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ARTICLE *in* ENVIRONMENTAL SCIENCE & TECHNOLOGY · MARCH 2012

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Bioaccumulation and Metabolism of Polybrominated Diphenyl Ethers in Carp (*Cyprinus carpio*) in a Water/Sediment Microcosm: Important Role of Particulate Matter Exposure

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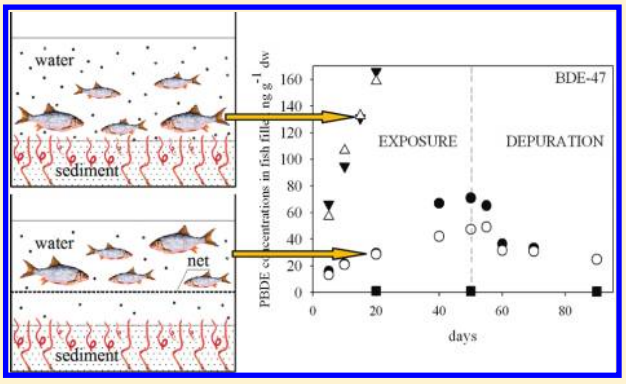
Supporting Information

ABSTRACT: Microcosms were built up to simulate a pond system with polybrominated diphenyl ether (PBDE) contaminated sediment and bioorganisms. The microcosms were divided into groups A and B. In group A, both benthic invertebrates (tubificid worms) and carp (*Cyprinu carpio*) were added, while in group B, only fish were added. After exposure for 20 d, the fish were sampled (exposure I). A net was fixed in the microcosms, and new fish were added (exposure II). These fish were prohibited from contacting the sediment by the net, and the accumulation and depuration of PBDEs in the fish were investigated. Among 11 monitored PBDE congeners (BDE-28, BDE-47, BDE-99, BDE-100, BDE-153, BDE-154, BDE-183, BDE-206, BDE-207, BDE-208, and BDE-209), only 5 congeners (BDE-28, BDE-47, BDE-100, BDE-153, and BDE-154) were detected in the carp fillets and liver. BDE-99 and BDE-183 were not detected in the fish because of the efficient metabolic debromination in carp tissues. The uptake of PBDEs in exposure I was significantly higher/faster than that in exposure II, since the fish in exposure I had an opportunity to take in more of the highly contaminated particles. The uptake kinetics (k_s) and elimination (k_e) rate coefficients showed a general trend of decreasing with increasing log K_{ow}. No significant difference was observed in uptake/depuration kinetics between groups A and B, indicating that the tubificids' reworking does not affect the bioaccumulation of sediment-associated PBDEs in fish significantly. All the PBDE congeners, including nona- and deca-BDEs, were bioaccumulated in the tubificid worms. The PBDE concentrations in the worms were significantly higher than those in the fish, and the congener profile of the sevem major congeners (BDE-28, BDE-47, BDE-99, BDE-100, BDE-153, BDE-154, and BDE-183) was distinctly different from that of fish tissues. The biota−sediment accumulation factors in the worms ranged from 0.01 to 5.89 and declined with increasing bromination and log K_{ow}.



INTRODUCTION

Polybrominated diphenyl ethers (PBDEs) are a class of additive brominated flame retardants that have been added to a variety of consumer products to reduce their flammability. There are three commercial formulas of PBDEs: penta-, octa-, and deca-BDE technical mixtures. Due to the wide presence and increasing level in the environment,[1] bioaccumulation ability, and potential adverse effects on wildlife and humans,[2,3] penta-BDE and octa-BDE were phased out in the European Union in 2004[4] and their production was stopped voluntarily in the United States. Tetra- through hepta-BDEs were added to the list of persistent organic pollutants (POPs) by the Stockholm Convention in 2009. Deca-BDE has also been banned throughout Europe since 2008 partly due to its potential to degrade to lower brominated congeners with higher toxicity.[5]

PBDEs are highly hydrophobic compounds with log K_{ow} in the range of 4.87−10 for tetra- through deca-BDEs.[6,7] Due to their high hydrophobicity, PBDEs tend to bind with particulate matter. As a result, sediment is an important reservoir for PBDEs and plays a very important role in their transport and fate in the environment. Sediment-associated PBDEs are potentially bioavailable to benthic invertebrates due to their intense ingestion and digestive activities to take in sediment.[8,9] Our previous study found that sediment-associated nona- and deca-BDEs were bioavailable to marine benthic invertebrates

Received: November 10, 2011
Revised: January 20, 2012
Accepted: February 7, 2012
Published: February 7, 2012

