Hydroxylated and methoxylated polybrominated diphenyl ethers in mollusks from Chinese coastal areas

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HIGHLIGHTS

- OH-PBDEs and MeO-PBDEs were determined in mollusks from Chinese coastal areas.
- Significant correlations were found between OH- and MeO-PBDEs.
- *Crassostrea talienwhanensis* accumulated more OH- and MeO-PBDEs.
- Temporal trends of OH- and MeO-PBDEs in mollusks were studied.

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ABSTRACT

Hydroxylated polybrominated diphenyl ethers (OH-PBDEs), methoxylated PBDEs (MeO-PBDEs) and PBDEs were determined in three mollusk species collected from three Chinese coastal regions in 2007, 2009, 2010 and 2011. The dominant MeO- and OH-PBDEs isomers detected in mollusks were 6-MeO-BDE-47, 2'-MeO-BDE-68, 6-OH-BDE-47 and 2'-OH-BDE-68. Concentrations of Σ MeO-PBDEs ranged from 9.20 to 2090 pg g^{-1} dry weight (mean: 450 pg g^{-1} dry weight). Concentrations of Σ OH-PBDEs ranged from 118 to 2540 pg g^{-1} dry weight (mean: 534 pg g^{-1} dry weight). Species differences in accumulation were found for the three mollusk species. Spatial distribution showed that OH- and MeO-PBDEs levels were higher in Weihai than in Tianjin. The temporal trends of OH- and MeO-PBDEs in mollusks were studied during period of 2007 to 2011, rising of Σ OH-PBDEs in Rap from Penglai and Ost from Weihai and declining of Σ MeO-PBDEs in Ost in Penglai were observed. Significant correlations were found between OH- and MeO-PBDEs, but neither between PBDEs and OH-PBDEs, nor between PBDEs and MeO-PBDEs, suggesting that OH- and MeO-PBDEs may have a common source or similar accumulation behavior in mollusks. OH- and MeO-PBDEs were likely not to originate from PBDE precursors.

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1. Introduction

Polybrominated diphenyl ethers (PBDEs) are a group of brominated flame retardants (BFRs) utilized in a variety of consumer products for the past several decades. PBDEs are toxic, persistent, and bioaccumulative, and have been ubiquitously distributed in the environment (Hites, 2004; de Wit et al., 2006). Structural analogues to PBDEs, mainly tetrabromo- and pentabromo-hydroxylated (OH)-PBDEs and methoxylated (MeO) PBDEs, have also been detected in algae, sponge, fish, bird, and mammal species from diverse aquatic environments (Unson et al., 1994; Sinkkonen et al., 2004; Wolkers et al., 2004; Malmvarn et al., 2005; Teuten et al., 2005).

For most toxicological endpoints, OH-PBDEs are more potent than the corresponding PBDEs. OH-PBDEs structurally resemble

the thyroid hormone (TH), thyroxine (T₄), and have been found to bind to transthyretin (TTR) (Hamers et al., 2008; Ucan-Marín et al., 2009; Li et al., 2010). OH-PBDEs also elicit many other toxic effects such as interruption of oxidative phosphorylation (Van Bostel et al., 2008), estrogenic and antiestrogenic activity (Meerts et al., 2001) and neurotoxicity (Dingemans et al., 2008; Hendriks et al., 2010) in exposed wildlife and humans.

