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Levels and distributions of PBDEs and PCBs in sediments of the Bohai Sea, North China

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Fifty-four surface sediments covering the whole water body of the Bohai Sea in North China were collected and analyzed for PBDEs and PCBs, to acquire information about their levels, distributions and possible sources. The results show that BDE 209 is the predominant congener with a mean value of 7000 pg g^{-1} dry weight, two orders of magnitude higher than other BDE congeners. The concentrations of $\Sigma PBDE_7$ (including BDE 28, 47, 99, 100, 153, 154 and 183) range from 220 to 900 pg g^{-1} dw. Significant correlations were found between BDE congeners and total organic content (TOC) (r^2 = 0.48–0.73). Pearson analysis shows that most tri- to hepta-BDE congeners were closely correlated (r^2 > 0.69). Congener patterns varied little among most of the samples and all the detected BDE congeners make a relatively equal mass contribution to $\Sigma PBDE_7$. Such a profile is notably different from any of the BDE commercial products. As for PCBs, only a few congeners were detected in certain samples. They ranged from nd-610 pg g^{-1} dw with a mean value of 145 pg g^{-1} dw, at the lower end of the range reported in remote areas of Europe and North America. The overall burdens of $\Sigma PBDE_7$ and BDE 209 within the upper 3 cm sediment layer were estimated to be 0.95–1.25 t and 11–19 t respectively. The latter accounts for about 0.008–0.014% of total BDE 209 produced in China from 1999 to 2006.

1. Introduction

Polybrominated diphenyl ethers (PBDEs) are a class of brominated flame-retardants (BFRs) widely used in plastics, textiles, electronics and other materials.[1] The main products of PBDEs consist of three commercial mixtures designated as deca-BDE, octa-BDE, penta-BDE. Deca-BDE is mainly composed of BDE 209 (97–98%). BDE 183 (>40%) is often taken as indicative of the octa-BDE mixture. Penta-BDE mixture consists of 41–42% of tetra-BDE (predominantly BDE 47) and 44–45% of penta-BDE (BDE 99 and 100).[2] With the ban of penta-BDE and octa-BDE in some western countries, deca-BDE has become the major BFR product occupying over 80% of the global market demand, while octa-BDE and penta-BDE account for less than 20%.[3] As additive flame retardants, PBDEs can enter the environment through the release from goods and products during their usage, as well as being bound to weathered and abraded particles.[4] The rapid increases of PBDE concentrations in humans and environment matrices and extensive ongoing usage of BFRs have raised more and more concerns from the public and environmental community.

Polychlorinated biphenyls (PCBs) are highly persistent molecules with similar structure and physicochemical properties. They have been widely used as capacitor fluids, engine oil additives, cable insulation, and wood preservation in western countries during the 1950–1980s until being banned.[5] In addition to industrial usage, research shows that these compounds can also be generated from thermal processes such as waste incinerations.[6–8] Some PCB congeners were proved to exhibit dioxin-like toxicities.[9,10] Because of their high hydrophobicity and lipophilicity, they tend to accumulate in the biota and cast a potential risk to human health.

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Environmental impact

This manuscript demonstrates the levels, distributions and possible sources of PBDEs and PCBs in sediments of the Bohai Sea. This is the first study reporting levels of PBDEs and PCBs in the whole water body of the Bohai Sea. We also estimate the PBDE burdens in the top 3 cm sediment layer in the Baohai Sea. Such results are important for national and even for global inventories of PBDEs. All these findings should be considered not only in planning future monitoring programs but also in preparing the national regulations. The results will expectedly contribute to national implementation plans under the Stockholm Convention on persistent organic pollutants.

China is an important manufacturing base for production of deca-BDE and electronics, two of the main PBDE sources. The Bohai Sea is surrounded by the biggest industrial area of northern China called Bohai Rim Region (BRR), which is made up of the Bohai Bay area, the Laizhou Bay area and the Liaodong Bay area. It has a population of up to 260 million people residing at BRR and this region developed rapidly in recent years. The consumption of PBDEs as well as the production of commodities containing PBDEs, notably electronics, has remarkably increased. The Bohai Bay area centered by Tianjin is becoming the third electronics centre after the Pearl River Delta (PRD) and the Yangtze River Delta (YRD). The Laizhou Bay area, centered by Weifang city of Shandong province, has developed into the biggest base of BFR research and manufacturing in China for the last decade, owing to the availability of low cost bromine-containing sea water sources. Over 10 deca-BDE manufacturers are located in the Laizhou Bay area. Both the electronics and BFR industries are newly developed high-tech industries vigorously encouraged and supported by the local government.

Sediments are known as major sinks for organic contaminants in aquatic environments. The study of sediments is an important step in mapping possible pollution sources and exposure pathways that make PBDEs bio-available to benthic organisms.[11] Considering the potential threat of PBDEs in biota, it has become essential to get a complete understanding about PBDEs in sediments offshore. Mai *et al.* investigated PBDEs in sediments of PRD, the largest manufacturing base for electronics in the world, and found it's among the highest concentrations reported in the literature.[12] In the Bohai Sea, however, few data of PBDEs are available. Only a few research surveys had been carried out.[13,14] Jin *et al.* analyzed PBDE in biota and sediments collected around BFR manufactories in the Laizhou Bay area and a high BDE 209 concentration was detected.[13] Wang *et al.* investigated congener specific distributions of PBDEs in sediments and mussels collected along the coastal cities of the Bohai Sea.[14] However, the number of sampling locations and samples in these studies were limited. As a result, the data were insufficient for evaluating distribution patterns, potential sources, fate, and effects of PBDEs on the entire Bohai Sea region. As for PCBs, so far very limited data is available.

