Levels and distribution of methoxylated and hydroxylated polybrominated diphenyl ethers in plant and soil samples surrounding a seafood processing factory and a seafood market

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ARTICLE INFO

Article history:

Received 29 November 2012

Received in revised form

14 January 2013

Accepted 18 January 2013

Keywords:

OH-PBDEs

MeO-PBDEs

Seafood processing factory

Seafood market

Plant sample

ABSTRACT

Polybrominated diphenyl ethers (PBDEs) along with hydroxylated polybrominated diphenyl ethers (OH-PBDEs) and methoxylated polybrominated diphenyl ethers (MeO-PBDEs) were found in plant and soil samples collected surrounding a seafood processing factory and a seafood market in China. The profiles of MeO-PBDE congeners were different between seafood processing factory and seafood market. The detection frequency and concentration of 6-OH-BDE-47 were lower than that of MeO-PBDEs. Near seafood processing factory, a decreasing trend of analyte concentrations in plants was found downstream the river where factory wastewater was discharged. Concentrations of Σ MeO-PBDEs in plant and soil samples showed difference as root > soil > leaf. However, at seafood market, the concentrations of Σ MeO-PBDEs were much higher in leaves than those in soil. The concentration of Σ MeO-PBDEs in leaves showed a remarkable difference between *Calystegia soldanella* (Linn.) R. Br. and *Setaira viridis* (L.) Beauv.

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1. Introduction

Polybrominated diphenyl ethers (PBDEs) have been used as flame retardants in many manufactured items and have received great attention due to their ubiquitous environmental distribution and bioaccumulation potential (Hites, 2004). Recently, focus has shifted to structural analogues of PBDEs, such as hydroxylated (OH) and methoxylated (MeO) PBDEs. OH-PBDEs are structurally similar to the thyroid hormone thyroxine (T₄). The toxicity of OH-PBDEs has been investigated and was considered more potent than that of PBDEs. Effects of OH-PBDEs on organisms include oxidative phosphorylation disruption, neurotoxicity and thyroid disruptions (Canton et al., 2008; Harju et al., 2007; Meerts et al., 2001; Mercado-Feliciano and Bigsby, 2008). Relative to OH-PBDEs, MeO-PBDEs were reported to have a greater effect on mRNA abundance of steroidogenic enzymes in the H295R cell line (He et al., 2008).

The marine environment is considered as the richest source of biogenic organohalogenes (Gribble, 2003). Up to now, OH-PBDEs and MeO-PBDEs were mainly detected in marine organisms such as algae, mussels and fish (Malmvarn et al., 2005; Teuten et al., 2005; Unson et al., 1994). There has been a considerable interest

in determining the sources and relationships among PBDEs, OH-PBDEs and MeO-PBDEs. 6-MeO-BDE-47, 2'-MeO-BDE-68, 6-OH-BDE-47, and 2'-OH-BDE-68 were the dominant MeO-PBDEs and OH-PBDEs found in marine organisms (Kelly et al., 2008; McKinney et al., 2006; Verreault et al., 2005; Wan et al., 2009). These *ortho*-substituted OH-PBDEs and MeO-PBDEs have been structurally identified and confirmed as natural compounds (Malmvarn et al., 2005, 2008). The *meta*- and *para*-substituted OH-PBDEs have been reported to be biotransformation products produced during PBDE exposure (Malmberg et al., 2005; Marsh et al., 2006; Qiu et al., 2007). Recently, Wan et al. demonstrated the interconversion of OH-PBDE and MeO-PBDE in Japanese medaka (Wan et al., 2010).