The origin of these OH- and MeO-PBDEs is under discussion, and two major sources have been suggested. Firstly, occurrence of higher concentrations of OH-PBDEs and MeO-PBDEs than PBDEs in marine organisms has led to the finding that these compounds may be formed naturally by marine algae or cyanobacteria (Malmvarn et al., 2005, 2008). Radiocarbon measurements of 6-MeO-BDE-47 and 2'-MeO-BDE-68 in whale collected from the North Atlantic demonstrated that these compounds were of natural origin (Teuten et al., 2005). Secondly, OH- and MeO-PBDEs were potential transformation products in organisms. OH-PBDEs were identified as metabolites of PBDEs in rats and mice (Orn and

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Klasson-Wehler, 1998; Hakk et al., 2002; Morck et al., 2003). MeO-PBDEs were also found in maize exposed to PBDEs (Wang et al., 2012). In addition, Wan et al. (2009) proposed that demethylation of MeO-PBDEs by cytochrome P450 rather than parent PBDEs contributed to the formation of OH-PBDEs. It was also shown that interconversion between 6-OH-BDE-47 and 6-MeO-BDE-47 could be observed in Japanese medaka (Wan et al., 2010). The origins of OH-PBDEs and MeO-PBDEs in marine biota have been of increasing scientific interest.

Mollusks have been commonly used to assess contamination in aquatic systems due to their relatively high lipid content and low metabolic enzyme activities (Isobe et al., 2007). The levels of PBDEs were investigated in a portion of samples in an earlier study of our group; however, no previous examination on OH- and MeO-PBDEs contaminations in selected mollusks from the study region has been reported. This study attempts to investigate and elucidate (1) contamination status, (2) species difference in accumulation, (3) spatial distribution, (4) temporal trends, and (5) possible source and potential exposure risks of OH- and MeO-PBDEs for the environment and human health, by analyzing PBDEs, OH-PBDEs and MeO-PBDEs in mollusks collected in Chinese coastal areas.

2. Experimental section

2.1. Chemicals and reagents

Target chemical standards included nine OH-PBDE congeners (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), nine MeO-PBDE congeners (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 five PBDE congeners (BDE-47, 66, 71, 85, 99). Based on the selected congeners of OH- and MeO-PBDEs, only corresponding tetra- and penta-BDEs which were abundant in the environment were selected here as target compounds to assess the statistical relationships among PBDEs, OH-PBDEs and MeO-PBDEs. Surrogate standards were ^{13}C -6-OH-BDE-47 and BDE-75. Chemical standards used in the present study were purchased from Accu-Standard (New Haven, CT, USA) and Wellington (Guelph, ON, Canada). All solvents were HPLC grade or pesticide grade and were obtained from Honeywell Burdick & Jackson (Seelze, Germany) and J.T. Baker (Phillipsburg, NJ, USA). Silica gel (100–200 mesh size) was purchased from Merck (Darmstadt, Germany).

2.2. Sampling

In August 2007, 2009, 2010 and 2011, three species of mollusks were collected separately from three coastal sites (Fig. 1) near the cities of Tianjin, Weihai and Penglai. Tianjin is located in Bohai Bay. Weihai is located along the Chinese Yellow Sea. Penglai is located near the boundary of Bohai Sea and Yellow Sea. The three selected species of mollusks were *Neverita didyma* (Nev), *Rapana venosa* (Rap) and *Crassostrea talienwhanensis* (Ost). The mollusks were transported to the laboratory on ice, and then cleaned by water in the laboratory. The soft tissue of the mollusks was thoroughly rinsed with Milli-Q water to remove impurities. For each species from a sampling site, about 1000 g of wet soft tissue (consisting of 5–10 individuals) was homogenized in a blender to form one composite sample. The samples were kept at $-20\text{ }^{\circ}\text{C}$ until analysis. A total of 36 composite soft tissue samples were obtained and analyzed.

2.3. Sample preparation

All samples were freeze-dried, homogenized and sieved. Sample pretreatment was based on our previous developed methods (Sun

