Environmental Chemistry

SORPTION OF PBDE IN LOW-DENSITY POLYETHYLENE FILM: IMPLICATIONS FOR BIOAVAILABILITY OF BDE-209

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Abstract—The coefficients of partitioning (K_{pew}) between low-density polyethylene (LDPE) film (50-μm thickness) and water for 23 polybrominated diphenyl ether (PBDE) congeners were determined based on a regression analysis of sorption kinetics over an extended exposure period (up to 365 d). A curvilinear relationship between log K_{pew} and log K_{OW} (octanol–water partition coefficient) was obtained for the target BDE congeners with the turning point at log K_{OW} approximately 8. Previously obtained dietary uptake efficiencies of BDE congeners in common carp (*Cyprinus carpio*) were also found to relate curvilinearly to log K_{OW}. In addition, field-measured relative abundances of BDE-209 compiled from previous investigations conducted in the Pearl River Delta of South China were significantly ($p < 0.001$) higher in abiotic samples ($n = 79$ from 11 matrices) than in biotic samples ($n = 73$ from 12 matrices), suggesting the likelihood for reduced bioavailability of BDE-209 in certain biota. Finally, a molecular-scale analysis indicated that the curvilinear relationship between log K_{pew} and log K_{OW} can be attributed to the energy barrier that a molecule has to overcome as it attempts to diffuse into the LDPE structure, which can become significant for larger molecules. Similarly, the reduced bioavailability of BDE-209 in many biological species can be regarded as a reflection of the magnitude of molecular interactions between cell membranes and BDE-209. Environ. Toxicol. Chem. 2011;30:1731–1738. © 2011 SETAC

Keywords—Low-density polyethylene film   Partition coefficient   Curvilinearity   Bioavailability   PBDE

INTRODUCTION

Polybrominated diphenyl ethers (PBDEs) are the main ingredients in the brominated fire retardants widely used in a variety of commercial products. They have considerable persistence in the environment, high accumulative ability in fatty tissues of organisms, substantial long-range transport potentials, and potential toxicity to ecosystems and humans [1–3]. Two groups of BDE congeners (tetrabromodiphenyl and pentabromodiphenyl ethers, and hexabromodiphenyl and heptabromodiphenyl ethers) were recently voted into the list of target organic contaminants under the Stockholm Convention on persistent organic pollutants ([4]; http://chm.pops.int/default.aspx). Although decabromodiphenyl ether (BDE-209) has not yet been targeted by the Stockholm Convention, probably because it is less toxic than lower brominated BDE congeners, concerns about its environmental fate are continuing to grow because it is presently the dominant component in brominated fire retardants and can be debrominated to presumably more toxic constituents. Whether BDE-209 is bioavailable, and to what extent, is a critical factor controlling its environmental fate and consequently its potential adverse impact on the health of the environment and humans.

Previous studies have demonstrated that the net dietary uptake efficiency (parallel to bioavailability) of BDE-209 in common carp (*Cyprinus carpio*) was much lower than those for BDE-28, -47, -99, -153, and -183 [5–7]. Two independent studies [8,9] also reported low dietary uptake of BDE-209 in rainbow trout (*Oncorhynchus mykiss*). The relatively lower

dietary uptake efficiency of BDE-209 compared to less brominated BDE congeners is consistent with the data compiled in the present study that the relative abundance of BDE-209 is generally lower in biota than in abiotic matrices. If the rates of biotransformation for individual BDE congeners in biota can be accounted for, it may be possible to assess the bioavailability of BDE-209 through a comparison of BDE compositional patterns in the biotic and abiotic matrices. However, such an approach is generally impractical due to the extreme difficulty in quantifying the biotransformation rates of BDE congeners under field conditions.

An alternative approach to the issue of bioavailability is the utility of passive sampling techniques capable of mimicking bioprocesses without the consequences of biotransformation. Polymer-coated (such as poly(dimethyl)siloxane [PDMS]) glass fibers [10] and low-density polyethylene (LDPE) films [11] have been used as biomimic probes, because they behave similarly to biological lipid. In such applications, the key step is to accurately determine the partition coefficients between the sorbent phase and water. However, this is not a trivial task, as demonstrated by Difilippo and Eganhouse [12] in the case of PDMS-water partition coefficients.

The present study was undertaken to accurately determine the LDPE-water partition coefficients (K_{pew}) for selected individual BDE congeners. In addition, the factors governing the bioavailability of BDE-209 were assessed in association with the dietary efficiency data from the literature and field-measured relative abundances of BDE-209 acquired in the Pearl River Delta (PRD) of South China (Supplemental Data, Fig. S1). To accomplish these objectives, laboratory experiments were carefully designed and executed to ensure the robustness of the measured K_{pew}. In addition, PBDEs have been detected in a variety of environmental matrices sampled in the PRD, providing reliable field data for assessments.

MATERIALS AND METHODS

Materials

Twenty-three target BDE congeners, including BDE-1, -15, -17, -28, -47, -66, -71, -85, -99, -100, -126, -138, -153, -154, -166, -181, -183, -190, -196, -204, -207, -208, and -209, were purchased from AccuStandard. Individual standard solutions of BDE-209 at 50 µg/ml in isooctane:toluene (9:1) and all other target BDE congeners at 50 µg/ml in isooctane were diluted with acetone to prepare spiking solutions of BDE-1 – BDE-190 at 1 µg/ml and BDE-196 – BDE-209 at 5 µg/ml. Surrogate standards (BDE-51, BDE-115, ^{13}C-labeled PCB-141, PCB-209, and ^{13}C-labeled BDE-209) and internal standards (BDE-69, ^{13}C-labeled PCB-208, and ^{13}C-labeled BDE-139) were acquired from Cambridge Isotope Laboratories. Hexane and methanol of high performance liquid chromatography grade were purchased from SK Chemical, whereas dichloromethane (DCM) and acetone was obtained locally and further purified by double distillation before use. High-purity water used as spiking medium was prepared from a Ro-DI^{TM} laboratory water purification system (Research Scientific Instruments).

Low-density polyethylene sheets (25-, 50-, and 100-µm film thicknesses) were purchased from TRM Manufacturing. Stripes of LDPE (2 ± 0.01 mg) fixed on copper wire were precleaned by soaking in DCM for 48 h, in methanol for 24 h, and in high-purity water for 24 h, and were cleaned again in high-purity water immediately before use to minimize possible cross-contamination. Laboratory glassware was cleaned with chromic acid mixture and oven-dried at 450°C for 4 h prior to use. Clean polytetrafluoroethylene-coated stirring bars were prepared from soaking in cold chromic acid mixture for 15 min and sonicating three times in DCM.

