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Improved Measurements of Partition Coefficients for Polybrominated Diphenyl Ethers

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 Supporting Information

ABSTRACT: Polybrominated diphenyl ethers (PBDEs) are a class of widely used brominated flame retardants with strong hydrophobicity. Due to their strong affinity for organic matter, accurate measurement of adsorption coefficients for PBDEs using conventional batch methods can be confounded by biases caused by their sorption to dissolved organic carbon (DOC). In this study, sorption isotherms were constructed for BDE-47 and BDE-99 in sediments by using different methods to measure the aqueous phase concentration C_w . Upon centrifugation, C_w measured by automated solid-phase microextraction (C_{w-SPME}) was consistently smaller than by liquid–liquid extraction (C_{w-LLE}), suggesting substantial association of PBDEs with DOC. Significant underestimations (1.2–106-fold) of sediment–water partition coefficient K_d occurred when C_w was measured by LLE. The log K_{DOC} values derived from the SPME measurements ranged from 5.10 to 8.02 for eight congeners from BDE-28 to BDE-183, suggesting a strong tendency for PBDEs to complex with DOC. This study showed that PBDE congeners have larger sorption coefficients than would be measured by the conventional method. The high affinity to DOC also means a potential for DOC-facilitated transport, thus enhancing the environmental mobility of PBDEs.

INTRODUCTION

Polybrominated diphenyl ethers (PBDEs) are a class of widely used flame-retardants found in commercial and household products with the characteristics of high hydrophobicity ($\log K_{ow} > 6$ for most congeners).¹ Toxicity studies show that liver, thyroid gland, and possibly developing reproductive organs are particular targets of PBDEs.^{2,3} After decades of production and use, PBDEs have become ubiquitous in the environment and increasingly concentrated in air, sewage sludge, sediments, wildlife, and also human tissues.^{4–9} For example, in North America, PBDE concentrations in the environment and in humans are believed to double every 4–6 years.¹⁰

One of the most important processes influencing the environmental fate and risks of hydrophobic organic contaminants (HOCs) such as PBDEs is phase partitioning. However, at present relatively few measured values for phase partition coefficients (e.g., organic-carbon normalized partition coefficient K_{OC} and dissolved organic carbon partition coefficient K_{DOC}) are available for PBDEs in the literature. For HOCs, accurate determination of K_d and K_{OC} becomes increasingly difficult as K_{ow} increases,¹¹ because HOCs with large $\log K_{ow}$ are sorbed not only to particulate organic matter but also to colloids such as dissolved organic carbon (DOC).^{12–17} As demonstrated for strongly hydrophobic pesticides, sorption to DOC could lead to greatly underestimated K_d or K_{OC} .^{15,18} This occurs because the conventional batch method relies on the measurement of aqueous-phase concentration C_w without excluding DOC or that C_w is inflated because of the coexistence of DOC.^{13,14} Various methods have been tested to reduce this bias, including complexation-flocculation,¹⁹ membrane dialysis,^{17,20} fluorescent quenching,²¹ and solubility enhancement.²²

However, some of these methods may affect the equilibrium (e.g., flocculation),²³ while others are time-consuming (e.g., membrane dialysis) or impractical.¹⁴

In recent years, studies from this and other groups have established solid-phase microextraction (SPME) as an effective method for detecting the freely dissolved concentration (C_{free}) in an aqueous matrix.^{15,16,24} Coupling SPME and the batch equilibration method thus offers a novel approach to improved K_d and K_{OC} measurements for HOCs. In this study we compared K_d and K_{OC} values for PBDEs in multiple sediments measured with the conventional method and the SPME-modified approach. The improved protocol may be similarly applied to other flame retardants, thus contributing to the establishment of a more reliable database of sorption coefficients for these emerging contaminants. In addition, the use of SPME for detecting C_w also afforded, for the first time, the experimental determination of K_{DOC} values for PBDEs for natural dissolved organic matter.

MATERIALS AND METHODS

Chemicals and Sediments. Standards of BDE-28, 47, 66, 99, 100, 153, 154, and 183 in isooctane (50 or 500 $\mu\text{g/mL}$) were purchased from AccuStandard (New Haven, CT). Surrogate deca-chlorobiphenyl was purchased from Fisher Scientific (Fairlawn, NJ). All other solvents and chemicals used in the present study were of gas chromatography (GC) or analytical grade.