The present study aims to investigate the status of PBDEs, and PCBs pollution in Bohai Sea *via* a large survey of surface sediments. A detailed description of the sampling sites within the Bohai Sea region is given elsewhere.[15] Fifty-four samples covering the whole water body were collected and analyzed to survey the spatial distribution and to examine the effects of the BRR's economic development on the Bohai Sea sediments. As an inner sea, the Bohai Sea is not that well exchanged with the neighboring open ocean—Northern Yellow Sea (NYS). This research is expected to assess the role it played during transportation and fate of PBDEs in BRR.

2. Materials and methods

2.1 Chemicals

All PBDE standards were purchased from Cambridge Isotopes Laboratories (Andover, MA USA) for quantification. 39 kinds of PBDE standards were used for confirming BDE congeners and a standard mixture of BDE 28, 47, 99, 100, 153, 154, 183 and 209 was used for quantification. Analysis of PCB was the same as a previous study.[16] 2,4,5,6-tetrachloro-*m*-xylene (TC*m*X), and PCB 209 were added as surrogates. PCB 54 and BDE 77 were used as internal standards for PCBs and PBDEs, respectively. Other chemicals and standards are described elsewhere.[15]

2.2 Cleanup and purification

Early research on aliphatic hydrocarbons of these samples has been reported.[15] Freeze-dried sediment samples were homogenized, pulverized and extracted with dichloromethane (DCM) in a Soxhlet apparatus for 48 h, with activated copper added to remove the sulfur in the samples. The extracts were concentrated to about 0.5 mL after solvent-exchanged with hexane. Half of the extracts were fractionated for the analysis of PBDEs and PCBs. The procedure followed is that described by Chen *et al.*[17] Briefly, the fractionated extracts were cleaned by passage through a multi-layer silica gel column containing anhydrous Na_2SO_4, 50% (w/w) sulfuric acid–silica gel, silica gel and Al_2O_3 from top to the bottom with successive eluants of 20 mL of 1 : 1 (w/w) hexane–DCM. After concentrated to approximately 50 μL by a gentle blow of N_2, the effluents were injected with 20 ng PCB 54 and BDE 77 for volume correction.

2.3 Instrumental analysis

PBDEs were detected with GC-NCI-MS (Agilent GC7890 coupled with 5975C MSD). A DB-5MS (30 m × 0.25 mm i.d., 0.25 μm film thickness) capillary column was used for the determination of PBDE congeners, except for BDE 209. The oven program is described elsewhere.[18] A 10 m VFS column (0.25 mm i.d., 0.25 μm film thickness, VFS) was used for BDE 209 analysis. Samples were injected at 290 °C in splitless mode. The oven program was 130 °C for 1 min, ramped at 12 °C min^{-1} to 155 °C, 4 °C min^{-1} to 215 °C, and further ramped at 3 °C min^{-1} to 300 °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.

GC-EI-MS applied with a 30 m DB-5ms column (0.25 mm i.d., 0.25 μm film thickness, J&W Scientific) was used for PCBs analysis. Samples were injected at 250 °C in splitless mode. The oven program was 130 °C for 1 min, ramped at 4 °C min^{-1} to 298 °C, and held for 10 min. PCBs were determined in selected ion mode (SIM).[16,19,20]

2.4 QA/QC

One procedural blank and one spiked blank consisting of all chemicals were run with every batch of 10 samples to assess potential sample contamination. Results show no target compounds were detected in laboratory blanks and the recovery for spiked blanks was 92.5 ± 8.5%. IDL and MDL were calculated according to US EPA method 5055. MDL for $PBDE_7$ (BDE 28, 47, 99, 100, 153, 154 and 183), BDE 209 and PCBs are 5–34 pg g^{-1} dw, 6 pg g^{-1} dw and 26–59 pg g^{-1} dw, respectively.

The surrogate recoveries in all samples (Both field collected and laboratory prepared) were between 89–107%. Two samples from the station with a low recovery (<30%) and a high one

(>150%) were omitted from subsequent analysis. The reported results were not surrogate recovery corrected.

