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**Bioaccumulation and Historical Deposition of Polybrominated
Diphenyl Ethers (PBDEs) in Deep Bay, South China**

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Abstract

To characterize the bioaccumulation and historical trends of polybrominated diphenyl ethers (PBDEs) in Deep Bay, an important water body between Hong Kong and mainland China with a Ramsar mangrove wetland (Maipo), marine organisms and core sediments were collected to determine their PBDEs concentrations. Sediment core dating was accomplished using the ^{210}Pb method. PBDEs concentrations in fish ranged from 0.17 to 4.16 ng g⁻¹ wet wt., with a mean value of 2.00 ng g⁻¹ wet wt. Temporal trends of the target PBDE congeners levels in core sediment generally increased from 1948 to 2003, with the highest levels in top sediment, suggesting an ongoing PBDEs input. The average sedimentation flux of PBDEs was 0.25 ng cm⁻² a⁻¹, and the double time of total PBDEs concentration was ca. 12.3 a. Correlations between the biota-sediment accumulation factors (BSAF) of PBDEs and their corresponding octanol-water partition coefficient (K_{ow}) were discussed.

Keywords: Polybrominated diphenyl ethers; Benthos; Cores; Bioaccumulation; Stable isotopes; Deep Bay, South China.

1. Introduction

Polybrominated diphenyl ethers (PBDEs) are the additive flame retardants and the next highest production group of brominated diphenyl ethers (BFRs) currently in use. PBDEs are widely used in manufactured products such as polymers, resins, electronic devices, building materials, textiles and polyurethane. PBDEs enter the environment via direct and indirect urban domestic/industrial sewage discharges and atmospheric deposition, and they have a tendency to accumulate in aquatic sediments and organisms due to their high octanol-water partition coefficients (Song et al., 2004). Some PBDE congeners exhibit substantially long environmental half-lives, potential bioaccumulation and possible adverse effects on wildlife and humans (de Wit, 2002; McDonald, 2002). They can impair attention, learning, memory and behavior in laboratory animals and possibly interfere with early neurodevelopment (Fowles et al., 1994; Darnerud, 2003; Brigden et al., 2005).

PBDEs have been widely detected in air, water, sediment, organism, and humans in recent years. Their levels in biota were estimated to double every 5 years, and were reported to increase by 60-fold in human breast milk in Sweden between 1972 and 1997 (Meironyt and Bergman, 1999; de Wit, 2002; Law et al., 2006). The estimated domestic production of predominant commercial deca-BDE mixture in China increased by 200% between 2000 and 2005, from 10 000 to about 30 000 metric tons (Chen et al., 2007). Furthermore, China appears to be a large dumping site of e-wastes imported from overseas legally and illegally in recent years (Brigden et al., 2005; Guo et al., 2007). A previous study using skipjack tuna to elucidate the global distribution

of PBDEs suggested that the coastal region off the East China Sea was supposedly a “hot spot” for PBDEs (Ueno et al., 2004). Apparently, the PBDEs contamination status in the environment of China and their effects on the ecosystem and humans remain to be fully understood.

Deep Bay, located in the eastern Lingdingyang of Pearl River Estuary, South China, is a natural, shallow estuarine bay with an average water depth of about 3 m, and a tidal range of about 1.4 m. It is 17.5 km long in SW-NE direction and 4~10 km in NW-SE direction (Fig. 1). The wetlands around Inner Deep Bay and Mai Po marshes are important to the migratory birds for many decades. The 1500 hectares of wetlands around the area was designated as a Wetland of International Importance under the Ramsar Convention in 1995. The consumption of PBDEs is believed to increase in this region because of the fast industrialization in the last two decades, which made the region the most important electronic manufacturing base in the world. Zheng et al. (2004) reported that the PBDE concentrations in green-lipped mussels from Hong Kong waters were among the highest in the world. Mai et al. (2005) reported that although the total PBDEs concentrations in sediments of the Pearl River Delta and adjacent South China Sea were mostly <50 ng/g, within the range for riverine and coastal sediments around the world, the BDE-209 concentrations at some sites were at the high end of the worldwide figures. Chen et al. (2007) investigated the time trend of PBDE concentration in sediment cores of Pearl River Estuary and results showed that total PBDEs (except for BDE 209) concentrations in all sediment cores increased gradually from the bottom (mid-1970s) to the middle layer (later 1980s and

early 1990s). PBDEs residue levels in fish from South China had been also measured (Meng et al., 2007; Xiang et al., 2007; Guo et al., 2008). Recent study showed that there was a fresh DDT input into the bay (Qiu et al., 2009a). To our knowledge, few studies on PBDEs in Deep Bay have been conducted. The present work aimed to (1) study the bioaccumulation of PBDEs in organisms of Deep Bay; (2) investigate the chronology of PBDE concentration and flux in Deep Bay as recorded in sediment core based on the ^{210}Pb dating; (3) analyze the compositions of PBDE congeners and the potential sources, and (4) discuss the relationships between the biota-sediment accumulation factors (BSAF) of PBDEs in Deep Bay and the corresponding octanol-water partition coefficient (K_{ow}).