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Table 1. Basic Physical and Chemical Properties of Sediments Used in This Study

sediment ^a	OC ^b (% dry weight)	DOC ^c (mg/L)	particle distribution (%)		
			sand	silt	clay
JLR	0.07 ± 0.01	2.97 ± 0.43	78	17	5
GCS	0.48 ± 0.04	3.39 ± 0.76	87	7	6
LLS	1.68 ± 0.08	6.60 ± 0.24	77	22	1
SDC	1.75 ± 0.14	6.49 ± 0.52	41	37	22

^aGCS = Greasy Creek sediment, Benton County, OR; JLR = Jordan Lake Reservoir sediment, Chatham County, NC; LLS = Leaf Lake sediment, El Dorado County, CA; SDC = San Diego Creek Sediment, Orange County, CA. ^bOC = organic carbon content in the bulk sediment. ^cDOC = dissolved organic carbon level in the supernatant after centrifugation.

Four sediments with no detectable PBDE residues were used, including Jordan Lake Reservoir sediment (JLR, Chatham County, NC), Greasy Creek sediment (GCS, Benton County, OR), Leaf Lake sediment (LLS, El Dorado County, CA), and San Diego Creek sediment (SDC, Orange County, CA). All sediments were wet-sieved through a 2-mm mesh and stored at 4 °C before use. Selected properties of the test sediments are listed in Table 1. The sediment OC content was determined by combustion on a nitrogen/carbon analyzer (Thermo Finnigan, Woods Hole, MA) after digestion with HCl (1 M) to remove carbonates.

Adsorption Isotherm Experiment. Two grams (dry weight equivalent) of sediment was placed in a 230-mL glass centrifuge bottle and spiked with 0.5 mL of a mixture of BDE-47 and BDE-99 in acetone to give initial concentrations of 0.5, 1, 1.5, 2, and 2.5 µg/g. After the carrier solvent was completely removed in a fume hood, 200 mL of 0.02 M NaCl water solution was added, and the samples were mechanically shaken end over end at 15 rpm for 16 h at room temperature. Preliminary experiments assessing adsorption kinetics showed that apparent equilibrium was quickly reached under the conditions used (see the Supporting Information, SI). Upon equilibrium, the samples were centrifuged at 500 g for 30 min. An aliquot of the supernatant was removed for measuring DOC level by combustion at 720 °C on an Apollo 9000 total OC analyzer (Tekmar-Dohrmann, Mason, OH) after acid digestion.

After the supernatant was decanted, the sediment phase was spiked with the surrogate and extracted twice, each time with 50 mL of methylene chloride-acetone (1:1, v/v) for 20 min in a Fisher Scientific IS30H ultrasound bath. The slurries were centrifuged at 500 g for 15 min, and the extract was filtered through a Whatman No. 41 filter paper filled with 20 g of anhydrous sodium sulfate (to remove the residual water). The extracts were combined and concentrated at 40 °C on a rotary evaporator to dryness. The residue was recovered in 25 mL of hexane, from which an aliquot was taken for GC-mass spectrometer (MS) analysis to derive C_s . The method recoveries as given by the surrogate were 85.7–116.6%, which were used in the concentration calculation.

After centrifugation, the same supernatant was analyzed separately by LLE and SPME. A subsample (150 mL) of the supernatant was transferred to a 500-mL glass separatory funnel and subjected to LLE to derive C_{w-LLE} . The supernatant in the separatory funnel was mixed with 40 mL of methylene chloride for 1 min. The methylene chloride phase was collected upon phase separation and filtered through Whatman No. 41 filter paper

filled with 20 g of anhydrous sodium sulfate. The remaining aqueous phase was extracted with fresh methylene chloride for two additional times. All the solvent extracts were combined and concentrated at 35 °C to near dryness. The sample was reconstituted in 1.0 mL of hexane and transferred to an autosampler vial for analysis on GC-MS. The method recoveries as given by the surrogate were 82.7–115.4%. The LLE method was exhaustive, and therefore C_{w-LLE} represented the total chemical concentration in the aqueous phase.

