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Polybrominated diphenyl ethers (PBDEs) in sediments of the coastal East China Sea: Occurrence, distribution and mass inventory

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ABSTRACT

Polybrominated diphenyl ethers (PBDEs) of sixty-three sediment samples from the coastal East China Sea (ECS), extending ~1000 km from the Yangtze River Estuary to the south, were measured. The levels of BDE-209 and $\sum PBDE_7$ (sum of BDE-28, 47, 99, 100, 153, 154, 183) were 0.3–44.6 ng/g (dry weight) and nd-8.0 ng/g, respectively. BDE-209 was the predominant congener, followed by BDE-99/100. This was consistent with the historical and current usage of PBDE mixtures in China. The compositions and distribution of PBDEs suggest that the PBDEs in this area could be mainly from the coastal electronic waste dismantling/recycling and Yangtze River input. The poor correlations between TOC, grain size of sediments with PBDEs imply that the PBDE distribution is more related to their land-based inputs rather than the sediment characters in the area. The coastal ECS is an important sink of PBDEs (7.5 t/yr) in the world.

1. Introduction

Polybrominated diphenyl ethers (PBDEs) have been widely used as flame retardants in the world since 1960s. They are added in various products such as plastics, textiles, electrical components and furnishing foam to reduce the fire hazards by interfering with the combustion of the polymeric materials (Rahman et al., 2001; Siddiqi et al., 2003; Martin et al., 2004). PBDEs have 209 theoretically possible congeners in 10 homologue groups (mono through deca) depending on the numbers and positions of the bromine atoms on the two phenyl rings. PBDEs can be easily escaped into the environment during material crushing because they are dissolved in the polymer without chemical bond (Rahman et al., 2001; Cynthia, 2002). PBDE residues have been now widely found in abiotic matrix (soils, sediments, waters and atmosphere) (Wang et al., 2005, 2007; Cai et al., 2008; Yogui and Sericano, 2009; Ramu et al., 2010) and biotic environment (marine animals, human milk, hair, blood, and adipose tissue) (Hites, 2004; Frederiksen et al., 2009; Kang et al., 2011) in recent years due to the rapid increase of PBDEs usage. Meanwhile, PBDEs have been become a concern in the world due to their persistence, bioaccumulation and toxicities in the environment (Darnerud et al., 2001; Martin et al., 2004).

China has been one of typical countries for producing and consuming PBDEs. The domestic production of brominated flame retardants (BFRs) was up to 10,000 tons with the main product of deca-BDE mixture in 2000 (Mai et al., 2005). In addition, the electronic waste (e-waste) imported into China contributed to be another important source of PBDEs in the environment (Martin et al., 2004; Wang et al., 2005; Leung et al., 2007). The PBDE contaminations have been received a widespread attention since the end of the 1990s in China, especially in some e-waste recyling areas, such as Guiyu (Guangdong province) (Leung et al., 2007) and Taizhou (Zhejiang province) (Zhao et al., 2008, 2009).

There are several reports on the occurrence, distribution and mass inventory of PBDEs in sediments in the coastal sea adjacent China Mainland, such as in the Pearl River Delta and adjacent South China Sea (Mai et al., 2005), Bohai Sea, North China (Pan et al., 2010). The Yangtze River Delta, adjacent to the East China Sea (ECS), was also investigated for PBDEs in surface sediments by Chen et al. (2006). However, to our knowledge, the study of PBDEs in sediments of the coastal ECS off the Zhejiang and Fujian provinces,

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extending ~1000 km from the Yangtze River Estuary (YRE) to the Minjiang River Estuary, has been untouched. The coastal ECS is a major sink of the Yangtze River-derived sediments and associated pollutants into the sea (Guo et al., 2003; Liu et al., 2006). Zhejiang and Fujian provinces are characterized by intensive industrial activities and urban development in China, where there are thousands of fast-growing factories including textiles, furniture, electric, electronic and toys. These factories use lots of PBDEs during their manufacturing processes as flame retardants. More importantly, the coast of Zhejiang province has become a booming recycling center for e-waste. PBDEs were detected in high level in soils, waters (Wang et al., 2011), air (Han et al., 2010), hairs and blood from children (Zhao et al., 2008; Zhang et al., 2011) in Zhejiang province.

The objectives of this study are to determine the levels, distribution and possible sources of PBDEs in sediments of the coastal ECS, and to estimate the mass inventory of PBDEs in the region.

2. Materials and methods

2.1. Sample collection

A detailed description of the sampling sites was shown in Fig. 1. Sixty-three surface sediment samples (0–3 cm) were collected during two cruises conducted by *R/V Dong Fang Hong 2* of the Ocean University of China in 2006 and *Science 1* of Institute of Oceanology, Chinese Academy of Science in 2007. Surface sediment samples were collected using a stainless steel box corer. Sediment samples were wrapped in aluminum foil and stored at −20 °C until analysis.

2.2. Materials

All standard mixtures were purchased from AccuStandard, Inc. (USA). A standard mixture of BDE-17, 28, 47, 66, 71, 85, 99, 100, 138, 153, 154, 183, 190 and 209 was used for quantification. 2,4,5,6-tetrachloro-m-xylene (TCmX) and PCB-209 were added as surrogates. BDE-77 was used as internal standard. Neutral silica gel (80–100 mesh) and alumina (100–200 mesh) were Soxhlet extracted with dichloromethane for 72 h prior to use. Sodium sulfate was baked at 450 °C and stored in sealed containers.

