Current levels and composition profiles of PBDEs and alternative flame retardants in surface sediments from the Pearl River Delta, southern China: Comparison with historical data

She-Jun Chen [a], An-Hong Feng [a,b], Ming-Jing He [a,b], Man-Ying Chen [a,b], Xiao-Jun Luo [a], Bi-Xian Mai [a,*]

[a] State Key Laboratory of Organic Geochemistry, Guangzhou Institute of Geochemistry, Chinese Academy of Sciences, Guangzhou 510640, China
[b] Graduate University of Chinese Academy of Sciences, Beijing 100049, China

HIGHLIGHTS

► PBDE levels in sediments have decreased substantially since China's RoHS directive.
► Contamination of novel DBDPE has exceeded that of deca-BDE in the PRD sediments.
► The congener profiles of PBDEs in the sediments have changed significantly.
► Significant biological or photolytic degradation of PBDEs may occur in the environment.

ARTICLE INFO

ABSTRACT

Polybrominated diphenyl ethers (PBDEs) and alternative flame retardants were measured in surface sediments collected during 2009–2010 from the Pearl River Delta, southern China (a large manufacturing base for electronics/electrical products), to evaluate the influence of China's RoHS directive (adopted in 2006) on their environmental occurrence. The concentrations in sediments from different water systems ranged from 3.67 to 2520 ng/g (average of 17.1–588 ng/g) for PBDEs and from 0.22 to 5270 ng/g (average of 11.3–454 ng/g) for the alternative retardants. Although the PBDE levels have decreased significantly compared with those in sediments collected in 2002 in this region, the levels of alternative decabromodiphenyl ethane (DBDPE) have exceeded those of BDE209 (two predominant halogenated flame retardants (HFRs) in China) in the majority of sediments. This finding suggests a different contaminant pattern of HFRs in current sediments due to the replacement of the deca-BDE mixture with DBDPE in this region. In addition, sediment concentrations of discontinued PBDEs in the rural area are clearly elevated due to e-waste dismantling. The congener profiles of PBDEs in the current sediments (with more abundant lower-brominated congeners) differed substantially from those in 2002 and from the technical products, suggesting that biological or photolytic debromination of PBDEs may have occurred in the environment.

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1. Introduction

Halogenated (usually brominated or chlorinated) flame retardants (HFRs) are chemicals that are extensively used in consumer products, including electronic equipment, textiles, furniture, and cars, to improve their resistance to fire (Batterman et al., 2010). A class of HFRs known as polybrominated diphenyl ethers (PBDEs), tetrabromobisphenol A (TBBPA), hexabromocyclododecane (HBCD), and Dechlorane Plus (DP) have become a topic of great concern because of their widespread occurrence in the environment and potential adverse effects on humans and wildlife (Cetin and Odabasi, 2007; Qiu et al., 2007; Harrad et al., 2009; Covaci et al., 2011; Ali et al., 2012). The phase-out of technical penta- and octa-BDE mixtures in many regions worldwide has caused their

manufacturers to seek alternatives to these products. For instance, 1,2-bis(2,4,6-tribromophenoxy)ethane (BTBPE) and decabromodiphenyl ethane (DBDPE) are used as replacements for technical octa- and deca-BDE mixtures, respectively (Kierkegaard et al., 2004; Hoh et al., 2005). Meanwhile, some historically used HFRs are being reintroduced to the market, such as hexabromobenzene (HBB) and pentabromoethylbenzene (PBEB) (Salamova and Hites, 2011). DP has also been reported as a possible candidate for deca-BDE replacement (Sverko et al., 2010). These chemicals have been detected in the environment at numerous locations (Covaci et al., 2011; Moller et al., 2011; Davis et al., 2012).

China is a large manufacturer and consumer of flame retardants, with a total annual production volume of 200 000 t, and the flame retardants used in more than 80% of the modified plastics in China are HFRs (Zhang and Lu, 2011). The annual production volumes have been estimated to be 20 000, 12 000, and 300 t for the deca-BDE mixture, DBDPE, and DP, respectively (Xiao, 2006). HBB, BTBPE, and pentabromotoluene (PBT)

are also manufactured in China, but production volumes are not available. No manufacturing information is available for PBEB in China. In 2006, the Chinese government declared the "Measures for Administration of the Pollution Control of Electronic Information Products", namely, China's Restriction of Hazardous Substances Directive (RoHS), and restricted the use of PBDEs with accepted maximum levels of 1000 mg/kg in electrical and electronic equipment (Zhou, 2006).

The Pearl River Delta (PRD), located in southern China, is one of the most highly urbanized and industrialized regions of China. In an earlier study, we reported the concentrations and distributions of PBDEs in the sediments collected in 2002 in the PRD (Mai et al., 2005). In the present study, riverine and estuarine surface sediments covering a larger geographical region were collected during 2009–2010 and were analyzed for PBDEs and alternative flame retardants, including DBDPE, BTBPE, DP, PBT, PBEB and HBB, to examine their current contamination status in the sediments in this region after the implementation of China's RoHS directive. The spatial distributions of these HFRs were predicted by Kriging interpolation analysis, and the correlations among the HFR compounds were analyzed to investigate their sources. Additionally, the HFR composition profiles in the sediments were examined and compared to understand the spatial and temporal variations as well as the processes for these chemicals that potentially occur in the environment.

