science & Technology* 47, 1024-1032.
- Cui, X., Jia, F., Chen, Y., Gan, J., 2011. Influence of single-walled carbon nanotubes on microbial availability of phenanthrene in sediment. *Ecotoxicology* 20, 1277-1285.
- Cui, X., Mayer, P., Gan, J., 2013. Methods to assess bioavailability of hydrophobic organic contaminants: principles, operations, and limitations. *Environmental Pollution* 172, 223-234.
- Eguchi, A., Isobe, T., Ramu, K., Tanabe, S., 2011. Optimisation of the analytical method for octa-, nona- and deca-brominated diphenyl ethers using gas chromatography-quadrupole mass spectrometry and isotope dilution. *International Journal of Environmental Analytical Chemistry* 91, 348-356.
- Gustafsson, O., Haghseta, F., Chan, C., MacFarlane, J., Gschwend, P.M., 1997. Quantification of the dilute sedimentary soot phase: Implications for PAH speciation and bioavailability. *Environmental Science & Technology* 31, 203-209.
- Hale, R.C., Alaei, M., Manchester-Neesvig, J.B., Stapleton, H.M., Ikononou, M.G., 2003. Polybrominated diphenyl ether flame retardants in the North American environment. *Environment International* 29, 771-779.
- Jeong, S., Wander, M.M., Kleineidam, S., Grathwohl, P., Ligouis, B., Werth, C.J., 2008. The role of condensed carbonaceous materials on the sorption of hydrophobic

- organic contaminants in subsurface sediments. *Environmental Science & Technology* 42, 1458-1464.
- Jia, F., Cui, X.Y., Wang, W., Delgado-Moreno, L., Gan, J., 2012. Using disposable solid-phase microextraction (SPME) to determine the freely dissolved concentration of polybrominated diphenyl ethers (PBDEs) in sediments. *Environmental Pollution* 167, 34-40.
- Jonker, M., Koelmans, A., 2002. Sorption of polycyclic aromatic hydrocarbons and polychlorinated biphenyls to soot and soot-like materials in the aqueous environment mechanistic considerations. *Environmental Science & Technology* 36, 3725-3734.
- Kleineidam, S., Schuth, C., Grathwohl, P., 2002. Solubility-normalized combined adsorption-partitioning sorption isotherms for organic pollutants. *Environmental Science & Technology* 36, 4689-4697.
- La Guardia, M., Hale, R., Harvey, E., 2006. Detailed polybrominated diphenyl ether (PBDE) congener composition of the widely used penta-, octa-, and deca-PBDE technical flame-retardant mixtures. *Environmental Science & Technology* 40, 6247-6254.
- Lacorte, S., Guillamon, M., Martinez, E., Viana, P., Barcelo, D., 2003. Occurrence and specific congener profile of 40 polybrominated diphenyl ethers in river and coastal sediments from Portugal. *Environmental Science & Technology* 37, 892-898.

- Liu, M., Tian, S., Chen, P., Zhu, L., 2011. Predicting the bioavailability of sediment-associated polybrominated diphenyl ethers using a 45-d sequential Tenax extraction. *Chemosphere* 85, 424-431.
- Mai, B.X., Chen, S.J., Luo, X.J., Chen, L.G., Yang, Q.S., Sheng, G.Y., Peng, P.G., Fu, J.M., Zeng, E.Y., 2005. Distribution of polybrominated diphenyl ethers in sediments of the Pearl River Delta and adjacent South China Sea. *Environmental Science & Technology* 39, 3521-3527.
- Meironyte, D., Noren, K., Bergman, A., 1999. Analysis of polybrominated diphenyl ethers in Swedish human milk. A time-related trend study, 1972-1997. *Journal of Toxicology and Environmental Health-Part A* 58, 329-341.
- Millward, R., Bridges, T., Ghosh, U., Zimmerman, J., Luthy, R., 2005. Addition of activated carbon to sediments to reduce PCB bioaccumulation by a polychaete (*Neanthes arenaceodentata*) and an amphipod (*Leptocheirus plumulosus*). *Environmental Science & Technology* 39, 2880-2887.
- Nylund, K., Asplund, L., Jansson, B., Jonsson, P., Litzen, K., Sellstrom, U., 1992. Analysis of some polyhalogenated organic pollutants in sediment and sewage-sludge. *Chemosphere* 24, 1721-1730.
- Oen, A.M.P., Beckingham, B., Ghosh, U., Krusa, M.E., Luthy, R.G., Hartnik, T., Henriksen, T., Cornelissen, G., 2012. Sorption of organic compounds to fresh and field-aged activated carbons in soils and sediments. *Environmental Science & Technology* 46, 810-817.

- Oleszczuk, P., Hale, S.E., Lehmann, J., Cornelissen, G., 2012. Activated carbon and biochar amendments decrease pore-water concentrations of polycyclic aromatic hydrocarbons (PAHs) in sewage sludge. *Bioresource Technology* 111, 84-91.
- Pignatello, J.J., Kwon, S., Lu, Y., 2006. Effect of natural organic substances on the surface and adsorptive properties of environmental black carbon (char): Attenuation of surface activity by humic and fulvic acids. *Environmental Science & Technology* 40, 7757-7763.
- Rahman, F., Langford, K.H., Scrimshaw, M.D., Lester, J.N., 2001. Polybrominated diphenyl ether (PBDE) flame retardants. *Science of the Total Environment* 275, 1-17.
- Rakowska, M.I., Kupryianchyk, D., Harmsen, J., Grotenhuis, T., Koelmans, A.A., 2012. In situ remediation of contaminated sediments using carbonaceous materials. *Environmental Toxicology and Chemistry* 31, 693-704.
- Ran, Y., Xing, B.S., Rao, P.S.C., Fu, J.M., 2004. Importance of adsorption (hole-filling) mechanism for hydrophobic organic contaminants on an aquifer kerogen isolate. *Environmental Science & Technology* 38, 4340-4348.
- Sun, X., Ghosh, U., 2008. The effect of activated carbon on partitioning, desorption, and biouptake of native polychlorinated biphenyls in four freshwater sediments. *Environmental Toxicology and Chemistry* 27, 2287-2295.
- ter Laak, T.L., Busser, F.J.M., Hermens, J.L.M., 2008. Poly(dimethylsiloxane) as passive sampler material for hydrophobic chemicals: Effect of chemical properties and

- sampler characteristics on partitioning and equilibration times. *Analytical Chemistry* 80, 3859-3866.
- ter Laak, T.L., Van Eijkeren, J.C.H., Busser, F.J.M., Van Leeuwen, H.P., Hermens, J.L.M., 2009. Facilitated transport of polychlorinated biphenyls and polybrominated diphenyl ethers by dissolved organic matter. *Environmental Science & Technology* 43, 1379-1385.
- Toms, L.-M.L., Hearn, L., Kennedy, K., Harden, F., Bartkow, M., Temme, C., Mueller, J.F., 2009. Concentrations of polybrominated diphenyl ethers (PBDEs) in matched samples of human milk, dust and indoor air. *Environment International* 35, 864-869.
- Wang, Z.Y., Zeng, X.L., Zhai, Z.C., 2008. Prediction of supercooled liquid vapor pressures and n-octanol/air partition coefficients for polybrominated diphenyl ethers by means of molecular descriptors from DFT method. *Science of the Total Environment* 389, 296-305.
- Werner, D., Hale, S.E., Ghosh, U., Luthy, R.G., 2010. Polychlorinated biphenyl sorption and availability in field-contaminated sediments. *Environmental Science & Technology* 44, 2809-2815.
- Xia, G.S., Ball, W.P., 1999. Adsorption-partitioning uptake of nine low-polarity organic chemicals on a natural sorbent. *Environmental Science & Technology* 33, 262-269.

- Xing, B.S., Pignatello, J.J., Gigliotti, B., 1996. Competitive sorption between atrazine and other organic compounds in soils and model sorbents. *Environmental Science & Technology* 30, 2432-2440.
- Yang, Y., Hunter, W., Tao, S., Crowley, D., Gan, J., 2009a. Effect of activated carbon on microbial bioavailability of phenanthrene in soils. *Environmental Toxicology and Chemistry* 28, 2283-2288.
- Yang, Y., Hunter, W., Tao, S., Gan, J., 2009b. Effects of black carbon on pyrethroid availability in sediment. *Journal of Agricultural and Food Chemistry* 57, 232-238.
- Yang, Y., Hunter, W., Tao, S., Gan, J., 2009c. Microbial availability of different forms of phenanthrene in soils. *Environmental Science & Technology* 43, 1852-1857.
- Yang, Z.Y., Zeng, E.Y., Xia, H., Wang, J.Z., Mai, B.X., Maruya, K.A., 2006. Application of a static solid-phase microextraction procedure combined with liquid-liquid extraction to determine poly(dimethyl)siloxane-water partition coefficients for selected polychlorinated biphenyls. *Journal of Chromatography A* 1116, 240-247.
- Yu, Y.-X., Zhang, S.-H., Huang, N.-B., Li, J.-L., Pang, Y.-P., Zhang, X.-Y., Yu, Z.-Q., Xu, Z.-G., 2012. Polybrominated diphenyl ethers and polychlorinated biphenyls in freshwater fish from Taihu Lake, China: Their levels and the factors that influence biomagnification. *Environmental Toxicology and Chemistry* 31, 542-549.

Tables

Table 3.1. Properties of biochar, charcoal and activated carbon

	OC (%)	SSA ^a	Volume _{total} ^b	Volume _{micro} ^c
Biochar	71.7 ± 0.8	35.9	19.5	8.3
Charcoal	84.7 ± 0.6	116.6	56.9	42.4
Activated Carbon	87.0 ± 0.5	706.2	294.6	162.2

^aSSA, BET specific surface area (m²g⁻¹)

^bVolume_{total}, the total pore volumes (cm³g⁻¹) measured with N₂

^cVolume_{micro}, the total micropore volumes (cm³g⁻¹) measured with N₂

Table 3.2. Measured PDMS-Water partition coefficients ($\log K_{\text{PDMS}}$) of PBDEs

	BDE 47	BDE 85	BDE 99	BDE 100	BDE 153	BDE 154
Name	2,2',4,4'-tetraBDE	2,2',3,4,4'-pentaBDE	2,2',4,4',5-pentaBDE	2,2',4,4',6-pentaBDE	2,2',4,4',5,5'-hexaBDE	2,2',4,4',5,6'-hexaBDE
No. of Br	4	5	5	5	6	6
MV ^a	770.68	856.13	853.92	844.47	902.27	892.00
Log K_{PDMS} (N=6)	5.89 ± 0.07	6.24 ± 0.08	6.68 ± 0.12	6.45 ± 0.06	6.80 ± 0.12	6.94 ± 0.08
log K_{ow} ^b	6.81 ± 0.08	7.37 ± 0.12	7.32 ± 0.14	7.24 ± 0.16	7.90 ± 0.14	7.82 ± 0.16

^aMV, molecular volume, 10^{-3} nm^3 (Yu et al., 2012)

^bValues measured using the slow-stir method (Braekevelt et al., 2003)

Table 3.3. The freely dissolved concentrations of PBDEs (C_{free} , ng/L) in unamended sediments and sediments amended with 1% of biochar, charcoal or activated carbon

Congener	Unamended	Biochar	Charcoal	Activated Carbon
San Diego Creek Sediment				
BDE 47	2.82±0.14	2.51±0.07	2.56±0.06	1.87±0.00
BDE 85	1.95±0.04	1.90±0.02	1.92±0.02	1.76±0.01
BDE 99	0.58±0.02	0.56±0.01	0.57±0.02	0.46±0.00
BDE 100	0.85±0.05	0.83±0.04	0.88±0.05	0.59±0.01
BDE 153	0.55±0.01	0.54±0.01	0.55±0.01	0.50±0.00
BDE 154	0.35±0.01	0.35±0.01	0.36±0.01	0.31±0.01
Jordan Lake Sediment				
BDE 47	13.84±0.29	3.05±0.09	3.11±0.11	0.24±0.00
BDE 85	4.03±0.09	1.91±0.02	1.94±0.05	0.24±0.01
BDE 99	2.03±0.06	0.63±0.03	0.64±0.04	0.07±0.00
BDE 100	4.23±0.14	1.38±0.11	1.50±0.12	0.09±0.00
BDE 153	1.28±0.05	0.64±0.02	0.64±0.03	0.07±0.00
BDE 154	1.17±0.06	0.62±0.02	0.62±0.02	0.05±0.00

Figures

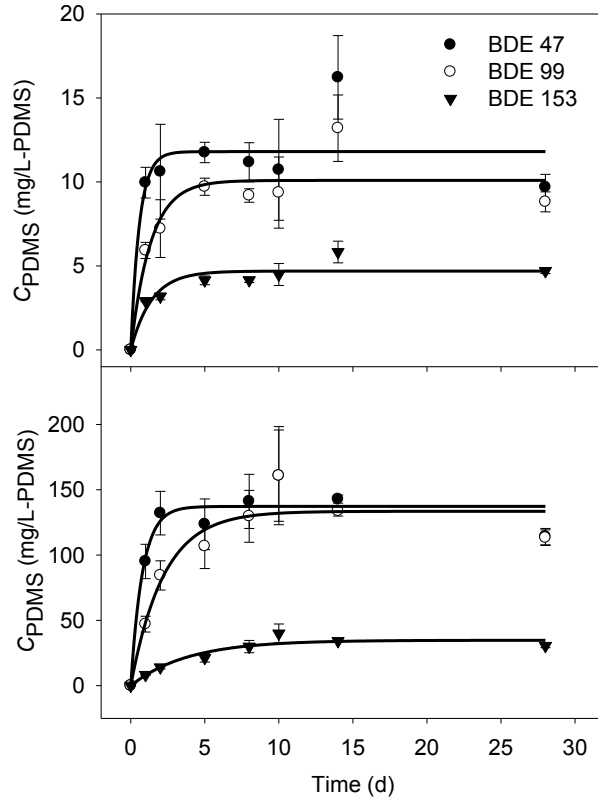


Figure 3.1. Uptake kinetics of BDE 47 (black circle), BDE 99 (white circle), and BDE 153 (black triangle) by PDMS fibers in sediments under mixing conditions.

San Diego Creek sediment (SD) (A); and Jordan Lake Reservoir sediment (JL) (B).

The data was fitted to a one-compartment rise to maximum equation to determine the

time to reach equilibrium: $C_{PDMS,t} = C_{PDMS,eq} \times (1 - e^{-kt})$, where $C_{PDMS,t}$ (mg/L) is the PBDE concentration on PDMS fiber at time t (d), $C_{PDMS,eq}$ is the PBDE concentration on PDMS fiber at equilibrium, and k (d^{-1}) is the uptake rate constant.

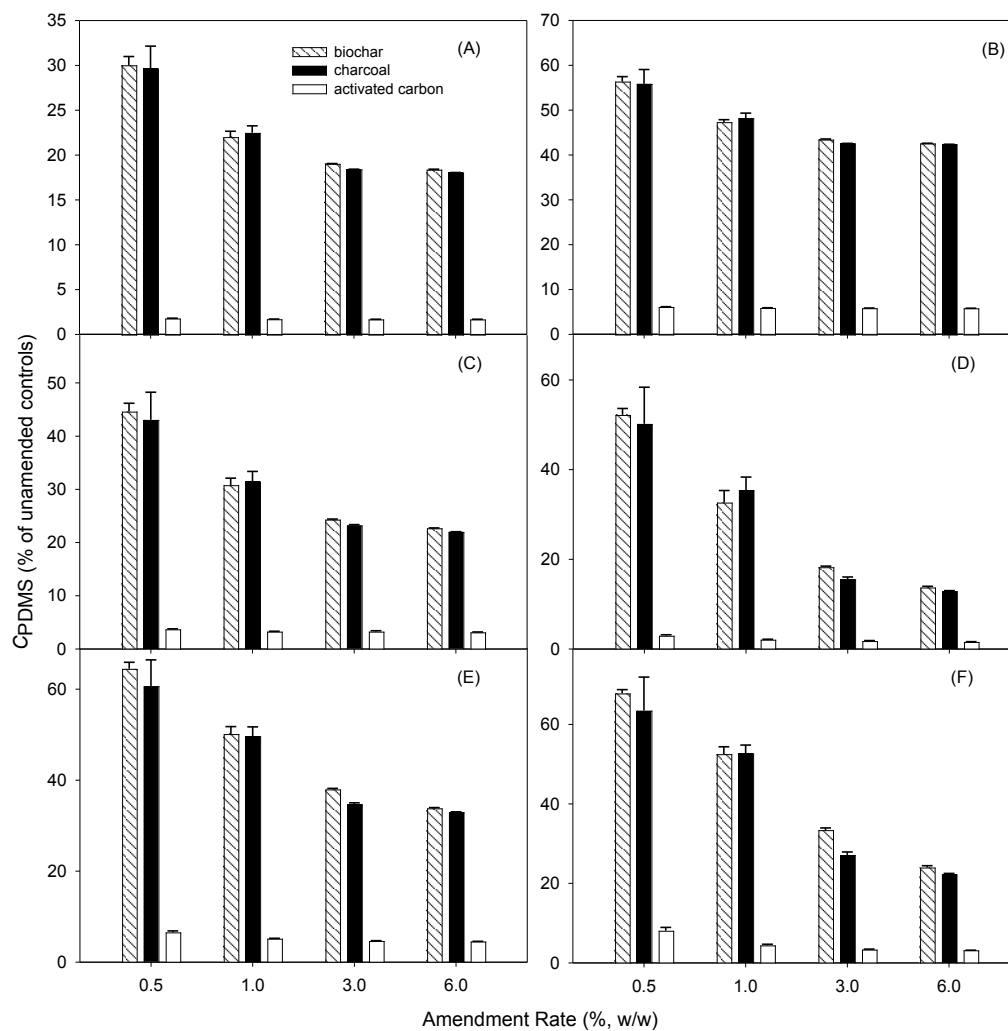


Figure 3.2. Concentrations of BDE 47 (A), 85 (B), 99 (C), 100 (D), 153 (E), and 154 (F) on PDMS fibers in Jordan Lake Reservoir sediment amended with different types of black carbon relative to the unamended controls.

