Environmental Pollution 171 (2012) 155–161

Contents lists available at SciVerse ScienceDirect

Environmental Pollution

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

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

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ARTICLE INFO

Article history:
Received 17 May 2012
Received in revised form
23 July 2012
Accepted 26 July 2012

Keywords:
PBDEs
Distribution
Sources
Deposition flux
The coastal East China Sea

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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http://dx.doi.org/10.1016/j.envpol.2012.07.039

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.

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.

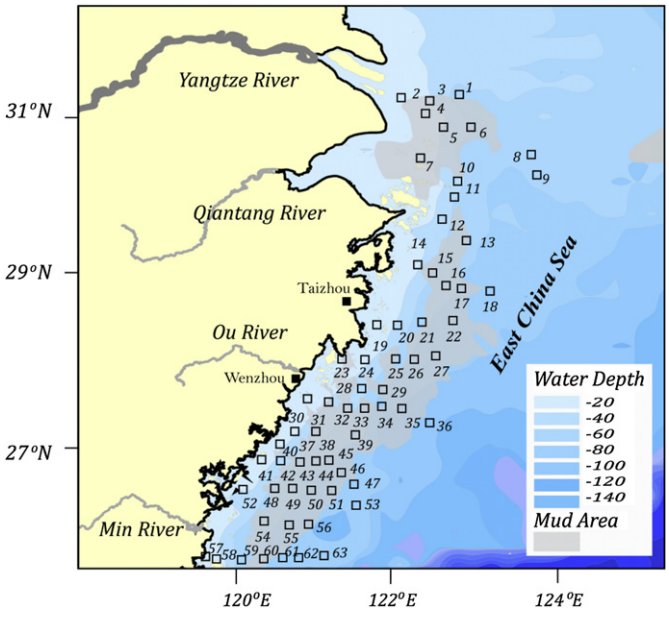

Fig. 1. Locations of the sampling sites in the coastal ECS.

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.

1.6 ± 1.4 ng/g. BDE-209 was found to be much more abundant than any other PBDE congeners with the concentrations ranging from 0.3 to 44.6 ng/g with a mean of 6.4 ± 4.8 ng/g.

Comparison of the PBDE concentrations in the coastal ECS sediments with other areas in the world is shown in Table 2. Although the detected PBDE congener numbers and kinds were somewhat different in these studies, BDE-47, 99, 100 and 209 were widely found in most study areas. Table 2 showed that the levels of BDE-209 in this study were lower than those in the Pearl River and Macao Coast South China (Mai et al., 2005), similar to the Yangtze River Delta and Xiamen offshore areas, East China (Chen et al., 2006; Li et al., 2010), while slightly higher than the Bohai Sea, North China (Pan et al., 2010), South China Sea (Mai et al., 2005) and Southwest Taiwan (Jiang et al., 2011). $\sum PBDE_7$ concentrations were lower than those in the Pearl River and Macao Coast (Mai et al., 2005), compared with the South China Sea (Mai et al., 2005) and Xiamen offshore areas (Li et al., 2010), and higher than the Bohai Sea (Pan et al., 2010), Yangtze River Delta (Chen et al., 2006) and Southwest Taiwan (Jiang et al., 2011). Compared with other area in the world, BDE-209 levels in sediments of the coastal ECS were significantly lower than those detected in the coastal waters of Korea (Moon et al., 2007b), Busan bay, Ulsan bay, Jinhae bay (Moon et al., 2007a), the Great Lakes (except Superior Lake) in USA (Song et al., 2005a, 2005b), while slightly higher than Superior Lake (Song et al., 2004). $\sum PBDE_7$ concentrations were higher than those reported in the coastal waters of Korea (Moon et al., 2007b), comparable to Busan bay, Ulsan bay, Jinhae bay (Moon et al., 2007a) and the Great Lakes in USA (Song et al., 2004, 2005a, 2005b).

3.2. Distribution

The distributions of BDE-209 and $\sum PBDE_7$ were shown in Fig. 2. Generally, there was a decreasing trend both for the BDE-209 and $\sum PBDE_7$ concentrations from the inshore areas toward the outer shelf in ECS (Fig. 2). The highest concentrations of BDE-209 and $\sum PBDE_7$ were observed at sites 20 and 40, respectively, which were close to the middle and northern Zhejiang province coast. Actually, Zhejiang province is a major manufactures center of textiles, toys and electronic in China. These factories used large amount of PBDEs as flame retardants. PBDEs could be probably released into the environment during the production process. Moreover, some coastal cities in Zhejiang province such as Taizhou and Wenzhou were well known as e-waste recycling factories (Fig. 1). Han et al. (2009) detected 13 PBDE congeners in the atmosphere of a major e-waste recycling area in Taizhou city, with the levels of 0.5 ng/m^3 in summer and 1.7 ng/m^3 in winter, which were about 7 times higher than that of the reference urban site without e-waste recycling. Soils and sediments collected from Fengjiang and Liushi (two typical e-waste cycling areas located in Taizhou and Wenzhou cities) were also found higher levels of PBDEs, which were several hundred magnitudes higher than the highest PBDE value in Ningbo city in Zhejiang province (Wang et al., 2011). The released PBDEs could be easily congregated in sediments of the coastal ECS by surface runoff and atmosphere deposition due to the proximity of the land-based contaminant inputs from those e-waste recycling areas.