3. Results and discussion

3.1 PBDEs

3.1.1 Target BDE congener levels and spatial distributions. The GC-MS chromatogram of the BDE congeners is shown in Fig. 1. Table 1 summarizes concentrations of target BDE congeners in Bohai Sea sediments. $\Sigma PBDE_7$ (sum of BDE 28, 47, 99, 100, 153, 154 and 183, except for BDE 209) ranged between 220–900 pg g^{-1} dw. The highest concentrations occurred in the Liaodong shoal, followed by the estuary of the Haihe River and the Luanhe River, while the lowest in the Laizhou Bay. This is not unexpected for the two rivers and the reasons will be explained later. The high concentration in the Liaodong shoal (including sites D9, D11 and D16) was mainly contributed by higher BDE 47 and 100 concentrations. The concentration of BDE 100 was 350, 370 and 200 pg g^{-1} dw at D9, D11 and D16, respectively, with a mean value of 80 pg g^{-1} dw for other sites. BDE 47 was 160, 210 and 180 pg g^{-1} dw at D11, D14 and D16, respectively, with a mean value of 80 pg g^{-1} dw for other sites. This may indicate a point source containing higher percent of BDE 100 and 47 or some specific mechanism of BDE transformation and degradation in this area. The lowest concentration in the Laizhou Bay may be attributed to its poor TOC content. Surface sediments in the Laizhou Bay are mainly composed of coarse sand, carried by the Yellow River and some drainage rivers in the northwest of Shandong Province, such as the Xiaoqing River, Bailang River and Weihe River. However, it is worth noticing that despite of poor TOC content, there were only slightly lower $\Sigma PBDE_7$ concentrations in the Laizhou Bay than other sites. Actually, after excluding the few special sites on Liaodong shoal (D9, D11, D12 and D16), most samples varied slightly between 300–600 pg g^{-1} dw with a mean value of 440 pg g^{-1} dw. As a result, Laizhou Bay has the highest TOC normalized burden of $\Sigma PBDE_7$, with a mean value of 203,700 pg g^{-1} TOC^{-1} in Laizhou Bay *versus* 127,700 pg g^{-1} TOC^{-1}in other sites of the Bohai Sea.

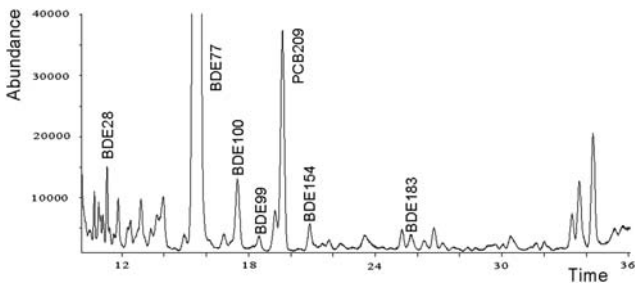

Fig. 1 GC-MS chromatograms of PBDE congeners of surface sediment at B2.

Table 1 Concentrations of target BDE congeners in sediments of the Bohai Sea (pg g^{-1} dw)

	Bohai Sea sediments (N = 52)			
	Min.	Max.	Mean	Median
BDE28	44	120	72	70
BDE47	45	210	81	76
BDE100	40	370	83	64
BDE99	42	84	62	60
BDE154	nd[b]	76	56	55
BDE153	48	94	70	68
BDE183	65	130	93	88
BDE209	1750	15100	7000	6430
$\sum PBDE_7$[a]	220	900	480	470

[a] $\sum PBDE_7$: sum of BDE 28, 47, 99, 100, 153, 154 and 183, excluding BDE 209. [b] nd = not detected.

BDE 209 in Bohai Sea ranged from 1760 to 15,100 pg g^{-1} dw with a mean value of 7000 pg g^{-1} dw, two orders of magnitude higher than other BDE congeners and one order higher than $\Sigma PBDE_7$. The highest concentrations occurred in the estuary of the Haihe River at sites B1, B2 and B4 with the value of 15,100, 13,900 and 10,900 pg g^{-1} dw, respectively, followed by the estuary of the Luanhe River, shown in Fig. 2a. It is similar with the spatial distributions of $\Sigma PBDE_7$ (Fig. 2c), which clearly show a riverine input influenced trend. Another hot spot of BDE 209 is the Laizhou Bay. BDE 209 concentration was below 10,000 pg g^{-1}dw in most samples of the Bohai Sea. However, elevated concentrations were found at stations B1, B2 and B4 mentioned above, and stations in the Laizhou Bay, A20, A23, and A26 with concentrations of 11,400, 11,700 and 12,700 pg g^{-1} dw, respectively. Since TOC content vary notably in Bohai Sea sediments, TOC normalized burden of BDE 209 was applied to obtain a more objective comparison, as shown in Fig. 2b. After normalized by TOC, an extremely high load of BDE 209 was observed in the Laizhou Bay with an average value of 5740 ng g^{-1} TOC^{-1}, compared to 1960 ng g^{-1} TOC^{-1} for all the other spots. This is probably due to the input of Bailang River which receives wastewater discharged from deca-BDE manufactures located in Weifang city. Extremely high BDE 209 concentrations (up to 1800 ng g^{-1} dw) were found in Bailang River sediment.[13] Besides, an exponential decrease in seaward trend of TOC burden of BDE 209 concentrations was observed from Laizhou Bay and estuaries of the two rivers leading to central Bohai Sea. This trend reflects the proximity of sampling station to the source regions.

As mentioned above, both the highest $\Sigma PBDE_7$ and BDE 209 concentrations occurred at the estuarine sites of the two rivers. The Haihe River receives domestic and industrial discharges and passes through the highly urbanized and populated Tianjin city. The biggest drainage river in Tianjin city, Dagu River, also merges with the Haihe River. Lu *et al.* (2007) analyzed PBDEs in a sediment core collected from the Dagu River in 2005. Comparable BDE concentrations with the present study and a clear temporal increased trend were found.[21] This agrees with the fact that the Dagu River joined into the Haihe River just at the mouth of the estuary. The Luanhe River flows through Tangshan city with heavy industrial activities as well as several small cities such as Leting, Qianxi and Luanxian city. Over 149 factories such as paper-making, mill running and petrochemistry are located around the Luanhe riverside. Due to the lack of efficient supervision, industrial waste as well as municipal sewages are discharged directly into the Luanhe River without treatments. Sewage has been emphasized as a potential source for PBDE contamination in some studies.[22,23] Moon *et al.* found sediments collected around petrochemical complex areas

