Environmental Pollution 233 (2018) 604–611

Contents lists available at ScienceDirect

Environmental Pollution

journal homepage: www.elsevier.com/locate/envpol

Hydroxylated and methoxylated polybrominated diphenyl ethers in a marine food web of Chinese Bohai Sea and their human dietary exposure☆

Yanwei Liu [a, b], Jiyan Liu [a, b, *], Miao Yu [a, b], Qunfang Zhou [a, b], Guibin Jiang [a, b]

[a] State Key Laboratory of Environmental Chemistry and Ecotoxicology, Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, Beijing 100085, China
[b] College of Resources and Environment, University of Chinese Academy of Sciences, Beijing 100049, China

ARTICLE INFO

Article history:
Received 19 June 2017
Received in revised form
3 October 2017
Accepted 26 October 2017

Keywords:
OH-PBDEs
MeO-PBDEs
Marine organisms
Trophic behavior
Dietary intake

ABSTRACT

Hydroxylated (OH-) and methoxylated (MeO-) polybrominated diphenyl ethers (PBDEs) have been identified ubiquitous in wildlife and environment. However, understanding on their trophic accumulation and human exposure was hitherto limited. In this study, the occurrences and trophic behaviors were demonstrated for OH- and MeO-PBDEs using the biota samples collected from Dalian, a coastal city near Chinese Bohai Sea. ∑OH-PBDEs exhibited a wider concentration range (<MDL (method detection limit) −25 ng/g dry weight (dw)) compared with ∑MeO-PBDEs (<MDL−2 ng/g dw) and ∑PBDEs (<MDL−2 ng/g dw). The congener profiles and distribution patterns revealed that majority of OH- and MeO-PBDEs in marine biota were naturally produced and largely attributed to preying on lower trophic level biota. Though tertiary consumers accumulated more MeO-PBDEs and PBDEs, these chemicals did not show statistically significant biomagnification in the selected food web. Conversely, trophic dilution was determined for ortho-substituted OH-tetraBDEs and OH-pentaBDEs, revealing that trophic dilution was prevalent for naturally produced OH-PBDEs. The dietary intake evaluation of OH-PBDEs (0.4 ng/kg/d) and MeO-PBDEs (0.8 ng/kg/d) via seafood consumption showed that coastal residents were in higher exposure risks to OH-PBDEs and MeO-PBDEs via the massive seafood consumption.

1. Introduction

Artificially synthesized polybrominated diphenyl ethers (PBDEs) have been widely applied as additive brominated flame retardants (BFRs) in consumer products since 1970s, leading to extensive release into the environment. Due to the characteristics of persistence, bioaccumulation, long-distance transportation and adverse health effects, penta-BDEs and octa-BDEs have been listed as persistent organic pollutants (POPs) in the Stockholm Convention in 2009. As the analogues of PBDEs, hydroxylated (OH-) and methoxylated (MeO-) PBDEs have also received public attentions.

Special concerns have been given to the deleterious health effects and toxicity mechanisms of OH-PBDEs and MeO-PBDEs. *In vivo* and *in vitro* studies have determined that OH-PBDEs were more potent than PBDEs and MeO-PBDEs on some toxicological effects (Wiseman et al., 2011; Kojima et al., 2009; Su et al., 2012). Due to the structural resemblance to thyroid hormones, OH-PBDEs showed high affinities to the thyroid hormone transporter and receptor, disrupting the thyroid hormone homeostasis (Wiseman et al., 2011). Besides, OH-PBDEs can cause steroidogenesis disturbance, endocrine-disrupting effects, developmental toxicity, dioxin-like activity, genotoxicity and neurotoxicity (Kojima et al., 2009; Legradi et al., 2017; Peng et al., 2016; Dingemans et al., 2008). It was considered that some of the serious adverse effects of PBDEs were caused by their hydroxylated metabolites (Wiseman et al., 2011; Kojima et al., 2009; Su et al., 2012). Comparatively, the adverse effects reported for MeO-PBDEs were rare. Dioxin-like activity and endocrine-disrupting effects were also identified for several MeO-PBDE congeners (Kojima et al., 2009; Su et al., 2012).