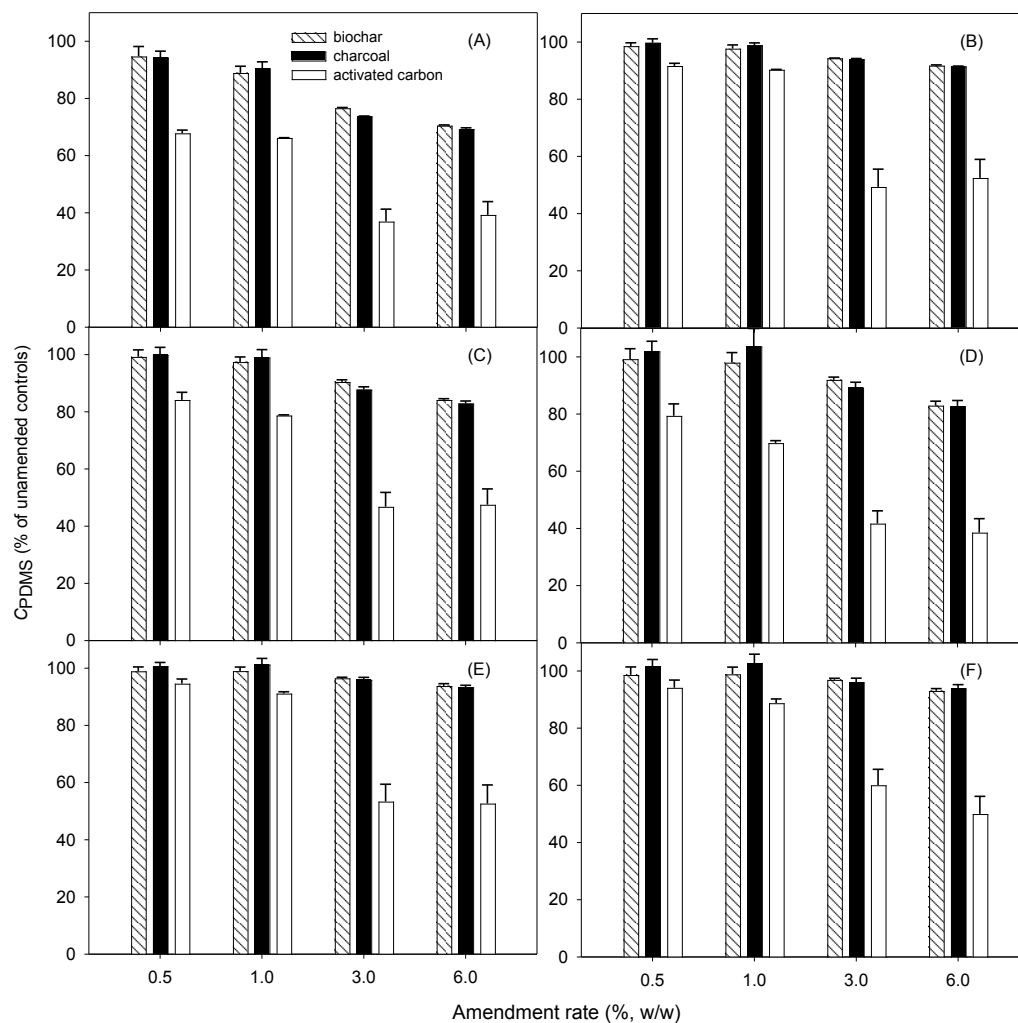


Figure 3.3. Concentrations of BDE 47 (A), 85 (B), 99 (C), 100 (D), 153 (E), and 154 (F) on the PDMS fibers in San Diego Creek sediment amended with different types of black carbon.

Chapter 4 Use of Isotope Dilution Method (IDM) to Predict Bioavailability of Organic Contaminants in Historically Contaminated Sediments

4.1. Introduction

Due to their high affinity for solid particles, hydrophobic organic contaminants (HOCs) preferentially deposit in soil or sediment in the environment, where they may cause direct ecological effects or become secondary contamination sources. As shown in recent studies, HOCs in the soil or sediment are distributed in heterogeneous regions of organic matter (Cornelissen et al., 2005; Luthy et al., 1997; Pignatello and Xing, 1996). Sequestration of HOCs in the “glassy” region of organic matter may lead to irreversible sorption or reduced bioaccessibility (Cornelissen et al., 2005; Luthy et al., 1997; Xing and Pignatello, 1997). Therefore, the use of the bulk chemical concentration may not convey the actual risk, because the total concentration could substantially over-express bioavailability (Ehlers and Luthy, 2003). Thus, predicting bioavailability that quantifies the actual amount of HOCs available for bioaccumulation or eliciting toxicity is essential for improving risk assessment (Reichenberg and Mayer, 2006).

Changes in bioavailability may be especially pronounced for recalcitrant HOCs (e.g., DDT, PCBs, PAHs) from historical contamination episodes, because aging and other sequestration processes are known to decrease contaminant bioavailability (Cornelissen et al., 2005; Hatzinger and Alexander, 1995; Tomaszewski et al., 2007). Methods such as mild solvent extraction and sequential desorption have been previously tested for measuring HOC bioaccessibility. In mild extraction, a variety of “soft” solvents (e.g., *n*-butanol, methanol, ethyl acetate) are used to estimate the readily extractable

fraction as an approximation of the bioavailable concentration (Kelsey et al., 1997; Khan et al., 2012; Tang and Alexander, 1999). However, in such applications, the measured value invariably depends on the strength of the selected solvent (Reichenberg and Mayer, 2006). Sequential desorption employing sorbents such as Tenax and cyclodextrin has also been used in many studies, where the polymeric sorbent traps the desorbed HOC to facilitate desorption measurement (Cornelissen et al., 2001; Cornelissen et al., 1997; Reid et al., 2000). However, the sequential desorption approach is extremely time consuming and laborious (Cornelissen et al., 2001). As an alternative, a single-point Tenax desorption has been tested (Cornelissen et al., 2001; Landrum et al., 2007), but studies comparing the single- and serial desorption schemes often showed under- or over-estimations (Cornelissen et al., 2001; Yang et al., 2008). Therefore, there is a great impetus to identify a simple and readily adoptable method for predicting bioaccessibility of HOCs in soil or sediment.

We recently explored the use of isotope dilution for predicting bioavailability of HOCs and evaluated the method using bifenthrin and pyrene as model contaminants in laboratory spiked freshwater sediments (Delgado-Moreno and Gan, 2013). The principle of isotope exchange was previously used for measuring metal bioavailability (Ahnstrom and Parker, 2001; Huang et al., 2011; Nolan et al., 2005; Sivry et al., 2011; Sterckeman et al., 2009; Tongtavee et al., 2005). However, sorption of metals to soil or sediment is known to differ mechanistically from that of organic molecules, as metal ions are adsorbed to specific charged sites (Davis and Leckie, 1978; Naidu and Harter, 1998). In this study, we extended the isotope dilution method (IDM) to sediments historically

contaminated with recalcitrant HOCs. Specifically, we evaluated the validity and performance of IDM for marine sediments from a Superfund site contaminated with DDT and PCBs from many decades ago, and demonstrated the predictability of IDM for contaminant bioavailability in extensively aged matrices.

4.2. Materials and Methods

4.2.1. Chemicals and Sediments

Seven legacy HOCs, including four DDT derivatives (*o,p'*-DDE, *p,p'*-DDE, *o,p'*-DDD and *p,p'*-DDD, denoted as DDXs) and three PCB congeners (PCB 52, PCB 70 and PCB 153), were considered in this study. Standards of PCB 67 and PCB 191 were used as external (recovery) surrogates, and PCB 30 and PCB 82 as internal standards. Stable isotope labeled HOCs (denoted as *HOCs herein) including ^{13}C -*o,p'*-DDD, ^{13}C -*o,p'*-DDE, ^{13}C -PCB 52, ^{13}C -PCB 153 and deuterated compounds *p,p'*-DDD-d₈, *p,p'*-DDE-d₄, and PCB 70-d₃ were used in the IDM method development and evaluation. Sources and purities of these chemicals may be found in the Supporting Information (SI).

Marine sediments (0-15 cm) historically contaminated with DDT and PCBs were collected at two sites (denoted as PV6C and PV8C) of the Palos Verdes Shelf (PVS) Superfund site off the coast of Los Angeles, California. Both sediments were sieved through a 2-mm mesh and stored at 4 °C before use. Contamination of the PVS ocean floor was due to many decades of discharge of wastewater by the Los Angeles County Sanitation District and disposal of wastewater containing DDT by the Montrose Chemical Company, once the largest DDT manufacturer in North America, from 1950s to 1970s. As a result, the PVS Superfund site encompasses about 44 km² of sediment that

is heavily contaminated with DDXs and PCBs. In some areas, levels of DDXs were as high as 200 mg/kg (U.S. EPA, 2009 and 2013). Monitoring showed that DDXs and PCBs at PVS have the potential to accumulate into marine benthic invertebrates and fish, posing human health risks via dietary exposure. The PV8C sediment was collected from the hot spot near the outfalls, whereas the PV6C sediment was relatively less contaminated (U.S. EPA, 2013). Sediment properties (texture and organic carbon content) were analyzed at the University of California Davis Analytical Laboratory using standard methods (Davis, CA). The measured organic carbon (OC) contents of PV6C and PV8C were 2.34% and 3.54%, respectively. The sand, silt, and clay contents were 36%, 51%, and 13% for PV6C, and 48%, 39%, and 13% for the PV8C sediment, respectively.

4.2.2. Characterization of HOC Phase Distribution

A batch equilibration experiment was carried out to determine the time for each native HOC to reach sorption equilibrium, and the apparent sediment-water partition coefficient K_d . Briefly, 2 g of the homogenized PV8C sediment (dry weight basis) was placed in 50-mL glass centrifuge tube and 20 mL of 32 ‰ artificial seawater containing 200 mg/L sodium azide was added. The tubes were sealed with aluminum foil lined caps and mixed at 120 rpm on a horizontal shaker. After 0.5, 1, 2, 4, 6, 12, 24, 48, or 96 h of mixing, triplicate samples were removed and centrifuged at 670 g for 30 min for phase separation. A similar protocol was used for the PV6C sediment, except that the samples were retrieved after 12, 24, and 48 h of mixing.

After centrifugation, the supernatant was collected and extracted using a liquid-liquid extraction (LLE) method. The details of the LLE method are given in SI. The final

extracts were reconstituted in 200 μL hexane. After addition of internal standards, an aliquot of the final extract was analyzed on a Varian 3800 GC equipped with a Varian 1200 triple quadrupole mass spectrometer (GC-MS/MS) (Varian, Sunnyvale, CA). Details of the instrumental analysis are provided in SI. Sediment samples were freeze-dried, and then extracted following a modified EPA method 3620C. The details of sediment extraction and method performance may be found in SI. The final extracts were reconstituted in 1 mL hexane and analyzed by GC-MS/MS.

4.2.3. Development of Isotope Dilution Method (IDM)

In the use of IDM for bioaccessibility prediction, the fraction of native HOC reversibly sorbed may be inferred from the sorption of the externally added, isotope-labeled HOC counterparts ($^*\text{HOC}$). The principle of IDM is based on assumptions that $^*\text{HOC}$ s added to the sediment distribute themselves just between the aqueous phase and the labile fraction after short-term mixing, and that the addition of $^*\text{HOC}$ s does not modify equilibrium of the native HOCs. Under these assumptions, the distribution of native HOCs in sediment may be expressed as:

$$C_T = (D \times C_w) + C_s^e + C_s^{\text{ne}} \quad (1)$$

where C_T ($\mu\text{g}/\text{kg}$) is the total HOC concentration in sediment, C_w ($\mu\text{g}/\text{L}$) is the HOC concentration in the solution phase, C_s^e ($\mu\text{g}/\text{kg}$) is the accessible concentration of sediment-sorbed HOC, C_s^{ne} ($\mu\text{g}/\text{kg}$) is the non-accessible concentration of sediment-sorbed HOCs, and D (L/kg) is the dilution factor equaling the ratio of the solution volume to the solid mass. The overall accessible concentration C_e ($\mu\text{g}/\text{kg}$) in sediment is:

$$C_e = (D \times C_w) + C_s^e \quad (2)$$

Thus, when the ^{*}HOC is introduced into a sediment-water binary system, it will readily redistribute itself between the solution and labile phases, which are in dynamic equilibrium:

$$\frac{{}^*C_w}{{}^*C_s^e} = \frac{C_w}{C_s^e} \quad (3)$$

where ^{*}C_w (μg/L) is the concentration of ^{*}HOC in the solution and ^{*}C_s^e (μg/kg) is the sorbed concentration of ^{*}HOC. The total concentration of ^{*}HOC in sediment (^{*}C₀, μg/kg) is:

$${}^*C_0 = D \times {}^*C_w + {}^*C_s^e \quad (4)$$

Combining Eq. 3 and 4, ^{*}C_s^e may be given as:

$$C_s^e = \frac{C_w}{{}^*C_w} \times ({}^*C_0 - D \times {}^*C_w) \quad (5)$$

Combining Eq. 2 and 5, accessible concentration C_e may be given as:

$$C_e = (D \times C_w) + C_s^e = \frac{C_w}{{}^*C_w} \times {}^*C_0 \quad (6)$$

Furthermore, the ratio of C_e over the total chemical concentration C_T gives the accessible fraction of the HOC, E:

$$E = \frac{C_e}{C_T} \quad (7)$$

A similar protocol to the above batch equilibration experiment was followed to evaluate partition kinetics of externally added ^{*}HOCs, and to estimate C_e and E from

simultaneous measurements of C_w and *C_w . Briefly, to a 2 g sediment and 20.0 mL artificial seawater, 10 μ L of a working solution containing each stable isotope-labeled HOC at 5 mg/L was added. The sediment-water slurry was mixed at 120 rpm on a horizontal shaker. Triplicate samples were removed after 0, 0.5, 2, 4, 6, 12, 24, 48, 96, or 192 h for both PV8C and PV6C sediments. Samples were centrifuged at 670 g for 30 min for phase separation and the supernatant was collected. Both the sediment and supernatant were separately analyzed for levels of HOCs following the same methods as described above. Determination of * HOCs in both the solution and solid phases allowed construction of isotope dilution kinetics and estimation of the time for isotope tracers to reach dilution equilibrium. When * HOCs in the aqueous phase reached a steady state, the measured C_w and *C_w , along with *C_0 were used to calculate C_e and E of the native HOCs in the target sediment samples using Eqs. 6 and 7.

4.2.4. Tenax-aided Desorption Experiment

To validate the performance of IDM, the same sediment samples were subjected to sequential desorption in which Tenax beads were used to recover the desorbed HOCs to facilitate measurement. Tenax-aided desorption has been previously used in a number of studies and fit of the desorption curve to a three-phase model gives estimates of the relative distribution of sorbed-HOCs in the rapid, slow and very slow desorption pools (Cornelissen et al., 2001; Cornelissen et al., 1997; Reid et al., 2000). Briefly, a 2-g aliquot of sediment was placed in a 50-mL polyethylene centrifuge tube. Tenax beads (0.15 g, Scientific Instrument Services, Ringoes, NJ) and 20 mL artificial seawater with 200 mg/L sodium azide were added. The tube was closed and mixed horizontally on a

mechanical shaker. For PV6C, after 1, 2, 6, 12, 24, 48, 96, 144, 192, or 312 h of shaking, the sample with Tenax was centrifuged at 670 *g* for 30-min. The Tenax beads were collected by passing the supernatant through a Whatman No. 41 filter paper (Whatman, Maidstone, UK). The trapped beads were rinsed thoroughly with the deionized water and air-dried before they were transferred to 20-mL glass vials, and then mixed in 3 mL of acetone-hexane (1:1, v:v) , followed by sonication in a Fisher Sonic 550 water bath for 5 min. The extraction was repeated for three times. The extracts were combined, concentrated under N₂ to near dryness, and reconstituted in 1 mL of hexane. The desorption step was repeated sequentially for additional increments. A similar protocol was used for PV8C sediment. However, owing to its high levels of DDXs and PCBs, the sequential desorption was continued up to 837 h to obtain the entire desorption kinetics.

The desorption kinetics up to 312 h for the PV6C sediment and up to 837 h for the PV8C sediment were used to construct the desorption curve and for estimating the rapid (F_r), slow (F_s), and very slow (F_{vs}) desorption fractions by fitting data to a triphasic model (Cornelissen et al., 1997) using SigmaPlot 11.0 (San Jose, CA):

$$\frac{S_t}{S_0} = F_r e^{-k_r t} + F_s e^{-k_s t} + F_{vs} e^{-k_{vs} t} \quad (8)$$

$$F_r + F_s + F_{vs} = 1 \quad (9)$$

where S_t and S_0 ($\mu\text{g}/\text{kg}$) are concentrations of HOCs in sediment after desorption time interval t (h) and before the initiation of desorption, respectively, and k_r , k_s , and k_{vs} are the rate constants (h^{-1}) for the rapid, slow and very slow desorption fractions, respectively.

