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Bioaccumulation characteristics of polybrominated diphenyl ethers in the marine food web of Bohai Bay

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HIGHLIGHTS

- Large differences of the concentration ratios between BDE99 and BDE100 in crab viscera (32:68) and in leg muscle (83:17) was found.
- BDE209 can be biodegraded to BDE47 through BDE154 and BDE99 in marine organism.
- Higher percentage of BDE154 was found in viscera than that in other tissues of marine organism of Bohai Bay.
- The BMF values of individual BDE congeners were different in muscle and viscera within feeding relationships.

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ABSTRACT

In recent years, polybrominated diphenyl ethers (PBDEs) are ubiquitous environmental contaminants, but its bioaccumulation and debromination in biota have remained largely unclear. In this study, we analyzed six PBDEs (BDE47, 99, 100, 153, 154, and 209) in various tissues (i.e., viscera, muscle, and gill) of 11 types of marine organisms including zooplankton, invertebrate and fish. The concentrations of six PBDE including BDE209 in marine organisms ranged from 0.75 to 7.29 ng/g dry weight, BDE209 from 0.46 to 6.78 ng/g dry weight, respectively. BDE209 was the dominant congener in all samples, followed by BDE47. The concentration ratio of BDE47, 99, 154 to ΣPBDEs in various tissues of organisms (i.e., *Rapana venosa*, shrimp, crab, cuttlefish, octopus, *Synechogobius hasta*, tonguefish and wolfish) increased, while the concentration ratio of BDE209 to ΣPBDEs decreased. Large differences of the concentration ratios between BDE99 and BDE100 in tissues of crab was found, ranging from 32:68 in crab viscera to 83:17 in crab leg muscle. Biomagnification factors for individual PBDE congeners ranged from 0.16 to 78.6. In general, the BMFs for BDE209 in muscle were higher than those in viscera within feeding relationships. The study results suggesting BDE209 can be biodegraded to BDE47 through BDE154 and BDE99 in marine organism, its metabolite importantly influenced by organism type not trophic level; higher percentage of BDE154 was found in viscera than that in other tissues in the analyzed marine organisms of Bohai Bay.

1. Introduction

Recent findings indicate that polybrominated diphenyl ethers (PBDEs) are ubiquitous environmental contaminants. The most worldwide used products are the penta-, octa- and decabrominated formulations. The penta- and octaBDE commercial mixtures have been banned in Europe due to their persistence and potential environmental and human health hazard; whereas commercial decaBDE, which is the principal component in flame retardants, is the only product that is still allowed for use after passing the risk assessment test (EUR, 20402 EN), but is restricted to use in electronic devices in the European Union (deWit, 2002; SFT, 2009).

The accumulation and transfer of PBDEs in aquatic food webs is an important criterion for assessing its ecological risk. The previous studies reported the accumulation of PBDEs in aquatic food webs, but the conclusions varied (Guo et al., 2008; Kuo et al., 2010; Wan et al., 2008; Hu et al., 2010; Law et al., 2006; and Kelly et al., 2008). For example, Guo et al. (2008) reported that the PBDE concentrations based on dry weight in fish tissues followed

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the sequence of liver > gill > skin > gastrointestinal tract and muscle, while Kuo et al. (2010) reported that there were no significant differences in PBDE concentrations based on lipid weight between liver and muscle, within fish species. In addition, Wan et al. (2008) and Hu et al. (2010) reported some PBDE congeners had trophic magnification in a marine food web of Bohai Bay and a freshwater food chain of Baiyangdian Lake, North China, also Law et al. (2006) reported that BDE 47 and BDE 209 had trophic magnification in a freshwater food web from Lake Winnipeg. Others (Kelly et al., 2008, Kuo et al., 2010) exhibited the absence of biomagnification for BDE209 in Canadian Arctic marine food web and in a food web of Lake Michigan. In recent years, it has been reported BDE209 can be metabolically transformed and degradation to lower brominated congeners (Stapleton et al., 2004, 2005, 2006; Kierkegaard et al., 1999). Kierkegaard et al. (1999) reported that BDE209 may be metabolized to the hexa and nona congeners by trout, and Labandeira et al. (2007) found that BDE209 was susceptible to accumulate in organisms in lower trophic level; Also, Bezres-Cruz et al. (2004) studied the solar photodecomposition of BDE209, they found that BDE209 transformed to BDE47 through primary intermediates (BDE206, 207, 197, 196, 183, 154, 153, 138, 100, 99, 85). Despite these previous efforts, bioaccumulation and debromination of PBDEs in biota have remained largely unclear. Because most previous studies have focused on fish muscle and liver, the available data are limited in addressing these issues. In addition, lipid content, depuration rates, size and food chain length and structure, as well as the contaminant levels in different tissues, have also been shown to be potential factors influencing bioaccumulation of these contaminants in aquatic organisms. Clearly, the bioaccumulation behavior of PBDEs in biota is complex and needs more field research, especially BDE209.

Bohai Bay is one of the three bays forming the Bohai Gulf, the innermost gulf of the Yellow Sea, in northeast China. It is a shallow water basin with a very mild-slope beach having mostly fine mud bottom. The water body receives both industrial and domestic wastewater discharge from Beijing, Tianjin and Hebei Province. The water exchange between Bohai Bay and Bohai Sea is low, and the physical self-cleaning capacity of Bohai Bay is poor.