The objectives of this work were to investigate the presence and distribution of OH-PBDEs and MeO-PBDEs in plants lived surrounding a seafood processing factory and a seafood market in Longkou, Shandong province, China. Plants play an important role in the terrestrial ecosystem. The uptake and metabolism of organic contaminants in the environment frequently occurred in plants and represent the first step of the food chain (Collins et al., 2006). Plant uptake of PBDEs was already observed (Tian et al., 2012), however, there have been few studies on the fate of OH-PBDEs and MeO-PBDEs in environmental plants. Seafood processing factories and seafood markets were important places where marine organisms were gathered in land and consumed by human. It was assumed in a previous work that the seafood factories discharge and the

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consumption of marine products by coastal residents were the possible major sources for the detected OH-PBDEs in sewage sludge of coastal cities (Sun et al., 2013). In Seafood processing factories, fish was treated in different ways. Head, viscera and skin of fish are generally the waste of filleting process. In seafood markets, a large amount of marine products were traded and also much waste was produced. The OH- and MeO-PBDEs existed in fish and mollusk could be released and transferred to the surrounding environment such as atmosphere, water and soil. Seafood processing factories and seafood markets were possible sources for OH- and MeO-PBDE in terrestrial environment. It is important to evaluate the potential exposure risks of OH- and MeO-PBDEs for the environment and human health.

2. Experimental section

2.1. Materials, standards and reagents

Commercial standards of MeO-PBDEs (4-MeO-BDE-42, 4'-MeO-BDE-49, 3-MeO-BDE-47, 5-MeO-BDE-47, 6-MeO-BDE-47, 2'-MeO-BDE-68, 6-MeO-BDE-85, 5'-MeO-BDE-99, and 6'-MeO-BDE-99) and OH-PBDEs (4-OH-BDE-42, 4'-OH-BDE-49, 3-OH-BDE-47, 5-OH-BDE-47, 6-OH-BDE-47, 2'-OH-BDE-68, 6-OH-BDE-85, 5'-OH-BDE-99, and 6'-OH-BDE-99) were purchased from AccuStandard (New Haven, CT, USA). Several PBDEs congeners which were potential precursors of above MeO- and OH-PBDEs including BDE-28, 47, 66, 68, 99 (AccuStandard, New Haven, CT, USA) were analyzed simultaneously to explore the possible sources of OH-PBDEs and MeO-PBDEs. Surrogate standards (BDE-75 and ^{13}C -6-OH-BDE-47) were purchased from Wellington (Guelph, ON, Canada). Working solutions of PBDEs (in hexane), MeO-PBDEs (in hexane), and OH-PBDEs (in acetonitrile) were prepared at 1 $\mu\text{g}/\text{mL}$ for quantitative analysis. Silica gel (100–200 mesh size) was obtained from Merck (Darmstadt, Germany). Deionized water (18.2 M Ω) was obtained from ultrapure water purification system (Barnstead International, Dubuque, USA). Acetonitrile (HPLC grade), methyl *tert*-butyl ether (MTBE) (HPLC grade), 2-propanol (HPLC grade), acetone (pesticide grade), hexane (pesticide grade) and dichloromethane (DCM) (pesticide grade) were purchased from J. T. Baker (Phillipsburg, NJ, USA). All other chemicals and reagents used were of analytical reagent grade or higher purity.

2.2. Sampling site description and sample collection

The sampling map and sites are shown in Fig. 1. Samples were collected around seafood processing factory (Fig. 1A) and seafood market (Fig. 1B), which are located in Longkou, Shandong province, in eastern China. The seafood processing factory started in 1998. The approximate annual amount of seafood products was 80–100 tons. The seafood market started in 1997. The annual amount of traded seafood was about 2200 tons. When sampling, grass which was similar in size and growth age was selected as sample. At each sampling site, one sample consisted of 3–5 plant individuals. Sampling sites A1, A2, A3, A4 and A5 were located in an area (grey color) inside the seafood processing factory, where head, viscera and skin of fish were discarded. Site A6 was located in a flower bed and did not contact seafood or any waste directly. The wastewater generated during fish processing was discharged into a river in the north of the factory through a sewage pipe. Site A7 was located at the end of sewage pipe where the effluent entered the riverway. Site A8, A9, A10, A11

was selected downstream along the riverside at specific intervals of about 10 m. Site A12 was a control sampling site which was 40 m upstream of site A7. Another control sampling site was site A13 which was one hundred meters away from the factory. Grass samples (*Capsella bursa-pastoris*) (expressed as Cb) was sampled at site A1, A4–A13 and *Erigeron annuus* (L.) Pers. (expressed as Ea) was sampled at site A2 and A3. The grass samples were divided into roots and leaves. The relevant rhizosphere soil was also collected. A fish sample, hairtail (*Coiliasspp*) which consisted of 5 individuals was collected inside the factory and wastewater from sewage pipe was collected at site A7.

