Effects of carbonaceous materials on microbial bioavailability of 2,2′,4,4′-tetrabromodiphenyl ether (BDE-47) in sediments

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HIGHLIGHTS

- CMs inhibited microbial debromination ratios of BDE-47 in sediments by 92.8–98.2%.
- The inhibitory effect of CMs on BDE-47 debromination increased with the CM content.
- CNTs decreased debromination of BDE-47 more remarkably than BC.
- Declined BDE-47 desorption from CMs explained reduction in BDE-47 bioavailability.
- The role of CMs in reducing BDE-47 bioavailability depended on their properties.

ARTICLE INFO

ABSTRACT

In this study, we investigated the influence of various types of carbonaceous materials (CMs) on the bioavailability of 2,2′,4,4′-tetrabromodiphenyl ether (BDE-47) to polybrominated diphenyl ether (PBDE)-degrading microorganisms in CM-amended sediments. The microbial debromination ratio of BDE-47 was reduced by 92.8%–98.2% in the 5.0% CM-amended sediment compared with in sediment without CM amendment after 100 d of anaerobic incubation. The concentrations of lower brominated products also decreased when the content of CMs increased from 0.2% to 5.0%. The inhibitory effects of CMs on BDE-47 debromination were CM content- and characteristic-specific. The reciprocals of BDE-47 debromination ratios and lower brominated product concentrations showed positive linear correlations with CM contents in sediments ($p < 0.01$), and the slopes of linear regression fitting generally correlated with specific surface areas (SSAs) of CMs. Desorption of BDE-47 from CMs indicated the declined desorbing fraction of BDE-47 was responsible for the reduction in BDE-47 bioavailability to microorganisms, thus decreasing its debromination in sediments amended with CMs. This study revealed that CM amendment could reduce the PBDE bioavailability to PBDE-degrading microorganisms in sediments, and it is expected to help deepen our understanding of the environmental behaviors and risks of PBDEs.

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1. Introduction

Polybrominated diphenyl ethers (PBDEs) are extensively used in industrial and consumer products as flame retardants worldwide for several decades [1,2]. Owing to their high lipophilicity, PBDEs tend to accumulate in human and animal bodies through various routes, including ingestion, inhalation and direct body contact [3–5]. It is well documented that PBDEs exhibited neurotoxic and endocrine disrupting effects on organisms [6,7]. Thus, the adverse environmental impacts of PBDEs have attracted attentions not only from the scientific community but also from administrative agencies, and commercial penta- and octa-BDE were listed in the Stockholm Convention as emerging persistent organic pollutants (POPs) in 2009.

Over past decades, PBDEs have been widely detected in various environmental components, such as air, soils, and aquatic systems [8–10]. As a typical class of hydrophobic organic compounds (HOCs), PBDEs would easily find their way into sediments, a vital

sink for HOCs in water environments [11,12]. It has been reported that microbial decomposition and degradation are the predominate pathways in removing HOCs from aquatic environments [13–15]. Furthermore, the biodegradability of HOCs in sediments largely depends on their bioavailability to microorganisms [16]. Hence, investigation of the microbial bioavailability of PBDEs in sediments would advance our understanding of their fate and transformations, and this is beneficial to minimizing their environmental hazards. Although numerous studies explored the bioavailability of sediment-associated HOCs (such as polycyclic aromatic hydrocarbons (PAHs) and polychlorinated biphenyls) to benthic animals during bioaccumulation processes [17–23], research on the PBDE bioavailability to microorganisms in sediments is rarely reported.

Black carbon (BC) and carbon nanotubes (CNTs) are two representatives of carbonaceous materials (CMs). BC is produced from incomplete combustion residues of biomass or fossil fuels under oxygen-limited and relatively low temperature (<700 °C) conditions. BC has potential for *in situ* remediation of polluted sediments due to its superior sorption capacity to organic contaminants [24–26]. CNTs are a type of one-dimensional carbonaceous nanomaterials with a radial dimension of nanometer scale and an axial dimension of micrometer scale [27]. The unique physicochemical properties of CNTs enable their promising applications in many fields [28–30]. Since the past century, BC and CNT production has increased rapidly as a result of intensive anthropogenic activities and accelerated industrial development [28,31]. Therefore, they would be inevitably discharged into the environments and affect the distribution, transfer, and bioavailability of HOCs [32–34]. For example, our previous work revealed that the biota-sediment accumulation factors of *Chironomus plumosus* larvae for PAHs decreased significantly due to increased sediment BC contents [35]. Also, the presence of $5 \, mg \, g^{-1}$ CNTs in soils could substantially reduce the PAHs mobility because of the strong PAH sorption to CNTs [36]. Similarly, Petersen et al. found that addition of CNTs to soils lowered the pyrene bioaccumulation in earthworms and enhanced the pyrene elimination rates [37]. Nevertheless, there is very limited research regarding the effects of CMs on PBDE bioavailability in sediments [38]. Meanwhile, research regarding the influence of CNTs on environmental behaviors of HOCs is still in its infancy compared with other CMs [39]. Moreover, to our knowledge, no existing study is concerned with how CMs would affect the PBDE bioavailability to microorganisms in aquatic sediments.

The main objective of this work was to investigate the impact of various CMs on the bioavailability of 2,2′,4,4′-tetrabromodiphenyl ether (BDE-47), a PBDE congener widely distributed in environments [40], to PBDE-degrading microorganisms in CM-amended sediments. BC (BC-cornstalk and BC-wood) and multi-walled carbon nanotubes (MWCNTs) (MWCNT-1 and MWCNT-2) with different physicochemical properties were used as typical CMs. The microbial debromination of BDE-47 in anaerobic sediments amended with various types and contents of CMs was first studied. Then, desorption of BDE-47 from CMs was further examined using the Tenax-assisted extraction method to investigate the influencing mechanism of CMs on BDE-47 bioavailability. This study is expected to enrich our knowledge on the environmental behaviors of PBDEs in aquatic systems and provide new insights in mitigating their ecological risks.

2. Materials and methods

2.1. Chemicals and reagents

Individual standards of PBDE congeners, including 2,2′-dibromodiphenyl ether (BDE-4), 2,2′,4-tribromodiphenyl ether (BDE-17), 2,4,4′-tribromodiphenyl ether (BDE-28), BDE-47 and

3,3′,4,4′-tetrabromodiphenyl ether (BDE-77), dissolved in isooctane and the standard solution of decachlorobiphenyl were purchased from AccuStandard (New Haven, CT). Dichloromethane, acetone and *n*-hexane were of HPLC grade and obtained from J. T. Baker (Phillipsburg, U.S.A.). Trichloroethylene, ethanol, resazurin, sodium propionate, and all the other inorganic reagents were of analytical grade (Sinopharm Chemical Reagent Co., Ltd., Beijing, China). The concentrated sulfuric acid was of guarantee grade. Vitamins (purity > 99%), neutral alumina (100–200 mesh), and silica gel (100–200 mesh) were purchased from J&K Scientific Ltd. (Beijing, China). Diatomite was obtained from Celite China Inc. (Beijing, China).

Tenax-TA resin (60–80 mesh), a porous polymer with high adsorption capacity to HOCs, was obtained from Kanglin Science and Technology Ltd. (Beijing, China) and used as an auxiliary extraction material in BDE-47 desorption experiments. The Tenax-TA beads were cleaned ultrasonically with deionized water, acetone, and *n*-hexane ($10 \, mL \, g^{-1}$ Tenax) successively for three times and oven-dried overnight at 75 °C prior to use.