Relatively higher levels of PBDEs were also observed in sediments of the YRE and the area to the south of the Hangzhou Bay, where is a significant deposition center of Yangtze-derived fine-grained sediments in the ECS (Liu et al., 2006). This suggests that PBDEs in the coastal ECS sediments could be partly attributed to the Yangtze River input. Furthermore, the levels of $\sum PBDE_7$ showed a gradual decreasing trend from the north to the south in the coastal mud areas, especially for the lower brominated BDE congeners (BDE-28 and 47 respectively) (Figs. 2b and 5). This loss of PBDEs could be attributed to the re-suspension, long-range transport and deposition of sediments from the north to the south in the coastal ECS since the lower brominated BDE congeners usually have larger aqueous solubility and smaller octanol–water partition coefficients (K_{OW}) (Tittlemier et al., 2002; Braekevelt et al., 2003). It has been reported that approximately 40% of the sediments discharged from the Yangtze River is deposited in the estuarine area north of 30° N; and the remaining 32% is believed to have been re-suspended in the YRE and transported southward, accumulating in the inner ECS shelf in winter triggered by the East Asian Monsoon (DeMaster et al., 1985; Liu et al., 2007).

It has been indicated that the TOC and grain size of sediments are two significant factors controlling the spatial distribution of POPs in the aquatic environment (Pan et al., 2010; Zheng et al., 2011). Similar to other POPs, PBDEs can be readily adsorbed on the particulate matters due to their high hydrophobicities (Rahman et al., 2001). However, very poor correlations were observed between TOC, median diameter (MD) of grain size with BDE-209 and $\sum PBDE_7$ (Fig. 3), implying that the spatial distribution of BDE-209 and $\sum PBDE_7$ were not constrained by the TOC or grain size of sediments. The similar results were reported in the South China Sea (Mai et al., 2005) and coastal locations in Korea (Moon et al., 2007b). In our previous studies, the poor correlations between TOC and OCPs in sediments of the coastal ECS were also found because of their heterogeneous sources and sedimentary process (Hu et al., 2011). The distribution of PBDEs

Table 2
Comparison of PBDEs concentrations in sediments of the coastal ECS with concentrations reported in other areas in the world.

Locations	Sample numbers	PBDE congeners numbers	BDE-209 (ng/g)	$\sum$PBDEs[a] (ng/g)	References
The coastal East China Sea	63	8	0.3–44.6	nd–8.0	This study
Bohai Sea	44	8	1.8–15.1	0.2–0.9	(Pan et al., 2010)
South China Sea	14	10	0.4–9.1	0.04–4.5	(Mai et al., 2005)
Pearl River	11	10	26.3–3580	1.1–49.3	
Macao Coast	9	10	6.7–149	0.6–41.3	
Yangtze River Delta	32	13	0.2–94.6	nd–0.6	(Chen et al., 2006)
Xiamen offshore areas	12	8	0.1–70.1	0.3–6.4	(Li et al., 2010)
Southwest Taiwan	57	14	nd–6.3	nd–1.8	(Jiang et al., 2011)
Coastal waters of Korea	25	20	0.2–493	0.05–0.9	(Moon et al., 2007b)
Busan bay	38	20	14.4–2253	0.38–5.9	(Moon et al., 2007a)
Ulsan bay	42	20	3.4–286	0.1–6.9	
Jinhae bay	31	20	2.0–145	0.03–6.0	
Superior Lake	6	10	4.3–17.5	0.5–3.1	(Song et al., 2004)
Huron Lake and Michigan Lake	6	10	21.5–95.6	1.0–4.0	(Song et al., 2005b)
Erie Lake and Ontario Lake	4	10	50.2–242	1.8–6.3	(Song et al., 2005a)

[a] The sum of all targeted PBDE congeners except BDE-209.