2. Materials and methods

2.1. Samples collection

Samples of benthic organisms and core sediment in seven stations from Deep Bay, as shown in Fig. 1, were collected in February 2004. A stainless steel static gravity corer (8 cm i.d.) was employed to collect the sediment which was sliced immediately at 1 cm intervals and stored in polyethene bags. The organism samples, with size ranging from 5 cm to 15 cm and lifespan approximately ranging 0.5–2 a, were collected by benthic trawling and stored in polyethene bags. The organism samples from seven stations were mixed into one to represent organisms in Deep Bay as it was not easy to collect enough samples from each station. Since most of the fishes were small benthos fish, they should be considered as local fish. All samples were transported to the laboratory at about 0 °C and frozen at -20 °C prior to treatments.

97

98 Fig. 1. Sampling locations in Deep Bay, South China

99

100 The specimens were identified in South China Institute of Oceanology, the Chinese
 101 Academy of Sciences. These included planktivorous, omnivorous, and carnivorous
 102 species, such as planktivorous fish (*Clupanodon thrissa*, *Clupanodon punctatus*,
 103 *Mugil cephalus*), small carnivorous fish (*Sillago japonica*, *Thrissa dussumieri*,
 104 *Leiognathus bindus*, *Leiognathus ruconius*, *Ilisha elongate*), carnivorous fish
 105 (*Inimicus cuvieri*, *Dasyatis zugei*, *Platycephalus indicus*), benthos feeders
 106 (*Collichthys lucidus*, *Nibea acuta*, *Cynoglossus robustus*), and omnivorous organisms
 107 (*Polynemus sextarius*, *Trypauchen vagina*, *Glossogobius giuris*, *Penaeus orientalis*
 108 and *Portunus pubescens*).

109 2.2. Chemical analysis

110 **Samples preparation.** Analytical procedures generally followed those of
 111 Richardson and Zheng (1999) and Zheng et al. (2004). Frozen organism samples were
 112 thawed and rinsed individually with purified water to remove possible impurities. The
 113 edible parts from about 3–5 specimens of the same specimens (17 fishes, one shrimp
 114 and one crab) collected from each location were pooled. Prior to extraction, the
 115 organism and sediment samples were freeze-dried and homogenized. Subsamples
 116 were dried to constant weight to determine the water contents. Dry samples were
 117 ground into powder with a stainless steel blender. Approximately 10 g of powder was
 118 placed in a round bottom flask, to which known quantities of ^{13}C -labeled PBDE

congeners (BDE-3, 15, 28, 47, 99, 153, and 183) were added. A hexane:acetone:dichloromethane (1:1:1) solution (150 ml) was added, and heated to 65 °C to gently boil the sediment powder in solvent for 4 h. After cooling, the mixture was filtered using a pre-cleaned glass filter, and the residue was washed three times with hexane and dichloromethane (total 30 ml each solvent). For organism samples, an aliquot of one tenth was used to gravimetrically determine the lipid content and the left solution was treated with concentrated sulfuric acid (5 ml $\times$ 3) to remove the bulk of lipids. The extraction solution both organism and sediment samples was reduced in volume to 1 ml by rotary evaporation prior to column chromatography. A chromatography column consisting of 6 g of pre-activated silica gel and 1 g of activated copper powder was washed with 15 ml acetone, followed by 15 ml of dichloromethane and 20 ml of hexane. The extraction aliquot (1 ml) was then added on the column and the PBDEs were eluted with a 30 ml mixture of dichloromethane and hexane (1:1), followed by 15 ml of dichloromethane. The combined eluate (45 ml) was reduced in volume to 300 μ l for quantitation by GC-MS spectrometry.

GC-MS analysis. PBDEs (< octa-PBDE) were analyzed in all samples using a Varian Saturn 2200 Ion Trap GC/MS/MS with a 30 m DB-1 capillary column (0.25 mm diameter and 0.25 μ m film thickness), with helium at a rate of 1 ml min⁻¹ as the carrier gas. BDE197, 207, 209 were analyzed with a similar but shorter column (10 m DB-1). The injector temperature was 280 °C. The GC oven temperature was programmed as follows: 90 °C for 2 min, increasing 20 °C per minute to 230 °C, followed by 2 °C per minute to 247 °C, then 20 °C per minute to a final temperature

of 280 °C, which was held for 25 min. The mass spectrometer was operated in the electron impact/selected ion monitoring (EI/SIM) mode. PBDE concentrations in core sediments (including BDE-17, 28, 32, 35, 37, 47, 49, 66, 71, 75, 77, 85, 99, 100, 119, 138, 153, 153, 154, 166, 181, 183 and 190) and organisms (including BDE-3, 15, 28, 47, 60, 85, 99, 100, 138, 153, 154, 183, 197, 207 and 209) were analyzed.

