

UC Riverside

UC Riverside Previously Published Works

Title

Comparing black carbon types in sequestering polybrominated diphenyl ethers (PBDEs) in sediments

Permalink

<https://escholarship.org/uc/item/3t59650w>

Authors

Jia, Fang
Gan, Jay

Publication Date

2014

DOI

10.1016/j.envpol.2013.08.009

Peer reviewed

Published in final edited form as:

Environ Pollut. 2014 January ; 184: 131–137. doi:10.1016/j.envpol.2013.08.009.

Comparing black carbon types in sequestering polybrominated diphenyl ethers (PBDEs) in sediments

Fang Jia* and Jay Gan

Department of Environmental Sciences, University of California, Riverside, CA 92521, USA

Abstract

Polybrominated diphenyl ethers (PBDEs) are widely found in sediments, especially congeners from the penta-BDE formula. Due to their strong affinity for black carbon (BC), bioavailability of PBDEs may be decreased in BC-amended sediments. In this study, we used a matrix-SPME method to measure the freely dissolved concentration (C_{free}) of PBDEs as a parameter of their potential bioavailability and evaluated the differences among biochar, charcoal, and activated carbon. Activated carbon displayed a substantially greater sequestration capacity than biochar or charcoal. At 1% amendment rate in sediment with low organic carbon (OC) content (0.12%), C_{free} of six PBDEs was reduced by 47.5–78.0%, 47.3–77.5%, and 94.1–98.3% with biochar, charcoal, and activated carbon, respectively, while the sequestration was more limited in sediment with high OC content (0.87%). Therefore, it is important to consider the type and properties of the BC and the sediment in BC-based remediation or mitigation.

Keywords

Solid phase microextraction; Black carbon amendment; Activated carbon; Charcoal; Biochar; Polybrominated diphenyl ether

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.

2. Materials and methods

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 isoctane (50 $\mu\text{g}/\text{mL}$) 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 mm PDMS was purchased from Polymicro Technologies (Phoenix, AZ). The volume of PDMS polymer coating per length was 51.1 $\mu\text{L}/\text{m}$. 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).

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 24 h, 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 (Pittsburgh, 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 1.

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 $\mu\text{g/L}$ 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 GCeMS. 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} :

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

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% NaN_3 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% NaN_3 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.

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 $\mu\text{g}/\text{kg}$ 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.

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 \times 0.25 mm \times 0.25 mm) (J&W Scientific, Folsom, CA) was used for separation. A 1- μL aliquot was injected in the inlet at 250 $^{\circ}\text{C}$ and in the pulsed splitless mode at 50 psi. The oven temperature was initiated at 80 $^{\circ}\text{C}$ for 1 min, then ramped at 20 $^{\circ}\text{C}/\text{min}$ to a temperature of 280 $^{\circ}\text{C}$ and held for 5 min, and finally ramped at 2 $^{\circ}\text{C}/\text{min}$ to 300 $^{\circ}\text{C}$ 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 $^{\circ}\text{C}$ and N_2 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.

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. Results and discussion

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 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.

3.2. Uptake kinetics in sediment

Fig. 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 (Fig. 1). For example, in the SD sediment, the time for attaining 95% of the equilibrium ($t_{0.95}$) 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 (Fig. 1). Accumulation was consistently more rapid in the SD sediment than in the JL sediment for the same PBDE congener. For example, $t_{0.95}$ 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. 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 (Fig. 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 (Fig. 2). In comparison, much greater decreases in C_{PDMS} consistently occurred in the activated carbon-amended sediment (Fig. 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 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 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 (Fig. 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 (Figs. 2 and 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 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.

3.4. 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 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). 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). 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.