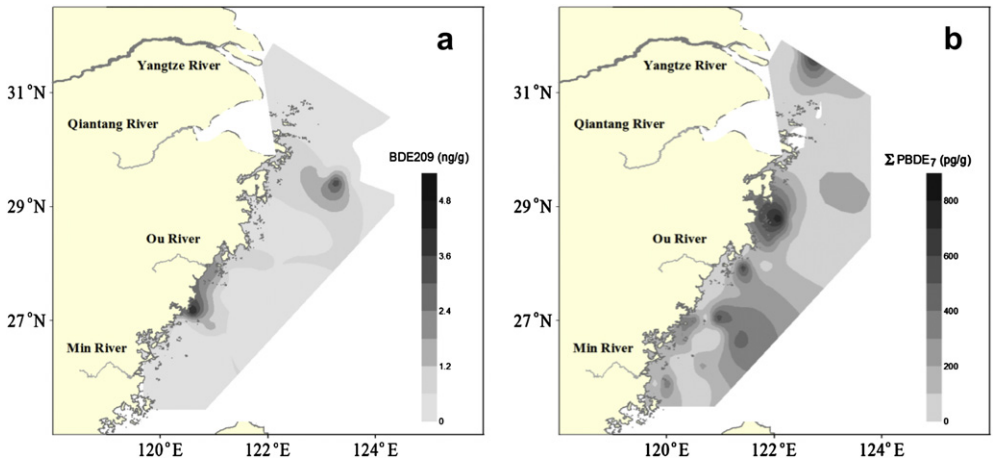

Fig. 2. Distributions of BDE-209 (a) and $\sum PBDE_7$ (b) in sediments of the coastal ECS.

in this study could be influenced by the intensive land-based inputs from the coastal e-waste cycling areas to their adjacent sea, and the degradation and re-apportionment of PBDEs in water column during re-suspension and long-range transport processes of sediments from the north to the south in the coastal ECS, possibly inducing the wakening of the effects of TOC and grain size of sediments on the distribution of PBDE congeners in the area.