2. Materials and methods

2.1. Sample collection

The PRD region has a temperate climate and numerous rivers discharging water into the South China Sea, mainly through the Pearl River Estuary (PRE) (Fig. 1). The rivers run through urban, electronics manufacturing, less-industrialized, rural, or electronic waste (e-waste) recycling areas that are potentially a characteristic of different pollution sources and levels. Sample collection was described in detail in a previous study (Feng et al., 2012) and is given briefly here. Surface sediment (top 5 cm) samples were collected from July 2009 to October 2010 in four major rivers and an estuary in the PRD region (Fig. 1): the Dongjiang River ($n = 42$), the Zhujiang River ($n = 19$), the Xijiang River ($n = 13$), the Beijiang River ($n = 14$), and the Pearl River Estuary (PRE) ($n = 13$). The Dongjiang and Zhujiang Rivers run through Dongguan (a center for electronics manufacturing) and Guangzhou (a megacity of southern China), respectively. The Beijiang River flows through both rural (B1–B4) and urban (B5–B14) areas. The Xijiang River flows mainly through rural and less-industrialized areas. The PRE receives fluvial inputs from these rivers. Eight sediment samples (SD1–SD8) were collected from the Shunde tributaries of the Xijiang and Beijiang Rivers, which are located in an industrial town (Shunde is a manufacturing center for household appliances). Sediment samples ($n = 13$) were also obtained from the Dayanhe River, which runs through an agricultural area (the upper reach) and an e-waste area (the lower reach). A previous study obtained sedimentation rates of 4–6 cm y^{-1} after the 1990s in the Zhujiang and Xijiang rivers and 1.5–3.9 cm y^{-1} in the PRE (Liu et al., 1998). Therefore, the top 5 cm of sediment was expected to represent recent inputs (less than 5 years). After collection, the samples were immediately transported to the laboratory and stored at −20 °C until further analysis.

2.2. Extraction and cleanup

Detailed procedures of extraction and cleanup have been given elsewhere (Zhang et al., 2009). Briefly, the sediment samples were freeze-dried, ground, and homogenized by sieving through a stainless steel 80-mesh sieve (0.2 mm). Samples (15–20 g) were spiked with surrogate standards (^{13}C-PCB141, BDE77, BDE181, and ^{13}C-BDE209) and Soxhlet-extracted with a mixture of acetone and hexane (1:1) for 24 h. Activated copper granules were added to the extraction

flasks during the extraction to remove elemental sulfur. The extracts were concentrated to 1–2 mL using a rotary evaporator and then purified through a 10-mm i.d. silica column, packed with neutral silica (8 cm, 3% deactivated), 44% sulfuric silica (8 cm), and anhydrous sodium sulfate (1 cm). The column was eluted with 30 mL hexane: dichloromethane (1:1, V/V). The concentrated extracts were reconstituted in 200 μL of *iso*-octane and spiked with quantification standards (^{13}C-PCB208, BDE118 and BDE128) prior to instrumental analysis.

2.3. Instrumental analysis

An Agilent 6890 gas chromatograph coupled to an Agilent 5975 mass spectrometer in electron capture negative ionization mode (GC-ECNI-MS) was used to analyze the target BFRs. Di- through hepta-BDEs, PBEB, HBB, pentabromotoluene (PBT), and DP isomers (*anti*- and *syn*-DP) were separated in a DB-XLB (30 m × 0.25 mm × 0.25 μm, J&W Scientific) capillary column. For octa- through deca-BDEs, DBDPE, and BTBPE, a DB-5HT (15 m × 0.25 mm × 0.10 μm, J&W Scientific) capillary column was used. More information on the instrumental parameters is available in a previous study (Zhang et al., 2009). The method detection limit, defined as a signal-to-noise ratio of 5:1, was 0.01–1.0 ng/g for PBDEs, 1.5 ng/g for DBDPE, 0.02–0.03 ng/g for DP isomers, and 0.01–0.06 ng/g for other compounds.

2.4. Quality control

The surrogate recoveries in all sediment samples were 109 ± 9.1% for BDE77, 94.2 ± 9.2% for BDE181, 89.1 ± 15.5% for ^{13}C-BDE209, and 95.1 ± 11.4% for ^{13}C-PCB141. Either a procedural blank or a spike recovery sample (pre-extracted sediment) was run, with each batch of 11 field samples. Except for BDE47, which was found in nearly all the procedural banks, BDE28, 66, 99, 153, 206, and 209 and *anti*-DP were found in less than one-third of the blanks, but their amounts were <8% of those in the corresponding sample extracts. The recoveries of PBDEs (BDE28, 47, 66, 85, 99, 100, 138, 153, 154, 183, and 209), DP, and DBDPE ranged from 73.5% to 123%, with mean values between 77.9% and 117% for the individual compounds. The relative standard deviations (RSDs) of the analytes in the three duplicate sediment samples were within the range of 1.7%–13.5%, except for DBDPE and HBB, with RSDs of 17.8% and 47.1%, respectively.