Around seafood market, eight sampling sites (B1–B8) were selected in different directions around the market. Grass samples, *Setaria viridis* (L.) Beauv (expressed as Sv) were sampled in all sampling sites. In site B4, another plant, *Calystegia soldanella* (Linn.) R. Br. (expressed as Cs), was also sampled to study the interspecies variability. Site B10 was a control sampling site far away in the other side of a river which was located western of the market. Leaves and soil samples were obtained in all sampling sites except for site B9, in the middle of the market, where have no grass but a kind of mollusk, *Crassostrea talienwhanensis*, was collected. In total, 22 leaf samples, 13 root samples, 22 soil samples, one wastewater sample, one fish sample, and one mollusk sample were collected. Before sampling, all the containers were pre-cleaned with acetone. All solid samples were packed in aluminum foil and sealed in Ziplock bags. Biological samples were stored in an ice-box after collection and kept at $-20\text{ }^{\circ}\text{C}$ until analysis. The wastewater sample was collected using glass bottles to avoid adsorption, stored at $4\text{ }^{\circ}\text{C}$ during transportation and analyzed as soon as possible after back to the laboratory.

2.3. Sample preparation

The sample preparation procedures for PBDEs, MeO-PBDEs and OH-PBDEs were modified from a previous developed method (Sun et al., 2013). In brief, solid samples were freeze-dried and then homogenized. Soils were sieved through a stainless steel 75-mesh sieve. The sieve was rinsed by acetone between samples to minimize cross-contamination. A suitable amount of the samples (800 mL for water and 2.0 g for solid samples) were spiked with BDE-75 and ^{13}C -6-OH-BDE-47. Wastewater sample was prefiltered through a $0.45\text{ }\mu\text{m}$ filter membrane and extracted twice with 40 mL of hexane/MTBE (1:1; v/v) after the addition of 4 mL of 2-propanol. The organic extracts were combined and evaporated to dryness. The solid samples were extracted three times in an ultrasonic bath with 10 mL of hexane/MTBE (1:1; v/v) after the addition of 2 mL of 2-propanol. The extracts were combined and dried under a gentle flow of high-purity nitrogen. The dried residues were then dissolved in 30 mL of DCM. Acidified silica gel (10 g, 44% H_2SO_4 acidified) was added to remove any lipids in the extract and the sulfuric acid residue was eliminated through an anhydrous Na_2SO_4 column. The extract was thereafter concentrated by rotary evaporation to $\sim 2\text{ mL}$ and fractionated on a silica (5 g, deactivated with 5% water) column. The column was first preconditioned by 30 mL of hexane and eluted by 60 mL of 20% DCM in hexane, and 70 mL of DCM in sequence. PBDEs and MeO-PBDEs were eluted in the first fraction and concentrated to a volume of 100 μL prior to GC–ECNI–MS analysis. OH-PBDEs were eluted in the second fraction and concentrated and solvent exchanged to 100 μL of acetonitrile for subsequent LC–MS/MS determination.

2.4. Instrumental analysis

Analysis of PBDEs, MeO-PBDEs and OH-PBDEs was performed based on a previously developed method (Sun et al., 2013). For PBDEs and MeO-PBDEs analysis,

Fig. 1. Sampling locations around the seafood processing factory (A) and seafood market (B).

a 7890A gas chromatograph (GC) coupled with a 7000B triple quadrupole mass spectrometer (Agilent, USA) operated in electron capture negative ionization (ECNI) mode was used. Compound separation was achieved using a DB-5 MS (J & W Scientific, Folsom, CA) fused silica capillary column (30 m, 0.25 mm i.d., 0.1 µm film thickness). Selected ion-monitoring (SIM) mode was used for quantitative determination. The monitored ions are ^{79}Br and ^{81}Br .