QA/QC. Retention times and mass spectra fragmentation for PBDEs 3, 15, 28, 47, 99, 153, and 183 were established by using ^{13}C -labeled PBDEs. Other PBDEs were identified based on the literature. All samples were run in duplicate. Concentrations of PBDEs in solvent blanks ($n = 2$) were low ($<0.08 \text{ ng g}^{-1}$), and the samples were considered valid when the concentrations exceeded three times that of the blank values. All reported values were corrected with a mean value (0.075 ng g^{-1}) of the blanks. Solution spike recoveries ranged between 76% (PBDE 183) and 108% (PBDE 47).

Isotope analysis. The organism samples were analyzed for $\delta^{15}\text{N}$ using an elemental analyzer EA (Flash EA 1112, CE) connected to an isotopic ratio mass spectrometer-IRMS (Delta plus XL, Finnigan). Approximately 0.8 mg of the sample was weighed in a tin cup and combusted in the elemental analyzer. Samples and standards were run in continuous flow with a standard deviation of 0.2‰ among replicate standard samples.

2.3. Sediment Dating

Sediment core dating was accomplished via ^{210}Pb analysis (Zhang et al., 2002; Qiu et al, 2009b). Briefly, the ^{210}Pb activities in sediment sub-samples were determined by

analysis of the α -radioactivity of its decay product ^{210}Po , on the assumption that the two are in equilibrium. The Po was extracted, purified, and self-plated onto silver discs at 75-80°C in 0.5 mole/L of HCl, with ^{209}Po (NIST, USA) used as yield monitor and tracer in quantification. Counting was conducted by computerised multi-channel α -spectrometry with gold-silicon surface barrier detectors. Supported ^{210}Po was obtained by indirectly determining the α -activity of the supporting parent ^{226}Ra , which was carried by co-precipitated BaSO_4 . As the core did not reach the critical depth of excessive $^{210}\text{Pb} \rightarrow 0$, only a *Constant Initial ^{210}Pb Concentration (CIC)* model was used, which assumes that dry mass entering the sediment pool has the same radioactivity concentration, to give an average sedimentation rate. Sedimentation age was calculated using a constant flux (CF) model (McCall et al., 1984):

$$t = -\lambda^{-1} \ln(1 - \xi)$$

where λ is the radioactive decay constant for ^{210}Pb (0.03114 a^{-1}), $\xi = \int_0^g A(g) dg / \int_0^\infty A(g) dg$, and dg is the thickness of each sediment interval ($\text{g cm}^{-2} \text{ a}^{-1}$). For sediment cores, the three undisturbed cores (A, B, E) were selected and analyzed for sediment dating. Since core A and E showed a mixing depth of ca. 7 cm and ca. 11.5 cm, respectively, only core B (total 39 cm long) was eventually selected to determine the PBDEs concentrations. In general, PBDEs concentrations in Shenzhen River estuary (site A and F) are expected to be influenced more by sewage discharge, while PBDEs concentrations in the mouth of the bay (site E) are potential to be affected more by the runoff of Pearl River. The simultaneous study showed that concentrations of hydrophobic organic compounds such as polycyclic aromatic

hydrocarbons in surface sediments of 7 sites (A, B, C, D, E, F and G) of Deep Bay were not significantly different (Qiu et al, 2009b). Moreover, Deep Bay is a relatively small bay and core B is located in the center of the bay. Therefore, it is reasonable to select core B as representing PBDEs distribution in the sediment of Deep Bay. Fig. S1 presents the distribution of excessive ^{210}Pb activity in the core-B, showing that the average sedimentation flux of the Core-B was $0.28 \text{ g cm}^{-2} \text{ a}^{-1}$, with an apparent sedimentation rate of 0.69 cm a^{-1} .

3. Results and Discussion

3.1. PBDEs in organisms

The concentrations of 15 PBDE congeners (BDE-3, 15, 28, 47, 60, 85, 99, 100, 138, 153, 154, 183, 197, 207 and 209) in organisms, as well as their ^{15}N values, are shown in Fig. 2. The mean total PBDEs concentrations in fish samples ($2.00 \pm 1.14 \text{ ng g}^{-1}$ wet wt.) were generally higher than those in shrimps (0.88 ng g^{-1} wet wt.) and those in crabs (1.44 ng g^{-1} wet wt.). PBDEs concentrations in wild fish of Deep Bay (mean: 2.00 , 0.17 – 4.16 ng g^{-1} wet wt. or mean: 62.9 , 20.9 – 166.4 ng g^{-1} lipid wt.) were higher than those wild fish of Daya Bay, South China (mean: 0.16 , 0.04 – 0.70 ng g^{-1} wet wt., Guo et al., 2008) and those in farmed fish of the coast of South China (mean: 0.15 , <0.0012 – 3.85 ng g^{-1} wet wt., Meng et al, 2007), but were lower than those wild biota in Pearl River Estuary where the median levels of the sum of BDEs 28, 47, 66, 85, 99, 100, 138, 153, 154, and 183 in large yellow croaker, silvery pomfret, flathead fish, robust tongue fish, and bombay duck were 67.3 , 123.9 , 114.4 , 181.2 , and 249.7 ng g^{-1}