(*Nereis succinea*, polychaetes) with a low biota−sediment accumulation factor (BSAF).[10] The sediment may be resuspended in the upper water column due to the strong stirring and disturbance of the large aquatic species, such as benthic fish. As a result, the suspended particulate matter (SPM) become a source of PBDEs for the species living in the upper layer. Several studies have been conducted to investigate the accumulation of sediment-associated PBDEs in benthic invertebrates, including deposit feeding species, oligochaetes (*Lumbriculus variegates*), and polychaetes (*N. succinea*), but little work has been done to examine the bioaccumulation of sediment-associated PBDEs in fish. There are many reports about the accumulation and biotransformation of PBDEs in fish. However, most of these studies were performed by feeding the fish with PBDE-spiked food.[11−14] None of them could mimic the real exposure scenario of fish to PBDEs in an aquatic system. Carp are omnivorous demersal fish in fresh water systems, and they have been widely used as model species to study the bioaccumulation and biotransformation of PBDEs.

In a static or semistatic water system, where the sediments are not subjected to frequent resuspension by strong water movement, tubificid oligochaetes have the greatest potential to disturb surface sediment due to their living habit, widespread distribution, and population density. Tubificids burrow in surfacial sediments, ingest sediment particulates (silt and clay particles), and egest them at the sediment/water interface as sand-sized fecal pellets. This process could promote the release of organic pollutants from sediment and increase their bioavailability.[15]

In the present study, microcosms were built up to simulate a pond system with PBDE-contaminated sediment. The microcosms were divided into groups A and B. In group A, both benthic invertebrates (tubificid worms) and carp (*Cyprinus carpio*) were added, while in group B, only fish were added. After exposure for 20 d, the fish were sampled and a net was fixed in the microcosms to prohibit fish from contacting the sediment. New fish were added, and the accumulation and depuration of PBDEs in the fish were investigated. The objectives of this study were to investigate (1) the accumulation and metabolism of sediment-associated PBDEs in benthic invertebrates and fish, (2) the impacts of particulate matter on the bioaccumulation of PBDEs in fish, and (3) the influence of bioturbation of tubificid oligochaetes on the bioaccumulation of sediment-associated PBDEs in carp (*C. carpio*) tissues.

MATERIALS AND METHODS

Standards and Reagents. Detailed information on the standards and reagents is provided in the Supporting Information. Eleven PBDE congeners (IUPAC nos. 28, 47, 100, 99, 154, 153, 183, 206, 207, 208, and 209) were monitored in the bioorganisms.

Sediment Preparation. The sediment was collected from a local site at Qilihai wetland (Tianjin, China). The sediment was inoculated and prepared following the procedures reported in our previous study.[10] Briefly, a small portion of sediment was spiked with the stock solutions of commercial products (DE-71, DE-79, and DE-83) in acetone. After the solvent was volatilized, the dry sediment was blended with 20 kg of sieved wet sediment (55% moisture) in a 50 L glass jar. The sediment was stirred with a motor stirrer in the dark for 3 weeks to ensure even partitioning of PBDEs in the sediment and then stored at 4 °C for 2 weeks prior to use. The PBDE concentrations were determined in the control (unspiked) and spiked sediments using the analytical procedures described below, and the results are listed in Table S1 in the Supporting Information.

Experimental Design. Experiments were conducted in five rectangular glass aquariums of 100 L. One of them was for the control test, in which clean sediment without spiking PBDEs was applied on the bottom. The other four aquariums were divided into two groups: one for fish exposure with oligochaete worms in the sediment (group A) and the other for fish exposure solely without worms (group B) (see Figure S1, Supporting Information). Wet sediment was put on the bottom of each aquarium with a height of around 3.0 cm. Filtered tap water was added to the aquariums slowly along the wall. The sediment/water system was allowed to equilibrate for 2 d. Adult freshwater tubificid oligochaetes (*Tubifex tubifex*) cultured in the laboratory were added into the group A and control aquariums with a density of around 1200 individuals m^{-2}. Carp (*C. carpio*), about 8 cm in length, were purchased from a local pet shop and acclimatized in the laboratory for 2 weeks prior to the exposure experiments.

Exposure I (Exp I). Fifty fish were added to each aquarium. Filtered dechlorinated tap water maintained at a temperature of 20 ± 2 °C was delivered to each tank to supply fresh water. The flow rate of the incoming water was approximately 0.01 L min^{-1}. The water in each aquarium was gently aerated to maintain oxygen saturation, and a 12 h light/12 h dark photoperiod was applied. The fish were fed with clean food daily in an amount equivalent to about 1% of their mean weight. Ten fish were sampled from each tank on days 5, 10, 15, and 20.

Exposure II (Exp II). At the end of exposure I, all the fish were removed from the tanks, and a nylon net of 2 mm mesh was fixed in each tank around 5 cm above the sediment to prevent the fish from touching the sediment. The sediment/water system was allowed to equilibrate for 1 d. Eighty fish were then added to each tank. The fish were exposed for 50 d. Seven fish were sampled from each tank on days 5, 10, 20, 40, and 50.