Wan et al. (2008) studied the trophodynamics of 13 PBDEs in the marine food web of Bohai Bay with only BDE28, 47, 100 and 119 exhibiting trophic magnification. Unfortunately, BDE209 was not included and trophic magnification factors of PBDEs calculated misleading. So in order to understand the bioaccumulation behavior of PBDEs in marine ecosystems of Bohai Bay, this study was undertaken to determine PBDEs in tissues i.e., viscera (containing liver, intestines and stomach, etc.), muscle, and gill, etc. or whole body of organisms of 11 types of marine organisms including zooplankton, invertebrate and fish from Bohai Bay, to evaluate characteristics of the tissue-specific and species-specific distribution of PBDE, and of bioaccumulation in tissues of viscera and muscle of organisms in marine food web of Bohai Bay.

2. Materials and methods

2.1. Sample collection

Marine organisms were randomly collected by fish trawling method in Beitankou intertidal zones of Bohai Bay (Fig. 1). Sediment samples and overlying waters (about 20 cm above the sediment) in triplicate were also collected. Beitankou, locating in the northern part of Bohai Bay, is a famous fishing port, with other activities including commerce, tourism, catering industry and entertainment. The marine organisms sampled include primary producers (zooplankton, n = 1), seven invertebrate species (bladder moon snail (*Neverita didyma*, n = 30), veined rapa whelk (*Rapana venosa*, n = 20), burrowing shrimp (*Upogebia* sp., n = 20), mantis shrimp (*Oratosquilla oratoria*, n = 20), crab (*Portunus trituberculatus*, n = 5), cuttlefish (*Sepia esculenta*, n = 12), octopus (*Octopus variabilis*, n = 10)), and four fish species (bartail flathead (*Platycephalus indicus*, n = 10), goby (*Synechogobius hasta*, n = 10), tonguefish (*Cynoglossus semilaevis*, n = 10), and wolffish (*Obontamblyopus rubicundus*, n = 10)) were collected in May, 2013. The zooplanton were obtained from vertical tows (bottom to surface) using 160 μm-mesh nets with 37 cm in i.d. and 140 m in length and pooled as one sample. Invertebrates and fish were caught with a bottom trawl, and were dissected to gills, head, muscles and viscera (containing liver, intestines and stomach, etc.). The same tissues were mixed for each species, wrapped with acetone-cleaned aluminum foil, sealed in plastic bags and stored in an ice box. The triplicate water samples (1L of each sample) were pooled as a sample, then filtered with 0.2 μm filter membrane, and the organisms were homogenized with homogenate machine (Waring Blender, 8011s, Waring® Commercial, USA). Suspended particulate matter retained on the filter membrane of overlying water, the sediment (500 g composited triplicates sediments associated with the marine organisms) and the homogenized organism were freeze–drying, and frozen at −20 °C until chemical analysis.

2.2. Analytical procedures

PBDEs in organism, sediment and the particle phase of overlying water were analyzed following USEPA method 1614. Briefly, about 1–2 g freeze–drying samples were homogenized with anhydrous sodium sulfate, spiked with $^{13}C_{12}$-labeled standards (EO-5277, including BDE28, 47, 99, 100, 154, 153, 183, 209, perchursed from Cambridge Isotope Laboratories, Inc. (MA, USA)) and allowed to equilibrate for 12–24 h. Then the samples were extracted with hexane and dichloromethane (v:v = 1:1) by ASE system (ASE300, Dionex, Sunnyvale, CA, USA). After rotated evaporate the extract to 2–3 mL, the extract was purified and fractionated with multi-layer silica gel column and florisil column. All fractions were concentrated and spiked with $^{13}C_{12}$-labeled injection standards (EO-5275, PCB52, 138, perchursed from Cambridge Isotope Laboratories, Inc. (MA, USA)) for HRGC/HRMS analysis. Quantification was performed using an isotope dilution method.

The water content and lipid content were only obtained from zooplankton, *R. venosa* (viscera and muscle), *S. hasta* (gill, viscera and muscle) and wolfish (head, viscera and muscle).

2.3. Quality assurance and quality control

Prior to analysis of the samples, the precision and recovery of PBDEs in muscle tissues of *S. hasta* were performed, with the relative standard deviation (RSD) less than 15%, and the recoveries of seven congeners (BDE47, 99, 100, 154, 153, 183, 209) ranging from 65 to 120%. The method quality control was done by regular analysis of procedural blanks and ongoing precision (RSD < 20%) and recovery. Due to the fact that BDE28 was not separated from BDE31, BDE28 was not determined. The limit of detection was estimated on the S/N ratio of 3:1 in the measurement of spiked samples. The method detection limits (MDLs) of BDE47, 99, 100, 154, 153, 183 and BDE209 ranged from 3 to 6 pg/g dry weight. The method blank values was below the MDLs for BDE47, 99, 100, 153, 154 and 183, however, the value of BDE209 in blank, which ranged from 20 to 40 pg/g dw, was higher than the MDLs (6 pg/g dw).