As far as we know, OH-PBDEs and MeO-PBDEs have no anthropogenic source and are considered as the transformation products of PBDEs. Biotransformation from PBDEs to MeO-PBDEs

☆ This paper has been recommended for acceptance by Maria Cristina Fossi.

* Corresponding author. State Key Laboratory of Environmental Chemistry and Ecotoxicology, Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, Beijing 100085, China.
E-mail address: liujy@rcees.ac.cn (J. Liu).

https://doi.org/10.1016/j.envpol.2017.10.105
0269-7491/

was identified in pumpkin (Yu et al., 2013; Sun et al., 2013c) and maize (Xu et al., 2016). OH-PBDEs were identified as PBDE metabolites in human hepatocytes, rats, mice and fish, with transformation ratios less than 1% (Wiseman et al., 2011; Stapleton et al., 2009). Those biotransformation processes were thought to be catalyzed by cytochrome P450 monooxygenase (CYP) enzymes. On the other hand, OH-PBDEs were able to be generated through oxidation of PBDEs in abiotic environment (Ueno et al., 2008). It was also verified that OH-PBDEs and MeO-PBDEs have natural origins. OH-PBDEs in marine sponge *Dysidea herbacea* were proved to be naturally produced by the symbiotic filamentous cyanobacterium *Oscillatoria spongeliae* (Unson et al., 1994). 6-MeO-BDE-47 and 2′-MeO-BDE-68 were demonstrated as natural products by radiocarbon analysis in a North Atlantic True's beaked whale (Teuten et al., 2005). Interconversion between OH-PBDEs and MeO-PBDEs found in Japanese Medaka, marine sediment, pumpkins and soybeans implied another environmental source (Zhang et al., 2012; Wan et al., 2010; Sun et al., 2014; Pan et al., 2016).

Because of the natural origin in marine environment, OH-PBDEs and MeO-PBDEs were generally at high concentrations in the primary producers and low-rank invertebrates, such as algae, marine sponges, and ascidians (Sionov et al., 2005; Fu et al., 1995; Schumacher and Davidson, 1995; Haraguchi et al., 2010). According to the available data, OH-PBDEs and MeO-PBDEs could be transferred through the food chain to fish, marine mammals and seabirds. However, their trophic transfer behaviors were not accurately evaluated since the primary producers and the low trophic level invertebrates were not concerned enough in the limited numbers of articles (Zhang et al., 2010a, 2012; Kelly et al., 2008; Dahlgren et al., 2016). OH-PBDEs and MeO-PBDEs existed in the seafood would be finally accumulated in human beings, and have been identified in human blood and breast milk samples (Eguchi et al., 2012; Chen et al., 2013; Lacorte and Ikonomou, 2009; Fujii et al., 2014; Wang et al., 2016), with higher concentrations in coastal residents' serum than inland e-waste recycling workers' (Eguchi et al., 2012). It has been found that environmental pollution and human exposure to OH-PBDEs and MeO-PBDEs around coastal areas were mainly attributed to the processing and consumption of tons of seafoods (Sun et al., 2013a, 2013b). Wang et al. (2011) found that marine fish contributed to higher dietary intakes of OH-PBDEs and MeO-PBDEs than freshwater fish (Wang et al., 2011). However, there is no scientific estimation on the dietary intakes and the human health risks of OH-PBDEs and MeO-PBDEs via various seafood consumption for coastal residents.

In this work, the frequently detected OH-PBDEs, MeO-PBDEs and PBDEs in the marine environment of Bohai Sea (Zhang et al., 2010a, 2012; Kelly et al., 2008; Sun et al., 2013a) were analyzed in marine algae, invertebrates and fish species. Our objectives were to i) characterize their distribution patterns in different marine organisms collected from Bohai Sea, ii) investigate their trophic transfer behaviors, and iii) estimate human dietary intakes of these compounds via seafood consumption. The contributions of the primary producers and low trophic level invertebrates to these compounds' fates were particular focused and evaluated in the selected food web.