2.2. Sediment microcosm setup and aging of BDE 47 in sediments

The details of preparing and characterizing BC and CNTs are described in Supporting Information (SI). Sediments with no detectable PBDEs were collected from the upper reaches of Hanjiang River in Shaanxi Province of China. The sediments were air-dried, passed through a 1-mm sieve and sterilized by γ-rays at a dosage of 25 kGy before use. The total organic carbon (1.02%) and BC content (0.19%) of the sediments were measured by a Vario EI elemental analyzer (Elementar Inc., Germany).

Aliquots of 0, 1.0, 2.5, 5.0, 7.5, 15.0, and 25.0 g CMs were blended thoroughly with 500 g of sediments to obtain artificial sediments containing 0%, 0.2%, 0.5%, 1.0%, 1.5%, 3.0%, and 5.0% CMs, respectively. One mL of BDE-47 stock solution ($500 \, \mu g \, mL^{-1}$) was spiked into 50 g of artificial sediment in a 125 mL headspace bottle to yield a final BDE-47 concentration of $10 \, \mu g \, g^{-1}$ in all sets of microcosms. After volatilization of the solvent, each bottle was added with 50 mL of sterile deionized water and sealed using a Teflon-silicon cap. Then the spiked sediments were aged aseptically and anaerobically at room temperature in the dark for 100 d.

2.3. Anaerobic debromination of BDE-47 in sediment microcosms

The PBDE-degrading microbial culture was originally isolated from a groundwater sample contaminated by chlorinated compounds and enriched with trichloroethene (TCE) anaerobically. The culture could dechlorinate TCE to ethene completely. In preliminary experiments, BDE-47 was anaerobically utilized by the culture as the sole electron acceptor and sequentially debrominated to lower brominated congeners, mainly including BDE-4, −17 and −28. The changes in the microbial community were examined by polymerase chain reaction-denaturing gradient gel electrophoresis (PCR-DGGE) analysis. It was found that *Acetobacterium* sp. in the enriched culture was most likely responsible for the microbial debromination of BDE-47.

After aging BDE-47 in CM-added sediments, each headspace bottle was filled with 30 mL of the basal medium, of which the preparation was described in SI. Then the bottles were sealed again, and syringe needles were inserted through the Teflon-silicon caps to discharge the air inside during the autoclave sterilization. After autoclaving at 121 °C for 30 min, the syringe needles were removed immediately to make the condition inside bottles anaerobic. Afterwards, 1 mL of phosphate buffer solution was added to each bottle, followed by addition of 0.3 mL of NaHCO$_3$ solution ($0.5 \, mol \, L^{-1}$), 0.3 mL of sodium propionate solution ($0.5 \, mol \, L^{-1}$), 0.3 mL of Na$_2$S solution ($1.0 \, mol \, L^{-1}$), 50 μL of vitamin solution, and

Table 1
Physicochemical properties of CMs.

Carbonaceous materials	Sources	Elemental analysis					Structural properties				
		Element content (%)			Molar ratio		SSA and pore structure			Tube structure of MWCNTs	
		C	H	N	H/C	N/C	SSA[a] ($m^2\,g^{-1}$)	V_{pore}[b] ($cm^3\,g^{-1}$)	D_{pore}[b] (nm)	Outer diameter (nm)	Length (μm)
BC-cornstalk	Cornstalk	66.6	4.10	1.68	0.74	0.02	11.6	4.51E-03	53.0	–	–
BC-wood	Wood	73.1	4.46	0.492	0.73	0.57	5.04	2.83E-03	46.3	–	–
MWCNT-1	–	97.5	0.762	–	0.09	–	159	0.870	22.0	10–20	~20
MWCNT-2	–	97.3	0.111	–	0.01	–	65.9	0.247	17.1	>50	~10

[a] SSAs were calculated from the desorption isotherm of N_2 at 77 K by the multipoint Brunauer-Emmett-Teller (BET) method.

[b] Pore volume (V_{pore}), and mean pore diameter (D_{pore}) were calculated from the desorption isotherm of N_2 at 77 K by the multipoint Barrett-Joyner-Halenda (BJH) method.

0.5 mL of trichloroethylene solution (200 mg L^{-1}). Finally, 1 mL of microbial culture suspension was inoculated into BDE-47 debromination experiment sets, and 0.5 mL of NaN$_3$ solution, a biocide to eliminate microbial activities, was added to control sets. All bottles were sealed air-tightly and incubated at 30 °C for 100 d with a shaking speed of 150 rpm.

2.4. Aging and desorption of BDE-47 on CMs

2.4.1. Aging

To elucidate the mechanism about the impact of CMs on microbial bioavailability of BDE-47, desorption of BDE-47 sorbed on various CMs was further investigated. A weight of 0.15 g CMs was put into a 50 mL PTFE centrifuge tube. Then, each tube was spiked with 0.2 mL of BDE-47 stock solution (500 μg mL^{-1}) and placed in a fume hood for 2–3 h to evaporate the solvent. Two mL of deionized water and 20 μL of NaN$_3$ solution (20 g L^{-1}) were added successively. Finally, the tubes were shaken (30 °C, 150 rpm) under the dark condition and aged for 100 d. Due to the extremely low water solubility of BDE-47 (~15 μg L^{-1}) [41,42], the amount of spiked BDE-47 dissolved in the 2 mL of water phase was below 0.03 μg, accounting for 0.03% of the total amount of BDE-47 spiked (100 μg) in the system. Therefore, it is reasonable to assume that almost all of spiked BDE-47 was sorbed on CMs in the aging process.

2.4.2. Desorption

After aging, 20 mL of deionized water and 200 μL of NaN$_3$ solution were added into each tube. A weight of 0.2 g Tenax-TA beads was put in a 200-mesh string bag made of stainless steel wires to prevent the attachment of CMs in the desorption experiment. Then, the centrifuge tubes were added by string bags containing the Tenax-TA beads and then shaken at 30 °C with the speed of 150 rpm. At predetermined time intervals (i.e. 1, 4, 9, 12, 24, 48, 72, 180, 336, 480 and 600 h), the string bags were removed from the tubes for subsequent extraction of BDE-47. Then the tubes were replenished by string bags with 0.2 g of new Tenax-TA beads and shaken continuously.

2.5. Extraction and cleanup of PBDEs

Extraction of residual BDE-47 and its lower borminated products from sediments was carried out using accelerated solvent extraction (ASE 300, Dionex, Sunnyvale, CA, U.S.A.) as described by de la Cal et al. [43]. Cleanup of concentrated extracts was performed using chromatography columns filled with silica gel and alumina [44]. Details about extraction and cleanup of PBDEs from the sediments, CMs and Tenax-TA resin could be found in SI.

2.6. GC–MS analysis

The PBDE extracts were analyzed by an Agilent 7890A gas chromatography (GC) coupled to an Agilent 5975C mass spectrometer (MS) with helium as carrier gas. The mass spectrometer was operated in electron impact ionization (70 eV). The settings and conditions of GC–MS are provided in SI.

2.7. Quality assurance and quality control

The ratios of signal to noise for PBDE congeners which were greater than 3 were considered as valid data. The detection limit for BDE-47 was 1 μg L^{-1}, and those for BDE-4, −17, and −28 were 0.5 μg L^{-1}. Correlation coefficients of the standard curves for all PBDE congeners were greater than 0.99. The recoveries of the PBDEs in all experiment sets were monitored using BDE-77 as the surrogate standard of which the mean recovery was 82%-96% for CMs and 78%-97% for sediments amended with CMs.

