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Distribution and partitioning of polybrominated diphenyl ethers in sediments from the Pearl River Delta and Guiyu, South China[☆]

Youda Huang^{a, b}, Dainan Zhang^a, Yu Yang^a, Xiangying Zeng^a, Yong Ran^{a, *}

^a State Key Laboratory of Organic Geochemistry, Guangzhou Institute of Geochemistry, Chinese Academy of Sciences, Guangzhou, 510640, China

^b University of Chinese Academy of Sciences, Beijing, 100049, China

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ABSTRACT

Polybrominated diphenyl ethers (PBDEs) were investigated by GC–NCI–MS in sediments collected from the Pearl River Delta (PRD) and Guiyu town, South China. The concentrations of \sum_{39} PBDEs and BDE 209 were in the ranges of 0.31–38.9 ng g⁻¹ and 12.2–488 ng g⁻¹ in the PRD, and 2.57–21,207 ng g⁻¹ and 7.02–66,573 ng g⁻¹ in Guiyu, respectively. The levels of PBDEs in Dongjiang River (DJ), Zhujiang River (ZJ), and Beijiang River (BJ), and Guiyu (GY) followed the order: GY > DJ > ZJ > BJ. The very high PBDE concentration (87,779 ng g⁻¹) was detected at G1 sediment in Guiyu compared with those in sediments from other regions around the world. The PBDE mixtures detected were mainly comprised of penta-, octa-, and deca-BDEs, in which deca-BDE was the dominant constituent. The abundant congeners, excluding BDE-209, were BDE-47, BDE-99, and BDE-183, suggesting the diverse use of commercial products containing these congeners in this region. The concentrations of major congeners were significantly correlated with total organic carbon (TOC) contents ($p < .01$). A good regression between the logarithmic TOC-normalized BDE average concentrations and their log K_{ow} confirmed that the sorption of PBDEs on sediment organic matter governed their spatial distribution, transport, and fate in the sediments. Furthermore, risk quotients (RQs) derived from concentrations of PBDEs in sediments from our study may pose high ecological risks to exposure of benthic organisms.

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1. Introduction

Polybrominated diphenyl ethers (PBDEs) are a group of additive flame-retardants, which have been widely utilized in many types of polymers such as plastics, paints, electrical components, textiles, foam, rubber, and other casing materials. In previous reports, PBDEs were found in many commercial and household products (Chen et al., 2009; Cheng et al., 2014; Hale et al., 2002; Ran et al., 2013). The commercial PBDE mixtures contain penta-BDE, octa-BDE, and deca-BDE, among which the penta- and octa-products include different BDE congeners, while deca-product mainly consists of BDE-209 (Hites, 2004; La Guardia et al., 2006). It was estimated that the worldwide demand for these compounds in 2001 was approximately 70,000 tons, among which 49%, 37%, and 12% were used in North America, Asia, and Europe, respectively (de Wit, 2002; Hites, 2004). However, PBDEs have attracted considerable

concerns in recent years due to their long persistence, bio-accumulation, increasing detectable frequency, and potential toxic effects on every level of living organisms including humans and wildlife (Gorgy et al., 2010; Macias-Zamora et al., 2016; Tombesi et al., 2017; Wang et al., 2015b).

Currently, e-waste recycling is considered to be a significant source of released PBDEs to the environment especially in developing countries. E-wastes are generated from the fast growing disposal of electronic products throughout the world, most of which are transported to developing countries and dismantled. It was reported by United Nations Environment Programme (UNEP) in 2005 that approximately 80% of the computer e-wastes were exported to Asia, 90% of which enters into China through illegal imports (UNEP, 2005). Usually, during e-waste recycling, valuable metals from electronics are recovered by primitive techniques, while other parts such as large amounts of plastic are either burned or subsequently dumped in the wide fields (Luo et al., 2011), leading to the release of a wide range of hazardous chemicals such as PBDEs into the surrounding environment. It has been reported that extremely high levels of PBDEs were found in combusted

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* Corresponding author.

E-mail address: yrans@gig.ac.cn (Y. Ran).

residues, soils, sediments, water, plants, aquatic species, and even human serum surrounding the typical e-waste sites in China and other countries (Cheng et al., 2014; Leung et al., 2007, 2010; Nnorom and Osibanjo, 2008). Consequently, the concentrations of PBDEs in the environment matrix surrounding the e-waste sites were found to be 2–3 magnitudes higher than those found in environment further far away from e-waste sites (Deng et al., 2007). Zhao et al. (2009) used *Cinnamomum camphora* leaves as biomonitors to investigate the diffusion of PBDEs from an e-waste recycling area to the surrounding regions, demonstrating that the contamination of PBDEs extended to a radius of at least 74 km. The above facts indicate that PBDE congeners emitted could easily transfer in different environmental compartments, enter the food chain transfer, and bioaccumulate in various trophic organisms. Therefore, the investigation on distribution and partitioning of PBDEs in soils, waters, and sediments could provide valuable information for further understanding their exposure risks and fates in contaminated environment (Besis and Samara, 2012; Leung et al., 2010; Macias-Zamora et al., 2016; Zhang et al., 2010).

The PRD is one of the most economically prosperous regions in China with an area of 41,700 km² and 41 million inhabitants. It is the largest production base for computers, electronic parts, and communication instruments. It is also the largest e-waste recycling processing site in China. Moreover, as it is located in the northern subtropical zone, frequent rainfalls during the year are abundant, which could facilitate the transport of different contaminants including PBDEs to aquatic environments. In addition, Guiyu town (GY) having a total area of 52 km² and a population of 150,000 is a well-known e-waste recycling site as 80% of families and nearly 10,000 migrants living in this town are engaged in e-waste recycling works. However, the dismantling methods to manage the electronic wastes are primitive, with little safety measures and attempts (gloves and breathing masks, etc) taken to control the exposure to complex chemicals presented in the e-wastes (Deng et al., 2006; Zhao et al., 2006), which pose a threat to the health of local residents and workers.