For OH-PBDEs analysis, an Agilent 1290 Series LC system coupled with an Agilent 6460 Triple Quadrupole MS/MS system (Agilent Technologies, Palo Alto, CA) was used. A C18 analytical column (100 mm × 2.1 mm, 2.2 µm particle size, Thermo Fisher Scientific, USA) was selected for separation. The flow gradient with acetonitrile (A) and water (B) was initiated at a composition of 55:45 (v/v) and increased to 75:25 with a flow rate of 0.38 mL/min in 20 min with a linear curve. Electrospray ionization was operated in the negative ion mode. Multiple reaction monitoring (MRM) mode was used for quantification. The $[\text{M} - \text{H}]^-$ precursor ion was m/z 578.6 for OH-pentaBDE and m/z 500.7 for OH-tetraBDE. The Product ions were $[\text{C}_6\text{H}_2\text{Br}_2\text{O}_2]^-$ and $[\text{Br}]^-$ for 4-OH-BDE-42 and 4'-OH-BDE-49; $[\text{C}_{12}\text{H}_5\text{Br}_3\text{O}_2]^-$ and $[\text{Br}]^-$ for 3-OH-BDE-47 and 5-OH-BDE-47; $[\text{Br}]^-$ for 6-OH-BDE-47, 2'-OH-BDE-68, 6-OH-BDE-85, 5'-OH-BDE-99 and 6'-OH-BDE-99.

2.5. Quality assurance and quality control

Method blank samples ($n = 5$) were analyzed to monitor interferences and contamination, showing an absence of background interference for all analytes. Recoveries for the surrogate standards, ^{13}C -6-OH-BDE-47 and BDE-75, were 71.3–93.2% and 74.6–95.1%, respectively. The concentrations were recovery corrected. The method limits of quantification (MLOQs) for individual compounds were estimated based on a signal to noise ratio of 10. MLOQs for each congener of PBDEs, MeO-PBDEs and OH-PBDEs were listed in Table 1.

3. Results and discussion

All concentrations reported were on a dry weight basis. Fig. 2 shows concentrations of detected $\Sigma\text{MeO-PBDEs}$, $\Sigma\text{OH-PBDEs}$ and ΣPBDEs in root, leaf and soil samples collected in seafood processing factory (A) and seafood market (B). Composition profiles of MeO-PBDE and OH-PBDE congeners in various matrices are shown in Fig. 3.

3.1. Seafood processing factory

In plant and soil samples inside and surrounding seafood processing factory, the detected MeO-PBDE congeners were mainly

Table 1
Method limits of quantification (MLOQs) ($S/N = 10$) of all target analytes for various matrices.

Compounds	MLOQs					
	Water (pg/L)	Root (pg/g dw)	Leaf (pg/g dw)	Soil (pg/g dw)	Mollusk (pg/g dw)	Fish (pg/g dw)
BDE-28	19	7	8	6	10	12
BDE-47	11	3	5	4	7	7
BDE-66	31	9	12	11	15	14
BDE-68	26	13	25	12	21	18
BDE-99	41	24	17	16	27	24
2'-MeO-BDE-68	16	7	12	10	8	16
6-MeO-BDE-47	12	5	11	7	9	10
3-MeO-BDE-47	15	8	18	13	12	17
5-MeO-BDE-47	19	15	9	16	21	15
4'-MeO-BDE-49	23	17	14	17	18	21
4-MeO-BDE-42	25	8	13	14	12	13
6'-MeO-BDE-99	36	21	32	22	27	29
5'-MeO-BDE-99	33	24	25	27	24	25
6-MeO-BDE-85	35	25	31	30	23	20
4-OH-BDE-42	13	18	15	16	13	18
3-OH-BDE-47	18	14	8	9	11	15
4'-OH-BDE-49	26	11	9	17	15	16
5-OH-BDE-47	14	7	14	8	11	13
6-OH-BDE-47	25	14	19	16	23	24
2'-OH-BDE-68	27	16	25	21	20	21
6-OH-BDE-85	43	22	31	24	30	31
5'-OH-BDE-99	36	31	25	28	33	36
6'-OH-BDE-99	38	33	28	27	32	37