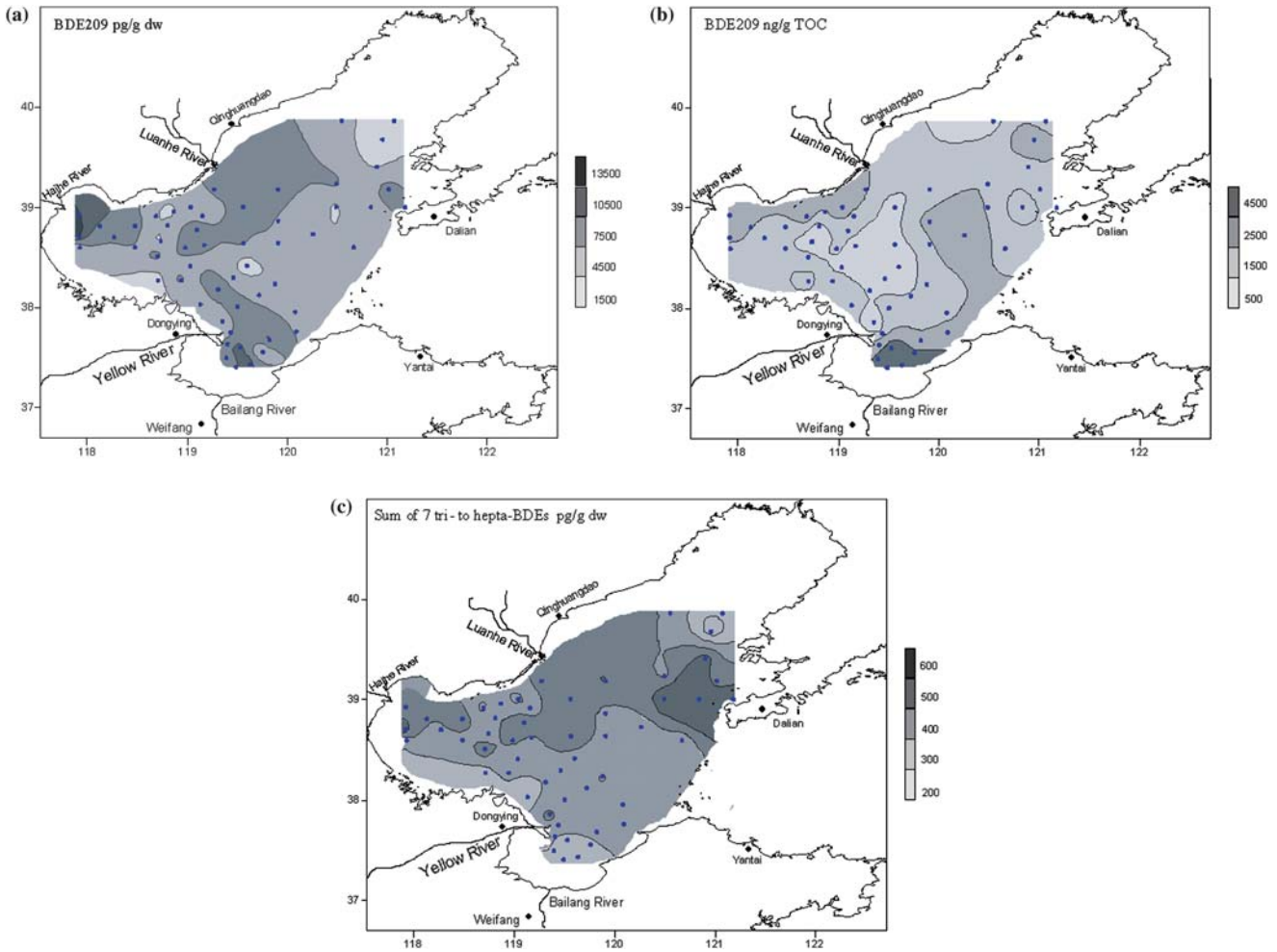

Fig. 2 Spatial distributions of (a) BDE 209 pg g^{-1} dw; (b) BDE 209 ng g^{-1} TOC^{-1}; (c) $\Sigma PBDE_7$ pg g^{-1} dw.

contained the highest PBDE concentrations and thus suggested that petrochemical complex is an important source of PBDE.[24] In the present study, both Tianjin and Tangshan are important petrochemical cities. Therefore, the wastewater discharged from human and industrial activities are probably the main contributors to the highest PBDE concentrations in the estuarine sites.

