

## Polybrominated diphenyl ethers (PBDEs) in the riverine and marine sediments of the Laizhou Bay area, North China†

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62 riverine and marine sediments were collected from the Laizhou Bay area, where the largest manufacturing base of brominated flame retardants (BFRs) in Asia is located. Eight polybrominated diphenyl ethers (PBDEs) were analyzed to investigate the impact of rapidly-developed bromine industries on the regional aquatic system. PBDE concentrations varied largely in riverine sediments.  $\Sigma_7$ PBDEs (including BDE 28, 47, 99, 100, 153, 154 and 183) and BDE 209 ranged from 0.01 to 53 ng g<sup>-1</sup> dw and from 0.74 to 285 ng g<sup>-1</sup> dw with a mean value of 4.5 ng g<sup>-1</sup> dw and 54 ng g<sup>-1</sup> dw, respectively, indicating a strong influence of direct pollution discharges from local factories. In marine sediments,  $\Sigma_7$ PBDEs and BDE 209 ranged from not detected (nd) to 0.66 ng g<sup>-1</sup> dw and from 0.66 to 12 ng g<sup>-1</sup> dw with a mean value of 0.32 ng g<sup>-1</sup> dw and 5.1 ng g<sup>-1</sup> dw, respectively. PBDE concentrations were mostly <10 ng g<sup>-1</sup> dw for  $\Sigma_7$ PBDEs and <50 ng g<sup>-1</sup> dw for BDE 209, which are at a relatively low level for monitored riverine and coastal sediments around the world. Even at the most contaminated sites in Laizhou Bay area, PBDE concentrations were not among the highest concentrations reported in the literature. Congener compositions were dominated by BDE 209 (57.2–99.9% of the sum of BDE congeners), with minor contributions from penta- and octa-BDE products. Tri- to octa-BDE congeners were well correlated among each other ( $r > 0.75$ ) and thus sources from similar mixing of penta- and octa-BDE products were suggested in this area. Compared with riverine sediments, a much better correlation between PBDE concentrations with TOC was observed in marine environment. The congener pattern changed and their correlation coefficients among each other were remarkably reduced. Contributions of BDE 28, 47 and 99 to  $\Sigma_7$ PBDEs were generally the same in almost all the marine sites, while it was distinctively higher for BDE 153. These are probably attributable to several reasons, such as contributions by atmospheric deposition and/or redistribution between particles of various sizes during and/or after fluvial transportation combined with the difference of physiochemical properties of BDE congeners.

### 1. Introduction

Polybrominated diphenyl ethers (PBDEs) are a class of brominated flame-retardants (BFRs) widely used in a variety of commercial and industrial products. They can enter the environment from various direct and indirect sources.<sup>1</sup> Many studies have reported their occurrence in all kinds of environmental compartments including biota worldwide.<sup>2,3</sup> Due to their lipophilic and hydrophobic characteristics, they tend to adsorb onto

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#### Environmental impact

Polybrominated diphenyl ethers (PBDEs) are flame retardants used extensively in commercial and industrial products. Although the use and production of penta- and octa-BDEs have been banned in the European Union and some USA states, Deca-BDEs are still in use globally. The Laizhou Bay area is the most important centre of Deca-BDEs production in China. In this study, we not only filled up the data gap of the occurrence of PBDEs in the riverine and marine sediments of Laizhou Bay area, but also show how the industrial activities impact the aquatic system by a systematic sampling campaign and analysis of common PBDEs.

fine particles, deposit on the seabed and further bioaccumulate in organisms. Wide concern has risen over the use and exposure of PBDEs.<sup>4</sup> PBDE products mainly include penta-, octa- and deca-BDE. Tetra-BDE (predominantly BDE 47) and penta-BDE (predominantly BDE 99 and 100) are main components of penta-BDE mixtures. BDE 183 (>40%) is often used as an indicator of the octa-BDE mixture. Deca-BDE product contains more than 98% of BDE 209.<sup>3</sup> Penta- and octa-BDEs have been listed under the Stockholm Convention and they have been banned in several countries.<sup>5</sup> In China however, both production and consumption of BFRs including some PBDE products have risen rapidly in recent years.

Laizhou Bay is one of the three main bays of Bohai Sea, making up 10% of the total area.<sup>6</sup> It is a shallow bay with smooth submarine topography and a submerged gentle slope from coast to the open sea. Its average water depth is less than 10 m with a maximum of 18 m. Due to the input of Yellow river, tidal current in the bay is very complex. Laizhou Bay is one of the bays most easily affected by storm tides in China. Due to its coastal morphology and its location on the intersection of warm and cold air masses, Laizhou Bay could be threatened by storm tide all the year around.<sup>7</sup>

Around the bay, industrial and urban developments have been booming in recent years. The famous chemical industrial base – Weifang Binhai Economic Development Zone (aka Binhai Zone), which utilizes abundant seawater and underground brine resources, is located to a large extent along the south coast of Laizhou Bay. Brominated chemical production is one of the mainstay industries in the Binhai Zone. The biggest research and development center of bromine-related products in China is located on the south coast of Laizhou Bay. Binhai Zone is also the biggest manufacturing base for BFRs in China, and a large number of plants which produce BFRs are scattered in this region. On the northwest coast, there is the second largest oilfield (Shengli oilfield) of China and thus petro-chemical industries are well developed due to the abundant oil resources. Huge amounts of domestic sewage and industrial wastewaters are discharged into Laizhou Bay. It was estimated to receive approximately 200 million tons of terrigenous sewage and over 100 thousand tons of maritime pollutants every year.