2.5. Data analysis

Kriging is a commonly used geostatistical method of spatial estimation (Vienneau et al., 2009). Ordinary Kriging interpolation analysis based on the spherical model was employed to predict and visualize the spatial distribution of the data for total analyzed HFRs in the riverine and estuarine sediments in the PRD region using ArcGIS 9.3 software. The formula for ordinary Kriging is

$$Z^*(\chi_0) = \sum_{i=1}^{n} iZ(i)$$

where $Z^*(\chi_0)$ is the estimated value at point χ_0, $Z(\chi_i)$ is the measured value at point χ_i, λ_i is the weight for the residual of $Z(\chi_i)$, and n is the number of measured samples (Bargaoui and Chebbi, 2009). The data were log-transformed to follow normal distributions. For correlation analysis, the concentrations were first log-transformed and were then plotted against each other. The statistical significance tests were conducted by ANOVA or the Mann–Whitney rank sum test using SigmaPlot 11.2.
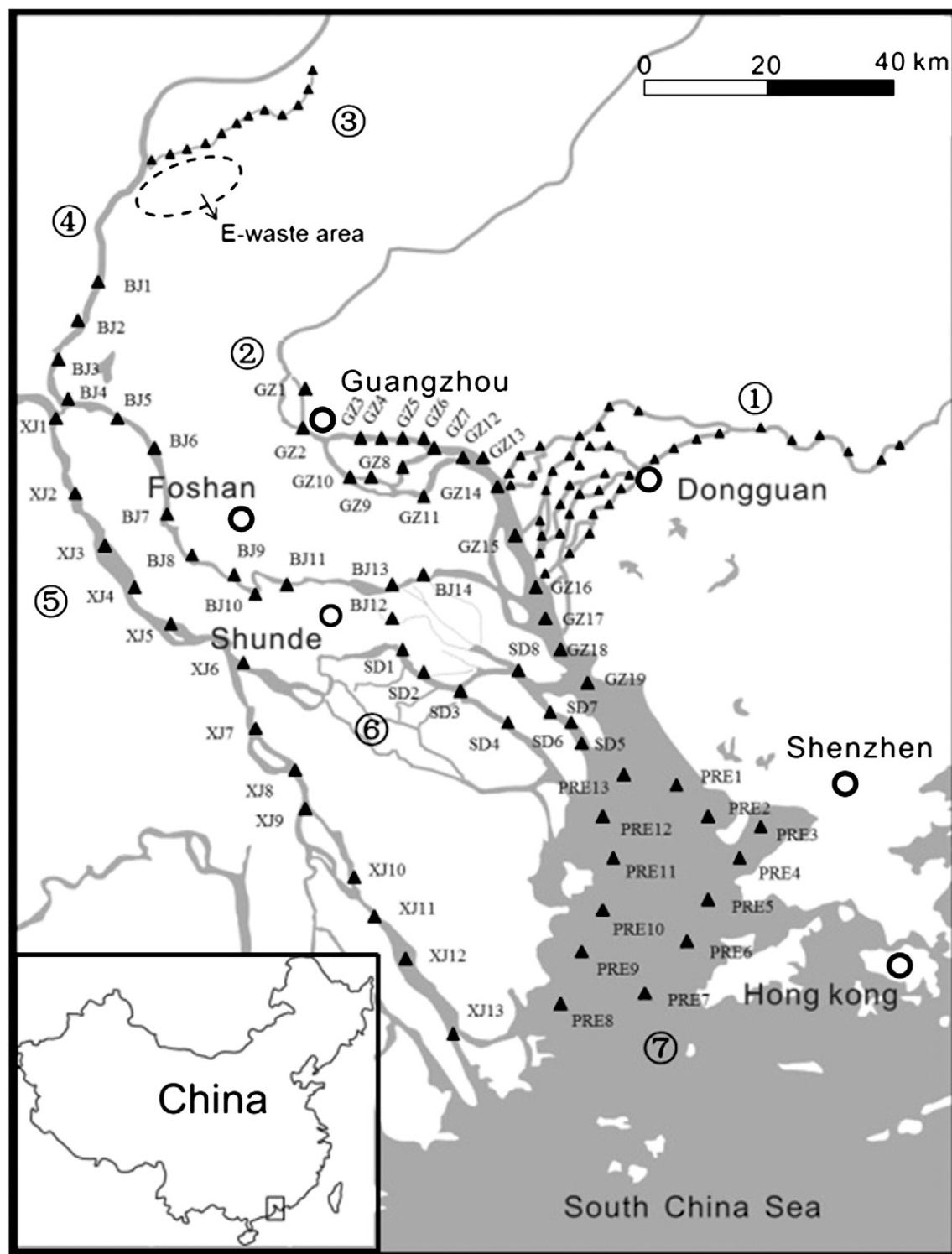
Fig. 1. Map of the Pearl River Delta (PRD) in southern China and locations of sampling sites (2009–2010). The rivers and estuary are numbered as follows: ① Dongjiang River, ② Zhujiang River, ③ Dayanhe River, ④ Beijiang River, ⑤ Xijiang Rivers, ⑥ Shunde tributaries, and ⑦ Pearl River Estuary.