Sorption kinetic experiments

Sorption kinetics were established from the measured concentrations of the target BDE congeners in LDPE and water at various timepoints. Each glass container with 2-L high-purity water was spiked with BDE-1 – BDE-190 at 0.04 µg/L and BDE-196 – BDE-209 at 0.1 µg/L and sodium azide at 0.2 g/L was added to prohibit bacterial activity. Three identical LDPE stripes were placed in each container. Sampling timepoints were 10, 18, 30, 60, 103, 132, 171, 222, 249, and 365 d for 50-µm LDPE and 15, 30, 60, 90, and 163 d for 25- and 100-µm LDPE. All containers were sealed, shielded from light, continuously agitated at 700 rpm, and maintained at 21 ± 2°C.

At each preset sampling timepoint, LDPE stripes were taken out and rinsed with high-purity water, and then extracted consecutively with 10-ml DCM for 24 h and 10-ml hexane for 24 h. The remaining water was transferred to a 2-L separator funnel and liquid–liquid extracted three times with 100, 80, and 60 ml of DCM, respectively. The surrogate standards (^{13}C-PCB-141 and PCB-209 at 0.03 µg/L, BDE-51 and BDE-115 at 0.007 µg/L, and ^{13}C-BDE-209 at 0.07 µg/L) were added to all water and LDPE samples prior to extraction. Each extract was concentrated to about 5 to 10 ml with a Zymark Turbo Vap II (Hopkinton) at 30°C, filtered through a sodium sulfate-filled funnel while hexane was used to wash the original vial, and further reduced to 1 ml with the Zymark Turbo Vap II. Finally, each extract volume was reduced to 0.5 ml under gentle N$_2$ stream. The internal standards, BDE-69, ^{13}C-PCB-208, and ^{13}C-BDE-139, were added to the final extracts before instrumental analysis.

Instrumental analysis

The concentrations of the target BDEs in all samples were determined with a Shimadzu 2010 gas chromatograph coupled with a QP 2010 plus mass spectrometer, equipped with a 15 m × 0.25 mm-i.d. (with a 0.10-µm film thickness) DB-5 column. A 1-µL aliquot of each extract was injected with an auto injector. The column temperature was programmed from 110°C (held for 5 min) to 200°C (held for 4 min) at 40°C/min, further increased to 260°C at 10°C/min and held for 1 min, and finally ramped to 310°C at 15°C/min where it was held for 15 min. The transfer line and injection port temperatures were maintained at 300°C and 290°C, respectively. Helium was used as the carrier gas at a constant flow of 1.5 ml/min, and methane was reagent gas for the negative chemical ionization source. In the selected ion monitoring mode, the ion source temperature was 260°C.

Quality assurance and quality control

Procedure blanks (high-purity water) and LDPE blanks were processed along with actual water and LDPE samples from each sampling timepoint. In addition, a selected number of LDPE samples extracted once were subject to a second extraction to monitor possible carryover. None of the analytes was detectable in procedural blanks, LDPE blanks, and reprocessed LDPE samples. The reporting limits were 0.3 and 3.3 ng/L for BDE-1 – BDE-208 and BDE-209 in water samples (2 L each) and 0.25 and 2.5 ng/mg for BDE-1 – BDE-208 and BDE-209 in LDPE (2 mg each), respectively. The concentrations of BDE-138, -153, -154, -181, -183, -190, and -209 in water at 222, 249, and 365 d were initially lower than their reporting limits with an extract volume of 0.5 ml. To ensure reliable quantitation, the final volumes of these three samples were further reduced to 0.1 ml; as a result, the measured concentrations exceeded the reporting limits. The average recoveries of the surrogate standards for extraction of LDPE and water were 112 ± 15% for ^{13}C-labeledPCB-141, 98 ± 9% for BDE-51, 113 ± 17% for BDE-115, 107 ± 14% for PCB-209, and 93 ± 25% for ^{13}C-labeled BDE-209. All concentrations are reported without surrogate recovery correction.

Data analysis

Until now, measured octanol-water partition coefficient (K_{OW}) values were available for a few BDE congeners only [13,14]; thus a regression analysis (Fig. S2) based on the method of Puzyn et al. [15] was conducted to estimate K_{OW} values for the target BDE congeners, which is detailed in the Supplemental Data, with the results being presented in Table S1. In addition, the sorption kinetics were regressed with an exponential function based on Fick's first law of diffusion, i.e.,

$$C = a\left(1 - e^{-bt}\right) \quad (1)$$

where C can be regarded as the effective concentration of an analyte sorbed in the sorbent phase, a and b are fitting parameters, and t is the extraction time. In the present study, C in Equation 1 is replaced with C_{pe}/C_w, where C_{pe} and C_w are the analyte concentrations in LDPE and water, respectively, as C_{pe}/C_w is a more stable measurable than C_{pe} in general. Therefore, Equation 1 can be revised to yield

$$C_{pe}/C_w = a\left(1 - e^{-bt}\right) \quad (2)$$

It is apparent from Equation 2 that C_{pe}/C_w becomes K_{pew} as t approaches infinity, i.e., K_{pew} is equal to the fitting parameter a.

Furthermore, the error associated with log K_{pew} (defined as Δlog K_{pew}) is given by

$$\Delta \log K_{pew} = \frac{\Delta a}{a \ln 10} \quad (3)$$

Due to kinetic experiments conducted within finite time periods, the practical time to equilibrium (t_{eq}) can be defined as the extraction time at which the relative difference between C_{pe}/C_w and K_{pew} is 5%, and is calculated by

$$t_{eq} = \frac{\ln 20}{b} \quad (4)$$

Regression analyses of the kinetic data were performed with SigmaPlot 10.0 (Systat Software). Other data were analyzed with SPSS 13.0 with a 95% confidence interval.

RESULTS AND DISCUSSION

Evaluation of spiked analyte concentrations

The selection of the spiked analyte concentrations (0.04 µg/L for BDE-1 – BDE-190 and 0.1 µg/L for BDE-196 – BDE-209; Table S2) was to ensure sufficiently high concentrations of the target analytes on LDPE and in the aqueous phase for accurate quantitation. On the other hand, large uncertainties in the measured C_{pe}/C_w and K_{pew} could have resulted from the low water solubilities of some heavily brominated BDE congeners; therefore, a thorough evaluation of the solubility issue is warranted. As expected, solubility data for BDE congeners are rare in the literature. Nevertheless, a compilation of the existing data (Table S2) indicates that all BDE congeners except for BDE-209 have water solubility values higher than the spiking concentrations used in the present study. More

important, the actual aqueous concentrations measured and then used in the determination of C_{pe}/C_w or K_{pew} values are those present in the aqueous phase at the preset sampling timepoints. As shown in Table S2, the measured concentrations of all the target analytes at the shortest and longest sampling timepoints of 10 and 365 d were substantially lower than their water solubilities. It should be noted that the use of acetone as the diluting solvent for all target BDE congeners also helped to increase the analyte solubility in the aqueous phase.