This study presents an investigation of the distribution and levels of PBDEs around Laizhou Bay area *via* a large survey of surface sediments throughout river systems. Each river is representative of different levels of anthropogenic activities, as well as in marine sediments of Laizhou Bay. Given the encouraged growth of marine chemical industries and marine fishery in Laizhou Bay, it is also our purpose to investigate the influence of highly developed bromine industries on the aquatic and sediment system in this area.

## 2. Materials and methods

### 2.1 Study area and sample collection

The study area and sampling sites are shown in Fig. 1. Twelve tributaries of different sizes flow into Laizhou Bay. They are the Yellow River (also named as Huanghe River, HH), Yihong River (YHH), Guangli River (GLH), Zimaigou River (ZMG), Xiaoqing River (XQH), Mihe River (MH), Bailan River (BLH),

Dihe River (DH), Yuhe River (YH), Weihe River (WH), Jiaoli River (JLH) and Dajiawa drainage system (DJW). HH is the biggest river with the largest river runoff and landslide discharge, followed by XQH, WH and JLH.

River sediments are here classified into three categories according to the surrounding environment that predominantly impacts them: (1) industrial; (2) urban; (3) rural. In the industrial group, DH1 and DH2 were sampled in an area with dyeing, printing, textile and sugar industries in addition to chemical plants. Other industrial sites were influenced mostly by chemical or petrochemical industries. The marine sediments are not included into any group. Site WFG was located within Weifang port, which was going through sea reclamation with large amounts of fresh soil transported and mixed. The sediments in this area were probably strongly influenced by current anthropogenic activities while being sampled and cannot reflect the true sedimentary information. It is not included into any group.

Samples were collected between September 14 and October 17, 2009, using a stainless steel grab sampler. There are thirty-two surface sediments (top 0–10 cm) from ten river and drainage system sites, four river estuary sites and twenty-six marine sites. All the samples were transported on ice to the laboratory and then stored at  $-20\text{ }^{\circ}\text{C}$  until analyzed.

### 2.2 Extract and cleanup

Freeze-dried sediment samples (20 g dry weight) were homogenized and Soxhlet extracted in dichloromethane (DCM) for 24 h, with 2,4,5,6-tetrachloro-*m*-xylene (TCMX) and PCB 209 added prior to extraction as recovery surrogates. The extract was reduced to 1 mL by rotary evaporation and then transferred to a glass column (15 cm long, 0.7 cm i.d.) filled with 1 cm anhydrous sodium sulfate and 3 cm acidified silica gel/sulfuric acid (50% (w/w) concentrated sulfuric acid). The extract was eluted with 15 mL hexane (HEX) and concentrated to 0.5 mL under a gentle  $\text{N}_2$  for cleanup on silica columns, packed with 3 cm pre-rinsed silica gel (3% deactivated) and 1 cm anhydrous  $\text{Na}_2\text{SO}_4$  on the top. Fractionation was achieved with the solvent sequences 15 mL of HEX (F1) and 15 mL of 1 : 1 DCM/HEX (F2). Fraction F1 contained all the PBDEs and was reduced to 25  $\mu\text{L}$  under a gentle stream of  $\text{N}_2$ . 20 ng of BDE 77 was added as internal standard before instrumental analysis.

### 2.3 Instrumental analysis

PBDEs were detected with GC-NCI-MS (Agilent GC7890 coupled with 5975C MSD). Details were described in a previous study.<sup>8</sup> A DB-5MS (30 m  $\times$  0.25 mm i.d., 0.25  $\mu\text{m}$  film thickness) capillary column was used for the determination of PBDE congeners, except for BDE 209. A 10 m VFS column (0.25 mm i.d., 0.25  $\mu\text{m}$  film thickness, VFS) was used for BDE 209 analysis. Samples were injected at 290  $^{\circ}\text{C}$  in splitless mode. The oven program was 130  $^{\circ}\text{C}$  for 1 min, ramped at 12  $^{\circ}\text{C min}^{-1}$  to 155  $^{\circ}\text{C}$ , 4  $^{\circ}\text{C min}^{-1}$  to 215  $^{\circ}\text{C}$ , and further ramped at 3  $^{\circ}\text{C min}^{-1}$  to 300  $^{\circ}\text{C}$  and held for 10 min. The ions  $m/z$  79 and 81 were monitored for BDE 28, 47, 99, 100, 153, 154 and 183, and ions  $m/z$  485, 487 for BDE 209. Peaks were quantified only if the signal/noise  $\geq$  4. The limit of detection (LOD), defined as