A subsample (18 mL) of the supernatant was transferred to a 20-mL screw-cap vial for analysis by SPME-GC-MS to derive C_{w-SPME} . An automated SPME method was developed through preliminary experiments and used in this study to determine C_{w-SPME} . The SPME analysis was carried out on a Varian 3800 (Varian Instruments, Sunnyvale, CA) coupled with a Varian 1200 triple-quadrupole mass spectrometer and a Combi Pal autosampler (CTC Analytics, Zwingen, Switzerland) that contained an automatic SPME assembly, an agitator device, and an SPME conditioning station. Sampling with SPME involved the use of 7-µm polydimethylsiloxane (PDMS) fiber (Supelco, Bellefonte, PA) that was initially conditioned by heating at 320 °C for 2 h. The fiber immersion depth was fixed at 10 mm from the top of the vial, allowing only the PDMS fiber to be exposed to the aqueous solution. Agitation of the sample was performed by the autosampler at 500 rpm. To avoid carry-over between samples, the fiber was desorbed for an additional 30 min at 320 °C in the SPME fiber conditioning station after each analysis. In preliminary experiments, incremental SPME sampling intervals (i.e., exposure time of fiber in sample) from 10 to 80 min were tested, from which a fixed sampled time of 40 min was selected for the actual analyses. External standards prepared in deionized water were analyzed under the same conditions.

Analysis of C_s and C_{w-LLE} was carried out on an Agilent 6890 GC coupled to an Agilent 5973 mass spectrometer (Agilent, Santa Clara, CA). The automated SPME analysis was performed on a Varian 3800 GC coupled with a Varian 1200 triple-quadrupole mass spectrometer. Detailed chromatographic conditions are provided in the SI.

Method Application. The same procedure as developed above was further applied to the sorption measurement of six additional PBDEs, i.e., BDE-28, 66, 100, 153, 154, and 183. These congeners were selected based on their environmental occurrences and also to represent a wide range of hydrophobicity. An initial spiking concentration of 0.5 µg/g was used for each congener.

Statistical Analysis. All experimental treatments were in three replicates. The regression lines of the sorption isotherms were compared using the STRATGRAPHICS Plus 5.1 (Statistical Graphic, Princeton, NJ). Significance between treatments was tested using a one-way analysis of variance (ANOVA) with SPSS 13.0.1 (SPSS, Chicago, IL).

RESULTS AND DISCUSSION

SPME Fiber Uptake Kinetics and Method Validation. In aqueous solutions, accumulation of BDE-47 and BDE-99 on the PDMS-coated SPME fiber was found to be proportional to the length of the sampling time interval from 10 to 80 min, and the response could be approximated by a linear relationship (Figure 1). This observation implied that the uptake of PBDEs onto the PDMS fiber was slow under the conditions used, and no apparent equilibrium was reached within 80 min. Due to the lack of phase

equilibrium, SPME sampling time (40 min) and other conditions such as immersion depth and mixing speed were precisely controlled through the use of the automated SPME injector to allow reproducible measurements.

External calibration for SPME analysis was performed using deionized water spiked with BDE-47 and -99 at 5, 10, 50, 100, 250, and 500 ng/L. Calibration curves were linear in the range used for each compound, with correlation coefficient (r^2) ≥ 0.99 for both compounds. The precision of the SPME method was evaluated by calculation of the relative standard deviation (RSD) of three replicates at each concentration level. The RSD values were between 0.22 and 12.05% for BDE-47 and 3.45–10.90% for BDE-99, suggesting good method repeatability.

Phase Distribution of PBDEs. Visual examination suggested that the sediment and aqueous phases were well separated upon centrifugation. The relationships between the sorbed

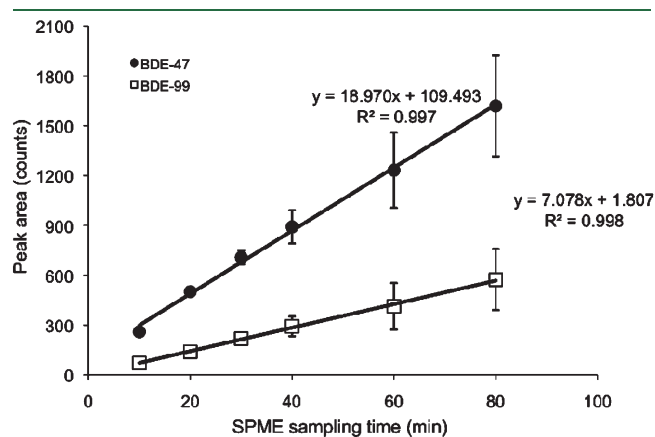


Figure 1. Chromatographic response in relation to fiber exposure time (i.e., sampling time) during analysis of PBDEs using automated solid-phase microextraction (SPME). Vertical bars represent standard deviations ($n = 3$).