At the end of exp II, tubificid worms were sifted from the sediments of group A and the control, washed with distilled water, and purged in filtered dechlorinated tap water for 48 h.

Depuration. At the end of exp II, all the remaining fish were taken out and transferred to individual tanks with clean filtered dechlorinated tap water for depuration, which lasted for 40 d. Seven fish were sampled from each tank on days 5, 10, 20, and 40.

At each sampling time, 1 L of overlying water was siphoned for determination of the content of SPM using a gravimetric method. At all samplings, the fish size and weight were recorded. The sampled fish were washed with distilled water and allowed to purge in filtered dechlorinated tap water for 48 h. Fish feces were collected by filtering the water at the end of depuration. The fish were dissected as fillet (without skin) and liver for the determination of PBDE concentrations. Other parts such as fish bones and intestines were discarded. Suspended particles and feces were analyzed for PBDEs.

Analysis of PBDEs. Analysis of PBDEs was performed following the procedure described by Zhu et al.[16] Detailed information on the sample extraction and cleanup, instrumental analysis, and lipid content determination is provided in the Supporting Information.

Quality Assurance and Control. Standards containing known amounts of BDE-28, BDE-47, BDE-77, BDE-99, BDE-100, BDE- 118, BDE-153, BDE-154, BDE-206, BDE-207, BDE-

Table 1. PBDE Concentrations (ng g^{-1} dw) in Carp Tissues on the 20th Day in Exp I and on the 50th Day in Exp II[a]

	exp I, group A		exp I, group B		exp II, group A		exp II, group B	
congeners	fillet	liver	fillet	liver	fillet	liver	fillet	liver
BDE-28	2.67	4.13	2.92	3.34	1.19	1.83	0.89	1.47
BDE-47	166	248	159	239	70.9	105	47.4	94.3
BDE-100	22.4	31.8	22.9	30.6	8.05	22.9	7.48	15.4
BDE-99	nd	nd	nd	nd	nd	nd	nd	nd
BDE-154	33.3	55.6	30.4	52.6	28.4	44.0	25.7	38.5
BDE-153	6.14	6.29	5.41	6.01	2.13	3.39	2.25	3.21
BDE-183	nd	nd	nd	nd	nd	nd	nd	nd
BDE-208	nd	3.90	nd	3.25	nd	nd	nd	nd
BDE-207	nd	7.90	nd	7.38	nd	nd	nd	nd
BDE-206	nd	5.88	nd	5.01	nd	nd	nd	nd
BDE-209	nd	nd	nd	nd	nd	nd	nd	nd

[a]The concentrations were the mean values of two replicates. The average relative standard deviation was less than 10%.

208, and BDE-209 were used to identify and quantify PBDE congeners. The pretreatment and cleanup processes were conducted in a clean room. One procedural blank was included with each batch of eight samples to ensure the performance of the analytical procedure. The recovery of the surrogate was in the range of 80−120%, and no recovery correction was made for the reported concentrations. The PBDE concentrations in the blank were relatively low compared with those in the samples. The method limits (MDLs) were defined as 3 times the average concentrations of PBDEs in the blank samples. BDE-47, BDE-99, BDE-153, BDE-183, and BDE-209 were detected in blank samples. The MDL was 0.15 ng g^{-1} dw for BDE-47 and BDE-99, 0.30 ng g^{-1} dw for BDE-183, and 30 ng g^{-1} dw for BDE-209. The MDLs for other congeners, which were not detected in blank samples, were defined as the minimum amounts detected by the instrument. The limits of detection were 0.02 ng g^{-1} dw for BDE-28, BDE-100, and BDE-154 and 0.30 ng g^{-1} dw for BDE-206, BDE-207, and BDE-208.

Fish Growth. Fish mortality was monitored throughout the experiments, and only one fish was dead in all the control and exposure tests. At each sampling time, the fish mass, length, and lipid content were measured, and the data are listed in TAble S2 (Supporting Information). No significant difference (paired Student's t test; $p < 0.05$) in fish mass and lipid content was observed between the control and exposure tests. In all the tests, the fish growth followed an exponential kinetics (see eq 1) with a very low growth rate of 3.2×10^{-3} g d^{-1}. The results indicate that the spiked PBDEs did not show obvious toxicity to the fish during the exposure period. Since all the fish were healthy and their growth parameters were similar, the results of PBDE accumulation and depuration in fish obtained in all conditions could be compared to each other.