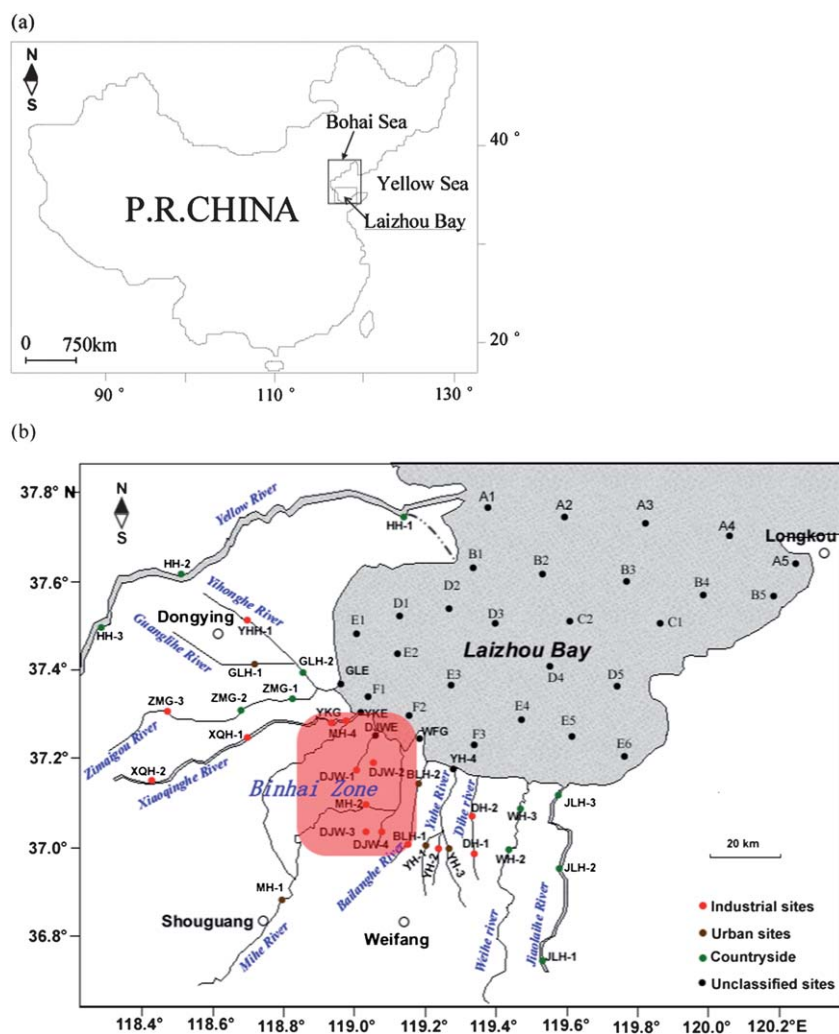


Fig. 1 (a) Location of Laizhou Bay in China; (b) Map of riverine and marine sampling sites.

a signal of 4 times the noise level, ranged from 0.01 to 0.08 ng g<sup>-1</sup> for all the congeners (Table 1).

Sediment total organic carbon (TOC) was determined with an elemental analyzer (CHNS Vario Ei III, Elementar) after removal of carbonates with 1 mol L<sup>-1</sup> hydrochloric acid.

## 2.4 QA/QC

For each batch of 20 field samples, a procedural blank (solvent with a filter paper identical to that used to wrap the sediment) and a sample duplicate were processed. Only small concentrations of BDE 209 were found in procedural blanks and they were appropriately subtracted from those in the sample extracts.

**Table 1** Concentrations of target BDE congeners in sediments of the Bohai Sea (ng g<sup>-1</sup> dw)<sup>c</sup>

	Detection limit	Riverine sediments (n = 36)			Marine sediments (n = 26)			%Det. ratio (n = 62)
		Range	Mean	Median	Range	Mean	Median	
BDE 28	0.01	nd <sup>b</sup> -15	1.1	0.27	nd-0.15	0.06	0.06	85
BDE 47	0.01	nd-9.0	0.72	0.25	nd-0.11	0.06	0.06	96
BDE 100	0.01	nd-0.7	0.13	0.02	nd-0.06	0.02	0.02	19
BDE 99	0.02	nd-4.8	0.45	0.2	nd-0.09	0.06	0.06	72
BDE 154	0.02	nd-2.4	0.22	0.03	nd-0.07	0.04	0.03	30
BDE 153	0.03	nd-18	0.98	0.03	nd-0.16	1	0.11	60
BDE 183	0.03	nd-16	0.84	0.03	nd-0.15	0.06	0.03	30
BDE 209	0.08	0.7-290	49	17	0.7-12	5.1	4.5	99
Σ <sub>7</sub> PBDEs <sup>a</sup>		nd-53	4.5	0.92	nd-0.66	0.34	0.33	99

<sup>a</sup> Σ<sub>7</sub>PBDEs refers the sum of all quantified PBDE congeners except BDE209. <sup>b</sup> nd, under detection limit. <sup>c</sup> Note: concentrations under detection limit were set to be LOD values when mean and median concentrations were calculated.