Many researches have focused on PBDEs in coastal or estuarial sediments as well as those around hot spots such as BFRs manufactories or e-waste sites. Only a few data on marine sediments are available. Generally, the level of $\Sigma PBDE_7$ concentration in the Bohai Sea was below 1000 pg g^{-1} dw which is similar to the background concentrations found in Denmark, Spain, Singapore, Japan, Korea, Macao, Qingdao near shore and Lake Maggiore Basin in Italy but higher than Northern South China Sea (NSCS) (139 pg g^{-1} dw[12]), Xijiang River (295 pg g^{-1} dw[12]), YRD (150 pg g^{-1} dw[25]) and Australia (396 pg g^{-1} dw[26]) (Fig. 3). For BDE 209, it is comparable to some low to moderately polluted lakes, rivers and coastal sea such as Lake Maggiore (1600–15,300 pg g^{-1} dw[11]) and YRD (13,400 pg g^{-1} dw[25]), but higher than NSCS (6495 in Bohai Sea *vs.* 1394 pg g^{-1} dw in NSCS at geometric value[12]), Xijiang River (4763 pg g^{-1} dw[12]), YRD outer sea (160–4000 pg g^{-1} dw[25]), Hong Kong marine sediments (nd-2920 pg g^{-1} dw[27]) and Denmark marine sediments (3670 pg g^{-1} dw[28]) (Fig. 4). After being normalized to TOC burden, it is at the same level as Macao coastal sediments (2038 ng g^{-1} TOC^{-1} in Bohai *vs.* 2025 ng g^{-1} TOC^{-1} in Macao[12]), although much lower in a dry weight concentration (6490 pg g^{-1} dw in Bohai *vs.* 20255 pg g^{-1} dw in Macao[12]). The highest TOC load of BDE

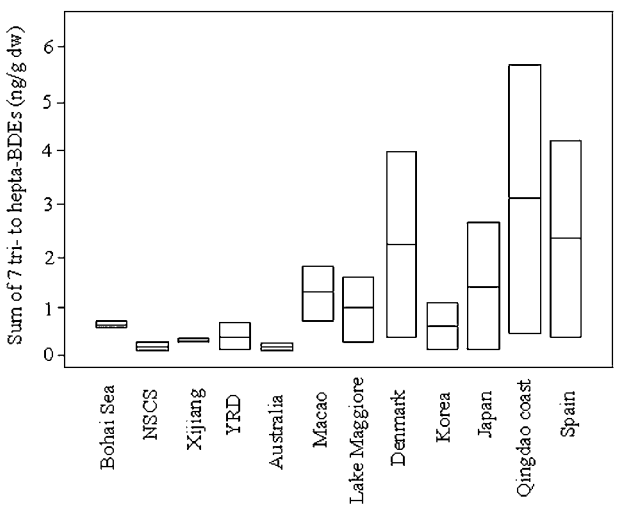

Fig. 3 Comparison of $\Sigma PBDE_7$ levels (ng g^{-1} dw) in sediments of the Bohai Sea with those from other regions worldwide.

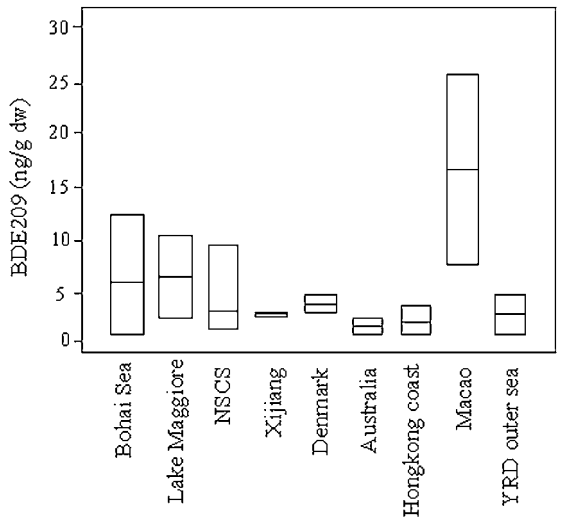

Fig. 4 Comparison of BDE 209 levels (ng g^{-1} dw) in sediments of the Bohai Sea with those sediments from other regions worldwide.

209 concentration reaches up to 11,800 ng g^{-1} TOC^{-1} in Laizhou Bay.

3.1.2 Correlations among BDE congeners, Organic Carbon and median grain size. Pearson correlation analyses were performed (Table 2). Good correlations were found among BDE 28, 99, 153, 154 and 183 (r^2>0.77). Specially, the latter 4 congeners show significantly strong correlations. Their Pearson efficiencies varied from 0.96 to 0.99. Poor correlations were found concerning with BDE 47 and 100. However, after eliminating the specific sites on Liaodong Shoal as described in section 3.1.1, their correlations with other congeners increased from below 0.2 to higher than 0.69. BDE 209 show moderate correlations with other BDE congeners (r^2 = 0.4–0.68).

Sediment TOC content is often a significant factor controlling the distribution of organic pollutants due to their high hydrophobicities. PBDEs were expected to be associated mainly with organic carbon-rich particles in soil and sediments. Generally, poor correlations (r^2<0.2) were observed in areas with input from point sources.[12,24] Moderate correlation (r^2 = 0.53) has been reported from Macao coastal sediments, a depositional zone in the PRD region.[12] In the present study, good correlation has been observed in Bohai Sea sediments (Table 2). Except for BDE 47 and BDE 100, the other BDE congeners show good correlation with TOC content (r^2>0.6). As described above, BDE 47 and 100 were locally affected on Liaodong shoal. After eliminating these stations (D9, D11, D12 and D16), better correlations were achieved. The coefficients were increased from 0.35 and 0.18 to 0.77 and 0.48 for BDE 47 and 100, respectively, while other congeners varied slightly. As a result, $\Sigma PBDE_7$ in Bohai Sea sediments were strongly controlled by TOC (r^2 = 0.73). It is similar to that of BDE 209. After excluding the BDE 209 data at stations B1, B2 and B4 in the estuary of the Haihe River and stations A19–A26 in the Laizhou Bay, the correlation coefficients in the remaining 43 samples were elevated from 0.27 to 0.63. Moderate correlations with median grain size were also found in the Bohai Sea. Pearson coefficients between BDE congeners and median grain size were between 0.29 and 0.72, with the highest value for BDE 28 and lowest for BDE 209. Other BDE congeners were moderately correlated (r^2 = 0.45–0.58). Hu *et al.* have found that TOC was very well correlated with the sediment size in the Bohai Sea, and thus suggested the influence of hydrodynamic effects on the SOM accumulation.[15] In the present study, good correlations of BDE congeners with TOC and sediment type suggested the key role of organic content in controlling the distributions of PBDEs in Bohai Sea sediments.