Data Analysis. The growth rate was calculated by fitting the fresh fish weight to an exponential model over the exposure time:

$$W_t = ae^{bt} \quad (1)$$

where W_t is the fish weight at time t (d), a is a constant, and b is the growth rate.

The elimination rate constant (k_e) was calculated by fitting the depuration data to a first-order decay model[17] using a nonlinear regression technique provided by SigmaPlot (SPSS Science, Chicago, IL):

$$C_t = C_{t=0}e^{-k_e t} \quad (2)$$

where C_t is the concentration of PBDEs in the fish fillet (ng g^{-1} dw) and k_e is the elimination rate constant.

The uptake rate constant (k_s) was estimated by fitting the uptake data to a first-order bioaccumulation model:[17]

$$C_t = \frac{k_s C_s}{k_e}(1 - e^{-k_e t}) \quad (3)$$

where C_t is the concentration of PBDEs accumulated in the fish fillet (ng g^{-1} dw), C_s is the concentration in the sediment (ng g^{-1} dw), k_s is the uptake rate coefficient (g of sediment g^{-1} of organism d^{-1}), and k_e is the elimination rate constant (d^{-1}).

Depuration half-lives ($t_{1/2}$) were calculated on the exponential part of the depuration curve using

$$t_{1/2} = \frac{\ln 2}{k_e} \quad (4)$$

RESULTS AND DISCUSSION

Partition and Metabolism of PBDEs in the Fish Tissues. The PBDE concentrations in fish tissues during the accumulation and elimination (in both groups A and B) are listed in the Supporting Information, Tables S3−S8. It is interesting that only five congeners (BDE-28, BDE-47, BDE-100, BDE-153, and BDE-154) were detected in the carp fillets and liver. BDE-206, BDE-207, and BDE-208 were only observed at low concentrations in fish liver on exposure for 20 d in exp I. The PBDE levels in carp tissues of the control group were distinctly lower than those of the exposure groups. For both exp I and exp II, PBDEs were accumulated at a higher level in the liver than in the fillet (Table 1). This is in accordance with the results reported in several previous studies.[18,19] Stapleton et al. exposed carp to PBDE-spiked food and found that PBDEs in the liver were 1.1−7.7 times higher than those in the whole-body tissues.[20] In the present study, the ratio was 1.8 on a dry-weight basis.

Figure 1 compares the congener profile of the seven major congeners, including BDE-28, BDE-47, BDE-100, BDE-99, BDE-154, BDE-153, and BDE-183, in the spiked sediments, SPM, fish tissues, and feces. The patterns in the sediments and SPM were similar to each other, with BDE-183 as the predominant congener (around 43%), followed by BDE-99

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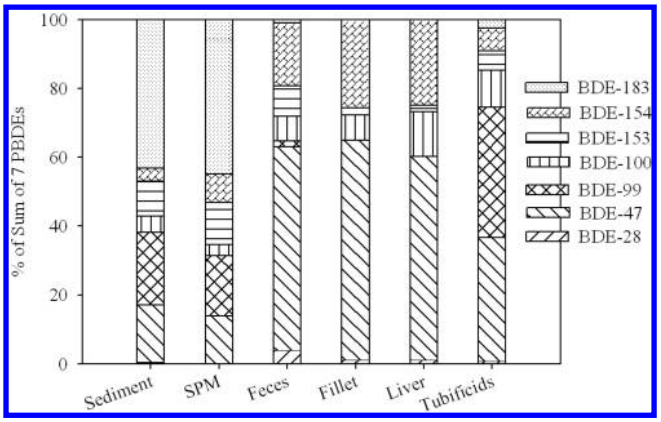

Figure 1. PBDE congener profiles in the spiked sediment, SPM, feces, fish fillet and liver, and tubificid worms in exp II, group A. The data were normalized to the sum of BDE-28, BDE-47, BDE-100, BDE-99, BDE-154, BDE-153, and BDE-183.

(21%) and BDE-47 (15%). However, a significantly different congener pattern was displayed in the fish. BDE-47 was the most abundant congener in the fish fillet and liver, accounting for more than 60% of the sum of the seven major congeners, followed by BDE-154, while BDE-99 and BDE-183 were not observed in the fish. Some studies found that BDE-47 made up approximately 60% of the total load of PBDEs.[21] The congener pattern in feces was in between that of the sediment and fish tissues. All seven congeners were observed in feces, with BDE-47 as the predominant congener, contributing around 55%.

