Environmental Science & Technology

Article

pubs.acs.org/est

Occurrences and Fates of Hydroxylated Polybrominated Diphenyl Ethers in Marine Sediments in Relation to Trophodynamics

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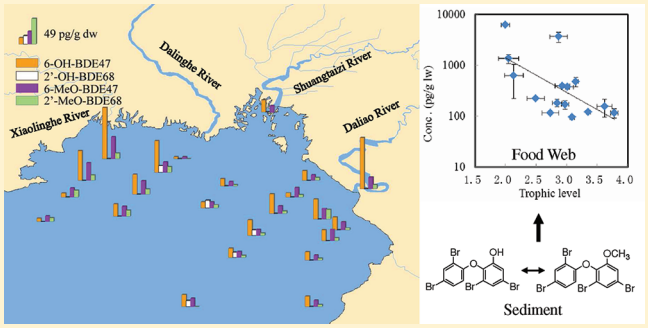
Supporting Information

ABSTRACT: While occurrences and origins of hydroxylated (OH-) polybrominated diphenyl ethers (PBDEs) in organisms have been reported, the fates of these compounds in abiotic matrixes and related trophodynamics are unclear. The present study measured concentrations of nine OH-PBDEs, twelve methoxylated (MeO-) PBDEs, and eleven PBDEs in marine sediments and explored the trophodynamics of OH-PBDEs in five invertebrates, eight fish, and two species of birds from Liaodong Bay, north China. While concentrations of PBDEs were less than the limit of quantification in sediments, concentrations of ΣOH-PBDEs and ΣMeO-PBDEs were 3.2−116 pg/g dry weight (dw) and 3.8−56 pg/g dw, respectively. When the detected compounds were incubated in native marine sediments the interconversion between 6-OH-BDE47 and 6-MeO-BDE47 was observed. This result is consistent with the similar spatial distributions and significant correlation between the concentrations of these naturally occurring compounds. 6-OH-BDE47 and 2′-OH-BDE68 were detected as the two major congeners in organisms collected from Liaodong Bay, and concentrations were 0.24 ± 0.005 ng/g lw (lipid weight) and 0.088 ± 0.006 ng/g lw, respectively. Biota-sediment accumulation factors (BSAFs) for invertebrates of 6-OH-BDE47 and 2′-OH-BDE68 were 0.017−0.96 and 0.19−1.5 (except for short-necked clam: 6.3), respectively. Lipid-normalized concentrations of 6-OH-BDE47 and 2′-OH-BDE68 decreased significantly with trophic level with TMFs of 0.21 and 0.15, respectively. The fates of OH-PBDEs in sediment together with their trophodynamics in marine food webs suggested that OH-PBDEs are partitioned into sediment and undergo biodilution in the marine food web.



INTRODUCTION

Polybrominated diphenyl ethers (PBDEs), an important group of brominated flame retardants, have emerged as contaminants of concern due to their widespread use, ubiquitous environmental occurrences, and bioaccumulation potential.[1−5] Their structural analogues, hydroxylated (OH-) and methoxylated (MeO-) PBDEs, are also detected in biotic media such as sponges and algae, blood/tissues of fish, birds, and marine mammals.[1−5] MeO-PBDEs have been found in animals, such as whales from the Canadian Arctic and North Atlantic, at concentrations sometimes hundreds of times higher than those of PBDEs.[4,6] OH-PBDEs are of particular interest due to their greater potencies for some effects such as disruption of thyroid hormone homeostasis, disruption of sex hormone steroidogenesis, and neurotoxic effects relative to PBDEs and MeO-PBDEs.[7−11] Maternal transfers have also been observed for OH-PBDEs in recent field investigations and laboratory studies and therefore posing a potential risk for offspring of wildlife and humans.[12,13]

The origins of the structural analogues of PBDEs were of particular interest due to their worldwide occurrences and potential adverse effects of exposure. With similar structures to PBDEs, OH-PBDEs and MeO-PBDEs were initially thought to be metabolites or byproducts of synthetic PBDEs.[14−16] However, radiocarbon abundance analysis[3,4] and laboratory exposure studies *in vitro* and *in vivo*[13,17] have found that the most abundant MeO-/OH-PBDE congeners (6-MeO-BDE47,

Received: September 12, 2011
Revised: January 16, 2012
Accepted: January 20, 2012
Published: January 20, 2012

2′-MeO-BDE68, 6-OH-BDE47, and 2′-MeO-BDE68), are naturally occurring compounds, and interconversion exists between 6-MeO-BDE47 and 6-OH-BDE47 in animals. Results of a recent study of the compounds in Chinese sturgeon (*Acipenser sinensis*) indicated that natural accumulation in the aquatic environment could be another important source of OH-PBDEs.[18] OH-PBDEs have also been detected in water samples (including surface water, rainfall, snow, and wastewater) from the upper Detroit River, Canada, as possible products formed via reaction of PBDEs with atmospheric OH radicals[19,20] and MeO-PBDEs have been detected in sediment cores from inland lakes, Michigan, USA.[21] Only one study reported the positive confirmation of two OH-triBDEs in sediments;[22] however, the exact congeners were not identified due to lack of the standards. Up to now, the fates of OH-PBDEs in abiotic environments remain unclear.

OH-PBDEs in abiotic samples could be an important source for organisms and therefore influencing their concentrations in organisms through trophic transfer. While occurrences of OH-PBDEs together with PBDEs and MeO-PBDEs have been reported in animals occupying higher trophic levels, characterizations of trophic transfer have only been investigated for PBDEs and MeO-PBDEs by using stable nitrogen isotopes to provide continuous trophic levels.[2,5,23,24] Concentrations of PBDEs and MeO-PBDEs have been reported to increase with trophic levels in the food web of the Bohai Sea, China, Lake Winnipeg, Canada, and Canadian Arctic.[2,5,23,24] Since OH-PBDEs have greater potential to elicit adverse effects in organisms compared to PBDEs and MeO-PBDEs,[7−11] there is a need to investigate the trophodynamics of OH-PBDEs in marine food web, which is a vital criterion for assessing the ecological risk of chemicals.

In this study, concentrations of PBDEs, MeO-PBDEs, and OH-PBDEs were measured in sediments from Liaodong Bay, north China. Transformations between MeO-PBDEs and OH-PBDEs were explored via laboratory tests of biodegradation in marine sediments. Trophodynamics of OH-PBDEs were further studied and compared to that of MeO-PBDEs in the same marine food web. The objective of this study was to clarify the occurrence of OH-PBDEs and the interconversions between MeO-PBDEs and OH-PBDEs in marine sediment and to better understand accumulations of these compounds in organisms through trophic transfer processes.