concentration C_s and the aqueous phase concentration C_w as measured by LLE (C_{w-LLE}) or SPME (C_{w-SPME}) are shown in Figure 2 for BDE-47 and Figure 3 for BDE-99. The C_{w-SPME} was consistently smaller than C_{w-LLE} , suggesting that a fraction of the dissolved PBDEs were actually sorbed to DOC and/or very fine particles that were not excluded from the aqueous phase by centrifugation. Analysis of the supernatant validated the presence of DOC in the aqueous phase. The levels of DOC ranged from about 3.0 to 6.6 mg/L (Table 1).

Assuming the difference between C_{w-LLE} and C_{w-SPME} was due to sorption to DOC, the concentration of PBDEs associated with DOC was calculated as

$$C_{DOC} = \frac{C_{w-LLE} - C_{w-SPME}}{[DOC]} \quad (1)$$

where $[DOC]$ is the level of DOC. The distribution of PBDEs in the sediment, water, and DOC phases as percentage of the recovered amount is shown in Table 2. The majority of PBDEs was found to be sorbed to the bulk sediment, accounting for $76.0 \pm 5.1\%$ to $97.7 \pm 0.9\%$ for BDE-47 and $82.0 \pm 5.1\%$ to $97.5 \pm 0.7\%$ for BDE-99. Only a very small fraction of PBDEs was freely dissolved in the water phase ($0.9 \pm 0.1\%$ to $6.2 \pm 1.5\%$ for BDE-47 and $0.7 \pm 0.4\%$ to $2.9 \pm 1.0\%$ for BDE-99). The fractions associated with DOC were in general similar or greater than the freely dissolved fraction. For instance, in the supernatant of the JLR sediment, the fraction attributed to sorption of BDE-47 on DOC was 17.8%, which was 2.9 times that of the freely dissolved form (6.2%). These results clearly demonstrated the strong affinity of PBDEs for organic carbon both in the bulk sediment phase and in the dissolved form.

Previous studies show that only the truly dissolved fraction of a chemical is available for processes such as volatilization and reactions such as direct photolysis¹⁴ or for biotic processes such as toxicity, bioaccumulation, or microbial transformations.^{25–30} The fraction of the apparently dissolved PBDEs that was truly dissolved (f_{diss}) was further determined, simply as the ratio of

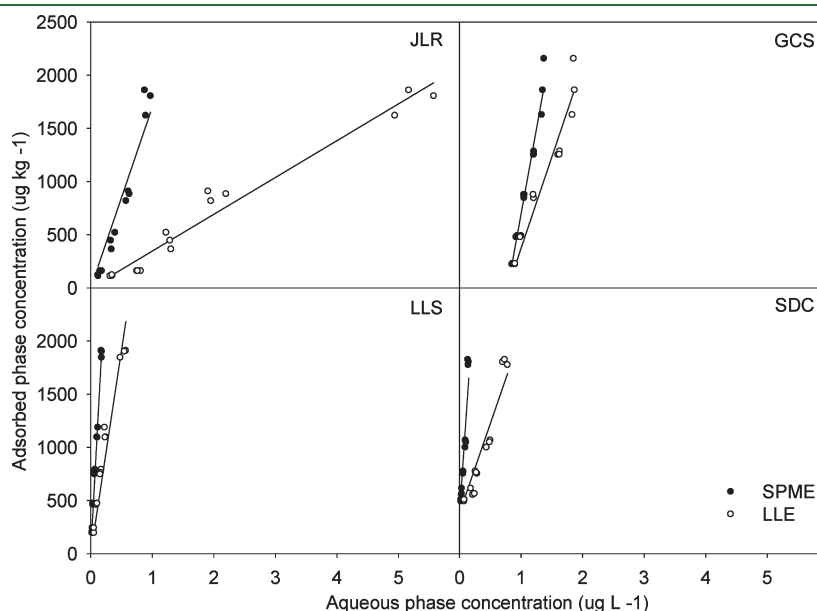


Figure 2. Sorption isotherms of BDE-47 in sediments measured using liquid–liquid extraction (LLE) or solid-phase microextraction (SPME) for detecting the aqueous-phase concentration C_w . GCS = Greasy Creek sediment, Benton County, OR; JLR = Jordan Lake Reservoir sediment, Chatham County, NC; LLS = Leaf Lake sediment, El Dorado County, CA; and SDC = San Diego Creek Sediment, Orange County, CA.