The present investigation was conducted to characterize the spatial distribution and partitioning of PBDEs in sediments from the PRD and Guiyu town in order to provide a better understanding the contamination extents, potential risks, and fates of PBDEs in the investigated region.

2. Materials and methods

2.1. Study area and sample collection

Three major tributaries of the Pearl River system were selected for sampling (<http://www.sciencedirect.com/science/article/pii/S0304389411007254> Fig. 1). Dongjiang River (DJ) and Zhujiang River (ZJ) are located in the northeast of the PRD. DJ serves as the drinking water source of Dongguan, Shenzhen, and Hong Kong. It runs across the city of Dongguan, where manufacturing and processing industries are well developed. ZJ flows through Guangzhou which is the biggest and highly urbanized city with a population of 12 million and various industries in South China. These two rivers join at the Shizhiyang Waterway and flow into the Pearl River Estuary (PRE) through the Humen outlet. On the other hand, Beijiang River (BJ), located in the southwest of the PRD, runs across less developed areas and flows into the estuary via the Jiaomen, Hongqimen, and Hengmen outlets. In this study, fifteen surface sediments (0–5 cm) were collected from DJ, ZJ, and BJ (Fig. 1) in July 2006 using a stainless steel grab sampler. Because the average sedimentation rates were 1.33 cm yr⁻¹ in the Zhujiang River (Zhang et al., 2002), the top 5-cm layer of sediments was expected to represent modern inputs. In order to investigate the contaminated

levels of PBDEs in point-source sites, five surface sediments were also collected from the e-waste site (GY) following the same procedures in February 2007 (Fig. 1). The sediment samples were kept at –20 °C until further analysis.

2.2. Chemicals

Mixed standards of 39 PBDE congeners (including BDE-1, -2, -3, -7, -8, -10, -11, -12, -13, -15, -17, -25, -28, -30, -32, -33, -35, -37, -47, -49, -66, -71, -75, -77, -85, -99, -100, -116, -118, -119, -126, -138, -153, -154, -155, -166, -181, -183, -190) and individual standard of BDE-209, were purchased from Accustandards (New Haven, CT). Two surrogate standards of ¹³C-PCB-141 and PCB-209 and also ¹³C-PCB-208 as an internal standard were obtained from Cambridge Isotope Laboratories (Andover, MA), Ultra Scientific (North Kingstown, RI) and Cambridge Isotope Laboratories (Andover, MA), respectively.

2.3. Samples pretreatment and analytical procedure

Analysis of PBDE congeners was performed through multi-step procedure including soxhlet extraction, chromatographic column purification, and GC-NCI-MS analysis following the method described previously (Zou et al., 2007). First, about 10 g freeze-dried and grinded samples were spiked with two surrogate standards (PCB-209 and ¹³C-PCB-141), extracted with acetone and hexane mixture (1:1 v:v) for 48 h by using Soxhlet extractors, and activated copper was added for desulphurization during the extraction. Then, the extracts were concentrated, cleaned, and consequently fractionated on a 1 cm i.d. silica/alumina column. The purified column was packed with neutral alumina (6 cm, 3% deactivated), neutral silica gel (2 cm, 3% deactivated), 25% sodium hydroxide silica (5 cm), neutral silica gel (2 cm, 3% deactivated), 50% sulfuric acid silica (8 cm), and anhydrous sodium sulfate (1 cm). The PBDE mixture was eluted with 30 ml of hexane and 60 ml of hexane:methylene chloride (1:1), and the final extract volume was reduced to 500 µL under a gentle N₂ stream. Prior to instrumental analysis, ¹³C-PCB-208 was added to each of the extracts as the internal standard, and finally the extracts were analyzed by GC-NCI-MS using an HP-5MS capillary column (30 m × 0.25 mm i.d. with 0.25 µm film thickness) (J&W Scientific Corp., CA, USA) and a DB-5MS capillary column (15 m × 0.25 mm i.d. with 0.25 µm film thickness) to separate 39 PBDE congeners and BDE-209, respectively.

2.4. TOC measurement

Measurement of TOC was accomplished according to previously reported method (Ran et al., 2007). Three grams of dried sediment sample were treated with 1M HCl to remove inorganic carbon and followed by washing three times with de-ionized water and drying overnight at 60 °C. Then, the total organic carbon was measured with an elemental analyzer (VarioEL III Elementar, Germany). Acetanilide was used as an external standard.

2.5. Ecological risk assessments of PBDEs in sediments

The risk quotient (RQ) approach is a widely used method in risk assessment studies on heavy metals and organic pollutants (Khairy et al., 2009; Wang et al., 2015a). It provides a quantitative estimate of the hazard associated with a single chemical or element (Environment Canada. Canadian Environmental Protection Act, 2013). In this study, the RQ values were determined by dividing the measured concentrations of PBDE congeners in the sediments by their respective sediment quality guidelines. Prior to the RQ