3. Results and discussion

3.1. Concentration levels

The concentrations of PBDEs and the alternatives in the surface sediments in the studied area are summarized in Table 1 and are provided in detail in Table S1 in the Supplementary material. PBDEs were detected in all the sediment samples, with concentrations ranging from 3.67 to 2520 ng/g dry weight. It was not surprising that the

highest PBDE concentrations were found in sediments from the Dongjiang River (with an average of 588 ng/g), which runs through a large electronics manufacturing center. The Zhujiang River (272 ng/g), which runs through a densely populated city, showed the second-highest average concentration. These concentrations were followed by those in sediments in the Shunde tributaries (117 ng/g), which are located in an industrial town, and the Dayanhe River (lower reach 128 ng/g and upper reach 35.9 ng/g), which is adjacent to an e-waste site. The Beijiang and Xijiang Rivers (55.0 and 29.7 ng/g, respectively),

Table 1
Concentrations (ng/g dry weight) of HFRs in the riverine and estuarine sediments from the Pearl River Delta in 2009–2010.

Sampling area	PBDEs[a]	DBDPE	BTBPE	DP	PBT + PBEB + HBB
Dongjiang River	3.83–2517 (588)	n.d.–1728 (193)	0.03–20.1 (2.86)	0.09–28.0 (3.56)	0.09–2.96 (0.69)
Zhujiang River	10.7–910 (272)	11.8–1180 (266)	0.13–41.8 (8.47)	0.41–45.0 (5.64)	0.11–2.30 (0.56)
Dayanhe River	13.5–161 (70.4)	22.4–362 (141)	n.d.–73.4 (7.54)	0.34–23.0 (4.25)	0.13–2.30 (0.48)
Beijiang River	9.99–183 (53.5)	n.d.–263 (81.4)	0.47–1.68 (0.92)	0.57–3.48 (1.48)	0.13–1.00 (0.25)
Xijiang River	4.12–65.0 (29.7)	2.86–80.4 (32.4)	n.d.–1.22 (0.39)	n.d.–0.95 (0.37)	n.d.–0.38 (0.10)
Shunde tributaries	5.78–242 (117)	2.90–302 (115)	0.22–5.87 (2.13)	0.09–3.43 (1.38)	0.10–0.54 (0.24)
Pearl River Estuary	3.67–45.6 (17.1)	n.d.–30.5 (10.2)	0.04–0.53 (0.20)	n.d.–2.13 (0.57)	0.09–1.98 (0.27)

[a] Sum of BDE28, 47, 66, 100, 99, 154, 153, 138, 183, 197, 203, 196, 208, 207, 206, and 209.

which flow through rural or less-industrialized areas, and the PRE have the lowest PBDE concentrations. The average concentrations of BDE209, an important PBDE congener in the environment, follow the same order of the total PBDEs in the sediments, varying from 14.2 ng/g in the PRE to 562 ng/g in the Dongjiang River.

Compared with the levels in the surface sediments collected in 2002 (Mai et al., 2005), the overall concentrations currently measured were approximately 4- and 3-fold lower in the Zhujiang River and 3- and 9-fold lower in the Dongjiang River for BDE209 and the other PBDEs (Σ_9PBDEs, sum of BDE28, 47, 66, 99, 100, 138, 153, 154, and 183), respectively ($p < 0.04$). The sediment PBDE concentrations in the PRE, receiving fluvial inputs mostly from the Zhujiang and Dongjiang Rivers, also decreased remarkably ($p \leq 0.01$) for Σ_9PBDEs (0.28 ng/g in 2010) relative to the concentrations in 2002 (3.13 ng/g) (Mai et al., 2005) and 2004 (2.93 ng/g) (Zheng et al., 2004), and they decreased moderately for BDE209 (14.2 in 2010 versus 18.5 ng/g in 2002). This finding clearly indicates a substantial decline in the release of PBDEs, especially the restricted congeners, into the rivers in recent years after the declaration of China's RoHS in 2006. The exception to this finding is that the average concentration in the Xijiang River increased by a factor of 1.6 for BDE209 (26.5 versus 16.1 ng/g) and leveled off for Σ_9PBDEs (0.38 versus 0.35 ng/g) compared with the values in 2002. It has been indicated that regional atmospheric transport from the industrial/urban areas is the main source of PBDEs in the Xijiang River sediments, especially for lower brominated PBDEs (Mai et al., 2005). The steady concentrations of Σ_9PBDEs (mainly from technical penta- and octa-BDE mixtures) in the Xijiang River suggest that these lower brominated BDE congeners are still being emitted into the atmosphere (e.g., from PBDE-treated products) after their regulation. It should be noted that the highest concentrations of Σ_9PBDEs (10.2–47.6 ng/g, average of 20.7 ng/g) were found in the lower reach of the Dayanhe River, which is located in a rural area affected by e-waste dismantling activities. The Σ_9PBDE concentrations in the Dayanhe River were significantly higher than those in the Xijiang River, which also runs through rural areas ($p = 0.006$). This result indicates that in contrast to the decreased sediment PBDE levels in urban areas, which are related to industrial/domestic sources, the contamination of PBDEs (especially the banned PBDEs) in some Chinese rural areas due to e-waste dismantling remains a considerable concern (Wang et al., 2005; Luo et al., 2007).