BDE-99 is a major congener in penta-BDE, and BDE-183 is the major congener in octa-BDE commercial product. They were not detected in any parts of the fish during the exposure in exp I and exp II. The absence of BDE-99 and BDE-183 in carp tissues could be explained by its efficient metabolism. Several field studies indicated that BDE-99 was detected in common carp (*C. carpio*) at extremely low concentration relative to other congeners.[22−24] In vivo and in vitro experiments proved that BDE-99 and BDE-183 could be metabolized rapidly in common carp.[20,25,26] An in vitro debromination study found that almost 80% of BDE-99 was biotranformed to BDE-47 in carp liver.[26] Streets et al. suggested that 10% of BDE-99 was debrominated to BDE-47 in lake trout in the Great Lakes.[27] A higher concentration of BDE-154 relative to BDE-153 was observed in the carp tissues, while the opposite trend was observed in the spiked sediment (Supporting Information, Table S1). Roberts et al. investigated in vitro hepatic subcellular debromination of PBDE congeners in common carp.[25] They found that BDE-47 and BDE-154 were resistant to metabolic debromination while BDE-153 and BDE-183 were liable to be metabolized with the formation of lower brominated congeners: BDE-153 was metabolized to BDE-47 and BDE-101, and BDE-183 was metabolized to BDE-153 and BDE-154. This may explain why BDE-183 was not detected in the carp while BDE-47 was accumulated and predominant in the carp (Figure 1).

BDE-209, which is the predominant congener in sediment, was not detected in any fish tissues. Only low levels of nona-BDEs were detected in the fish liver in exp I, in which the fish could contact the contaminated sediment directly. However, a relatively high concentration of BDE-209 was detected in the feces (Supporting Information, Tables S3−S8). In group A, the BDE-209 concentration in the feces was comparable to that in the SPM and sediment, and it accounted for 89% ± 1.8% of the total PBDEs (∑PBDEs) in the feces, suggesting that BDE-209 was taken up by carp but was eliminated without bioaccumulation in the tissues. This also implies that carp mainly take up PBDEs by ingestion of SPM because the PBDE concentrations in water are very low, especially for higher brominated congeners. In our previous study, we found that BDE-209 could be taken up by benthic organisms through gut uptake with extremely low efficiency.[10] It was reported that the gut uptake of BDE-209 by rainbow trout from food was less than 1%.[11,13] Stapleton et al. exposed common carp to BDE-209-contaminated food and found that only 3.2% of BDE-209 could be assimilated by the carp.[11] They did not find BDE-209 in the body homogenate of the carp even after 60 d of exposure. Debromination products such as one octa-PBDE (BDE-202), two hepta-PBDEs (BDE-179 and BDE-188), and three hexa-PBDEs (BDE-154, BDE-155, and one unidentified hexa-BDE) were identified, indicating that carp could metabolize BDE-209 to lower brominated congeners. Roberts et al. also reported that BDE-209 could be metabolized to BDE-197, BDE-207, and BDE-208.[25] Low assimilation efficiency combined with metabolic debromination attributed to the lack of BDE-209 in carp tissues.

Bioaccumulation and Depuration. Figure 2 illustrates the uptake and depuration kinetics of the accumulated

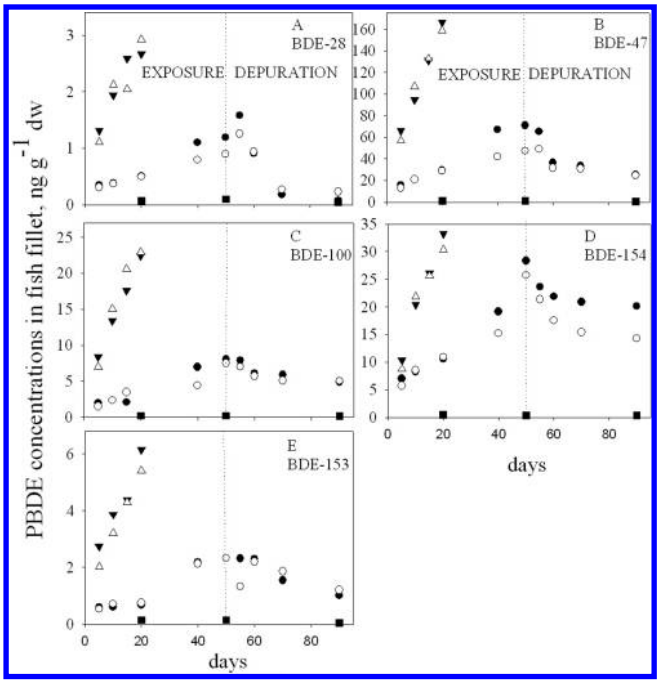

Figure 2. Accumulation and depuration of PBDEs in carp fillets. Solid triangular symbols represent exp I, group A, hollow triangular symbols represent exp I, group B, solid circular symbols represent exp II, group A, hollow circular symbols represent exp II, group B, and square symbols represent the control. Each point is the mean of two replicates with a standard deviation of less than 10%.