lipid wt., respectively (Xiang et al., 2007). This is consistent with the fact that Pearl River Estuary was more polluted than Daya Bay and Deep Bay. PBDEs concentrations in wild fish of Deep Bay were comparable to those in skipjack tunas *Katsuwonus pelamis* from offshore waters in Asia-Pacific regions and Indian Ocean (<0.1–53 ng g⁻¹ lipid wt., Ueno et al. 2004) and those in farmed Atlantic salmon *Salmo salar* (0.49–10.92 ng g⁻¹ wet wt., Hites et al. 2004), but were lower than those in crappie *Pomoxis annularis* and bluegill *Lepomis macrochirus* from Hadley Lake in the United States (1500–1900 ng g⁻¹ lipid wt., Dodder et al. 2002). In the present study, relatively higher total PBDE concentrations were observed in benthic fish (e.g., *Cynoglossus robustus*) and carnivorous fish (e.g., *Inimicus cuvieri*), while relatively lower PBDEs concentration was found in planktivorous fish (e.g., *Mugil cephalus*) indicating a positive correlation between fish PBDEs burden and their food habit.

Fig. 2. The PBDEs concentrations and $\delta^{15}\text{N}$ values in organisms collected from Deep Bay.

Increases in contaminant concentrations from the prey to the predator can be successfully defined using the relative abundances of naturally occurring stable isotopes of nitrogen (i. e., $\delta^{15}\text{N}$ values; Hobson and Welch, 1992). The increase in $\delta^{15}\text{N}$ is generally 3 to 5‰ between each trophic level (Minigawa and Wada, 1984), though a consumer's diet often consists of prey organisms from different trophic levels, depending on the availability of prey organisms (Ruus et al, 2002). In the present study, planktivorous fish *Mugil cephalus* showed a lower $\delta^{15}\text{N}$ value (7.1‰)

than carnivorous fish *Inimicus cuvieri* (14.4‰) in Deep Bay. As shown in Fig. 2, positive correlations between total PBDEs (normalized to lipid content) and $\delta^{15}\text{N}$ values in planktivorous fish were apparently observed, whereas negative correlations between them in small carnivorous fish were also found. Relationships between log PBDEs (ng/g lipid wt.) and $\delta^{15}\text{N}$ values in the organisms of Deep Bay were shown in Fig. 3-a. The same pattern was also observed for BDE-47. A weak bioaccumulation of hydrophobic chemicals in organism of the tropical-subtropical waters may be interpreted by enhanced partition of hydrophobic chemicals between water and organisms due to higher temperature, as well as by relatively quick metabolism and short resident time of the chemicals in organisms (Guo et al., 2008). There was a significant correlation between log PBDEs (ng/g wet wt.) and log percent lipid in the organisms from Deep Bay ($R^2=0.54$; $P<0.01$; Fig. 3-b), confirming the fact that PBDEs are hydrophobic in nature and easily bioaccumulated in organisms.

Fig. 3. The relationships between PBDEs concentrations and $\delta^{15}\text{N}$ values and lipid percents in organisms from Deep Bay

3.2. PBDE in core sediment

Total $\Sigma_{22}\text{PBDEs}$ (BDE-17, 28, 32, 35, 37, 47, 49, 66, 71, 75, 77, 85, 99, 100, 119, 138, 153, 154, 166, 181, 183 and 190) concentrations in the core sediment from Deep Bay ranged from 0.07 to 4.85 ng/g dry wt, with median value of 0.68 ng/g dry wt (or 65 ng/g organic carbon). In the neighboring area, i.e. the Pear River Estuarine

region (Mai *et al.*, 2005), the average concentration of BDE-209 in surface sediment was 18.5 ng/g (range: 0.7–111.9 ng/g), while the sum of 10 PBDE congeners (BDE-28, -47, -66, -100, -99, -138, -153, -154, -183) concentrations in surface sediments was 3.13 ng/g (range: 0.3–21.8 ng/g), which was higher than those in Deep Bay for the same 10 congeners (2.22 ng/g). Total Σ_{22} PBDEs levels in surface sediments in the present study (3.31 ng/g dry wt, top 2 cm in core sediment) were generally comparable to those in surface sediment samples collected in Pearl River Estuary of South China (0.11–13.03 ng/g, Zheng *et al.*, 2004), those in the coastal region of Korea (1.1–33.8 ng/g, Moon *et al.*, 2002), and those in the river and coastal areas of Portugal (0.5–20 ng/g, Lacorte *et al.*, 2003), but were generally lower than those in Osaka Bay of Japan (8–352 ng/g, Ohta *et al.*, 2002) and those in San Francisco Estuary of US (BDL–212 ng/g, Oros *et al.*, 2005). PBDEs levels in surface sediment in Deep Bay were generally at the low-intermediate ranges in the world.

The down-core variations of PBDE concentrations and TOC contents in the core as a function of the deposition year are shown in Fig. 4. In general, the levels of PBDE congeners started to increase from the late 1960s onward and reached the second highest values in 1990s and the highest values in 2003 (top layer). These increases coincided with the production and usage figures of penta-mixture in the world since the 1970s. The second peak PBDE concentrations occurred in the 1990s, which might indicate a critical time for the widespread use of the BFR-related substances in Pearl River Delta. There was a continuous and obvious increase of PBDEs concentrations toward the surface layer after 1982, suggesting the fresh PBDEs inputs into Deep Bay.