Sorption kinetics of target BDE congeners

The main objective of the kinetic studies was to acquire accurate K_{pew} by fitting the measured sorption curves with Equation 2. As a result, the quality of data fitting dictates the robustness of K_{pew} values. In the present study, although kinetic experiments were performed with 25-, 50-, and 100-µm LDPE films, only the kinetics with the 50-µm LDPE film were investigated in detail. Hence, the following discussions will focus on the 50-µm LDPE film; however, the sorption kinetics for all three LDPE films are considerably similar and the conclusions derived herein can be applied to all three LDPE films.

The sorption kinetics varied with BDE congeners (Fig. 1). The first group of BDE congeners (BDE-1, -15, -17, -28, -47, -66, and -71) and BDE-209 appear to have reached equilibrium between LDPE and water upon 10 d of extraction, the first timepoint sampled in the experiments (Fig. 1a,d). All kinetic points for these congeners will then be treated equally in the determination of K_{pew}. For all other BDE congeners, equilibrium parameters were obtained by extrapolating the kinetic curves to $t \rightarrow \infty$ (Table 1). It should be noted that the fitted parameters in Table 1 were acquired excluding the data points at
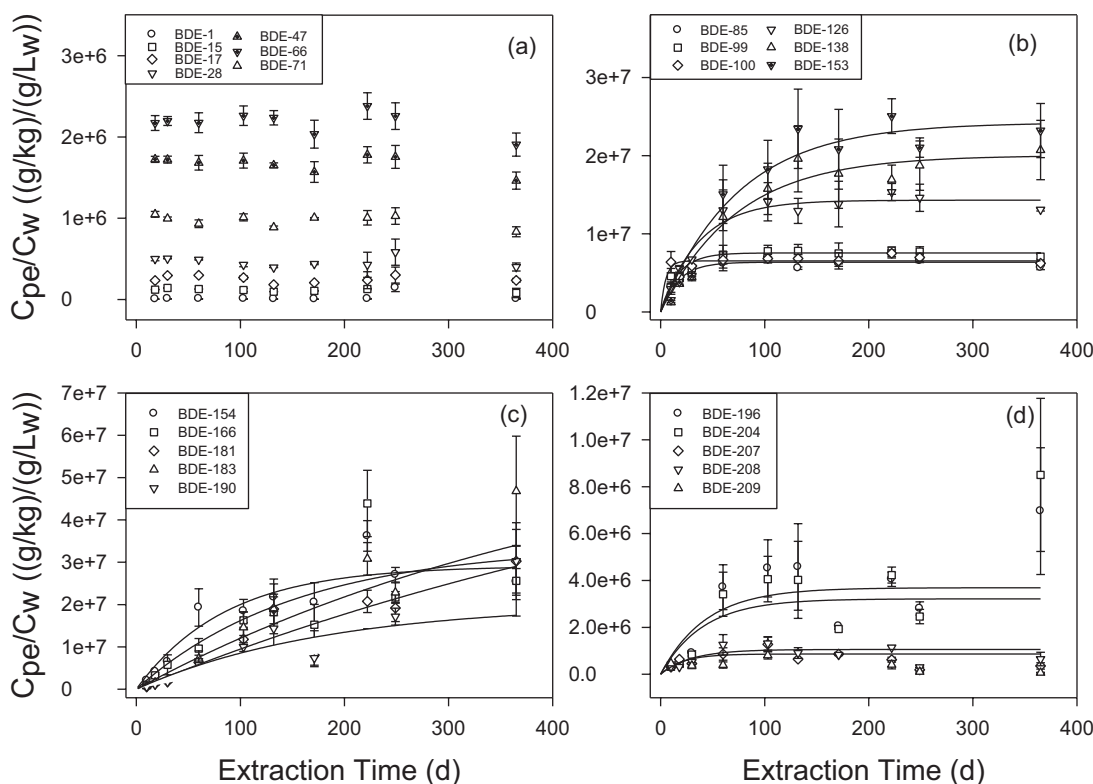

Fig. 1. Sorption kinetics of target polybrominated diphenyl ethers (PBDEs) congeners on 50-µm low density polyethylene (LDPE) film expressed as C_{pe}/C_w versus time (day), where C_{pe} and C_w are the concentrations of an analyte in LDPE film and water, respectively. The target PBDE congeners were divided into four groups: (**a**) BDE-1 – BDE-71; (**b**) BDE-85 – BDE-153; (**c**) BDE-154 – BDE-190; and (**d**) BDE-191 – BDE-209.

Table 1. Fitted parameters from a regression of measured data with Fick's first law of diffusion, $C_{pe}/C_w = a\,(1 - e^{-bt})$, except for brominated diphenyl ethers - BDE-1, -15, -17, -28, -47, -66, -71 and -209

Congener	log K_{OW}[a]	r^2	$p(a)$[b]	$p(b)$[b]	t_{eq}[c]	log K_{pew}[d]	log (C_{pe}/C_w) (t = 60 d)
BDE-1	4.34	N/A[e]	N/A	N/A	N/A	3.86 ± 0.19	N/A
BDE-15	5.82	N/A	N/A	N/A	N/A	5.08 ± 0.17	N/A
BDE-17	5.63	N/A	N/A	N/A	N/A	5.43 ± 0.14	N/A
BDE-28	6.24	N/A	N/A	N/A	N/A	5.69 ± 0.12	N/A
BDE-47	6.80	N/A	N/A	N/A	N/A	6.25 ± 0.10	N/A
BDE-66	7.00	N/A	N/A	N/A	N/A	6.37 ± 0.10	N/A
BDE-71	6.54	N/A	N/A	N/A	N/A	6.02 ± 0.11	N/A
BDE-85	7.27	0.90	< 0.0001	< 0.0001	51 ± 6	6.80 ± 0.01	6.79 ± 0.02
BDE-99	7.38	0.89	< 0.0001	< 0.0001	49 ± 6	6.88 ± 0.01	6.87 ± 0.02
BDE-100	7.09	0.79	< 0.0001	0.0042	15 ± 5	6.82 ± 0.01	6.82 ± 0.01
BDE-126	7.86	0.91	< 0.0001	< 0.0001	111 ± 14	7.16 ± 0.01	7.06 ± 0.03
BDE-138	8.17	0.87	< 0.0001	< 0.0001	219 ± 40	7.30 ± 0.03	7.05 ± 0.08
BDE-153	7.86	0.89	< 0.0001	< 0.0001	222 ± 36	7.38 ± 0.02	7.13 ± 0.07
BDE-154	7.62	0.89	< 0.0001	< 0.0001	175 ± 28	7.36 ± 0.02	7.17 ± 0.06
BDE-166	8.11	0.79	< 0.0001	0.0001	150 ± 35	7.18 ± 0.04	7.03 ± 0.08
BDE-181	8.61	0.81	0.0003	0.018	731 ± 285	7.47 ± 0.11	6.81 ± 0.25
BDE-183	8.61	0.81	< 0.0001	0.001	441 ± 123	7.39 ± 0.06	6.91 ± 0.16
BDE-190	8.61	0.77	< 0.0001	0.001	277 ± 77	7.12 ± 0.04	6.79 ± 0.13
BDE-196	9.29	0.63	< 0.0001	0.006	130 ± 44	6.57 ± 0.04	6.44 ± 0.11
BDE-204	9.26	0.62	< 0.0001	0.007	122 ± 42	6.51 ± 0.04	6.39 ± 0.10
BDE-207	9.65	0.56	< 0.0001	0.003	63 ± 19	5.94 ± 0.03	5.91 ± 0.05
BDE-208	9.65	0.56	< 0.0001	0.005	88 ± 29	6.02 ± 0.03	5.96 ± 0.08
BDE-209	9.87	N/A	N/A	N/A	N/A	5.61 ± 0.22	N/A