Three duplicate samples reported RSDs within 20% for all the target chemicals. The recoveries for TCmX and PCB209 were  $87.1 \pm 12.5\%$ ,  $85.8 \pm 9.8\%$ . However, it should be noted that these surrogates we used might behave differently with PBDEs, particularly with BDE 209. Since BDE 209 can degrade in the injector of the GC, the actual recoveries may actually be lower than estimated from the recovery standards. Reported values were not corrected by surrogate recovery.

### 3. Results and discussion

#### 3.1 PBDE concentrations and spatial distributions

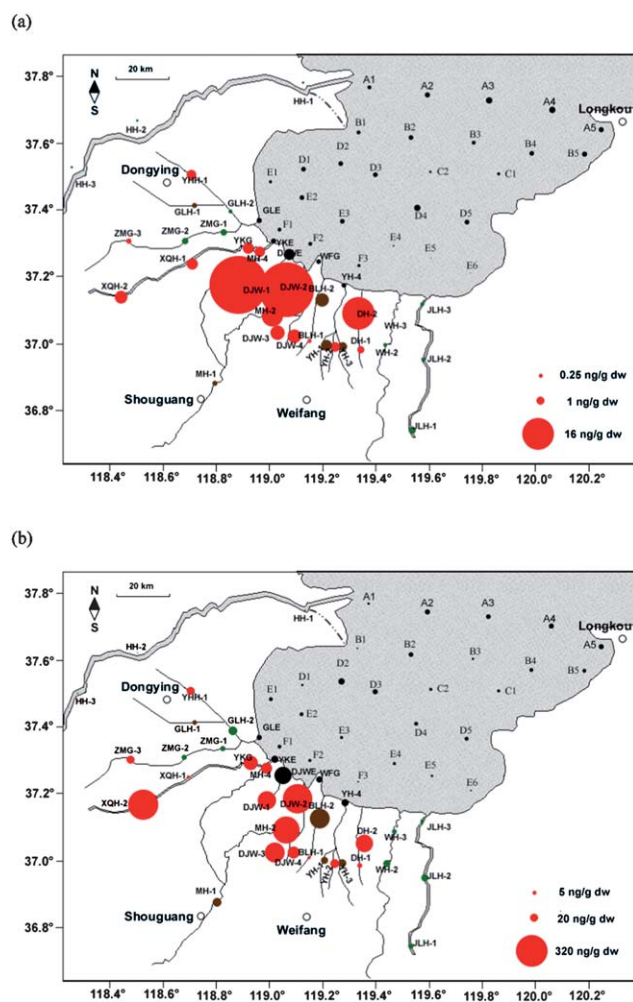
PBDE concentrations are shown in Fig. 2. Eight BDE congeners were analyzed including BDE 28, 47, 99, 100, 154, 153 183 and 209, Table 1.  $\Sigma_7$ PBDEs (sum of BDE 28, 47, 99, 100, 154, 153 and 183, except for BDE 209) in riverine sediments ranged from 0.01 to  $53 \text{ ng g}^{-1}$  dw with a mean value of  $4.5 \text{ ng g}^{-1}$  dw. BDE 209 ranged from 0.74 to  $280 \text{ ng g}^{-1}$  dw with a mean value of  $54 \text{ ng g}^{-1}$  dw. Over 90% and 70% of all the riverine samples ( $n = 36$ ) were in the range of nd– $10 \text{ ng g}^{-1}$  dw and nd– $50 \text{ ng g}^{-1}$  dw for  $\Sigma_7$ PBDEs and BDE 209, respectively. The remaining few sites with higher concentrations occurred mostly at industrial areas, such as

Dajiawa drainage system and Xiaoqinghe River. The highest concentrations of  $\Sigma_7$ PBDEs were found at sites DJW1 ( $53 \text{ ng g}^{-1}$  dw) and DJW2 ( $48 \text{ ng g}^{-1}$  dw), while the highest concentrations of BDE 209 were at site XQH2 ( $285 \text{ ng g}^{-1}$  dw) and DJW2 ( $274 \text{ ng g}^{-1}$  dw), about ten and four times higher than their respective average levels. PBDE concentrations in riverine sediments varied substantially, indicating the PBDE contamination is probably derived from direct discharge from local factories. The lowest concentrations were found in Yellow River, Jiaolai River and Weihe River. This is probably attributable to these rivers flowing through vast farmlands combined with their sediments having abundant sandy characteristics. In marine sediments, PBDE concentrations varied slightly. They ranged from not detected (nd) to  $0.66 \text{ ng g}^{-1}$  dw and from 0.66 to  $12 \text{ ng g}^{-1}$  dw for  $\Sigma_7$ PBDEs and BDE 209, with a mean value of  $0.32 \text{ ng g}^{-1}$  dw and  $5.1 \text{ ng g}^{-1}$  dw, respectively.