Similar distribution profiles have been also observed in the sediment cores from Macao (Chen *et al.*, 2007), Osaka Bay (Sakai *et al.* 2002), Western Europe (Zegers *et al.*, 2003) and the Great Lakes (Song *et al.*, 2004). While different patterns occurred in the sediment cores of Tokyo Bay where PBDEs levels increased up to the mid-1990s and decreased afterwards (Minh *et al.*, 2007). In addition, the absence of all PBDE congeners in the older layers (before the late 1950s) in the present study indicated the absence of natural production of the target BDE congeners. This situation also occurred in sediment cores from the Drammenfjord (Norway), the western Wadden Sea (The Netherlands), and the freshwater Lake Woserin (Germany) (Zegers *et al.*, 2003). The apparent early arrival of PBDEs (late 1950s) in present study might actually reflect bioturbation, which can move contaminants deeper into the core.

Fig. 4. PBDE concentrations in the sediment core by year of deposition

Based on ^{210}Pb dating results, the current sedimentation flux of PBDEs was $0.92 \text{ ng cm}^{-2} \text{ a}^{-1}$, with the average of $0.25 \text{ ng cm}^{-2} \text{ a}^{-1}$. In order to understand the pollution rate, the time required for the concentration of PBDEs to double (T_2) was estimated from data measured in sediment core from Deep Bay. The T_2 value of PBDEs concentrations was 12.3 a ($r^2=0.80$), which was longer than those in sediment cores from the adjacent Pearl River Estuary ($T_2=6\sim7 \text{ a}$, Chen *et al.*, 2007), but was comparable to those in Lake Michigan of US ($T_2=11.2 \text{ a}$, Zhu *et al.*, 2005). The T_2 value in the present study was approximately 1-2 folds higher than the 4-6 a reported

for biota and humans (Hites, 2004).

Due to their high hydrophobic properties, PBDE congeners are expected to be associated mainly with the organic carbon-rich particles in the sediment. In the present sediment core, total organic carbon (TOC) contents ranged from 0.67% to 1.41%, with an average of 1.01%. Statistical analysis showed that TOC contents explained 52% of the variability in total PBDEs concentrations, implying the role played by organic matters in the transport and redistribution of PBDEs in Deep Bay.

3.3. Compositions and Sources

Among the 15 PBDEs (BDE-3, 15, 28, 47, 60, 85, 99, 100, 138, 153, 154, 183, 197, 207 and 209) measured in organisms in the present study, BDE-47 and BDE-100 were the predominant congeners, accounting for 46.5% and 13.5% of total PBDEs in organisms from Deep Bay, respectively (Fig. S2-a). This is consistent with the fact that BDE-47 and BDE-100 are the most bioaccumulative congeners among the commercial Penta-BDE mixtures (Oros et al., 2005). It is noteworthy that, despite the large quantity of BDE-209 used in Asia/China (Ueno et al., 2004) as well as its high concentrations in some of the sediments from the Pearl River Delta (Mai et al., 2005), BDE-209 comprised only <1.3% of the total PBDEs in the organisms of Deep Bay. This may imply that BDE-209 has a low bioaccumulation potential to organisms (Boon et al., 2002; Guo et al., 2008).

Of the 22 PBDE congeners (BDE-17, 28, 32, 35, 37, 47, 49, 66, 71, 75, 77, 85, 99, 100, 119, 138, 153, 154, 166, 181, 183 and 190) in the present study, BDE-47, -49, -99 and -183 were the abundant congeners in core sediment, accounting for

21.4%, 10.9%, 13.8% and 17.4% of total PBDEs concentrations, while in surface sediment (top 2 cm) they accounted for 30.6%, 13.9%, 14.0% and 7.2% of total PBDEs concentrations, respectively (Fig. S2-b). It should be noted that BDE-209 was the most predominant congener in sediment of the adjacent Pearl River Estuary, accounting approximately 86% of total PBDEs (Mai et al., 2005). In the present study, BDE-47 and BDE-49 in surface sediments were higher than the average values in sediment core, whereas BDE-183 was on the contrary. Recent studies showed that octa-BDE (BDE-196, -197 and -203) can be debrominated to hepta-BDE 183, and hexa-BDE 153, as well as the two most commonly detected PBDEs in the environment, penta-BDE 99 and tetra-BDE 47, by anaerobic dehalogenating bacteria (Robrock et al., 2008). Our results suggest that some proportion of BDE-183 in sediment core may be produced in situ by debromination, but not for BDE-47 and BDE-49. Environmental debromination in sediments was not evident in Deep Bay. The same pattern was also observed on the west coast of Canada (Johannessen et al., 2008). In general, highly brominated congeners can be transformed to lower brominated congeners or metabolites, which could become an important source of low brominated BDEs in the environment (Keum and Li, 2005).