4.2.5. Bioaccumulation Experiment

The usefulness of IDM was further demonstrated by evaluating the correlation between C_e and uptake of HOCs into a marine deposit feeder *Neanthes arenaceodentata*. The selected marine polychaete is a predominant benthic invertebrate in the surface and subsurface macrofauna community in the PVS area and is an important food source for the bottom feeding flatfish California halibut (*Paralichthys californicus*) (Anderson et al., 1998). The overall method for the bioaccumulation test was modified from the American Society for Testing and Materials (ASTM) sediment toxicity test with polychaetous annelids (ASTM, 2013). Briefly, 2-3 week old *N. arenaceodentata* worms (Aquatic Toxic Support, Bremerton, WA) were acclimated in aerated artificial seawater at the room temperature ($20 \pm 1^\circ\text{C}$) for 1 wk and fed with dry algae. After the acclimation, 15 worms were transferred to a 1-L beaker containing 20 g (dry weight basis) of PV8C or PV6C sediment and 350 mL artificial seawater. The worms were exposed at 20°C for 4 d with air bubbled into the overlying water. The water level, salinity, and ammonia contents were checked daily and kept constant throughout the exposure. A control group without exposure to the sediment was included. After 4-d of exposure, the worms were retrieved by sieving and depurated in clean artificial seawater (32‰) for 48 h. The analysis of the tissue samples for DDXs and PCBs and lipid content are given in SI.

4.2.6. Quality Assurance and Quality Control

Several practices were used to assure the accuracy and reproducibility of sample analysis. First, the recoveries of target HOCs and surrogate standards spiked in the sediment and worm tissue samples were verified in method development (SI). Second,

both external surrogates and internal standards were spiked in all samples to monitor the extraction efficiency and check for instrument drift insensitivity (SI). In addition, a laboratory blank was included with every batch of 9 samples to monitor for potential contamination from laboratory materials and solvents. Furthermore, a standard reference material, SRM 1947 Lake Michigan Fish Tissue, was purchased from the National Institute of Standards and Technology (NIST) and used for validating the analysis of tissue samples of *N. arenaceodentata* in this study. The calibration curve standards were prepared daily and were used only when the regression coefficient was greater than 0.999. Difference between different treatments was determined by one-way analysis of variance (ANOVA) and Tukey test, using SPSS 15.0 (SPSS, Chicago, IL).

4.3. Results and Discussion

4.3.1. Phase Partition Kinetics

The measurement of DDXs and PCBs in the sediment phase (C_s) and in the aqueous phase (C_w) over time allowed the characterization of phase distribution kinetics of the extensively aged HOCs in the marine sediments. Figures S4.1 and S4.2 display the relative phase distribution of HOCs in the PV8C and PV6C sediments at different time intervals. In the PV8C sediment, an apparent phase equilibrium was reached within 12 h of mixing and K_d remained constant for up to 96 h. One-way ANOVA analysis showed that there was no difference among the distribution values beyond 12 h for PCBs ($p = 0.163 - 0.365$), DDEs ($p = 0.227 - 0.528$) or DDDs ($p = 0.433 - 0.911$). In the PV6C sediment (Figure S4.2), it appears that *o,p'*-DDD and *p,p'*-DDD reached an apparent equilibrium within 12 h, while all PCBs and DDEs reached a steady state after 24 h. This

observation was in agreement with other studies, where phase equilibrium was reached between sediment and liquid phases for DDT and its metabolites within 4 h (Van den Hoop et al., 1999). Therefore, 24 h was considered as the time duration adequate for achieving phase distribution equilibrium for the native HOCs in the historically contaminated sediments in this study.

The time necessary for the externally added * HOCs to reach phase distribution equilibrium was subsequently determined. Upon introduction to the sediment slurry, * HOCs rapidly partitioned to the sediment phase and an apparent phase distribution equilibrium was reached after a short period of mixing. Figure 4.1 shows the changes of aqueous ($^*C_w/^*C_0$) or sediment phase fraction ($^*C_s/^*C_0$) of ^{13}C -PCB 52 and d_8-p,p' -DDE as a function of mixing time. The kinetics of other * HOCs may be found in SI (Figure S4.3). The strong sorption of * PCBs and * DDXs to the sediment resulted in rapid dilution of the added isotope tracers in the aqueous phase, as reflected from the rapid decreases in $^*C_w/^*C_0$ (Figure 4.1). For example, after 2 h of mixing, 90.2% and 89.1% of the initially added ^{13}C -PCB 52 and d_8-p,p' -DDE were found in the sediment phase for the PV8C sediment, or the original concentration in the solution phase was diluted by 10.2 and 9.1 times, respectively. High percentages of dilution were also found for the other isotope labeled HOCs (7.9 – 28.9 fold) in the PV8C sediment at 2 h (Figure S4.3). Fast partitioning of * HOCs was also observed for the PV6C sediment (Figure S4.4). Dilution beyond 2 h interval was much more gradual. From 24 to 192 h, the fractions of * HOCs in both sediment and aqueous phases were essentially constant, suggesting that phase distribution of the isotope tracers reached an apparent equilibrium. One-way ANOVA

analysis showed no significant change in the fraction of *HOCs in the sediment or solution phases ($p = 0.276 - 0.890$ for *PCBs, $p = 0.536 - 0.624$ for *DDEs and $p = 0.388 - 0.769$ for *DDD) for the PV8C sediment between 24 and 192 h (Figures 4.1 and S4.3). Similar results ($p = 0.109 - 0.878$) were also observed for the PV6C sediment (Figure S4.4). At the steady state, less than 2% of the introduced *HOCs remained in the aqueous phase for both PV8C and PV6C sediments.

The K_d values calculated for native HOCs using the derived C_s and C_w (Figure S4.5) showed no detectable influence from the addition of isotope analogues. The K_d values of each HOC obtained from the previous batch sorption experiment and the ones after the addition of isotope tracers were found to be essentially identical (Table 4.1 and Table S4.2). This finding suggested that addition of isotope tracers did not alter the phase distribution of the native HOCs, validating one of the prerequisites for IDM. This was expected as the tracers were isotope labeled counterparts of the native HOCs and should have very similar physico-chemical properties (Mechlinska et al., 2010).

4.3.2. Accessibility of HOCs Estimated by Isotope Dilution Method (IDM)

When the isotope dilution reached an apparent equilibrium (e.g., ≥ 24 h), the accessible concentration C_e was estimated using Eq. 6 with the derived C_w , *C_w , and *C_0 (pre-determined). The C_e values of PCBs or DDXs in PV8C were much higher than those in PV6C (Table 4.2), which coincided with the overall higher contamination levels of HOCs at the PV8C location (U.S. EPA, 2013). The overall C_e of DDXs and PCBs were estimated at 14052 and 223 $\mu\text{g}/\text{kg}$ for the PV8C sediments, respectively, which was

consistent with the overall higher levels of DDXs in these sediments than PCBs (U.S. EPA, 2009 and 2013).

The relative accessibility E was calculated as the ratio of C_e over C_T for each HOC in the sediments (Table 4.2). The use of E eliminated the effect of different contamination levels, allowing more straightforward comparison of contaminant accessibility. The derived E values were all smaller than 1, with most E values < 0.50 for the HOCs in the PV8C sediment (Table 4.2), clearly suggesting that a significant fraction of the native HOCs was in regions of sediment that were not accessible by the externally added *HOCs. The derived E values of PCBs and DDXs in the PV8C sediment were consistently smaller than those in the PV6C sediment, which may be attributed to the higher OC content in the PV8C sediment (3.54%) as compared to that in the PV6C sediment (2.34 %). For example, the averaged E values of DDEs and DDDs were 0.37 and 0.28, respectively, in the PV8C sediment, which were smaller than those in the PV6C sediment (0.60 for DDEs and 0.65 for DDDs). In the same sediment, E also varied among the different HOCs. For example, in the PV6C sediment, E values for PCB 52 (0.89), PCB 70 (0.62), and PCB 153 (0.58) displayed a decreasing trend as the chlorine substitution or K_{ow} increased (Hawker and Connell, 1988). In the PV8C sediment, a similar trend was not observed, and the E values for the different PCB congeners were statistically the same. This suggests that there were other factors (e.g., aging time) affecting the accessibility of HOCs. Contact time or aging has been often found to diminish the availability of PCBs in sediments (Alexander, 2000; Hale et al., 2011; Xu et al., 2008).

4.3.3. Validation of IDM by Sequential Tenax Desorption and Bioaccumulation Assays

The sequential Tenax-aided desorption was applied to the same PV8C and PV6C sediments to evaluate HOC accessibility by fitting the desorption curves (Figure S4.6) to the triphasic model to derive F_r , F_s , and F_{vs} . The regression fit to the model was excellent for all sediment-HOC treatments (Table S4.3). The estimated rapid fraction (F_r) was consistently smaller in the PV8C sediment than that in the PV6C sediment for the same compound. For example, the averaged F_r values were 0.15, 0.08, and 0.10 for PCBs, DDEs, and DDDs in the PV8C sediment, which were smaller than those in the PV6C sediment (0.30, 0.30, and 0.33, respectively). However, F_r of HOCs was only about a half of E given by IDM for the same HOC. For example, in the PV8C sediment, the E and F_r of PCB 52 were 0.49 and 0.22, respectively. Similar differences were observed in a previous study where spiked sediments (pyrene and bifenthrin) were considered (Delgado-Moreno and Gan, 2013). Studies showed that in addition to F_r , the slow desorption fraction F_s also contributed to bioavailability (Birdwell and Thibodeaux, 2009; Cui et al., 2010; Kraaij et al., 2002; Wells et al., 2005). For instance, when the rapid desorption fraction was removed, PAHs in the slow desorption compartment migrated to the rapid desorption pool over time (Birdwell and Thibodeaux, 2009). When benthic deposit feeders were exposed to sediments with the rapid desorption fraction removed, there was still accumulation of PCBs and PAHs (Kraaij et al., 2002). The biodegradation of PAHs by bacteria also exceeded the measured F_r in sediments (Wells et al., 2005). These observations together suggest that bioaccessibility of sediment-borne HOCs may encompass both F_r and F_s as estimated from desorption kinetics.

A good linear relationship ($R^2 = 0.86$, $p < 0.01$) was observed between the E values and the sum of F_r and F_s (Figure 4.2). The linear slope (1.12 ± 0.13) was close to 1, implying that the accessibility predicted by IDM was close to the sum of F_r and F_s estimated from desorption kinetics and likely a better indicator for bioavailability than F_r . The concentrations of PCB 153 in the PV8C and PV6C sediments were relatively low (26.3 and 11.4 $\mu\text{g}/\text{kg}$), resulting in a large variance in the estimated F_r , F_s , and F_{vs} values for this PCB congener. For example, F_r , F_s and F_{vs} of PCB 153 in the PV6C sediment were 0.10 ± 0.33 , 0.38 ± 3.42 and 0.52 ± 3.74 , respectively. If the data points for PCB 153 were excluded from the correlation, the linear relationship further improved substantially ($R^2 = 0.93$, $p < 0.01$).

The performance of IDM was further evaluated by comparing the measured C_e of HOCs with 4-d accumulation of HOCs into the marine polychaete *N.arenaceodentata*. A previous study showed that the uptake of HOCs by the polychaete reached a steady state after 4 d of exposure (Bao et al., 2013). After 4 d of exposure, tissue residue (C_b) of HOCs was analyzed and expressed on both dry weight (d.w.) and lipid weight (l.w.) bases. Owing to the relatively low levels of PCBs in the sediment, only DDEs and DDDs were reliably detected in the tissue samples. For example, C_b of DDEs was 1595.0 ± 326.8 $\mu\text{g}/\text{kg}$ (d.w.) for the PV6C sediment exposure and 3282.0 ± 192.9 $\mu\text{g}/\text{kg}$ (d.w.) for the PV8C sediment. The values for DDDs were 42.1 ± 11.7 and 161.2 ± 20.6 $\mu\text{g}/\text{kg}$ (d.w.), respectively. Strong linear relationships were found between C_e ($\mu\text{g}/\text{kg}$) normalized by OC content and C_b ($\mu\text{g}/\text{kg}$) normalized by lipid content for DDEs and DDDs in the PV8C ($R^2 = 0.84$) and PV6C ($R^2 = 0.94$) sediments (Figure 4.3). The slopes

for the linear relationships were 1.88 ± 0.57 and 1.20 ± 0.22 for PV8C and PV6C sediments, respectively. Therefore, the accessible concentration C_e derived by IDM was clearly predictive of the bioaccessibility of DDT derivatives in the historically contaminated marine sediments.

4.4. Considerations in Use of IDM for Predicting Bioaccessibility

As demonstrated in this study, the use of IDM to derive C_e or E involves only a few simple steps, i.e., addition of isotope-labeled analogues to a sediment sample, mixing the sample for a relatively short duration (e.g., 24 h), and analyze the aqueous concentrations of both labeled and non-labeled (native) HOCs using a MS-equipped chromatographic system. Standards labeled with ^{13}C or deuterium are widely available nowadays, especially for legacy contaminants. At present, MS-equipped instruments are also found in most research and commercial laboratories. In fact, many laboratories already use stable-isotope labeled standards as recovery surrogates or internal standards in routine analysis of environmental samples. Therefore, the measurement of C_e or E may require only minor modifications to existing procedures.

In this study, the PV6C and PV8C sediments contained very different levels of DDXs and PCBs. The isotope-labeled analogues were added at a fixed rate (i.e., 25 $\mu\text{g}/\text{kg}$) to the sediment samples, regardless of the bulk sediment concentrations of the individual HOCs. When expressed as the ratio to the native HOC level, $^*C_0/C_T$ varied from 0.09% to 82.4% for the PV8C sediment, and from 1.3% to 301% for the PV6C sediment. Therefore, results of this study suggested that it is not necessary to control the ratio of $^*C_0/C_T$ in the use of IDM. This offers the advantage that the concentrations of

native HOCs in a contaminated sample need not to be known before hand, and that a single rate of isotope labeled tracers may be used irrespective of the levels of native HOCs. This lends a great versatility to the method because field contaminated samples often contain a mix of HOCs over a wide range of concentrations.

Another important consideration in the use of IDM is the time for the externally introduced isotope tracers to reach dilution equilibrium. In the present study, 24 h was selected based on the observed isotope dilution kinetics. There was no significant difference in the time to equilibrium among the different HOCs or between different sediments. As shown in this study, isotope dilution did not change appreciably during 24-192 h for both sediments and all HOCs considered. Therefore, after dilution equilibrium is reached, the specific time interval used for mixing is not critical, which adds flexibility to the method. Moreover, a mixing interval of 24 h is relatively short and convenient, contributing to a high sample throughput and hence feasibility.

The PV Shelf Superfund site represents a vast contaminated area where a multitude of factors could have affected the concentration profiles of DDXs and PCBs at a given location, including effluent discharge history, distance to the outfalls, topography of the ocean floor, and sediment deposition, burial, and resuspension caused by ocean currents. The two locations considered in this study, PV8C and PV6C were around 2 km apart, with PV8C close to the outfalls. As shown in this study, contaminant accessibility as estimated by IDM ranged from 0.28 to 0.89 and was substantially smaller than 1 for most HOCs, suggesting that aging and other factors may have significantly decreased the bioavailability of HOCs at this Superfund site. Thus, the use of bioavailability-relevant

measurements over bulk sediment levels may provide improved risk assessment that is valuable in decision making, in e.g., designation of specific areas for remediation. In addition, findings from the current study also offered a preliminary comparison between locations at the PV Shelf site. The relative accessibility of DDXs and PCBs in the PV8C sediment was consistently smaller than in the PV6C sediment. The underlying mechanisms for changes in contaminant accessibility merit further research. Although this study only considered marine sediments and a select group of HOCs, the principle of IDM should be similarly applicable to other solid matrices (e.g., soil) and contaminants, and should be further explored.

References

- ASTM, 2013. Standard guide for conducting sediment toxicity tests with polychaetous annelids (E1611-00). American Society for Testing and Materials, 100 Barr Harbor Drive, PO Box C700, West Conshohocken, PA 19428-2959. United States, pp. 1-26.
- Ahnstrom, Z.A.S., Parker, D.R., 2001. Cadmium reactivity in metal-contaminated soils using a coupled stable isotope dilution-sequential extraction procedure. *Environmental Science & Technology* 35, 121-126.
- Alexander, M., 2000. Aging, bioavailability, and overestimation of risk from environmental pollutants. *Environmental Science & Technology* 34, 4259-4265.
- Anderson, B.S., Hunt, J.W., Phillips, B.M., Tudor, S., Fairey, R., Newman, J., Puckett, H.M., Stephenson, M., Long, E.R., Tjeerdema, R.S., 1998. Comparison of marine sediment toxicity test protocols for the amphipod *Rhepoxynius abronius* and the polychaete worm *Nereis (Neanthes) arenaceodentata*. *Environmental Toxicology and Chemistry* 17, 859-866.
- Bao, L.J., Jia, F., Crago, J., Zeng, E.Y., Schlenk, D., Gan, J., 2013. Assessing bioavailability of DDT and metabolites in marine sediments using solid-phase microextraction with performance reference compounds. *Environmental Toxicology and Chemistry* 32, 1946-1953.
- Birdwell, J.E., Thibodeaux, L.J., 2009. PAH repartitioning in field-contaminated sediment following removal of the labile chemical fraction. *Environmental Science & Technology* 43, 8092-8097.