3.1.3 Congener patterns and possible sources. The dominance of BDE 209 in the total PBDEs is apparent. The contribution of BDE 209 ranged from 86 to 97% of the total PBDEs with a mean value of 93%. The ratio of BDE 209 to $\Sigma PBDE_7$ ranged from 6 to 32 with a mean value of 15. The predominance of BDE 209 in sediment has been found in various regions around the world,[13] no matter whether they were from a river,[12] an estuary,[25] a lake,[29] or a sea.[28] These findings agree with the fact that deca-BDE mixtures account for most of the total PBDEs mixtures production and usage around the world.[30] The dominance of BDE 209 in this study indicated that deca-BDE is the main commercial mixture produced and used within BRR.

Among the 7 tri- to hepta-BDE congeners, BDE 47 and 100 were the dominated ones (except for sites at Liaodong Shoal). BDE congener patterns among most of the stations (Fig. 5) showed slight variations. It's probably due to the relatively mild seabed of the Bohai Sea and fewer fierce ocean currents than the South China Sea, which makes the Bohai Sea a huge and fine depositional zone for pollutants. Usually, the resemblance of patterns to BDE formulations were found in sediments, either

Table 2 Pearson correlation coefficients among BDE congeners and TOC[a]

	BDE28	BDE47	BDE100	BDE99	BDE154	BDE153	BDE183	BDE209	$\Sigma PBDE_7$
BDE47	0.15 (0.73)[b]								
BDE100	0.01 (0.45)[b]	0.63							
BDE99	0.77	−0.27 (0.92)[b]	0.13 (0.76)[b]						
BDE154	0.80	0.11 (0.91)[b]	0.19 (0.74)[b]	0.97					
BDE153	0.82	0.21 (0.88)[b]	0.08 (0.73)[b]	0.98	0.99				
BDE183	0.80	0.15 (0.87)[b]	0.02 (0.69)[b]	0.95	0.99	0.98			
BDE209	0.45	0.077 (0.44)[b]	−0.04 (0.40)[b]	0.48	0.68	0.53	0.43		
TOC	0.61	0.35 (0.77)[b]	0.17 (0.48)[b]	0.73	0.61	0.70	0.69	0.27 (0.63)[c]	0.54 (0.73)[b]

[a] Correlation is significant at the 0.01 level (2-tailed). [b] Sites on Liaodong Shoal D9, D11, D12, D16 were excluded. [c] Sites in Laizhou Bay A19–A26 were excluded.

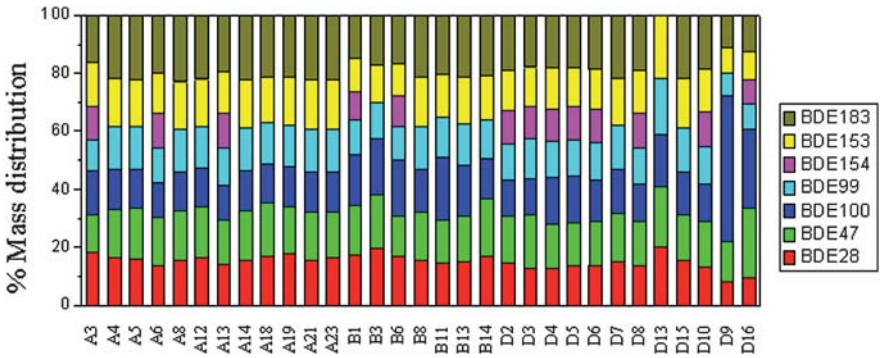

Fig. 5 Percent of individual BDE congeners to $\Sigma PBDE_7$ in parts of the Bohai Sea sediments.

with the dominance of BDE 47 and 99, or that of BDE 183. These congeners were respective indicatives of penta-BDE and octa-BDE sources, as mentioned in the introduction. Our study suggested however, that the Bohai Sea seemed to be specific. All the detectable BDE congeners in this study make a nearly equal mass percent contribution to $\Sigma PBDE_7$. The mean value of main congeners (excluding the special spots described above), calculated as percentage of total PBDEs, were as follows: BDE 28, 17 $\pm$ 9%; BDE 47, 17 $\pm$ 3.5%; BDE 100, 15 $\pm$ 4.5%; BDE 99, 13.5 $\pm$ 5.5%; BDE 153, 15.5 $\pm$ 6.5%; BDE 154, 10 $\pm$ 6%; and BDE 183, 18.5 $\pm$ 7.5%. BDE 183 was slightly higher than other congeners. So far, no commercial products were reported to show similar profiles (Fig. 6). Therefore, a mixture of different sources or some kind of transformation must have happened for the BDE pollutants during the courses of transportation or after they had been received in the Bohai Sea.

