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Occurrence of polybrominated diphenyl ethers in fish and shellfish downstream from electronic-waste recycling plants

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Abstract

We measured 39 polybrominated diphenyl ethers (PBDEs) in the muscle tissue of three species of fish (*Sciaenops ocellatus*, *Sparus macrocephalus*, and *Lateolabrax japonicus*) and four species of shellfish (*Tegillarca granosa*, *Cyclina sinensis*, *Sinonovacula constricta*, and *Ostrea cucullata*) that were collected downstream of electronic-waste recycling plants in Taizhou, China. A total of 24 PBDE congeners ($PBDE_{24}$) in the samples were detected. The $\sum PBDE_{24}$ (total PBDE) ranged from 545.4 to 1688.7 ng/kg ww (wet weight). The mean $\sum PBDE_{24}$ concentration was 1382.6 ng/kg ww in fish and 858.1 ng/kg ww in shellfish. The lower brominated congeners were detected at relatively high concentrations in all species. The penta-products, produced from e-waste, were found at relatively low levels. A principal component analysis suggested a significant correlation among di-, tri-, tetra-, and hepta-BDEs for the three species of fish. Similarly, we found a significant correlation between mono- and tri-BDEs in the shellfish. Our results suggested that the processes of PBDE metabolism and elimination were similar in both fish and shellfish. In addition, the primary source of PBDEs appeared to be from the debromination of high brominated PBDEs.

Key words: bioaccumulation; polybrominated diphenyl ethers; congener

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Introduction

Polybrominated diphenyl ethers (PBDEs) are a group of persistent organic pollutants. There are 209 PBDE congeners, distinguished by the number and position of their bromine atoms. Many of these compounds are commonly used in building materials, furnishing textiles, and electronic equipment. The tetra-, penta-, and deca-BDEs are the most commonly used congeners (Brown et al., 2006; Kuiper et al., 2008). Two of the three commercial PBDE mixtures (penta-BDE and octa-BDE) have been banned by the European Union and several U.S. States due to their toxic, mutagenic, and carcinogenic effects (Darnerud et al., 2001; Stoker et al., 2004; Zhou et al., 2001). However, deca-BDE commercial mixtures are still used widely, without regulation for their usage and disposal. Debromination of deca-BDEs occurs during the use of electronic equipment. This results in the formation of octa- and nona-congeners in e-wastes (Lou et al., 2009). Lower brominated congeners, such as tetra- and penta-BDE mixtures, are commonly found in human milk (Zhu et al., 2009), eggs (Lam et al., 2007), and terrestrial and aquatic biota (Liang et al., 2008; Hermanussen et al., 2004; Boon et al., 2002). These PBDEs are released during the recycling of electronic waste (e-waste). In many cases this process is unregulated which can lead to a release of PBDEs into the environment (Luo et al., 2007).

E-waste includes electronic products such as computers, printers, photocopy machines, and television sets. Obsolete electronic products are often exported to developing countries for recycling due to the lower labor costs and less stringent environmental regulations (Lou et al., 2007). In recent years, facilities for the dismantling of used electric appliances have grown rapidly in the offshore areas of Taizhou, China. Although the economic benefit to the region is considerable, the e-waste represents an increasingly large source for the emission of PBDEs into the local environment (Liang et al., 2008; Zhao et al., 2008). Since 2005, the local government has adopted a series of environmental protection measures. However, the effect of these measures has not been thoroughly evaluated.

Our objective was to measure the levels of PBDEs in fish and shellfish collected from aquaculture facilities in the Taizhou region and determine the potential point sources of contamination. We also evaluated the distribution of congeners, both among and within the species. This information is valuable for the sustainable development of the e-waste recycling industry and the protection of marine aquaculture.