Previous studies showed that BDE-47 and BDE-99 were the most common congeners in air, water, and sediment, as well as in people, fish, birds, and mammals (de Wit, 2002; Watanabe and Sahai, 2003; Law et al., 2006). The pattern of the major congeners in sediment from Deep Bay remained similar to that of the industrial formulation Bromkal 70-5DE, which may be related to the widely used penta- and

octa-BDE commercial products and is probably the original source. For example, BDE-99 is a major component in penta-BDE commercial products (48.6% in DE-71 [Great Lakes Chemical] and 44.8% in Bromkal 70-5DE [Chemische Fabrik Kalk], La-Guardia et al., 2006), and in the present study, its relative abundance in the core samples was 13.8%. Compared to those in other environmental compartments of local areas, the proportion of BDE-99 in core sediment of Deep Bay was lower than those in water of Pearl River (27%, Guan et al., 2007), air of Gunagzhou (28%, Chen et al., 2006), and sediments of the Pearl River Delta and northern South China Sea (38%, Mai et al., 2005). BDE-47 is another abundant congener in penta-BDE products (38.2% in DE-71 and 42.8% in Bromkal 70-5DE, La-Guardia et al., 2006), and was predominant in all samples, with a mean percentage content of 24%, which was generally close to those in riverine runoff (35%, Guan et al., 2007), air (39%, Chen et al., 2006), and sediments (28%, Mai et al., 2005). BDE-183, considered as a marker compound for the octa-mix PBDE formulation (42% in DE-79; Great Lakes Chemical; La-Guardia et al., 2006), was also found in the core sediment of Deep Bay at relatively high median concentrations, equivalent to 0.12 ng/g (15% of total PBDEs), suggesting the extensive use of technical octa-BDEs in local areas. The high proportion of BDE-183 (8%-16%) in the waterbirds of South China has also been reported (Luo et al., 2009). These results were completely different from those in three cores collected from Western Europe where BDE183 was systematically absent (Zegers et al., 2003). E-waste and waste discharges in surrounding areas were reported as the potential sources (Mai et al., 2005; Wu et al., 2008).

In core sediment, significant positive correlations were found among PBDE congeners except for BDE-181, -166 and -71 which were at very low levels (Table S1), suggesting that these congeners had similar source inputs and underwent similar deposition and decomposition processes. Principal component analysis (PCA) showed that the first two factors accounted for 75% of the total variance in the dataset (Fig. S3). Tri- to penta-BDE congeners primarily contributed to factor 1 which explained 63% of the total variance, indicating that these contaminants may originate from penta-BDE commercial products and their metabolites. Hexa- and hepta-BDEs formed another group and contributed primarily to factor 2. They might have been formed from the mixed octa-BDE products and by the degradation of deca-BDE through microorganism and photolysis (Söderström et al., 2004; Gerecke et al., 2005). Correlations among PBDE congeners in organisms are also summarized in Table S2 and Fig. S4.

3.4. BSAF of PBDE

Hydrophobic and lipophilic organic contaminants can easily accumulate in organisms such as fish mainly *via* bioconcentration directly from the water environment (LeBlanc, 1995), and/or biomagnification through trophic transfer (Kiriluk et al., 1995). Aquatic organism especially benthic organisms can absorb contaminants from sediment, and its ability can be expressed by the biota-sediment accumulation factors (BSAF), defined as a ratio of the lipid-normalized concentration of the chemical in tissue and the organic carbon-normalized concentration of the chemical in sediment. In this study, we selected the PBDE congeners measured both

383 in organisms and sediment (top 2 cm) to calculate the BSAF for individual PBDE
 384 congeners in each specimen. Individual BDE congeners with descending values of
 385 BSAFs (in parentheses) for all specimens in Deep Bay followed the sequence of
 386 BDE-100 (0.72) > BDE-154 (0.68) > BDE-85 (0.48) > BDE-153 (0.39) > BDE-28
 387 (0.30) > BDE-47 (0.29) > BDE-138 (0.016) > BDE-183 (0.014) > BDE-99 (0.001). In
 388 the adjacent Pear River Estuary (Xiang *et al.*, 2007), the median values of BSAF for
 389 biota followed the sequence of BDE-100 (17.35) > BDE-47 (11.18) > BDE-154 (4.49)
 390 > BDE-99 (3.36) > BDE-66 (2.81) > BDE-153 (2.58) > BDE-28 (1.46) > BDE-183
 391 (0.04) > BDE-138 (0.00) > BDE-209 (0.00). In Deep Bay and Pearl River Estuary, the
 392 highest BSAF value was BDE-100 while the lower BSAF values were BDE-138 and
 393 BDE-183. The BASF values of the target PBDE congeners (<0.8) in the present study
 394 were lower than those in fish from the lakes of the northeastern United States (16–38,
 395 Dodder *et al.*, 2002), suggesting a weaker bioaccumulation of PBDE in organisms of
 396 Deep Bay. The relatively longer age (3–4 a) of the target fish (*Pomoxis annularis* and
 397 *Lepomis macrochirus*) in the above study may partly contribute the higher BASF
 398 values. Correlations between the BSAF of PBDE and the corresponding K_{ow} in Deep
 399 Bay were shown in Fig. 5. As the bromine substituted number of PBDE congener
 400 increases, the corresponding K_{ow} and hydrophobic properties increase, leading to the
 401 higher ability for bioaccumulating contaminants. On the other hand, as the bromine
 402 substituted number of PBDE congener increases, the molecular volume and the steric
 403 effect also increase, resulting in a lower ability for bioaccumulating contaminants. In
 404 the present study, 3–6 Br PBDE except for BDE-99 and BDE-138 had the higher

ability of bioaccumulation, while Dodder et al. (2002) reported that 4–6 Br PBDE in fishes from the northeastern United States had the higher ability of bioaccumulation. It was reported that the maximum bioaccumulation for PBDE in British Columbia grizzly bears was found to be in the mid-range of PBDE log K_{ow} (Christensen et al., 2005).