2.3. Extraction and instrumental analysis

In the laboratory, sediment samples were freeze-dried, pulverized, and sieved through 80-mesh stainless steel. About 10 g samples were spiked with TCmX and PCB-209 and extracted with dichloromethane in a Soxhlet apparatus for 48 h. Activated copper was added to remove the sulfur in the samples. The extracts were concentrated and solvent-exchanged to n-hexane using a rotary evaporator. Concentrated extracts were cleaned and fractionated on an 8 mm i.d. alumina/silica column packed, from the bottom to top, with neutral alumina (3 cm, 3% deactivated), neutral silica gel (3 cm, 3% deactivated), 50% (on a weight basis) sulfuric acid silica (2 cm), and anhydrous sodium sulfate (1 cm). The PBDE fraction was eluted with 50 mL of dichloromethane/n-hexane (1:1), and solvent-exchanged to n-hexane and concentrated to 0.5 mL under a gentle nitrogen stream. A known quantity of BDE-77 was added as an internal standard prior to instrumental analysis.

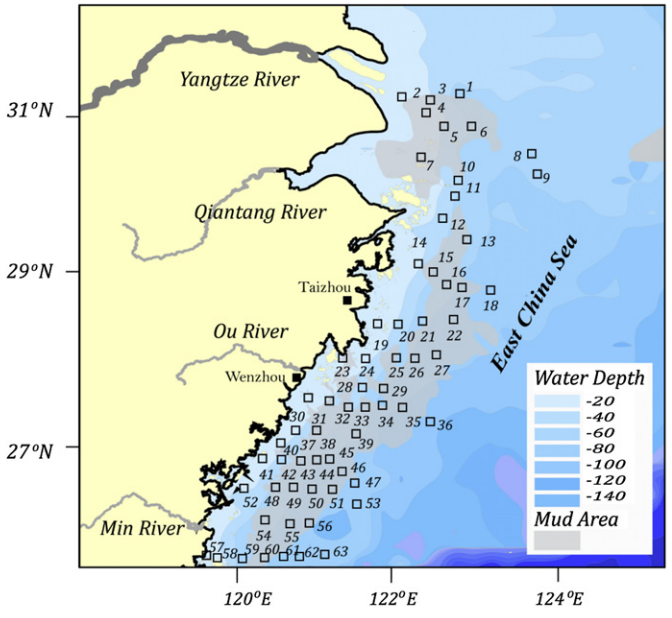

Fig. 1. Locations of the sampling sites in the coastal ECS.

PBDEs were measured by GC–NCI–MS (Agilent GC7890 coupled with 5975C MSD). A DB-5MS capillary column (30 m × 0.25 mm i.d. × 0.25 μm film thickness) was used for the determination for the PBDE congeners excepted for BDE-209. BDE-209 was detected using a DB-5MS column (15 m × 0.25 mm i.d. × 0.25 μm film thickness). The oven temperature began at 130 °C for 1 min, increased to 155 °C at 12 °C/min, 215 °C at 4 °C/min, then up to 300 °C at 3 °C/min and hold for 10 min. Injector temperature was 290 °C. Splitless injection of a 1 μL sample was performed with a 5 min solvent delay time. Ion fragments m/z 79 and 81were monitored for tri-to hepta-BDE, and m/z 79, 81, 486.7 and 488.7 for BDE-209, besides, PCB-209 was monitored using m/z 496, 498 and 500.

2.4. QA/QC

A procedural blank (solvent with a filter paper identical to that used to wrap the sediment) and a spiked blank (14 PBDE congeners spiked into solvent with the filter paper) were processed for each batch of 10 samples for quality assurance and control. No target compounds were detected in procedural blanks, and the mean recovery for spiked blanks was 92.0 ± 6.5%. The average surrogate recoveries in 63 samples were 86.2 ± 12.5% for TCmX and PCB-209. Nominal detection limits were 50 pg/g for BDE-209 and 0.5 pg/g for other individual PBDE congeners.

2.5. Total organic carbon (TOC) and grain size of sediments

After freeze-dried and pulverized, the samples for TOC were treated with 4 N HCl to remove carbonate, and then dried 12 h at 60 °C. TOC of the carbonate-free samples were measured in duplicates in a Vario EL-III Elemental Analyzer. Replicate analysis of one sample ($n = 8$) gave a precision of ±0.02 wt % for TOC. The sample for grain size analysis was determined using a laser Particle Size Analyzer (Mastersizer 2000, Malven Instruments Ltd., UK). The particle sizes were <4 μm for clay, 4–63 μm for silt and >63 μm for sand. The relative error of the duplicate samples was less than 3% ($n = 6$).

3. Results and discussion

3.1. Occurrence

The detection frequencies and concentrations of PBDE congeners in sediments of the coastal ECS were summarized in Table 1. Eight PBDE congeners were detected as followed: BDE-28, 47, 99, 100, 153, 154, 183 and 209. BDE-209 was detected at all sites, followed by BDE-47 with the detection frequencies of 84%. BDE-183 was the least detected congener (29%). High detection frequencies of BDE-209 and 47 indicated that the two PBDE congeners had a widespread distribution in sediments of the coastal ECS. Concentrations of $\sum$PBDE$_7$ (sum of BDE-28, 47, 99, 100, 153, 154, 183) ranged from nd (not detected) to 8.0 ng/g, with an average of

Table 1
Detection frequencies and concentrations of PBDE congeners in the coastal ECS sediments.

PBDE congeners	Detection frequencies (%)	Concentrations (ng/g)		
		Max	Min	Mean
BDE-28	76	1.2	nd[a]	0.1
BDE-47	84	2.7	nd	0.3
BDE-99	62	2.2	nd	0.4
PBD-100	75	3.7	nd	0.4
BDE-153	57	0.7	nd	0.1
BDE-154	71	0.8	nd	0.1
BDE-183	29	0.9	nd	0.07
PBDE-209	100	44.6	0.3	6.4
$\sum$PBDE$_7$		8.0	nd	1.6

[a] nd-not detected.