All experiment sets were carried out in the dark to avoid photochemical degradation of BDE-47. Each experiment was performed in triplicate and the relative standard deviations of parallel samples were below 10%. Method blank and control sample were included in each experiment set. The level of BDE-47 detected in method blank of desorption experiments was far below (<0.1%) the levels in Tenax-TA beads. The debromination ratios of BDE-47 in all sterilized controls were below 0.5%.

3. Results and discussion

3.1. BC and CNT characterization

The physicochemical characteristics of CMs are listed in Table 1. The H/C ratios of BC-cornstalk and BC-wood were both lower than 1, suggesting a high degree of carbonization and aromaticity [45]. This is consistent with the H/C ratios of BC produced with woods and straws under similar pyrolysis condition reported by Kloss et al. [46]. Another important parameter for CMs is the specific surface area (SSA) which influences their interaction with organic contaminants. The SSA of BC-cornstalk was two fold higher than that of BC-wood; this was likely due to the much larger pore volume of BC-cornstalk in contrast with BC-wood while their pore diameters were close to each other (Table 1). It also suggested that the cornstalk-pyrolyzed BC had a higher porosity than the BC derived from wood. The SSAs of BC herein were similar with the results from other research [47] but smaller than the average SSA (62.6 $m^2\,g^{-1}$) compiled by Ahmad et al. [26]. Since the SSA of BC increases with pyrolysis temperatures [45], the main reason might be the relatively higher average pyrolysis temperature (470 °C) reported by Ahmad et al. [26] than 400 °C used herein.

Table 1 shows that both MWCNT-1 and MWCNT-2 had a high purity as their carbon content were nearly 100% based on the element analysis. The SSAs of MWCNT-1 and MWCNT-2 were 159.6 and 65.94 $m^2\,g^{-1}$, respectively, comparable to results from previous studies [48,49]. Although the difference in pore diameters between them was not remarkable, the SSA of MWCNT-1 was approximately two fold larger than MWCNT-2. This suggested a more abundant mesopority in MWCNT-1, which was consistent
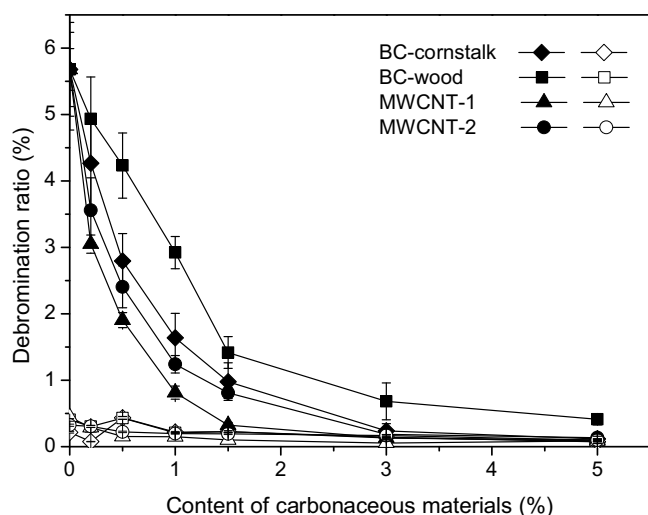
Fig. 1. Effects of CMs on debromination of BDE-47 by microorganisms in CM-amended sediments. Solid symbols and hollow symbols represent the samples with and without PBDE-degrading microorganisms, respectively. Data represent the mean value ± standard deviation (n = 3).

with the greater pore volume for MWCNT-1 than for MWCNT-2 ($0.870\,cm^3\,g^{-1}$ versus $0.247\,cm^3\,g^{-1}$). Thus, cmpared with BC, MWCNTs had considerably higher aromatic-like structures, SSAs and pore volumes, indicative of their stronger affinity and sorption capacity to HOCs [50].

3.2. Anaerobic microbial debromination of BDE-47 in CM-amended sediments

Based on our preliminary experiments and previous studies on anaerobic microbial debromination pathways of BDE-47 [51–53], BDE-4, −17, and −28 are the main lower brominated products. Thus, the debromination ratio was calculated by dividing the total amount of lower brominated products by the initial amount of parent BDE-47 spiked in sediments. As shown in Fig. 1, after 100 d of anaerobic incubation in sediments amended with CMs, debromination of BDE-47 was observed in all microcosms inoculated with the PBDE-degrading microbial culture but not in the sterilized control samples added with NaN_3. This demonstrated the PBDE-degrading microbes were responsible for BDE-47 debromination in anaerobic sediments. Microbially mediated anaerobic biodegradation is regarded as a crucial way to eliminate PBDEs in sludge and soils [54,55]. The debromination ratio of BDE-47 in sediment without CM amendment was 5.68%, while it dropped drastically below 0.50% and reduced by 92.8%–98.2% in the presence of 5.0% CMs (Fig. 1). This indicates that the CM amendment could substantially inhibit the microbial debromination of BDE-47 in sediments.

As shown in Fig. 1, the inhibitory effect of CMs on BDE-47 debromination exhibited a CM content-dependent trend, and it became increasingly prominent as the CM contents ascended from 0.2% to 5.0%. Notably, when the CM amendment exceeded 3.0%, BDE-47 debromination was considerably suppressed (Fig. 1). For instance, the debromination ratio of BDE-47 was 2.92% when the amendment of BC-wood was 1.0%, whereas it descended to 0.50% in sediment with 5.0% BC-wood addition. Similar observations were also reported elsewhere. Recently, Eibisch et al. found that addition of 5.0% either pyrochar or hydrochar to soils inhibited mineralization of isoproturon more significantly than the 0.5% amendment [56]. Likewise, the extent of phenanthrene degradation by indigenous microorganisms declined remarkably from 45.4% to 15.2% as the concentration of CNTs increased from 0% to 1.0% in soils [57]. Additionally, we assumed that the microbial debromination of BDE-

47 in CM-amended sediments conformed to the first-order kinetics and determined the half-lives of BDE-47 in the anaerobic sediments (Table S1). The half-life of BDE-47 in sediment without CM amendment was 1185.3 d, which is comparable to the half-live of BDE-209 (700 d) in anaerobic sewage sludge reported by Gerecke et al. [58] CM amendment resulted in much higher half-lives of BDE-47 ranging from 1371.0 d to 69280 d and the half-lives increased remarkably with the contents of CMs added. This indicates that it would cost longer time for PBDE-degrading microorganisms to eliminate BDE-47 from the sediments amended with CMs.

Furthermore, we analyzed the anaerobic debromination products of BDE-47 in CM-amended sediments as shown in Fig. 2. The three daughter PBDE congeners were present in all sediments samples except in the sterilized ones after 100 d anaerobic incubation. The concentration of the three daughter congeners increased in the sequence of BDE-17 > BDE-4 > BDE-28, in agreement with the results reported by Zhu et al. [59]. The relatively higher levels of BDE-4 and BDE-17 than BDE-28 were possibly due to the preferential removal of *para* bromines from BDE-47 molecules in microbial reductive debromination under anaerobic conditions [51]. As it did to the parent BDE-47, CM addition also reduced the yields of all lower brominated products which declined with the increased CM contents in sediments as well (Fig. 2).