#### 3.2 Global comparison of sediment PBDEs

PBDE concentrations in sediments have been reported from various regions around the world and most samples analyzed contained less than  $50 \text{ ng g}^{-1}$  of  $\Sigma_7$ PBDEs. A number of European and American samples had extremely high concentrations of PBDEs. For example, up to 368 and  $898 \text{ ng g}^{-1}$  for BDE-47 and BDE-99, respectively, were detected in the Tees Estuary, the downstream area of a BFR manufacturing plant, in the United Kingdom, and up to 212 and  $148 \text{ ng g}^{-1}$  for  $\Sigma_7$ PBDEs were found in San Francisco bay and a site in the Niagara river of the USA (impacted by industrial and urban areas), respectively.<sup>9–11</sup> Higher concentrations of  $\Sigma_7$ PBDEs were also found in Dongjiang river of China ( $94.7 \text{ ng g}^{-1}$ ), which receives wastewater from the world's largest manufacturing base for electronics/electrical products.<sup>12</sup> In comparison, most riverine samples in our study had  $\Sigma_7$ PBDE levels less than  $10 \text{ ng g}^{-1}$ . This is lower than most of the riverine and coastal sediments reported in North America and Europe, such as Niagara river ( $20.4 \text{ ng g}^{-1}$ ), Cinea river and marine coast in Spain ( $0.16\text{--}34.1 \text{ ng g}^{-1}$ ) and Danube river in Austria ( $10.4 \text{ ng g}^{-1}$ ), and similar to those in some regions of Asia, like Kuwait ( $0.08\text{--}3.8 \text{ ng g}^{-1}$ ), Korea ( $5.3 \text{ ng g}^{-1}$ ) and Singapore (Table 2) ( $6.2 \text{ ng g}^{-1}$ ).<sup>8–22</sup> Despite the different congeners analyzed in these studies (see footnotes in Table 2), the eight congeners studied in the present study are the most commonly detected and predominant congeners in their studies. Therefore, the concentrations have comparability. Three sediment samples collected from DJW area with higher levels are slightly lower than the highest concentrations found in Dongjiang river of the Pearl River Delta (PRD) and just a twentieth to a third of the highest found in the UK and the USA, respectively. Although manufacturing scale and process could be influential, the differences in BFR market might be a key point. In China or Asia, deca-BDE is the dominant product of PBDEs while in formerly North America and Europe, penta-BDE and/or octa-BDE products accounted for the most.<sup>2,3</sup>

BDE 209 concentrations in sediments varied substantially worldwide, from not detected (nd) to  $11600 \text{ ng g}^{-1}$  in river sediment of Japan, which is the highest concentration found so far.<sup>13</sup> Generally, most sites have concentrations lower than  $500 \text{ ng g}^{-1}$  (Table 2), while the few sites that exceed  $1000 \text{ ng g}^{-1}$  can be classified as hot spots contaminated by BDE 209. These are often



**Fig. 2** PBDE concentration distributions for  $\Sigma_7$ PBDEs (a) and BDE 209 (b) (different colors represent the same sampling information as Fig. 1b).



**Table 2** Comparison of PBDEs levels in surface sediments from other PBDE contaminated regions around the world (ng g<sup>-1</sup> dw)<sup>a</sup>

Locations	Sampling surroundings	ΣPBDEs (ng g <sup>-1</sup> dw)	BDE 209 (ng g <sup>-1</sup> dw)
Riverine and coast, Laizhou Bay	Industrial, urban and rural areas	0.01–53(4.4)	0.74–290(51)
Laizhou Bay, this study	Marine	nd–0.6(0.32)	0.66–12(5)
Hadley lake, USA <sup>20</sup>	Proximity to a suspected PBDE manufacturing facility, air deposition is the only known method for PBDEs to enter Hadley Lake	5.2–37.6(13.9)	19–36(28.8)
Niagara river, USA <sup>9</sup>	Rural, urban, industrial areas	nd–148(20.4) <sup>b</sup>	nd
Great Lakes, USA <sup>21–23</sup>	At locations where the effects of local point sources could be minimized	0.3–6.3 <sup>b</sup>	4–242
North Sea, Germany <sup>24</sup>	Marine		0.03–6.5
Swedish rivers <sup>25</sup>	Rural, urban and industrial areas	8–50 <sup>c</sup>	68–7100
Cinea river and marine coast, Spain <sup>26</sup>	Industrial area, the upstream of the river and marine	0.16–34.1 <sup>d</sup>	2.1–132.1
Danube, Austria <sup>27,28</sup>	Unknown	10.4	0.08–84
Marine in Korea <sup>3</sup>	Marine	1.1–33.8(5.3)	
Kuwait marine coast <sup>29</sup>	Marine	0.08–3.8 <sup>d</sup>	
Singapore marine coast <sup>30</sup>	Marine	3.4–13.8(6.2) <sup>c</sup>	
Tokyo Bay, Japan <sup>31</sup>	Marine	0.05–3.6 (0.94) <sup>c</sup>	0.89–85 (20)
Pearl river estuary, China <sup>32</sup>	Marine	0.33–21.8(3.1)	0.6–112(18.5)
North South China Sea <sup>12</sup>	Marine	0.04–4.5(0.46)	0.41–9.1(3)
Yangtze river delta, China <sup>33</sup>	Marine	Nd–0.55(0.15)	0.16–95(13)
Bohai Sea, China <sup>8</sup>	Marine	0.22–0.9	1.76–15(7)
Zhujiang, China <sup>9</sup>	Industrial, urban areas	1.1–49.3 (12.9)	26.3–3580 (890)
Dongjiang, China <sup>12</sup>	Industrial, urban areas	2.2–94.7 (27.3)	21.3–7340 (1440)