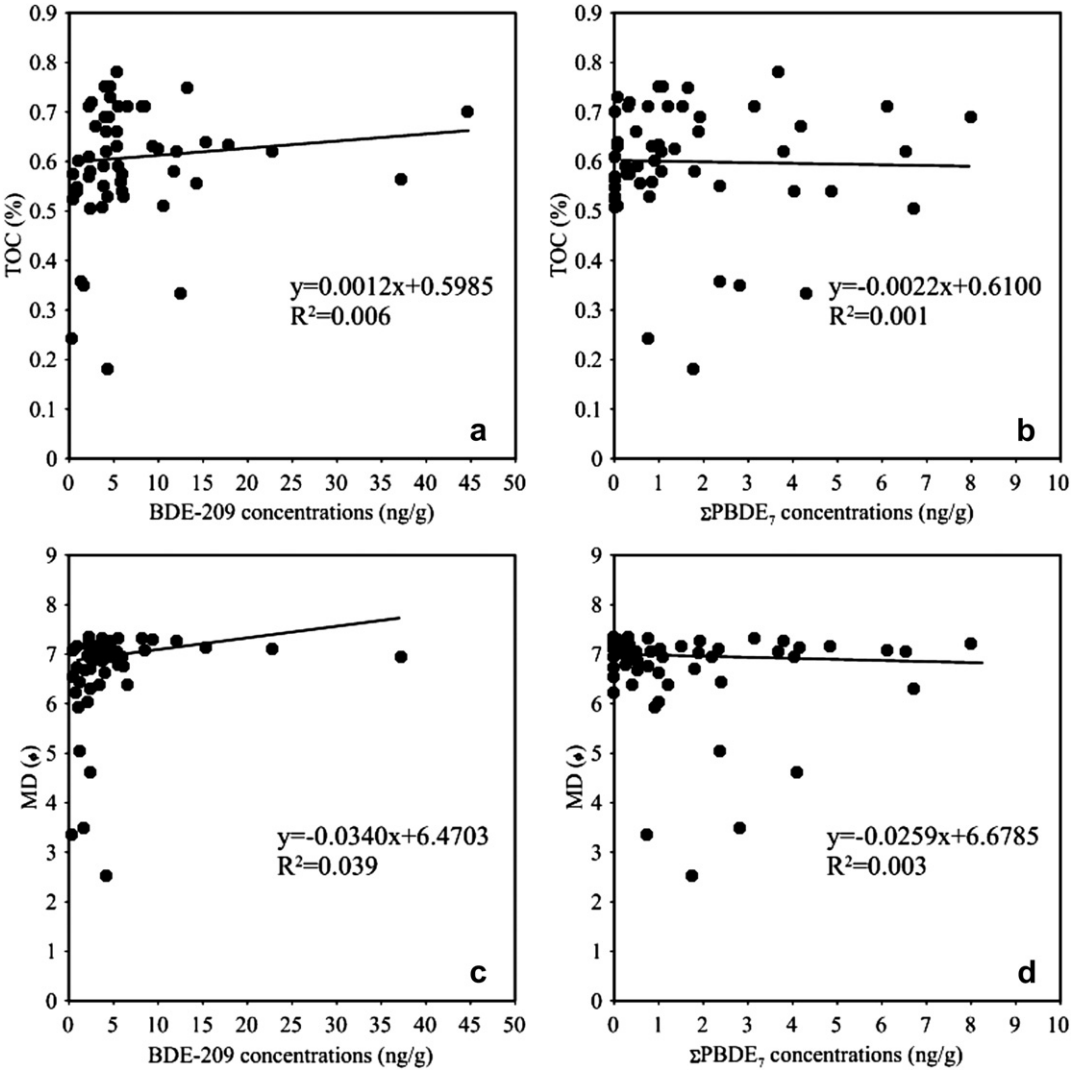

Fig. 3. Correlations of TOC with BDE-209 (a) and $\sum PBDE_7$ (b), and correlations of median diameter (MD) with BDE-209 (c) and $\sum PBDE_7$ (d) in sediments of the coastal ECS.

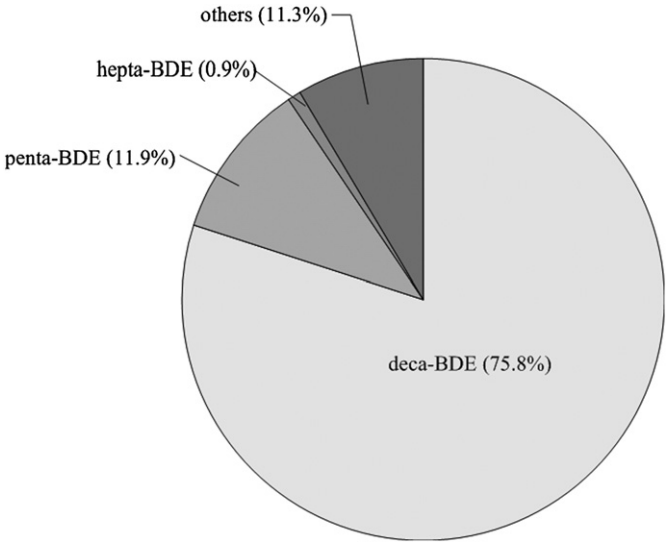

Fig. 4. Percentages of PBDE congeners of the measured PBDEs in sediments of the coastal ECS.

3.3. Congener profiles of PBDEs and potential sources

Generally, PBDEs are commercially available in three technical mixtures as penta-, octa- and deca-BDE mixtures (Siddiqi et al., 2003). Penta-BDE is a mixture of penta-BDE (50–62%), tetra-BDE (24–38%) and hexa-BDE (4–8%), while octa-BDE contains hepta-BDE (43–44%), octa-BDE (31–35%), hexa-BDE (10–12%) and nona-BDE (9–11%). Deca-BDE is constituted with BDE-209 (97–98%) (Darnerud et al., 2001). In this study, the congener pattern was dominated by deca-BDE (BDE-209), constituting between 16.3% and 100% with a mean value of 75.8 ± 19.9% of the total PBDE concentrations (Fig. 4). The predominance of deca-BDE was reported in various media of the environment, such as the sediments, water, human and animals in China (Wang et al., 2009, 2011; Zhang et al., 2011). According to the statistics, WTO reported that the annual global consumption of PBDEs was about 40,000 tons, of which approximately 10% was commercial penta-, 15% octa-, and 75% deca-BDE (Rahman et al., 2001). As penta- and octa-BDE were banned in some western countries, deca-BDE has become the more prevalent product widely used in textiles and electronics equipment due to their lower toxicity compared with penta- and octa-BDE (La Guardia et al., 2006). China, as a large consumption country of deca-BDE, was usually dominant in the occurrence of BDE-209 in the environment (Cai et al., 2008).

The mean value of other PBDE congeners, calculated as percent of $\sum$PBDE$_7$, were as followed: BDE-99, 20.9 ± 17.4% (nd-74.9%); BDE-100, 20.7 ± 17.3% (nd-96.0%); BDE-47, 15.1 ± 13.5% (nd-72.7%); BDE-28, 8.9 ± 7.0% (nd-44.5%); BDE-153, 8.3 ± 9.2% (nd-48.6%); BDE-154, 7.7 ± 8.2% (nd-85.2%); BDE-183, 4.2 ± 6.8% (nd-30.2%). As shown in Fig. 5, percentages of those 7 PBDE congeners varied with sampling sites. BDE-99 and 100 were dominant in most sampling sites. On the whole, BDE-99 and 100 (penta-BDE), the main constituents of the technical penta-BDE mixture, accounted for 48.4% of $\sum$PBDE$_7$, except nine sampling sites where the $\sum$PBDE$_7$ were not detected. By a comparison, BDE-183 (hepta-BDE), a major component of technical octa-BDE mixture, was not largely detected in this area. The higher brominated BDE congeners can be degraded to lower brominated BDE congeners, as a result, the degradation of higher brominated BDE congeners might be one of the significant source for the lower brominated BDE congeners in some areas (He et al., 2006). However, there were poor correlations among PBDE congeners ($R^2 < 0.4$) (Table 3), implying that the degradation of higher brominated BDE congeners was not a notable source for other lower brominated BDE congeners detected. Thus, the direct