The data points at 365 d for BDE-183, -190, -196 and -204 were excluded in regression analysis.
[a] Regressed values presented in Table S1.
[b] p values for fitting parameters a and b.
[c] Defined as equilibrium time t when $(K_{pew} - C_{pe}/C_w)/K_{pew} < 0.05$ (Eqn. 4 in the main text.) K_{pew} is the polyethylene (PE)-water partition coefficient).
[d] $K_{pew} = C_{pe}/C_w$ as $t \rightarrow \infty$ (Eqn. 2 in the main text) and the errors were calculated with Eqn. 3 in the main text.
[e] Not applicable.

365 d for BDE-183, -190, -196, and -204. These data points show large deviations from the fitted kinetic curves, and can lead to large uncertainties for the fitted equilibrium parameters (Table S3). Therefore, they were rejected in the current data analyses. However, as discussed in the next section, the general pattern of the correlation between log K_{pew} and log K_{OW} is not significantly altered with or without the use of these data points. Another issue that has been carefully considered is the consequence of losses of the target analyte due to adsorption onto the glass container and stirring bar surfaces (Fig. S3). However, C_{pe}/C_w or K_{pew} values were acquired in the present study by directly measuring the analyte concentrations in LDPE and the aqueous phase, making any third-phase interference irrelevant. In fact, Yang et al. [16] verified with a radiolabeled approach that the sorption to glassware and stir bar surfaces had no effect on the measured PDMS–water partition coefficients of polychlorinated biphenyl (PCB) congeners 52, 77, and 153, phenanthrene, benzo[a]pyrene, 1,1,1-trichloro-2,2-bis(p-chlorophenyl)ethane (p,p'-DDT), and 1,1-bis-(4-chlorophenyl)-2,2-dichloroethene (p,p'-DDE).

In general, the quality of kinetic data fitting is reasonable, as demonstrated by the range of 0.56–0.91 for the least-square regression coefficients (r^2) and the p values for fitted a and b all less than 0.05 (all but one less than 0.01) (Table 1). The time to equilibrium (t_{eq}) estimated with Equation 4 exhibits an interesting pattern, i.e., it first increases with increasing log K_{OW}, reaches a plateau at log K_{OW} approximately 8.5, and then decreases with the continuing rise of log K_{OW} (Table 1). The more rapid approach to equilibrium for sorption of heavily brominated BDE congeners, such as octa- (BDE-204), nona-BDEs (BDE-207 and -208) and BDE-209, compared to moderately brominated congeners (such as hexa- and hepta-BDEs) was somewhat unexpected, because it would be more difficult

for the heavily brominated BDEs to diffuse into LDPE structure. A close look at Figure 1 suggests that the amounts of the heavily brominated BDEs required to reach the sorption plateaus were smaller than those of the moderately brominated congeners, thus shorter times may be needed for the heavily brominated BDEs to reach the state of equilibrium partitioning.

Curvilinear relationship between measured log K_{pew} and log K_{OW}

The sorption of BDE-1, -15, -17, -28, -47, -66, -71, and -209 reached equilibrium within 10 d of exposure (Fig. 1a,d), so the measured data points (three replicates for each extraction date) were used to yield average K_{pew} with the exception of BDE-1, where two data points at 249 d were excluded. These two C_{pew}/C_w values carry relative differences of 570% and 950%, respectively, compared to the average, and log K_{pew} for BDE-1 is improved to 3.86 ± 0.19 from 4.24 ± 0.94 when these two values are rejected.

A comparison of the fitted log K_{pew} and log (C_{pe}/C_w) at 60 d (Table 1) indicates no alteration to the general pattern for the log K_{pew} and log K_{OW} correlative relationship (Fig. 2). Even if the data points at 365 d for BDE-183, -190, -196, and -204 are included in the correlation plot, the above-mentioned pattern remains intact (Fig. S4). These assessments suggest that, although the times to equilibrium vary with individual BDE congeners (Table 1), an extraction time of 60 d is able to reconstruct the curvilinearity for the correlation between log K_{pew} and log K_{OW} (Fig. 2). In environmental applications of LDPE techniques, C_w is determined from measured C_{pe} and laboratory-calibrated K_{pew}. Practically, K_{pew} is often calibrated within a short time period, raising concerns about whether C_{pe}/C_w determined at a finite time t can be used as K_{pew} with reasonable accuracy. To address this issue for PBDEs, the
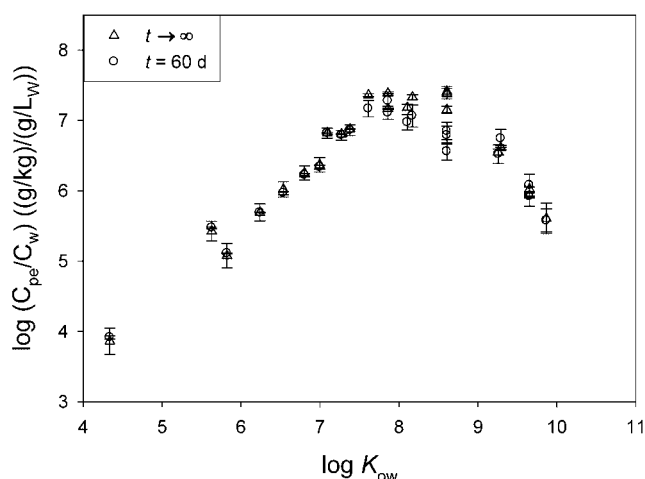
Fig. 2. Correlations between the polyethylene (PE)-water partition coefficients (log K_{pew}) on 50-μm low-density PE (LDPE) film obtained from the kinetics of C_{pe}/C_w versus time t and octanol-water partition coefficients (log K_{OW}), where C_{pe} and C_w are the concentrations of an analyte in LDPE film and water, respectively. Two sets of log K_{pew} values are presented: the first set of data contains those derived from equilibrium extraction time (triangle), i.e., t approaches infinity (Fig. 1), whereas the second set of data contains those based on an extraction time of 60 d (circle). The procedure to acquire log K_{OW} values (Table S1) for the target BDE congeners is presented in the Supplemental Data.

relative difference between K_{pew} and C_{pe}/C_w, defined as $100\% \times (K_{pew} - C_{pe}/C_w)/K_{pew}$, was calculated at various time-points chosen in the present study. This relative difference ranges from 0 to 70% at 60 d with an average of $30 \pm 24\%$, falls below 20% for all but one congener (BDE-181, with a relative difference of 37%) at 240 d, and diminishes at 365 d (the relative difference for BDE-181 stands at 22%) (Table S4). Clearly, a calibration time of 60 d, a time duration often used in fish exposure experiments [5–7], can yield reasonable accuracy when C_w is determined with the laboratory-calibrated C_{pe}/C_w.