6-MeO-BDE-47, 2'-MeO-BDE-68 and 4'-MeO-BDE-49. 6-MeO-BDE-47 was the primary MeO-PBDE congener that was consistent with the results obtained in many marine organisms (Kelly et al., 2008; Malmvarn et al., 2008; Nomiya et al., 2011). Only one OH-PBDE congener, 6-OH-BDE-47, was detected in a small number of samples with much lower concentrations comparing to MeO-PBDEs. The detected PBDE congeners were BDE-28, BDE-47, BDE-66 and BDE-99. ΣPBDEs ranged from <LOD to 1285.4 pg/g (mean of 245.5 pg/g) for plants, and from <LOD to 274.9 pg/g (mean of 116.3 pg/g) for soil samples. In hairtail (*Coiliassp*) samples that were processed as products of the factory, 6-MeO-BDE-47 (973.6 pg/g), 2'-MeO-BDE-68 (433.5 pg/g), 4'-MeO-BDE-49 (389.4 pg/g), 6-OH-BDE-47 (174.3 pg/g) were detected at much higher concentrations than those in plant and soil samples (Fig. 2A). Concentration of ΣPBDEs was 725.7 pg/g in hairtail. Besides, a small amount of 5-MeO-BDE-47 (43.5 pg/g), 6'-MeO-BDE-99 (63.3 pg/g) and 2'-OH-BDE-68 (57.8 pg/g) which were usually found in marine organisms (Kelly et al., 2008; Marsh et al., 2004; Routti et al., 2009) was also identified in these fish. The results showed that MeO- and OH-PBDEs in the soil and plant samples may come from the marine products that processed in the factory.

Inside the seafood processing factory (sites A1–A5), concentrations of $\Sigma\text{MeO-PBDEs}$ were in the range of 162.2–838.8 pg/g for soil samples and 60.6–635.6 pg/g for plant samples. 6-OH-BDE-47 was only detected in leaf samples obtained in site A1, A4 and A5 with concentrations of 11.4, 12.8 and 14.3 pg/g, respectively. Similar status was found in reports of marine animals. OH-PBDEs were not detectable in fish and marine wildlife in Canadian Arctic marine food web, but MeO-PBDEs were detected (Kelly et al., 2008). It was also reported that the total concentrations of OH-PBDEs were much lower than that of MeO-PBDEs in market fish of Hong Kong (Wang et al., 2011). Since fish head, fish viscera and fish skin were discarded everywhere in this area (Fig. 1), MeO- and OH-PBDEs existed in marine products were released and contaminated the soil. The plants grew in the soil were able to take up these organic pollutants through root and then translocate the pollutants from roots to shoots. The direct contact of plants with marine products and waste was also one of the pathways for plants accumulating MeO- and OH-PBDEs. On the other hand, air transportation may contribute to some extent to the accumulation of these compounds. In site A6, the control sampling site inside the factory without any direct seafood or waste contact, MeO-PBDEs were also found in plant and soil samples. However, the concentrations of $\Sigma\text{MeO-PBDEs}$ in various samples in site A6 were all much lower than those in site A1–A5. It was indicated that a portion of MeO-PBDEs were likely contaminating soil and plants via atmospheric transmission, but the contribution of atmosphere transportation is relatively lower comparing to direct contact of soil and grass with seafood (or waste) and the plant uptake from soil. It was noticeable that 6-MeO-BDE-47, the predominant congener in fish, soil and plant samples, was not detected in site A6, maybe due to the relatively low transportation or accumulation potential.

Different plant species having different accumulation and distribution behavior to the same contaminants was observed at sites A1–A5. Though the two sampled plant species grew in the same condition at site A1–A5, 6-OH-BDE-47 was only detected in leaf samples of *Capsella bursa-pastoris*, and not detected in *Erigeron annuus* (L.) Pers. $\Sigma\text{MeO-PBDEs}$ in *Capsella bursa-pastoris* ranked as root < leaf < soil, whereas, $\Sigma\text{MeO-PBDEs}$ in *Erigeron annuus* (L.) Pers. ranked as leaf < root < soil. In addition, either plant species showed different accumulation behavior for MeO-PBDEs and PBDEs.