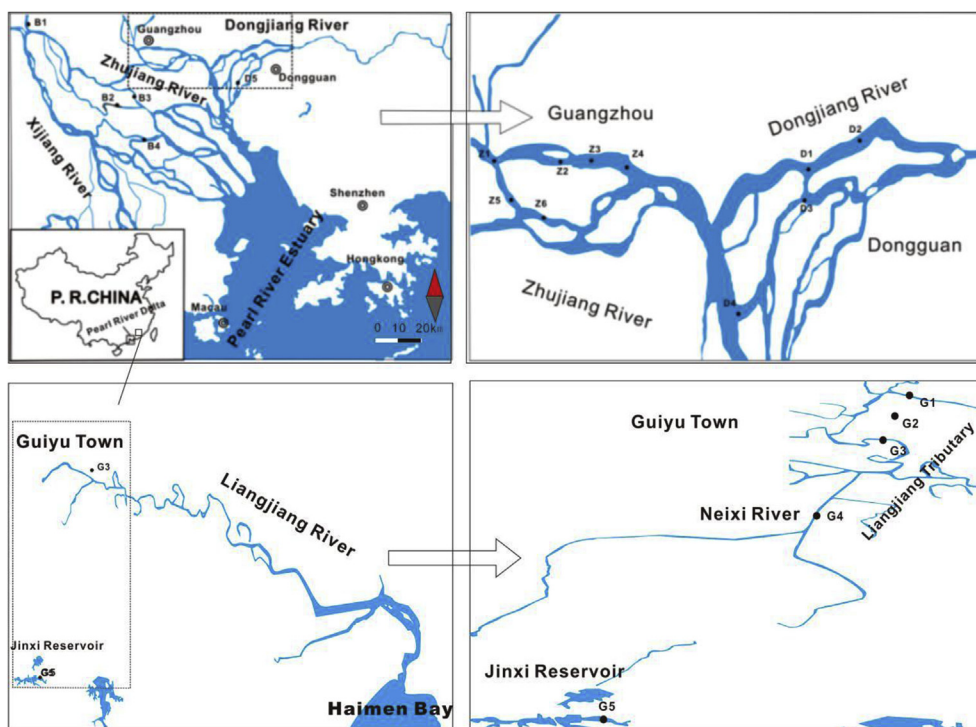


Fig. 1. Map of the study area and sampling sites of the PRD and Guiyu Town.

calculation, the concentrations of PBDE congeners in the sediment samples were normalized to 1% organic carbon. The guidelines for interpreting RQ values are as follows: $0.01 \leq RQ < 0.1$, low risk; $0.1 \leq RQ < 1$, medium risk; and $RQ \geq 1$, high risk to sediment-dwelling organisms (Environment Canada, Canadian Environmental Protection Act February 2013).

2.6. Quality assurance/quality control (QA/QC)

The QA/QC samples included procedural blanks, spiked blanks, and spiked matrix samples. Only negligible, trace concentrations of BDE-8, -47, and -209 were detected in the procedural blank samples, which were 0.011 ng g^{-1} , 0.009 ng g^{-1} and 0.043 ng g^{-1} . The limits of quantification, defined as ten times the ratio of signal to noise of each congener, were $5\text{--}20 \text{ pg/g}$ for tri- to hepta-BDEs and 200 pg/g for BDE-209. The recovery efficiency of PBDE congeners in spiked blanks and spiked matrix samples were 106.2%–127.3% and 95.6%–119.6%, respectively. The relative standard deviations for individual PBDE congeners measured in duplicate samples were $<15\%$. The average recoveries of $^{13}\text{C-PCB-141}$ and PCB-209 were $69.0 \pm 11.0\%$ and $71.0 \pm 19.0\%$, respectively, with the relative standard deviations $<20\%$. The reported data were not corrected by surrogate recoveries. The experiments were performed in dark (during extraction, concentration and analysis, etc) to minimize photodegradation.

3. Result and discussion

3.1. Levels and distribution of PBDEs in sediments

The concentrations of PBDEs in the sediment samples were presented in Table 1 and Fig. 2. Although di-, tri-, tetra-, penta-, hexa-, hepta-, and deca-BDEs were detected in all the samples, BDE-1, -2, -3 were only detected in the GY samples. In particular, BDE-209 showed 1–2 orders of magnitude higher than any of other

congeners in most of the samples, indicating that large quantities of deca-BDE were used in these regions. In addition, the levels of tetra-, penta-, hexa-, and hepta-BDEs were respectively higher than those of di- and tri-BDE. Moreover, the concentrations of $\sum_{39}\text{PBDEs}$ (excluding BDE-209) and BDE-209 in the PRD ranged from 0.308 to 38.9 ng g^{-1} and from 12.2 to 488 ng g^{-1} , respectively, whereas in the point-source sediments (GY) the concentrations were in the range of $2.57\text{--}21207 \text{ ng g}^{-1}$ and $7.02\text{--}66573 \text{ ng g}^{-1}$, respectively (Table 1).

With respect to the spatial distribution, the concentrations of $\sum_{39}\text{PBDEs}$ and BDE-209 were much higher in GY than in the PRD. The highest concentrations of PBDEs were observed at the G1 site collected from the tributary of Liangjiang river in Guiyu. The concentrations of $\sum_{39}\text{PBDEs}$ and BDE-209 were $21,207 \text{ ng g}^{-1}$ and $66,573 \text{ ng g}^{-1}$, respectively, which are the highest concentrations of PBDEs reported in river sediments around the world except for those observed in the similar e-waste sites (Labunska et al., 2013). The sites G3 and G4, located in Lianjiang wharf and Neixi river in Guiyu, also showed high concentrations of PBDEs, which was most likely related to domestic sewage and industrial wastewater discharges in the town. The concentrations of $\sum_{39}\text{PBDEs}$ and BDE-209 at G2 collected from a paddy field were 108 ng g^{-1} and 371 ng g^{-1} , respectively. Even though the measured concentrations at G2 were 2 orders of magnitude lower than at the other polluted sites in this study, they were similar to those in other reported point-source sediments (Cheng et al., 2014; Ma et al., 2016). However, they were much higher than those reported in the paddy fields (Shang et al., 2013; Wang et al., 2015b). In contrast, G5 collected from a drinking water reservoir in GY showed the lowest concentrations of PBDEs. Its $\sum_{39}\text{PBDEs}$ and BDE-209 concentrations were 2.57 ng g^{-1} and 7.02 ng g^{-1} , respectively.

In the PRD, the levels of PBDEs in the DJ sediments were relatively high. D1 and D2 showed the highest concentrations, which could be related to the developed industry in Zhongtang, a town nearby. D4 and D5 showed low concentrations of PBDEs as they are

Table 1The contents and compositional profiles of BDE congeners in the sediment samples (n = 20, ng g⁻¹).