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1 Materials and methods

1.1 Study area and sample collection

The study was conducted in Jiang-xia Town, Taizhou. Taizhou is a center for merchandise trade, e-waste dismantling, and recycling in South China. In August 2008, fish and shellfish samples were collected from four sites, located 20–30 km downstream from a number of e-waste dismantling and recycling plants. Three species of fish (*Sciaenops ocellatus*, *Sparus macrocephalus*, and *Lateolabrax japonicus*) were sampled from marine cages at each sites, and four species of shellfish (*Tegillarca granosa*, *Cyclina sinensis*, *Sinonovacula constricta* and *Ostrea cucullata*) were sampled from the ponds of aquaculture facilities at each site. All fish and shellfish were of a similar age and were selected based on their weight (*S. ocellatus*: 566–712 g; *S. macrocephalus*: 580–650 g; *L. japonicus*: 603–715 g; *T. granosa*: 12.0–14.4 g; *C. sinensis*: 12.0–15.3 g; *S. constricta*: 13.1–14.8 g; *O. cucullata*: 40–52.7 g). Sampling animals in aquaculture facilities offers a number of advantages over using wild fish. For example, the fish/shellfish experience the same natural seawater environment, but feed and growth are controlled. In addition, the life history of each group is known and all individuals are confined to specific regions of the ocean. All samples were transported to the laboratory within 6 hr. We measured the weight of each animal then dissected and filleted the muscle with a clean stainless steel knife. The tissue was packed in aluminum foil. The tissue samples were then frozen at –20°C until further analysis.

1.2 Chemicals and instrumentation

The PBDE analytical standard solution was purchased from Acros Organics, USA. The solution contained three mono-BDEs (BDE-1, 2 and 3), seven di-BDEs (BDE-7, 8, 10, 11, 12, 13, and 15), eight tri-BDEs (BDE-17, 25, 28, 30, 32, 33, 35, and 37), six tetra-BDEs (BDE-47, 49, 66, 71, 75, and 77), seven penta-BDEs (BDE-85, 99, 100, 105, 116, 119, and 126), five hexa-BDEs (BDE-138, 153, 154, 155, and 166), and three hepta-BDEs (BDE-181, 183, and 190). The concentrations of each compound ranged from 100 ng/mL for the mono-congeners to 250 ng/mL for the hepta congeners. We used the standard solution to construct a calibration curve and measure recovery efficiency from spiked samples.

We pre-cleaned the silica gel (100–200 mesh) by heating at 450°C for 6 hr in a shallow metallic enamel tray. Similarly, we pre-cleaned the anhydrous sodium sulfate by heating at 120°C for 6 hr in a shallow metallic enamel tray. All organic solvents were of chromatographic grade or equivalent. We used Milli-Q water (Millipore, USA) for all experiments.

Gas chromatography coupled to mass spectrometry with negative chemical ionization (GC-NCI-MS) using a gas chromatograph (GC 3800) connected to a mass spectrometer (240 MS: Varian, Palo Alto, USA) with a VF-5 ms (30 m × 0.25 mm × 0.25 μm, Varian, USA) was used. The rotary evaporator (RE-52AA) was purchased from the Shanghai Kanghua Biology Medical Instrument Factory (China).

1.3 PBDE extraction and purification

We treated the tissue samples (10 g) with anhydrous sodium sulfate to remove water. The samples were then subjected to Soxhlet extraction using a mixture of 100 mL *n*-hexane/methylene dichloride (1:1, *V/V*) for 48 hr in a water bath (60°C). The extract was condensed to 10 mL in the rotary evaporator then eluted with sulfuric acid until the sulfuric acid layer was colorless. Following this, the extract was eluted with a 20% sodium sulfate solution. Then anhydrous sodium sulfate was added to remove trace amounts of water. The extract (2 mL total volume) was then concentrated using the rotary evaporator. The concentrated extract was passed through a glass column (inside diameter: 1 cm) packed (in order, from the base) with 4 cm of alumina, 2 cm of silica gel (100–200 mesh), 3 cm of alkaline silica gel, 2 cm of silica gel, 5 cm of acidic silica gel, and 1 cm anhydrous sodium sulfate. The glass column was also pre-eluted with hexane then eluted with 20 mL methylene dichloride/*n*-hexane (1:1, *V/V*). The sample extracts were then condensed to 0.5 mL and dried with nitrogen. The PBDEs in the samples were dissolved in 1 mL of pure *n*-hexane and filtered through a 0.45-μm filter paper. The samples were then analyzed using GC/MS.

1.4 Chemical analyses

The column oven temperature was programmed from 110°C to 180°C at 8°C/min, and held for 1 min, then increased to 210°C at 2°C/min and held for 1 min, followed by increasing to 300°C at 5°C/min and held for 5 min. The injector and detector temperatures were kept at 280 and 300°C, respectively. Helium gas (purity: 99.999%) was use as both carrier gas (1.0 mL/min) and make up gas for the detector (60 mL/min). The samples were injected in a split mode (split ratio: 5:1). The injection volume was 1.0 μL.