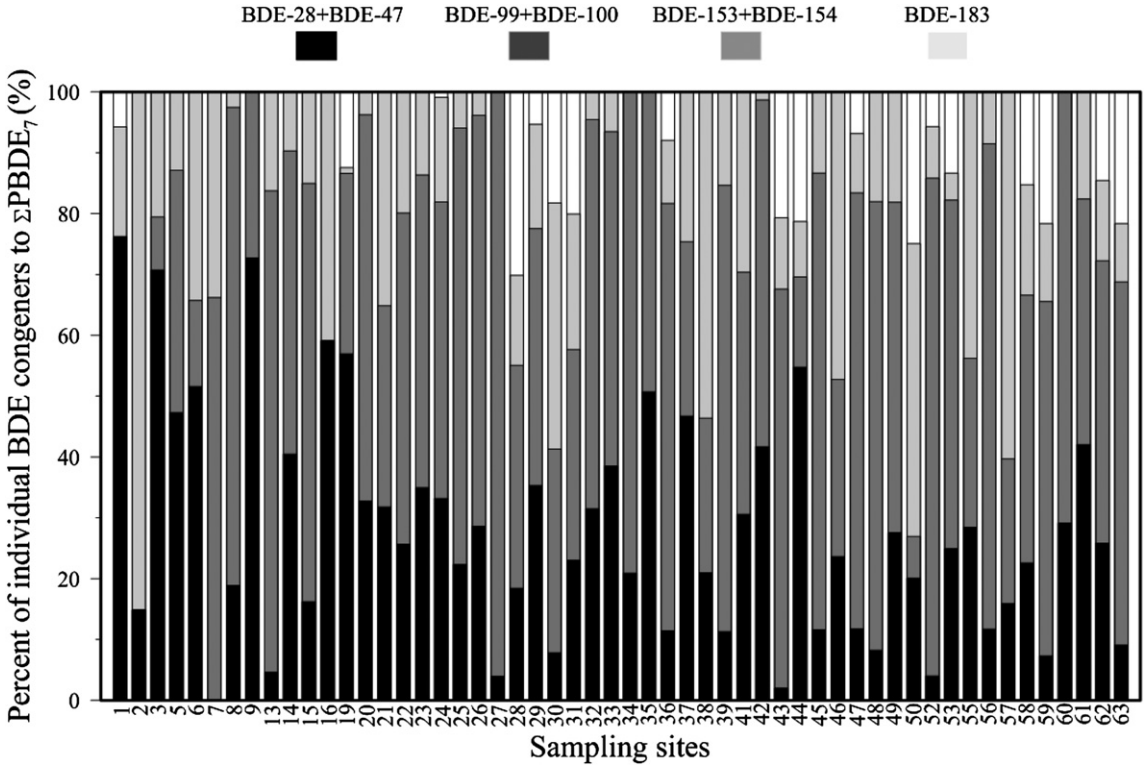

Fig. 5. Percentages of tri-hepta-BDE congeners to $\sum$PBDE$_7$ in sediments of the coastal ECS (except nine sample sites where the $\sum$PBDE$_7$ were not detected in the area).

Table 3
Pearson correlation coefficients among PBDE congeners.

	BDE-28	BDE-47	BDE-99	BDE-100	BDE-153	BDE-154	BDE-183	BDE-209
BDE-28	1							
BDE-47	0.256	1						
BDE-99	0.290	0.118	1					
BDE-100	0.394	0.130	0.275	1				
BDE-153	0.204	0.074	0.166	0.068	1			
BDE-154	0.060	0.107	0.066	0.042	0.117	1		
BDE-183	0.001	0.026	0.100	0.021	0.008	0.006	1	
BDE-209	0.022	0.022	0.004	0.008	0.009	0.003	0.003	1

inputs of technical deca and penta-BDE mixtures rather than octa-BDE mixture were two probably major sources in the coastal ECS sediments.

3.4. Deposition flux

Surface sediments in the coastal ECS are dominated by fine-grained mud except for relict sands on the out mud areas (Liu et al., 2007). This could induce an accumulation of PBDEs in the coastal ECS sediments owing to strong adsorption ability for PBDEs. The mass inventory of PBDEs was estimated according to Chen et al. (2006b). The study area was divided into 63 parts, and make sure each of the 63 sampling sites was allocated in the center of own part. The sediment concentrations from this site were chosen as representative for the entire compartment. The mass inventory (I) was estimated according to the following equation:

$$I = CAdp;$$

Where C is the concentration of PBDEs in the sediments; A is the water area; d is the recommended sediment dry density of 1.2 g/cm^3 according to Liu et al. (2007); and p is the sedimentary rate. The corresponding sedimentary rate value of each site was used according to DeMaster et al. (1985) and Liu et al. (2006).