et al., 2012a) with modifications. Briefly, an aliquot of 2 g of mollusk sample was spiked with surrogate standard and extracted thrice with 10 mL of hexane/MTBE (1:1; v/v) after the addition of 2 mL 2-propanol. The extracts were combined and dried under gentle flow of nitrogen gas. The dried residues were then dissolved in 20 mL of DCM and cleaned by acidified silica gel (10 g, 44% H_2SO_4 acidified). Then, a glass column filled with anhydrous Na_2SO_4 was used to filter the extract. The concentrated extract was further cleaned up and fractionated by elution with 60 mL of 80% hexane in DCM and 70 mL of DCM on a column packed with, from bottom to top, 5 g of silica deactivated with 5% water (w/w) and 1 g of anhydrous sodium sulfate. PBDEs and MeO-PBDEs were eluted in the first fraction and concentrated to a volume of 100 μL for subsequent gas chromatography/mass spectrometry (GC/MS) analysis. OH-PBDEs were eluted in the second fraction. The eluate was concentrated to dryness by evaporation and gentle stream of nitrogen gas and solvent exchanged to 100 μL of acetonitrile prior to liquid chromatography/tandem quadrupole mass spectrometry (LC-MS/MS) determination.

2.4. Instrumental analysis

OH-PBDEs were analyzed using a high-performance liquid chromatograph (Agilent 1290) coupled with a triple-quadrupole mass spectrometer (Agilent 6460). The quantification of PBDEs and MeO-PBDEs was carried out using a gas chromatograph (Agilent 6890) equipped with a mass spectrometer detector (Agilent 5973C) operated in electron capture negative ionization (ECNI) mode. More detailed descriptions of the instrument operational procedures can be found in our previously developed method (Sun et al., 2012a,b).

2.5. Quality assurance and quality control (QA/QC)

QA/QC was implemented to ensure the correct identification and accurate quantification of the target compounds. All pretreatment equipments rinses were carried out with acetone and hexane to avoid cross contamination. A laboratory blank and a matrix spike were injected for every batch of 6 samples during the instruments analysis. No target compounds were found in blanks and no memory effects were observed between consecutive runs. Identification was based on a comparison of the retention times and mass spectra of analytes in samples to those of authentic standards. All analyte concentrations were recovery corrected. The method detection limits (MDLs) for all the investigated analytes by GC-MS and LC-MS/MS was estimated based on a signal-to-noise ratio (S/N) of 3 using the lowest concentration standard. For OH-PBDEs, MDLs were $3.83\text{--}6.72\text{ pg g}^{-1}$ dry weight (dw). For PBDEs and MeO-PBDEs, MDLs were $1.22\text{--}8.61\text{ pg g}^{-1}$ dw. Recoveries for spiked samples were 71.4–94.7% for PBDEs and MeO-PBDEs, and 67.5–85.6% for OH-PBDEs. The results of PBDEs analysis were in good agreement with those for reported values as described in previous report done by our group (Zhu et al., 2012).

3. Results and discussion

3.1. Congener profiles and concentrations

Fig. 2 shows concentrations of detected $\Sigma\text{MeO-PBDEs}$, $\Sigma\text{OH-PBDEs}$ and ΣPBDEs in all analyzed mollusk samples. Composition profiles of MeO-PBDE and OH-PBDE congeners in each mollusk sample are shown in Fig. 3.

The detected MeO-PBDE congeners were 6-MeO-BDE-47, 2'-MeO-BDE-68, 4-MeO-BDE-42, 5-MeO-BDE-47, 4'-MeO-BDE-49, 6-MeO-BDE-85, 5'-MeO-BDE-99 and 6'-MeO-BDE-99, with

Fig. 1. Map of sampling locations in Chinese coastal areas. (★, sampling site).

detection frequency of 97%, 94%, 36%, 28%, 6%, 8%, 8% and 33%, respectively. 6-MeO-BDE-47 (concentration range from <LOD to 947 pg g^{-1} dry weight (dw); mean: 167 pg g^{-1} dw) and 2'-MeO-BDE-68 (concentration range from <LOD to 750 pg g^{-1} dw; mean: 188 pg g^{-1} dw) were the most predominant congeners. The combined levels of 6-MeO-BDE-47 and 2'-MeO-BDE-68 accounted for 47–100% of the sum of all identified MeO-PBDEs. Higher contributions of the two MeO-PBDE congeners have been reported in bivalve (*Mytilus edulis*) from the Canadian Arctic marine food web (Kelly et al., 2008) and mollusk species (*Ruditapes philippinarum*,