<sup>a</sup> Note: data in brackets are mean concentrations. <sup>b</sup> Apart from the eight congeners analyzed in present study, BDE 66, 85 and 138 were also analyzed and not detected. <sup>c</sup> Only BDE 47, 99 and 100 were analyzed. <sup>d</sup> 40 congeners were analyzed and only the eight congeners similar with our study were detected. <sup>e</sup> Apart from the eight congeners analyzed in present study, BDE 3, 15, 197, 207 were also included with minor contributions.

impacted by industries or local discharge. For example, up to 7340 ng g<sup>-1</sup> and 3580 ng g<sup>-1</sup> were found in Dongjiang and Zhujiang river of the Pearl River Delta of China, respectively.<sup>12</sup> High concentrations of BDE 209 were also found in Busan Bay of Korea (2253 ng g<sup>-1</sup>), which is a heavily industrialized region where many factories in this area produce petrochemical products, machinery, non-ferrous metals, automobiles, and ships.<sup>14</sup> In our study, the highest BDE 209 concentrations were found in two tributaries receiving direct sewage discharge from a BFR plant and a petrochemical complex, respectively. By comparison, BDE 209 level in the Laizhou Bay area is much lower than in the PRD with intensive deca-BDE usage and is definitely not among the highest concentrations reported in the literature. As a center of bromine-related products in China and the biggest manufacturing base of BFRs in Asia though, the impact by PBDE contamination is much better than expectations from other areas.

Regarding marine sediments, the findings were consistent with our previous study on Bohai Sea.<sup>8</sup> The levels of Σ<sub>7</sub>PBDEs fall in the low end of the global range, and are similar to those in the Pearl River estuary, northern South China Sea and Yangtze River delta. The levels of BDE 209 are similar to North Sea in Germany and some coastal regions of China, such as the northern part of the South China Sea, coastal sediments of Hong Kong and Yangtze River delta, and they are also relatively low compared to other marine sediments in the world.<sup>23–25</sup>

### 3.3 PBDE congener patterns and their correlations

Similar to many studies from various regions around the world, BDE 209 was the predominant congener, accounting for 57–100% of the total PBDEs detected in all the samples with a mean value of 93%.<sup>12,14–17</sup> This is consistent with the expectations based

on deca-BDE commercial mixtures accounting for the largest market demand among PBDEs in Asia compared to penta- and octa-BDE.<sup>18,19</sup> Among the 7 lower brominated congeners, BDE 28 and 47 were the most frequently detected congeners, followed by BDE 99. BDE 28 and 47 were detected in almost all of the samples (n = 62). The other three congeners – BDE 100, 154 and 183 were only detected in less than 30% of all the samples.

In riverine sediments, congener profiles varied among sampling groups. Few congeners mainly BDE 28 and/or 47 were detected in the rural group, while at industrial and urban groups, BDE 28, 47, 99, 153 and 183 were commonly detected and their detection ratios were higher than those of BDE 100 and 154. The proportions between these congeners seemed quite similar at most industrial and urban sites, despite a few exceptional samples. For instance, BDE 47 and 99 were dominant at XQH2, while BDE 153 and 183 were remarkably higher than other congeners at DJW1 and YH1. The variation may directly reflect the characteristics of surrounding emission sources. Pearson correlations were made between BDE congeners, as shown in Table 3. All the data were ln-transformed to reduce assumptions of normality and constant variances. It can be seen from Table 3 that the seven lower chlorinated congeners analyzed in our study are well correlated (r > 0.75 between six BDE congeners except BDE 100) with each other in riverine sediments. while in general, it is not that good between BDE 209 and lighter congeners. Thus there are generally similar proportions between BDE congeners (except for BDE 209) at most industrial and urban sites as mentioned above.

As described before, PBDE products mainly include penta-, octa- and deca-BDE. Congener patterns of typical penta- and octa-BDE products were also shown in Fig. 3a.<sup>12</sup> From the comparisons it can be suggested that despite different emissions, PBDE sources might be from the similar mixing of penta- and