- Cornelissen, G., Gustafsson, O., Bucheli, T.D., Jonker, M.T.O., Koelmans, A.A., Van Noort, P.C.M., 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* 39, 6881-6895.
- Cornelissen, G., Rigterink, H., ten Hulscher, D.E.M., Vrind, B.A., van Noort, P.C.M., 2001. A simple Tenax (R) extraction method to determine the availability of sediment-sorbed organic compounds. *Environmental Toxicology and Chemistry* 20, 706-711.
- Cornelissen, G., vanNoort, P.C.M., Govers, H.A.J., 1997. Desorption kinetics of chlorobenzenes, polycyclic aromatic hydrocarbons, and polychlorinated biphenyls: Sediment extraction with Tenax(R) and effects of contact time and solute hydrophobicity. *Environmental Toxicology and Chemistry* 16, 1351-1357.
- Cui, X.Y., Hunter, W., Yang, Y., Chen, Y.X., Gan, J., 2010. Bioavailability of sorbed phenanthrene and permethrin in sediments to *Chironomus tentans*. *Aquatic Toxicology* 98, 83-90.
- Davis, J.A., Leckie, J.O., 1978. Effect of adsorbed complexing ligands on trace-metal uptake by hydrous oxides. *Environmental Science & Technology* 12, 1309-1315.
- Delgado-Moreno, L., Gan, J., 2013. A stable isotope dilution method for measuring bioavailability of organic contaminants. *Environmental Pollution* 176, 171-177.
- Ehlers, L.J., Luthy, R.G., 2003. Contaminant bioavailability in soil and sediment. *Environmental Science & Technology* 37, 295A-302A.

- Hale, S.E., Hanley, K., Lehmann, J., Zimmerman, A.R., Cornelissen, G., 2011. Effects of chemical, biological, and physical aging as well as soil addition on the sorption of pyrene to activated carbon and biochar. *Environmental Science & Technology* 45, 10445-10453.
- Hatzinger, P.B., Alexander, M., 1995. Effect of aging of chemicals in soil on their biodegradability and extractability. *Environmental Science & Technology* 29, 537-545.
- Hawker, D.W., Connell, D.W., 1988. Octanol water partition-coefficients of polychlorinated biphenyl congeners. *Environmental Science & Technology* 22, 382-387.
- Huang, Z.Y., Chen, T., Yu, J.A., Zeng, X.C., Huang, Y.F., 2011. Labile Cd and Pb in vegetable-growing soils estimated with isotope dilution and chemical extractants. *Geoderma* 160, 400-407.
- Kelsey, J.W., Kottler, B.D., Alexander, M., 1997. Selective chemical extractants to predict bioavailability of soil-aged organic chemicals. *Environmental Science & Technology* 31, 214-217.
- Khan, M.I., Cheema, S.A., Shen, C., Zhang, C., Tang, X., Shi, J., Chen, X., Park, J., Chen, Y., 2012. Assessment of phenanthrene bioavailability in aged and unaged soils by mild extraction. *Environmental Monitoring and Assessment* 184, 549-559.

- Kraaij, R., Seinen, W., Tolls, J., 2002. Direct evidence of sequestration in sediments affecting the bioavailability of hydrophobic organic chemicals to benthic deposit-feeders. *Environmental Science & Technology* 36, 3525-3529.
- Landrum, P.F., Robinson, S.D., Gossiaux, D.C., You, J., Lydy, M.J., Mitra, S., Ten Hulscher, T.E.M., 2007. Predicting bioavailability of sediment-associated organic contaminants for *Diporeia* spp. and *Oligochaetes*. *Environmental Science & Technology* 41, 6442-6447.
- Luthy, R.G., Aiken, G.R., Brusseau, M.L., Cunningham, S.D., Gschwend, P.M., Pignatello, J.J., Reinhard, M., Traina, S.J., Weber, W.J., Westall, J.C., 1997. Sequestration of hydrophobic organic contaminants by geosorbents. *Environmental Science & Technology* 31, 3341-3347.
- Mechlinska, A., Wolska, L., Namiesnik, J., 2010. Isotope-labeled substances in analysis of persistent organic pollutants in environmental samples. *Trac-Trends in Analytical Chemistry* 29, 820-831.
- Naidu, R., Harter, R.D., 1998. Effect of different organic ligands on cadmium sorption by and extractability from soils. *Soil Science Society of America Journal* 62, 644-650.
- Nolan, A.L., Zhang, H., McLaughlin, M.J., 2005. Prediction of zinc, cadmium, lead, and copper availability to wheat in contaminated soils using chemical speciation, diffusive gradients in thin films, extraction, and isotopic dilution techniques. *Journal of Environmental Quality* 34, 496-507.

- Pignatello, J.J., Xing, B.S., 1996. Mechanisms of slow sorption of organic chemicals to natural particles. *Environmental Science & Technology* 30, 1-11.
- Reichenberg, F., Mayer, P., 2006. Two complementary sides of bioavailability: accessibility and chemical activity of organic contaminants in sediments and soils. *Environmental Toxicology and Chemistry* 25, 1239-1245.
- Reid, B.J., Stokes, J.D., Jones, K.C., Semple, K.T., 2000. Nonexhaustive cyclodextrin-based extraction technique for the evaluation of PAH bioavailability. *Environmental Science & Technology* 34, 3174-3179.
- Sivry, Y., Riotte, J., Sappin-Didier, V., Munoz, M., Redon, P.-O., Denaix, L., Dupre, B., 2011. Multielementary (Cd, Cu, Pb, Zn, Ni) stable isotopic exchange kinetic (SIEK) method to characterize polymetallic contaminations. *Environmental Science & Technology* 45, 6247-6253.
- Sterckeman, T., Carignan, J., Srayeddin, I., Baize, D., Cloquet, C., 2009. Availability of soil cadmium using stable and radioactive isotope dilution. *Geoderma* 153, 372-378.
- Tang, J., Alexander, M., 1999. Mild extractability and bioavailability of polycyclic aromatic hydrocarbons in soil. *Environmental Toxicology and Chemistry* 18, 2711-2714.
- Tomaszewski, J., Werner, D., Luthy, R., 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*, 2143-2150.

- Tongtavee, N., Shiowatana, J., McLaren, R.G., Gray, C.W., 2005. Assessment of lead availability in contaminated soil using isotope dilution techniques. *Science of the Total Environment* 348, 244-256.
- U.S. EPA, 2009. Interim record of decision: Palos Verdes Shelf operable unit 5 of Montrose Chemical Corporation Superfund site, Los Angeles County, CA. Region IX, United States Environmental Protection Agency.
- U.S. EPA, 2013. Revised final data report for the fall 2009 sediment sampling program: Palos Verdes Shelf (OU 5 of the Montrose Chemical Corporation Superfund site) Los Angeles County, California, San Francisco, California. United States Environmental Protection Agency.
- Van den Hoop, M., Kreule, P., Loch, J.P.G., 1999. Sorption kinetics and transformation of DDT in sediment. *Water Air and Soil Pollution* 110, 57-66.
- Wells, M., Wick, L.Y., Harms, H., 2005. Model polymer release system study of PAH bioaccessibility: The relationship between “rapid” release and bioaccessibility. *Environmental Science & Technology* 39, 1055-1063.
- Xing, B.S., Pignatello, J.J., 1997. Dual-mode sorption of low-polarity compounds in glassy poly(vinyl chloride) and soil organic matter. *Environmental Science & Technology* 31, 792-799.
- Xu, Y., Gan, J., Wang, Z., Spurlock, F., 2008. Effect of aging on desorption kinetics of sediment-associated pyrethroids. *Environmental Toxicology and Chemistry* 27, 1293-1301.

Yang, Y., Hunter, W., Tao, S., Gan, J., 2008. Relationships between desorption intervals and availability of sediment-associated hydrophobic contaminants. *Environmental Science & Technology* 42, 8446-8451.

Tables

Table 4.1. Log K_d values of PCBs and DDXs in PV8C sediments before (N = 9) and after (N = 30) the addition of isotope-labeled analogues

Compound	log K_d (before)	log K_d (after)
PCB 52	3.70 ± 0.20	3.56 ± 0.22
PCB 70	3.74 ± 0.19	3.57 ± 0.20
PCB 153	3.50 ± 0.38	3.30 ± 0.19
<i>o,p'</i> -DDE	3.37 ± 0.13	3.56 ± 0.19
<i>p,p'</i> -DDE	3.37 ± 0.18	3.57 ± 0.22
<i>o,p'</i> -DDD	3.54 ± 0.25	3.67 ± 0.25
<i>p,p'</i> -DDD	4.07 ± 0.44	3.99 ± 0.43

Table 4.2. The accessible concentrations (C_e , $\mu\text{g}/\text{kg}$) and fractions (E) of PCBs and DDXs determined by the isotope dilution method in the PV8C and PV6C sediments.

	PV8C		PV6C	
	C_e	E	C_e	E
PCB 52	99.6 ± 21.2	0.49 ± 0.17	9.2 ± 1.6	0.89 ± 0.12
PCB 70	107.1 ± 18.8	0.42 ± 0.10	9.6 ± 1.9	0.62 ± 0.08
PCB 153	15.9 ± 2.7	0.52 ± 0.07	4.8 ± 1.6	0.58 ± 0.20
<i>o,p'</i> -DDE	1250.9 ± 165.3	0.37 ± 0.11	179.5 ± 57.8	0.63 ± 0.24
<i>p,p'</i> -DDE	9168.3 ± 1380.4	0.37 ± 0.13	1082.4 ± 426.5	0.57 ± 0.20
<i>o,p'</i> -DDD	528.6 ± 153.3	0.29 ± 0.09	13.6 ± 1.6	0.62 ± 0.08
<i>p,p'</i> -DDD	3104.3 ± 1948.5	0.28 ± 0.23	78.3 ± 3.9	0.69 ± 0.03

Figures

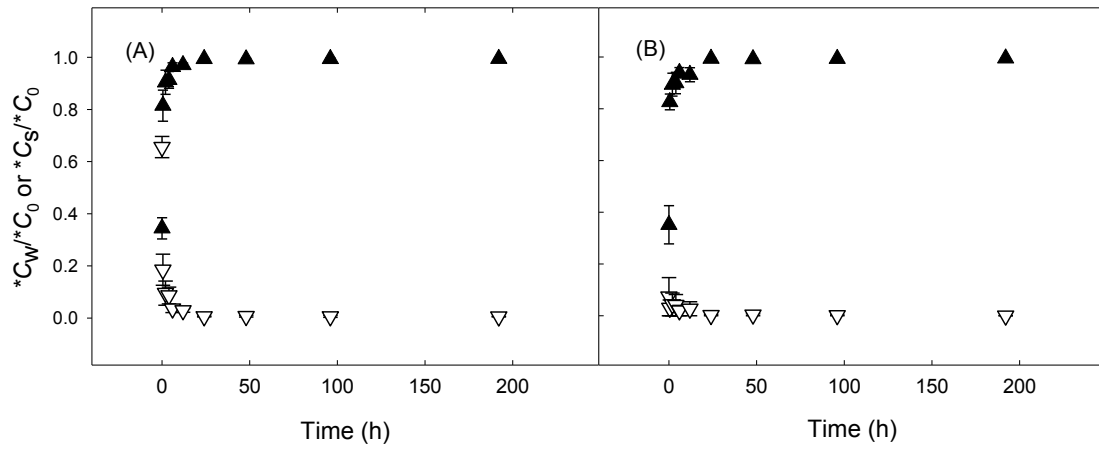


Figure 4.1. Fractions of isotope tracers ($^*\text{HOC}$) in the sediment (solid triangle) and liquid phase (open triangle) in the PV8C sediment slurry as a function of mixing time (A) ^{13}C -PCB 52; (B) d_4 - p,p' -DDE.

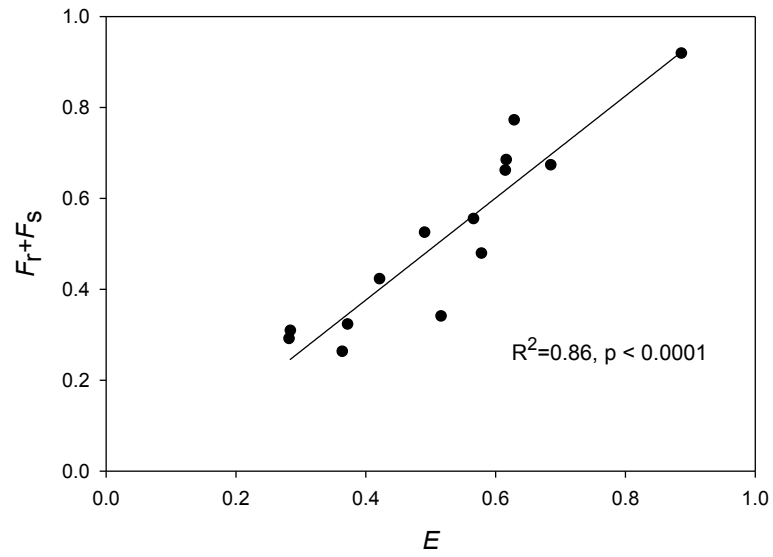


Figure 4.2. Linear correlation between the accessibility (E) given by the isotope dilution method and the sum of rapid and slow desorption fractions (F_r+F_s) derived by Tenax desorption (slope = 1.12 ± 0.13 , $R^2=0.86$, $p < 0.0001$)

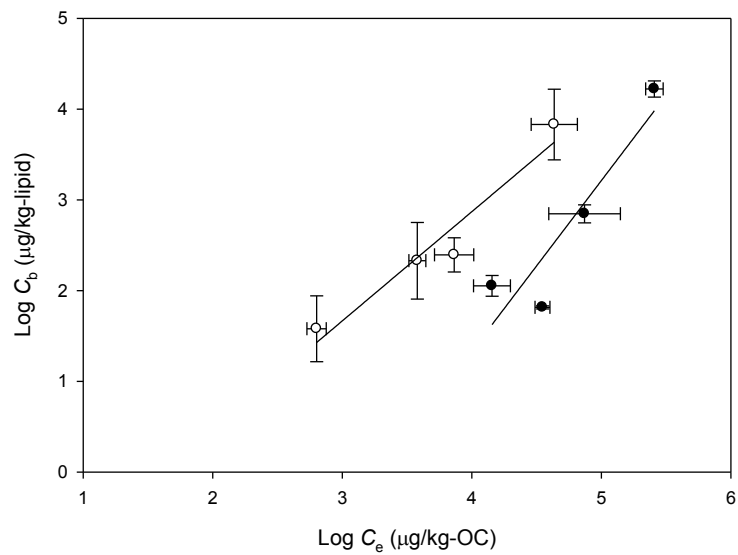


Figure 4.3. Linear correlation between the lipid content-normalized tissue residues of DDXs ($\text{Log } C_b$, $\mu\text{g/kg-lipid}$) in *N.arenaceodentata* and the organic carbon-normalized accessible HOC concentrations ($\text{Log } C_e$, $\mu\text{g/kg-OC}$)

Supporting Information

S4.1. Materials and Methods

S4.1.1. Chemicals and Sediments

1,1-dichloro-2,2-bis-(chlorophenyl)ethane (*p,p'*-DDD), 1,1-dichloro-2,2-bis-(chlorophenyl)ethylene (*p,p'*-DDE), 1,1-dichloro-2,4-bis-(chlorophenyl)ethane (*o,p'*-DDD), 1,1-dichloro-2,4-bis-(chlorophenyl)ethylene (*o,p'*-DDE), 2,2',5,5'-Tetrachlorobiphenyl (PCB 52), 2,3',4',5'-Tetrachlorobiphenyl (PCB 70), 2,2',4,4',5,5'-Hexachlorobiphenyl (PCB 153), external surrogates 2,3',4,5'-Tetrachlorobiphenyl (PCB 67) and 2,3,3',4,4',5',6-Heptachlorobiphenyl (PCB 191), internal standards 2,4,6-Trichlorobiphenyl (PCB 30) and 2,2',3,3',4-Pentachlorobiphenyl (PCB 82) were purchased from AccuStandard (New Haven, CT). Isotope analogues ^{13}C -*o,p'*-DDD, ^{13}C -*o,p'*-DDE, ^{13}C -PCB 52, and ^{13}C -PCB 153 were purchased from Cambridge Isotope Laboratories (Tewksbury, MA); deuterated compounds *p,p'*-DDD- d_8 , *p,p'*-DDE- d_4 , and PCB 70- d_3 were purchased from C/D/N Isotopes (Pointe-Claire, Quebec, Canada).