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 PM. Assessing the combined roles of natural organic matter and black carbon as sorbents in sediments. *Environ. Sci. Technol.* 2002; 36:21–29. [PubMed: 11811485]
- Barring H, Bucheli TD, Broman D, Gustafsson O. Soot-water distribution coefficients for polychlorinated dibenzo-p-dioxins, polychlorinated dibenzofurans and polybrominated diphenylethers determined with the soot cosolvency-column method. *Chemosphere.* 2002; 49:515–523. [PubMed: 12430638]
- Beckingham B, Ghosh U. Field-scale reduction of PCB bioavailability with activated carbon amendment to river sediments. *Environ. Sci. Technol.* 2011; 45:10567–10574. [PubMed: 22077959]
- Braekevelt E, Tittlemier S, Tomy G. Direct measurement of octanol-water partition coefficients of some environmentally relevant brominated diphenyl ether congeners. *Chemosphere.* 2003; 51:563–567. [PubMed: 12615110]
- Chai Y, Currie RJ, Davis JW, Wilken M, Martin GD, Fishman VN, Ghosh U. Effectiveness of activated carbon and biochar in reducing the availability of polychlorinated dibenzo-p-dioxins/dibenzofurans in soils. *Environ. Sci. Technol.* 2012; 46:1035–1043. [PubMed: 22136630]
- Chen B, Zhou D, Zhu L. Transitional adsorption and partition of nonpolar and polar aromatic contaminants by biochars of pine needles with different pyrolytic temperatures. *Environ. Sci. Technol.* 2008; 42:5137–5143. [PubMed: 18754360]
- Choi Y, Cho Y-M, Gala WR, Luthy RG. Measurement and modeling of activated carbon performance for the sequestration of parent- and alkylated-polycyclic aromatic hydrocarbons in petroleum-impacted sediments. *Environ. Sci. Technol.* 2013; 47:1024–1032. [PubMed: 23240641]
- Cui X, Jia F, Chen Y, Gan J. Influence of single-walled carbon nanotubes on microbial availability of phenanthrene in sediment. *Ecotoxicology.* 2011; 20:1277–1285. [PubMed: 21656161]
- Cui X, Mayer P, Gan J. Methods to assess bioavailability of hydrophobic organic contaminants: principles, operations, and limitations. *Environ. Pollut.* 2013; 172:223–234. [PubMed: 23064200]
- Eguchi A, Isobe T, Ramu K, Tanabe S. Optimisation of the analytical method for octa-, nona- and deca-brominated diphenyl ethers using gas chromatography-quadrupole mass spectrometry and isotope dilution. *Int. J. Environ. Anal. Chem.* 2011; 91:348–356.
- Gustafsson O, Haghseta F, Chan C, MacFarlane J, Gschwend PM. Quantification of the dilute sedimentary soot phase: implications for PAH speciation and bioavailability. *Environ. Sci. Technol.* 1997; 31:203–209.
- Hale RC, Alaei M, Manchester-Neesvig JB, Stapleton HM, Ikonomou MG. Polybrominated diphenyl ether flame retardants in the North American environment. *Environ. Int.* 2003; 29:771–779. [PubMed: 12850095]
- Jeong S, Wander MM, Kleinedam S, Grathwohl P, Ligouis B, Werth CJ. The role of condensed carbonaceous materials on the sorption of hydrophobic organic contaminants in subsurface sediments. *Environ. Sci. Technol.* 2008; 42:1458–1464. [PubMed: 18441788]