In addition, as shown in Figs. 1 and 2, when the CM amendment was 1.5% or less, the inhibitory effect on the BDE-47 biodebromination for different CM types was in the order of MWCNT-1 > MWCNT-2 > BC-cornstalk > BC-wood, in line with their SSA ranking (Table 1). For example, in comparison with sediment without CM amendment, debromination ratios of BDE-47 decreased by 69.2%, 61.6%, 58.5% and 33.1% at 0.5% CM amendment for MWCNT-1, MWCNT-2, BC-cornstalk and BC-wood, respectively, and their SSAs were 159, 65.9, 11.6 and $5.04\,m^2\,g^{-1}$, respectively. Cui et al. found that single-walled carbon nanotubes (SWCNTs) could inhibit ^{14}C-phenanthrene mineralization more significantly than biochar or charcoal at the amendment rate of $1\,mg\,g^{-1}$, and they assumed that the five fold to six fold higher SSA of SWCNTs than biochar and charcoal was responsible for the greater mineralization reduction [60]. However, it is noteworthy that the differences in inhibitory effects among various CMs diminished substantially as the CM addition was higher than 3.0% (Fig. 1). This suggested that the SSA of CMs could exert a significant influence on debromination of BDE-47 at relatively low CM amendment, while the role of SSA would be overshadowed by high CM content which turned into a dominant factor as the amount of CMs increased. Similarly, it was reported that the variations in impacts of biochar on isoproturon mineralization in soils were pronounced and dependent on the physicochemical properties of biochar when 0.5% char was added, while the variations became less significant at 5.0% amendment [56].

Further analysis, as shown in Figs. S1-S4, revealed that the reciprocals of both BDE-47 debromination ratio ($1/R$) and concentration of lower brominated congeners ($1/C$) had a significant positive linear correlation with the CM content amended in sediments (f_{CM}) ($p < 0.01$), following the relationships as below:

$$1/R = A_1 \times f_{CM} + B_1 \tag{1}$$

$$1/C = A_2 \times f_{CM} + B_2 \tag{2}$$

where A_1, A_2, B_1 and B_2 are constants. Similar results were also observed in our previous study on the influences of BC amendment on PAH bioaccumulation in *Chironomus plumosus* larvae, which revealed that the bioavailable concentration of PAHs in pore water (C_{iw}) positively correlated with the BC content in sediments (f_{char}) significantly ($p < 0.01$) [61]. It suggests that the increased CM amendment in sediments would introduce more adsorption sites available for more BDE-47 molecules to attach on. This could lead
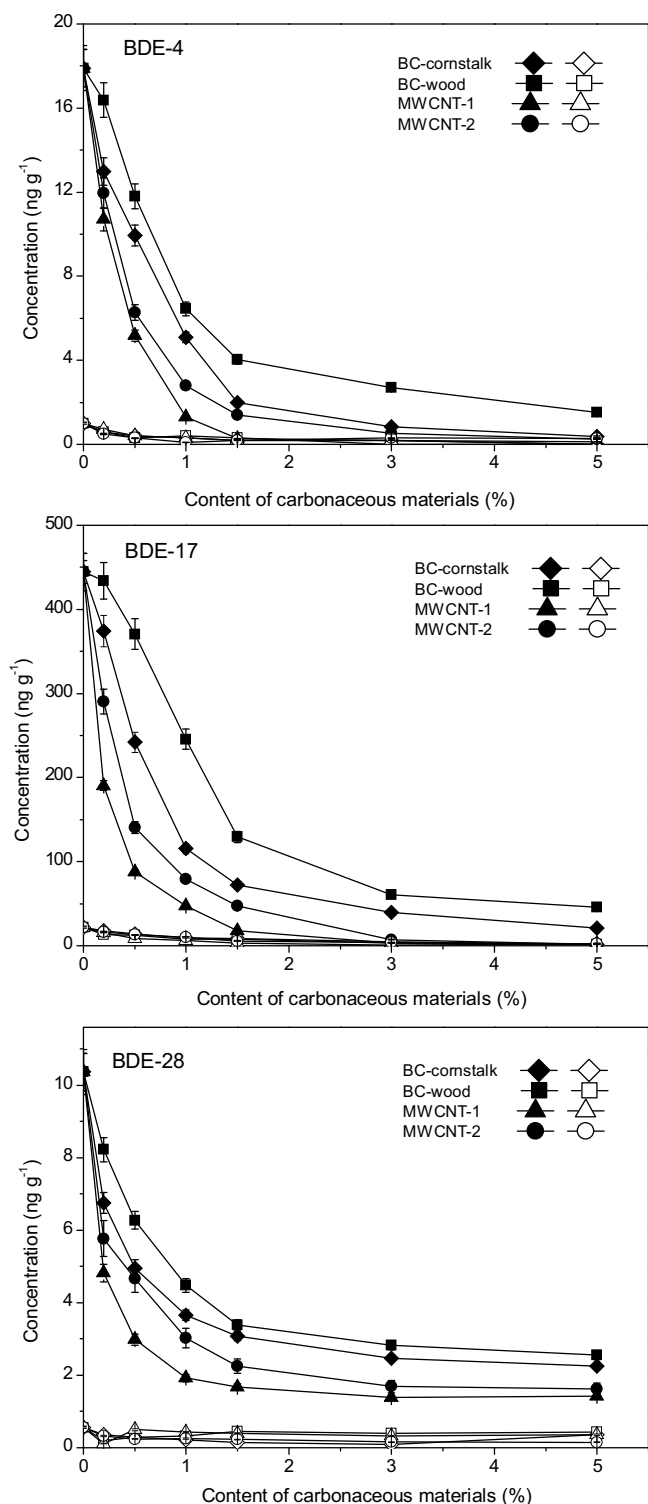
Fig. 2. Levels of lower brominated PBDE congeners in sediments amended with various contents and types of CMs. Solid symbols and hollow symbols represent the samples with and without PBDE-degrading microorganisms, respectively. Data represent the mean value ± standard deviation (n = 3).

to fewer amounts of BDE-47 desorbing from CMs and thus reduce the bioavailable portion of BDE-47 to microbial utilization which consequently limited its debromination. Additionally, constant A_1 and A_2 in equation (1) and (2), the slopes of linear regression fitting, reflect the sorption capacity of CMs to BDE-47. As shown in Figs. S1-S4, for different types of CMs, the slope generally followed the
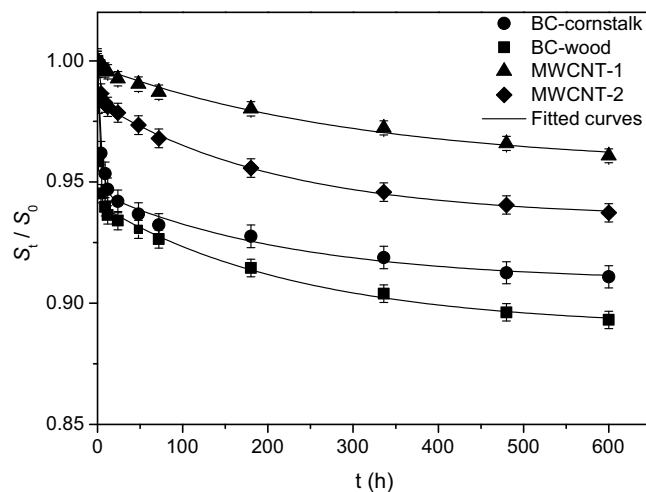

Fig. 3. Desorption kinetics of BDE-47 sorbed on CMs. Data represent the mean value ± standard deviation (n = 3).

sequence: MWCNT-1 > MWCNT-2 > BC-cornstalk > BC-wood, consistent with their respective SSAs.

3.3. Desorption of BDE-47 associated with CMs

For the HOCs in sediments, the bioavailable fraction is generally recognized as the proportion which could desorb from sediments reversibly rather than the total amount of sediment-bound HOCs [62]. Also, it is usually believed that microorganisms could only utilize the desorbable parts of the sorbed HOCs in sediments [16]. Therefore, in order to probe the mechanism about impacts of CMs on BDE-47 bioavailability to microorganisms, desorption of BDE-47 from various CMs was investigated.