S4.1.2. Liquid Sample Extraction

The liquid samples were added with surrogates and extracted with 10 mL of hexane by vortex for 1 min in 40-mL TOC vials. The samples were frozen at $-80\text{ }^\circ\text{C}$ for 1h and the hexane layer was passed through sodium sulfate and transferred into the test tubes for concentration under N_2 . A second extraction was repeated if there was emulsion after mixing the solvent with samples. The extracts were combined and concentrated to around 200 μL . After spiking with internal standards, an aliquot (1 or 2 μL) of the final extract was analyzed on a Varian 3800 GC equipped with a Varian 1200 triple

quadrupole mass spectrometer (GC-MS/MS) (Varian, Sunnyvale, CA). The method recoveries for the spiked liquid samples (n=3) were 75.5 – 105.5% for PCBs, 78.8 – 84.3% for DDEs, and 77.1 – 73.7% for DDDs, respectively. Averaged recoveries of surrogates (n=57) during the PV8C sediment analysis were 92.7% for PCB 67 and 81.0% for PCB 191, and those in the PV6C sediment (n=40) were 98.0% for PCB 67 and 75.9% for PCB 191.

S4.1.3. Sediment Sample Extraction and Analysis

Sediment samples were freeze-dried for 1 d using a freeze dry system (Labconco, Kansas City, MO) and stored at -21 °C until analysis. For extraction, each sediment sample was added with 10 µL of external surrogates (5 mg/L of PCB-67 and PCB-191 in acetone) and sonicated for 20 min in 40 mL of acetone-dichloromethane (1:1, v:v). The mixture was centrifuged at 670 g for 10 min, and the supernatant was passed through sodium sulfate into a 250-mL round bottom flask. The extraction was repeated for three times. The extracts were combined and condensed to < 1 mL on a vacuumed rotary evaporator at 42 °C, and then re-dissolved in hexane and concentrated to around 1 mL. For cleanup, the extract was loaded onto a Florisil cartridge (2g, Thermo Scientific, Bellefonte, PA) and eluted with 20 mL of acetone-hexane (1:9, v:v) following a modified EPA method 3620C. The eluate was concentrated to near dryness under N₂, spiked with 10 µL of internal standards (5 mg/L of PCB-30 and PCB-82 in hexane), and reconstituted to 1 mL with hexane in a GC vial. An aliquot (1 µL) of the final extract was taken for analysis on GC-MS/MS. For concentrations beyond the range of calibration standards, the samples were diluted before injection. The method recovery for the spiked sediment

samples was (n=3) 88-136%. The averaged recoveries of surrogates (n=57) in the PV8C sediment were 108.3 % for PCB-67 and 61.6% for PCB-191, and that in the PV6C sediment (n=40) was 81.5% for PCB-67 and 64.2% for PCB-191.

S4.1.4. Tissue Sample Extraction and Analysis

Upon depuration, the worms were transferred into pre-weighed glass centrifuge tubes, freeze-dried and stored at -21 °C until analysis. The dry mass of the worms was recorded. The tissue was sonicated in 40 mL of acetone-dichloromethane (1:1, v:v) for 20 min and the extraction process was repeated two more times. The extracts were combined and concentrated to around 10 mL. One fifth of the sample was taken for analysis of lipid content, and the remaining sample was concentrated to < 1.0 mL in hexane. The sample was further cleaned up by passing through a 20-mL solid phase cartridge (Supelco, Bellefonte, PA) packed with 2-cm height of acidic silica gel in hexane. The sample was eluted with 25 mL of hexane-dichloromethane (1:1, v: v) and concentrated to around 200 μ L under a gentle stream of N₂. An aliquot (2 μ L) of internal standards (5 mg/L in hexane) was spiked into the sample prior to instrumental analysis. Preliminary experiments showed that the spiked recoveries of DDXs and PCBs were 94-141%. The Standard Reference Material 1947 (SRM 1947) purchased from the National Institute of Standards and Technology (NIST) was used for validation of the current method, and the recoveries for the selected PCBs and DDXs were 76 – 83% and 81 – 116%, respectively.

S4.1.5. Chromatographic Conditions

The samples (1 or 2 μ L) were injected at 200°C in the pulsed splitless mode at 45 psi with purge valve closed for 1.0 min. A DB-5MS Ultra Inert capillary column (60m ×

0.25 mm × 0.25 μm, Agilent, Wilmington, DE) was used for separation. The initial column temperature was set at 80 °C for 1 min, ramped to 210 °C at 10 °C/min, further ramped to 300 °C at 5 °C/min, and held at 300 °C for 5 min. High purity helium (99.999%) was used as the carrier gas at a flow rate of 1mL/min.

The triple-quadrupole mass spectrometer was operated in the electron ionization (EI) mode at 70 eV with selected reaction monitoring (SRM). The transfer line, ionization source, and manifold temperatures were 300, 250, and 40 °C, respectively. A filament multiplier delay of 17.0 min was used to prevent system damages. The detector multiplier voltage was used in the extended dynamic range (EDR). Argon (99.999%) in the range of 1.66 – 1.67 mTorr was used as a collision gas. The scan time was 0.4 s and the peak widths of m/z 2.0 and 2.0 were set in the first (Q1) and third (Q3) quadrupoles, respectively. A Varian workstation was used for instrumental control and data analysis. Calibration standards were prepared in n-hexane and analyzed under the same conditions on the same day of analysis. The specific GC-MS/MS conditions are shown in Table S4.1.

Table S4.1. Conditions of GC-MS/MS method for analytes

Chemical	Segment	Precursor ion (m/z)	Product ion (m/z)	Collision energy (eV)
PCB 30 (IS)	1	257	186	25
PCB 52	1	291	220	25
¹³ C-PCB 52	1	303	232	25
PCB 67 (SS)	1	291	220	25
PCB 70	2	291	220	18
d ₄ -PCB 70	2	294	224	25
<i>o,p'</i> -DDE	2	247	176	30
¹³ C- <i>o,p'</i> -DDE	2	258	188	30
<i>p,p'</i> -DDE	3	247	176	25
d ₈ - <i>p,p'</i> -DDE	3	255	184	30
<i>o,p'</i> -DDD	3	235	165	25
¹³ C- <i>o,p'</i> -DDD	3	247	176	25
PCB 82 (IS)	3	255	184	30
<i>p,p'</i> -DDD	4	235	165	20
d ₈ - <i>p,p'</i> -DDD	4	243	173	22
PCB 153	4	359	289	20
¹³ C-PCB 153	4	371	300	35
PCB 191 (SS)	5	397	323	30

Table S4.2. Log K_d values of PCBs and DDXs in PV6C sediments before (N = 6) and after (N = 31) the addition of isotope-labeled analogues

PV6C	log K_d (before)	log K_d (after)
PCB 52	3.76 ± 0.07	3.23 ± 0.15
PCB 70	nd ^a	nd
PCB 153	3.09 ± 0.07	3.08 ± 0.11
<i>o,p'</i> -DDE	3.95 ± 0.11	3.55 ± 0.20
<i>p,p'</i> -DDE	3.81 ± 0.09	3.44 ± 0.18
<i>o,p'</i> -DDD	3.89 ± 0.16	3.52 ± 0.17
<i>p,p'</i> -DDD	3.60 ± 0.11	3.43 ± 0.18

^and=not detected.

Table S4.3. Mean regression parameters from fitting Tenax desorption data of PCBs and DDXs in PV8C and PV6C sediments to a triphasic desorption model

	F_r^a	k_r (h ⁻¹)	F_s	k_s (h ⁻¹)	F_{vs}	k_{vs} (h ⁻¹)	R ²
PV8C sediment							
PCB 52	0.218	0.152	0.306	1.84E-2	0.476	7.00E-4	0.999
PCB 70	0.183	0.111	0.238	1.42E-2	0.579	4.00E-4	0.999
PCB 153	0.063	0.226	0.276	1.00E-2	0.661	3.00E-4	0.999
<i>o,p'</i> -DDE	0.098	0.125	0.224	1.45E-2	0.678	3.00E-4	0.999
<i>p,p'</i> -DDE	0.058	0.177	0.204	1.52E-2	0.738	3.00E-4	0.999
<i>o,p'</i> -DDD	0.106	0.132	0.202	1.57E-2	0.692	2.00E-4	0.999
<i>p,p'</i> -DDD	0.094	0.125	0.196	1.61E-2	0.710	3.00E-4	0.999
PV6C sediment							
PCB 52	0.448	5.02E-2	0.470	2.90E-3	0.082	2.91E-10	0.996
PCB 70	0.334	6.16E-2	0.326	4.30E-3	0.334	9.67E-12	0.998
PCB 153	0.102	3.80E-2	0.375	5.00E-3	0.522	2.03E-17	0.998
<i>o,p'</i> -DDE	0.359	5.44E-2	0.412	5.10E-3	0.229	1.15E-18	0.999
<i>p,p'</i> -DDE	0.235	5.51E-2	0.319	6.30E-3	0.445	2.00E-4	0.999
<i>o,p'</i> -DDD	0.329	6.60E-2	0.355	4.40E-3	0.317	6.78E-13	0.999
<i>p,p'</i> -DDD	0.331	6.38E-2	0.341	4.30E-3	0.328	4.29E-12	0.999

^a F_r , F_s and F_{vs} are the rapid, slow and very slow desorption fractions, respectively; k_r , k_s and k_{vs} are the corresponding desorption rate constants.

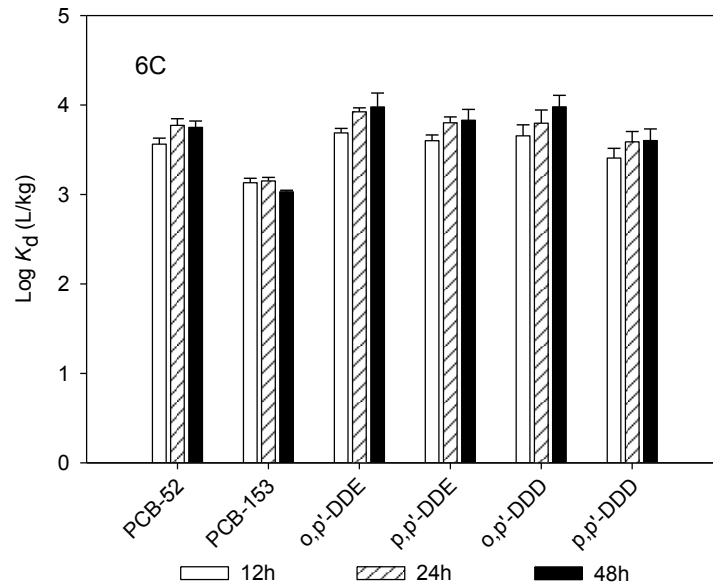


Figure S4.1. Logarithm of sediment-water partition coefficients ($\log K_d$) of PCB 52, PCB 153, *o,p'*-DDE, *p,p'*-DDE, *o,p'*-DDD and *p,p'*-DDD with time in the PV6C sediments.

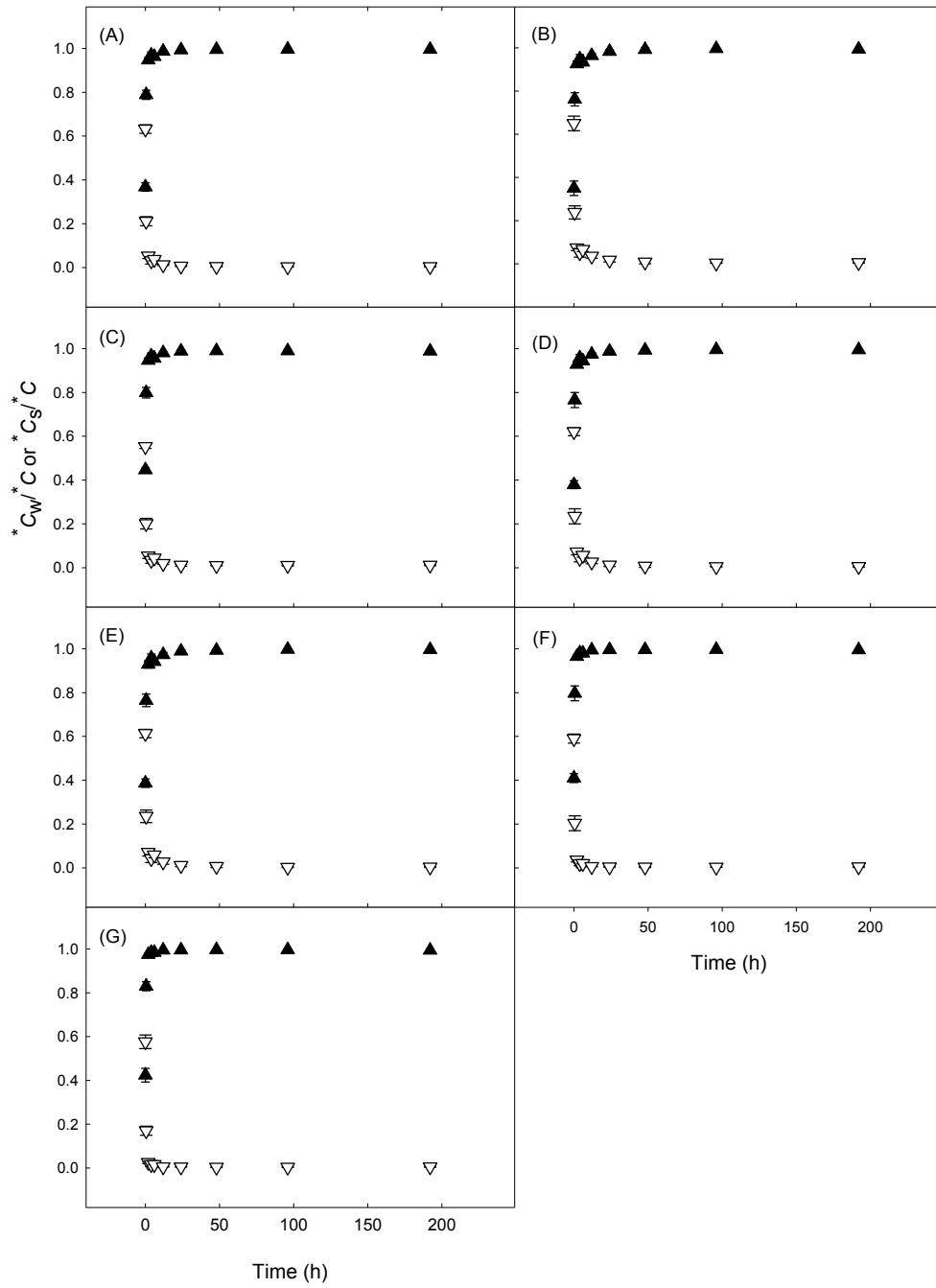


Figure S4.2. Stable isotope dilution fractions of isotope tracers (*HOC) in the sediment (black triangle) and liquid phase (white triangle) in the PV6C sediment-water system: (A) ^{13}C -PCB 52, (B) ^{13}C -PCB 153, (C) d_3 -PCB 70, (D) ^{13}C -*o,p'*-DDE, (E) d_4 -*p,p'*-DDE, (F) ^{13}C -*o,p'*-DDD, and (G) d_8 -*p,p'*-DDD

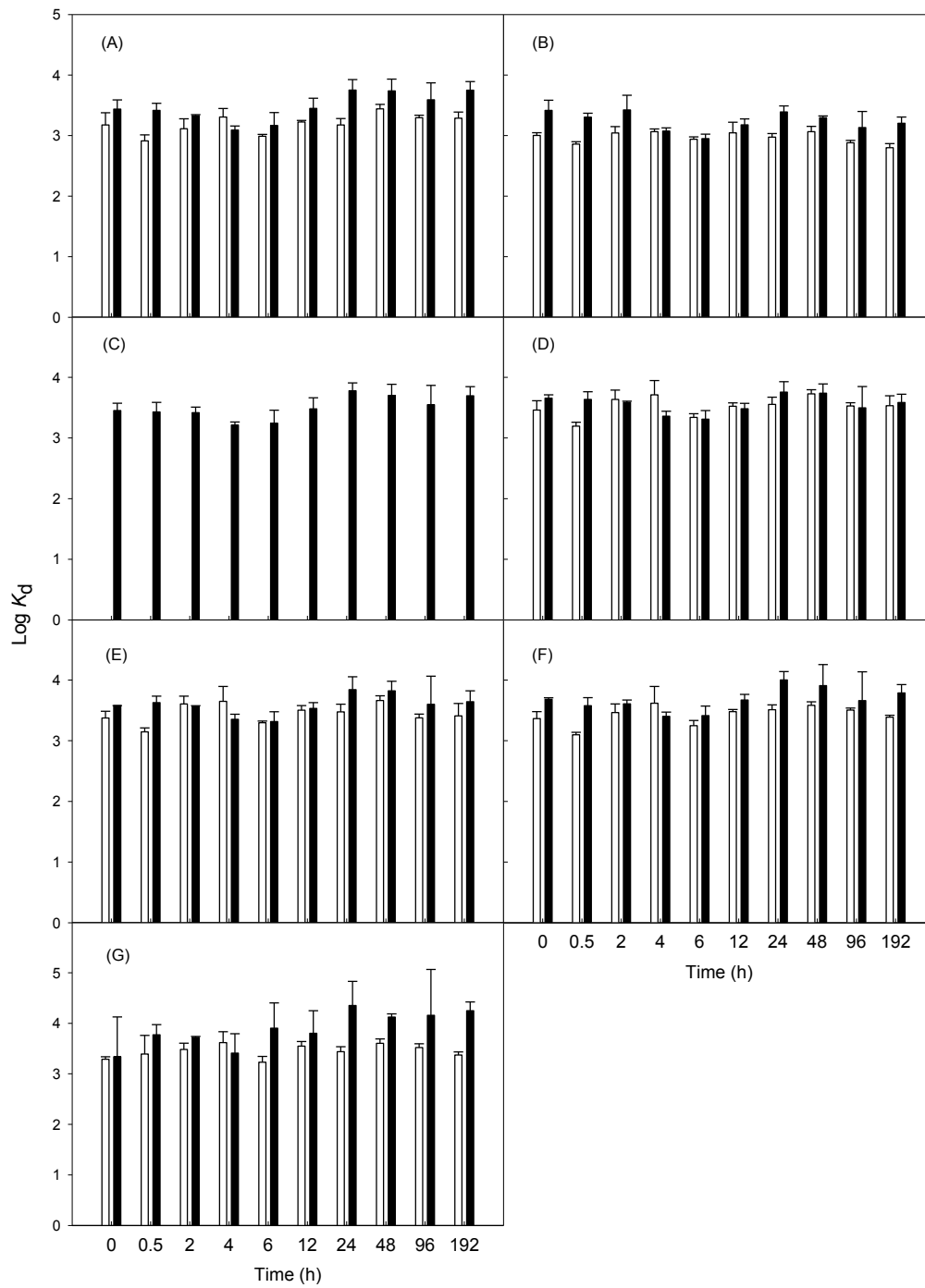


Figure S4.3. Logarithm of sediment-water partitioning coefficients ($\text{Log } K_d$) of (A) PCB 52, (B) PCB 153, (C) PCB 70, (D) *o,p'*-DDE, (E) *p,p'*-DDE, (F) *o,p'*-DDD, (G) *p,p'*-DDD in the PV6C (white bar) and PV8C (black bar) sediments during the isotope dilution kinetics.