congeners, including BDE-28, BDE-47, BDE-100, BDE-154, and BDE-153 in the fish fillet. The uptake of these BDEs in exp I was significantly higher/faster than that in exp II. There are several pathways for the carp to be exposed to PBDEs: ingesting SPM occasionally when they eat the feed and breathing through the gills. In exp I, the carp could contact the spiked sediment directly. Meanwhile, as a result of the strong swirling disturbance of fish, the SPM in overlying water in exp I

Table 2. Bioaccumulation and Elimination Parameters of Selected PBDE Congeners

		k_s (10^{-2} ng g^{-1} d^{-1})			
congener	log K_{ow}	exp I[b]	exp II[b]	k_e (10^{-2} d^{-1})[b]	$t_{1/2}$ (d)
BDE-28	5.98[a]	15.7 ± 1.40	8.72 ± 2.82	4.80 ± 1.21	14.4
BDE-47	6.81[a]	9.30 ± 1.02	5.40 ± 2.44	2.65 ± 1.10	26.2
BDE-99	7.32[a]				
BDE-100	7.24[a]	2.38 ± 0.14	1.10 ± 0.67	1.24 ± 1.60	55.9
BDE-153	7.90[a]	0.34 ± 0.38	0.27 ± 0.28	1.53 ± 0.41	45.3
BDE-154	7.82[a]	5.70 ± 1.04	3.60 ± 2.30	1.21 ± 0.62	57.5
BDE-183	8.27[a]				
BDE-206	9.70[c]				
BDE-207	9.70[c]				
BDE-208	9.70[c]				
BDE-209	10.3[c]				

[a]Reported by Braekevelt et al.[7] [b]Mean value ± standard deviation. [c]Calculated by the equation log K_{ow} = 0.621(number of Br atoms) + 4.12.[7]

was 0.5 ± 0.2 g/L, significantly higher than 0.09 ± 0.03 g/L in exp II. The average concentration of ∑PBDEs in the SPM in exp I was 1927 ng g^{-1} dw, much higher than 1134 ng g^{-1} dw in exp II. Herein, the fish in exp I had the opportunity to take in more of the highly contaminated particles and accumulated a higher level of PBDEs. Our previous study found that benthic fish accumulated more PBDEs than pelagic fish.[19] This implies that benthic organisms have more opportunities for PBDE exposure by ingesting a large amount of sediment and SPM than pelagic ones.

The uptake kinetics increased linearly, and depuration followed an exponential decay model. The uptake did not reach the steady state in 50 d of exposure. Similar accumulation and depuration kinetics were reported by Tomy et al. and Munschy et al., who exposed lake trout (*Salvelinus namaycush*) and common sole (*Solea solea* L.) to spiked food.[12,14] A first-order kinetic model was used to fit the accumulation data with r^2 = 0.83−0.99 (eq 3), and the uptake rate coefficients (k_s) were calculated and are listed in Table 2.

Elimination of the accumulated PBDEs followed a first-order kinetic (eq 2) well (r^2 = 0.69−0.91) during the 40 d depuration period (Figure 2). The elimination rate coefficients (k_e) were estimated from the model fit and are shown in Table 2. Figure 3A illustrates the relationship of k_s (in exp I and exp II) with log K_{ow}. The k_s of the same congener was higher in exp I than that in exp II and showed a general trend of decreasing with increasing log K_{ow} (Figure 3A). It was reported that the uptake rate coefficient increases with log K_{ow} of organic chemicals when log K_{ow} is in the range of 0−3; but it displays a decreasing trend if log K_{ow} is higher.[28] With the increase of K_{ow}, hydrophobic organic chemicals prefer to bind with sediment particles and even become sequestrated during aging. As a result, desorption of these chemicals from sediment into interstitial water becomes very difficult, and the assimilation efficiency from ingested particles becomes very low. As listed in Table 2, all the studied PBDE congeners have log K_{ow} > 5.9. The extremely high hydrophobicity increases the resistance of mass transfer through aqueous phases, and this becomes the dominant barrier for uptake. Therefore, the k_s values of the PBDEs decreased with their log K_{ow} values. The relatively high k_s of BDE-154 could be due to the debromination of BDE-183 in the fish. The elimination rate coefficients (k_e) also decreased with increasing log K_{ow}. This agrees with the general assumption that the depuration rate decreases with log K_{ow}.[29] This is perhaps due to the difficulty of releasing hydrophobic chemicals from the lipid compartment of organisms.[30]