Districts	Sites	1Br	2Br	3Br	4Br	5Br	6Br	7Br	BDE-209	∑ ₃₉ PBDEs	∑ _{all} PBDEs
BJ	B1	nd	0.015	0.041	0.154	0.061	0.018	0.019	12.2	0.308	12.5
	B2	nd	0.296	1.05	2.39	0.889	0.292	0.065	41.2	4.99	44.9
	B3	nd	0.038	0.112	0.499	0.075	0.052	0.036	18.1	0.811	18.5
	B4	nd	0.147	0.491	2.40	1.25	0.602	0.850	115	5.74	117
DJ	D1	nd	nd	0.870	21.9	12.3	2.20	1.52	488	38.9	524
	D2	nd	0.077	0.185	2.56	1.96	0.026	0.228	407	5.04	409
	D3	nd	0.158	0.364	3.89	2.58	0.441	0.334	335	7.77	340
	D4	nd	0.081	0.135	0.857	0.466	0.099	0.089	239	1.73	239
	D5	nd	0.207	0.450	2.23	1.21	0.433	0.064	90.4	4.59	93.9
ZJ	Z1	nd	0.144	0.236	2.24	1.04	0.423	0.613	116	4.69	120
	Z2	nd	0.160	0.488	6.64	0.973	1.08	1.46	226	10.8	235
	Z3	nd	0.043	0.028	0.175	0.081	0.063	0.109	44.7	0.499	44.9
	Z4	nd	0.058	0.156	2.59	1.65	0.386	0.350	382	5.19	382
	Z5	nd	0.143	0.219	1.65	0.887	0.338	0.584	123	3.82	127
	Z6	nd	nd	nd	4.69	4.70	0.578	1.17	272	11.1	282
	Z7	nd	358	1216	8946	7969	2454	264	66,573	21,207	87,779
GY	G1	nd	358	1216	8946	7969	2454	264	66,573	21,207	87,779
	G2	11.1	4.13	7.09	39.0	29.2	9.50	7.77	371	108	479
	G3	3.00	3.74	11.8	84.6	60.0	23.3	27.8	8840	214	9054
	G4	6.72	1.48	4.96	62.8	85.3	125	500	49,426	786	50,212
	G5	nd	0.110	0.170	1.23	0.800	0.140	0.130	7.02	2.57	9.59
	Min	nd	nd	nd	0.154	0.061	0.018	0.019	7.02	0.308	9.59
	Max	11.1	358	1216	8,946	7,969	2,454	500	66,573	21,207	87,779
	Median	nd	0.144	0.300	2.48	1.23	0.428	0.467	233	5.11	237

nd: not detected.

located near the estuary, and the sediments may be diluted by tidal seawater. Moreover, the concentrations of PBDEs in the ZJ sediments were high, and the average concentrations of ∑₃₉PBDEs and BDE-209 were 6.02 ng g⁻¹ and 198.6 ng g⁻¹, respectively. The concentrations of PBDEs in the ZJ tributary (Z1–Z4) showed a fluctuated distribution from upstream to downstream. The concentrations in the BJ sediments were relatively low as the average ∑₃₉PBDEs and BDE-209 concentrations were 2.96 ng g⁻¹ and 48.3 ng g⁻¹, respectively. This tributary is located in remote region, the population is low, its industry is less developed, and its river flow is high.

Generally speaking, the pollution of PBDEs in the point-source sites (GY) was very serious. In the PRD, the levels of PBDEs were higher in DJ than in ZJ and in BJ, which is similar to the reported distribution in sediments (Mai et al., 2005) and soils (Zou et al., 2007) in the PRD. The contamination of PBDEs was related to the population, industry, waste discharge, and hydrological processes in the watershed. As Guiyu is a well-known e-waste recycling site, pollution of PBDEs from dismantling emission is serious. Dongguan and Guangzhou are the main production sites for electronic and communication products in the PRD, leading to high emission of PBDEs in the investigated watershed.

3.2. Comparison of sediment PBDEs

The PBDEs levels in the sediments were compared with those in other regions around the world (Table 2). It was found that the concentrations of PBDEs in several sediments from Guiyu were much higher than most of those from other places around the world. The levels of PBDEs in the PRD in this study were lower than those reported in the same region (Mai et al., 2005; Chen et al., 2009, 2013), similar to those in Fuhe River (Hu et al., 2010), and higher than those in Xiamen offshore (Li et al., 2010), Hai River basin (Zhao et al., 2012), mangrove swamps in Hong Kong (Zhu et al., 2014), and Shanghai rivers (Wang et al., 2015b).

In addition, the PBDE concentrations in the PRD and GY exhibited higher levels than most of the reported values around the world, such as those in the Great Lakes (Zhu and Hites, 2005; Song et al., 2005), Maggiore Lake in Italy (Mariani et al., 2008), Niagara River in Canada (Richman et al., 2013), Llobregat River basin in

Spain (Barón et al., 2014), Diep and Kuils Rivers in South Africa (Daso et al., 2016), Bahía Blanca estuary in Argentina (Tombesi et al., 2017), even higher than the values from e-waste recycling sites in Vietnam (Matsukami et al., 2015; Anh et al., 2017). High concentrations of PBDEs were observed in Lake Shihwa in Korea (Moon et al., 2012), which were comparable to those in Guiyu. According to the above result, it is concluded that the sediments in the PRD, especially in Guiyu, were heavily contaminated by PBDEs.

3.3. Congener patterns of PBDEs in sediments

Penta-BDE was calculated from the percentage of the sum of the major congeners BDE-47, BDE-99, and BDE-100 in the technical mixture Bromkal 70-5DE, and octa-BDE was calculated from the percentage of BDE-183 in DE-79 (La Guardia et al., 2006). It was assumed that deca-BDE mainly consists of BDE-209. Table S1 listed the concentrations of penta-, octa-, and deca-BDE. It is known from Table S1 that deca-BDE constituted 73.4–99.3% of the total PBDE (mean 93.1%, median 94.6%) and was the dominant congener in all of the samples (Figure S1), illustrating the extensive use of technical formulations containing deca-BDE in the regions (Mai et al., 2005; Zou et al., 2007). Moreover, penta-BDE consisted of 0.27–21.5% of the total PBDE (mean 9.13%, median 1.04%), while octa-BDE accounted for 0.30–16.6% of the total PBDE (mean 5.00%, median 1.60%) (Figure S1), suggesting that the use of penta- and octa-BDE technical products were moderate.