Fig. 5. The biota-sediment accumulation factors (BSAF) of PBDE congeners in Deep Bay and their relation with the logarithm of octanol-water partition coefficient (K_{ow})

4. Conclusions

In this paper, we provide detailed information about PBDEs in benthos and core sediment of Deep Bay, South China. The PBDEs concentrations in benthic organisms were at intermediate levels compared with those reports in other parts of the world. BDE-47 was the most predominant congener in both organisms and core sediments (not including BDE-209 in sediment), accounting for 46.5% and 21.4% of total target PBDEs, respectively. Owing to the recent rapid regional economic development, PBDEs contamination in the bay revealed increasing time trends in core sediment, suggesting an ongoing PBDEs input into the bay. E-waste and waste discharges may be the potential sources of contamination in Deep Bay.

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Supporting Information

Table S1. Correlations between PBDE congeners and total organic carbon (TOC) in core sediments of Deep Bay, South China

Table S2. Correlations between PBDE congeners and lipid contents in organisms of Deep Bay, South China

Fig. S1. Distribution of sedimentation age and excessive ^{210}Pb activity in the sediment core B

Fig. S2. The percentage of PBDE congeners in organism and sediment of Deep Bay, South China

Fig. S3. Rotated factor pattern for PBDEs in core sediments of Deep Bay, South China

Fig. S4. Rotated factor pattern for PBDEs in organisms of Deep Bay, South China

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Figure captions and table list**Figures:**

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Fig. 2. The PBDEs concentrations and $\delta^{15}\text{N}$ values in organisms collected from Deep Bay.

Fig. 3. The relationships between PBDEs concentrations and $\delta^{15}\text{N}$ values and lipid percents in organisms from Deep Bay.

Fig. 4. PBDE concentrations in the sediment core by year of deposition (BDE209 was not included in the total PBDEs).

Fig. 5. The biota-sediment accumulation factors (BSAF) of PBDE congeners in Deep Bay and their relation with the logarithm of octanol-water partition coefficient (K_{ow}).

599 Fig. 1. Sampling locations in Deep Bay, South China

600

601

Fig. 2. The PBDEs concentrations and $\delta^{15}\text{N}$ values in organisms collected from Deep Bay.

Planktivorous fish (1. *Mugil cephalus*, 2. *Clupanodon punctatus*, 3. *Clupanodon thrissa*), small carnivorous fish (4. *Leiognathus ruconius*, 5. *Leiognathus bindus*, 6. *Ilisha elongate*, 7. *Thrissa dussumieri*, 8. *Sillago japonica*), carnivorous fish (9. *Dasyatis zugei*, 10. *Platycephalus indicus*, 11. *Inimicus cuvieri*), benthos feeder (12. *Nibea acuta*, 13. *Collichthys lucidus*, 14. *Cynoglossus robustus*) and omnivorous organisms (15. *Trypauchen vagina*, 16. *Portunus pubescens*, 17. *Polynemus sextarius*, 18. *Penaeus orientalis*, 19. *Glossogobius giuris*).

Fig. 3. The relationships between PBDEs concentrations and $\delta^{15}\text{N}$ values and lipid percents in organisms from Deep Bay

Fig. 4. PBDE concentrations in the sediment core by year of deposition (BDE209 was not included in the total PBDEs)

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Supporting Information

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Table S1. Correlations between PBDE congeners and total organic carbon (TOC) in core sediments of Deep Bay, South China