The BDE-47 desorption from CMs was performed by sequential Tenax-assisted extractions and described using the first-order kinetics model with three compartments as below [63]:

$$S_t/S_0 = F_r \times e^{-k_r \times t} + F_s \times e^{-k_s \times t} + F_{vs} \times e^{-k_{vs} \times t} \qquad (3)$$

$F_r + F_s + F_{vs} = 1$ (4) where S_0 and S_t correspond to the amount of CM-sorbed BDE–47 at the beginning and time t (h) during the desorption process, respectively; F_r, F_s, and F_{vs} are the rapidly, slowly, and very slowly desorbing fraction of BDE-47, respectively; k_r, k_s, and k_{vs} (h^{-1}) are the rate constants for respective desorbing compartments. Due to the strong hydrophobicity of BDE-47 (log K_{ow} = 6.81) and the excellent adsorption capacity of Tenax- TA resin, BDE-47 concentration in water phase was assumed to be negligible throughout desorption period [64]. Another assumption was that desorption of BDE-47 from CMs in three compartments were independent of each other.

Fig. 3 shows the desorption kinetics data of BDE-47 sorbed on CMs fitted by equations (3) and (4). The fitting curves for all CMs exhibit an initial relatively rapid desorption of BDE-47, followed with a slower desorption stage and finally a stage with a much slower release of the remaining sorbed BDE-47. As shown in Table 2, the fitting curves for all CMs had high correlation coefficients ($r^2 > 0.97$), demonstrating the successful description of BDE-47 desorption from CMs by the 3-compartment first-order kinetics model. This is aligned with previous research on desorption of other HOCs [16,65]. Furthermore, the desorbing fractions of CM-associated BDE-47 after 600 h desorption experiment were in the range of 3.9%–10.7% (Fig. 3). These results were significantly lower than the desorbing percentage of pyrene from charcoals ranging from 33% to 55% reported by Zhou et al. [66]. This discrepancy might result from both the greater hydrophobicity of BDE-47 than pyrene

Table 2
Fitting parameters of desorption kinetics for BDE-47 sorbed on BC and CNTs.

	F_r (%)	k_r (h^{-1})	F_s (%)	k_s (h^{-1})	F_{vs} (%)	k_{vs} (h^{-1})	r^2
BC-cornstalk	5.2 ± 0.3	0.26 ± 0.11	3.7 ± 0.4	0.0044 ± 0.0020	91 ± 0.4	5.1E-102	0.988
BC-wood	5.9 ± 0.4	1.2 ± 0.71	5.1 ± 0.4	0.0042 ± 0.0011	89 ± 0.5	8.2E-116	0.993
MWCNT-1	4.1 ± 0.5	0.0032 ± 0.01	5.8 ± 0.3	0.00040 ± 0.0001	90 ± 0.2	4.8E-118	0.976
MWCNT-2	1.8 ± 0.1	0.30 ± 0.06	4.8 ± 0.1	0.0047 ± 0.0048	93 ± 0.1	8.7E-140	0.998

Table 3
Correlations between the desorbing fractions of BDE-47 and SSAs of CMs.

	Desorbing fraction[a]				
	F_{12h}	F_{48h}	F_{180h}	F_{480h}	F_{600h}
SSA Pearson's r	−0.934	−0.947	−0.967[*]	−0.962[*]	−0.954[*]
r^2	0.872	0.897	0.935	0.925	0.910
Sig.	0.066	0.053	0.033	0.038	0.046

[a] F_{12h}, F_{48h}, F_{180h}, F_{480h}, and F_{600h} denote desorbing fraction at 12, 48, 180, 480 and 600 h, respectively.
[*] Significant at the 95% confidence level.

and the differences in physicochemical properties between CMs herein and the charcoals used in their research.

Relevant parameters for the fitting model of BDE-47 desorption kinetics are listed in Table 2. According to Table 2, the F_r and F_s were much lower than the F_{vs} which accounted for approximately 90% of the total desorbing fraction, indicating the dominant role of the F_{vs} in governing the BDE-47 desorption from CMs. Liu et al. found that the F_r, F_s, and F_{vs} of BDE-47 desorbing from different sediments were 8.22–19.1%, 7.49–13.1%, and 67.7–84.3%, respectively [64]. Our results show smaller F_r and F_s but greater F_{vs} compared with theirs. This difference might be ascribed to two reasons. First, the aging time in their study was just 14 d, much shorter than the 100 d in this work. Longer contact time would facilitate the movement of BDE-47 molecules from CM surfaces into inner pores which might undergo conformational modification or structural rearrangement [67,68]. Such alterations of pores were able to entrap BDE-47 inside and strengthen their resistance to desorption from CMs, thus leading to the decreased F_r accompanied with increased F_v. The other reason is that the affinity of pure CMs used herein to BDE-47 is higher than natural sediments due to their abundant aromatic and porous structures relative to the heterogeneous sediment organic matter [31]. This would result in tighter association and greater sequestration of BDE-47 with CMs and the difficulty in BDE-47 desorbing from CM-amended sediments. Consequently, it is reasonable to conclude that when sediments were amended with CMs, the preferable and powerful sorption of BDE-47 to CMs in sediments would strikingly limit BDE-47 desorption and decrease the F_r. This led to the reduction in the bioavailable fraction of BDE-47 to PBDE-degrading microorganisms, since F_r was widely found to be positively correlated with the bioavailability of HOCs in soils and sediments [62]. This could explain the declined microbial debromination of BDE-47 in CM-amended sediments as shown in Figs. 1 and 2.

Furthermore, Fig. 3 shows that the desorbing fraction of CM-associated BDE-47 for various CMs ranked as: BC-wood > BC-cornstalk > MWCNT-2 > MWCNT-1, in accordance with the order of their SSAs (Table 1). To better explore the role of SSAs in affecting the BDE-47 desorption, the correlations between desorbing fractions at different time interval (i.e. F_{12h}, F_{48h}, F_{180h}, F_{480h}, and F_{600h}, respectively) and SSAs of CMs were analyzed. According to Table 3, desorbing fractions of BDE-47 showed good negative correlations with SSAs of CMs, and F_{180h}, F_{480h}, and F_{600h} significantly correlated with CM SSAs at the 95% confidence level ($p < 0.05$). In other words, the amount of CM-sorbed BDE-47 which could be released into aqueous phase during desorption period decreased

with the increase in SSAs of CMs. This indicates that the SSA is an important factor in determining BDE-47 desorption from CMs. It has been reported that the increase in SSAs of BC and CNTs could raise their adsorption capacity to HOCs, such as PAHs [27] and organophosphate pesticides [69]. Therefore, as the SSAs of CMs increased, greater adsorption of BDE-47 induced the decline in the desorbing fraction and thus reduced the BDE-47 bioavailability to PBDE-degrading microorganisms. This probably explains the more remarkable impacts of CNTs than BC on inhibiting microbial debromination of BDE-47 (Figs. 1 and 2).