MATERIALS AND METHODS

Sample Collection. Liaodong Bay is located in the north region of the Bohai Sea, northern China, with an approximate area of 10,000 km^2 and maximum depth of 32 m. The study areas and sampling locations are shown in Figure S1, Supporting Information. Twenty-three samples of sediments were collected from the subsurface zone (0−30 cm depth) in Liaodong Bay in May 2006. Sediments were freeze-dried, grounded, and sieved through a 0.2 mm mesh before storage at −20 °C. Components of the aquatic food web were collected in November 2006 (40°42N; 121°46E) as described previously.[5] The food web included three species of mollusk, the short-necked clam (*Ruditapes philippinarum*), Mactra quadrangularis (*Mactra veneriformis, Reeue*), and rock shell (*Rapana venosa*), two crustaceans, the mole cricket (*Upogebia major* (*de Haan*) and Chinese mitten-handed crab (*Eriocheir sinensis H. Milne-Eswards*), eight fishes, the red-eye mullet (*Liza hematocheila*), goby (*Synechogobius hasta*), small yellow croaker (*Pseudosciaena polyactis*), China anchovy (*Thrissa kammalensis*), half-smooth tongue-sole (*Cynoglossus semilaevis*), Japanese Spanish mackerel (*Scomberomrus niphonius*), flathead fish (*Platycephalus indicus*), and black spot-fed bass (*Lateolabrax japonicas*), and two species of seabird, the black-tailed gull (*Larus crassirostris*) and black-headed gull (*Larus ridibundus*). Invertebrates and fish were caught with a bottom trawler, and seabirds were captured before their winter migration commenced. All samples were stored at −20 °C prior to analysis. Concentrations of the PBDEs, OH-PBDEs, and MeO-PBDEs as well as ratios of stable isotopes were measured in soft tissues of invertebrates (n = 3 for each species) and muscle tissues from fishes (n = 3 for each species) and seabirds (n = 16 for black-tailed gull, and n = 7 for black-headed gull). Muscle was chosen for both isotope and chemical analysis, because different turnoff rates of isotope ratios exist among tissues, and the turnoff rates in muscle were relatively slow.[25]

Biotranformation in Marine Sediments. Marine sediments and seawater used in this study were collected from the coastal area around the Bohai Sea, north China. Marine sediments and seawaters were stored at 4 °C after sampling and used for biotranformation reactions within 24 h. An aliquant of 1 g of marine sediment and 4 mL of seawater were used to make slurry. The slurry was incubated with individual congeners (6-MeO-BDE47 and 6-OH-BDE47) at 3 μg/g of wet sediment or the carrier solvent acetone alone (sterile controls). The percentage of acetone in the incubation was less than 0.1%. Sterile controls were autoclaved three times before the biotranformation test was initiated. After spiking, the flasks were shaken at 120 rpm at 30 °C in darkness. Concentrations of target compounds were measured on days 0, 1, 4, 25, 42, and 66. All experiments were performed in triplicate, and sterile controls were monitored at the same times.

Extraction and Cleanup of Sediment and Biota Samples. PBDEs, OH-PBDEs, and MeO-PBDEs were identified and quantified by use of methods that have been validated and described previously.[17] Approximately 1−5 g of dried sediment or biota samples was spiked with a mixture of ^{13}C-labeled PBDEs and native 6-OH-BDE17 surrogates, which has been checked to be absent from the samples. The samples were extracted by accelerated solvent extraction (Dionex ASE-200, Sunnyvale, CA) with two 10 min cycles. The first cycle was performed with n-hexane/dichloromethane (DCM) (1:1) at 100 °C and 1500 psi, followed by a second cycle with n-hexane/methyl tert-butyl ether (MTBE) (1:1) at a temperature of 60 °C and pressure of 1000 psi. The two extraction fractions were combined and rotary evaporated to near dryness.

To determine the lipid content of the analyzed samples, one-fifth of the extract was used to determine the lipid content by rotary evaporating to dry and heating at 65 °C for about 30 min, after which the lipid content was determined gravimetrically. The remaining extract was then transferred to 15 mL glass tubes by 8 mL of hexane, and 4 mL of 0.5 M KOH in 50% ethanol was added. The aqueous layer (KOH) was extracted three times with 8 mL of n-hexane to produce a neutral fraction. After extraction, 1.5 mL of 2 M HCl was added into the 15 mL tubes, and the phenolic compounds were extracted three times with n-hexane/MTBE (9:1; v/v) to produce a phenolic fraction.

The neutral fraction of biota samples was not analyzed since concentrations of PBDEs and MeO-PBDEs in the marine food web from Lidodong Bay have been reported previously.[5] The neutral fraction of sediment samples was concentrated to approximately 2 mL and passed through a glass column packed

with 1 g of Na_2SO_4 and 8 g of acidified silica (48% H_2SO_4). After application of the sample, the column was eluted with 15 mL of n-hexane and 10 mL of DCM. The eluate was further cleaned on a neutral alumina column (4 g of sodium sulfate, 4 g of neutral alumina, 4 g of sodium sulfate). The first fraction eluted from the alumina column with 20 mL of hexane was discarded. The second fraction, which contained PBDEs and MeO-PBDEs, was obtained by elution with 25 mL of 60% DCM in n-hexane. The eluate was evaporated to dryness under a gentle stream of nitrogen, then 30 μL nonane and 10 μL internal standards (^{13}C-BDE138) were added for analysis of PBDEs and MeO-PBDEs.

After being dried by a gentle stream of nitrogen, the phenolic fraction was redissolved in 480 μL of aliquot of the derivatization solvent (acetonitrile/methanol/water/pyridine (5:2:2:1; v/v/v/v)), and then 40 μL of methyl chloroformate (MCF) was added. The reaction mixture was shaken on a vortex at room temperature for 1 h and then diluted with 1.2 mL of pure water. The aqueous solution was extracted three times with 6 mL of n-hexane. Extracts were concentrated and subjected to acidified silica gel chromatography as described above, eluted with 30 mL of n-hexane and 30 mL of DCM. The eluate was concentrated to 40 μL for MCFO-PBDEs (derivatives of OH-PBDEs) analysis.

Extraction and Cleanup of Sediment Biotranformation Mixtures. Instead of the derivatization with MCF, which is suitable for environmental samples, a simpler and time-saving method, using dansyl chloride as derivatization reagent, was applied for analysis of incubation mixtures, and the details of the method was reported previously.[26] Incubation mixtures were transferred into amber tubes and spiked with a mixture of surrogates (^{13}C-labeled PBDEs and 6-OH-BDE17). After addition of 20 mL of nanopure water (18 MΩ), 0.5 mL of hydrochloric acid (HCl, 37%), and 30 mL of 2-propanol, samples were extracted three times with 30 mL of hexane/MTBE (1:1; v/v). Extracts were then washed four times with 20 mL of nanopure water to remove residual acid, and the hexane extracts were concentrated and dried under nitrogen.

Dried residues were dissolved in 200 μL of aqueous 100 mM sodium bicarbonate (adjusted to pH 10.5 with sodium hydroxide), and 200 μL of dansyl chloride (1 mg/mL in acetone) was added. After vortex mixing for 1 min, the samples were incubated at 70 °C for 10 min. Then, 1 mL of pure water and 3 × 3 mL of hexane were added, and the organic solvent layer was removed and transferred onto a silica gel carriage (500 mg, 6 cc, Waters, USA) for fractionation. After application of the extract, the column was eluted with 3 mL of hexane/DCM (3:2, v/v) and then 3 mL of ACE/DCM (3:7, v/v). The first fraction was evaporated to dryness and reconstituted with 50 μL of nonane for analysis of PBDEs and MeO-PBDEs. The second fraction was evaporated to dryness and reconstituted with 50 μL of acetonitrile:water (60:40) for liquid chromatography-tandem mass spectrometry (LC-MS/MS) analysis of OH-PBDEs.