We previously obtained a curvilinear relationship between the logarithm of PDMS-water partition coefficient (log K_f) and log K_{OW} for PCBs with the turning point at log K_{OW} approximately equal to 7 to 7.5 [17,18], which is similar to the field-observed correlations between log-based bioconcentration factor and log K_{OW} [19–21]. This curvilinearity was attributed to the difference in the Gibbs free energies for cavity formation in PDMS and octanol that can become significant for larger molecules [18]. Jonker and van der Heijden [22] instead ascribed the curvilinearity, or hydrophobicity cutoff in their term, to insufficient time to equilibrium and the presence of a third phase, but their conclusion of no hydrophobicity cutoff was only applicable to compounds with log K_{OW} up to 7.5. In the present study, 23 target BDE congeners with log K_{OW} spanning from 4.34 to 9.87, among which nine congeners have log K_{OW} greater than 8, were selected for the kinetic experiments. This, along with the extended exposure timepoints from 10 to 365 d (Fig. 1), greatly ensures that the fitted kinetic profiles have statistical significance. Furthermore, even if the log K_{pew} value for BDE-209 is excluded because of the debatable issue about the solubility of BDE-209, the curvilinearity displayed in Figure 2 remains intact.

As mentioned above, the sorption kinetics with 25-μm and 100-μm LDPE films were not measured in detail (Figs. S5 and S6) compared to 50-μm LDPE. Nevertheless, partitioning of BDE-1, -15, -17, -28, -47, -66, -71, -100, and -209 between LDPE and water was deemed equilibrium and the related data

can be used to assess the sorption similarity of LDPE with different thicknesses. Figure S7 indicates that these LDPEs are essentially identical in that regard.

Dietary uptake efficiency of BDE congeners

The similar curvilinearity discussed above was also observed in the cases of dietary uptake efficiency and biomagnification potential in relation to log K_{OW}. Limited data on dietary uptake of PBDEs have been acquired through laboratory studies [5–9,23] and are summarized in Table S4. For northern pike (*Esox lucius*), dietary uptake efficiency decreases singly from BDE-47 ($92 \pm 20\%$) to BDE-99 ($62 \pm 10\%$) and to BDE-153 ($40 \pm 10\%$) [23] with increasing log K_{OW} (Table 1). Common carp (*Cyprinus carpio*) also shows the same decreasing trend for BDE-47, -99, and -153, but a maxima occurs at BDE-47 (log $K_{OW} = 6.80$) when BDE-28, -183, and -209 are also included (Fig. S8). Because dietary uptake involves passage of chemicals through biological membranes, somewhat similar to diffusion across LDPE surface, the nonlinear relationship shown in Figure S4 may also be explained by the similar mechanism for the curvilinearity between log K_{pew} and log K_{OW} (Fig. 2).

Field-measured relative abundances of BDE-209

A large set of data on the relative abundances of BDE-209 in 23 environmental matrices sampled from the PRD was compiled from the literature [24–37] and is graphically displayed in Figure 3. An independent samples t test for equality of means indicates that there is a significant difference ($p < 0.001$) in the relative abundances of BDE-209 between the abiotic ($n = 79$ from 11 matrices) and biotic ($n = 73$ from 12 matrices) samples, i.e., the average relative abundances of BDE-209 were $74 \pm 29\%$ and $35 \pm 30\%$ in abiotic and biotic samples, respectively. In addition, 61 out of 79 abiotic samples, compared to 27 out of 73 biotic samples, had relative abundances of BDE-209 greater than 50%. Given the fact that these samples were collected from multiple locations at various time periods and contained PBDEs at levels varying over several orders of magnitude, the substantial relative abundance difference between the abiotic and biotic samples (Fig. 3) clearly points to reduced bioavailability of BDE-209 in certain biota compared to other BDE congeners.

The reduced bioavailability of BDE-209 in certain biota can be further confirmed by another previous study [38] that collected and analyzed a set of abiotic and biotic samples from four freshwater fish ponds at Dongguan and Shunde of the PRD (Fig. S1). Among the 32 composite samples analyzed [38], all 12 fish samples contained BDE-209 with relative abundance lower than 15% and all but one abiotic composite sample had relative abundances of BDE-209 greater than 50% (Fig. 4). It should be noted that air samples, particularly the gaseous and dissolved phase samples, also had low relative abundances of BDE-209 (Figs. 3, 4), which is obviously attributable to the low volatile and high hydrophobic properties of BDE-209.