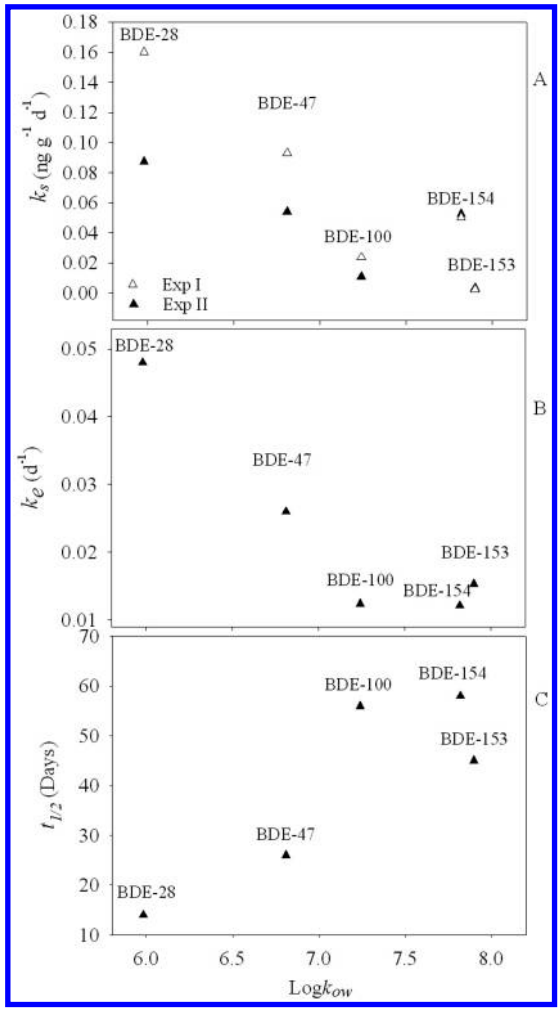

Figure 3. Calculated uptake rate coefficients (k_s) (A), elimination rate coefficients (k_e) (B), and half-lives ($t_{1/2}$) (C) of individual PBDEs relative to their log K_{ow} values.

It is well recognized that molecules with higher log K_{ow} have a stronger affinity for lipidlike biomolecules and thus increase their lifetimes in the tissues of bioorganisms. The half-lives ($t_{1/2}$) of PBDEs in the carp tissues in the present study also displayed a general trend of increasing in the range of 14 d for BDE-28 to 58 d for BDE-154 and were comparable to the $t_{1/2}$ values of PBDEs in juvenile rainbow trout exposed to spiked

dx.doi.org/10.1021/es204011k | Environ. Sci. Technol. 2012, 46, 2951−2958

food.[12] However, alternative elimination routes, such as metabolism, would affect the lifetimes of PBDEs in biota tissues. For example, the $t_{1/2}$ of BDE-153 was shorter than that of BDE-154 even though they have similar log K_{ow} values, which could be explained by the debromination of BDE-153 in the carp. Stapleton et al. also observed a short half-life of BDE-153 in common carp.[11]

No significant difference in uptake/depuration kinetics was observed between groups A and B, as shown in Figure 2. The results indicate that the tubificids' reworking does not affect the bioaccumulation of sediment-associated PBDEs in fish significantly. The SPM contents in groups A and B were similar to each other without a significant difference. Neither was there a significant difference in PBDE concentrations in the SPM between groups A and B, suggesting that tubificids do not significantly affect the resuspension of bottom sediment and release of PBDEs from the sediment. Karlchhoff et al. reported that the pollutant release into the water column was not comparably enhanced in the presence of the tubificid worms.[15]

Accumulation in Tubificid Oligochaetes. The tubificid worms were exposed to the spiked sediment for almost 80 d. Our previous study found that accumulation of PBDEs in polychaete *N. succinea* attained the steady state in 30 d.[10] Other studies reported that accumulation by oligochaete *L. variegatus* exposed to sediment-associated PBDEs reached the steady state around 7 d.[8,9] It is reasonable to assume that the accumulation by the worms reached the steady state in 80 d at the end of exp II. The PBDE concentrations in tubificid worms are listed in Table 3, and the congener pattern of the most common seven congeners is shown in Figure 1. It is interesting that all the PBDE congeners, including nona- and deca-BDEs, were found in the worms. The concentrations of PBDEs in the worms were significantly higher than those in the fish in both exp I and exp II. The worms actively ingest sediment through the gut, and the opportunity for PBDE exposure is greatly enhanced as compared to that of the fish, leading to the high PBDE concentrations in the worm tissues. The high PBDE concentrations accumulated in the benthic worms could have significant environmental implications given that they are prey of some higher trophic bioorganisms.