Instrumental Conditions. Identification and quantification of PBDEs, MeO-PBDEs, and MFCO-PBDEs (derivatives of OH-PBDEs) were performed by use of a Hewlett-Packard 5890 series II high-resolution gas chromatograph interfaced to a Micromass Autospec high-resolution mass spectrometer (HRGC-HRMS) (Micromass, Beverly, MD). Chromatographic separation was achieved on a DB-5MS capillary column (30 m length, 0.25 mm ID, 0.1 μm film thickness, Agilent, Carlsbad, CA). A splitless injector was used, and the injector was held at 285 °C. The interface temperature was maintained at 320 °C, and ion temperature was kept at 285 °C. The carrier gas was helium. The electron ionization energy was 37 eV, and the ion current was 750 μA. Data acquisition was conducted in selected ion monitoring mode. For PBDEs, the temperature program was from 110 °C (10 min) to 250 at 25 °C/min and then increased to 260 at 1.5 °C/min and then to 323 °C (15 min) at 25 °C/min. For MCFO-PBDEs (derivatives of OH-PBDEs), the temperature program was from 150 °C (2 min) to 320 °C (2 min) at 10 °C/min. For MeO-PBDEs, the temperature program was from 150 °C (2 min) to 245 °C (2 min) at 2 °C/min and then increased to 320 °C (2 min) at 30 °C/min. Ions monitored for HRMS of PBDEs, MeO-PBDEs, and MCFO-PBDEs were described previously.[17]

Quantification of OH-PBDEs in the incubation mixtures was conducted using an Acquity UPLC system (Waters, Milford, MA, USA) connected to a Waters Micromass Quattro Premier XE (triple−quadrupole) detector equipped with an electrospray ionization source (Micromass, Manchester, UK) in the positive ion mode. A C8 column (100 × 2.1 mm, 1.7 μm particle size) from Waters (Milford, MA, USA) was used for chromatographic separation at room temperature and a flow rate of 0.3 mL/min. Injection volume was 20 μL. Acetonitrile and water containing 0.1% formic acid were used as mobile phase. Gradient conditions were initiated with 75% acetonitrile followed by a linear increase to 90% acetonitrile in 1.5 min. The proportion of acetonitrile was then increased to 95% in 4 min and held for 1 min. Data acquisitions were performed by use of a mass spectrometer equipped with a turbo ion spray source operated in the positive multireaction monitoring (MRM) mode, and the MRM transition channels are listed in Table S1, Supporting Information. Optimal MS conditions were as follows: source temperature, 110 °C; desolvation temperature, 350 °C; capillary voltage, 3.50 kV; desolvation gas flow, 800 L/h; cone gas flow, 100 L/h; and multiplier, 650 V.

Quality Assurance and Quality Control (QA/QC). Details of the QA/QC of the method have been described previously.[18,26] The standards used in biotransformation reactions were from the same stock solutions used in a previous study, which found that the presence of impurities did not affect conclusions drawn from the studies.[13] Concentrations of all congeners were quantified by the internal standard isotope-dilution method which used the mean relative response factors determined from each standard calibration run. PBDEs and MeO-PBDEs were quantified relative to ^{13}C-PBDEs, and OH-PBDEs were quantified relative to 6′-OH-BDE17. Recoveries of ^{13}C-PBDEs and 6′-OH-BDE17 were 67.9 ± 1.29% − 75.6 ± 2.2% and 117.2 ± 2.5%, respectively. For incubation samples, the method was validated with spiked sediments. The spiking concentrations were at least three times the original matrix concentrations in sediment. Recoveries for spiked sediments were 73−83% for OH-PBDEs and 89−102% for MeO-PBDEs/PBDEs, respectively. All equipment was rinsed with acetone and hexane to avoid contamination. During analysis, a laboratory blank was incorporated with every batch of 12 samples. OH-PBDEs and MeO-PBDEs were not detected in blanks, and the method detection limits (MDL) were set to the instrumental minimum detectable amounts. MDLs for quantification of OH-PBDEs (MCFO-PBDEs) by GC-HRMS were 1−2 pg/g ww for biota samples and 1−2 pg/g dw for sediment samples, and the MDLs were 1.6−6.4 pg/g dw for PBDEs and 1.6 pg/g dw for MeO-PBDEs in sediment

samples. For LC-MS/MS analysis, the MDLs for all target OH-PBDEs were 4–25 pg/g ww.

Biota-Sediment Accumulation Factor (BSAF) and Trophic Magnification Factor (TMF). Biota-sediment accumulation factors of OH-PBDEs and MeO-PBDEs were calculated by dividing the lipid-normalized concentrations in invertebrates by the concentration in sediment normalized to the concentration of total organic carbon (eq 1)

$$BSAF = \frac{C_{biota}/f_{lipid}}{C_{sediment}/f_{oc}} \quad (1)$$

where C_{biota} is the concentration of individual OH-PBDEs and MeO-PBDEs congener in invertebrate samples, $C_{sediment}$ is the concentration of individual OH-PBDEs and MeO-PBDEs congener in sediments, f_{oc} is the fraction of organic carbon in sediments, and f_{lipid} is the fraction of lipid in invertebrate and fish samples.

Trophic magnification factors were calculated by use of a following relationship as previous studies.[5] Concentrations of OH-PBDEs on lipid and wet weight basis were both used in the statistical analysis (eq 2)[5]

$$\text{Log OH-PBDEs concentration} = a + b\,TL \quad (2)$$

Trophic levels, determined by stable nitrogen isotopes, ranged from 2.0 to 4.2 in all individual organisms (Figure S2, Supporting Information), which have been reported in our previous study.[5] The b in eq 2 was used to calculate TMF (eq 3)

$$TMF = 10^{b} \quad (3)$$

Statistical Analysis. Concentrations in samples were represented as "geometric mean ± geometric standard deviation". Linear regression analysis was used to determine relationships between log-transformed concentrations of OH-PBDE and trophic levels. When the p value was less than 0.05, the linear regression was regarded as significant. An estimation of TMFs based on observations in which nondetect data are present has been considered to be appropriate as reported previously.[27] In this study, TMFs were calculated by substituting the concentrations lower than the detection limits with one-half of the MDL, original values and values derived from regression order statistics (ROS), respectively. Statistical analyses were conducted using SPSS software (SPSS, Inc.).

RESULTS AND DISCUSSION

Occurrences in Sediment. Of the 10 OH-PBDEs, 6-OH-BDE47 and 2′-OH-BDE68 were detected in sediment samples with detection frequency of 100% and 26%, respectively. Concentrations of 6-OH-BDE47 and 2′-OH-BDE68 were 22 ± 2.3 pg/g dw (dry weight) and 1.9 ± 3.1 pg/g dw, respectively. The predominance of the two compounds has been reported in organisms from the Detroit River[1] and Norwegian Arctic[28] and humans in Nicaragua and South Korea.[12,29] To our knowledge, this is the first report that describes the concentrations of OH-PBDEs in the sediment samples. The geographical distributions of OH-PBDEs in sediments from Liaodong Bay are shown in Figure 1. Maximum concentrations were observed in samples from locations nearest to the Daliaohe River and the Xiaolinghe River, while lesser concentrations were observed in samples collected from offshore locations.