In terms of rate constants for BDE-47 desorption from various CMs, they all followed the ranking of $k_r > k_s \gg k_{vs}$, and the k_r and k_s values were generally in the range of 10^{-1}–10^{-2} and 10^{-3}–10^{-4}, respectively (Table 2). These results were in line with other studies on desorption of pentachlorophenol and phenanthrene from CM-containing sediments [70,71]. It is notable that the k_r for BDE-47 desorption from MWCNT-1 was around two orders of magnitude lower than other CMs, and meanwhile it also had the largest SSA (159 m^2 g^{-1}) as well as the greatest pore volume (0.870 cm^3 g^{-1}) of all the CMs (Table 1). These characteristics could equip MWCNT-1 with stronger affinity and sorption capacity to BDE-47, which slowed down the desorption rate of BDE-47 during the rapid desorption phase. This might account for the least bioavailability of BDE-47 in sediment amended with MWCNT-1. Furthermore, the k_{vs} values for MWCNT-1 and MWCNT-2 were generally lower than those for BC-wood and BC-cornstalk. On the one hand, this might be attributed to the unique structures of CNTs with high-energetic adsorption sites which would strengthen their π-π interaction with the aromatic rings of BDE-47 molecules, bringing about tighter association between BDE-47 and CNTs [27,50]. On the other hand, besides the adsorption, it was proposed that pore-filling was also a primary mechanism for the sorption of BDE-47 to CMs [72]. Hence, the larger pore diameters of BC than CNTs were favorable to the elimination of pore-entrapped BDE-47. This would accelerate desorption of BC-associated BDE-47 during the very slowly desorbing stage and thus lead to the relatively higher k_{vs} for BC. Therefore, the relatively lower k_{vs} of CNTs than BC might be responsible for the less microbial bioavailability of BDE-47 in CNT-amended sediments.

Apart from adsorption and pore-filling mechanisms controlling desorption of sorbed BDE-47, the hysteresis effect likely played an important role in decreasing the BDE-47 bioavailability as well. CNTs could easily bond with each other forming aggregates in environmental matrixes due to the Van der Waals forces among them. The adsorption sites of BDE-47 on CNT aggregates mainly distributed in four areas: inner pores, external surfaces, interstitial channels, and groove areas [27,50]. The inner pores and interstitial channels could lock the sorbed BDE-47 inside, inducing irreversible adsorption and desorption hysteresis of BDE-47 in CNT-added sediments. As a result, the stronger desorption hysteresis of BDE-47 from CNTs than BC would also contribute to more remarkable reduction in BDE-47 bioavailability to microbes in sediments as shown in Figs. 2 and 3.

4. Conclusions

CMs in sediments are of great concern because of their impacts on environmental behaviors, fate and adverse biological effects

of HOCs. To our knowledge, this research is the first to investigate the influence of CM amendment on the PBDE bioavailability to PBDE-degrading microorganisms in anaerobic sediments. Our results show that the addition of CMs in sediments could remarkably lower the anaerobic microbial debromination of BDE-47, and the effects of CMs on BDE-47 debromination were dependent on their contents and physicochemical properties. Further investigation on desorption of BDE-47 from CMs revealed that the decrease in debromination probably derived from the reduced bioavailable fraction of sorbed BDE-47 in sediments with CM amendment. This study illustrated that the strong association of BDE-47 with CMs would make it difficult for BDE-47 to desorb from CMs so that amendment of CMs into sediments would lead to the declined BDE-47 bioavailability to PBDE-degrading microbes. This was advantageous to alleviate the environmental risks of PBDEs to aquatic animals, but meanwhile, it would also limit the removal of PBDEs from sediments by microbial degradation.

Acknowledgements

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.jhazmat.2016.03.065.

References

[1] A. Hassanin, K. Breivik, S.N. Meijer, E. Steinnes, G.O. Thomas, K.C. Jones, PBDEs in European background soils: levels and factors controlling their distribution, Environ. Sci. Technol. 38 (2004) 738–745.

[2] J. Ge, M.X. Liu, X.Y. Yun, Y.Y. Yang, M.M. Zhang, Q.X. Li, J. Wang, Occurrence, distribution and seasonal variations of polychlorinated biphenyls and polybrominated diphenyl ethers in surface waters of the East Lake, China, Chemosphere 103 (2014) 256–262.

[3] S.D. Shaw, D. Brenner, M.L. Berger, F. Fang, C.S. Hong, R. Addink, D. Hilker, Bioaccumulation of polybrominated diphenyl ethers in harbor seals from the northwest Atlantic, Chemosphere 73 (2008) 1773–1780.

[4] A. Sudaryanto, N. Kajiwara, O.V. Tsydenova, T. Isobe, H.X. Yu, S. Takahashi, S. Tanabe, Levels and congener specific profiles of PBDEs in human breast milk from China: implication on exposure sources and pathways, Chemosphere 73 (2008) 1661–1668.

[5] A. Sjodin, D.G. Patterson Jr., A. Bergman, A review on human exposure to brominated flame retardants–particularly polybrominated diphenyl ethers, Environ. Int. 29 (2003) 829–839.

[6] S.C. Lema, I.R. Schultz, N.L. Scholz, J.P. Incardona, P. Swanson, Neural defects and cardiac arrhythmia in fish larvae following embryonic exposure to 2,2',4,4'-tetrabromodiphenyl ether (PBDE 47), Aquat. Toxicol. 82 (2007) 296–307.

[7] S.C. Roberts, A.C. Bianco, H.M. Stapleton, Disruption of type 2 iodothyronine deiodinase activity in cultured human glial cells by polybrominated diphenyl ethers, Chem. Res. Toxicol. 28 (2015) 1265–1274.

[8] Y. Dong, L. Li, P.J. Bie, S.L. Jia, Q. Wang, Z. Huang, X.H. Qiu, J.B. Zhang, J.X. Hu, Polybrominated diphenyl ethers in farmland soils: source characterization, deposition contribution and apportionment, Sci. Total Environ. 466 (2014) 524–532.

[9] R. Lohmann, J. Klanova, P. Kukucka, S. Yonis, K. Bollinger, Concentrations, fluxes, and residence time of PBDEs across the tropical atlantic ocean, Environ. Sci. Technol. 47 (2013) 13967–13975.

[10] J. Ma, X.H. Qiu, J.L. Zhang, X.L. Duan, T. Zhu, State of polybrominated diphenyl ethers in China: an overview, Chemosphere 88 (2012) 769–778.

[11] I.S. Lee, K.S. Kim, S.J. Kim, J.H. Yoon, K.H. Choi, S.D. Choi, J.E. Oh, Evaluation of mono- to deca-brominated diphenyl ethers in riverine sediment of Korea with special reference to the debromination of DeBDE209, Sci. Total Environ. 432 (2012) 128–134.

[12] I.S. Lee, H.H. Kang, U.J. Kim, J.E. Oh, Brominated flame retardants in Korean river sediments, including changes in polybrominated diphenyl ether concentrations between 2006 and 2009, Chemosphere 126 (2015) 18–24.

[13] G. Cornelissen, O. Gustafsson, T.D. Bucheli, M.T.O. Jonker, A.A. Koelmans, P.C.M. Van Noort, Extensive sorption of organic compounds to black carbon, coal, and kerogen in sediments and soils: mechanisms and consequences for distribution bioaccumulation, and biodegradation, Environ. Sci. Technol. 39 (2005) 6881–6895.

[14] A.K. Haritash, C.P. Kaushik, Biodegradation aspects of polycyclic aromatic hydrocarbons (PAHs): a review, J. Hazard. Mater. 169 (2009) 1–15.

[15] J.F. Quensen 3rd, J.M. Tiedje, S.A. Boyd, Reductive dechlorination of polychlorinated biphenyls by anaerobic microorganisms from sediments, Science 242 (1988) 752–754.

[16] J.M. Spasojevic, S.P. Maletic, S.D. Roncevic, D.V. Radnovic, D.I. Cucak, J.S. Trickovic, B.D. Dalmacija, Using chemical desorption of PAHs from sediment to model biodegradation during bioavailability assessment, J. Hazard. Mater. 283 (2015) 60–69.