Macrta veneriformis Reeve and *Rapana venosa*) from Chinese Liaodong Bay (Zhang et al., 2010a). The profiles of MeO-PBDEs were also similar to those in other marine organism such as red algae and cyanobacteria in the Baltic Sea (Malmvarn et al., 2008), fish from Japanese coastal waters (Nomiya et al., 2011b), albatross from the Indian and South Atlantic Oceans (Wan et al., 2009), and polar bear from Northern and Western Alaska (Wan et al., 2009). Concentrations of $\Sigma\text{MeO-PBDEs}$ ranged from 9.20 to 2090 pg g^{-1} dw (mean: 450 pg g^{-1} dw) in mollusks in this study, which were greater than those in sediment from nearby Liaodong

Fig. 2. Concentrations of detected $\Sigma\text{MeO-PBDEs}$, $\Sigma\text{OH-PBDEs}$ and ΣPBDEs in mollusk samples.

Fig. 3. Composition profiles of MeO-PBDE and OH-PBDE congeners in mollusk samples.

Bay ($3.8\text{--}56\text{ pg g}^{-1}\text{ dw}$) (Zhang et al., 2012). When concentrations were expressed on a lipid weight (lw) basis, the average concentrations of $\Sigma\text{MeO-PBDEs}$ in mollusk in this work ($3.63 \pm 3.53\text{ ng g}^{-1}\text{ lw}$) were lower than those in mollusks from Liaodong Bay ($15.9 \pm 11.8\text{ ng g}^{-1}\text{ lw}$) (Zhang et al., 2010a) and in mollusk from the Canadian Arctic (mean: $14\text{ ng g}^{-1}\text{ lw}$) (Kelly et al., 2008).

Two of nine target OH-PBDE congeners, 6-OH-BDE-47 and 2'-OH-BDE-68, were found in all mollusk samples. Concentrations of 6-OH-BDE-47 were in the range of $89.7\text{--}2090\text{ pg g}^{-1}\text{ dw}$ (mean: $388\text{ pg g}^{-1}\text{ dw}$). Concentrations of 2'-OH-BDE-68 were in the range of $10.0\text{--}701\text{ pg g}^{-1}\text{ dw}$ (mean: $147\text{ pg g}^{-1}\text{ dw}$). 6-OH-BDE-47 and 2'-OH-BDE-68 have also been reported as predominant OH-PBDE congeners frequently detected in aquatic organisms. Higher proportions of the two compounds were observed in fish collected from the Detroit River (Valters et al., 2005), ringed seals from the Baltic Sea (Routti et al., 2009), Chinese sturgeon from the Yangtze River (Zhang et al., 2010b), and cetaceans from Japanese coastal waters (Nomiyama et al., 2011a). On the basis of lipid weight, the corresponding average values of $\Sigma\text{OH-PBDEs}$ in mollusks ($5.81 \pm 5.43\text{ ng g}^{-1}\text{ lw}$) were greater than those in Chinese sturgeon from the Yangtze River ($0.81 \pm 0.18\text{ ng g}^{-1}\text{ lw}$) (Zhang et al., 2010b) and in beluga whales from the Canadian Arctic ($<0.001\text{--}0.23\text{ ng g}^{-1}\text{ lw}$) (Kelly et al., 2008). For the selected PBDE congeners which were potential precursors of the commonly identified MeO- and OH-PBDEs in mollusks, the concentrations and profile of individual PBDE were similar to those previously reported (Zhu et al., 2012). BDE-47 was the primary contaminant with detection frequency of 100%. Concentrations ranges of ΣPBDEs were $63.9\text{--}2300\text{ pg g}^{-1}$ for all mollusk samples, comparable to the concentrations of OH-PBDEs and MeO-PBDEs. While the reported proportions of metabolites during biotransformation of PBDEs were generally very small in the lab exposure experiments. 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 all less than 1% (Hamers et al., 2008). Therefore, OH- and MeO-PBDEs in mollusks were not the biotransformation products of PBDEs. Bioaccumulation from natural origin may be the predominant pathway that led to the occurrence of OH- and MeO-PBDEs in mollusks.