As possible precursors for OH-PBDEs, PBDEs, and MeO-PBDEs were also investigated in sediment from Liaodong Bay. Concentrations of PBDE congeners, including BDE28, BDE47,

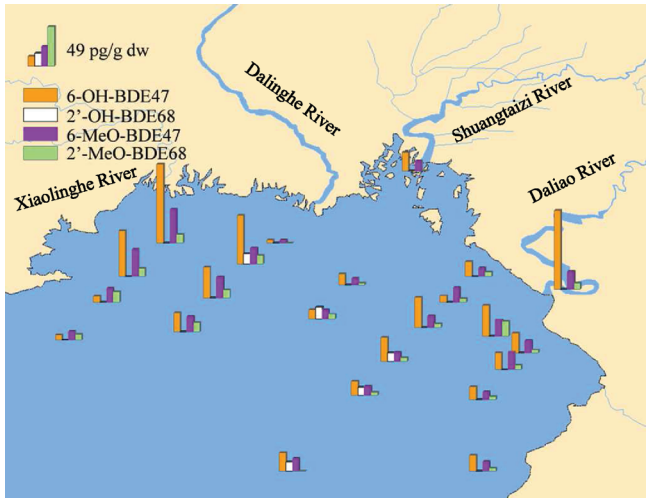


Figure 1. Concentrations of MeO-PBDEs and OH-PBDEs in sediment samples from Liaodong Bay.

BDE66, BDE77, BDE100, BDE99, BDE85, BDE154, BDE153, BDE138, and BDE183, were less than the MDLs (1.6–6.4 pg/g dw). Relatively low concentrations of PBDEs were also reported for sediments from the Daliao River Estuary, Liaodong Bay (nondetect-7.01 pg/g dw).[30] Of the twelve MeO-PBDEs, 6-MeO-BDE47, 2′-MeO-BDE68, 6-MeO-BDE17, 4-MeO-BDE17, 5-MeOBDE47, and 4′-MeO-BDE101 were detected in sediments with detection frequencies of 100%, 87%, 35%, 39%, 4%, and 4%, respectively. Concentrations of ΣMeO-PBDEs ranged from 3.8 to 56 pg/g dw in Liaodong Bay, which were similar to those in the Kootenay River in Genelle, British Columbia, Canada (0.61 to 43.7 pg/g dw),[22] but less than those in Muskegon Lake, Michigan, USA (3.5 to 120 pg/g dw).[21] 6-MeO-BDE47 (15 ± 1.6 pg/g dw) and 2′-MeO-BDE68 (5.5 ± 1.9 pg/g dw) were the predominant congeners, which accounted for 66 ± 19% and 21 ± 12% of the ΣMeO-PBDEs, respectively (Table S2, Supporting Information). Similar profiles have been observed in sediment and biota from Canada and the USA.[2,22,31] The relative greater concentrations of the two major MeO-PBDE congeners were also found in sites along the coast, where similar geographical distributions to those of OH-PBDEs were observed (Figure 1).

Occurrences in Biota. Of the 10 OH-PBDEs, 6-OH-BDE47, 2′-OH-BDE68, 3-OH-BDE47, 4-OH-BDE49, and 5-OH-BDE47 were detected in biota from Liaodong Bay, and their detection frequencies are listed in Table S3, Supporting Information. Similar to the profile in sediment, 6-OH-BDE47 (6.7 ± 1.4 pg/g ww in invertebrates, 2.8 ± 1.3 pg/g ww in fishes, and 4.4 ± 1.4 pg/g ww in birds) exhibited the greatest concentration among OH-PBDEs, followed by 2′-OH-BDE68 (3.2 ± 1.3 pg/g ww in invertebrates, 1.1 ± 1.1 pg/g ww in fishes, and 1.3 ± 1.2 pg/g ww in birds). When concentrations were expressed on a lipid weight basis, the average concentrations of ΣOH-PBDEs in biota from Liaodong Bay (invertebrates: 1.7 ± 0.002 ng/g lw; fishes: 0.28 ± 0.001 ng/g lw; and birds: 0.084 ± 0.001 ng/g lw) were greater than those in organisms of the marine food web from the Canadian Arctic (<0.001–0.23 ng/g lw)[2] but similar to those in muscle of Chinese sturgeon from the Yangtze River, China (0.81 ± 0.18 ng/g lw)[18] and in the blubber of ringed seals from East Greenland (0.7 ± 0.5 ng/g lw).[28] Only one previous study explored the zebrafish acute toxicity of 6-OH-BDE47, and the no adverse effect level (NOAEL) value was

dx.doi.org/10.1021/es203195s | Environ. Sci. Technol. 2012, 46, 2148–2155

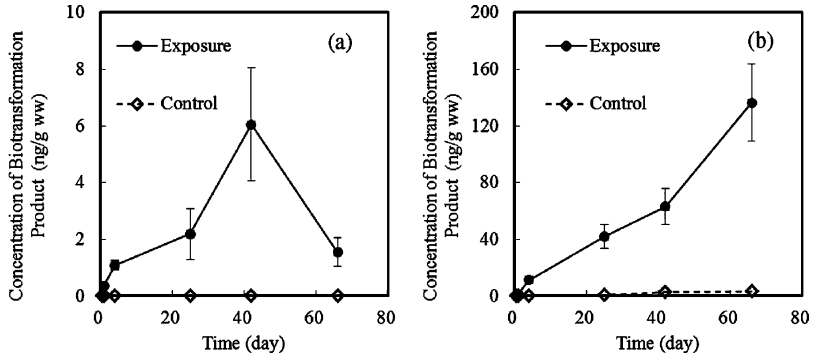


Figure 2. (a) Formation of 6-OH-BDE47 in the biodegradation test of marine sediments incubated with 6-MeO-BDE47. (b) Formation of 6-MeO-BDE47 in marine sediments incubated with 6-OH-BDE47. Error bars indicate standard deviation.

reported to be 150 nM.[32] Concentrations of 6-OH-BDE47 in fishes from Liaodong Bay were approximately 5 orders of magnitude lower than the NOAEL value, showing little hazard of 6-OH-BDE to fishes.

The major OH-PBDE congeners detected, 6-OH-BDE47 and 2′-OH-BDE68, have been identified as compounds of natural origin such as sponges and algae[3,4] or converted products from their corresponding natural MeO-PBDE analogues in previous studies.[17] There was a significant correlation between concentrations of 6-OH-BDE47 and 6-MeO-BDE47 in fishes (R^2 = 0.651, p = 0.016), and such correlation is consistent with the interconversion of the two compounds in Japanese medaka as reported recently.[13] These results further indicated that the *ortho*-substituted OH-PBDEs in the organisms from Liaodong Bay were of the natural origins. Alternatively, some *meta-/para*-substituted OH-PBDEs, being absence in sediment, were detected in biota samples. Previous studies have reported some *ortho*-substituted OH-PBDEs (6-OH-BDE47, 6-OH-BDE66) and *meta-/para*-substituted OH-PBDEs (e.g., 4-OH-BDE42, 4′-OH-BDE49, 3-OH-BDE47, and 5-OH-BDE47) as metabolites via *in vivo* biotransformation of PBDEs.[15,33,34] Therefore, the occurrence of *meta-/para*-substituted OH-PBDEs (3-OH-BDE47, 5-OHBDE47, and 4-OH-BDE49) in organisms from Liaodong Bay would be originated from biotransformation of PBDEs, and the ecological risk assessment of PBDEs in organisms should consider potential contributions of these compounds.