1.5 Quality control

Blank samples were prepared in the same manner as the tissue samples, and analyzed concurrently with the field samples to measure interference and laboratory contamination. A solvent and procedural blank was included for every batch of 10 samples. The recovery efficiency for the PBDEs was between 66.6%–113.6%. The detection limit for animal tissues was between 0.001–0.025 ng/g. The concentration of each congener was quantified using the external calibration method, based on a five-point calibration curve for 39 PBDEs.

2 Results and discussion

2.1 Organismal levels of polybrominated diphenyl ethers (PBDEs)

We measured the tissue concentrations of 39 mono- to hepta-brominated PBDE congeners. A total of 24 PBDE congeners ($PBDE_{24}$) in the samples was detected. The $PBDE_{24}$ tissue concentrations and total PBDE levels

($\sum PBDE_{24}$) varied widely among the fish and shellfish samples (Table 1). The results suggest that bioaccumulation of PBDEs was highly species-specific. The highest $\sum PBDE_{24}$ level (wet weightt (ww)) was detected in *S. macrocephalus* (1688.7 ng/kg), followed by *L. japonicus* (1427.9 ng/kg), *S. constricta* (1421.9 ng/kg), *S. ocellatus* (1031.2 ng/kg), *C. sinensis* (759.5 ng/kg), *T. granosa* (705.7 ng/kg), and *O. cucullata* (545.4 ng/kg). The mean $\sum PBDE_{24}$ level was higher in fish (1382.6 ng/kg) than that in shellfish (858.1 ng/kg). The mean $\sum PBDE_{24}$ level in all species of fish was at least two times higher than that in the majority of the shellfish species, except *S. constricta*. These differences may be explained by the feeding ecology of the organisms (Guo et al., 2007). The fish typically feed on small fish, shrimp, and shellfish whereas the shellfish feed primarily on diatoms and organic debris. Thus, the contaminants are transported from lower trophic levels to higher trophic levels, and accumulated. Our results are consistent with those reported by Tittlemier et al. (2004).

$\sum PBDE_{24}$ levels differed significantly among the three species of teleosts. The levels were the lowest in *S. ocellatus* and highest in *S. macrocephalus* (Table 1). This is likely

Table 1 Concentrations of PBDEs measured in organisms (ng/kg ww) collected downstream from e-waste recycling plants in Taizhou, China

Sample	*Sciaenops ocellatus*		*Sparus macrocephalus*		*Lateolabrax japonicus*	
	Range	Average	Range	Average	Range	Average
BDE-1	nd	0.0	nd	0.0	nd–171.8	76.5
BDE-2	nd–141.0	92.1	nd–403.5	206.8	nd–330.7	147.0
BDE-3	nd	0.0	nd–157.0	39.3	nd–433.2	128.4
BDE-8	14.2–15.5	14.9	17.1–37.2	22.8	18.7–23.7	20.5
BDE-10	64.1–86.8	71.8	nd–56.1	14.0	nd–140.1	79.0
BDE-11	21.1–25.3	22.7	23.8–42.3	29.7	22.5–33.8	27.9
BDE-12	40.3–45.2	42.0	nd–49.4	22.4	nd–51.3	23.9
BDE-17	60.5–64.9	63.1	58.3–87.8	69.9	50.8–82.1	74.1
BDE-25	43.4–43.7	43.6	39.9–51.6	46.3	44.4–49.0	45.9
BDE-28	26.5–32.3	30.2	30.0–77.7	54.2	15.1–56.7	42.5
BDE-33	41.1–48.9	46.0	44.8–122.1	83.9	22.2–84.2	51.0
BDE-35	nd–17.5	11.0	nd–27.0	16.9	15.3–19.0	17.4
BDE-37	18.9–25.5	21.3	22.7–41.9	31.8	20.9–29.9	26.5
BDE-47	135.5–208.8	170.3	199.9–687.9	410.2	105.8–352.1	215.4
BDE-49	57.1–124.5	94.5	77.9–131.5	111.3	nd–182.2	102.9
BDE-66	60.7–132.7	100.7	83.0–140.2	118.6	nd–194.4	109.8
BDE-71	14.8–16.4	15.6	20.6–30.2	25.7	17.8–72.4	33.9
BDE-77	78.2–87.4	82.3	nd–72.8	18.2	nd–100.5	74.1
BDE-99	nd	0.0	nd–73.8	35.4	nd–93.6	41.1
BDE-100	29.9–47.5	37.9	45.5–121.6	75.3	26.5–63.7	43.5
BDE-119	nd	0.0	nd	0.0	nd–75.8	18.9
BDE-153	nd	0.0	nd–142.2	69.7	nd	0.0
BDE-154	nd	0.0	96.2–170.1	129.6	nd–110.7	27.7
BDE-181	nd–213.7	71.2	nd–226.8	56.7	nd	0.0
∑PBDEs		1031.2		1688.7		1427.9