As it is seen in Fig. 3, the percentages of low bromine PBDE congeners, except BDE-209, were highly variable among the sediments in different regions. The low bromine PBDE congeners in the DJ sediments were similar, as they mainly contained BDE-47 and BDE-99 with the relative percentages of 36.4–43.4% and 25.6–41.1%, respectively. The pattern was similar to that of commercial product 70-5DE (La Guardia et al., 2006), indicating that low bromine PBDEs in the DJ region were mainly originated from this product. The congener pattern of PBDEs in the ZJ sediments was similar to that from DJ, suggesting that a uniform commercial formula was used in the PRD region (Mai et al., 2005). In addition, as hepta-BDE (mainly BDE-183) showed higher percentages ranging from 10.7% to 29.5% in the ZJ sediments than in the DJ

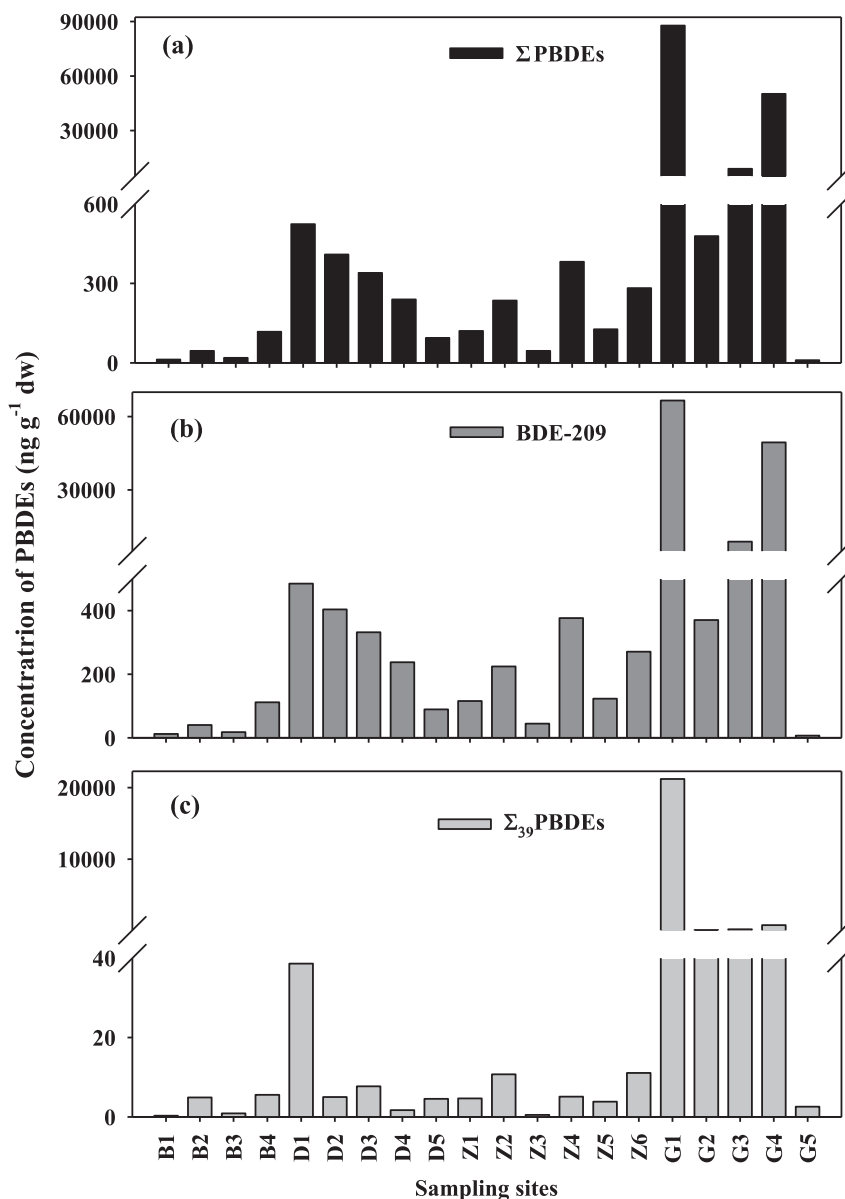


Fig. 2. Levels of PBDEs (ng g^{-1}) in sediments of the PRD and Guiyu. B, D, Z, G represent the samples from Beijing River, Dongjiang River, Zhujiang River and Guiyu, respectively.

sediments, suggesting the wide use of hepta-BDE in the Guangzhou region. In the BJ samples, the percentage of BDE-183 was 19.7% at B4, which is likely to be related to point source pollution. Other three samples showed a similar pattern of low bromine PBDEs, which consisted of BDE-47 (45.6–50.4%) and BDE-99 (16.5–19.0%). The contribution of BDE-47 were higher in BJ than in ZJ and in DJ, which might related to the fact that BJ receive atmospherically transported contaminants from other highly industrialized and urbanized regions around the PRD. As to the point source sediments in GY, the pattern of PBDEs at G3 was similar to the commercial product 79-8DE, and the percentage of BDE-183 reached 66.8%. But the congener pattern in the other samples was similar to that of 70-5DE, suggesting the diverse source of PBDEs in GY.