Interconversion of 6-OH-BDE47 and 6-MeO-BDE47 in Sediment. Geographical distributions of concentrations of the primary MeO-PBDEs and OH-PBDEs were similar in sediment from Liaodong Bay (Figure 1), and a significant correlation was found between concentrations of 6-MeO-BDE47 and 6-OH-BDE47 (r^2 =0.571, $p < 0.001$) (Figure S3, Supporting Information). Similarities in occurrences and significant correlation between these two compounds observed in biota samples in previous studies have been demonstrated to be due to the interconversion between 6-OH-BDE47 and 6-MeO-BDE47 based on the *in vitro* and *in vivo* exposures.[13,17] Since bacterial methylation and demethylation have been reported to occur in sediment,[35,36] it is possible that similar interconversion between 6-OH-BDE47 and 6-MeO-BDE47 could occur in sediment. So interconversion of 6-MeO-BDE47 and 6-OH-BDE47 was investigated by use of a water sediment test system. Figure 2 shows the formation of biotransformation products in 6-MeO-BDE47-exposed and 6-OH-BDE47-exposed sediment after 66-day incubation. Measurable concentrations of 6-OH-BDE47 (6.0 ng/g ww on day 42) were detected in 6-MeO-BDE47 exposed sediment (exposure concentration: 590 ng/g ww), while no formation of 6-OH-BDE47 was observed in the sterile control within 66 days (Figure 2a). The concentration ratios on a molar basis between biotransformation products and their parent compounds (6-OH-BDE47/6-MeO-BDE47) in sediment incubated with 6-MeO-BDE47 was 0.010 ± 0.002. These results are consistent with 6-MeO-BDE-47 being a source of the 6-OH-BDE47 in sediment from Liaodong Bay. The opposite reaction was also observed. When sediment was spiked with 170 ng/g ww 6-OH-BDE47, 130 ng/g ww of 6-MeO-BDE47 was observed after 66 days (Figure 2b). Negligible concentrations of 6-MeO-BDE-47 (3.3 ng/g) were detected in control sediment on day 66, which could be due to residual bioactivities that survived autoclaving. The concentration ratio of 6-MeO-BDE47/6-OH-BDE47 on a molar basis was 0.824 ± 0.052 in sediment incubated with 6-OH-BDE47. These results further demonstrate that 6-OH-BDE47 can be biotransformed to 6-MeO-BDE-47 in sediment. While previous studies have speculated that some MeO-PBDEs would be formed via methylation of OH-PBDEs in sediment,[37] the results presented here are the first experimental evidence of the formation of a MeO-PBDE from an OH-PBDE in sediment. Considering that PBDEs would be degraded to form OH-PBDEs, incubations of a slurry spiked with individual BDE47 (3 μg/g of wet sediment) was also conducted for one month. In the replicate experiment, similar concentrations of 6-OH-BDE47 (3.3 ± 1.5 ng/g ww) and 6-MeO-BDE47 (44 ± 1.0 ng/g ww) were detected in sediment incubated with 6-MeO-BDE47 and 6-OH-BDE47 on day 28, respectively. OH-PBDEs and MeO-PBDEs were not detected during the 28 days' incubation of BDE47. These results indicated that OH-PBDEs and MeO-PBDEs could not be originated from biotransformation of PBDEs in sediment from Liaodong Bay. Overall, the sediment biotransformation test indicated that the interconversion between 6-OH-BDE47 and 6-MeO-BDE47 occurred in sediment via biotransformation pathways, although rates of biotranformation obtained under laboratory conditions would be different from environmentally relevant conditions in coastal marine bottom sediments. Recent studies have reported that both 6-OH-BDE47 and 6-MeO-BDE47 are natural products based on radiocarbon measurements.[3,4] The interconversion of the two compounds in sediment and biological matrix is consistent of their natural origins in aquatic environment.

BSAFs and TMFs of OH-PBDEs: Comparison to MeO-PBDEs. The accumulation of OH-PBDEs from sediments to invertebrates and organisms of various trophic levels in the marine food web was assessed (Table 1). Similarly to previous studies,[2,38−40] lipid corrected concentrations of OH-PBDEs were mainly used, since OH-PBDEs were lipophilic compounds

Table 1. Mean Biological Parameters and Concentrations of Total OH-PBDEs in Marine Sediments (pg/g dry weight) and Biota (pg/g wet weight) Collected from Liaodong Bay, North China[a]

species	SED	RP	MVR	RV	ESME	UM	LH	SH	PP	TK	SN	CS	PI	LJ	LR	LC
TL	-	2.00 ± 0.07	2.05 ± 0.09	2.87 ± 0.09	2.74 ± 0.14	2.93 ± 0.12	2.14 ± 0.15	2.50 ± 0.14	2.85 ± 0.08	2.98 ± 0.06	3.01 ± 0.09	3.09 ± 0.04	3.15 ± 0.04	3.36 ± 0.03	3.78 ± 0.10	3.62 ± 0.30
N	23	3	3	3	3	3	3	3	3	3	3	3	3	3	7	16
length (cm)	-	-	-		-	-	38 ± 1.7	24 ± 1.2	27 ± 2.3	14 ± 0.58	47 ± 1.2	30 ± 1.7	33 ± 2.3	78 ± 1.2	33 ± 0.76	45 ± 7
weight (g)	-	-	-	-	-	-	671 ± 31	76 ± 8.7	168 ± 31	16 ± 1.2	525 ± 12	170 ± 12	175 ± 58	3540 ± 170	344 ± 32	679 ± 326
TOC content (%)	0.48 ± 0.04	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
lipid content (%)	-	0.28 ± 0.08	1.04 ± 0.03	0.30 ± 0.16	0.64 ± 0.06	1.68 ± 0.49	1.11 ± 0.23	0.33 ± 0.12	1.85 ± 0.37	9.80 ± 0.11	2.29 ± 0.45	0.79 ± 0.06	1.23 ± 0.06	0.62 ± 0.06	7.20 ± 0.53	6.48 ± 1.32
6-OHBDE47	22 ± 2.3	18 ± 1.0	14 ± 1.3	11 ± 1.5	ND	6.7 ± 1.1	3.8 ± 4.6	ND	3.3 ± 1.3	16 ± 1.4	8.6 ± 1.2	ND	5.7 ± 1.4	ND	4.6 ± 5.6	4.3 ± 4.1
2-OHBDE68	1.9 ± 3.1	10 ± 1.2	1.8 ± 4.4	2.7 ± 1.3	N.D	8.4 ± 1.3	1.3 ± 1.7	ND	ND	ND	4.5 ± 1.4	ND	1.5 ± 1.8	ND	1.0 ± 2.2	1.5 ± 2.6
5-OHBDE47	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	1.5 ± 2.6
4-OHBDE49	ND	ND	1.7 ± 4.2	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	1.2 ± 2.3	ND	ND
3-OHBDE47	ND	ND	ND	ND	ND	ND	2.1 ± 2.4	ND	ND	ND	ND	ND	ND	1.3 ± 2.4	1.2 ± 3.4	1.1 ± 2.3
∑OH-PBDEs	24 ± 2.3	28 ± 1.1	19 ± 1.7	14 ± 1.4	ND	15 ± 1.2	5.3 ± 5.7	ND	3.3 ± 1.3	16 ± 1.4	13 ± 1.2	ND	6.9 ± 1.6	1.5 ± 3.5	5.4 ± 6.5	5.7 ± 5.3

[a]SED = sediment; RP = short-necked clam (*Ruditapes philippinarum*); MVR = mactra quadrangularis (*Mactra veneriformis,Reeue*); RV = rock shell (*Rapana venosa*); ESME = Chinese mitten-handed crab (*Eriocheir sinensis H. Milne-Eswards*); UM = mole cricket (*Upogebia major(de Haan)*); LH = redeye mullet (*Liza haematocheila*); SH = goby (*Synechogobius hasta*); PP = small yellow croaker (*Pseudosciaena polyactis*); TK = China anchovy (*Thrissa kammalensis*); SN = Japanese spanish mackerel (*Scomberomrus niphonius*); CS = half-smooth tongue-sole (*Cynoglossus semilaevis*); PI = flathead fish (*Platycephalus indicus*); LJ = black spotfed bass (*Lateolabrax japonicas*); LR = black-headed Gulls (*Larus ridibundus*); LC = black-tailed Gull (*Larus crassirostris*). TL, trophic level; ND, not detected. TL and lipid content in biota are from ref 5.

with log K_{ow} of 4.5−10.7[2] and preferential accumulation of OH-PBDEs in adipose compared with tissue with low lipid content such as muscle in sturgeon.[18] On the other hand, accumulation of OH-PBDEs could be affected by other factors such as protein (e.g., TTR),[12] concentrations of OH-PBDEs on wet weight basis were also used for calculation of BSMF and TMFs.