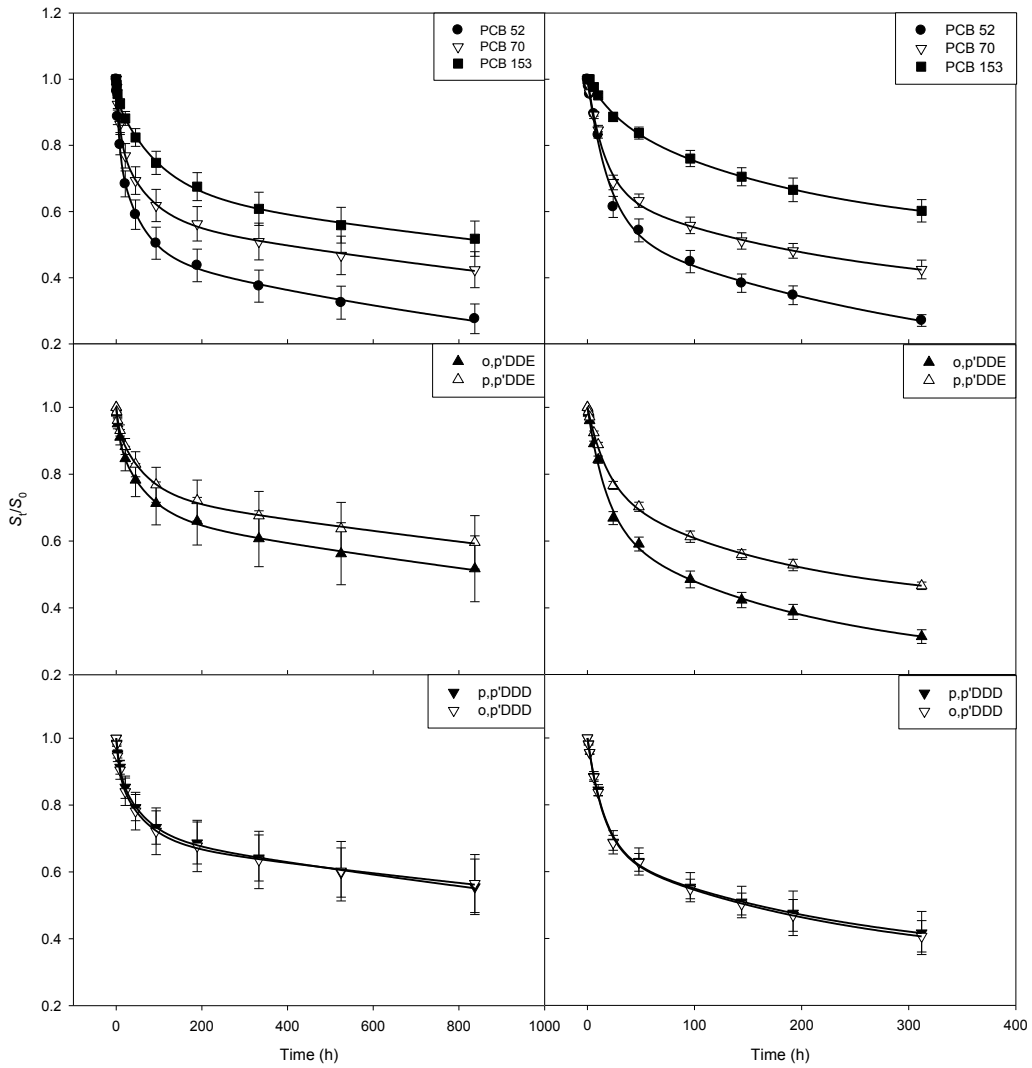


Figure S4.4. Sequential desorption curves of PCB 52, PCB 70, PCB 153, *o,p'*-DDE, *p,p'*-DDE, *o,p'*-DDD, and *p,p'*-DDD by Tenax in PV8C (left) and PV6C (right) sediment.

Chapter 5 Comparing Different Methods for Assessing Contaminant Bioavailability in Sediments Following Amendment Treatments

5.1. Introduction

Due to their high affinity for organic carbon particles, hydrophobic organic compounds (HOCs) preferentially deposit onto the bed sediment in surface aquatic systems, where HOCs are sorbed by geosorbents and the sorption generally results in decreased bioaccumulation or toxicity to benthic organisms (Luthy et al., 1997). Such contaminant sorption or sequestration may be further enhanced by the intentional addition of strong sorbents such as black carbon materials (Cornelissen et al., 2005; Ghosh et al., 2011). It is well recognized that the use of bulk chemical concentrations may lead to substantial overestimation of the bioavailability or risks of HOCs in these scenarios (Ehlers and Luthy, 2003). Therefore, measurement of bioavailability and applying it in a before-and-after manner is valuable for evaluating the effectiveness or progress of remediation operations (Ehlers and Luthy, 2003; Semple et al., 2004).

A range of bioavailability estimation methods have been introduced and tested over the last two decades. Bioavailability measurement methods generally fall into two types, i.e., passive samplers that detect the freely dissolved concentration C_{free} and methods that measure a fraction of the sorbed chemical as an indicator of bioaccessibility (Reichenberg and Mayer, 2006). A number of passive samplers, such as polyethylene device (PED), semi-permeable membrane device (SPMD) and solid phase microextraction (SPME) have been used for measuring C_{free} of HOCs in the sediment porewater (Fernandez et al., 2009; Hawthorne et al., 2011; Hawthorne et al., 2009;

Huckins et al., 1993; Poerschmann et al., 1997). Various extraction or desorption-based methods have been tested for predicting the bioavailable fraction, which include mild solvent extraction (Kelsey et al., 1997; Khan et al., 2012; Tang and Alexander, 1999), Tenax-aided sequential desorption (Cornelissen et al., 1998; Cornelissen et al., 2001), cyclodextrin extraction (Reid et al., 2000; Stokes et al., 2005) and the isotope dilution method (IDM) (Delgado-Moreno and Gan, 2013; Jia et al., 2014). However, while these methods have been used with success in individual studies, few researchers have compared their suitability or elucidate advantages and disadvantages for use in the evaluation of remediation performance. The lack of method comparison has likely contributed to the seemingly arbitrary selection of methods in some studies, inconsistent results and also the difficulty to analyze data across different studies.

In this study, we applied three different methods for measuring the bioavailability of *p,p'*-DDT and its metabolite *p,p'*-DDE in sediments following amendment with activated carbon, charcoal or sand. Addition of black carbon materials has been often shown to be effective at sequestering or immobilizing HOCs in many bench-scale and pilot studies (Cho et al., 2009; Tomaszewski et al., 2007; Werner et al., 2010), while capping with gravel or sand has been used to physically separate the contaminated sediment bed from its overlaying water to minimize exposure (Hyun et al., 2006; Lampert et al., 2011; McDonough et al., 2007). Three methods, SPME, Tenax-aided desorption test and IDM, were used on the same unamended and amended sediment samples. Method performance and limitations were analyzed and discussed. Information

from this study may be used for improving data interpretation and guiding method selection in similar efforts to assess efficiency or progress of remediation treatments.

5.2. Materials and Methods

5.2.1. Chemicals, SPME Fibers and Tenax

Standards of 1,1,1-trichloro-2,2-bis(*p*-chlorophenyl)ethane (*p,p'*-DDT) and its metabolite 1,1-dichloro-2,2-bis(*p*-chlorophenyl)ethylene (*p,p'*-DDE), and internal standard 2,2',3,3',4-pentachlorobiphenyl (PCB 82) were purchased from AccuStandard (New Haven, CT). Stable isotope labeled analogues *p,p'*-DDT- d_4 and *p,p'*-DDE- d_4 and surrogate *o,p'*-DDT- d_8 were purchased from C/D/N Isotopes (Pointe-Claire, Quebec, Canada). Thin fiber (430- μm diameter) coated with 35 μm PDMS was purchased from Polymicro Technologies (Phoenix, AZ). The volume of PDMS polymer per fiber length was 51.1 $\mu\text{L}/\text{m}$. The PDMS fiber was pre-cleaned by Soxhlet extraction with ethyl acetate for 72 h and cut to 1-cm pieces with a razor blade before use (Jia et al., 2012). Tenax TA resin (60-80 mesh) was purchased from Scientific Instrument Services (Ringoos, NJ). All other solvents and chemicals used were of analytical or gas chromatography (GC) grade.

5.2.2. Sediments and Amendment Materials

Two river sediments with no detectable DDT residues were used, including San Diego Creek sediment (SD, Orange County, CA) and Jordan Lake Reservoir sediment (JL, Chatham County, NC). Both sediments were wet-sieved through a 2-mm mesh and stored at 4 °C before use. The sediment OC content was measured by combustion on a nitrogen-carbon analyzer (Thermo Finnigan, Woods Hole, MA) after removing the

inorganic carbon with 1 M HCl. The black carbon (BC) content was determined by combusting an aliquot in a muffle furnace at 375 °C for 24 h, digestion with 1 M HCl, and then analyzing on the elemental analyzer (Gustafsson et al., 1997). The measured OC contents were 0.87% and 0.12% for the SD and JL sediments, respectively. The measured BC content was 0.11% for the SD sediment, but below detection limit for the JL sediment.

Three types of amendment materials were used, including sand and two types of black carbon, i.e., activated carbon and charcoal. The activated carbon was purchased from Calgon Carbon (Pittsburg, PA). The charcoal was derived from the combustion of macrocarpa in New Zealand at 400 °C (Jia and Gan, 2014). The sand was collected from San Diego Creek, air-dried and stored at room temperature. All amendment materials were further ground in a mortar, passed through a No. 100 mesh (< 0.15 mm) before use. The OC contents, specific surface areas (SSA) and microporosity of the black carbon materials were determined and reported elsewhere (Jia and Gan, 2014).

The sediments were spiked with *p,p'*-DDT and *p,p'*-DDE following the U.S. EPA guidelines (2001). Briefly, the stock solution with *p,p'*-DDT and *p,p'*-DDE in acetone was first applied to 5 g of silica sand (passed through a 0.15-mm mesh before use) in a 125-mL wide-mouth jar. After the carrier solvent was evaporated in the fume hood, 50 g (dry weight equivalent) of sediment was added and an amendment material (sand or activated carbon, or charcoal) was incorporated into the sediment at 0, 1 and 5% (dry weight basis) using a stainless steel spatula. The spiked sediments were mixed at 120 rpm on a shaker for 7 d and then aged for over 1 month before use. Aliquots of the incubated

sediments were removed and analyzed for the bulk sediment concentration following solvent extraction. Details on the analysis of bulk sediment concentration (C_T) may be found elsewhere (Jia et al., 2014). Preliminary experiments showed that the recoveries of *p,p'*-DDE and *p,p'*-DDT in the sediments ranged from 88% to 136%. The nominal sediment concentrations were 463.8 ± 105.2 and 101.4 ± 18.1 $\mu\text{g}/\text{kg}$ (d.w.) for *p,p'*-DDE and *p,p'*-DDT, respectively in the SD sediment, and were 400.5 ± 87.1 and 150.1 ± 27.9 $\mu\text{g}/\text{kg}$ (d.w.) in the JL sediment. The dissipation of DDT was observed during sediment incubation (Van den Hoop et al., 1999), therefore the recovered concentration was used as the total bulk concentration (C_T).

5.2.3. Bioavailability Measurement Using Different Methods

5.2.3.1. Solid Phase Microextraction (SPME)

Analysis of C_{free} of *p,p'*-DDT and *p,p'*-DDE in the sediment samples was carried out using a method similar to Jia and Gan (2014). Briefly, an aliquot (2.0 g dry weight) of the treated sediment, one piece of 1-cm PDMS fiber, and 2 mL of 200 mg/L sodium azide solution were placed in a 20-mL glass vial. The vials were equilibrated under agitated condition for 7 d at room temperature. The PDMS fibers were carefully retrieved, extracted and analyzed. The C_{free} was calculated by dividing the concentration in the PDMS polymer (C_{PDMS}) over the PDMS-water partition coefficient K_{PDMS} . The K_{PDMS} values of DDT and DDE were adopted from an earlier study (Bao et al., 2013).

5.2.3.2. Isotope Dilution Method

The principle of IDM for bioavailability estimates was discussed previously, and involves the addition of isotope-labeled analogues of the target HOCs (denoted as $^*\text{HOC}$)

and measurement of aqueous phase concentrations of both the native and labeled HOCs (Delgado-Moreno and Gan, 2013). Briefly, the accessible fraction of HOC in a sediment sample (C_e , $\mu\text{g}/\text{kg}$) includes the concentration of HOC in the aqueous phase (C_w , $\mu\text{g}/\text{L}$) and the accessible concentration of sediment-sorbed HOC (C_s^e , $\mu\text{g}/\text{kg}$), which may be estimated as:

$$C_e = (D \times C_w) + C_s^e = \frac{C_w}{C_w^*} \times C_0 \quad (1)$$

where C_w and C_w^* ($\mu\text{g}/\text{L}$) are the aqueous phase concentrations of native HOC and the introduced $^*\text{HOC}$, D (L/kg) is the dilution factor equaling the ratio of aqueous phase volume to solid mass, and C_0 ($\mu\text{g}/\text{kg}$) is the initial concentration of $^*\text{HOC}$ introduced into the sediment-water system.

The accessible fraction of HOCs, E , may be expressed as the ratio of C_e over the bulk sediment concentration C_T ($\mu\text{g}/\text{kg}$)

$$E = \frac{C_e}{C_T} \quad (2)$$

In this study, C_e and E of p,p' -DDT and p,p' -DDE were determined following the method given in Delgado-Moreno et al. (2010). Briefly, an aliquot (2 g) of the treated sediment was placed in a 50-mL glass centrifuge tube and 20.0 mL of 200 mg/L sodium azide in ultrapure water was added to adjust the sediment-water ratio to 1:10 (w:v) and suppress microbial activity. The sample tube was sealed with aluminum foil lined cap and mixed at 120 rpm on a horizontal shaker for 24 h. Preliminary experiments showed that both DDT and DDE reached an apparent partition equilibrium within 12 h. To each sample, 10 μL of an acetone solution containing p,p' -DDT- d_4 and p,p' -DDE- d_4 , each at 5

mg/L, was added. The sample tubes were recapped and vortexed for 10 s, followed by mixing at 120 rpm. Preliminary experiments showed that the distribution of isotope-labeled analogues between the sediment and aqueous phases reached a steady state within 24 h and did not vary for up to 192 h. In this study, 48 h of mixing was used to accomplish isotope dilution.

The sample mixture was centrifuged at 670 g for 30 min and the supernatant was collected. After addition of 20 μ L of acetone solution containing *o,p'*-DDT and *o,p'*-DDT- d_8 at 5 mg/L each (as surrogates), the liquid sample was extracted with 10 mL hexane by vortexing for 1 min in a TOC vial. After placing the mixture in a freezer (-80 °C) for 1 h, the hexane layer was decanted and passed through sodium sulfate into a test tube. The same extraction step was repeated for an additional time, and the extracts were combined. The sample extract was concentrated under N_2 to 100 μ L. An aliquot (2 μ L) of the final extract was analyzed. The mean method recoveries (n=3) were 84.3% for *p,p'*-DDE and 97.9% for *p,p'*-DDT, respectively. Simultaneous analyses of *p,p'*-DDT and *p,p'*-DDE and their deuterated analogues in the aqueous phases allowed for the calculation of C_e using Eq. 1, and consequently E using the bulk sediment concentration in Eq. 2.