Table 3. Concentrations of PBDEs in Tubificid Worms (ng g^{-1} dw) and the Calculated BSAFs

congener	concn[a]	BSAF
BDE-28	6.26 ± 1.23	5.89
BDE-47	317 ± 42.6	4.38
BDE-100	95.8 ± 34.3	4.74
BDE-99	332 ± 46.1	3.09
BDE-154	57.3 ± 15.2	4.14
BDE-153	50.2 ± 6.60	1.09
BDE-183	22.2 ± 0.51	0.99
BDE-208	0.34 ± 0.02	0.04
BDE-207	5.17 ± 0.40	0.05
BDE-206	0.86 ± 0.51	0.02
BDE-209	25.0 ± 14.7	0.01

[a]Mean data of four replicates ± standard deviation.

As shown in Figure 1, the congener profile of the seven congeners was distinctly different from that of fish tissues. BDE-99 and BDE-47 were the dominant congeners, contributing 38% and 38%, respectively, while BDE-99 was absent in fish. BDE-183 was also detected in the worms while not in the fish. These differences suggest that the worms have very low metabolism capacity to debrominate PBDEs as compared to carp.

Since the worms accumulate PBDEs from sediment and do not debrominate them significantly, they can be used as a biomarker to reflect the bioavailability of sediment-associated PBDEs. The BSAF was calculated as the ratio of lipid-normalized tissue concentration to organic carbon-normalized sediment concentration at the steady state. The BSAF in the worms ranged from 0.01 to 5.89 for tri- through deca-BDEs (Table 3). The BSAFs were comparable to those reported by Liang et al., who studied BSAFs of PBDEs in earthworms.[31] The relationship of BSAF versus log K_{ow} of PBDEs is illustrated in Figure 4. Overall, the BSAF declined with log K_{ow} and the number of bromine atoms. This is in agreement with the reports about PBDE exposure in earthworms.[31,32] The BSAF of BDE-154 was higher than that of BDE-153. Wang et al. reported that the BSAF of PBDEs in blue mussel in the Bo Sea declined with log K_{ow} except for BDE-154 and explained that BDE-154 could be due to the biotransformation of BDE-209.[33] Tubificid worms accumulated nona- and deca-BDEs with low BSAF values of 0.01−0.05, which are comparable to those of nona- and deca-BDEs in polychaete *N. succinea*[10] and the results of some field studies.[34−37] The extremely low BSAFs of nona-BDEs and BDE-209 may be accounted for by their extremely high hydrophobicity and large molecular size. Compared to the nona-BDE profile in spiked sediment, BDE-206 contributed less in tubificid worms, while BDE-207 contributed more. This phenomenon was also observed in the accumulation of sediment-associated DE-83 by polychaete *N. succinea*.[10] This could be the result of the biotransformation of BDE-209 to BDE-207 and BDE-208 in tubificids. Another plausible reason is that BDE-207 and BDE-208 are easier to accumulate by bioorganisms as compared to BDE-206 and BDE-209.

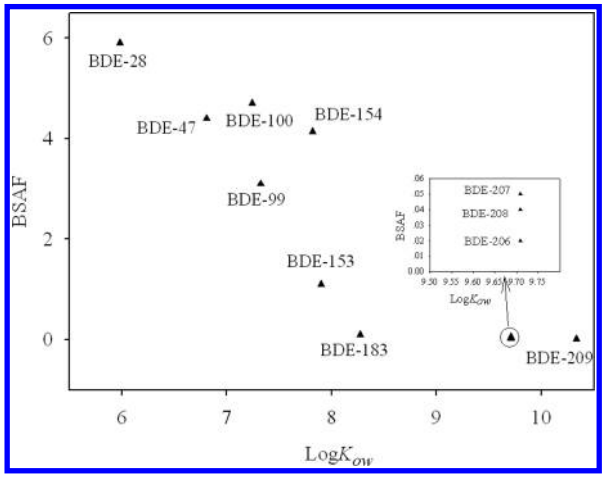

Figure 4. Relationship of BSAFs of PBDEs in tubificid worms with log K_{ow} values. BSAFs were calculated on the basis of the mean concentrations of PBDEs in worms after exposure for 80 d.

■ ASSOCIATED CONTENT

Supporting Information

Text describing the chemicals, sample extraction and cleanup, instrumental analysis, and lipid content analysis, figure showing the experimental design, and tables giving the PBDE concentrations in spiked sediment, concentrations of the

main PBDE congeners in carp tissues during exp I and exp II in groups A and B and the control group, and concentrations of PBDEs in feces, SPM, and sediment at the end of exp I and exp II. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

This study was supported by the Chinese Natural Science Foundation (Funding Numbers 20877044 and 21077060), Ministry of Education (Grants 20070055031 and 708020), Ministry of Science and Technology (Grants 2009DFA92390 and 2009BAC60B01), Ministry of Environmental Protection (Grant 201009026), Tianjin Municipal Science and Technology Commission (Grant 10SYSYJC27200), and China-U.S. Center for Environmental Remediation and Sustainable Development.

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