The total deposition fluxes of PBDEs estimated for the coastal ECS with area of 78,000 km^2 were 5.6 t/yr for BDE-209 and 1.9 t/yr for $\sum$PBDE$_7$, respectively. It was reported that the deposition flux in the Bohai Sea with area of 77,000 km^2 was 11–19 t/yr for BDE-209 and 1.3–1.9 t/yr for $\sum$PBDE$_7$ (Pan et al., 2010). Consequently, the flux of BDE-209 in the coastal ECS was lower than that in the Bohai Sea, and the reverse was true for the $\sum$PBDE$_7$. Compared with the $\sum$PBDE$_9$ flux (0.01 t/yr for Superior, 0.04 t/yr for Michigan, 0.03 t/yr for Huron, 0.06 t/yr for Erie and 0.03 t/yr for Ontario) and BDE-209 flux (0.10 t/yr for Superior, 0.75 t/yr for Michigan, 0.58 t/yr for Huron, 1.62 t/yr for Erie and 1.31 t/yr for Ontario) in sediments of the Great Lakes in the US (Li et al., 2006), it is indicated that the coastal ECS should be a significant sink of PBDEs in the world.

4. Conclusions

The high levels of PBDEs in sediments were observed in the inshore area off the Zhejiang province, the YRE and the area to the south of the Hangzhou Bay. These suggest that the local sources from the e-waste recycling areas and the Yangtze River input could be the main sources for PBDEs in the coastal ECS. Meanwhile, there was a slight decrease for $\sum$PBDE$_7$ level in sediments from the north to the south which could be attributed to their different solubility in water. The technical deca and penta-BDE mixtures rather than octa-BDE mixture were two major sources in the coastal ECS. The distribution of PBDEs was not controlled by the sediment characters in the region. The total deposition flux of PBDEs for the coastal ECS with area of 78,000 km^2 was estimated to be 5.6 t/yr for BDE-209 and 1.9 t/yr for $\sum$PBDE$_7$, respectively.

Acknowledgments

This work was supported by the Key Laboratory of Marine Hydrocarbon Resources and Environmental Geology, Ministry of Land and Resources of China (No: GZH201100203), and the Natural Science Foundation of China (NSFC) (Nos: 41076015, and 41103046). We wish to thank the crew of *R/V Dong Fang Hong 2* of the Ocean University of China and *Science 1* of Institute of Oceanology for collecting the sediment samples.

References

Braekevelt, E., Tittlemier, S.A., Tomy, G.T., 2003. Direct measurement of octanol–water partition coefficients of some environmentally relevant brominated diphenyl ether congeners. Chemosphere 51, 563–567.
Cai, Q.Y., Mo, C.H., Wu, Q.T., Katsoyiannis, A., Zeng, Q.Y., 2008. The status of soil contamination by semivolatile organic chemicals (SVOCs) in China: a review. Science of the Total Environment 389, 209–224.
Chen, S.J., Gao, X.J., Mai, B.X., Chen, Z.M., Luo, X.J., Sheng, G.Y., Fu, J.M., Zeng, E.Y., 2006. Polybrominated diphenyl ethers in surface sediments of the Yangtze River Delta: levels, distribution and potential hydrodynamic influence. Environmental Pollution 144, 951–957.
Chen, S.J., Luo, X.J., Mai, B.X., Sheng, G.Y., Fu, J.M., Zeng, E.Y., 2006b. Distribution and mass inventories of polycyclic aromatic hydrocarbons and organochlorine pesticides in sediments of the Pearl River Estuary and the Northern South China Sea. Environmental Science & Technology 40, 709–714.
Cynthia, A. d.W., 2002. An overview of brominated flame retardants in the environment. Chemosphere 46, 583–624.
Darnerud, P.O., Eriksen, G.S., Jóhannesson, T., Larsen, P.B., Viluksela, M., 2001. Polybrominated diphenyl ethers: occurrence, dietary exposure, and toxicology. Environmental Health Perspectives 109, 49–68.
DeMaster, D.J., McKee, B.A., Nittrouer, C.A., Qian, J.C., Cheng, G.D., 1985. Rates of sediment accumulation and particle reworking based on radiochemical measurements from continental shelf deposits in the East China Sea. Continental Shelf Research 4, 143–158.
Frederiksen, M., Vorkamp, K., Thomsen, M., Knudsen, L.E., 2009. Human internal and external exposure to PBDEs – a review of levels and sources. International Journal of Hygiene and Environmental Health 212, 109–134.
Guo, Z.G., Yang, Z.S., Fan, D.J., Pan, Y.J., 2003. Seasonal variation of sedimentation in the Changjiang Estuary mud area. Journal of Geographic Science 13, 348–354.
Han, W.L., Feng, J.L., Gu, Z.P., Chen, D.H., Wu, M.H., Fu, J.M., 2009. Polybrominated diphenyl ethers in the atmosphere of Taizhou, a major e-waste dismantling area in China. Bulletin of Environmental Contamination and Toxicology 83, 783–788.
Han, W.L., Feng, J.L., Gu, Z.P., Wu, M.H., Sheng, G.Y., Fu, J.M., 2010. Polychlorinated biphenyls in the atmosphere of Taizhou, a major e-waste dismantling area in China. Journal of Environmental Sciences 22, 589–597.
He, J.Z., Robrock, K.R., Alvarez-Cohen, L., 2006. Microbial reductive debromination of polybrominated diphenyl ethers (PBDEs). Environmental Science & Technology 40, 4429–4434.
Hites, R.A., 2004. Polybrominated diphenyl ethers in the environment and in people: a meta-analysis of concentrations. Environmental Science & Technology 38, 945–956.
Hu, L.M., Lin, T., Shi, X.F., Yang, Z.S., Wang, H.J., Zhang, G., Guo, Z.G., 2011. The role of shelf mud depositional process and large river inputs on the fate of organochlorine pesticides in sediments of the Yellow and East China Seas. Geophysical Research Letters 38, L03602.
Jiang, J.J., Lee, C.L., Fang, M.D., Ko, F.C., Baker, J.E., 2011. Polybrominated diphenyl ethers and polychlorinated biphenyls in sediments of southwest Taiwan: regional characteristics and potential sources. Marine Pollution Bulletin 62, 815–823.
Kang, Y., Wang, H.S., Cheung, K.C., Wong, M.H., 2011. Polybrominated diphenyl ethers (PBDEs) in indoor dust and human hair. Atmospheric Environment 45, 2386–2393.