5.2.3.3. Tenax-aided Desorption Method

The Tenax-aided desorption at 24 h was performed by following the method described elsewhere (Xu et al., 2008), with minor modifications. Briefly, 1.0 g aliquot of sediment was placed in a 50-mL polyethylene centrifuge tube, and 0.1 g Tenax beads and 10.0 mL of 200 mg/L sodium azide solution were added. The tube was closed and then

mixed at 120 rpm for 24 h. After centrifugation at 670 *g* for 20 min, the Tenax beads were collected by passing the supernatant through a Whatman No. 41 filter paper (Whatman, Maidstone, UK). The trapped beads were rinsed with deionized water, air-dried, and then transferred to a 20-mL glass scintillation vial. The Tenax beads were extracted by sonicating in 3 mL acetone-hexane (1:1, v/v) for 5 min. The extraction procedure was repeated a total of three times. The extracts were combined in a test tube, concentrated under N₂ to near dryness and reconstituted in 1 mL of hexane with 10 µL of internal standards (Jia et al., 2014). The amount of *p,p'*-DDT or *p,p'*-DDE desorbed from the sediment sample was divided over the bulk sediment concentration to yield the 24-h desorption fraction F_{24} . All Tenax-aided desorption determination was conducted in triplicates.

5.2.4. Chemical Analysis

The quantitative analysis of *p,p'*-DDT, *p,p'*-DDE, and their deuterated analogues was carried out on a Varian 3800 GC equipped with a Varian 1200 triple quadrupole mass spectrometer (GC-MS/MS; Varian, Sunnyvale, CA). The samples (1 or 2 µL) were injected at 200 °C in the pulsed splitless mode at 45 psi with the purge valve closed for 1.0 min. A DB-5MS Ultra Inert capillary column (60m × 0.25 mm × 0.25 µm, Agilent, Wilmington, DE) was used for the separation. The initial column temperature was set at 80 °C for 1 min, ramped to 210 °C at 10 °C/min, further ramped to 300 °C at 5 °C/min, and held at 300 °C for 5 min. High purity helium (99.999%) was used as the carrier gas at a flow rate of 1.0 mL/min. The MS/MS was operated in electron ionization (EI) mode at

70 eV with selected reaction monitoring (SRM). The transfer line, ionization source, and manifold temperatures were 300, 250, and 40 °C, respectively.

5.2.5. Quality Assurance and Quality Control

Several practices were used to assure the accuracy and reproducibility of sample analysis. Both external surrogates and internal standards were introduced into all samples before analysis to monitor extraction efficiency and instrument drift. The recoveries of external surrogates for the aqueous and solid phases were $83.2 \pm 5.2\%$ and $108.3 \pm 16.4\%$, respectively. A laboratory blank was included in every batch of 9 samples to check for potential contamination arising from laboratory materials and solvents used in sample preparation. The calibration curve standards were prepared daily in hexane and the regression was used only when the regression coefficient was greater than 0.999. Difference between treatments was determined by one-way analysis of variance (ANOVA) using SPSS 15.0 (SPSS, Chicago, IL).

5.3. Results and Discussion

5.3.1. Effects of Amendment on Bioavailable Concentrations

Among the three methods used to assess bioavailability of *p,p'*-DDT and *p,p'*-DDE in this study, SPME measurement produced a concentration value C_{free} while the other two methods resulted in accessible fractions. Compared to the unamended sediment, addition of black carbon materials resulted in significant decreases in C_{free} of *p,p'*-DDT and *p,p'*-DDE (Table 5.1). For example, when activated carbon was amended at 1%, the average C_{free} values of *p,p'*-DDE were only 0.2 and 0.1 ng/L in the SD and JL sediments, respectively, which were a small fraction of those measured in the unamended

sediments (12.8 and 169.0 ng/L). A similar trend was also found for C_{free} of *p,p'*-DDT (Table 5.1). In comparison to activated carbon, addition of charcoal was less effective at reducing C_{free} (Table 5.1). For example, in the JL sediment, 1% of charcoal amendment decreased the average C_{free} of *p,p'*-DDE to 6.1 ng/L or *p,p'*-DDE to 23.5 ng/L. Furthermore, as the amendment rate increased to 5%, C_{free} of *p,p'*-DDT and *p,p'*-DDE further decreased, and the decrease was also greater for activated carbon than charcoal (Table 5.1). In fact, C_{free} was below the detection limit (limit of detection, LOD= 0.04 and 0.33 ng/L for *p,p'*-DDE and *p,p'*-DDT, respectively) in most samples amended with activated carbon at 5%, while very low values of C_{free} were observed for sediment samples with 5% charcoal amendment (Table 5.1).

The difference between activated carbon and charcoal may be attributed to their OC contents and likely also differences in their microporosity (Kleineidam et al., 2002; Xia and Ball, 1999). In this study, the activated carbon ($87.0 \pm 0.5\%$) had a higher OC content than charcoal ($84.7 \pm 0.6\%$) and its BET specific surface area and micropore volumes were 6.06- and 3.83-fold of those for charcoal, respectively.

In contrast to the strong effects of black carbon materials, addition of sand at 1 or 5% of the sediment mass did not cause any significant change to the measured C_{free} as compared to the unamended control (Table 5.1). The derived C_{free} values were statistically identical ($p > 0.05$) between the unamended and sand-amended sediments. This observation suggested that sand was a poor sorbent to compete against the sediment for the sorption of *p,p'*-DDT or *p,p'*-DDE. However, it must be noted that sand capping as a remediation practice serves the purpose to physically isolate the contaminated

sediment bed from the overlaying water, creating a barrier to minimize contaminant availability while allowing time for natural attenuation to progress (Hyun et al., 2006; Lampert et al., 2011; McDonough et al., 2007). However, as shown by this study, if sand is mixed into sediment due to, e.g., current or bioturbation induced resuspension or mixing, sand would likely have little effect on the bioavailable concentration of HOCs in the sediment.

5.3.2. Effects of Amendment on Bioavailable Fractions

Both IDM and Tenax-aided desorption were used in this study to estimate the accessible fraction of *p,p'*-DDT and *p,p'*-DDE in the sediments. In the use of IDM, the derived C_e was used to calculate E , which is the fraction of accessible concentration over the bulk sediment concentration (Table 5.2). In the unamended sediment, the averaged E values of *p,p'*-DDE and *p,p'*-DDT in the JL sediment were consistently higher than those in the SD sediment (Table 5.2). The difference reflects the fact that the SD sediment (0.87%) had a higher OC content than the JL sediment (0.12%) and that organic carbon was a driving force for HOC sequestration (Luthy et al., 1997). Addition of black carbon materials consistently decreased E values of *p,p'*-DDT or *p,p'*-DDE in both sediments. For example, in the SD sediment, amendment of charcoal at 1% decreased the average E value of *p,p'*-DDE from 0.545 to 0.265, while addition of 1% activated carbon decreased the average E to only 0.065 (Table 5.2). Even greater reductions from black carbon amendment were found in the JL sediment. For instance, addition of charcoal at 1% decreased the average E in the JL sediment from 0.711 to 0.063, and amendment of activated carbon at 1% decreased E to only 0.019 (Table 5.2). Similar reductions were

also observed with *p,p'*-DDT. The stronger effect of black carbon in the JL sediment may be attributed to its relatively low OC content, suggesting that black carbon competed with the native OC in sequestering HOCs. This finding also implies that for high-OC sediments, it would be necessary to amend black carbon materials at comparatively higher rates to achieve the same degree of reduction in contaminant bioavailability than in low OC sediments. In sediments with 5% charcoal or activated carbon, the derived E values were further reduced. In particular, with 5% activated carbon amendment, E fell below the detection limit.

When Tenax-aided desorption was used to measure the desorbed fraction over a 24-h interval, the derived F_{24h} values were consistently smaller than E in the same sediments (Tables 5.2 and 5.3). For instance, in the unamended SD sediment, averaged F_{24h} values were 0.147 and 0.324 for *p,p'*-DDE and *p,p'*-DDT, which were only 27% and 59.7%, respectively, of the E values for the same compounds. This suggests that F_{24h} was likely an underestimation of the overall chemical accessibility. Amendment of black carbon materials caused similar degrees of suppression to the estimated F_{24h} values (Table 5.3). Addition of 1% charcoal changed F_{24h} of *p,p'*-DDE from 0.147 to 0.059 in the SD sediment and to 0.028 in the JL sediment (Table 5.3). Amendment at the 5% level caused additional decreases, with F_{24h} estimated at 0.007-0.019 for both compounds in the SD sediment, and 0.014-0.022 in the JL sediment (Table 5.3).

In contrast, sand amendment did not appreciably change E or F_{24h} of *p,p'*-DDT and *p,p'*-DDE in both sediments (Tables 5.2 and 5.3). When compared to the unamended control, these values were statistically identical. The lack of effect from sand amendment

on E or F_{24h} was in agreement with that for C_{free} , validating that if mixed into the sediment, sand would have no effect on contaminant bioavailability.

5.3.3. Comparison of Different Methods for Evaluating Amendment Effects

The effect of the various amendment treatments on the potential bioavailability of p,p' -DDT and p,p' -DDE in the sediments was analyzed in a before-and-after manner. A ratio was calculated using C_{free} , E or F_{24h} in the amended sediment over that in the unamended control, i.e., $C_{free}/C_{free,0}$, E/E_0 or $F_{24h}/F_{24h,0}$ (where the subscript 0 indicates the absence of an amendment in a sediment). When the calculated ratios were plotted against each other, as shown in Figure 5.1, highly significant linear correlations were observed for all ratios, with $R^2 \geq 0.92$, and $p < 0.001$ (Figure 5.1). More importantly, the slopes of these linear relationships were all statistically similar to 1 (Figure 5.1). The fact that the slopes of the linear correlations were unity clearly suggest that all three methods were equally capable of predicting the effect of amendment on bioavailability of p,p' -DDT and p,p' -DDE. This conclusion is significant given that these methods operated on different principles and that different compartments of a sediment sample (i.e., aqueous phase vs. solid phase) were targeted for chemical analysis. Although other methods were not included in this study, considering that passive samplers (e.g., SPMD, PED) use a similar principle (i.e., equilibrium partitioning theory, EqP) as SPME, and that other accessibility methods (e.g., mild solvent extraction, cyclodextrin desorption) also aim to determine the readily desorbable fraction as in Tenax-aided desorption or IDM, the above conclusion may be also valid for the various bioavailability estimation methods in general. This further implies that there may be a great degree of flexibility in method

selection for evaluating the efficiency or progress of remediation treatments, so long as the analysis is made in a before-and-after manner.

However, different methods have inherent strengths and limitations (Cui et al., 2013; Macrae and Hall, 1998; Reichenberg and Mayer, 2006), and therefore method selection should consider application circumstances and objectives. Among the three methods tested in this study, SPME was the least sensitive, and C_{free} of p,p' -DDT was below the detection limit in all activated carbon amended samples, and was close to the detection limit for all p,p' -DDE samples (Table 5.1). In comparison, $F_{24\text{h}}$ was measurable in all amended sediments for both p,p' -DDE and p,p' -DDT (Table 5.3). This difference may be attributed to the fact that only a fraction of the aqueous phase concentration was used for detection by SPME, whereas $F_{24\text{h}}$ was a measurement of the desorbed fraction over an extended time duration (24 h). Under the experimental conditions used in this study, the amount of analytes introduced into the GC-MS/MS system for analysis was 7.6 – 162.1 times greater for the Tenax desorption approach than the SPME method. The sensitivity of IDM was between the Tenax-aided desorption and SPME measurements in this study, with E below the method limit only in the SD sediment with 5% activated carbon amendment (Table 5.2). Although also using the desorbed fraction for analysis, as shown in Eq. 2, the sensitivity of IDM is influenced by the amount of isotope labeled analogues added to a sediment sample. In this study, the amount of deuterated p,p' -DDT or p,p' -DDE was only at 8.5 – 13.1% of the non-labeled HOCs. Therefore, it is likely that the method sensitivity of IDM may approach that of Tenax-aided desorption if the isotope-labeled analogues are added at levels similar to that of the native HOCs.

5.4. Conclusions

By applying three different methods to the same sediments, we showed that all methods were capable of accurately predicting the effect of the simulated remediation treatments on the bioavailability of *p,p'*-DDT and *p,p'*-DDE. This suggests that there may be coherent relationships among these methods, allowing interchangeable or complementary use of these methods for bioavailability evaluation in remediation practices. However, desorption based methods such as Tenax extraction and IDM consistently showed better sensitivity than the SPME method that aimed to measure the freely dissolved concentration C_{free} in the aqueous phase. Given that legacy contaminants such as PCBs, PAHs, dioxins and PBDEs are generally strongly hydrophobic with very large K_{ow} values, C_{free} in the aqueous phase of a sediment sample is inevitably very small. It must be noted that *p,p'*-DDT and *p,p'*-DDE were spiked into the sediments at relatively high levels (101.4 – 463.8 $\mu\text{g}/\text{kg}$) in this study. It is likely that some field contaminated sediments may contain HOCs at lower concentrations, which may further diminish the ability for passive samplers such as SPME to detect C_{free} . On the other hand, passive samplers such as SPME and PED are more appropriate for in situ applications, where these devices may be buried at the site and retrieved periodically to monitor the progress of a remediation treatment. In comparison, methods such as Tenax-aided desorption or IDM use discreet sediment samples that are collected and used for ex situ analysis. Therefore, while the consistency in predicting bioavailability changes offers a great flexibility in method selection, other factors such as contamination levels and measurement objectives (e.g., in situ vs. ex situ monitoring) should also be considered

when choosing a method. Applicability and limitation of different methods should be further validated on other contaminants, and with different environmental matrices (e.g., soil).

References

- Bao, L.J., Jia, F., Crago, J., Zeng, E.Y., Schlenk, D., Gan, J., 2013. Assessing bioavailability of DDT and metabolites in marine sediments using solid-phase microextraction with performance reference compounds. *Environmental Toxicology and Chemistry* 32, 1946-1953.
- Cho, Y.-M., Ghosh, U., Kennedy, A.J., Grossman, A., Ray, G., Tomaszewski, J.E., Smithenry, D.W., Bridges, T.S., Luthy, R.G., 2009. Field application of activated carbon amendment for in-situ stabilization of polychlorinated biphenyls in marine sediment. *Environmental Science & Technology* 43, 3815-3823.
- Cornelissen, G., Gustafsson, O., Bucheli, T.D., Jonker, M.T.O., Koelmans, A.A., Van Noort, P.C.M., 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* 39, 6881-6895.
- Cornelissen, G., Rigterink, H., Ferdinandy, M.M.A., Van Noort, P.C.M., 1998. Rapidly desorbing fractions of PAHs in contaminated sediments as a predictor of the extent of bioremediation. *Environmental Science & Technology* 32, 966-970.
- Cornelissen, G., Rigterink, H., ten Hulscher, D.E.M., Vrind, B.A., van Noort, P.C.M., 2001. A simple Tenax (R) extraction method to determine the availability of sediment-sorbed organic compounds. *Environmental Toxicology and Chemistry* 20, 706-711.

- Cui, X., Mayer, P., Gan, J., Cui, X.Y., 2013. Methods to assess bioavailability of hydrophobic organic contaminants: principles, operations, and limitations. *Environmental Pollution* 172.
- Delgado-Moreno, L., Gan, J., 2013. A stable isotope dilution method for measuring bioavailability of organic contaminants. *Environmental Pollution* 176, 171-177.
- Delgado-Moreno, L., Wu, L., Gan, J., 2010. Effect of dissolved organic carbon on sorption of pyrethroids to sediments. *Environmental Science & Technology* 44, 8473-8478.
- Ehlers, L.J., Luthy, R.G., 2003. Contaminant bioavailability in soil and sediment. *Environmental Science & Technology* 37, 295A-302A.
- Fernandez, L.A., Macfarlane, J.K., Tcaciuc, A.P., Gschwend, P.M., 2009. Measurement of freely dissolved PAH concentrations in sediment beds using passive sampling with low-density polyethylene strips. *Environmental Science & Technology* 43, 1430-1436.
- Ghosh, U., Luthy, R.G., Cornelissen, G., Werner, D., Menzie, C.A., 2011. In-situ sorbent amendments: A new direction in contaminated sediment management. *Environmental Science & Technology* 45, 1163-1168.
- Gustafsson, O., Haghseta, F., Chan, C., MacFarlane, J., Gschwend, P.M., 1997. Quantification of the dilute sedimentary soot phase: Implications for PAH speciation and bioavailability. *Environmental Science & Technology* 31, 203-209.
- Hawthorne, S.B., Jonker, M.T.O., van der Heijden, S.A., Grabanski, C.B., Azzolina, N.A., Miller, D.J., 2011. Measuring picogram per liter concentrations of freely

- dissolved parent and alkyl PAHs (PAH-34), using passive sampling with polyoxymethylene. *Analytical Chemistry* 83, 6754-6761.
- Hawthorne, S.B., Miller, D.J., Grabanski, C.B., 2009. Measuring low picogram per liter concentrations of freely dissolved polychlorinated biphenyls in sediment pore water using passive sampling with polyoxymethylene. *Analytical Chemistry* 81, 9472-9480.
- Huckins, J.N., Manuweera, G.K., Petty, J.D., Mackay, D., Lebo, J.A., 1993. Lipid-containing semipermeable-membrane devices for monitoring organic contaminants in water. *Environmental Science & Technology* 27, 2489-2496.
- Hyun, S., Jafvert, C.T., Lee, L.S., Rao, P.S.C., 2006. Laboratory studies to characterize the efficacy of sand capping a coal tar-contaminated sediment. *Chemosphere* 63, 1621-1631.
- Jia, F., Bao, L.-J., Crago, J., Schlenk, D., Gan, J., 2014. Use of isotope dilution method (IDM) to predict bioavailability of organic contaminants in historically contaminated sediments. In review.
- Jia, F., Cui, X.Y., Wang, W., Delgado-Moreno, L., Gan, J., 2012. Using disposable solid-phase microextraction (SPME) to determine the freely dissolved concentration of polybrominated diphenyl ethers (PBDEs) in sediments. *Environmental Pollution* 167, 34-40.
- Jia, F., Gan, J., 2014. Comparing black carbon types in sequestering polybrominated diphenyl ethers (PBDEs) in sediments. *Environmental Pollution* 184, 131-137.