Sample	*Tegillarca granosa*		*Cyclina sinensis*		*Sinonovacula constricta*		*Ostrea cucullata*	
	Range	Average	Range	Average	Range	Average	Range	Average
BDE-1	nd–134.9	36.6	nd–295.0	115.3	nd–57.7	11.5	61.6–61.7	61.7
BDE-2	nd–245.6	100.3	nd–144.9	94.9	nd–105.8	76.0	65.9–68.0	67.0
BDE-3	nd–329.2	62.6	nd–405.6	69.2	nd–36.7	14.5	nd–42.0	21.0
BDE-8	nd–25.3	15.6	nd–23.9	13.4	nd–25.1	14.3	nd–25.5	12.8
BDE-10	nd–30.4	0.0	nd	0.0	nd–35.1	19.9	nd	0.0
BDE-11	nd–35.1	19.9	18.8–34.6	29.2	nd–33.5	31.4	34.3–34.9	34.6
BDE-12	nd–51.2	12.9	nd–43.8	20.0	nd–25.2	10.1	nd–26.8	13.4
BDE-17	26.1–70.8	35.6	24.5–48.3	31.5	27.5–126.2	49.2	nd–26.9	13.4
BDE-25	nd–54.1	12.6	0.2–42.5	10.8	1.3–72.0	16.1	0.4–0.6	0.5
BDE-28	nd–31.0	7.2	1.1–10.2	3.8	3.3–83.1	18.2	0.5–2.5	1.5
BDE-33	3.4–55.2	27.8	4.7–26.4	19.1	23.3–128.0	48.2	20.3–22.8	21.5
BDE-35	16.5–30.3	27.4	nd–45.7	18.3	nd–28.9	22.8	nd–29.7	14.9
BDE-37	nd–33.2	24.9	nd–30.4	11.1	30.1–43.9	33.6	32.0–32.9	32.4
BDE-47	31.2–317.1	96.4	33.7–129.3	65.5	65.4–816.0	237.4	35.3–47.4	41.4
BDE-49	nd–104.4	40.8	nd–68.7	22.6	41.7–331.5	105.3	nd–28.9	14.4
BDE-66	nd–111.2	43.4	nd–73.0	24.1	44.4–353.7	112.2	nd–30.6	15.3
BDE-71	nd–51.4	18.1	nd–37.9	20.4	nd–29.1	19.6	nd–30.0	15.0
BDE-77	nd–45.0	12.4	nd–51.8	6.5	30.8–158.1	61.6	nd	0.0
BDE-99	nd–168.0	21.0	nd–66.5	42.3	nd–413.5	140.7	nd–53.8	26.9
BDE-100	19.0–49.8	38.5	31.4–79.1	42.2	41.4–99.5	55.8	44.8–45.5	45.1
BDE-119	nd	0.0	nd–73.1	14.1	nd–144.2	67.6	nd	0.0
BDE-153	nd	0.0	nd–109.7	13.7	nd–192.3	93.4	nd–66.1	33.0
BDE-154	nd	0.0	nd–94.1	22.8	nd–259.6	100.9	59.0–60.3	59.6
BDE-181	nd–221.1	51.6	nd–195.9	48.6	nd–214.5	61.8	nd	0.0
∑PBDEs		705.7		759.5		1421.9		545.4

nd: not detected.

related to differences in growth rate. *S. macrocephalus* grows at a slower rate so has a greater cumulative exposure to contaminants at any given bodyweight. The $\sum PBDE_{24}$ levels also differed among the shellfish species. The levels measured in *S. constricta* were 2–3 orders of magnitude higher than that in the other shellfish species (Table 2).