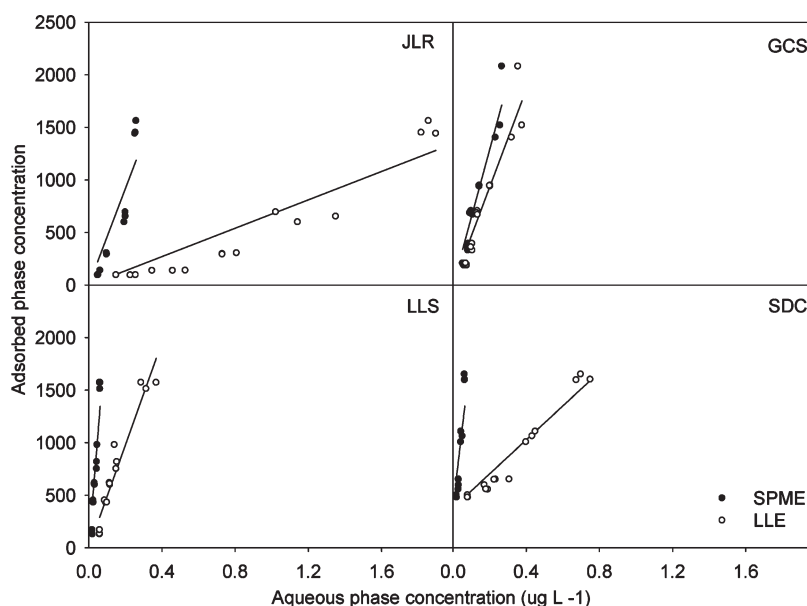


Figure 3. Sorption isotherms of BDE-99 in sediments measured using liquid–liquid extraction (LLE) or solid-phase microextraction (SPME) for detecting the aqueous-phase concentration C_w . GCS = Greasy Creek sediment, Benton County, OR; JLR = Jordan Lake Reservoir sediment, Chatham County, NC; LLS = Leaf Lake sediment, El Dorado County, CA; and SDC = San Diego Creek Sediment, Orange County, CA.

Table 2. Phase Distribution of PBDEs at Equilibrium in the Different Phases Calculated As the Percentage of the Recovered amount (Mean \pm Standard Deviation; $n = 3$)

sediment ^a	freely dissolved	DOC	sediment	f_{diss}^b
BDE-47				
JLR	6.20 \pm 1.46	17.76 \pm 4.80	76.04 \pm 5.07	26.50 \pm 6.93
GCS	3.47 \pm 0.23	2.35 \pm 0.81	94.17 \pm 0.86	60.63 \pm 8.34
LLS	0.90 \pm 0.12	1.37 \pm 0.30	97.74 \pm 0.33	40.15 \pm 5.75
SDC	1.24 \pm 0.26	4.66 \pm 1.63	94.10 \pm 1.77	21.75 \pm 4.72
BDE-99				
JLR	2.87 \pm 0.95	14.92 \pm 4.70	82.21 \pm 5.11	16.56 \pm 5.65
GCS	1.88 \pm 0.59	0.62 \pm 0.15	97.50 \pm 0.70	74.87 \pm 4.09
LLS	0.65 \pm 0.36	1.69 \pm 0.58	97.66 \pm 0.91	24.11 \pm 4.98
SDC	0.92 \pm 0.43	5.24 \pm 1.21	93.84 \pm 1.42	14.57 \pm 5.79

^a GCS = Greasy Creek sediment, Benton County, OR; JLR = Jordan Lake Reservoir sediment, Chatham County, NC; LLS = Leaf Lake sediment, El Dorado County, CA; and SDC = San Diego Creek Sediment, Orange County, CA. ^b f_{diss} the percentage of freely dissolved in the supernatant.