La Guardia, M.J., Hale, R.C., Harvey, E., 2006. Detailed polybrominated diphenyl ether (PBDE) congener composition of the widely used penta-, octa-, and deca-PBDE technical flame-retardant mixtures. Environmental Science & Technology 40, 6247–6254.

Leung, A.O.W., Luksemburg, W.J., Wong, A.S., Wong, M.H., 2007. Spatial distribution of polybrominated diphenyl ethers and polychlorinated dibenzo-p-dioxins and dibenzofurans in soil and combusted residue at Guiyu, an electronic waste recycling site in southeast China. Environmental Science & Technology 41, 2730–2737.

Li, A., Rockne, K.J., Sturchio, N., Song, W.L., Ford, J.C., Buckley, D.R., Mills, W.J., 2006. Polybrominated diphenyl ethers in the sediments of the Great Lakes. 4. Influencing factors, trends, and implications. Environmental Science & Technology 40, 7528–7534.

Li, Q.Z., Yan, C.Z., Luo, Z.X., Zhang, X., 2010. Occurrence and levels of polybrominated diphenyl ethers (PBDEs) in recent sediments and marine organisms from Xiamen offshore areas, China. Marine Pollution Bulletin 60, 464–469.

Liu, J.P., Li, A.C., Xu, K.H., Velozzi, D.M., Yang, Z.S., Milliman, J.D., DeMaster, D.J., 2006. Sedimentary features of the Yangtze River-derived along-shelf clinoform deposit in the East China Sea. Continental Shelf Research 26, 2141–2156.

Liu, J.P., Xu, K.H., Li, A.C., Milliman, J.D., Velozzi, D.M., Xiao, S.B., Yang, Z.S., 2007. Flux and fate of Yangtze River sediment delivered to the East China Sea. Geomorphology 85, 208–224.

Mai, B.X., Chen, S.J., Luo, X.J., Chen, L.G., Yang, Q.S., Sheng, G.Y., Peng, P.G., Fu, J.M., Zeng, E.Y., 2005. Distribution of polybrominated diphenyl ethers in sediments of the Pearl River Delta and adjacent South China Sea. Environmental Science & Technology 39, 3521–3527.

Martin, M., Lam, P.K.S., Richardson, B.J., 2004. An Asian quandary: where have all of the PBDEs gone? Marine Pollution Bulletin 49, 375–382.

Moon, H.B., Kannan, K., Choi, M., Choi, H.G., 2007a. Polybrominated diphenyl ethers (PBDEs) in marine sediments from industrialized bays of Korea. Marine Pollution Bulletin 54, 1402–1412.

Moon, H.B., Kannan, K., Lee, S.J., Choi, M., 2007b. Polybrominated diphenyl ethers (PBDEs) in sediment and bivalves from Korean coastal waters. Chemosphere 66, 243–251.