Both penta-BDE and octa-BDE products are probably widely used in the Bohai Sea area, which causes equivalent mass contributions from minor components like BDE 100, 153, 154 and the major ones like BDE 47, 99 and 183. However, according to the literature,[31] minor components made up <5% in commercial mixtures, while major ones took up more than 35%. Therefore, it's impossible for the minor components to be equivalent to the major ones unless additional degradation or transformation happens.

BDE 209 can be degraded to lower brominated BDE congeners including BDE 154, 99, 47 and 49 when exposed to natural sunlight or by anaerobic microbial degradation.[32–34] In this study, the BDE 209 concentration was two orders of magnitude higher than other congeners. Thus the contribution of lower brominated congeners from BDE 209 degradation may not be negligible. Besides, nona-BDE congeners can also be degraded into lower molecular congeners.[33] Jin *et al.* reported nona-BDE congeners exist in deca-BDE technical formulations produced in Shandong Province.[13] Therefore, degradation of higher brominated BDE congeners might be a contributor to lower molecular congeners in Bohai Sea sediments.

There is also evidence revealing that BDE 183, 154, 153 and 99 can also be biotransformed.[33] In the present study, BDE 154 was only identified in 22 of 54 samples. Considering the significant correlations among BDE 99, 153, 154 and 183 (r^2>0.95), it can be suggested that these BDE congeners might be mainly from the common sources, which means the anaerobic environment of the Bohai Sea might have changed the original pattern when they were just transported to Bohai Sea. This is also a probable reason for exhibiting a different pattern of PBDEs in the Bohai Sea from industrial sources.

A few studies investigated the distribution of PBDEs on surface sediments of the coastal Bohai Sea region and a sediment core in the Bailang River near Laizhou Bay.[13,14] Similar congener patterns in the surface and subsurface sediments of the core were found, except for slightly lower BDE 100 and higher BDE 153 proportions (Fig. 6). In the coastal surface sediment research, resemblance of PBDE profile to penta-BDE was found.

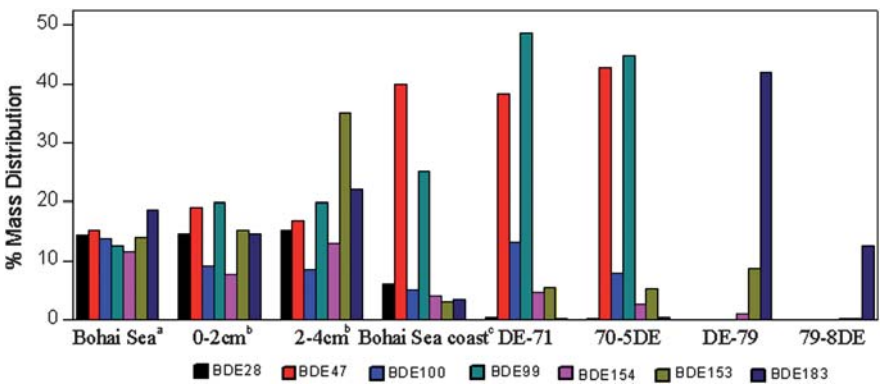

Fig. 6 Profiles comparison of Bohai Sea sediment with commercial mixtures and other related studies: a-present study; b-sediment core of Bailang River near Laizhou Bay;[13] c-surface sediments of Bohai Sea coast.[14]

However, the present study reveals no commercial mixtures dominant. The possible reasons for the discrepancy of PBDE patterns between the Bohai Sea open area (our study) and the coastal zone[14] are explained. Firstly, there were only a few sampling sites of the coastal sediments, which might have been severely influenced by point octa-BDE sources. Besides, little information about either congener patterns or sampling sites for all the samples is available from this literature. Secondly, different instrument analysis methods were applied in these two studies which might have caused large deviations. However, both methods were proved to be efficient on analyzing PBDEs.[35,36] Thirdly, Hexa- and hepta-BDE congeners (BDE 153, 154, 183) were theoretically supposed to have shorter long-range transport distances than lighter congeners. If octa-BDE accounted for a rather small amount of BDE usage as demonstrated in the coastal sediment research, the decrease of BDE 47 and 99, or the increase of BDE 153, 154 and 183 from the coast to the sea can only be explained by photodegradation of lower brominated BDE congeners during transportation or microbial degradation of high brominated BDE congeners like BDE 209 and nona-BDE. The photodegradation assumption could be further proved by the abundance of BDE 28. BDE 28 was usually detected in air although it was not identified in any commercial products. Researches have shown BDE 28 was mainly attributed to possible photodegradation of highly brominated congeners during atmospheric transport. The photolytic debromination of PBDEs under experimental and natural conditions has been demonstrated in various studies.[37–40]

3.1.4 Sediment burden of PBDEs. As a semi-enclosed sea, the Bohai Sea is more fragile to ecological risk than other open seas such as the South China Sea and the East China Sea. Thus, based on this study, we attempted to assess the sediment burden of PBDEs in the Bohai Sea to give information for Bohai Sea pollution. The mass inventory of PBDEs in the Bohai Sea was calculated according to Lin *et al.*, 2009.[41]