$C_{w\text{-SPME}}$ over $C_{w\text{-LLE}}$. The estimated f_{diss} varied from 21.8 to 60.6% for BDE-47 and 16.6 to 74.9% for BDE-99 (Table 2). Zarnadze and Rodenburg³¹ also studied the partitioning of PBDEs among the particle phase, the truly dissolved phase, and the colloidal phase in the water column. Instead of direct measurements, the authors used the following relationships to estimate f_{diss}

$$f_{\text{diss}} = \frac{1}{1 + K_{\text{DOC}}[\text{DOC}]} \quad (2)$$

$$K_{\text{DOC}} = m \cdot K_{\text{ow}} \quad (3)$$

where the constant of proportionality (m) describing the effectiveness of DOC relative to octanol was inferred from values for

Table 3. Sediment–Water Partition Coefficient K_d Values of BDE-47 and BDE-99 in Sediments with Aqueous Concentration Measured by Liquid–Liquid Extraction (LLE) or Solid-Phase Microextraction (SPME) (Mean \pm Standard Deviation; $n = 3$)

sediment ^a	JLR	GCS	LLS	SDC
BDE-47 ($\times 10^3$)				
LLE	0.34 \pm 0.01	1.37 \pm 0.05	3.35 \pm 0.08	2.33 \pm 0.05
SPME	2.02 \pm 0.05	2.83 \pm 0.06	10.40 \pm 0.28	12.25 \pm 0.75
BDE-99 ($\times 10^3$)				
LLE	0.76 \pm 0.02	5.17 \pm 0.08	4.92 \pm 0.11	2.20 \pm 0.03
SPME	6.06 \pm 0.21	7.51 \pm 0.06	31.50 \pm 0.71	31.03 \pm 0.95

^a GCS = Greasy Creek sediment, Benton County, OR; JLR = Jordan Lake Reservoir sediment, Chatham County, NC; LLS = Leaf Lake sediment, El Dorado County, CA; and SDC = San Diego Creek Sediment, Orange County, CA.

PCBs. The derived f_{diss} was 54% for BDE-47 and 14% for BDE-99. Therefore, to our knowledge, this is the first study to experimentally measure f_{diss} for PBDEs. While the results reaffirmed the strong affinity of PBDEs for DOC, they also showed that sources and levels of DOC could greatly affect f_{diss} , suggesting a necessity for direct measurement.

Evaluation of K_d and K_{oc} Underestimation by the Conventional Approach. The sorption isotherms were fitted to a linear relationship to estimate K_d . The good linear relationships ($r^2 > 0.90$) were likely due to the use of a relatively small concentration range. Large K_d values were obtained for both BDE-47 ($0.34\text{--}3.35 \times 10^3$ for LLE and $2.02\text{--}12.3 \times 10^3$ for SPME) and BDE-99 ($0.76\text{--}5.17 \times 10^3$ for LLE and $3.10\text{--}75.1 \times 10^3$ for SPME) (Table 3), validating that these compounds have exceptionally high affinity for the solid sediment phase.

The K_d values obtained for the same sediment but with different methods for measuring C_w were statistically compared.

Table 4. Log K_{OC} and Log K_{DOC} Values of PBDE Congeners Estimated Using Solid-Phase Microextraction (SPME) (Mean \pm Standard Deviation; $n = 3$)