[17] C.T.A. Moermond, I. Roessink, M.T.O. Jonker, T. Meijer, A.A. Koelmans, Impact of polychlorinated biphenyl and polycyclic aromatic hydrocarbon sequestration in sediment on bioaccumulation in aquatic food webs, Environ. Toxicol. Chem. 26 (2007) 607–615.

[18] M. Lyytikainen, P. Hirva, P. Minkkinen, H. Hamalainen, A.L. Rantalainen, P. Mikkelson, J. Paasivirta, J.V.K. Kukkonen, Bioavailability of sediment-associated PCDD/Fs and PCDEs: relative importance of contaminant and sediment characteristics and biological factors, Environ. Sci. Technol. 37 (2003) 3926–3934.

[19] D. Meric, A.N. Alshawabkeh, J.P. Shine, T.C. Sheahan, Bioavailability of hydrophobic organic compounds in thin-layered capped sediments, Chemosphere 103 (2014) 281–289.

[20] A. Cachada, R. Pereira, E.F. da Silva, A.C. Duarte, The prediction of PAHs bioavailability in soils using chemical methods: state of the art and future challenges, Sci. Total Environ. 472 (2014) 463–480.

[21] E.M. Mackenbach, Y. Jing, M.A. Mills, P.F. Landrum, M.J. Lydy, Application of a Tenax model to assess bioavailability of PCBs in field sediments, Environ. Toxicol. Chem. 31 (2012) 2210–2216.

[22] M. Crampon, F. Bureau, M. Akpa-Vinceslas, J. Bodilis, N. Machour, F. Le Derf, F. Portet-Koltalo, Correlations between PAH bioavailability, degrading bacteria, and soil characteristics during PAH biodegradation in five diffusely contaminated dissimilar soils, Environ. Sci. Pollut. Res. 21 (2014) 8133–8145.

[23] J. You, A.D. Harwood, H. Li, M.J. Lydy, Chemical techniques for assessing bioavailability of sediment-associated contaminants: sPME versus Tenax extraction, J. Environ. Monit. 13 (2011) 792–800.

[24] A. Cabrera, L. Cox, K. Spokas, M.C. Hermosin, I. Cornejo, W.C. Koskinen, Influence of biochar amendments on the sorption-desorption of aminocyclopyrachlor, bentazone and pyraclostrobin pesticides to an agricultural soil, Sci. Total Environ. 470 (2014) 438–443.

[25] M. Parween, A. Ramanathan, P.S. Khillare, N.J. Raju, Persistence, variance and toxic levels of organochlorine pesticides in fluvial sediments and the role of black carbon in their retention, Environ. Sci. Pollut. Res. 21 (2014) 6525–6546.

[26] M. Ahmad, A.U. Rajapaksha, J.E. Lim, M. Zhang, N. Bolan, D. Mohan, M. Vithanage, S.S. Lee, Y.S. Ok, Biochar as a sorbent for contaminant management in soil and water: a review, Chemosphere 99 (2014) 19–33.

[27] O.G. Apul, T. Karanfil, Adsorption of synthetic organic contaminants by carbon nanotubes: a critical review, Water Res. 68 (2015) 34–55.

[28] M.S. Mauter, M. Elimelech, Environmental applications of carbon-based nanomaterials, Environ. Sci. Technol. 42 (2008) 5843–5859.

[29] G. Cirillo, S. Hampel, U.G. Spizzirri, O.I. Parisi, N. Picci, F. Iemma, Carbon nanotubes hybrid hydrogels in drug delivery: a perspective review, Biomed. Res. Int. 2014 (2014) 1–17.

[30] R.H. Baughman, A.A. Zakhidov, W.A. de Heer, Carbon nanotubes—the route toward applications, Science 297 (2002) 787–792.

[31] A.A. Koelmans, M.T.O. Jonker, G. Cornelissen, T.D. Bucheli, P.C.M. Van Noort, O. Gustafsson, Black carbon: the reverse of its dark side, Chemosphere 63 (2006) 365–377.

[32] W.Q. Zhou, J. Shan, B.Q. Jiang, L.H. Wang, J.F. Feng, H.Y. Guo, R. Ji, Inhibitory effects of carbon nanotubes on the degradation of C-14-2,4-dichlorophenol in soil, Chemosphere 90 (2013) 527–534.

[33] E.J. Petersen, L. Zhang, N.T. Mattison, D.M. O'Carroll, A.J. Whelton, N. Uddin, T. Nguyen, Q. Huang, T.B. Henry, R.D. Holbrook, K.L. Chen, Potential release pathways, environmental fate, and ecological risks of carbon nanotubes, Environ. Sci. Technol. 45 (2011) 9837–9856.

[34] K.T. Semple, M.J. Riding, L.E. McAllister, F. Sopena-Vazquez, G.D. Bending, Impact of black carbon on the bioaccessibility of organic contaminants in soil, J. Hazard. Mater. 261 (2013) 808–816.

[35] M. Shen, X. Xia, F. Wang, P. Zhang, X. Zhao, Influences of multiwalled carbon nanotubes and plant residue chars on bioaccumulation of polycyclic aromatic hydrocarbons by *Chironomus plumosus* larvae in sediment, Environ. Toxicol. Chem. 31 (2012) 202–209.

[36] S.B. Li, U. Turaga, B. Shrestha, T.A. Anderson, S.S. Ramkumar, M.J. Green, S. Das, J.E. Canas-Carrell, Mobility of polyaromatic hydrocarbons (PAHs) in soil in the presence of carbon nanotubes, Ecotoxicol. Environ. Saf. 96 (2013) 168–174.

[37] E.J. Petersen, R.A. Pinto, P.F. Landrum, W.J. Weber, Influence of carbon nanotubes on pyrene bioaccumulation from contaminated soils by earthworms, Environ. Sci. Technol. 43 (2009) 4181–4187.

[38] C. Di Paolo, N. Gandhi, S.P. Bhavsar, M. Van den Heuvel-Greve, A.A. Koelmans, Black carbon inclusive multichemical modeling of PBDE and PCB biomagnification and -transformation in estuarine food webs, Environ. Sci. Technol. 44 (2010) 7548–7554.

[39] M.J. Riding, F.L. Martin, K.C. Jones, K.T. Semple, Carbon nanomaterials in clean and contaminated soils: environmental implications and applications, Soil 1 (2015) 1–21.

[40] Z.W. Tang, Q.F. Huang, J.L. Cheng, Y.F. Yang, J. Yang, W. Guo, Z.Q. Nie, N. Zeng, L. Jin, Polybrominated diphenyl ethers in soils, sediments, and human hair in a plastic waste recycling area: a neglected heavily polluted area, Environ. Sci. Technol. 48 (2014) 1508–1516.

[41] S.A. Tittlemier, T. Halldorson, G.A. Stern, G.T. Tomy, Vapor pressures, aqueous solubilities, and Henry's law constants of some brominated flame retardants, Environ. Toxicol. Chem. 21 (2002) 1804–1810.

[42] E. Papa, S. Kovarich, P. Gramatica, Development, validation and inspection of the applicability domain of QSPR models for physicochemical properties of polybrominated diphenyl ethers, QSAR Comb. Sci. 28 (2009) 790–796.

[43] A. de la Cal, E. Eljarrat, D. Barcelo, Determination of 39 polybrominated diphenyl ether congeners in sediment samples using fast selective pressurized liquid extraction and purification, J. Chromatogr. A 1021 (2003) 165–173.

