

Time Trends of Polybrominated Diphenyl Ethers in Sediment Cores from the Pearl River Estuary, South China

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The present study provides information on the time trend of PBDEs in three sediment cores from the Pearl River Estuary (PRE), South China, using ²¹⁰Pb dating technique. The ΣPBDEs (except for BDE 209) concentrations in all sediment cores increased gradually from the bottom (mid-1970s) to the middle layer (later 1980s and early 1990s) followed by different temporal trends in different locations to the surface sediments, reflecting the variations in the consumption of commercial penta-BDEs mixture in different regions of the Pearl River Delta. The BDE 209 concentrations remained constant until 1990 and thereafter increased exponentially to the present, with doubling times of 2.6 ± 0.5 – 6.4 ± 1.6 years, suggesting the increasing market demands for deca-BDE mixture after 1990 in China. The inventories of ΣPBDEs and BDE 209 in sediments of the PRE were 56.0 and 368.2 ng cm⁻², respectively, and the total burden of PBDEs in the PRE were estimated at 8.6 metric tons. The current ΣPBDEs and BDE 209 fluxes to the PRE were 2.1 and 29.7 ng cm⁻² yr⁻¹, respectively. The concurrent increase of BDE 209 fluxes and the annual gross industrial output values of electronics manufacturing revealed that the rapid growth of electronics manufacturing in this region since the early 1990s was responsible for the sharp rise of BDE 209 fluxes in the past decade. The PBDE congener compositions of the cores indicated the various input pathways for PBDEs transport to different locations of the estuary.

Introduction

During the past few decades, great concerns about polybrominated diphenyl ethers (PBDEs) have arisen due to their ubiquitous presence and persistence in the environment and potential toxicities such as thyroid hormone disrupting, neurotoxic, and developmental effects to wildlife and humans (1). PBDEs are released to the environment during the production, use, and disposal of PBDE-containing products. Like many other semivolatile organic compounds, they can enter the water column via direct and indirect urban

domestic/industrial sewage discharges and atmospheric deposition, and they have a tendency to accumulate in aquatic sediments due to their high octanol–water partition coefficients (2).

Historical trends of PBDEs in various environmental compartments and humans have been reported mostly in Europe and North America (3–6). Concentrations of PBDEs have increased from the 1960s or 1970s to the 1990s and then decreased or leveled off in Europe, whereas they continue to increase in different environmental media in North America in the past decade (7–10). The discrepancy is likely a result of difference in the timelines of production and use of technical PBDE products between the two continents. For instance, penta-BDE mixture has been restricted for over 10 years and banned within Europe since 2003 (11, 12), however, in North America, Great Lakes Chemical Corp. voluntarily stopped penta- and octa- mixtures production at the end of 2004, and they were subsequently discontinued in certain states in the United States (13). Currently, information on the temporal trends of PBDEs in the environment of Asia is limited, except for several reports on PBDEs in sediment cores and human milk from Japan (14–16).

The domestic consumption of PBDEs is believed to increase in China because of the rapid growth of manufacturing activities for electronic and telecommunication equipment (ETE), such as computer, phone, printer, and household electric equipment. The estimated domestic production of predominant commercial deca-BDE mixture in China increased by 200% between 2000 and 2005, from 10 000 to about 30 000 metric tons (17). On the other hand, China appears to be a large dumping site of e-wastes imported from overseas legally and illegally in recent years (18). Apparently, the PBDEs contamination status in the environment of China and their effects on the ecosystem and humans remain to be fully understood.

The Pearl River Delta (PRD), the largest ETE manufacturing base in China, has been subjected to significant PBDEs pollution in air, water, and biota (19–21). Our recent study has revealed the substantially high BDE 209 levels in riverine sediments and their increasing trends in two sediment cores in the Pearl River Estuary (PRE) (19). The PRE is regarded as an important reservoir of pollutants generated in the PRD. The present study aimed to (1) investigate the chronology of PBDE concentration and flux in the PRE as recorded in three sediment cores (including the two cores in our previous study) based on the ²¹⁰Pb dating; (2) assess the influence of the rapidly increasing ETE manufacturing activities in the PRD region on the PBDEs accumulation in the coastal ecosystem by estimating the inventories, burdens, and fluxes; (3) assess the transport pathways for PBDEs to the PRE.

Experimental Section

Sample Collection. A detail description of the sampling area was given elsewhere (22). Three sediment cores were taken from the eastern and western sides of the PRE in April 2004 for core no. 1 (N 22° 28.5', E 113° 46.5') and core no. 2 (N 22° 16.0', E 113° 42.0') and in January 2006 for core no. 3 (N 22° 1.5', E 113° 34.2') (Figure 1). Sediment cores were collected by a Plexiglas gravity corer with four subcores (55 cm × 8 cm i.d.), with lengths of 34, 31, and 50 cm for core nos. 1, 2, and 3, respectively, and sectioned at 2 cm intervals in the ship. Samples were sealed in precleaned bottles and stored at 0 °C. All samples were transported on ice to the laboratory and stored at –20 °C until further analysis.