Pan, X.H., Tang, J.H., Li, J., Guo, Z.G., Zhang, G., 2010. Levels and distributions of PBDEs and PCBs in sediments of the Bohai Sea, North China. Journal of Environmental Monitoring 12, 1234–1241.

Rahman, F., Langford, K.H., Scrimshaw, M.D., Lester, J.N., 2001. Polybrominated diphenyl ether (PBDE) flame retardants. Science of the Total Environment 275, 1–17.

Ramu, K., Isobe, T., Takahashi, S., Kim, E.Y., Min, B.Y., We, S.U., Tanabe, S., 2010. Spatial distribution of polybrominated diphenyl ethers and hexabromocyclododecanes in sediments from coastal waters of Korea. Chemosphere 79, 713–719.

Siddiqi, M.A., Laessig, R.H., Reed, K.D., 2003. Polybrominated diphenyl ethers (PBDEs): new pollutants–old diseases. Clinical Medicine & Research 1, 281–290.

Song, W.L., Ford, J.C., Li, A., Mills, W.J., Buckley, D.R., Rockne, K.J., 2004. Polybrominated diphenyl ethers in the sediments of the great lakes. 1. Lake superior. Environmental Science & Technology 38, 3286–3293.

Song, W.L., Ford, J.C., Li, A., Sturchio, N.C., Rockne, K.J., Buckley, D.R., Mills, W.J., 2005a. Polybrominated diphenyl ethers in the sediments of the Great Lakes. 3. Lakes Ontario and Erie. Environmental Science & Technology 39, 5600–5605.

Song, W.L., Li, A., Ford, J.C., Sturchio, N.C., Rockne, K.J., Buckley, D.R., Mills, W.J., 2005b. Polybrominated diphenyl ethers in the sediments of the great lakes. 2. Lakes Michigan and Huron. Environmental Science & Technology 39, 3474–3479.

Tittlemier, S.A., Halldorson, T., Stern, G.A., Tomy, G.T., 2002. Vapor pressures, aqueous solubilities, and Henry's law constants of some brominated flame retardants. Environmental Toxicology and Chemistry 21, 1804–1810.

Wang, D.L., Cai, Z.W., Jiang, G.B., Leung, A., Wong, M.H., Wong, W.K., 2005. Determination of polybrominated diphenyl ethers in soil and sediment from an electronic waste recycling facility. Chemosphere 60, 810–816.

Wang, Y.W., Jiang, G.B., Lam, P.K.S., Li, A., 2007. Polybrominated diphenyl ether in the East Asian environment: a critical review. Environment International 33, 963–973.

Wang, Z., Ma, X.D., Lin, Z.S., Na, G.S., Yao, Z.W., 2009. Congener specific distributions of polybrominated diphenyl ethers (PBDEs) in sediment and mussel (Mytilus edulis) of the Bo Sea, China. Chemosphere 74, 896–901.

Wang, J.X., Lin, Z.K., Lin, K.F., Wang, C.Y., Zhang, W., Cui, C.Y., Lin, J.D., Dong, Q.X., Huang, C.J., 2011. Polybrominated diphenyl ethers in water, sediment, soil, and biological samples from different industrial areas in Zhejiang, China. Journal of Hazardous Materials 197, 211–219.

Yogui, G.T., Sericano, J.L., 2009. Polybrominated diphenyl ether flame retardants in the U.S. marine environment: a review. Environment International 35, 655–666.

Zhang, X.Y., Ruan, X.L., Yan, M.C., Zhao, Y.X., Wei, W.J., Qin, Z.F., Yang, Y.J., Xu, H.M., Li, Y., 2011. Polybrominated diphenyl ether (PBDE) in blood from children (age 9–12) in Taizhou, China. Journal of Environmental Sciences 23, 1199–1204.

Zhao, G.F., Wang, Z.J., Dong, M.H., Rao, K.F., Luo, J.P., Wang, D.H., Zha, J.M., Huang, S.B., Xu, Y.P., Ma, M., 2008. PBBs, PBDEs, and PCBs levels in hair of residents around e-waste disassembly sites in Zhejiang Province, China, and their potential sources. Science of The Total Environment 397, 46–57.

Zhao, G.F., Wang, Z.J., Zhou, H.D., Zhao, Q., 2009. Burdens of PBBs, PBDEs, and PCBs in tissues of the cancer patients in the e-waste disassembly sites in Zhejiang, China. Science of the Total Environment 407, 4831–4837.

Zheng, B.H., Zhao, X.R., Liu, L.S., Li, Z.C., Lei, K., Zhang, L., Qin, Y.W., Gan, Z.F., Gao, S.Z., Jiao, L.X., 2011. Effects of hydrodynamics on the distribution of trace persistent organic pollutants and macrobenthic communities in Bohai Bay. Chemosphere 84, 336–341.