Analyzing the contribution of individual PBDEs to the total load is useful for tracking the contaminant source and illustrating the fate and transportation of PBDEs in the environment. Of the 39 PBDE congeners analyzed in this study, BDE-8, 11, 17, 25, 28, 33, 37, 47, 71, and 100 were present in the three species of fish. The concentration of BDE-47 was relatively high in all three teleosts species (mean 265.3 ng/kg), followed by BDE-2, 66, 49, 17, and 77 (148.6, 109.7, 102.9, 69.0, and 58.2 ng/kg, respectively). However, of these 39 PBDE congeners, only BDE-33, 47, and 100 were present in the four species of shellfish. Interestingly, BDE-47 was also the dominant congener in the shellfish (mean: 110.2 ng/kg), followed by BDE-2, 99, 1, 66, 154, and 49 (84.6, 57.7, 56.3, 48.8, 45.8, and 45.8 ng/kg, respectively). A number of studies have also reported that BDE-47 is the most abundant congener in fish and bivalves (Dodder et al., 2002; Shaw et al., 2008, Kiviranta et al., 2004). We measured very high levels of BDE-47 and BDE-154 in *S. constricta*, which contributed to the high $\sum PBDE_{24}$ level in this species. Guo et al. (2002) also reported high levels of BDE-154 in shellfish. Few studies have documented the levels of BDE-2 in fish and bivalves. Inter-study comparisons of PBDE levels are complicated because each laboratory may analyze for a different suite of PBDE congeners. However, the key congeners, with respect to their accumulation in the biota, are included in each studies, allowing for adequate comparisons (Hermanussen et al., 2008). The appearance of lower brominated congeners occurs due to the debromination of high brominated congeners that are discharged into the environment (Stapleton et al., 2004). Low-molecular weight PBDEs are absorbed and accumulated more easily than high molecular weight PBDEs.

2.2 Comparison with other studies

We separated aquatic organisms into "fish" and "shellfish" for the purposes of assessing exposure. Each category incorporated both marine and freshwater species (Lorber, 2008). The average total PBDE concentration in the muscle of the three fish species (mean 1382.6 ng/kg ww) and four shellfish species (mean 858.1 ng/kg ww) sampled in our study was lower than that in fish from other regions. For example, a series of PBDE surveys were conducted in Europe, including Italy (Mariani et al., 2008) and Norway (Mariussen et al., 2008); North America, including the United States (Oros et al., 2005) and Canada (Kelly et al., 2008); and the Asia-Pacific region, including Korea (Moon et al., 2007), Hong Kong (Liu et al., 2005), Singapore (Bayen et al., 2003), and China (Luo et al., 2007). The levels of PBDEs differed significantly among the fish in these studies. The highest total PBDE level (15,600 ng/g ww) was measured in *C. carpio* from Vero River, Spain (Eljarrat et al., 2007), and the concentration of BDE-47 in *C. carpio* was 3714.3 ng/g. Conversely, the lowest total PBDE level (48 pg/g ww) was measured in shrimp from Canada (Tittlemier et al., 2004). The data also suggest that PBDE contamination is regionally distributed. For example, PBDEs are an increasing problem in Laizhou Bay due to the production of brominated flame retardants. In this region, PBDEs concentrations in shellfish range from 230–720 ng/g lipid wt (Jin et al., 2008). Other regions, such as Guiyu, China, have experienced similar increases in PBDE contamination due to industrialization (Leung et al., 2007; Luo et al., 2007).

The concentrations of PBDEs measured in the study were in the low range of the concentrations that have been reported in other countries (Mariussen et al., 2008; Brown et al., 2006; Kelly et al., 2008). Furthermore, the levels were much lower than the samples from other regions in China, especially Guangzhou in southern China, where has

Table 2 Comparison of BDE-47 and ∑PBDEs concentrations in organisms samples from Taizhou with other studies (ng/g, ww)