A recent review compiled the concentration data for PBDEs in birds collected from multiple locations around the world; the concentrations of BDE-209 were found to be approximately one order of magnitude lower than those of total PBDEs minus BDE-209 in terrestrial birds [39]. Because concentration data from a specific location were largely acquired by the same authors [39] and BDE-209 has been the predominant component in brominated fire retardants used worldwide in recent years, this observation again points to the reduced bioavail-
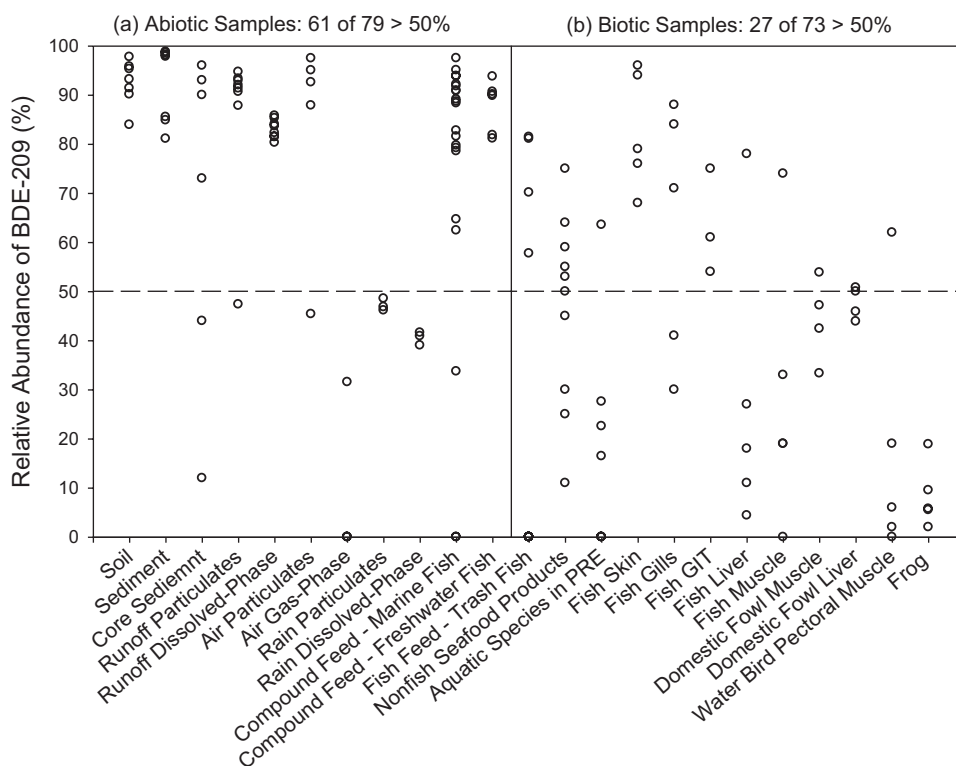
Fig. 3. Relative abundances of decabromodiphenyl ether (BDE-209) in various environmental matrices sampled in the Pearl River Delta of South China [24–37]. An independent samples *t* test for equality of means indicates that the difference in the relative abundances of BDE-209 between the abiotc ($n = 79$) and biotic ($n = 73$) samples is significant ($p < 0.001$).

ability of BDE-209 in biota—in this case global terrestrial birds.

Molecular-scale explanation for curvilinearity

As mentioned above, we previously ascribed the similar curvilinear relationship between log K_f and log K_{OW} for polychlorinated biphenyls to the difference in Gibbs free energies required to create cavity in PDMS and octanol, respectively, i.e., log K_f – log K_{OW} approximately equal to ($G_{cavity–octanol}$ – $G_{cavity–PDMS}$)/(2.303·RT) [18]. Clearly, this energy difference is negligible for small molecules but may become significant for larger molecules. The implication of this hypothesis is that the analyte concentration in the sorbent phase (PDMS or LDPE in our studies) may be lower than expected but is still able to maintain thermodynamic equilibrium with that in water (truly dissolved phase).

Herein we offer a molecular-scale explanation for the curvilinearity based on a revised version of the scheme by Ai [40]. As shown in Figure 5, the LDPE–water system is presumably constructed from a bulk LDPE phase, an LDPE surface layer of perhaps a few molecules in thickness, and water. Therefore, the volume of the bulk LDPE phase (defined as V_{bulk}) is much greater than that of the LDPE surface layer (designated $V_{surface}$), i.e., $V_{bulk} \gg V_{surface}$. In addition, the diffusion layer in water as proposed by Ai [40] is neglected here because strong agitation was always applied in our sorption experiments. In this scenario, equilibrium partitioning of a molecule between LDPE and water leads to

$$K_{pew} = C'_{pe}/C_w \qquad (5)$$

For a large molecule (e.g., BDE-209), its equilibrium concentrations are higher in the LDPE surface layer than in the bulk LDPE phase, i.e., $C'_{pe} > C_{pe}$, due to the energy barrier (or difference) mentioned above that the molecule has to overcome as it attempts to cross the boundary between the bulk phase and surface layer. On the other hand, the parameter usually measured is the total mass (m_{pe}) in $V_{bulk} + V_{surface}$, i.e.,

$$m_{pe} = C_{pe} V_{bulk} + C'_{pe} V_{surface} \qquad (6)$$

When $V_{bulk} \gg V_{surface}$, Equation 6 becomes $m_{pe} \approx C_{pe} V_{bulk}$. In essence, we always assume $K_{pew} = C_{pe}/C_w$ in calculating the LDPE-water partition coefficients, but instead Equation 5 should be used to obtain K_{pew}. Obviously, $C'_{pe}/C_w > C_{pe}/C_w$ at equilibrium because $C'_{pe} > C_{pe}$ as rationalized above, resulting in a decreasing trend for measured log K_{pew} with increasing log K_{OW} after log K_{OW} reaches approximately 8 (Fig. 2).