DBDPE was measured in 97% of the sediment samples, with concentrations ranging from non-detectable to 1730 ng/g. The highest average concentrations of DBDPE were measured in sediments from the Zhujiang (266 ng/g) and Dongjiang (267 ng/g) rivers, after the six samples from the upper reach of the Dongjiang River that are not impacted by direct industrial effluent from Dongguan (the electronics manufacturing center) were excluded. The DBDPE concentrations in the other water systems decreased in the following order: the Dayanhe River (lower reach 205 ng/g and upper reach 98.3 ng/g) > the Shunde tributaries (115 ng/g) > the Beijiang River (81.4 ng/g) > the Xijiang River (32.4 ng/g) > the PRE (10.2 ng/g). The concentrations of BTBPE and DP, with averages of 0.20–8.47 and 0.56–5.64, respectively, were approximately two orders of magnitude lower than those for PBDEs and DBDPE, and they decreased in the same order: the Zhujiang

River > the Dongjiang River > the Dayanhe River > the Shunde tributaries > the Beijiang River > the Xijiang River > the PRE. However, the BTBPE and DP concentrations were significantly higher ($p < 0.03$) in the lower reach of the Dayanhe River (18.7 for BTBPE and 9.43 ng/g for DP) compared with the other measurements. The concentrations of PBT, PBEB, and HBB were much lower, with combined average concentrations ranging from 0.10 to 0.69 ng/g, reflecting that the rivers and the estuary are dominated by diffuse sources for these pollutants in this region.

The concentrations of tri- to hepta-BDEs (0.02–1.33 ng/g), BDE209 (3.94–103 ng/g), DP (0.69–7.00 ng/g), and PBEB (0.07–1.90 ng/g) found in surficial sediments from the Dalian coastal area in China, which is affected by industrial and domestic sources, were within the range of our concentrations (Wang et al., 2011). The concentrations of PBDEs (without BDE209) (<8 ng/g) in the riverine and coastal sediments from Indonesia were comparable to our results, while the concentrations of BDE209 (<27 ng/g) were substantially lower than most values in this study (Ilyas et al., 2011). The PBDE concentrations in the San Francisco Bay sediments were found to range from 2 to 8 ng/g (median 4 ng/g) (Klosterhaus et al., 2012), a much lower range than in our results. High sediment concentrations of PBDEs (up to 18 700 ng/g) were recently reported in an artificial Lake in Korea (Moon et al., 2012). The average DP concentration (4.93 ng/g) in sediments in a canal near a DP manufacturing plant in China (Wang et al., 2010) was comparable to those in the Zhujiang, Dongjiang, and Dayanhe Rivers. These concentrations were lower than the sediment DP concentrations (21–310 ng/g) recently reported in the Niagara River in the U.S., which was affected by DP manufacturing sources (Shen et al., 2011). The concentrations of DBDPE (4.8–23 ng/g) and BDE209 (4.1–82 ng/g) in sediments from Llobregat River basin, Spain (Guerra et al., 2010), were generally similar to the levels in the Xijiang River in this study. More data for comparison are listed in Table S2.