BSAF values of 6-OH-BDE47 and 2′-OH-BDE68 based on lipid weight concentrations were 0.017−0.96 g TOC/g lipid and 0.19−1.5 g TOC/g lipid (except for short-necked clam: 6.3) in invertebrates from Liaodong Bay, respectively (Table 2).

Table 2. Biota-Sediment Accumulation Factors (g TOC/g lipid) of Major OH-PBDEs and MeO-PBDEs in the Invertebrates from Liaodong Bay[a]

species	6-OHBDE47	2-OHBDE68	6-MeO-BDE47	2′-MeO-BDE68
RP	0.96	6.3	4.5	0.40
MVR	0.20	0.61	2.2	2.1
RV	0.56	1.5	7.2	1.0
ESME	0.017	0.19	0.48	0.14
UM	0.06	0.85	0.14	0.22

[a]RP = short-necked clam (*Ruditapes philippinarum*); MVR = mactra quadrangularis (*Mactra veneriformis, Reeue*); RV = rock shell (*Rapana venosa*); ESME = Chinese mitten-handed crab (*Eriocheir sinensis H. Milne-Eswards*); UM = mole cricket (*Upogebia major*(*de Haan*)).

BSAF values based on wet weight concentrations were 0.025−0.59 and 0.23−3.2 g wet weight/g dry weight for 6-OH-BDE47 and 2′-OH-BDE68, respectively. The BSAF values of 6-MeO-BDE47 and 2′-MeO-BDE68 were 0.48−7.2 g TOC/g lipid and 0.14−2.1 g TOC/g lipid, respectively, which were greater than those of OH-PBDEs (Table 2). The BSAFs of MeO-PBDEs in Liaodong Bay were less than those of PBDEs with similar log K_{ow} in marine mussels from the Bohai Sea, China (BDE47: 0.23−16.15; BDE-99: 0.34−7.59)[41] and Vancouver Island, Canada (BDE47: 49.1−572; BDE99: 50.1−490).[42] The results indicated that bioaccumulation potential of OH-PBDEs were less than those of MeO-PBDEs and PBDEs.

Trophodynamics of OH-PBDEs were investigated in the food web of Liaodong Bay to assess the accumulation of the compounds from invertebrates to organisms with relative high trophic levels. No significant correlations were observed between trophic levels and the concentrations of OH-PBDEs based on wet weight. On the other hand, lipid normalized concentrations of 6-OH-BDE47 and 2′-OH-BDE68 decreased significantly with increasing trophic levels (Figure 3). All approaches used to treat concentrations that were less than the detection limits yielded an overall conclusion that the TMFs of OH-PBDEs were significantly less than 1.0, while the regression slope obtained by substituting one-half the detection limit was slightly less than those by other two methods (Table S4, Supporting Information). TMF values of 6-OH-BDE47 and 2′-OH-BDE68 were 0.21 (lower-upper 95% CI: 0.068−0.64, r^2 = 0.414, p = 0.010, n = 62) and 0.15 (lower-upper 95% CI: 0.037−0.64, r^2 =0.384, p = 0.014, n = 62), respectively, when concentrations below detection limits were substituted with one-half the MDL (Figure 3, Table S4, Supporting Information). This result suggested that OH-PBDEs undergo trophic dilution in the marine food web. For MeO-PBDEs, positive relationships were found for 6-MeO-BDE47 and 2′-MeO-BDE68 in the same food web without birds, while no statistically significant relationships were obtained between concentrations of MeO-PBDE

dx.doi.org/10.1021/es203195s | Environ. Sci. Technol. 2012, 46, 2148−2155

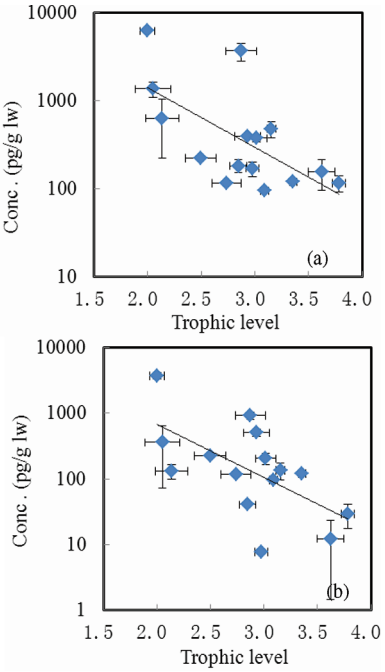


Figure 3. Relationships between concentrations of OH-PBDE congeners and trophic levels in biota samples in Liaodong Bay, north China: (a) 6-OH-BDE47 (TMF = 0.21, r^2 = 0.414, p = 0.010) and (b) 2′-OH-BDE68 (TMF = 0.15, r^2 = 0.384, p = 0.014).

congeners and trophic levels.[5] These two chemicals exhibited significant concentration increases via trophic levels with TMFs of 2.3 and 2.6, respectively, in the marine food web of the Canadian Arctic.[2] Such a difference in trophic transfer between MeO-PBDEs and OH-PBDEs is consistent with the greater biotransformation of OH-PBDEs in organisms, based on the fact that concentration ratios between transformation products and their parent compounds in OH-PBDE exposed organisms (0.998 ± 0.269) were greater than those in MeO-PBDE exposed organisms (0.021 ± 0.013).[13] This result suggested that biotransformation would be the main factor influencing the trophodynamics of OH-PBDEs in the marine food web. In addition, the lesser concentrations of both MeO-PBDEs and OH-PBDEs in birds from Liaodong Bay is possibly due to greater biotransformation of the two compounds that have been observed in microsomes of chicken compared with that of trout.[17]

Overall, this work reported the occurrences of OH-PBDEs in marine sediments from Liaodong Bay and demonstrated interconversion of OH-PBDEs and MeO-PBDEs in marine sediment. Fates of OH-PBDEs in sediment together with their trophodynamics in the marine food web further indicated that OH-PBDEs preferentially partitioned in sediments. Bioaccumulation from natural sources is one of the contributors of *ortho*-substituted OH-PBDEs in marine organisms from Liaodong Bay, and the occurrence of *meta-/para*-substituted OH-PBDEs could be originated from metabolism of PBDEs. These results provide information for assessing the ecological risk of OH-PBDEs and suggested that it is cautious to consider the contribution of OH-PBDEs to PBDEs-induced risks in sediment.