3.2. Species differences in accumulation

Nev, Rap and Ost are commonly found in Chinese seas. Concentrations of $\Sigma\text{MeO-PBDEs}$ and $\Sigma\text{OH-PBDEs}$ were compared between Nev and Ost, and Rap and Ost collected from the same locations in the same year using concentration ratios (concentration in Ost is as 1). Concentration ratios in Nev ranged from 0.01 to 0.34 (mean of 0.08) for MeO-PBDEs, and from 0.07 to 0.94 (mean of 0.44) for OH-PBDEs. Concentration ratios in Rap ranged from 0.04 to 1.46 (mean of 0.27) for MeO-PBDEs, and from 0.07 to 3.45 (mean of 0.87) for OH-PBDEs. Apparently, MeO-PBDEs and OH-PBDEs were accumulated more in Ost than in Rap and Nev. MeO-PBDEs and OH-PBDEs may have similar mechanisms of bioaccumulation in mollusks. Ost are Lamellibranchia bivalve and filter feeders feeding on plankton. Nev and Rap are carnivorous snails and feed on shellfish including Ost. The mean trophic levels of Ost, Nev and Rap are 3.0, 3.2, and 3.4, respectively, according to the previous report (Zhu et al., 2012). Trophic dilution rather than magnification were observed and were consistent with the results obtained by Zhu et al. (Zhu et al., 2012). The lipid contents of Ost, Nev and Rap are $15.7\% \pm 2.2\%$, $6.2\% \pm 0.1\%$, and $6.7\% \pm 1.8\%$, respectively. Results showed the lipid contents had stronger relationships with $\Sigma\text{OH-PBDEs}$ and $\Sigma\text{MeO-PBDEs}$ than trophic levels. It was assumed that Ost which have relatively higher lipid contents have greater bioaccumulative abilities of MeO-PBDEs and OH-PBDEs than Nev and Rap. The levels of $\Sigma\text{OH-PBDEs}$ were mainly higher than that of $\Sigma\text{MeO-PBDEs}$ in all mollusks except Ost collected from Tianjin and Penglai, suggesting the existence of selective enrichment of pollutants for mollusk species to some extent. Species differences in profiles of OH-PBDE and MeO-PBDE congeners were also studied (Fig. 3). In mollusk from both Tianjin and Penglai, the proportion of 6-OH-BDE-47 in the sum of OH- and MeO-PBDEs ranked as Ost < Rap < Nev. The proportion of 2'-OH-BDE-68 was lower in Ost than in Rap and Nev, however, the proportion of 2'-MeO-BDE-68 was much higher in Ost than in Rap and Nev. 6-MeO-BDE-85 can only be found in Ost. 4-MeO-BDE-42 and 6'-MeO-BDE-99 can be detected in a portion of Rap and Ost samples, but were undetectable in all Nev samples. These profiles differences may be attributed to congener-specific dietary exposure or different biotransformation capacities between mollusk species.