Organism	Sampling location	Year	BDE-47	∑PBDEs	Reference
Sciaenops ocellatus	Taizhou, China	2008	0.2	1.0	This study
B. Sparus macrocephalus			0.4	1.7	
C. Lateolabrax japonicus			0.2	1.4	
Perca fluviatilis	Vltava and Elbe, Germany	2005	2.4	3.8	Hajslová et al., 2007
Oreochromis spp.	Guiyu, China	2004	69.0	115.0	Luo et al., 2007
Cyprinus carpio[a]	Vero River, Spain	2004	3670.0	15600	Eljarrat et al., 2007
Salmo trutta Linnaeus	Mjosa, Norway	2004	55.0	407.0	Mariussen et al., 2008
Corbicula fluminea[c]	San Francisco Estuary, USA	2002	180.0	316.7	Oros et al., 2005
Mactra chinensis[b]	Laizhou Bay, China	2005	857.7	3428.6	Jin et al., 2008
Ruditapes philippinarum[b]	Laizhou Bay, China	2005	3714.3	12000	Jin et al., 2008
Crassostrea gigas[c]	San Francisco Estuary, USA	2002	125.0	200.0	Oros et al., 2005
Mytilus edulis[b]	Hudson Bay, Canada	1999–2003	414.3	771.4	Kelly et al., 2008
Perna viridis	Singapore	2002	0.09–1.5	2.0–38.0	Bayen et al., 2003
Mytilus californianus	San Francisco Estuary, USA	2002	85.0	145.0	Oros et al., 2005
Mytilus edulis[c]	Hong Kong's marine environment, China	2004	0.3–1.7	27.0–83.7	Liu et al., 2005
Bivalves (*Mytilus coruscus*, *Mytilus edulis*, *Crassostrea gigas*)	Coastal locations in Korea	2004	0.3	2.9	Moon et al., 2007
Cyclina sinensis	Taizhou, China	2008	0.07	0.8	This study
Ostrea cucullata			0.04	0.6	

[a] Water content and lipid content are arithmetic 70% and 10%, respectively, in the fish; [b] water content and lipid content are arithmetic 80% and 3.5%, respectively, in the shellfish; [c] water content is arithmetic 80% in the shellfish.

an one of the world's largest electronic-waste recycling centers (Leung et al., 2007; Luo et al., 2007). Interestingly, the concentration of PBDEs in fish and shellfish in Taizhou were much lower than in human hair and foraging hens, which were also sampled in Taizhou (Liang et al., 2008; Zhao et al., 2008). However, a direct comparison of these data are difficult due to differences in the species, age, gender, weight, and lipid content of the individual samples and differences in the analytical methods. In addtion, the number of congeners was highly variable among the studies due to local differences in BDE sources or the availability of BDE congener standards for the analytical laboratories (Dodder et al., 2002). To allow comparison with other studies, the BDE-47 and $\sum PBDE_{24}$ levels, shown in Table 2, are referenced to a standard level due to the higher toxicity of BDE-47 (Darnerud, 2003) (the concentrations are presented as wet weight, based on a water and lipid content of 70% and 10%, respectively, in fish and 80% and 3.5%, respectively, in shellfish).

The concentrations of BDE-47 and total $PBDE_{24}$ ranged from 0.17 to 0.41 ng/g and 1.03 to 1.69 ng/g, respectively, in the three fish species. These levels are lower than those reported in other species throughout the world, such as *Cottus gobio* Linnaeus from Hudson Bay, Canada (Kelly et al., 2008), *Perca fluviatilis* from Vltava and Elbe, Germany (Hajslová et al., 2007), *Oreochromis* spp. from Guiyu, China (Luo et al., 2007), *Oncorhynchus tschawytscha* from Hudson Bay, Canada (Kelly et al., 2008), *Cyprinus carpio* L from the Vero River, Spain (Eljarrat et al., 2007), and Salmo trutta Linnaeus from Mjosa, Norway (Mariussen et al., 2008).

There are limited data on shellfish, the majority focusing on clams, oysters, and mussels. BDE-47 and $\sum PBDE_{24}$ concentrations in bivalves from Taizhou are much lower than those in *M. chinensis* and *R. philippinarum*, from Laizhou Bay, China (Jin et al., 2008), and *C. fluminea* and *Crassostrea gigas* from the San Francisco Estuary, USA (Oros et al., 2005). However, the levels were similar to those reported in Zhousan, a coastal city in eastern China (Miyake et al., 2008). Conversely, BDE-47 and $\sum PBDE_{24}$ levels were over 5 times higher in *Mytilus edulis* from Hong Kong's marine environment, China (Liu et al., 2005), *Perna viridis* from Singapore (Bayen et al., 2003), *M. edulis* from Hudson Bay, Canada (Kelly et al., 2008), and bivalves (*Mytilus coruscus*, *M. edulis*, and *C. gigas*) from coastal locations in Korea (Moon et al., 2007) than the concentrations measured in our study.