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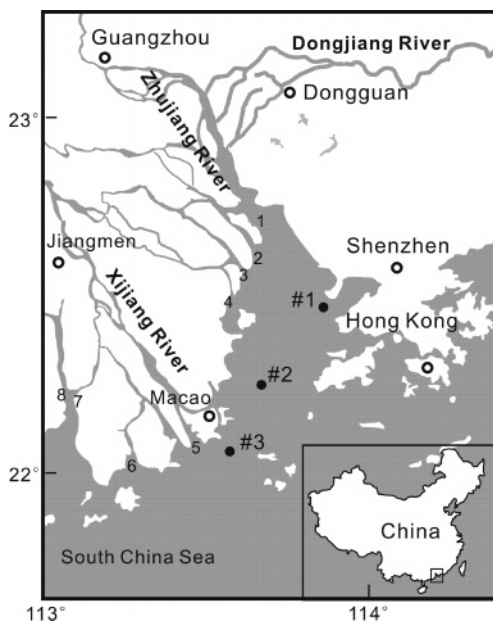


FIGURE 1. Map of study area and sampling sites. 1–8 represent the eight main outlets to the Pearl River Estuary: 1, Humen; 2, Jiaomen; 3, Hongqimen; 4, Hengmen; 5, Modaomen; 6, Jitimen; 7, Hutiaomen; 8, Yamen.

Analytical Procedure and Quality Control. Eleven PBDE congeners were analyzed for core nos. 1 and 2, including tri- through hepta-BDEs (BDE 28, 47, 66, 85, 99, 100, 138, 153, 154, and 183) and deca-BDE (BDE 209). Six additional octa- and nona-BDE congeners (BDE 196, 197, 203, 206, 207, and 208) were also measured for core no. 3. Detailed analytical procedure and instrumental analysis conditions were given elsewhere (19). The surrogate recoveries in all the samples were 79.9–118.4%, with a mean value of 100.6% for ^{13}C -PCB 141 and 80.3–116.8%, with a mean value of 99.7% for PCB 209, respectively. Recoveries of 10 PBDE congeners (BDE 28, 47, 66, 100, 99, 154, 153, 138, 183, and 209) ranged from 53.5 to 111.3%, 82.6% on average, in the spiked blank samples. Only considerably low concentrations of BDE 47 (<0.04 ng per sample) were found in procedural blanks, and they were appropriately subtracted from those in the sample extracts.

Dating of the Sedimentary Core. The ^{210}Pb activities in sediment subsamples were determined by analysis of the radioactivity of its decay product ^{210}Po . The Po was extracted, purified, and self-plated onto silver disks at 75–80 °C in 0.5 M HCl, with ^{209}Po used as yield monitor and tracer in quantification. Counting was conducted by computerized multichannel spectrometry with gold-silicon surface barrier detectors. Supported ^{210}Po was obtained by indirectly determining the activity of the supporting parent ^{226}Ra . Constant initial ^{210}Pb concentration (CIC) model was used for core no. 2, obtaining an average sedimentation rate (23).

Data Analysis. PBDEs concentrations were reported on a dry weight basis. The inventory (I) of PBDEs was defined as the total integrated mass of PBDEs per unit area from the bottom to the surface sediments. The fluxes (F) were estimated by the sedimentation rates and the concentrations of PBDEs. They were calculated using the equations, $I = \sum C_i \rho_b d$ and $F = C_i R_i$, respectively, where C_i (ng/g) is the concentration in sediment segment i , ρ_b (g cm^{-3}) is the dry mass density of sediment segment i , d (cm) is the thickness of segment, and R_i ($\text{g cm}^{-2} \text{yr}^{-1}$) is the sedimentation rate.

Results and Discussion

Sediment Rates. An average sedimentation rate of $0.97 \text{ g cm}^{-2} \text{ yr}^{-1}$ was obtained for core no. 2. A previous study reported the average sedimentation rates of 0.59 and 2.35 g

$\text{cm}^{-2} \text{ yr}^{-1}$ in the eastern and western sides of the PRE, respectively (23). Caused by the prevailing southwestward coastal current in the PRE, freshly discharged materials from rivers tend to be transported to the western rather than the eastern side of the estuary, resulting relatively high sedimentation rates in the western PRE than the eastern side. Our sedimentation rate at core no. 2 is between these reported values. An average sedimentation rate of $1.52 \text{ g cm}^{-2} \text{ yr}^{-1}$ in the previous study was determined in a sediment core nearby core no. 3 in our study (23), and this average sedimentation rate was applied to core no. 3. Therefore, both the top 31 cm in core no. 2 and 50 cm in core no. 3 represent approximate 30 years of depositional records. Core no. 1 was located near Shenzhen Bay, west of a sediment core in the bay that has a sedimentation rate of $0.59 \text{ g cm}^{-2} \text{ yr}^{-1}$ (23). Presumably, core no. 1 may have a higher sedimentation rate than this value, and thereby the top 34 cm in core no. 1 was encompassed at least 30–40 years of depositions. Considering this dating uncertainty for core no. 1, the chronology of PBDEs in sediments was reported only for core nos. 2 and 3.