It has become clear from the above discussions that further validation of the hypothesis for the curvilinearity can be conducted with thin sorbent films of various thicknesses comparable to the thickness of the surface layer. The curvilinearity is expected to progressively diminish as the thickness of the sorbent phase becomes sufficiently small (i.e., $m_{pe} \rightarrow C'_{pe} V_{surface}$ and C'_{pe}/C_w is actually measured to obtain K_{pew}), if the hypothesis holds true. This hypothesis also implicates that the reduced bioavailability of BDE-209 observed in many biological species is essentially a reflection of the magnitude of molecular interactions between cell membranes and BDE-209. In this regard, for example, a more rigid cell structure would result in a lower bioavailability for BDE-209 than a less rigid one.
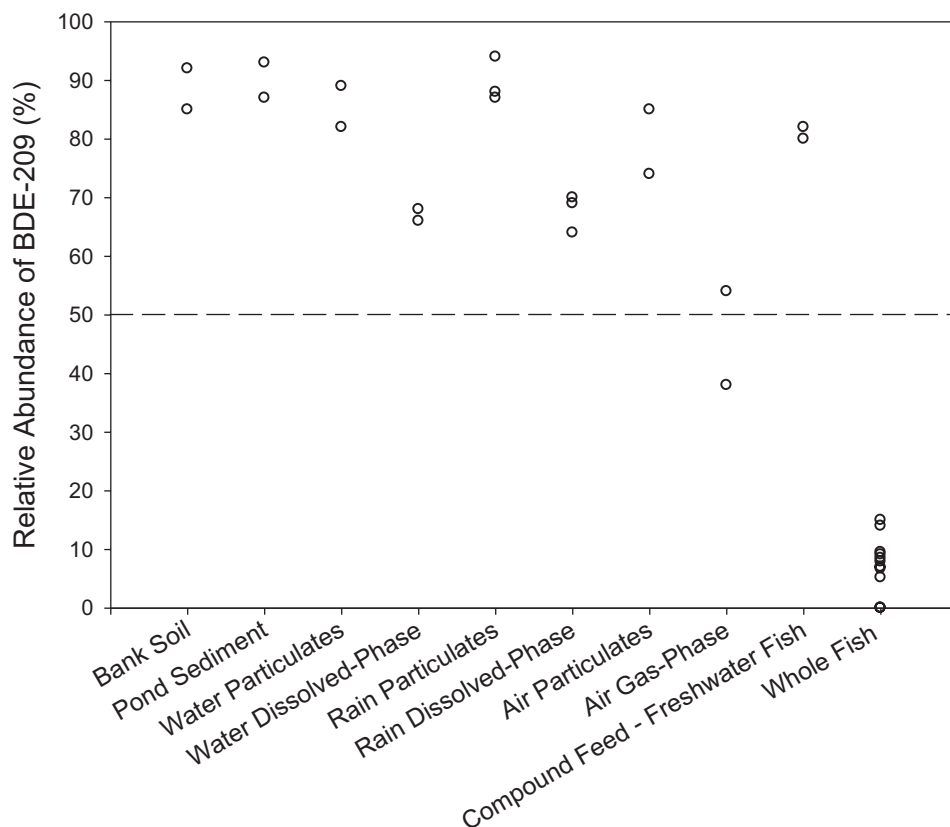
Fig. 4. Relative abundances of decabromodiphenyl ether (BDE-209) in various environmental matrices sampled from typical freshwater cultured fish ponds of South China [38].
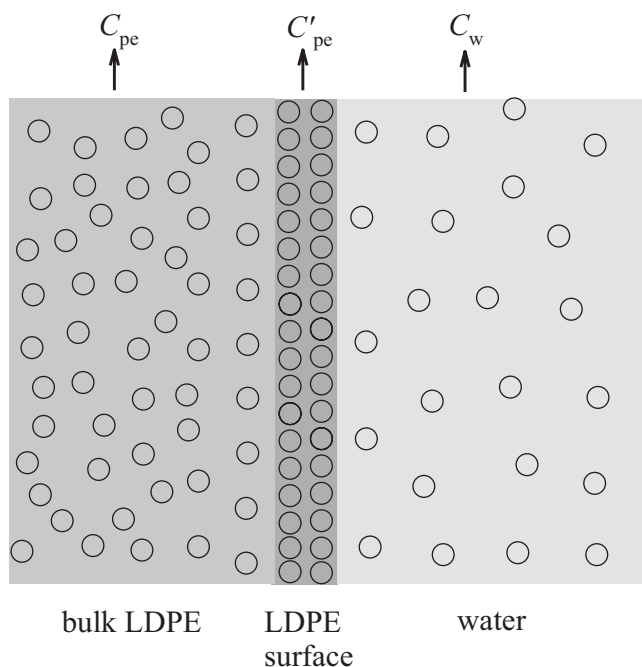

Fig. 5. Schematic showing equilibrium partitioning of an analyte among the bulk low-density polyethylene (LDPE) phase, LDPE surface layer of perhaps a few molecules in thickness, and water, based on a revised version of the scheme proposed by Ai [40]. The concentrations of the molecule in these phases are denoted as C_{pe}, C'_{pe}, and C_w.

CONCLUSIONS

The present study demonstrates a curvilinear relationship between log K_{pew} and log K_{OW} for BDE congeners, which can be attributed to the energy barrier that a target analyte has to overcome as it attempts to diffuse into the LDPE structure. The energy barrier can become significant for larger molecules. Similarly, the reduced bioavailability of BDE-209 observed in many biological species is likely a reflection of the magnitude of molecular interactions between cell membranes and BDE-209.

SUPPLEMENTAL DATA

Tables and figures containing regressed K_{OW} values, kinetic and equilibrium parameters of BDE congeners, and compiled dietary uptake efficiency data from the literature. (1,090 KB).

REFERENCES

1. Ter Schure AFH, Larsson P, Agrell C, Boon JP. 2004. Atmospheric transport of polybrominated diphenyl ethers and polychlorinated biphenyls to the Baltic Sea. *Environ Sci Technol* 38:1282–1287.
2. Hites RA. 2004. Polybrominated diphenyl ethers in the environment and in people: A meta-analysis of concentrations. *Environ Sci Technol* 38:945–956.

3. Darnerud PO, Eriksen GS, Jóhannesson T, Larsen PB, Viluksela M. 2001. Polybrominated diphenyl ethers: Occurrence, dietary exposure, and toxicology. *Environ Health Perspect* 109 (Suppl 1): 49–68.

4. United Nations Environment Program. 2004. Stockholm Convention on Persistent Organic Pollutants (POPs). Geneva, Switzerland.

5. Stapleton HM, Alaee M, Letcher RJ, Baker JE. 2004. Debromination of the flame retardant decabromodiphenyl ether by juvenile carp (*Cyprinus carpio*) following dietary exposure. *Environ Sci Technol* 38:112–119.

6. Stapleton HM, Letcher RJ, Li J, Baker JE. 2004. Dietary accumulation and metabolism of polybrominated diphenyl ethers by juvenile carp (*Cyprinus carpio*). *Environ Toxicol Chem* 23:1939–1946.

7. Stapleton HM, Letcher RJ, Baker JE. 2004. Debromination of polybrominated diphenyl ether congeners BDE 99 and BDE 183 in the intestinal tract of the common carp (*Cyprinus carpio*). *Environ Sci Technol* 38:1054–1061.

8. Stapleton HM, Brazil B, Holbrook RD, Mitchelmore CL, Benedict R, Konstantinov A, Potter D. 2006. In vivo and in vitro debromination of decabromodiphenyl ether (BDE 209) by juvenile rainbow trout and common carp. *Environ Sci Technol* 40:4653–4658.

9. Kierkegaard A, Balk L, Tjärnlund U, De Wit CA, Jansson B. 1999. Dietary uptake and biological effects of decabromodiphenyl ether in rainbow trout (*Oncorhynchus mykiss*). *Environ Sci Technol* 33:1612–1617.

10. Mayer P, Vaes WHJ, Wijnker F, Legierse KCHM, Kraaj R, Tolls J, Hermens JLM. 2000. Sensing dissolved sediment porewater concentrations of persistent and bioaccumulative pollutants using disposable solid-phase microextraction fibers. *Environ Sci Technol* 34:5177–5183.

11. Friedman CL, Burgess RM, Perron MM, Cantwell MG, Ho KT, Lohmann R. 2009. Comparing polychaete and polyethylene uptake to assess sediment resuspension effects on PCB bioavailability. *Environ Sci Technol* 43:2865–2870.

12. Difilippo EL, Eganhouse RP. 2010. Assessment of PDMS-water partition coefficients: Implications for passive environmental sampling of hydrophobic organic compounds. *Environ Sci Technol* 44:6917–6925.

13. Braekevelt E, Tittlemier SA, Tomy GT. 2003. Direct measurement of octanol-water partition coefficients of some environmentally relevant brominated diphenyl ether congeners. *Chemosphere* 51:563–567.

14. Choi K-I, Lee S-H, Osako M. 2009. Leaching of brominated flame retardants from TV housing plastics in the presence of dissolved humic matter. *Chemosphere* 74:460–466.