Outside the seafood processing factory (sites A7–A13), a distinct spatial distribution was observed that the concentrations of target compounds in soil and plant samples gradually decreased

from site A7 to A11 along the direction of the river. MeO-PBDEs, OH-PBDEs and PBDEs were all detected from leaf, root and soil samples collected at site A7. Σ MeO-PBDEs ranged from 932.3 pg/g (root sample) at site A7 to <LOD after site A10. The same MeO- and OH-PBDE congener profiles were observed in wastewater sampled at site A7 (Fig. 3). However, the concentration of Σ MeO-PBDEs in wastewater was lower than that in soil and plant samples. It was indicated that soil and plants were able to accumulate these contaminants after the wastewater was discharged. Bio-magnification was observed since Σ MeO-PBDEs shows the concentration order of wastewater < soil < roots at site A7. At site A10 and A11 that was 30–40 m downstream of the outlet of the wastewater, MeO-PBDEs were not detectable. At site A12 which was located upstream of the outlet, and another control sampling site A13, neither MeO-PBDEs nor OH-PBDEs were found. These results strongly indicated that the factory and its wastewater was a pollution source of MeO-PBDEs and OH-PBDEs for surrounding environment but the atmospheric transmission of MeO-PBDEs and OH-PBDEs was in a very limited scope.

Compare the plant samples of *Capsella bursa-pastoris* obtained at A1, A4, A5 and A7, the diverse pollution source and accumulation pathway in different sampling sites resulted in the different distribution trends of OH- and MeO-PBDEs in plants. At site A7, A8 and A9, the concentration of Σ MeO-PBDEs in samples showed as root > soil > leaf. Different from the grey area inside the factory in Fig. 1, there was neither obvious atmospheric transmission of contaminants from the factory nor direct contact of seafood with plants at the riverside outside the factory. Therefore, root uptake from soil was the significant pathway for the accumulation of OH- and MeO-PBDEs in plants outside factory, leading to the difference from the plants inside the factory with concentration in leaf higher than that in root.

3.2. Seafood market

In plant and soil samples collected at site B1–B8 surrounding the seafood market, the detected MeO-PBDE congeners were only 2'-MeO-BDE-68 and 4'-MeO-BDE-49. Similar to the samples collected from site A6, 6-MeO-BDE-47 was also not detected in any leaf or soil samples surrounding seafood market (Fig. 3). Concentrations of Σ MeO-PBDEs ranged from <LOD to 584.1 pg/g, lower than those in seafood processing factory. 6-OH-BDE-47 was only detected in leaf samples collected at site B1, B2 and B3. The concentration of 6-OH-BDE-47 was similar to those in seafood processing factory and also lower than MeO-PBDEs. For *Crassostrea talienwhanensis* collected at site B9 inside the market, the detected congeners were the same as hairtail (*Coiliaspp*) collected from the seafood processing market. In a previous work, *Crassostrea talienwhanensis* was proved as suitable bioindicator of contamination by PBDEs in the Chinese Bohai Sea (Zhu et al., 2012). Concentrations of PBDEs were comparable in both studies. The levels of MeO- and OH-PBDEs in seafood samples were relatively higher than in plants and soil. This further supported the assumption that MeO- and OH-PBDEs existed in marine animals of both the factory and market were released and contaminated the surrounding environment. At site B10, all target compounds were below the detection limits, suggesting the seafood market should be the main source of PBDEs, MeO- and OH-PBDEs for the nearby environment.

The concentrations of Σ MeO-PBDEs and Σ PBDEs were much higher in leaves than in soil and OH-PBDE only detected from leaves, suggesting that contaminants existed in these leaves should be mostly come from air. It was consequently assumed that the adsorption of leaves is an important accumulation pathway for plants. The concentration of MeO-PBDEs in leaves showed a remarkable difference between the two obtained plant species at

site B4. Σ MeO-PBDEs in leaves of Sv and Cs were 584.1 pg/g and 109.2 pg/g, respectively. The leaf of Sv is thin lanceolate with relatively higher specific surface area and lots of cilia on surface could help enhance the adsorptive ability, while the leaf of Cs is thick reniform with relatively lower specific surface area. Thus the effects of plant species were further confirmed.