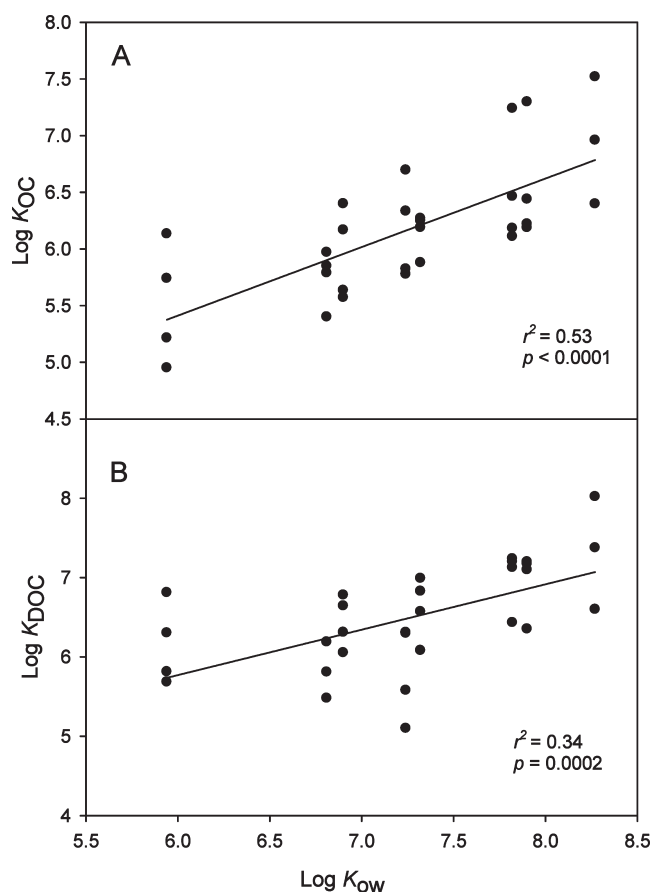
compound	JLR ^a	GCS	LLS	SDC
Log K_{OC}				
BDE-28	5.74 \pm 0.00	4.95 \pm 0.05	5.21 \pm 0.06	6.13 \pm 0.04
BDE-47	6.44 \pm 0.01	5.77 \pm 0.01	5.79 \pm 0.02	5.85 \pm 0.03
BDE-66	6.40 \pm 0.04	5.57 \pm 0.10	5.63 \pm 0.06	6.17 \pm 0.04
BDE-99	6.92 \pm 0.02	6.19 \pm 0.01	6.27 \pm 0.01	6.25 \pm 0.02
BDE-100	6.70 \pm 0.01	5.77 \pm 0.12	5.82 \pm 0.08	6.33 \pm 0.00
BDE-153	7.30 \pm 0.01	6.19 \pm 0.02	6.22 \pm 0.03	6.43 \pm 0.01
BDE-154	7.24 \pm 0.02	6.10 \pm 0.12	6.18 \pm 0.06	6.46 \pm 0.00
BDE-183	7.52 \pm 0.01	6.40 \pm 0.08	6.96 \pm 0.05	— ^b
Log K_{DOC}				
BDE-28	5.81 \pm 0.01	5.68 \pm 0.02	6.30 \pm 0.07	6.81 \pm 0.03
BDE-47	6.19 \pm 0.11	5.48 \pm 0.02	5.48 \pm 0.01	5.81 \pm 0.03
BDE-66	6.31 \pm 0.05	6.05 \pm 0.09	6.64 \pm 0.07	6.78 \pm 0.02
BDE-99	6.31 \pm 0.02	5.10 \pm 0.02	5.58 \pm 0.01	6.30 \pm 0.03
BDE-100	6.57 \pm 0.02	6.08 \pm 0.10	6.83 \pm 0.09	6.99 \pm 0.04
BDE-153	7.20 \pm 0.04	6.43 \pm 0.22	7.24 \pm 0.22	7.13 \pm 0.04
BDE-154	7.10 \pm 0.05	6.35 \pm 0.17	7.20 \pm 0.05	7.18 \pm 0.01
BDE-183	7.38 \pm 0.02	6.60 \pm 0.06	8.02 \pm 0.04	— ^b

^a GCS = Greasy Creek sediment, Benton County, OR; JLR = Jordan Lake Reservoir sediment, Chatham County, NC; LLS = Leaf Lake sediment, El Dorado County, CA; and SDC = San Diego Creek Sediment, Orange County, CA. ^b The aqueous phase concentration was below the detection limit.

K_d derived from the SPME measurement was significantly greater ($P < 0.05$) than that from LLE for all sediment-compound combinations. On average, K_d values obtained by the SPME method were 2.1–5.9-fold greater than that by LLE for BDE-47, and the differences were 1.5–14.1 times for BDE-99 (Table 3). Since C_s was unaffected by the method used for detecting C_w , the increases in K_d measured by the SPME method were attributed directly to the smaller C_w values as given by C_{w-SPME} that discounted the fraction sorbed to DOC in the supernatant.

The underestimation of K_d by the conventional batch equilibrium-solvent extraction procedure was also consistently found for BDE-28, 66, 100, 153, 154, and 183 (artificially depressed K_d by 1.2–106-fold for selected PBDE congeners, data not shown). The underestimation in K_d by the conventional approach for PBDEs was similar to that observed for synthetic pyrethroids in a previous study, where the conventional method artificially depressed K_d by 0.6–21.7-fold.¹⁵ It was further shown³² that the underestimation diminished as centrifugation speed was increased or solid-to-solution ratio was decreased, or that K_d approached the true value when extreme centrifugation speed or solid-to-solution ratio was used. In this study, the solid-to-solution ratio, at 2:200 (w/w), was very small. Much greater underestimations may occur if larger solid-to-solution ratios are used, as would be commonly encountered in sorption measurements for soils or sediments.