$$I = CAdp$$

Where C is the concentration of PBDEs in sediment, d is the assumed sediment density of 1.0 g cm^{-3}, A is the water area of Bohai Sea (77000 km^2),[15] and p is sediment thickness (in this study it is 3 cm). Concentration data of 52 samples of Bohai Sea were used. The mean value of BDE 209 and $\Sigma PBDE_7$ were 7000 pg g^{-1} dw and 480 pg g^{-1} dw (with the median values of 6430 pg g^{-1} dw and 470 pg g^{-1} dw), respectively, after excluding the four abnormally high values. Since the median value and mean value are very close, the lower quartile (410 pg g^{-1} dw for $\Sigma PBDE_7$, 4830 pg g^{-1} dw for BDE 209) and upper quartile (540 pg g^{-1} dw for $\Sigma PBDE_7$, 8190 pg g^{-1} dw for BDE 209) were adopted as the lower limit and the upper limit, respectively. The calculated mass inventories of the Bohai Sea ranged 11–19 t and 0.95–1.25 t for BDE 209 and $\Sigma PBDE_7$, respectively. It was estimated that outputs of deca-BDE in China increased from 2500 t in 1999 to 50000 t in 2006.[42] Thus, a total of 139,000 t of BDE 209 was produced in China from 1999 to 2006 (an equal rise ratio was assumed). In that case, Bohai Sea sediments contain 0.008–0.014% of the total BDE 209 production in China. Researches have revealed high BDE 209 concentration often occurred at places concerned with electronics industry, furniture factories, plastics and electronics wastes, and such industries have been rapidly developed around/within BRR very much in step with deca-BDE. Compared to the total amount produced in China, the minor amount of BDE 209 in the Bohai Sea indicate that most of this BFR were still retained in the products or in the source region.

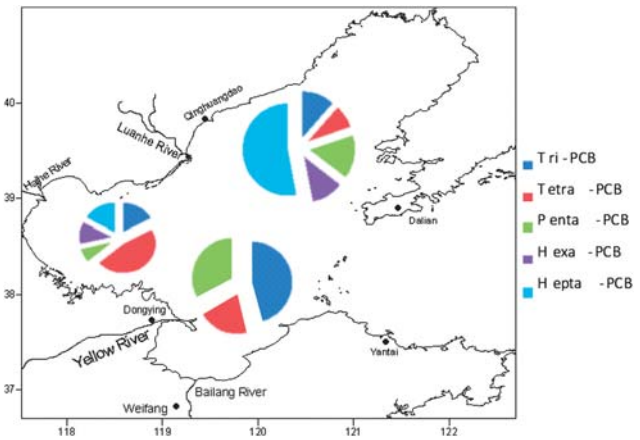

Fig. 7 Congener patterns of PCBs in different parts of the Bohai Sea.

3.2 PCBs

In Bohai Sea sediments, 16 PCB congeners were detected, including 5 priority pollutants PCB 28, 101, 138, 153 and 180. The PCBs level ranged from nd-610 pg g^{-1} dw with a mean value of 145 pg g^{-1} dw. PCB 28 and 101 have higher detectable ratios over 50%, while the others below 30%. Compared to the levels found worldwide, the Black Sea (0.3–6.8 ng g^{-1} dw[43]), the Caspian Sea (0.03–6.4 ng g^{-1} dw[44]), Southwestern of Baltic Sea (0.1–11 ng g^{-1} dw[45]), Gulf of Alaska (0.1–2 ng g^{-1} dw[46]), Kara Sea (nd-1.5 ng g^{-1} dw[47]), PCBs in Bohai Sea sediments were at the lowest end of the range reported in remote areas of Europe and North America. Low levels of PCBs were reported in other coastal regions of China, such as Jiaozhou Bay (0.57–31.6 ng g^{-1} dw[48]), Xiamen harbor (0.01–0.32 ng g^{-1} dw[49]) and Pearl River Delta (3.5–48.3 ng g^{-1} dw[50]).

In sediments of the Bohai Sea, different congener patterns were observed in different areas (Fig. 7). In Bohai Bay and Laizhou Bay, mainly lower chlorinated PCBs tri-PCB and tetra-PCB were detected, consistent with some other research on distribution patterns of PCBs in air and sediment of Beijing and Tianjin.[51–53] While in samples collected in northern Bohai Sea, near Liaodong Peninsular, higher chlorinated PCBs including penta-PCB, hexa-PCB and hepta-PCB, accounts for more than 70% of total PCBs. This difference indicates that PCBs in the Bohai Sea might be from mixed contribution of various sources from different areas such as re-emission of previous industrial usage, release from incineration and unlawfully usage nowadays.

4. Conclusion

The PBDEs concentrations in the Bohai Sea sediments were investigated and their levels were comparable to those of moderately polluted rivers, estuaries, or industrial bays reported

in various studies. BDE 209 was the predominant congener, consistent with previous studies that deca-BDE is the major commercial product used in China. Significant correlations were observed between most of BDE congeners and TOC content. Detected lower brominated BDE congeners (except BDE 209) also showed good correlation with TOC. It can be therefore concluded that the Bohai Sea is a fine depositional zone for PBDEs around the BRR area. Remarkable distinction of congener patterns existed between Bohai Sea sediments and commercial BDE products. The specific congener profiles may be attributed to photodegradation during transportation and bio-processes such as biodegradation and transformations. PCBs were at the lower end of the range reported in remote areas of Europe and North America. Different congener patterns of PCBs were observed in different areas, which indicated that various pollution sources of PCBs still exist in China. The overall burdens of $\Sigma PBDE_7$ and BDE 209 within the upper 3 cm sediment layer were estimated to be 0.95–1.25 t and 11–19 t, respectively. The latter accounts for about 0.008–0.014% of total BDE 209 produced in China from 1999 to 2006.

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