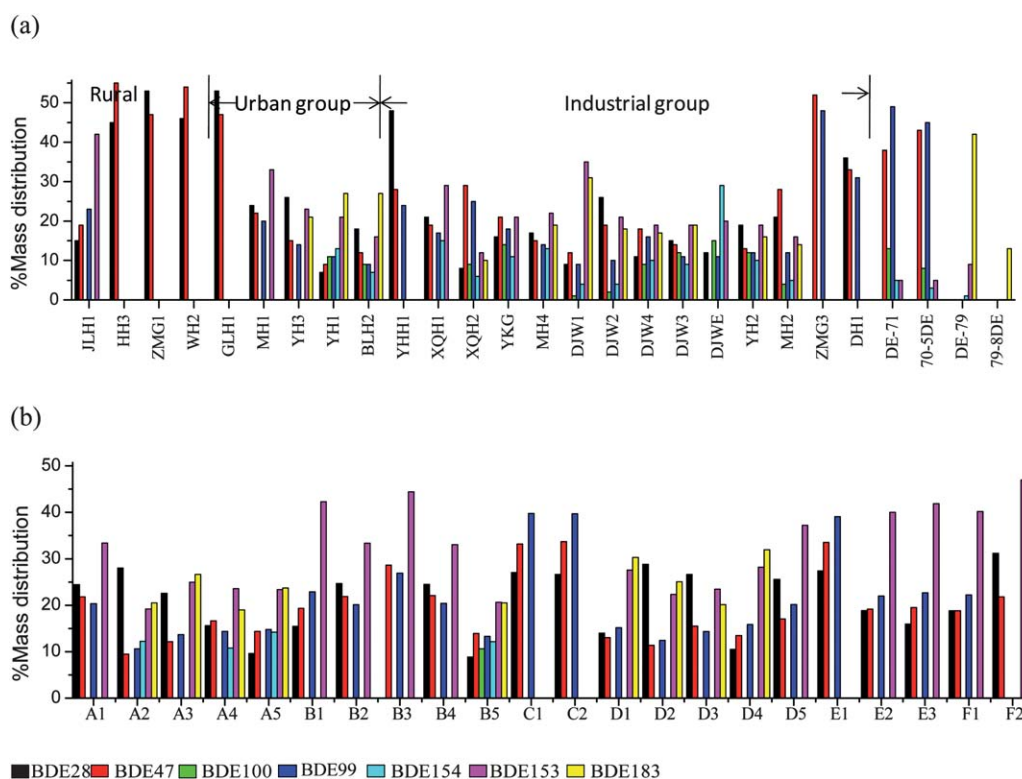
**Table 3** Pearson correlation coefficients among all the congeners

		BDE 28		BDE 47		BDE 100		BDE 99		BDE 154		BDE 153		BDE 183		BDE 209	
		R	M	R	M	R	M	R	M	R	M	R	M	R	M	R	M
BDE 28	r	1	1														
	N	31	25														
BDE 47	r	0.96 <sup>a</sup>	0.45 <sup>b</sup>	1	1												
	N	31	25	35	28												
BDE 100	r	0.83 <sup>a</sup>	—	0.77 <sup>a</sup>	—	1	1										
	N	11	1	11	1	11	1										
BDE 99	r	0.91 <sup>a</sup>	0.36	0.99 <sup>a</sup>	0.89 <sup>a</sup>	0.76 <sup>b</sup>	—	1	1								
	N	20	23	22	24	11	1	22	24								
BDE 154	r	0.92 <sup>a</sup>	0.13	0.89 <sup>a</sup>	0.16	0.79 <sup>a</sup>	—	0.93 <sup>b</sup>	0.51	1	1						
	N	14	6	14	6	11	—	14	6	14	6						
BDE 153	r	0.92 <sup>a</sup>	0.2	0.91 <sup>a</sup>	0.64 <sup>a</sup>	0.75 <sup>a</sup>	—	0.95 <sup>a</sup>	0.93 <sup>a</sup>	0.99 <sup>a</sup>	0.7	1	1				
	N	17	21	17	23	11	1	17	21	14	6	17	23				
BDE 183	r	0.92 <sup>a</sup>	-0.07	0.90 <sup>a</sup>	0.34	0.75 <sup>b</sup>	—	0.92 <sup>a</sup>	0.67 <sup>b</sup>	0.98 <sup>a</sup>	0.97 <sup>a</sup>	0.99 <sup>a</sup>	0.86 <sup>a</sup>	1	1		
	N	12	10	12	10	9	1	12	10	11	5	12	10	12	10		
BDE 209	r	0.69 <sup>a</sup>	0.62 <sup>a</sup>	0.73 <sup>a</sup>	0.37	0.56	—	0.61 <sup>a</sup>	0.3	0.29	-0.19	0.42	0.28	0.45	-0.27	1	1
	N	30	25	34	28	11	1	22	24	14	6	17	23	12	10	33	28

<sup>a</sup> Correlation is significant at the 0.01 level (2-tailed). <sup>b</sup> Correlation is significant at the 0.05 level (2-tailed). Data with independent variables or dependent variables missing are excluded before Pearson correlation was calculated. R: riverine sediments; M: marine samples.

octa-BDE products in this area. While at the few sites including XQH1, DJW1 and YH1 mentioned above, the proportion of penta- to octa-BDE products might be different, which resulted in the dominance of a few congeners mainly contained in one certain product. Though, it was indicated from the correlations that they have little impact on the statistical results.