Table 4 lists the OC-normalized partition coefficient K_{OC} values for the selected PBDE congeners based on SPME-derived K_d data. In a previous study, partitioning of some PBDEs between the particulate and dissolved phases in Lake Michigan

**Figure 4.** Correlation of experimentally derived partition coefficients with log K_{ow} for selected PBDE congeners: (A) K_{OC} and (B) K_{DOC} .

water was measured.³³ Glass-fiber filters were used to collect the particles, and glass columns packed with XAD-2 resin were used to capture the apparent dissolved phase.³³ The values of log K_{OC} were estimated to be 6.2 ± 0.8 for BDE-47 and 6.5 ± 0.04 for BDE-99, which were similar to those observed in the present study (Table 4). A significant correlation ($r^2 = 0.53$, $p < 0.0001$) was found between the derived log K_{OC} values and log K_{ow} ^{34,35} for the selected congeners (Figure 4A). However, it is evident that log K_{OC} values varied over a wide range for the same congener but in different sediments. This suggests that K_{OC} of PBDEs is affected not only by the hydrophobicity of congeners but also by the properties of the solids. Therefore, K_{OC} values for PBDEs should be experimentally measured, instead of through estimation using empirical relationships.

Estimation of K_{DOC} . The partition coefficient between DOC and water phases is a useful parameter for predicting toxicity and bioaccumulation potentials of HOCs in sediments or soils. In its sediment quality guidelines, U.S. EPA suggested the use of K_{DOC} in relating chemical concentrations to toxicity to benthic organisms.³⁶ However, K_{DOC} values are scarce for most HOCs, apparently due to the lack of techniques to completely separate water and DOC phases. In this study, the detection of C_{free} by SPME and the simultaneous measurement of total aqueous concentrations by LLE afforded the estimation of K_{DOC} using a simple relationship

$$K_{DOC} = \frac{C_{DOC}}{C_{free} \cdot [DOC]} \quad (4)$$

Using the measured DOC levels in the supernatant, K_{DOC} was estimated to be 3.1×10^5 to 1.6×10^6 for BDE-47 ($\log K_{\text{DOC}} 5.76 \pm 0.34$) and 1.33×10^5 to 2.4×10^6 for BDE-99 ($\log K_{\text{DOC}} 5.92 \pm 0.56$) (Table 4). These values were similar or slightly smaller than the K_{OC} values for the same sediments. Ter Laak et al.¹⁸ reported $\log K_{\text{DOC}}$ in Aldrich humic acid to be 5.96 for BDE-47 and 6.35 for BDE-99, somewhat higher than those obtained in this study. A few studies suggested that the commercial Aldrich humic acid had different affinities to HOCs from naturally occurring DOC sources.³⁷ When plotting the derived $\log K_{\text{DOC}}$ values against $\log K_{\text{ow}}$, a significant correlation ($r^2 = 0.34$, $P = 0.0002$) was observed, although substantial data scattering was evident for individual congeners (Figure 4B).

The overall high K_{OC} and K_{DOC} values found in this and other studies suggest that PBDEs have extraordinary affinity for the bed sediment as well as DOC in the water column or in sediment porewater. This has several implications on the fate, transport, and ecotoxicological effects by PBDEs. The fact that PBDEs are sorbed favorably to DOC implies that in natural surface streams DOC may act as an effective carrier in surface runoff or streamflow for PBDEs and thus enable PBDEs to move over relatively long distances. The overall positive relationship between K_{DOC} and K_{ow} also suggests that DOC-enhanced mobility should be more pronounced for the more highly brominated PBDE congeners. On the other hand, as shown for other HOCs, bioavailability to aquatic invertebrates, measured as acute toxicity or uptake, is often related to C_{free} .^{28–30} In water column or sediment porewater, DOC is always present, and the levels are generally higher in sediment porewater than in surface water. This would mean that sorption to DOC or C_{free} must be known to more accurately predict bioaccumulation, toxicity, or even transformation rates of PBDEs in the environment. The SPME method developed in this study may be conveniently used for such purposes. PBDEs and other brominated flame retardants comprise of a large number of compounds with varying hydrophobicity or K_{ow} . A systematic effort to generate a database of improved K_{OC} and K_{DOC} values is a valuable exercise for the fate and risk assessment of these emerging contaminants.

■ ASSOCIATED CONTENT

S Supporting Information. Additional details on sorption equilibration and chromatographic conditions. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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