- Jia F, Cui XY, Wang W, Delgado-Moreno L, Gan J. Using disposable solid-phase microextraction (SPME) to determine the freely dissolved concentration of polybrominated diphenyl ethers (PBDEs) in sediments. *Environ. Pollut.* 2012; 167:34–40. [PubMed: 22522316]
- Jonker M, Koelmans A. Sorption of polycyclic aromatic hydrocarbons and polychlorinated biphenyls to soot and soot-like materials in the aqueous environment mechanistic considerations. *Environ. Sci. Technol.* 2002; 36:3725–3734. [PubMed: 12322744]
- Kleineidam S, Schuth C, Grathwohl P. Solubility-normalized combined adsorption-partitioning sorption isotherms for organic pollutants. *Environ. Sci. Technol.* 2002; 36:4689–4697. [PubMed: 12433183]
- La Guardia M, Hale R, Harvey E. Detailed polybrominated diphenyl ether (PBDE) congener composition of the widely used penta-, octa-, and deca-PBDE technical flame-retardant mixtures. *Environ. Sci. Technol.* 2006; 40:6247–6254. [PubMed: 17120549]
- Lacorte S, Guillamon M, Martinez E, Viana P, Barcelo D. Occurrence and specific congener profile of 40 polybrominated diphenyl ethers in river and coastal sediments from Portugal. *Environ. Sci. Technol.* 2003; 37:892–898. [PubMed: 12666918]
- Liu M, Tian S, Chen P, Zhu L. Predicting the bioavailability of sediment-associated polybrominated diphenyl ethers using a 45-d sequential Tenax extraction. *Chemosphere.* 2011; 85:424–431. [PubMed: 21890174]
- Mai BX, Chen SJ, Luo XJ, Chen LG, Yang QS, Sheng GY, Peng PG, Fu JM, Zeng EY. Distribution of polybrominated diphenyl ethers in sediments of the Pearl River Delta and adjacent South China Sea. *Environ. Sci. Technol.* 2005; 39:3521–3527. [PubMed: 15952354]
- Meironyte D, Noren K, Bergman A. Analysis of polybrominated diphenyl ethers in Swedish human milk. A time-related trend study, 1972–1997. *J. Toxicol. Environ. Health A.* 1999; 58:329–341.
- Millward R, Bridges T, Ghosh U, Zimmerman J, Luthy R. Addition of activated carbon to sediments to reduce PCB bioaccumulation by a polychaete (*Neanthes arenaceodentata*) and an amphipod (*Leptocheirus plumulosus*). *Environ. Sci. Technol.* 2005; 39:2880–2887. [PubMed: 15884389]
- Nylund K, Asplund L, Jansson B, Jonsson P, Litzen K, Sellstrom U. Analysis of some polyhalogenated organic pollutants in sediment and sewage-sludge. *Chemosphere.* 1992; 24:1721–1730.
- Oen AMP, Beckingham B, Ghosh U, Krusa ME, Luthy RG, Hartnik T, Henriksen T, Cornelissen G. Sorption of organic compounds to fresh and field-aged activated carbons in soils and sediments. *Environ. Sci. Technol.* 2012; 46:810–817. [PubMed: 22128748]
- Oleszczuk P, Hale SE, Lehmann J, Cornelissen G. Activated carbon and biochar amendments decrease pore-water concentrations of polycyclic aromatic hydrocarbons (PAHs) in sewage sludge. *Bioresour. Technol.* 2012; 111:84–91. [PubMed: 22391590]
- Pignatello JJ, Kwon S, Lu Y. 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. *Environ. Sci. Technol.* 2006; 40:7757–7763. [PubMed: 17256524]
- Rahman F, Langford KH, Scrimshaw MD, Lester JN. Polybrominated diphenyl ether (PBDE) flame retardants. *Sci. Total Environ.* 2001; 275:1–17. [PubMed: 11482396]
- Rakowska MI, Kupryianchyk D, Harmsen J, Grotenhuis T, Koelmans AA. In situ remediation of contaminated sediments using carbonaceous materials. *Environ. Toxicol. Chem.* 2012; 31:693–704. [PubMed: 22389227]
- Ran Y, Xing BS, Rao PSC, Fu JM. Importance of adsorption (hole-filling) mechanism for hydrophobic organic contaminants on an aquifer kerogen isolate. *Environ. Sci. Technol.* 2004; 38:4340–4348. [PubMed: 15382862]
- Sun X, Ghosh U. The effect of activated carbon on partitioning, desorption, and biouptake of native polychlorinated biphenyls in four freshwater sediments. *Environ. Toxicol. Chem.* 2008; 27:2287–2295. [PubMed: 18517308]
- ter Laak TL, Busser FJM, Hermens JLM. Poly(dimethylsiloxane) as passive sampler material for hydrophobic chemicals: effect of chemical properties and sampler characteristics on partitioning and equilibration times. *Anal. Chem.* 2008; 80:3859–3866. [PubMed: 18422340]