In marine sediments, BDE 28, 47, 99 and 153 are the main congeners. A remarkable difference with riverine sediments is the variation of proportion between BDE congeners. Contributions of BDE 28, 47 and 99 were generally the same to  $\Sigma_7$ PBDEs in almost all the marine sites, while BDE 153 was distinctively higher, as shown in Fig. 3b. This could be attributable to several reasons. First of all, unlike river particles, especially for those



**Fig. 3** Mass distributions of tri- to octa-BDE congeners in riverine (a) and marine (b) sediments. Note: the rest sites with only BDE 28 and/or BDE 47 detected are not included in part (a). They are six rural sites having similar patterns with WH2, and two industrial sites.

influenced by direct discharge from nearby emissions, marine particles are mixed from different sources. Further, since Laizhou Bay is a shallow bay with frequent storm tide, deposited sediments of different periods may be mixed due to turbulences on the sea bed. Finally, compared to river sediments, more time is allowed for sediments to achieve equilibrium partitioning with the surrounding water phase. Therefore, due to the difference of physiochemical properties of BDE congeners, such as the higher binding affinity to particles due to larger molecular size and lower velocity of desorbing from aged particles of higher brominated congeners, the congener patterns may have changed during these processes from their emissions to marine environment. These can also explain their consequential reduced Pearson correlation coefficients and higher proportion of heavier congeners in marine environment.

### 3.4 Correlations between PBDEs and total organic carbon

TOC often has a high affinity to many organic pollutants such as polycyclic aromatic hydrocarbons (PAHs) and organic chlorinated pesticides (OCPs), and this is expected to be similar with PBDEs. In the present study, no clear correlations were found between PBDEs and TOC in riverine sediments (Fig. 4). This is not surprising because of contributions mainly from direct emission sources. However, their correlations in marine sediments were remarkably elevated. Although it is not well correlated from a statistical point of view, considering the natural variability of processes going on in marine systems, this general correlation seems as good as can be expected. There are several possible explanations to account for this. Marine sediments receive particles from various sources, including atmospheric deposition as well as fluvial input from different areas. The addition of fine particles from other sources especially from atmospheric deposition might be a big contributor to their better correlation between PBDE and TOC in marine environment. Another possibility is that, since more time has occurred from the direct PBDE emissions in the marine environment than the riverine environment, the PBDE had more time to distribute itself to the TOC phase; and thus, what is seen in the marine environment is more representative of a steady-state distribution condition than the dynamic situation in the rivers close to the emission source. Most likely, it is a combination of these two reasons.

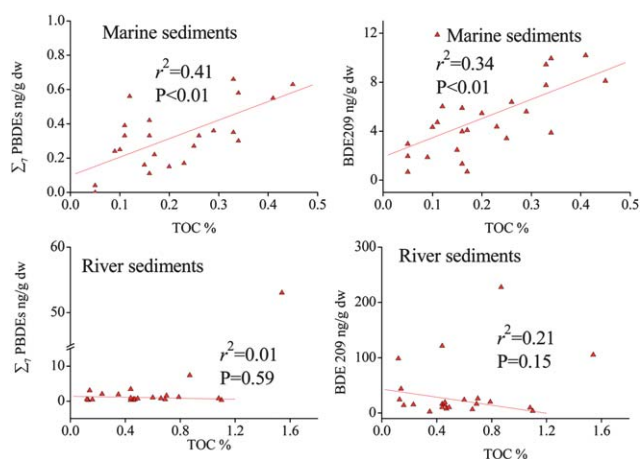


Fig. 4 Correlations between TOC and PBDE concentrations.

In the present study, PBDE contamination in the Laizhou Bay area was studied. However, due to more and more concern about its high toxicity and the restriction on PBDE usage in many countries, enterprises of BFRs are gradually developing new products to replace PBDEs, such as tetrabromobisphenol A (TBBPA), hexabromocyclododecane (HBCD), brominated epoxy resin (BEO), brominated polystyrene (BPS) and poly-(pentabromobenzyl acrylate) (PBBPA). In China, deca-BDE and TBBPA account for over 50% of the total BFR production and the BEO production has increased rapidly in recent years. Thus our research on PBDE contamination provides implications for contamination by other BFRs and the consequential uncertain risks.

## 4 Conclusions

PBDE contamination in the Laizhou area – the largest manufacturing base of BFRs in Asia was studied. The PBDE concentration is at a relatively low level for riverine and coastal sediments around the world. Even at the most contaminated sites, it is not among the highest concentrations reported in the literature. The riverine sampling areas were mainly impacted by direct emission sources from local factories. BDE 209 is the predominant congener, with minor contributions from similar mixing of penta- and octa-BDE products at most industrial and urban sites. Compared with riverine sediments, a much better correlation between PBDE concentrations with TOC was observed in marine environment. Congener pattern changed and their correlation coefficients among each other were remarkably reduced, which may be attributable to several reasons, such as contributions by atmospheric deposition and/or redistribution between particles of various sizes during and/or after fluvial transportation combined with the difference in physiochemical properties of BDE congeners. In conclusion, as only one group of pollutants of various BFR products, this study provides many implications for further study on other BFR contaminants.

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