3.3. Spatial distribution

Three representative sampling sites were selected to assess the spatial distribution of OH- and MeO-PBDEs in mollusks. The highest concentration of Σ MeO-PBDEs and Σ OH-PBDEs were all found in Ost sample collected in Weihai. Average Σ MeO-PBDEs concentration and average Σ OH-PBDEs concentration among four years in mollusk species from different cities were shown in Fig. 4. The average levels in mollusk mainly gradually increased in order of Tianjin < Penglai < Weihai. Statistical analysis was executed with SPSS 16.0. OH-PBDEs levels in mollusks were statistically different between Tianjin and Weihai ($p < 0.01$) using the Tukey test. There was no known anthropogenic source for OH- and MeO-PBDEs, so the spatial distribution of these chemicals may not be related to industrial activities and population of the three cities. Sampling sea area may be a potential affecting factor. Tianjin is located along Bohai Sea which is China's continental sea. This semi closed sea area is far away from ocean and strongly affected by surrounding continent. Therefore, the temperature and salinity of seawater were distinctly different from oceans (Chen, 2009). Weihai is located along the Yellow Sea which is marginal sea of the Pacific Ocean. This sea area has unobstructed seawater exchange with ocean. Since most detected OH- and MeO-PBDEs in oceans were regarded as marine natural products, diverse marine environment may lead to the different levels of OH- and MeO-PBDEs in organisms. Penglai is located between Bohai Sea and Yellow Sea. So, the mollusks lived in this area were affected by both seas. That is why Σ MeO-PBDEs and Σ OH-PBDEs in most mollusk samples collected in Penglai were higher than that of Tianjin and lower than that of Weihai.

3.4. Temporal trends

The temporal trends of Σ MeO-PBDEs and Σ OH-PBDEs in mollusks were illustrated in this work, as shown in Fig. 2. Σ OH-PBDEs in Rap from Penglai increased from 289 pg g^{-1} dw in 2007 to 853 pg g^{-1} dw in 2011 (Spearman's rank correlation coefficient: $r^2 = 0.97$, $p < 0.01$), and that in Ost from Weihai increased from 1110 pg g^{-1} dw in 2007 to 2540 pg g^{-1} dw in 2011 ($r^2 = 0.74$, $p = 0.09$). Σ MeO-PBDEs in Ost in Penglai decreased from 1610 pg g^{-1} dw in 2007 to 772 pg g^{-1} dw in 2011 ($r^2 = 0.88$, $p < 0.05$). For other mollusk samples, no gradually declining or rising concentration between 2007 and 2011 was observed. There

was also no obvious temporal trend found for the proportion of OH- and MeO-PBDE congeners in mollusks during the sampling period. To the best of our knowledge, there were no reported data about the temporal trends of OH- and MeO-PBDEs concentrations in marine animals in several years. It is still difficult to clarify the reason why some mollusks showed obvious temporal variation.

3.5. Correlations between PBDEs, MeO-PBDEs and OH-PBDEs

The statistical relationships between PBDEs, OH-PBDEs and MeO-PBDEs were studied to further explore the possible sources of OH-PBDEs and MeO-PBDEs in mollusks. Fig. 5 shows the correlations between target compounds in all mollusk species. In this study, Σ OH-PBDEs and Σ PBDEs ($r = 0.12$, $p = 0.50$), and Σ MeO-PBDEs and Σ PBDEs ($r = 0.28$, $p = 0.052$) showed no significant correlations, suggesting that OH- and MeO-PBDEs did not mainly originate from PBDEs. Σ MeO-PBDEs and Σ OH-PBDEs ($r = 0.49$, $p = 0.001$) showed significant positive correlation. Moreover, individual isomers: 6-OH-BDE-47 and 2'-OH-BDE-68 ($r = 0.84$, $p < 0.001$), 6-MeO-BDE-47 and 2'-MeO-BDE-68 ($r = 0.72$, $p < 0.001$), and 6-OH-BDE-47 and 6-MeO-BDE-47 ($r = 0.51$, $p < 0.001$) showed significant positive correlation. From these results, several assumptions can be obtained as follows: (1) MeO-PBDEs and OH-PBDEs may share a common source in marine environment such as biosynthesis by red algae (Malmvarn et al., 2005); (2) MeO-PBDEs and OH-PBDEs may have similar bioaccumulation potential in mollusks; (3) Biotransformation process may happen between MeO-PBDEs and OH-PBDEs in mollusks. MeO-PBDEs were regarded as an important contributor to the formation of OH-PBDEs (Wan et al., 2009), OH-PBDEs were also found to form MeO-PBDEs via methylation reaction (Wan et al., 2010). 2'-OH-BDE-68 and 2'-MeO-BDE-68 ($r = 0.19$, $p = 0.28$) showed no significant correlation, maybe due to their low interconversion potential in mollusks. No significant linear relationships were found between 6-OH-BDE-47 and precursor BDE-47 ($r = 0.08$, $p = 0.64$), and 6-MeO-BDE-47 and precursor BDE-47 ($r = 0.13$, $p = 0.44$), which further supported the hypothesis that PBDE was not a primary origin for OH- and MeO-PBDEs in mollusks.