- ter Laak TL, Van Eijkeren JCH, Busser FJM, Van Leeuwen HP, Hermens JLM. Facilitated transport of polychlorinated biphenyls and polybrominated diphenyl ethers by dissolved organic matter. *Environ. Sci. Technol.* 2009; 43:1379–1385. [PubMed: 19350907]
- Toms L-ML, Hearn L, Kennedy K, Harden F, Bartkow M, Temme C, Mueller JF. Concentrations of polybrominated diphenyl ethers (PBDEs) in matched samples of human milk, dust and indoor air. *Environ. Int.* 2009; 35:864–869. [PubMed: 19351571]
- Wang ZY, Zeng XL, Zhai ZC. Prediction of supercooled liquid vapor pressures and n-octanol/air partition coefficients for polybrominated diphenyl ethers by means of molecular descriptors from DFT method. *Sci. Total Environ.* 2008; 389:296–305. [PubMed: 17897703]
- Werner D, Hale SE, Ghosh U, Luthy RG. Polychlorinated biphenyl sorption and availability in field-contaminated sediments. *Environ. Sci. Technol.* 2010; 44:2809–2815. [PubMed: 19961220]
- Xia GS, Ball WP. Adsorption-partitioning uptake of nine low-polarity organic chemicals on a natural sorbent. *Environ. Sci. Technol.* 1999; 33:262–269.
- Xing BS, Pignatello JJ, Gigliotti B. Competitive sorption between atrazine and other organic compounds in soils and model sorbents. *Environ. Sci. Technol.* 1996; 30:2432–2440.
- Yang Y, Hunter W, Tao S, Crowley D, Gan J. Effect of activated carbon on microbial bioavailability of phenanthrene in soils. *Environ. Toxicol. Chem.* 2009a; 28:2283–2288. [PubMed: 19572767]
- Yang Y, Hunter W, Tao S, Gan J. Effects of black carbon on pyrethroid availability in sediment. *J. Agric. Food Chem.* 2009b; 57:232–238. [PubMed: 19090765]
- Yang Y, Hunter W, Tao S, Gan J. Microbial availability of different forms of phenanthrene in soils. *Environ. Sci. Technol.* 2009c; 43:1852–1857. [PubMed: 19368182]
- Yang ZY, Zeng EY, Xia H, Wang JZ, Mai BX, Maruya KA. 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. *J. Chromatogr. A.* 2006; 1116:240–247. [PubMed: 16580005]
- Yu Y-X, Zhang S-H, Huang N-B, Li J-L, Pang Y-P, Zhang X-Y, Yu Z-Q, Xu Z-G. Polybrominated diphenyl ethers and polychlorinated biphenyls in freshwater fish from Taihu Lake, China: their levels and the factors that influence biomagnification. *Environ. Toxicol. Chem.* 2012; 31:542–549. [PubMed: 22190383]

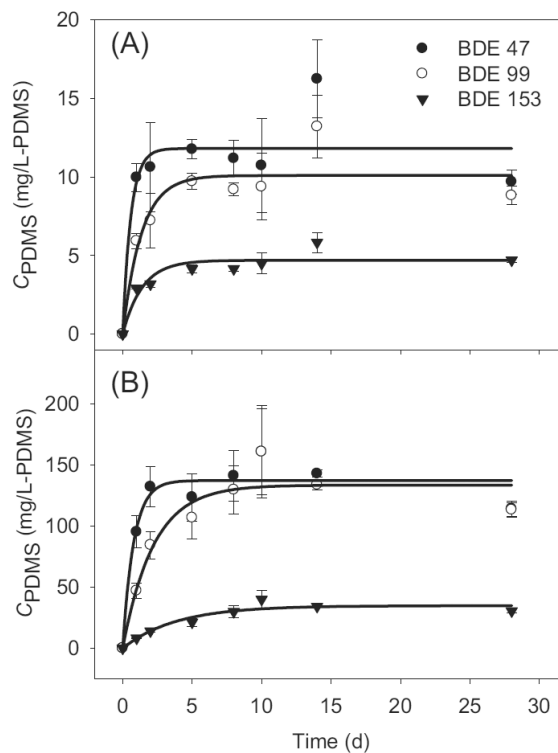


Fig. 1. Uptake kinetics of BDE 47 (●), BDE 99 (○), and BDE 153 (▼) by PDMS fibers in sediments under mixing conditions. (A) San Diego Creek sediment (SD); and (B) Jordan Lake Reservoir sediment (JL). The data was fitted to a one-compartment rise to maximum equation to determine the time to reach equilibrium: $C_{PDMS;t} = C_{PDMS;eq} \times (1 - e^{-kt})$, 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.