3.4. Organic carbon properties in the sediments of the PRD

The elemental analysis in the sediments of the PRD is listed in Table S2. The TOC contents ranged from 0.40% to 12.7% with a

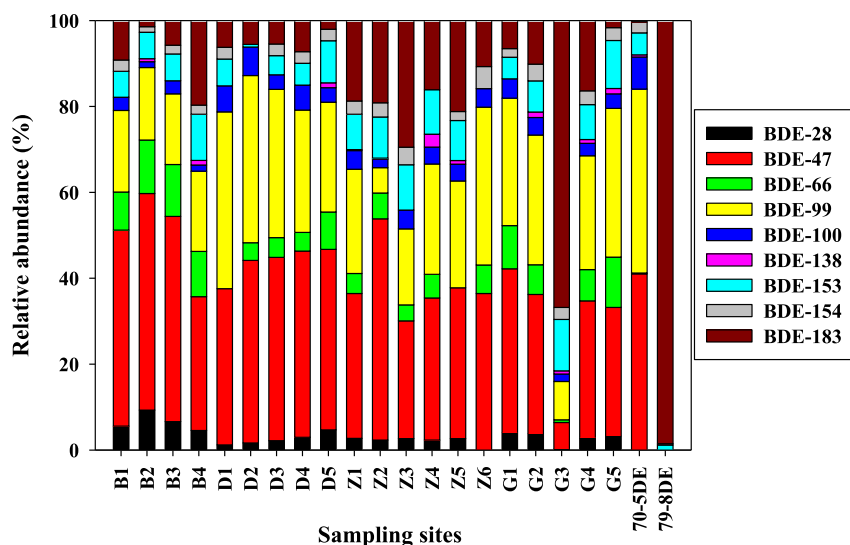
median of 1.88%. The contents of total nitrogen (TN) ranged from not detected to 0.84% with a median of 0.17%. Generally, the TOC contents were correlated to the PBDE concentrations. The TOC contents were relatively high in DJ and ZJ, ranging from 1.51% to 7.86% and from 1.72 to 12.73%, respectively, while they were low in BJ, ranging from 0.44% to 1.28%.

The ratios of C/N could be used as an index for the identification of organic matter source (Krishnamurthy et al., 1986) since the ratios of C/N higher than 8 indicate that the organic matter is originated from terrestrial source. The ratios of C/N in the sediments ranged from 13.1 to 34.3 with an average of 17.4 (Table S2). These values are close to the values of terrestrial higher plants, indicating that organic matter in the sediments were majorly originated from terrestrial input. In addition, the regression analysis showed that the TN contents were highly significantly related to the TOC contents ($R^2 = 0.885$, $p < 0.01$) (Figure S2).

Table 2Comparisons of PBDE concentrations (ng g^{-1}) in the investigated sediment with those in other locations around the world.

Location	n ^a	Σ PBDEs ^b	BDE-209	References
Guiyu, China	40	2.57–21207	7.02–66573	This study
Pearl River Delta, China	40	0.310–38.9	12.2–488	This study
Pearl River Delta, China	10	0.1–94.7	1.9–7340	Mai et al. (2005)
Pearl River Delta, China	10	0.120–19.7	1.26–2446	Chen et al. (2014)
Beijiang River, China	10	0.020–186	0.230–1558	Chen et al. (2009)
Fuhe River, China	8	0.130–6.39	11.8–293	Hu et al. (2010)
Xiamen offshore areas, China	9	0.300–6.40	0.100–70.1	Li et al. (2010)
Hai River basin, China	20	0.060–2.04	nd–0.13	Zhao et al. (2012)
Mangrove sediments in Hong Kong, China	8	0.570–14.4	1.53–75.9	Zhu et al. (2014)
Shanghai rivers, China	52	0.205–119	nd–189	Wong et al. (2015)
Lake Michigan, USA	9	1.70–4.00	43.9–95.6	Song et al. (2005)
Lake Erie, USA	18	1.10	39.0	Zhu and Hites (2005)
Maggiore Lake, Italy	8	0.020–27.1	nd–24.5	Mariani et al. (2008)
Lake Shihwa, Korea	23	0.160–943	0.820–17800	Moon et al. (2012)
Niagara River, Canada	17	nd–18.0	nd–170	Richman et al. (2013)
Llobregat River basin, Spain	7	1.50–44.3	1.47–43.6	Barón et al. (2014)
Bui Dau river, Vietnam	14	nd–30.0	0.430–320	Matsukami et al. (2015)
Diep and Kuils Rivers, South Africa	9	0.040–11.4	nd–3.50	Daso et al. (2016)
Trieu khuc, Hanoi city, Vietnam	8	21.6–474	0.900–386	Anh et al. (2017)
Bahía Blanca estuary, Argentina	10	0.050–1.95	0.130–1.95	Tombesi et al. (2017)

nd: not detected.

^a Number of PBDEs congeners analyzed in sample.^b The sum of all target PBDE congeners except for BDE 209.**Fig. 3.** The relative abundance of BDE congeners (include BDE-28, -47, -66, -99, -100, -138, -153, -154, -183) of the sediments and two commercial products.

3.5. Partitioning of PBDEs between sediments and waters in the PRD

The sorption and desorption of hydrophobic organic compounds on organic matter are critical to their distribution, bioavailability, risk, and fate of hydrophobic organic chemicals (Pignatello and Xing, 1996; Ran et al., 2007) in aquatic environment. Previous investigation showed that PBDEs in soils and sediments were mainly associated with organic matter (Gouin and Harner, 2003). In order to investigate the important role of organic carbon in partitioning of PBDEs between sediments and waters, correlation analyses were conducted between TOC and BDE congeners (Fig. 4 and Figure S3). It showed that TOC contents were strongly related to Σ_{39} PBDEs ($R^2 = 0.873$, $p < 0.01$) and Σ_{all} PBDEs ($R^2 = 0.635$, $p < 0.01$) except for the Z5 sample (Fig. 4). Moreover, the correlation coefficients (R^2) for all of the congeners were as follows: 0.489 $p < 0.01$ for BDE-28, 0.866, $p < 0.01$ for BDE-47, 0.430,

$p < 0.01$ for BDE-66, 0.808, $p < 0.01$ for BDE-99, 0.846, $p < 0.01$ for BDE-100, 0.068, $p = 0.368$ for BDE-138, 0.690, $p < 0.01$ for BDE-153, 0.658, $p < 0.01$ for BDE-154, 0.537, $p < 0.01$ for BDE-183, and 0.596, $p < 0.01$ for BDE-209 (Figure S3). It is noted that the concentrations of BDE-138 were not correlated with the TOC contents due to its low detectable frequency, and will not be discussed in the following analysis. The linear relationship of BDE-47 with TOC was highly significant ($R^2 = 0.866$, $p < 0.01$), similar to previous investigations (Hassanin et al., 2004; Zou et al., 2007).