Spatial distributions of Σ MeO-PBDEs and Σ PBDEs in leaf of Sv showed that the concentration in site B4 was the highest, and the lowest concentrations were found in site B5, B7 and B8. The possible reasons are hypothesized as: (1) the predominant wind direction was mainly southeastern in the period of plant growth and sampling. This may reduce the accumulation of pollutants in sampling site in southeast. (2) There is a river located closely in the west of the market. Some garbage generated from the market was discarded in the riverbank. (3) The west gate and north gate were main entrances of seafood market. The transportation aisle and storage position of seafood were closer to site B4 and B2.

3.3. Statistical relationships

The statistical relationships among PBDEs, OH-PBDEs and MeO-PBDEs were assessed to further explore the possible sources of OH-PBDEs and MeO-PBDEs. Relatively high concentration of Σ PBDEs (1285.4 pg/g) was found in leaves of Sv collected in site B4. BDE-47 was the primary BDE congener among the target PBDEs. Significant linear relationships were found between the concentrations of BDE-47 and 6-MeO-BDE-47 (Spearman's rank correlation coefficient: $r = 0.47$, $p < 0.01$), BDE-47 and 4'-MeO-BDE-49 ($r = 0.79$, $p < 0.01$), BDE-47 and 2'-MeO-BDE-68 ($r = 0.81$, $p < 0.01$), and Σ PBDEs and Σ MeO-PBDEs ($r = 0.59$, $p < 0.01$). This suggested that they may have a common source or similar accumulation potential in plants and soil. 6-MeO-BDE-47, 2'-MeO-BDE-68 and 6-OH-BDE-47 have been considered as naturally occurring products in marine organisms (Malmvarn et al., 2005, 2008). The three compounds have a similarity in structure that they all have a methoxyl or hydroxyl group in the *ortho* position relative to the ether bond. Seafood consumption and processing were considered to contribute to the load of MeO- and OH-PBDEs in biosolids in wastewater treatment plants (Sun et al., 2013). They may also be an important source for plants in the terrestrial ecosystem. On the other hand, metabolic process may take place in plants. The occurrence of OH-PBDEs has been reported in several controlled PBDE exposure studies (Chen et al., 2006; Hakk et al., 2002; Staskal et al., 2006). MeO-PBDEs were reported as potential metabolites of PBDEs in maize (Wang et al., 2012). Inter-conversion of OH-PBDEs and MeO-PBDEs was demonstrated in Japanese medaka (Wan et al., 2010). In this research, it is difficult to confirm whether biotransformation occurred in analyzed plants. However, concentration ratios between metabolites and parent compounds were mainly very low (Wiseman et al., 2011). For example, the concentration ratios between metabolites (2'-OH-BDE-66, 3-OH-BDE-47, 4-OH-BDE-42, 4'-OH-BDE-49, 5-OH-BDE-47 and 6-OH-BDE-47) and exposed BDE-47 were approximately 0.30%, 0.84%, 0.10%, 0.54%, 0.074%, and 0.022%, respectively (Hamers et al., 2008). While in this study concentrations of MeO-PBDEs detected in plants and soil were comparable to PBDEs, suggesting bio-accumulation maybe the dominant pathway that led to the occurrence of MeO- and OH-PBDEs in plants and soil.

4. Conclusions

MeO-PBDEs and PBDEs were ubiquitous in the environment surrounding seafood processing factory and seafood market in China. OH-PBDEs can only be detected in a portion of samples with much lower concentrations. Seafood processing factory and seafood market were important sources that MeO- and OH-PBDEs

entered fresh water, plants and soil. Uptake by root, adsorption by leaves and direct contact of plants with marine products were three potential accumulation pathways for terrestrial plants. However, the atmosphere transportation range of these pollutants was very limited and their concentrations in the environment were relatively low.

Acknowledgements

This work was jointly supported by the National Basic Research Program of China (No. 2009CB421603), the National Natural Science Foundation of China (Nos. 21277153, 21177147), and Important Directional Item of the Chinese Academy of Sciences (No. KZCX2-EW-QN409).

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