3.2. Spatial distribution and correlation analysis

The spatial distribution of the total HFRs is displayed in Fig. 2. It is clear that the most highly contaminated zones were located in the Dongjiang and Zhujiang Rivers, followed by the Dayanhe River (which was not shown in Fig. 2 because this river is very narrow) and the Shunde tributaries. Treated or untreated industrial effluents in Dongguan and Shunde were the major sources of HFRs for the Dongjiang River and Shunde tributaries. The industrial, commercial, and domestic sources in densely populated Guangzhou are largely responsible for the occurrence of HFRs in the Zhujiang Rivers (Feng et al., 2012). HFRs in the sediments of the Dayanhe River are associated with e-waste dismantling activities. The HFR contamination in the Beijiang River sediment is lower than in the rivers above, whereas elevated concentrations were found in sediments near the outlet of the Dayanhe River. The Xijiang River and the PRE showed the lowest HFR contamination. The concentrations of total HFRs increased downstream slightly in the Xijiang River, while the estuary receiving riverine runoff showed decreasing HFR concentrations in the sediments from the outlets to the coast. Relatively higher concentrations occurred at the western side of the PRE than the eastern side due to
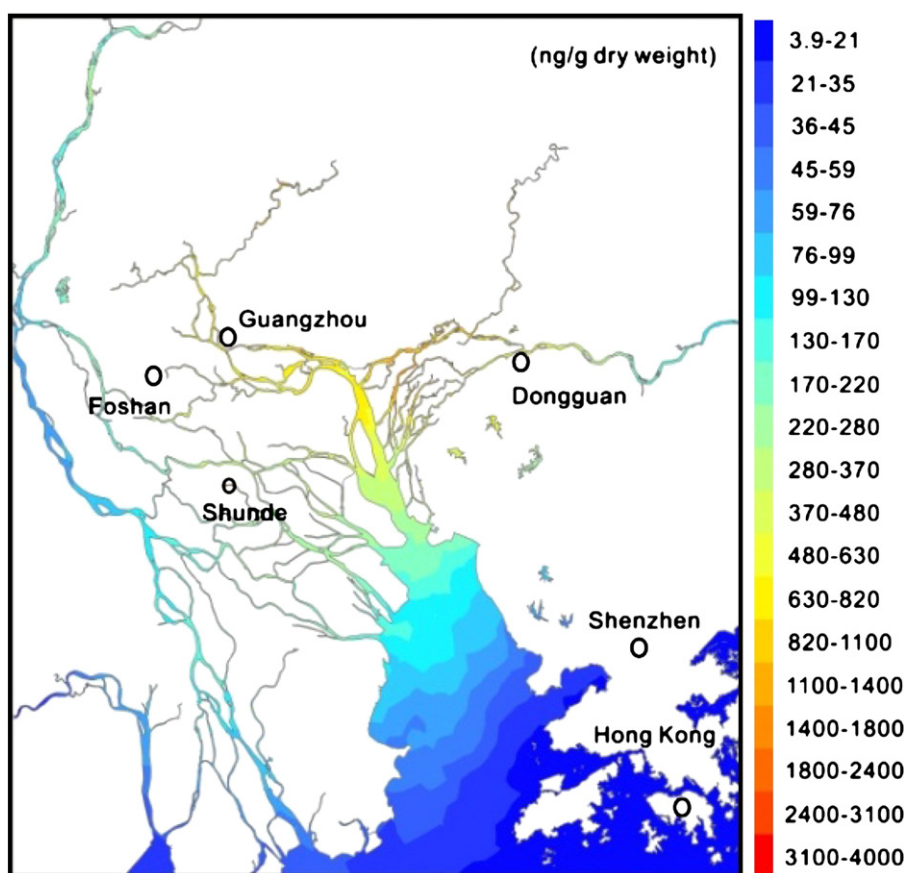
Fig. 2. Spatial distributions of total HFRs (PBDEs, DBDPE, BTBPE, HBB, PBEB, PBT, and DP) in the surface sediments from the Pearl River Delta constructed by the Kriging interpolation method.

the prevailing upwelling coastal current at the eastern side and the riverine current at the western side in the PRE (Mai et al., 2005).

The correlation analysis (Table S3) revealed that the sediment HFR concentrations generally showed significant correlations in the rivers where local input sources exist (the Dongjiang, Zhujiang, and Dayanhe Rivers and the Shunde tributaries), suggesting a common source for most of these HFRs in these rivers. Nevertheless, the HFR concentrations in the estuary and in the rivers without local sources (the Beijiang and Xijinag Rivers) showed less significant correlations. This result suggests diverse sources or environmental processes of HFRs to these rivers and the estuary. It is noteworthy that DBDPE, a replacement of deca-BDE, had strong correlations with BDE209 in all of the sediments except for the Beijiang River, also in line with their similar environmental behavior due to their similarity in structure.

3.3. Composition profiles and implications for environmental processes

The HFRs in the sediments of the PRD were dominated by PBDEs and DBDPE, which accounted for 34%–76% and 23%–64% (on average) of the total HFRs, respectively, due to their use in large quantities (Xiao, 2006). Of the PBDEs, BDE209 was predominant, with average relative contributions ranging from 78% to 92%. This result suggests that the deca-BDE mixture and DBDPE were the predominant HFR products used in this region in recent years. The fractions of DBDPE [DBDPE/(DBDPE + BDE209)] were greater than 0.5 in most sediment samples (Fig. 3), suggesting that the contamination of novel DBDPE has exceeded that of the deca-BDE mixture in most places in the PRD. The fractions in the Dongjiang River and the PRE (with mean values of 0.25 and 0.39, respectively) were significantly lower than in the other rivers ($p \leq 0.03$, except for PRE vs. the Xijiang River), indicating that the use of the deca-BDE mixture is still significant in this electronics manufacturing center (Dongguang). Ten archived

sediments collected from different rivers in the PRD in 2002 were analyzed again to obtain the DBDPE fractions. The fractions ranged from 0.01 to 0.17 (with a mean value of 0.06), which were significantly lower than those in the current sediments ($p < 0.001$). The values of DBDPE/(DBDPE + BDE209) in the current sediments in the Dongjiang River (0.25 ± 0.14) were also moderately higher than those in the surface sediments collected in 2006 in the same river (0.23 ± 0.13), as reported by Zhang et al. (2009). The results reflect an increasing use of DBDPE in the PRD region. The similar fraction ranges in the Dongjiang River and the PRE are evidence that the Dongjiang River runoff is primarily responsible for the presence of HFRs in the PRE. This result is consistent with our previous results indicated by the diastereoisomer compositions and enantiomeric fractions of HBCD in the sediments in these areas (Feng et al., 2012).