	TOC(%)	BDE17	BDE28	BDE32	BDE35	BDE37	BDE47	BDE49	BDE66	BDE71	BDE75	BDE77	BDE85	BDE99	BDE100	BDE119	BDE138	BDE153	BDE154	BDE166	BDE183	BDE190	PBDEs
TOC(%)	1	0.70	0.65	0.40	0.60	0.61	0.66	0.70	0.63	0.44	0.40	0.46	0.43	0.62	0.60	0.26	0.57	0.58	0.70	0.24	0.58	0.47	0.72
BDE17		1	0.97	0.63	0.92	0.84	0.97	1.00	0.95	0.26	0.87	0.90	0.86	0.84	0.88	0.61	0.67	0.46	0.58	0.26	0.38	0.70	0.95
BDE28			1	0.61	0.97	0.90	0.96	0.98	0.98	0.21	0.89	0.94	0.90	0.83	0.89	0.61	0.65	0.45	0.55	0.21	0.32	0.69	0.94
BDE32				1	0.62	0.57	0.62	0.64	0.60	0.14	0.60	0.52	0.56	0.57	0.57	0.41	0.47	0.35	0.34	0.14	0.39	0.49	0.63
BDE35					1	0.90	0.92	0.94	0.97	0.16	0.87	0.94	0.92	0.78	0.84	0.65	0.65	0.44	0.48	0.21	0.36	0.74	0.90
BDE37						1	0.81	0.86	0.90	0.38	0.76	0.83	0.82	0.69	0.76	0.71	0.64	0.48	0.54	0.46	0.39	0.68	0.85
BDE47							1	0.97	0.93	0.19	0.84	0.88	0.84	0.90	0.92	0.54	0.66	0.50	0.60	0.18	0.39	0.69	0.96
BDE49								1	0.97	0.26	0.88	0.91	0.88	0.85	0.89	0.62	0.67	0.47	0.58	0.24	0.37	0.70	0.96
BDE66									1	0.21	0.90	0.95	0.92	0.81	0.88	0.66	0.65	0.46	0.52	0.24	0.32	0.70	0.92
BDE71										1	0.17	0.05	0.12	0.16	0.14	0.42	0.22	0.30	0.34	0.68	0.43	0.23	0.32
BDE75											1	0.91	0.93	0.72	0.79	0.65	0.56	0.27	0.27	0.15	0.13	0.67	0.80
BDE77												1	0.92	0.73	0.83	0.63	0.54	0.30	0.38	0.12	0.13	0.65	0.83
BDE85													1	0.78	0.85	0.72	0.67	0.38	0.36	0.20	0.20	0.78	0.84
BDE99														1	0.97	0.46	0.83	0.73	0.74	0.15	0.47	0.80	0.94
BDE100															1	0.53	0.83	0.69	0.73	0.16	0.38	0.80	0.94
BDE119																1	0.46	0.28	0.26	0.70	0.30	0.67	0.60
BDE138																	1	0.82	0.79	0.31	0.54	0.89	0.79
BDE153																		1	0.88	0.36	0.78	0.70	0.68
BDE154																			1	0.36	0.63	0.61	0.72
BDE166																				1	0.54	0.43	0.32
BDE183																					1	0.55	0.55
BDE190																						1	0.80
PBDEs																							1

* $p < 0.01$ as coefficient is larger than 0.40, while $p < 0.05$ as coefficient ranges 0.30~0.40 (n=38). Principal Component Analysis (PCA) was performed to get the rotated factor pattern of PBDEs in core sediment using varimax with Kaiser normalization.

666 Table S2. Correlations between PBDE congeners and lipid contents in organisms of

667 Deep Bay, South China

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	Lipid	BDE3	BDE15	BDE28	BDE47	BDE60	BDE85	BDE100	BDE99	BDE154	BDE153	BDE138	BDE183	BDE197	BDE207	BDE209	PBDEs
Lipid	1	0.12	0.65	0.17	0.52	0.56	0.50	0.33	0.12	0.29	0.58	0.12	0.54	0.54	0.32	0.29	0.69
BDE 3		1	-0.20	-0.14	-0.40	0.51	-0.10	0.24	1.00	-0.20	0.53	1.00	0.62	-0.16	-0.36	-0.28	-0.17
BDE15			1	0.36	0.54	0.15	0.18	-0.02	-0.20	0.08	0.16	-0.20	0.14	0.39	0.56	0.66	0.56
BDE28				1	0.38	-0.02	0.33	-0.03	-0.14	-0.02	0.09	-0.14	-0.13	0.07	0.37	0.45	0.54
BDE47					1	-0.06	0.59	-0.06	-0.40	0.47	0.10	-0.40	0.03	0.56	0.68	0.60	0.85
BDE60						1	0.12	0.72	0.51	-0.01	0.92	0.51	0.62	0.46	-0.20	-0.09	0.34
BDE85							1	0.10	-0.10	0.74	0.34	-0.10	0.20	0.54	0.23	0.29	0.74
BDE100								1	0.24	-0.06	0.71	0.24	0.35	0.47	-0.25	0.00	0.32
BDE99									1	-0.20	0.53	1.00	0.62	-0.16	-0.36	-0.28	-0.17
BDE154										1	0.16	-0.20	0.14	0.44	0.41	0.25	0.50
BDE153											1	0.53	0.68	0.57	-0.12	0.04	0.51
BDE138												1	0.62	-0.16	-0.36	-0.28	-0.17
BDE183													1	0.22	-0.17	-0.08	0.24
BDE197														1	0.24	0.36	0.74
BDE207															1	0.71	0.54
BDE209																1	0.60
PBDEs																	1

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Fig. S1. Distribution of sedimentation age and excessive ^{210}Pb activity in the sediment
core B

Fig. S2. The percentage of PBDE congeners in organism and sediment of Deep Bay, South China *

* It should be noted that BDE-209 was not included in sediment.

679 Fig. S3. Rotated factor pattern for PBDEs in core sediments of Deep Bay, South

680 China

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683 Fig. S4. Rotated factor pattern for PBDEs in organisms of Deep Bay, South China

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