The partition behavior of PBDEs in the sediments was investigated by calculating the organic carbon normalized partition coefficients (K_{oc}) as follows:

$$K_{oc} = q_e / C_e f_{oc} \quad (1)$$

Where q_e ($\mu\text{g g}^{-1}$) is the equilibrium solid-phase concentration, C_e ($\mu\text{g L}^{-1}$) is the aqueous-phase concentration, and f_{oc} is the fraction

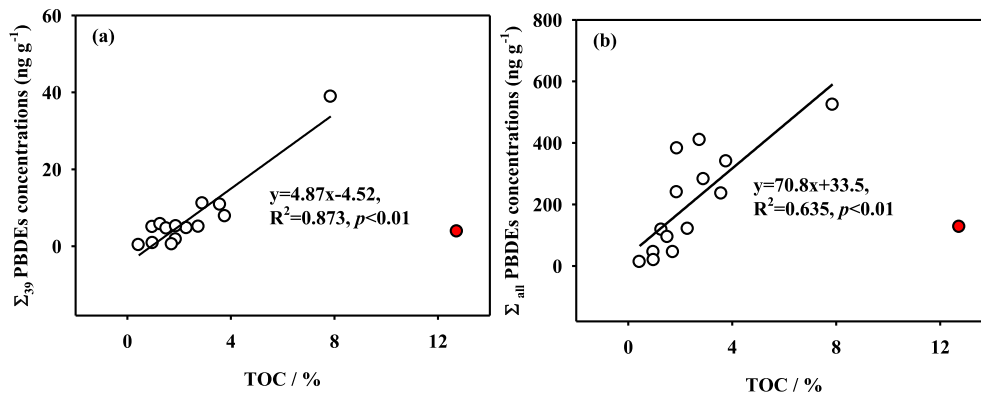


Fig. 4. Correlation between TOC and PBDEs in sediments of the PRD. Red circle represents outlier of sample Z5. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

of organic carbon in sediment. Further, K_{oc} can be estimated by the following equation (Gawlik et al., 1997):

$$\log K_{oc} = a \log K_{ow} + b \quad (2)$$

Combining the two equations gives:

$$\log (q_e/f_{oc}) = a \log K_{ow} + b + \log C_e \quad (3)$$

Where q_e/f_{oc} is the TOC-normalized concentration of PBDE congener (slope in Figure S3). The plot of logarithmic TOC-normalized BDE values versus their $\log K_{ow}$ (Fig. 5) provided an approximate regression equation ($R^2 = 0.694$, $p < 0.01$), confirmed that the distribution of PBDEs was mainly governed by the TOC-related sorption.

The b value could be obtained by using the reported K_{oc} – K_{ow} regression equation for other hydrophobic organic contaminants. If this value is -0.35 (Karickhoff, 1981), the aqueous concentration of BDE congeners could be estimated from equation (3) and the slope of the regression equation in Fig. 5. The estimated aqueous

concentration of any BDE was 1.62 ng L^{-1} in the sediments. As aqueous solubility of many BDE congeners is below 0.1 ng L^{-1} , the high concentrations of PBDEs estimated may be related to quite abundant colloids or dissolved organic matter in porewaters, which may enhance the solubility of PBDE congeners (Brownawell and Farrington, 1986; Maskaoui et al., 2002). However, if the estimated concentrations of PBDEs were compared with PBDE concentrations reported in sediment porewaters (Jia et al., 2012; Li et al., 2010), it was found that they were in the same order of magnitude, demonstrating that the partitioning of PBDEs on sediment organic matter is the dominating process.

3.6. Ecological risk assessments of PBDEs in sediments

As shown in Table 3, although the RQs of tri-BDE, tetra-BDE, and hexa-BDE in the PRD sediments were below 1, they were higher than 1 in 86.7% and 46.7% of the sediment samples for deca-BDE and penta-BDE, respectively, indicating that PBDEs in the river sediments from the PRD posed potential high ecological risks at

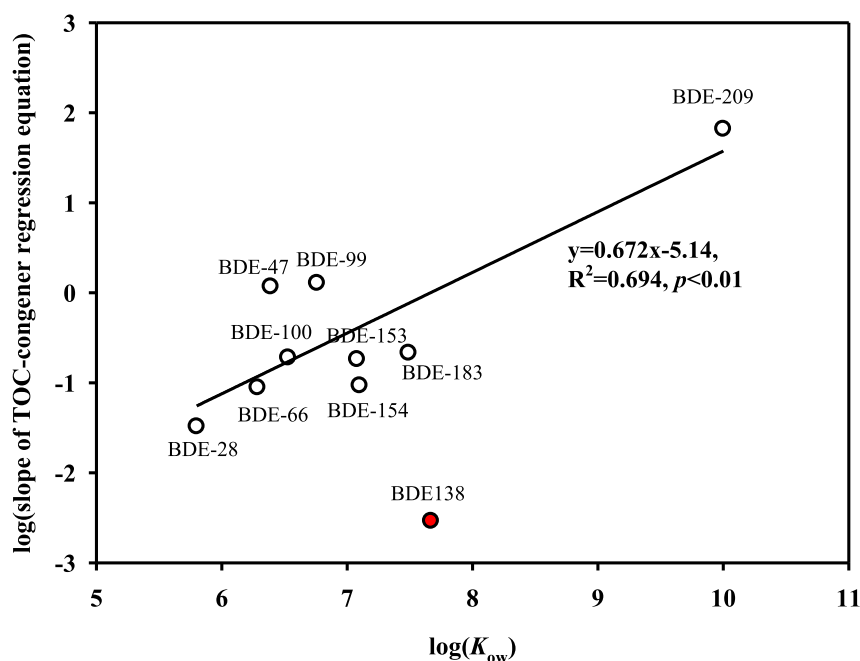


Fig. 5. Correlation between logarithms of slope of TOC-congener equation and the $\log(K_{ow})$ value of each BDEs in sediments of the PRD.