Fig. 4 demonstrates the composition profiles of the legacy PBDEs (tri- through hepta-BDE congeners) that were mainly derived from penta- and octa-BDE mixtures in the sediments. The congener profiles were substantially different from those observed in the sediments collected in 2002 (including the Zhujiang, Dongjiang, and Xijiang Rivers and the PRE, Fig. S1 in the Supplemental material), which were similar to the profiles of the common technical penta-BDE mixtures (DE-71 and 70-5DE). First, the contributions from BDE183 in the current sediments were significantly elevated compared with those collected in 2002 ($p < 0.001$), except for the Xijiang River and the PRE for two possible reasons: i) the release of PBDEs derived from the penta-BDE mixture decreased by a greater degree than BDE183 (a main ingredient of the octa-BDE mixture) after their regulation in 2006 in China, and/or ii) more BDE183 was generated from the microbial or photolytic debromination of highly brominated BDEs relative to other BDE congeners (Bezares-Cruz et al., 2004; He et al., 2006). Second, there was an apparent change (although not statistically significant for all cases) in the ratio of BDE47/(BDE47 + BDE99) between the current and previous
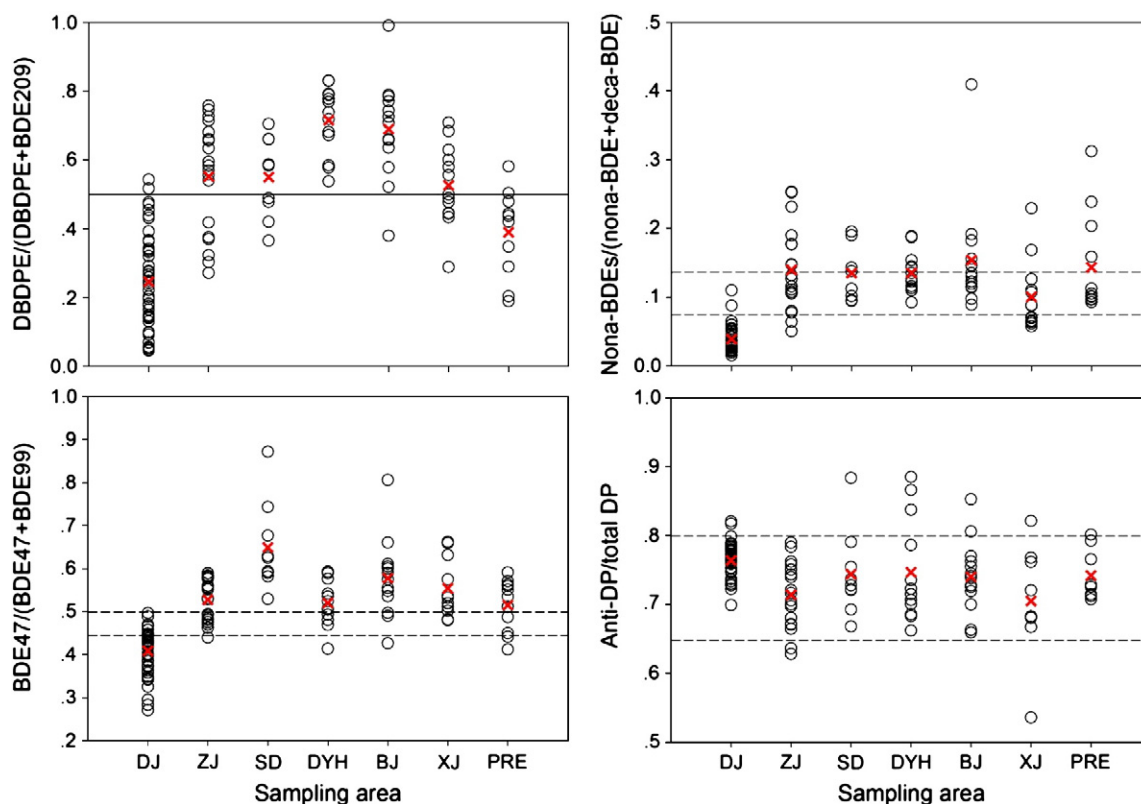
Fig. 3. Ratios of DBDPE/(DBDPE + BDE209), BDE47/(BDE47 + BDE99), nona-BDEs/(nona-BDE + deca-BDE), and *anti*-DP/total DP concentrations in the surface sediments from the Pearl River Delta. The dotted lines represent the maximum and minimum ratios reported in technical mixtures. The solid line (value = 0.5) represent an equal concentration of DBDPE and BDE209. ZJ, Zhujiang River; SD, Shunde tributaries; DJ, Dongjiang River; DYH, Dayanhe River; BJ, Beijiang River; XJ, Xijiang River; PRE, Pearl River Estuary.