2.3 PBDE composition

Samples containing a low concentration of one compound may have high concentrations of other compounds. The mono- to tetra-homologs were relatively abundant in the majority of fish and shellfish species (Fig. 1), and the tetra- to hexa-homologs were most common in *S. constricta*.

The tetra-BDEs were the dominant PBDE homolog in the three fish species. These accounted for 44.9%, 40.5%, and 37.5% of the total PBDEs in *S. ocellatus*, *S. macrocephalus*, and *L. japonicus*, respectively. The dominant congener was BDE-47. The tri-BDEs accounted for 20.9%, 17.9%, and 18.0% of the total PBDEs for *S. ocellatus*, *S. macrocephalus*, and *L. japonicus*, respectively. There was no significant difference in the concentration of tetra- and tri-BDEs among the fish species. The lower brominated congeners were detected at relatively high concentrations whereas the higher brominated congeners were detected at relatively low concentrations in all the fish. The PBDE composition was similar among the 3 fish species, suggesting that the PBDEs were derived from the same point source. Interestingly, the relative abundance of commercial penta-products, produced in e-waste, was very low. Thus, we hypothesize that debromination enhances depuration of the higher brominated congeners and slows depuration of the lower brominated congeners (e.g., tetra-BDEs) due to the formation of lower molecular weight reaction products (Kelly et al., 2008).

We observed a significant difference in the concentration of BDE congeners among the shellfish. The tetra-BDEs

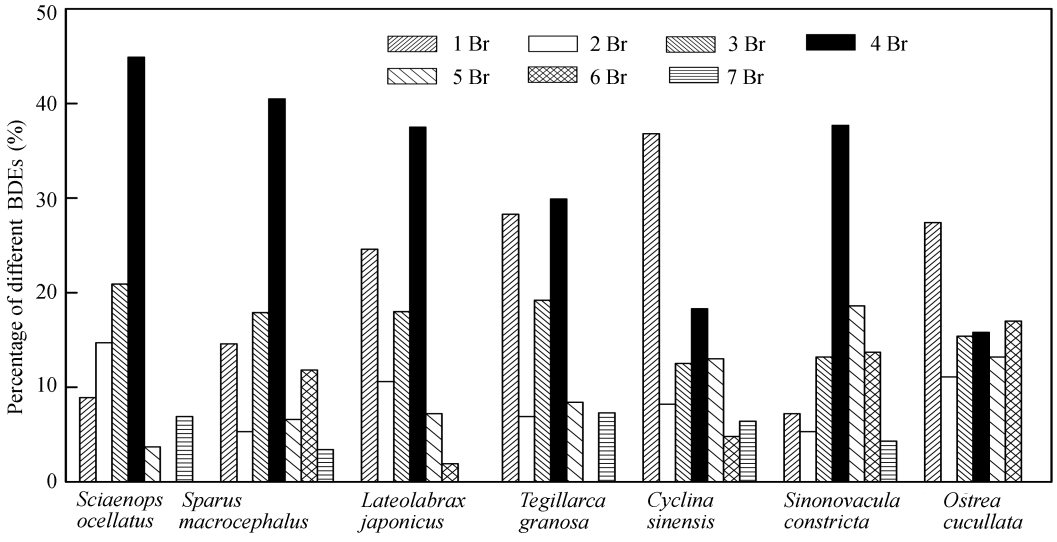

Fig. 1 Percentage of the different bromine atoms measured in the muscle samples.

were dominant in *T. granosa* and *S. constricta*, accounting for 29.9% and 37.7% of the total PBDEs, respectively. Conversely, the mono-BDEs were dominant in *C. sinensis* and *O. cucullata*, accounting for 36.8% and 27.4% of the total PBDEs, respectively, followed by the tetra-BDEs (18.3% and 15.8%, respectively) and the tri-BDEs (12.5% and 15.4%, respectively). The composition of PBDE congeners in *S. constricta* differed from that in the other species.

The commercial penta-BDE mixture consists primarily of tetra-PBDEs and penta-PBDEs. The two dominant congeners are BDE-99 and BDE-47 (LaA Guardia et al., 2006). The PBDE congeners are distributed among the gaseous and particle phases once released into the environment. They then undergo degradation and/or long-range atmospheric transport to areas outside the e-waste dismantling zone (Luo et al., 2009). Because filter-feeding bivalves live primarily in marine sediments, it is reasonable to conclude that the major source of PBDE contamination in shellfish is associated with water and sediment pollution. In addition, congener-specific biotransformation of PBDEs undoubtedly plays an important role in the bioaccumulation of PBDEs. Species-specific differences in the rate of PBDE transformation may also be responsible for the wide ranging estimation for PBDE biomagnification (Muir et al., 2006).