■ ASSOCIATED CONTENT

Supporting Information

Text, figures, and tables addressing (1) chemicals and standards, (2) LC-MS/MS analysis of OH-PBDEs; (3) concentrations of individual MeO-PBDEs in sediments and relationship between the concentrations of 6-OH-BDE47 and 6-MeO-BDE47 in sediments; (4) the detection frequencies of OH-PBDEs; (5) regression parameters for TMFs; (6) sampling locations in Liaodong Bay and trophic levels of organisms. 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

Financial support from the National Nature Science Foundation of China (41171385, 20837003) are gratefully acknowledged. We thank Dr. Michael H. W. Lam, Department of Biology and Chemistry and State Key Laboratory in Marine Pollution, City University of Hong Kong, Kowloon, Hong Kong SAR, China, for providing standards.

■ REFERENCES

(1) Valters, K.; Li, H. X.; Alaee, M.; D'Sa, I.; Marsh, G.; Bergman, A.; Letcher, R. J. Polybrominated diphenyl ethers and hydroxylated and methoxylated brominated and chlorinated analogues in the plasma of fish from the Detroit River. *Environ. Sci. Technol.* **2005**, *39* (15), 5612−5619.

(2) Kelly, B. C.; Ikonomou, M. G.; Blair, J. D.; Gobas, F. A. P. C Hydroxylated and methoxylated polybrominated diphenyl ethers in a Canadian Arctic marine food web. *Environ. Sci. Technol.* **2008**, *42* (19), 7069−7077.

(3) Guitart, C.; Slattery, M.; Ankisetty, S.; Radwan, M.; Ross, S. J.; Letcher, R. J.; Reddy, C. M. Contemporary C-14 radiocarbon levels of oxygenated polybrominated diphenyl ethers (O-PBDEs) isolated in sponge-cyanobacteria associations. *Mar. Pollut. Bull.* **2011**, *62* (3), 631−636.

(4) Teuten, E. L.; Xu, L.; Reddy, C. M. Two abundant bioaccumulated halogenated compounds are natural products. *Science* **2005**, *307* (5711), 917−920.

(5) Zhang, K.; Wan, Y.; An, L. H.; Hu, J. Y. Trophodynamics of polybrominated diphenyl ethers and methoxylated polybrominated diphenyl ethers in a marine food web. *Environ. Toxicol. Chem.* **2010**, *29* (12), 2792−2799.

(6) Mckinney, M. A.; De Guise, S.; Martineau, D.; Beland, P.; Lebeuf, M.; Letcher, R. J. Organohalogen contaminants and metabolites in beluga whale (*Delphinapterus leucas*) liver from two Canadian populations. *Environ. Toxicol. Chem.* **2006**, *25* (5), 1246−1257.

(7) Meerts, I. A. T. M.; van Zanden, J. J.; Luijks, E. A. C.; van Leeuwen-Bol, I.; Marsh, G.; Jakobsson, E.; Bergman, A.; Brouwer, A. Potent competitive interactions of some brominated flame retardants and related compounds with human transthyretin *in vitro*. *Toxicol. Sci.* **2000**, *56* (1), 95−104.

(8) Meerts, I. A. T. M.; Letcher, R. J.; Hoving, S.; Marsh, G.; Bergman, A.; Lemmen, J. G.; van der Burg, B.; Brouwer, A. *In vitro* estrogenicity of polybrominated diphenyl ethers, hydroxylated PBDEs, and polybrominated bisphenol A compounds. *Environ. Health Perspect.* **2001**, *109* (4), 399−407.

(9) Dingemans, M. M. L.; de Groot, A.; van Kleef, R. G. D. M.; Bergman, A.; van den Berg, M.; Vijverberg, H. P. M.; Westerink. RHS Hydroxylation increases the neurotoxic potential of BDE-47 to affect exocytosis and calcium homeostasis in PC12 cells. *Environ. Health Perspect.* **2008**, *116* (5), 637−643.

(10) Mercado-Feliciano, M.; Bigsby, R. M. Hydroxylated metabolites of the polybrominated diphenyl ether mixture DE-71 are weak