15. Puzyn T, Suzuki N, Haranczyk M. 2008. How do the partitioning properties of polyhalogenated POPs change when chlorine is replaced with bromine. *Environ Sci Technol* 42:5189–5195.

16. Yang Z-Y, Greenstein D, Zeng EY, Maruya KA. 2007. Determination of poly (dimethyl) siloxane - water partition coefficients for selected hydrophobic organic chemicals using 14C-labeled analogs. *J Chromatogr A* 1148:23–30.

17. Yang Z-Y, Zeng EY, Xia H, Wang J-Z, Mai B-X, Maruya KA. 2006. Application of a static solid-phase microextraction procedure combined with liquid-liquid extraction to determine poly(dimethyl)siloxane-water partition coefficients for selected polychlorinated biphenyls. *J Chromatogr A* 1116:240–247.

18. Yang ZY, Zhao YY, Tao FM, Ran Y, Mai BX, Zeng EY. 2007. Physical origin for the nonlinear sorption of very hydrophobic organic chemicals in a membrane-like polymer film. *Chemosphere* 69:1518–1524.

19. Bremle G, Okla L, Larsson P. 1995. Uptake of PCBs in fish in a contaminated river system: Bioconcentration factors measured in the field. *Environ Sci Technol* 29:2010–2015.

20. Meylan WM, Howard PH, Boethling RS, Aronson D, Printup H, Gouchie S. 1999. Improved method for estimating bioconcentration/bioaccumulation factor from octanol/water partition coefficients. *Environ Toxicol Chem* 18:664–672.

21. Gerofke A, Kömp P, McLachlan MS. 2005. Bioconcentration of persistent organic pollutants in four species of marine phytoplankton. *Environ Toxicol Chem* 24:2908–2917.

22. Jonker MTO, van der Heijden SA. 2007. Bioconcentration factor hydrophobicity cutoff: An artificial phenomenon reconstructed. *Environ Sci Technol* 41:7363–7369.

23. Bureau S, Axelman J, Broman D, Jakobsson E. 1997. Dietary uptake in pike (*Esox Lucius*) of some polychlorinated biphenyls, polychlorinated naphthalenes and polybrominated diphenyl ethers administered in natural diet. *Environ Toxicol Chem* 16:2508–2513.

24. Mai BX, Chen SJ, Luo XJ, Chen LG, Yang QS, Sheng GY, Peng PA, Fu JM, Zeng EY. 2005. Distribution of polybrominated diphenyl ethers in sediments of the Pearl River Delta and adjacent South China Sea. *Environ Sci Technol* 39:3521–3527.

25. Chen LG, Mai BX, Bi XH, Ran Y, Luo XJ, Chen SJ, Sheng GY, Fu JM, Zeng EY. 2006. Concentration levels, compositional profiles, and gas-particle partitioning of polybrominated diphenyl ethers in the atmosphere of an urban city in South China. *Environ Sci Technol* 40:1190–1196.

26. Guo J-Y, Wu F-C, Mai B-X, Luo X-J, Zeng EY. 2007. Polybrominated diphenyl ethers in seafood products of South China. *J Agric Food Chem* 55:9152–9158.

27. Guan YF, Wang JZ, Ni HG, Luo XJ, Mai BX, Zeng EY. 2007. Riverine inputs of polybrominated diphenyl ethers from the Pearl River Delta (China) to the coastal ocean. *Environ Sci Technol* 41:6007–6013.

28. Chen SJ, Luo XJ, Lin Z, Luo Y, Li KC, Peng XZ, Mai BX, Ran Y, Zeng EY. 2007. Time trends of polybrominated diphenyl ethers in sediment cores from the Pearl River Estuary, South China. *Environ Sci Technol* 41:5595–5600.

29. Xiang C-H, Luo X-J, Chen S-J, Yu M, Mai B-X, Zeng EY. 2007. Polybrominated diphenyl ethers in the biota and sediments of the Pearl River Estuary, South China. *Environ Toxicol Chem* 26:616–623.

30. Zou MY, Ran Y, Gong J, Mai BX, Zeng EY. 2007. Polybrominated diphenyl ethers in watershed soils of the Pearl River Delta: Occurrence, inventory, and fate. *Environ Sci Technol* 41:8262–8267.

31. Guo Y, Meng XZ, Tang H-L, Mai BX, Zeng EY. 2008. Distribution of polybrominated diphenyl ethers in fish tissues from the Pearl River Delta, China: Levels, compositions and potential sources. *Environ Toxicol Chem* 27:576–582.

32. Guo Y, Yu H-Y, Zhang B-Z, Zeng EY. 2009. Persistent halogenated hydrocarbons in fish feeds manufactured in South China. *J Agric Food Chem* 57:3674–3680.

33. Zhang BZ, Guan YF, Li SM, Zeng EY. 2009. Occurrence of polybrominated diphenyl ethers in air and precipitation of the Pearl River Delta, South China: Annual washout ratios and depositional rates. *Environ Sci Technol* 43:9142–9147.

34. Luo X-J, Liu J, Luo Y, Zhang X-L, Wu J-P, Lin Z, Chen S-J, Mai B-X, Yang Z-Y. 2009. Polybrominated diphenyl ethers (PBDEs) in free-range domestic fowl from an e-waste recycling site in South China: Levels, profile and human dietary exposure. *Environ Pollut* 35:253–258.

35. Luo X-J, Zhang X-L, Liu J, Wu J-P, Luo Y, Chen S-J, Mai B-X, Yang Z-Y. 2009. Persistent halogenated compounds in waterbirds from an e-waste recycling region in South China. *Environ Sci Technol* 43:306–311.

36. Wu J-P, Luo X-J, Zhang Y, Chen S-J, Mai B-X, Guan Y-T, Yang Z-Y. 2009. Residues of polybrominated diphenyl ethers in frogs (*Rana limnocharis*) from a contaminated site, South China: Tissue distribution, biomagnification, and maternal transfer. *Environ Sci Technol* 43:5212–5217.

37. Yu H-Y, Guo Y, Bao L-J, Qiu Y-W, Zeng EY. 2011. Persistent halogenated compounds in two typical marine aquaculture zones of South China. *Mar Pollut Bull* (in press). DOI: 10.1016/j.marpolbul.2010.12.006

38. Zhang B-Z, Ni H-G, Guan Y-F, Zeng EY. 2010. Occurrence, bioaccumulation and potential sources of polybrominated diphenyl ethers in typical freshwater cultured fish ponds of South China. *Environ Pollut* 158:1876–1882.

39. Chen D, Hale RC. 2010. A global review of polybrominated diphenyl ether flame retardant contamination in birds. *Environ Int* 36:800–811.

40. Ai J. 1997. Solid phase microextraction for quantitative analysis in nonequilibrium situations. *Anal Chem* 69:1230–1236.