Naturally occurring OH- and MeO-PBDEs have a similarity in structure that they all have a methoxyl or hydroxyl group in the *ortho* position relative to the ether bond (Maervoet et al., 2004), such as 6-MeO-BDE-47, 2'-MeO-BDE-68, 6-OH-BDE-47 and 2'-OH-BDE-68 which were the dominant OH- and MeO-PBDE congeners in mollusks. The current thinking is that OH- and MeO-PBDEs found in mollusks are mostly a consequence of accumulation via natural sources in marine environments. However, mutual transformation pathway between OH- and MeO-PBDEs may also play an important role in their occurrence in mollusk species. Marine products are an important part of the diet of coastal residents. Seafood consumption were considered to contribute to the load of OH-PBDEs in biosolids in wastewater treatment plants (Sun et al., 2012b). Seafood processing factory and seafood market have been found as important sources that MeO- and OH-PBDEs entered soil and plants (Sun et al., 2013). Consumption of marine products could represent an important source of OH-PBDEs and MeO-PBDEs exposure for humans. The results in this study are important to help to evaluate the potential exposure risks of OH- and MeO-PBDEs for the environment and human health.

4. Conclusion

In this study, OH-PBDEs and MeO-PBDEs were measured in three mollusk species collected from three coastal cities. Eight MeO-PBDE congeners and two OH-PBDE congeners were identified. 6-MeO-BDE-47, 2'-MeO-BDE-68, 6-OH-BDE-47 and 2'-OH-

Fig. 4. Average Σ MeO-PBDEs concentrations and average Σ OH-PBDEs concentrations among four years in mollusks from different cities.

Fig. 5. Correlation between concentrations (ng g⁻¹ dry weight) of (A): ΣPBDEs and ΣOH-PBDEs, (B): ΣPBDEs and ΣMeO-PBDEs, (C): ΣOH-PBDEs and ΣMeO-PBDEs, (D): 6-OH-BDE-47 and 2'-OH-BDE-68, (E): 6-OH-BDE-47 and 6-MeO-BDE-47, (F): 2'-OH-BDE-68 and 2'-MeO-BDE-68, (G): 6-MeO-BDE-47 and 2'-MeO-BDE-68, (H): BDE-47 and 6-OH-BDE-47, (I): BDE-47 and 6-MeO-BDE-47 in 36 mollusk samples. p Values: Spearman's rank correlation coefficients.

BDE-68 were the predominant contaminants. Species differences in accumulation showed the levels of OH- and MeO-PBDEs were higher in Ost than in Nev and Rap. Different sampling sea area can lead to distinct spatial distribution that OH- and MeO-PBDEs concentrations were generally higher in Weihai than in Tianjin. Temporal trends of OH- and MeO-PBDEs in mollusks of Chinese coastal areas were investigated for the first time in this work. For a portion of mollusks, a declining or rising concentration trend from 2007 to 2011 was observed. Statistical relationships between PBDEs, OH-PBDEs and MeO-PBDEs showed that PBDE was not a primary source for the existence of OH- and MeO-PBDEs in marine environment. Significant correlations were observed between OH-PBDEs and MeO-PBDEs, suggesting they may have mutual transformation processes or share a common source or similar accumulation behavior in mollusks.

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