[44] B. Mai, S. Chen, X. Luo, L. Chen, Q. Yang, G. Sheng, P. Peng, J. Fu, E.Y. Zeng, Distribution of polybrominated diphenyl ethers in sediments of the Pearl River Delta and adjacent South China Sea, Environ. Sci. Technol. 39 (2005) 3521–3527.

[45] O.D. Nartey, B.W. Zhao, Biochar preparation, characterization, and adsorptive capacity and its effect on bioavailability of contaminants: an overview, Adv. Mater. Sci. Eng. (2014) 12.

[46] S. Kloss, F. Zehetner, A. Dellantonio, R. Hamid, F. Ottner, V. Liedtke, M. Schwanninger, M.H. Gerzabek, G. Soja, Characterization of slow pyrolysis biochars: effects of feedstocks and pyrolysis temperature on biochar properties, J. Environ. Qual. 41 (2012) 990–1000.

[47] R.A. Brown, A.K. Kercher, T.H. Nguyen, D.C. Nagle, W.P. Ball, Production and characterization of synthetic wood chars for use as surrogates for natural sorbents, Org. Geochem. 37 (2006) 321–333.

[48] B. Shrestha, T.A. Anderson, V. Acosta-Martinez, P. Payton, J.E. Canas-Carrell, The influence of multiwalled carbon nanotubes on polycyclic aromatic hydrocarbon (PAH) bioavailability and toxicity to soil microbial communities in alfalfa rhizosphere, Ecotoxicol. Environ. Saf. 116 (2015) 143–149.

[49] X. Wang, J. Lu, B. Xing, Sorption of organic contaminants by carbon nanotubes: influence of adsorbed organic matter, Environ. Sci. Technol. 42 (2008) 3207–3212.

[50] B. Pan, B. Xing, Adsorption mechanisms of organic chemicals on carbon nanotubes, Environ. Sci. Technol. 42 (2008) 9005–9013.

[51] K.R. Robrock, P. Korytar, L. Alvarez-Cohen, Pathways for the anaerobic microbial debromination of polybrominated diphenyl ethers, Environ. Sci. Technol. 42 (2008) 2845–2852.

[52] J.A. Tokarz 3rd, M.Y. Ahn, J. Leng, T.R. Filley, L. Nies, Reductive debromination of polybrominated diphenyl ethers in anaerobic sediment and a biomimetic system, Environ. Sci. Technol. 42 (2008) 1157–1164.

[53] H.W. Zhu, Y. Wang, X.W. Wang, T.G. Luan, N.F.Y. Tam, Intrinsic debromination potential of polybrominated diphenyl ethers in different sediment slurries, Environ. Sci. Technol. 48 (2014) 4724–4731.

[54] A.C. Gerecke, P.C. Hartmann, N.V. Heeb, H.P. Kohler, W. Giger, P. Schmid, M. Zennegg, M. Kohler, Anaerobic degradation of decabromodiphenyl ether, Environ. Sci. Technol. 39 (2005) 1078–1083.

[55] M.K. Song, C.L. Luo, F.B. Li, L.F. Jiang, Y. Wang, D.Y. Zhang, G. Zhang, Anaerobic degradation of polychlorinated biphenyls (PCBs) and polychlorinated biphenyls ethers (PBDEs), and microbial community dynamics of electronic waste-contaminated soil, Sci. Total Environ. 502 (2015) 426–433.

[56] N. Eibisch, R. Schroll, R. Fuss, Effect of pyrochar and hydrochar amendments on the mineralization of the herbicide isoproturon in an agricultural soil, Chemosphere 134 (2015) 528–535.

[57] A.O. Oyelami, K.T. Semple, The impact of carbon nanomaterials on the development of phenanthrene catabolism in soil, Environ. Sci. Process Impacts 17 (2015) 1302–1310.

[58] A.C. Gerecke, W. Giger, P.C Hartmann, N.V. Heeb, H.P.E. Kohler, P. Schmid, M. Zennegg, M. Kohler, Anaerobic degradation of brominated flame retardants in sewage sludge, Chemosphere 64 (2006) 311–317.

[59] H.W. Zhu, Y. Wang, N.F.Y. Tam, Microcosm study on fate of polybrominated diphenyl ethers (PBDEs) in contaminated mangrove sediment, J. Hazard. Mater. 265 (2014) 61–68.

[60] X.Y. Cui, F. Jia, Y.X. Chen, J. Gan, Influence of single-walled carbon nanotubes on microbial availability of phenanthrene in sediment, Ecotoxicology 20 (2011) 1277–1285.

[61] F. Wang, Q.W. Bu, X.H. Xia, M.H. Shen, Contrasting effects of black carbon amendments on PAH bioaccumulation by *Chironomus plumosus* larvae in two distinct sediments: role of water absorption and particle ingestion, Environ. Pollut. 159 (2011) 1905–1913.

[62] M.J. Lydy, A.D. Harwood, S.A. Nutile, P.F. Landrum, Tenax extraction of sediments to estimate desorption and bioavailability of hydrophobic contaminants: a literature review, Integr. Environ. Assess. Manag. 11 (2015) 208–220.

[63] G. Cornelissen, P.C.M. van Noort, J.R. Parsons, H.A.J. Govers, Temperature dependence of slow adsorption and desorption kinetics of organic compounds in sediments, Environ. Sci. Technol. 31 (1997) 454–460.

[64] M. Liu, S.Y. Tian, P. Chen, L.Y. Zhu, Predicting the bioavailability of sediment-associated polybrominated diphenyl ethers using a 45-d sequential Tenax extraction, Chemosphere 85 (2011) 424–431.

[65] J. You, A.D. Harwood, H.Z. Li, M.J. Lydy, Chemical techniques for assessing bioavailability of sediment-associated contaminants: SPME versus Tenax extraction, J. Environ. Monitor. 13 (2011) 792–800.

[66] Z.L. Zhou, H.W. Sun, W. Zhang, Desorption of polycyclic aromatic hydrocarbons from aged and unaged charcoals with and without modification of humic acids, Environ. Pollut. 158 (2010) 1916–1921.

[67] F. Wong, T.F. Bidleman, Aging of organochlorine pesticides and polychlorinated biphenyls in muck soil: volatilization, bioaccessibility, and degradation, Environ. Sci. Technol. 45 (2011) 958–963.

[68] Y. Song, F. Wang, X.L. Yang, C.Y. Liu, F.O. Kengara, X. Jin, X. Jiang, Chemical extraction to assess the bioavailability of chlorobenzenes in soil with different aging periods, J. Soils Sediments 11 (2011) 1345–1354.

[69] X.Y. Yu, G.G. Ying, R.S. Kookana, Reduced plant uptake of pesticides with biochar additions to soil, Chemosphere 76 (2009) 665–671.

[70] A.H. Rhodes, M.J. Riding, L.E. McAllister, K. Lee, K.T. Semple, Influence of activated charcoal on desorption kinetics and biodegradation of phenanthrene in soil, Environ. Sci. Technol. 46 (2012) 12445–12451.

[71] G.H. Cheng, L.C.H. Zhu, M.Y. Sun, J.Y. Deng, H.Y. Chen, X.H. Xu, L.P. Lou, Y.X. Chen, Desorption and distribution of pentachlorophenol (PCP) on aged black carbon containing sediment, J. Soils Sediments 14 (2014) 344–352.

[72] J. Xin, R.L. Liu, H.B. Fan, M.L. Wang, M. Li, X. Liu, Role of sorbent surface functionalities and microporosity in 2,2′,4,4′-tetrabromodiphenyl ether sorption onto biochars, J. Environ. Sci.-China 25 (2013) 1368–1378.