2.4 Source identification based on principal component analysis

We used principal component analysis (PCA) to investigate potential pollution sources and distribution patterns (Table 3). All data were normalized to the percentage of PBDEs having the same bromine atomic number. The most likely factors were those with an eigenvalue > 1 that could explain 80% of the data variance. We detected a significant correlation among the di-, tri-, tetra-, and hepta-BDEs for the three species of fish. Although the correlation was lower for the hexa-BDEs, the correlation coefficient was higher than for the mono- and penta-BDEs. Similarly, we found a significant correlation among the mono- and tri-BDEs in the shellfish. When all seven species were considered, the correlation coefficient of the mono-BDEs was higher than any of the remaining congeners. These results suggest that mono-BDE is the primary contributor to PBDE contamination in fish and shellfish in Taizhou.

The PCA results indicate that the PBDE composition of most samples was similar, suggesting that the contamination originated from the same source. However, the commercial penta-BDE products, widely used in e-wastes, were poorly correlated. Previous research has shown that the sources of lower-molecular-weight PBDEs often differ from the sources of higher-molecular-weight PBDEs. There are differences in the partitioning of the lower brominated PBDE congeners and the higher brominated PBDE congeners in the aquatic environment (Moon et al., 2004). Approximately 80% of the PBDEs produced consist of deca-BDE. However, marine organisms predominantly accumulate lower brominated congeners (Stapleton et al., 2004; Tomy et al., 2004). This is likely due to the lower bioavailability of higher brominated PBDEs and debromination during metabolism (Martin et al., 2004). The capacity to metabolize PBDEs varies widely among organisms. For example, decapod crustaceans have a relatively high capacity for metabolizing PBDEs (Bodin et al., 2007). Our results suggest that fish and shellfish have a similar capacity to metabolize and eliminate PBDEs. Thus, the PBDEs measured in fish and shellfish from Taizhou were likely derived from the debromination of higher brominated PBDEs.

3 Conclusions

We detected 24 BDE congeners in fish and shellfish samples from the Taizhou region. The highest levels of PBDEs were found in *S. macrocephalus* and the lowest in *O. cucullata*. The levels of PBDEs tended to be lower in fish than that in shellfish. The most common congener in both fish and shellfish was BDE-47, followed by BDE-2. The concentrations of BDE-49 and BDE-66 were also relatively high.

The lower brominated congeners were detected at relatively high concentrations and the higher brominated congeners were detected at relatively low concentrations. The PBDE levels in this region were in the low concentration range that have been reported throughout the world. Furthermore, the relative abundance of penta-BDEs, produced in e-waste, was very low. Together, our results suggested that the containment measures in place at the

Table 3 Principal component analysis for the three species of fish, the four species of shellfish, and for both groups

Samples	Fish		Shellfish		All organisms studied		
	Factor 1	Factor 2	Factor 1	Factor 2	Factor 1	Factor 2	Factor 3
∑mono-BDEs	–	–	0.860	0.368	–	0.890	0.036
∑di-BDEs	0.747	–	0.329	0.937	0.512	0.378	–
∑tri-BDEs	0.987	–	0.600	–	0.919	0.022	–
∑tetra-BDEs	0.960	0.281	–	–	0.726	–	0.085
∑penta-BDEs	–	–	–	0.048	–	–	0.180
∑hexa-BDEs	–	0.855	–	0.628	–	–	–
∑hepta-BDEs	0.927	–	0.431	–	0.341	0.121	0.863
Eigenvalue	5.31	1.70	3.12	2.87	3.22	1.63	1.23
Variance (%)	75.8	24.2	44.6	40.9	45.99	23.32	17.52
Cumulative (%)	75.8	100	44.6	85.6	45.99	69.30	86.83

Extraction method: principal component analysis; rotation method: Varimax with Kaiser normalization; eigenvalue > 1.00 and factor loading > 0.10 are listed.

e-waste plants in Taizhou were successful. Based on principal component analysis, we concluded that the processes of PBDE metabolism and elimination were similar in both fish and shellfish. The analysis also suggested that the PBDEs are derived primarily by the debromination of higher brominated PBDEs.

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