Table 3

The RQ of each PBDE congener in the PRD based on Federal Sediment Quality Guidelines (FSeQGs) proposed by Environment Canada (n = 20).

Districts	Sites	BDE-28	BDE-47	BDE-66	BDE-99	BDE-100	BDE-153	BDE-154	BDE-209
BJ	B1	0.0006	0.0056	0.0011	0.230	0.034	0.0001	0.0000	1.46
	B2	0.0075	0.0459	0.0114	1.50	0.124	0.0005	0.0001	2.17
	B3	0.0010	0.0077	0.0019	0.258	0.048	0.0001	0.0000	0.946
	B4	0.0034	0.0261	0.0088	1.53	0.117	0.0008	0.0002	4.60
DJ	D1	0.0009	0.0289	0.0000	3.18	0.470	0.0004	0.0002	3.25
	D2	0.0006	0.0162	0.0016	1.45	0.245	0.0000	0.0000	7.73
	D3	0.0008	0.0177	0.0019	1.39	0.137	0.0002	0.0001	4.63
	D4	0.0004	0.0073	0.0007	0.470	0.095	0.0001	0.0000	6.69
	D5	0.0022	0.0222	0.0046	1.32	0.174	0.0005	0.0001	3.12
ZJ	Z1	0.0009	0.0123	0.0017	0.860	0.154	0.0003	0.0001	2.65
	Z2	0.0011	0.0279	0.0033	0.312	0.104	0.0005	0.0002	3.30
	Z3	0.0001	0.0015	0.0002	0.061	0.023	0.0001	0.0000	1.36
	Z4	0.0006	0.0097	0.0016	0.731	0.113	0.0003	0.0000	10.55
	Z5	0.0001	0.0020	0.0000	0.135	0.021	0.0000	0.0000	0.508
	Z6	0.0000	0.0349	0.0064	3.43	0.404	0.0000	0.0004	4.92
	Z7	0.0001	0.0015	0.0002	0.061	0.023	0.0001	0.0000	1.36
GY	G1	2.31	24.5	9.54	2755	270	0.808	0.215	701
	G2	0.0130	0.128	0.0271	11.6	1.57	0.0025	0.0014	3.90
	G3	0.0224	0.277	0.0633	22.5	2.47	0.0063	0.0025	93.1
	G4	0.0087	0.236	0.0233	33.4	6.48	0.0407	0.0095	520
	G5	0.0004	0.0039	0.0010	0.295	0.0450	0.0000	0.0000	0.0739

most of the sampling sites. Penta-BDE and deca-BDE were the major ecological risk drivers for sediment dwelling organisms.

Taking the point-source sediments in GY into account, an estimated organic carbon content of 5% was used in the RQ calculation for each of the samples because of the lack of exact analysis values. From Table 3, the RQs of all the BDE congeners in the GY samples except G5 were much higher than in the PRD samples. Especially the sample G1 had the RQs much higher than 1 for most of the BDE congeners. It could be concluded that PBDEs in the point-source sediments posed serious ecological risks. The major ecological risks were derived from penta-BDE and deca-BDE. In addition, tri-BDE and tetra-BDE were potential drivers in some of the GY sediments. However, it should be noted that there is considerable uncertainty in the toxicity thresholds (Environment Canada, Canadian Environmental Protection Act, 2013). Thus, the actual risks of PBDEs in the sediments need further investigation.

In previous investigations, major sources of persistent organic pollutants in estuaries were thought to be legacy pools of past point-source released by manufacturing and from non-point sources associated with the general use, storage, and disposal of contaminants (Walker et al., 1999). Estuaries are also hydrologically open systems affected by long-distance transport of contaminants from upstream and downstream areas, suggesting that more diffuse, non-point sources of contaminants may be important (Walker et al., 1999; Foster et al., 2000) or that other factors may be involved in sediment contamination (King et al., 2004). In the PRD, the total input of PBDEs for the eight major riverine outlets of the PRD was estimated at 2.14 ton yr⁻¹ (Guan et al., 2009). Chen et al. (2007) reported that PBDE concentrations in the PRE increased exponentially after 1990, with the average annual flux of 31.8 ng cm⁻² yr⁻¹ and the total burden of 8.6 ton. Considering the increasing levels of PBDEs in the PRD sediments, a considerable amount of PBDEs from the PRD was inputted into the PRE and South China Sea, which requires effective efforts for source management and pollution control.

4. Conclusions

The present investigation showed that PBDEs were ubiquitous in the sediments from the Pearl River Delta and Guiyu town, South China. The level of PBDEs contamination were higher than most of the reported values, especially in Guiyu samples. The

contamination of PBDEs was related to the population, industry, waste discharge, and hydrological processes in the watershed. A good regression of TOC-normalized BDE values with their log *K*_{ow} in the sediments confirmed that TOC-related sorption of PBDEs predominantly governed their distribution. Moreover, the risk quotients for risk assessment of PBDEs in the sediments showed high ecological risks at all of the sampling sites, with penta-BDE and deca-BDE being the major ecological risk drivers for the benthic organisms.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at <https://doi.org/10.1016/j.envpol.2017.12.049>.

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