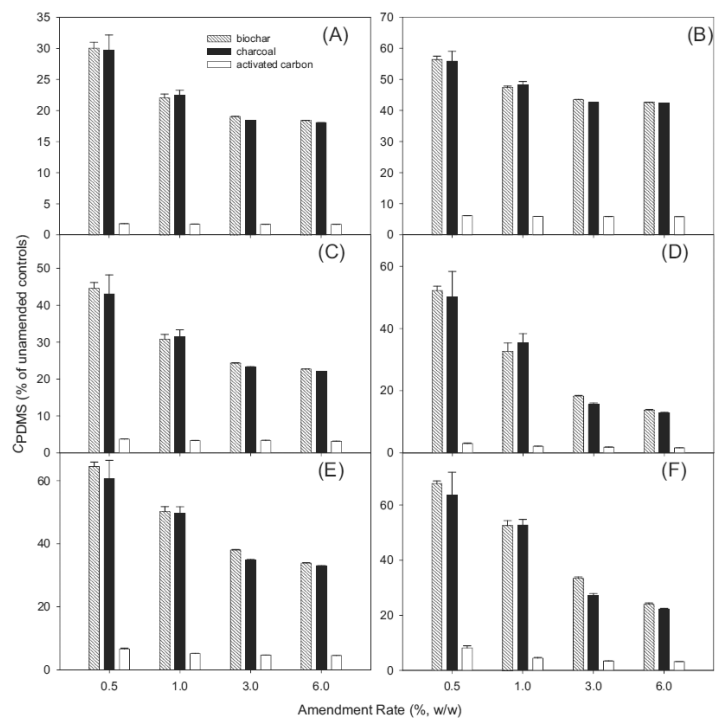


Fig. 2. Concentrations of BDE 47 (A), 85 (B), 99 (C), 100 (D), 153 (E), and 154 (F) on PDMS fibers in Jordan Lake Reservoir sediment amended with different types of black carbon relative to the unamended controls.

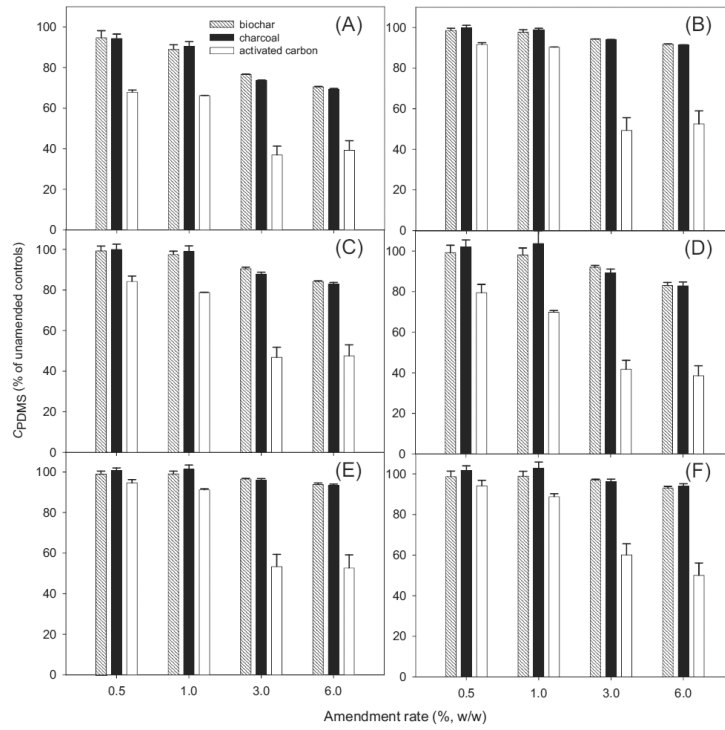


Fig. 3. Concentrations of BDE 47 (A), 85 (B), 99 (C), 100 (D), 153 (E), and 154 (F) on the PDMS fibers in San Diego Creek sediment amended with different types of black carbon.

Table 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 (m² g⁻¹).

^bVolume_{total}, the volume of total pores (cm³ g⁻¹) measured with N₂.

^cVolume_{micro}, the volume of total micropores (cm³ g⁻¹) measured with N₂.

Table 2Measured PDMSe-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

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
<i>San Diego Creek sediment</i>				
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
<i>Jordan Lake sediment</i>				
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