2. Materials and methods

2.1. Chemicals and reagents

Standards of target compounds included ten OH-PBDE standards (50 μg/mL for 5-OH-BDE-47, 3′-OH-BDE-28 and 3-OH-BDE-47; 10 μg/mL for 2′-OH-BDE-68, 6-OH-BDE-85, 4-OH-BDE-42, 4′-OH-BDE-49, 6-OH-BDE-47, 5′-OH-BDE-99 and 6′-OH-BDE-99), ten MeO-PBDE standards (50 μg/mL for 5-MeO-BDE47, 3′-MeO-BDE28 and 3-MeO-BDE47; 10 μg/mL for 2′-MeO-BDE-68, 6-MeO-BDE-47, 4′-MeO-BDE-49, 4-MeO-BDE-42, 6′-MeO-BDE-99, 5′-MeO-BDE-99 and 6-MeO-BDE-85) and seven PBDE standards (50 μg/mL for BDE-28, BDE-47, BDE-66, BDE-99, BDE-85, BDE-154, BDE-153). BDE-75 (50 μg/mL) and ^{13}C-6-OH-BDE-47 (50 μg/mL) were selected as surrogated standards for PBDEs, MeO-PBDEs and OH-PBDEs. All standards were purchased from AccuStandard (New Haven, CT, USA) and Wellington (Guelph, ON, Canada).

Acetonitrile (ACN), methyl *tert*-butyl ether (MTBE) and 2-propanol were of HPLC grade. Acetone, hexane (HX) and dichloromethane (DCM) were of pesticide grade. All solvents were purchased from J. T. Baker (Phillipsburg, NJ, USA). Milli-Q water (18.3 MΩ cm) was generated by a Milli-Q system (Millipore, Billerica, MA). Silica gel (100–200 mesh size) was purchased from Merck (Darmstadt, Germany). Analytical reagent grade anhydrous sodium sulfate was purchased from Sinopharm Chemical Reagent, Inc. (Beijing, China). Silica gel and anhydrous sodium sulfate were heated at 140 °C for 7 h and 660 °C for 6 h before use, respectively.

2.2. Sample collection and preparation

Marine biological samples of Bohai Sea were collected from costal area of Dalian in 2012. A total of 20 marine species were involved, including five species of marine fish, ten species of invertebrates and five species of algae. The details on organism species, sample number, trophic levels (TL), water contents (water %), lipid contents (lipid%), and stable isotope ratios were shown in Table S1. Among all the selected seafood types, the marine species of fish, crab, shrimp, cephalopod, bivalve and algae were the seafood most commonly consumed by local residents. The collected samples were immediately transported to laboratory on ice and cleaned by water. Stainless steel scalpel blades were used to get the target tissue, including flesh of fish, soft tissue of invertebrates and the whole algae. Wet tissues of several individual organisms were then freeze-dried and homogenized to form one composite sample. Each composite sample was formed from a certain number of individuals of algae, invertebrates and fish. Finally, samples were stored at −20 °C until analysis. All the tools were rinsed by acetone between samples to avoid cross contamination.

The sample extraction and purification method adopted in current study showed good recoveries (71–113%) and repeatability (4–12% RSD) in various matrix (water, soil, sediment, plant, mollusk and fish) (Sun et al., 2012). An amount of 2 g biological samples was successively spiked with surrogate standards and 15 mL of HX/MTBE mixture (1:1, *v/v*). After ultrasonic extraction for 20 min twice, the extracts were combined and dried under a nitrogen flow, re-dissolved in DCM and mixed with 10 g 44% acidified silica gel (H_2SO_4: silica gel = 44:66; *m/m*) to remove lipid. Then the organic phase was loaded on an anhydrous sodium sulfate column to remove water. After rinsing the column, the combined organic phase was concentrated to 2 mL by rotary evaporation. A silica column (5 g, deactivated with 5% water) preconditioned by hexane was used for further cleanup and separation. PBDEs, MeO-PBDEs and OH-PBDEs were successively eluted by 50 mL of 3% DCM in hexane, 60 mL of 20% DCM in hexane and 70 mL of DCM. Finally, the eluents of PBDEs and MeO-PBDEs were combined and concentrated to a final volume of 100 μL in hexane. The eluent of OH-PBDEs was concentrated to 100 μL in acetonitrile.

2.3. Instrumental analysis

Analysis of OH-PBDEs was performed on an Agilent 1290 liquid chromatograph (LC) interfaced with an Agilent 6460 triple-quadrupole mass spectrometer (MS/MS) using electrospray ionization (ESI) in the negative ion multiple-reaction monitoring