estrogen receptor-alpha ligands. *Environ. Health Perspect.* **2008**, *116* (10), 1315−1321.
(11) Canton, R. F.; Scholten, D. E. A.; Marsh, G.; De Jong, P. C.; Van den Berg, M. Inhibition of human placental aromatase activity by hydroxylated polybrominated diphenyl ethers (OH-PBDEs). *Toxicol. Appl. Pharmacol.* **2008**, *227* (1), 68−75.
(12) Wan, Y.; Choi, K.; Kim, S.; Ji, K.; Chang, H.; Wiseman, S.; Jones, P. D.; Khim, J. S.; Park, S.; Park, J.; Lam, M. H, W.; Giesy, J. P. Hydroxylated polybrominated diphenyl ethers and bisphenol A in pregnant women and their matching fetuses: Placental transfer and potential risks. *Environ. Sci. Technol.* **2010**, *44* (13), 5233−5239.
(13) Wan, Y.; Liu, F. Y.; Wiseman, S.; Zhang, X. W.; Chang, H.; Hecker, M.; Jones, P. D.; Lam, M. H. W.; Giesy, J. P. Interconversion of hydroxylated and methoxylated polybrominated diphenyl ethers in Japanese medaka. *Environ. Sci. Technol.* **2010**, *44* (22), 8729−8735.
(14) Hakk, H.; Huwe, J. K.; Murphy, K.; Rutherford, D. Metabolism of 2,2′,4,4′-tetrabromodiphenyl ether (BDE-47) in chickens. *J. Agric. Food Chem.* **2010**, *58* (15), 8757−8762.
(15) Marsh, G.; Athanasiadou, M.; Athanassiadis, I.; Sandholm, A. Identification of hydroxylated metabolites in 2,2′,4,4′-tetrabromodiphenyl ether exposed rats. *Chemosphere* **2006**, *63* (4), 690−697.
(16) Stapleton, H. M.; Kelly, S. M.; Pei, R.; Letcher, R. J.; Gunsch, C. Metabolism of polybrominated diphenyl ethers (PBDEs) by human hepatocytes *in vitro*. *Environ. Health Perspect.* **2009**, *117* (2), 197−202.
(17) Wan, Y.; Wiseman, S.; Chang, H.; Zhang, X. W.; Jones, P. D.; Hecker, M.; Kannan, K.; Tanabe, S.; Hu, J. Y.; Lam, M. H. W.; Giesy, J. P. Origin of hydroxylated brominated diphenyl ethers: Natural compounds or man-made flame retardants? *Environ. Sci. Technol.* **2009**, *43* (19), 7536−7542.
(18) Zhang, K.; Wan, Y.; Giesy, J. P.; Lam, M. H. W.; Wiseman, S.; Jones, P. D.; Hu, J. Y. Tissue concentrations of polybrominated compounds in Chinese sturgeon (*Acipenser sinensis*): Origin, hepatic sequestration, and maternal transfer. *Environ. Sci. Technol.* **2010**, *44* (15), 5781−5786.
(19) Ueno, D.; Darling, C.; Alaee, M.; Pacepavicius, G.; Teixeira, C.; Campbell, L.; Letcher, R. J.; Bergman, A.; Marsh, G.; Muir, D. Hydroxylated polybrominated diphenyl ethers (OH-PBDEs) in the abiotic environment: Surface water and precipitation from Ontario, Canada. *Environ. Sci. Technol.* **2008**, *42* (5), 1657−1664.
(20) Hua, W. Y.; Bennett, E. R.; Letcher, R. J. Triclosan in waste and surface waters from the upper Detroit River by liquid chromatography-electrospray-tandem quadrupole mass spectrometry. *Environ. Int.* **2005**, *31* (5), 621−630.
(21) Bradley, P. W.; Wan, Y.; Jones, P. D.; Wiseman, S.; Chang, H.; Lam, M. H. W.; Long, D. T.; Giesy, J. P. PBDEs and methoxylated analogues in sediment cores from two Michigan, USA, inland lakes. *Environ. Toxicol. Chem.* **2011**, *30*, 1236−1242.
(22) Lacorte, S.; Ikonomou, M. G.; Fischer, M. A comprehensive gas chromatography coupled to high resolution mass spectrometry based method for the determination of polybrominated diphenyl ethers and their hydroxylated and methoxylated metabolites in environmental samples. *J. Chromatogr., A* **2010**, *1217* (3), 337−347.
(23) Kelly, B. C.; Ikonomou, M. G.; Blair, J. D.; Gobas, F. A. P. C Bioaccumulation behaviour of polybrominated diphenyl ethers (PBDEs) in a Canadian Arctic marine food web. *Sci. Total Environ.* **2008**, *401* (1−3), 60−72.
(24) Wan, Y.; Hu, J. Y.; Zhang, K.; An, L. H. Trophodynamics of polybrominated diphenyl ethers in the marine food web of Bohai Bay, North China. *Environ. Sci. Technol.* **2008**, *42* (4), 1078−1083.
(25) Jardine, T. D.; Kidd, K. A.; Fisk, A. T. Applications, considerations, and sources of uncertainty when using stable isotope analysis in ecotoxicology. *Environ. Sci. Technol.* **2006**, *40* (24), 7501−7511.
(26) Chang, H.; Wan, Y.; Naile, J.; Zhang, X. W.; Wiseman, S.; Hecker, M.; Lam, M. H. W.; Giesy, J. P.; Jones, P. D. Simultaneous quantification of multiple classes of phenolic compounds in blood plasma by liquid chromatography-electrospray tandem mass spectrometry. *J. Chromatogr., A* **2010**, *1217* (4), 506−513.
(27) Borga, K; Kidd, K. A.; Muir, D. C. G.; Berglund, O.; Conder, J. M.; Gobas, F. A. P. C; Kucklick, J.; Malm, O.; Powell, D. E. Trophic magnification factors: Considerations of ecology, ecosystems, and study design. *IEAM* **2012**, *8* (1), 64−84.
(28) Verreault, J.; Gabrielsen, G. V.; Chu, S. G.; Muir, D. C. G.; Andersen, M.; Hamaed, A.; Letcher, R. J. Flame retardants and methoxylated and hydroxylated polybrominated diphenyl ethers in two Norwegian Arctic top predators: Glaucous gulls and polar bears. *Environ. Sci. Technol.* **2005**, *39* (16), 6021−6028.
(29) Athanasiadou, M.; Cuadra, S. N.; Marsh, G.; Bergman, A.; Jakobsson, K. Polybrominated diphenyl ethers (PBDEs) and bioaccumulative hydroxylated PBDE metabolites in young humans from Managua, Nicaragua. *Environ. Health Perspect.* **2008**, *116* (3), 400−408.
(30) Zhao, X. F.; Zhang, H. J.; Ni, Y. W.; Lu, X. B.; Zhang, X. P.; Su, F.; Fan, J. F.; Guan, D. M.; Chen, J. P. Polybrominated diphenyl ethers in sediments of the Daliao River Estuary, China: Levels, distribution and their influencing factors. *Chemosphere* **2011**, *82* (9), 1262−1267.
(31) Stapleton, H. M.; Dodder, N. G.; Kucklick, J. R.; Reddy, C. M.; Schantz, M. M.; Becker, P. R.; Gulland, F.; Porter, B. J.; Wise, S. A. Determination of HBCD, PBDEs and MeO-BDEs in California sea lions (*Zalophus californianus*) stranded between 1993 and 2003. *Mar. Pollut. Bull.* **2006**, *52* (5), 522−531.
(32) Van Boxtel, A. L.; Kamstra, J. H.; Cenijn, P. H.; Pieterse, B.; Wagner, M. J.; Antink, M.; Krab, K.; Van Der Burg, B.; Marsh, G.; Brouwer, A.; Legler, J. Microarray analysis reveals a mechanism of phenolic polybrominated diphenylether toxicity in zebrafish. *Environ. Sci. Technol.* **2008**, *42* (5), 1773−1779.
(33) Morck, A.; Hakk, H.; Orn, U.; Wehler, E. K. Decabromodiphenyl ether in the rat: Absorption, distribution, metabolism, and excretion. *Drug Metab. Dispos.* **2003**, *31* (7), 900−907.
(34) Yu, Z. Q.; Zheng, K. W.; Ren, G. F.; Zheng, Y. Y.; Ma, S. T.; Peng, P. G.; Wu, M. H.; Sheng, G. Y.; Fu, J. M. Identification of hydroxylated octa- and nona-bromodiphenyl ethers in human serum from electronic waste dismantling workers. *Environ. Sci. Technol.* **2010**, *44* (10), 3979−3985.
(35) Schafer, J.; Castelle, S.; Blanc, G.; Dabrin, A.; Masson, M.; Lanceleur, L.; Bossy, C. Mercury methylation in the sediments of a macrotidal estuary (Gironde Estuary, south-west France). *Estuarine, Coastal Shelf Sci.* **2010**, *90* (2), 80−92.
(36) Marvin-Dipasquale, M. C.; Oremland, R. S. Bacterial methylmercury degradation in Florida Everglades peat sediment. *Environ. Sci. Technol.* **1998**, *32* (17), 2556−2563.
(37) Haglund, P. S.; Zook, D. R.; Buser, H. R.; Hu, J. W. Identification and quantification of polybrominated diphenyl ethers and methoxy-polybrominated diphenyl ethers in Baltic biota. *Environ. Sci. Technol.* **1997**, *31* (11), 3281−3287.
(38) Letcher, R. J.; Gebbink, W. A.; Sonne, C.; Born, E. W.; McKinney, M. A.; Dietz, R. Bioaccumulation and biotransformation of brominated and chlorinated contaminants and their metabolites in ringed seals (*Pusa hispida*) and polar bears (*Ursus maritimus*) from East Greenland. *Environ. Int.* **2009**, *35* (8), 1118−1124.
(39) Liu, J. A.; Luo, X. J.; Yu, L. H.; He, M. J.; Chen, S. J.; Mai, B. X. Polybrominated Diphenyl Ethers (PBDEs), Polychlorinated Biphenyles (PCBs), Hydroxylated and methoxylated-PBDEs, and methylsulfonyl-PCBs in bird serum from south China. *Arch. Environ. Contam. Toxicol.* **2010**, *59* (3), 492−501.
(40) Lacorte, S.; Ikonomou, M. G. Occurrence and congener specific profiles of polybrominated diphenyl ethers and their hydroxylated and methoxylated derivatives in breast milk from Catalonia. *Chemosphere* **2009**, *74* (3), 412−420.
(41) Wang, Z.; Ma, X. D.; Lin, Z. S.; Na, G. S.; Yao, Z. W. Congener specific distributions of polybrominated diphenyl ethers (PBDEs) in sediment and mussel (*Mytilus edulis*) of the Bo Sea, China. *Chemosphere* **2009**, *74* (7), 896−901.
(42) DeBruyn, A. M. H.; Meloche, L. M.; Lowe, C. J. Patterns of bioaccumulation of polybrominated diphenyl ether and polychlorinated biphenyl congeners in marine mussels. *Environ. Sci. Technol.* **2009**, *43* (10), 3700−3704.