- Kelsey, J.W., Kottler, B.D., Alexander, M., 1997. Selective chemical extractants to predict bioavailability of soil-aged organic chemicals. *Environmental Science & Technology* 31, 214-217.
- Khan, M.I., Cheema, S.A., Shen, C., Zhang, C., Tang, X., Shi, J., Chen, X., Park, J., Chen, Y., 2012. Assessment of phenanthrene bioavailability in aged and unaged soils by mild extraction. *Environmental Monitoring and Assessment* 184, 549-559.
- Kleineidam, S., Schuth, C., Grathwohl, P., 2002. Solubility-normalized combined adsorption-partitioning sorption isotherms for organic pollutants. *Environmental Science & Technology* 36.
- Lampert, D.J., Sarchet, W.V., Reible, D.D., 2011. Assessing the effectiveness of thin-layer sand caps for contaminated sediment management through passive sampling. *Environmental Science & Technology* 45, 8437-8443.
- Luthy, R.G., Aiken, G.R., Brusseau, M.L., Cunningham, S.D., Gschwend, P.M., Pignatello, J.J., Reinhard, M., Traina, S.J., Weber, W.J., Westall, J.C., 1997. Sequestration of hydrophobic organic contaminants by geosorbents. *Environmental Science & Technology* 31, 3341-3347.
- Macrae, J.D., Hall, K.J., 1998. Comparison of methods used to determine the availability of polycyclic aromatic hydrocarbons in marine sediment. *Environmental Science & Technology* 32, 3809-3815.

- McDonough, K.M., Murphy, P., Olsta, J., Zhu, Y., Reible, D., Lowry, G.V., 2007. Development and placement of a sorbent-amended thin layer sediment cap in the Anacostia River. *Soil & Sediment Contamination* 16, 313-322.
- Poerschmann, J., Zhang, Z.Y., Kopinke, F.D., Pawliszyn, J., 1997. Solid phase microextraction for determining the distribution of chemicals in aqueous matrices. *Analytical Chemistry* 69, 597-600.
- Reichenberg, F., Mayer, P., 2006. Two complementary sides of bioavailability: Accessibility and chemical activity of organic contaminants in sediments and soils. *Environmental Toxicology and Chemistry* 25, 1239-1245.
- Reid, B.J., Stokes, J.D., Jones, K.C., Semple, K.T., 2000. Nonexhaustive cyclodextrin-based extraction technique for the evaluation of PAH bioavailability. *Environmental Science & Technology* 34, 3174-3179.
- Semple, K.T., Doick, K.J., Jones, K.C., Burauel, P., Craven, A., Harms, H., 2004. Defining bioavailability and bioaccessibility of contaminated soil and sediment is complicated. *Environmental Science & Technology* 38, 228A-231A.
- Stokes, J.D., Wilkinson, A., Reid, B.J., Jones, K.C., Semple, K.T., 2005. Prediction of polycyclic aromatic hydrocarbon biodegradation in contaminated soils using an aqueous hydroxypropyl-beta-cyclodextrin extraction technique. *Environmental Toxicology and Chemistry* 24, 1325-1330.
- Tang, J., Alexander, M., 1999. Mild extractability and bioavailability of polycyclic aromatic hydrocarbons in soil. *Environmental Toxicology and Chemistry* 18, 2711-2714.

- Tomaszewski, J., Werner, D., Luthy, R., 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*, 2143-2150.
- U.S. EPA, 2001. Methods for collection, storage and manipulation of sediments for chemical and toxicological analyses: Technical manual. United States Environmental Protection Agency, Washington, DC 20460.
- Van den Hoop, M., Kreule, P., Loch, J.P.G., 1999. Sorption kinetics and transformation of DDT in sediment. *Water Air and Soil Pollution* 110, 57-66.
- Werner, D., Hale, S.E., Ghosh, U., Luthy, R.G., 2010. Polychlorinated biphenyl sorption and availability in field-contaminated sediments. *Environmental Science & Technology* 44, 2809-2815.
- Xia, G.S., Ball, W.P., 1999. Adsorption-partitioning uptake of nine low-polarity organic chemicals on a natural sorbent. *Environmental Science & Technology* 33.
- Xu, Y., Gan, J., Wang, Z., Spurlock, F., 2008. Effect of aging on desorption kinetics of sediment-associated pyrethroids. *Environmental Toxicology and Chemistry* 27, 1293-1301.

Tables

Table 5.1. The freely dissolved concentrations (C_{free} , ng/L) of *p,p'*-DDT and *p,p'*-DDE measured by the solid phase microextraction (SPME) in sediments following different amendments

Sediment	<i>p,p'</i> -DDT		<i>p,p'</i> -DDE	
	SD ^a	JL	SD	JL
Unamended	17.1 ± 2.3	318.4 ± 32.4	12.8 ± 2.8	169.0 ± 6.4
1% AC ^b	nd ^c	nd	0.3 ± 0.2	0.1 ± 0.1
1% CC	10.1 ± 1.0	23.5 ± 8.6	6.7 ± 0.6	6.1 ± 2.3
1% Sand	13.9 ± 1.5	344.5 ± 8.6	12.4 ± 1.2	171.9 ± 3.7
5% AC	nd	nd	0.2 ± 0.1	nd
5% CC	2.6 ± 0.4	nd	1.1 ± 0.2	0.2 ± 0.1
5% Sand	15.2 ± 1.2	305.8 ± 10.4	12.9 ± 0.5	158.3 ± 2.6

^aSD= San Diego Creek sediment, Orange County, CA; JL= Jordan Lake Reservoir sediment, Chatham Country, NC.

^bAC = activated carbon; CC = charcoal. ^cnd= not detected.

Table 5.2. The accessible fraction (E) of p,p' -DDT and p,p' -DDE measured by the isotope dilution method (IDM) in sediments following different amendments

Sediment	p,p' -DDT		p,p' -DDE	
	SD ^a	JL	SD	JL
Unamended	0.543 ± 0.073	0.704 ± 0.072	0.545 ± 0.025	0.711 ± 0.037
1% AC ^b	0.044 ± 0.009	0.045 ± 0.008	0.065 ± 0.011	0.019 ± 0.001
1% CC	0.352 ± 0.042	0.181 ± 0.026	0.265 ± 0.026	0.063 ± 0.007
1% Sand	0.407 ± 0.040	0.570 ± 0.042	0.487 ± 0.011	0.699 ± 0.069
5% AC	nd ^c	0.049 ± 0.008	nd	0.021 ± 0.009
5% CC	0.091 ± 0.018	0.165 ± 0.015	0.086 ± 0.007	0.048 ± 0.008
5% Sand	0.545 ± 0.070	0.668 ± 0.098	0.552 ± 0.033	0.726 ± 0.015

^aSD= San Diego Creek sediment, Orange County, CA; JL= Jordan Lake Reservoir sediment, Chatham Country, NC.

^bAC = activated carbon; CC = charcoal. ^cnd= not detected.

Table 5.3. The desorption fraction of *p,p'*-DDT and *p,p'*-DDE at 24 h (F_{24h}) measured by the Tenax desorption method in sediments following different amendments

Sediment	<i>p,p'</i> -DDT		<i>p,p'</i> -DDE	
	SD ^a	JL	SD	JL
Unamended	0.324 ± 0.083	0.301 ± 0.026	0.147 ± 0.022	0.124 ± 0.006
1% AC ^b	0.036 ± 0.002	0.045 ± 0.008	0.009 ± 0.001	0.018 ± 0.003
1% CC	0.196 ± 0.021	0.100 ± 0.016	0.059 ± 0.001	0.028 ± 0.003
1% Sand	0.310 ± 0.020	0.357 ± 0.024	0.139 ± 0.006	0.134 ± 0.014
5% AC	0.019 ± 0.003	0.022 ± 0.004	0.007 ± 0.001	0.014 ± 0.001
5% CC	0.062 ± 0.006	0.066 ± 0.013	0.017 ± 0.001	0.026 ± 0.003
5% Sand	0.276 ± 0.024	0.283 ± 0.057	0.138 ± 0.009	0.144 ± 0.027

^aSD= San Diego Creek sediment, Orange County, CA; JL= Jordan Lake Reservoir sediment, Chatham Country, NC.

^bAC = activated carbon; CC = charcoal.

Figures

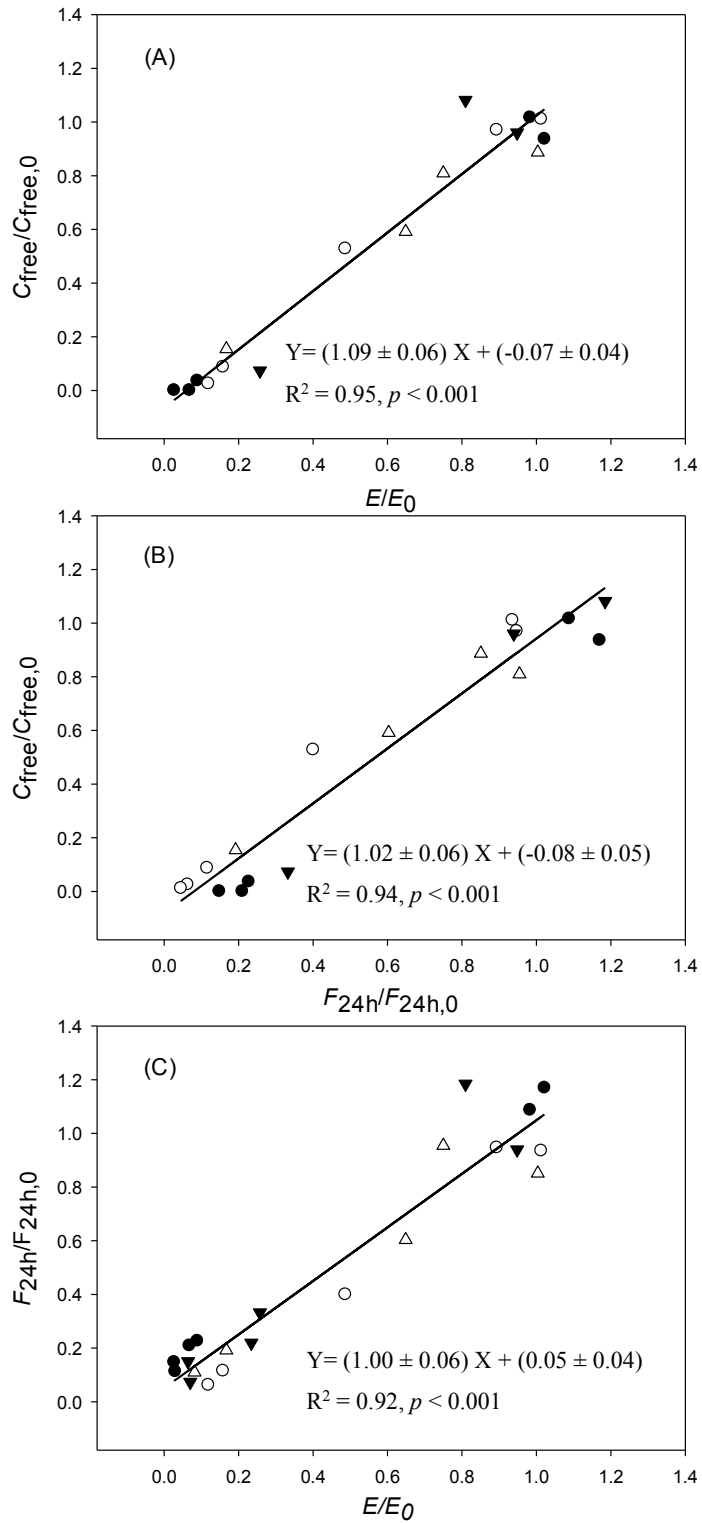


Figure 5.1. Correlations between the E/E_0 and $C_{\text{free}}/C_{\text{free},0}$ (A), $C_{\text{free}}/C_{\text{free},0}$ and $F_{24\text{h}}/F_{24\text{h},0}$ (B), and E/E_0 and $F_{24\text{h}}/F_{24\text{h},0}$ (C) for p,p' -DDT in black carbon or sand amended SD (blank triangle) and JL (filled triangle) sediments, and p,p' -DDE in black carbon or sand amended SD (blank circle) and JL (filled circle) sediments, respectively. The subscript 0 indicates levels in the sediment without amendments.

Chapter 6 General Conclusions and Future Research Needs

6.1. General Conclusions

For HOCs, it is bioavailability, rather than the bulk chemical concentration, that regulates the bioaccumulation or potential toxicity to organisms. In this project, three different bioavailability methods, including SPME, matrix-SPME and IDM, were developed and applied in different scenarios for improving our understanding of the environmental fate and ecotoxicological effects of HOCs, including PBDEs, PCBs, and DDT and DDT metabolites in freshwater and marine sediments.

When exploring the use of disposable PDMS fibers for measuring bioavailability of PBDEs in sediments, we found that C_{free} of PBDEs in sediment porewater decreased with increasing degree of bromination of PBDEs or OC content in a sediment. Consequently, the potential bioaccumulation or aquatic toxicity of BDE 47, 99, or 153 would be 1.3–10.5 times greater in a sediment with low OC content (0.24%) than in a sediment with high OC content (1.4 – 2.5%).

In a subsequent study, a matrix-SPME method was further developed and used to compare the efficiency of sequestration capacity of different BC materials on PBDEs. The results showed that activated carbon had substantially greater efficacy than biochar or charcoal in inhibiting the bioavailability of PBDEs, which was attributed to its higher OC content, large BET surface area and micropore volumes. The effect of BC amendment on bioavailability of PBDEs was more pronounced in low OC sediments than in high OC sediments. Therefore, when using BC for amendment, it is important to consider the type of BC material and the sediment properties.

Isotope dilution has been extensively used in understanding bioavailability of metals; however, similar applications have not been extended to HOCs. We attempted to explore a similar isotope dilution method (IDM) to determine the bioaccessible fraction of sediment-borne HOCs. The bioaccessible fraction E given by IDM involves the use of stable isotope labeled analogues and simple analytical steps. For DDT and DDT metabolites and PCBs, after addition of isotope labeled analogues, a steady state in the distribution of the labeled standards between the sediment and aqueous phase was reached within 24 h of mixing. The measured E correlated very well with the sum of the rapid and slow desorption fractions given by the sequential Tenax desorption test. The derived accessible concentration C_e was shown to be a good indicator for bioaccumulation of DDTs and PCBs by the marine benthic polychaete *Neanthes arenaceodentata*.

In the last study, we compared different methods for their advantages and limitations for use in the evaluation of remediation efficiency. Sediments were amended with charcoal, activated carbon or sand at 1 or 5% to simulate some of the popular remediation treatments. When compared to the unamended sediments, the SPME, Tenax desorption and IDM predicted essentially the same degrees of reductions in bioavailability from various amendments. After normalizing with unamended sediment, measurements given by these methods were linearly correlated with the slopes close to 1. This finding suggests that it is not critical to choose a specific bioavailability estimation method, as long as the evaluation is done in a before-and-after fashion. However, SPME and likely other passive samplers that aim to predict bioavailability by measuring C_{free} ,

were substantially less sensitive than the Tenax desorption test or IDM. This information may be used for guiding method selection in efforts to evaluate efficacy or monitor progress of remediation treatments.

6.2. Future Research Needs

This project has developed different tools to estimate bioavailability of HOCs in sediments and in specific applications of the bioavailability measurement methods. However, more work needs to be carried out to improve our understanding of the fate and risks of HOCs in sediments or soils, including contamination of HOCs from historical episodes and HOCs in different matrices (e.g., run-off water, soil).

Some studies have shown that as the HOCs persist in the sediment, they become gradually less available for bioaccumulation or biodegradation. Therefore, contact time or aging is likely a significant factor to consider for HOCs from historical contamination events. The effect of aging should be characterized to complement risk assessment of contaminated sites and to monitor the effectiveness and progress of risk mitigation operations.

In addition, aging may further impose an effect on sorbents such as black carbon that is incorporated into sediment or soil to sequester or immobilize the contaminants. The sorption sites on sorbents may be increasingly blocked by colloids or natural organic matter, leading to decreased capacity for binding HOCs over time. It is also likely that over time, HOC molecules may migrate into inner pores or isolated regions of sorbents (e.g., black carbon), which would result in a decrease in bioavailability of the sorbed HOCs.

Furthermore, similar to the particulate OC in the sediment, the presence of dissolved organic matter (DOM) in the water phase may decrease C_{free} of HOCs, owing to their high affinity to DOM. Even though many studies have demonstrated that particulate OC is highly effective at sequestering HOCs and diminishing their bioavailability, the bioavailability of DOM-associated HOCs is less understood. Further research on the bioavailability of DOM-associated HOCs will improve our overall understanding of the fate and effects of HOCs in surface water ecosystems and likely also soil-water systems.