sediments. The mean BDE47/(BDE47 + BDE99) ratios ranged from 0.39 to 0.49 in the sediments collected in 2002, with most values below the ratios in the technical mixture (0.44 and 0.50) (Fig. S2), while the ratios in the current sediments were mostly larger than 0.5 (with mean values of 0.52–0.55), except for the Dongjiang River (0.4). Third, the contributions of BDE28 and 66 in this study were also apparently higher than those reported previously. For example, the average contributions ranged from 6% (Dongjiang River) to 30% (PRE) in the present study, whereas they ranged from 1% to 7% in 2002 (Mai et al., 2005). We speculated that the degradation of highly brominated BDEs (from both the deca-BDE mixture and the legacy PBDEs) in the environment may have led to the considerable variations in the PBDE profiles in the sediments because of the reduced fresh inputs of PBDEs into the rivers and estuary. Additional evidence

for this explanation is the significantly ($p < 0.02$) higher ratios (0.06–0.52) of nona-BDEs/(nona-BDE + deca-BDEs) in most sediments compared with those in the technical deca-BDE mixtures (0.03–0.10) (La Guardia et al., 2006). In general, the lowest ratios (0.02–0.11) were found in the Dongjiang River, which is attributed to the ongoing release of PBDEs derived from the deca-BDE mixture in this electronics manufacturing center, as mentioned above. It is noteworthy that the PBDE profiles in the sediments in the Dayanhe River were distinct between the upper and lower reaches (Fig. S3). The upper reach (upstream of the e-waste source) showed clearly high contributions of BDE28 (24%) and ratios of BDE47/(BDE47 + BDE99) (0.55) compared with the lower reach (7% and 0.47, respectively), which flows across the e-waste area.

Technical DP mainly consists of *syn*- and *anti*-isomers. The fraction of the *anti*-DP to the total DP concentration (f_{anti}) in the sediment samples was calculated. The f_{anti} values reported in Chinese technical DP products were within the range of 0.65–0.79 measured in our laboratory and by Wang et al. (2010), similar to those (0.65–0.80) reported previously (Hoh et al., 2006; Tomy et al., 2007). The f_{anti} values in most of the sediment samples were in this range, suggesting no pronounced stereoselective enrichment of *anti*-DP in the sediment in the PRD.

4. Conclusions

The current contamination status of PBDEs and alternative compounds was examined in the surface sediments in the PRD, southern China, and compared with historical levels in this region prior to the implementation of China's RoHS directive. The PBDE levels have decreased for both Σ_9PBDEs and BDE209 compared with the concentrations in 2002, primarily due to a reduction in use of PBDEs in the electrical and electronic manufacturing industries. However, the contamination levels of novel DBDPE have exceeded those of deca-BDE in
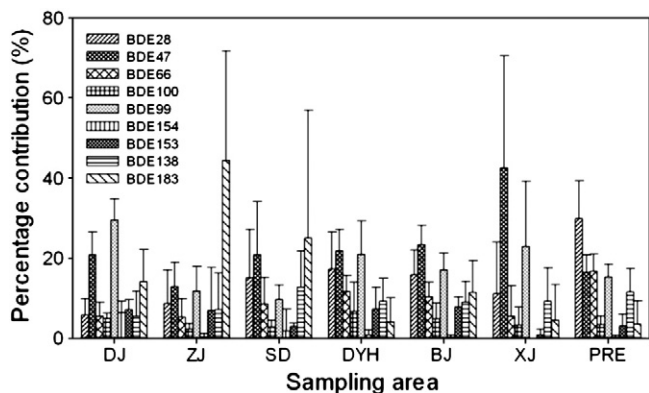
Fig. 4. Congener profiles of PBDEs (tri- through hepta-BDEs) in surface sediments from the Pearl River Delta. ZJ, Zhujiang River; SD, Shunde tributaries; DJ, Dongjiang River; DYH, Dayanhe River; BJ, Beijiang River; XJ, Xijiang River; PRE, Pearl River Estuary.

most sediments. The results demonstrate the influence of China's RoHS directive, adopted in 2006, on the HFR contamination patterns in the sediments. In contrast, e-waste dismantling resulted in clearly elevated concentrations of the discontinued PBDEs in sediments in the rural area. The congener profiles of the PBDEs in the current sediments have changed greatly compared with the profiles in previous sediments and in the technical PBDE products, suggesting an influence of significant biological or photolytic debromination of PBDEs in the environment because of the reduced fresh inputs to the sediments. This finding also raises concerns over the degradation of highly brominated compounds into lower-molecular compounds in the environment.

Acknowledgments

Appendix A. Supplementary data

Supplementary data to this article can be found online at http://dx.doi.org/10.1016/j.scitotenv.2012.11.104.

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