Time Trends of PBDE Concentrations. PBDEs were measurable in all segments of the three sediment cores (Table 1). The concentrations are illustrated in Figure 2 as a function of sediment depth of the three cores and also against the deposition year for core nos. 2 and 3. In the rest of the paper, Σ PBDEs refers to the tri- through hepta-BDEs measured in this study. The TOC normalized PBDEs concentrations do not change the sediment profiles and differences in contamination magnitude within and among the cores. The Σ PBDEs concentrations generally showed an increasing trend from the bottom (~ 1975) to a middle sediment layer at 20–24 cm in core no. 1, 14–18 cm in core no. 2, and 20–22 cm in core no. 3. These sediment layers approximately corresponded to the late 1980s (1989) and early 1990s (1994) in core nos. 2 and 3, respectively. These increases were coincident with the production and use figures of pentamixture in the world since the 1970s. This profile has also been observed in most of dated sediment cores from the Great Lakes (2, 24–26), Western Europe, and the Baltic Sea (9, 27). The times for the concentrations to double, t_2 , in the sediments are 7.1 ± 1.5 years at core no. 2 and 6.0 ± 1.4 years at core no. 3 estimated by data measured in segments deposited prior to 1990 (Table 1). These t_2 values are comparable to the t_2 values calculated from dated sediment cores in other studies from North America and Europe (3, 9, 24, 26), but somewhat longer than the 3–5 years reported for biota and humans (3). In sediments deposited after the first peak, the Σ PBDEs profiles were quite different among the three cores (Figure 2). The Σ PBDEs concentrations in core no. 1 showed a dramatically decrease from a peak at depth of 22–24 cm to the section at 18–20 cm and then leveled off to the surface, probably indicating that the use of penta- mixture has been reduced in Shenzhen, as this location is influenced directly by domestic sewage and industrial effluent from the city of Shenzhen via Shenzhen Bay. In core no. 2, the Σ PBDEs concentrations are fluctuated with a zigzag pattern in sediments deposited after 1989. This location, situated in the western part of the PRE, receives fluvial suspended particles from most watersheds of the delta including the Zhujiang, Dongjiang, and Beijiang Rivers through Humen, Jiaomen, Hongqilimen, and Hengmen outlets. These watersheds run across the large urbanized and industrialized areas of the PRD, such as the cities of Guangzhou and Dongguan, two important sources of PBDEs of the PRD as demonstrated in our previous study (19). The complicated sediment record of Σ PBDEs in core no. 2 may reflect the changes in the production and use of the pentamixture in the major urbanized and industrialized areas or was likely resulted from the sediment disturbance and mixing. However, it is difficult to verify this supposition because data

TABLE 1. Concentration, Doubling Times, Surface Flux, and Inventory of PBDEs in the Sediments of the Pear River Estuary, China

core	concn. range ^a (ng/g)						surface concn. (ng/g)	
	Σ PBDEs ^b		BDE 209		octa- and nona-BDEs		Σ PBDEs	BDE 209
	before ~1990 ^c	after ~1990	before 1990 ^d	after 1990	before 1990	after 1990		
1	2.85–5.3 (3.8)	0.07–0.93 (0.3)	0.43–0.63 (0.52)	1.11–6.8 (7.4)	na ^e	na	0.15	13.5
2	1.2–7.0 (3.7)	1.5–5.8 (3.4)	2.0–3.3 (2.9)	2.5–13.9 (9.0)	na	na	3.9	13.9
3	0.01–0.13 (0.03)	0.03–0.63 (0.23)	0.1–1.6 (0.8)	2.4–61.5 (18.2)	nd–0.3 (0.03)	nd–6.6 (1.9)	0.38	30.3

core	doubling time, t_2 (year)				inventory (ng cm ⁻²)		surface flux (ng cm ⁻² yr ⁻¹)	
	Σ PBDEs		BDE 209		Σ PBDEs	BDE 209	Σ PBDEs	BDE 209
	before ~1990	after ~1990	before 1990	after 1990				
1	na		na	na	na	na		
2	7.1 ± 1.5	na	na	6.4 ± 1.6	106.2	172.8	3.7	13.4
3	6.0 ± 1.4	2.2 ± 0.4	na	2.6 ± 0.5	5.8	563.6	0.58	46.0

^a Values in parentheses are average concentrations. ^b Σ PBDEs refers to the sum of tri- through hepta- BDEs. ^c Depth at 20 cm for core no. 1, 1989 for core no. 2, and 1994 for core no. 3. ^d Depth at 20 cm for core no. 1. ^e Not available.

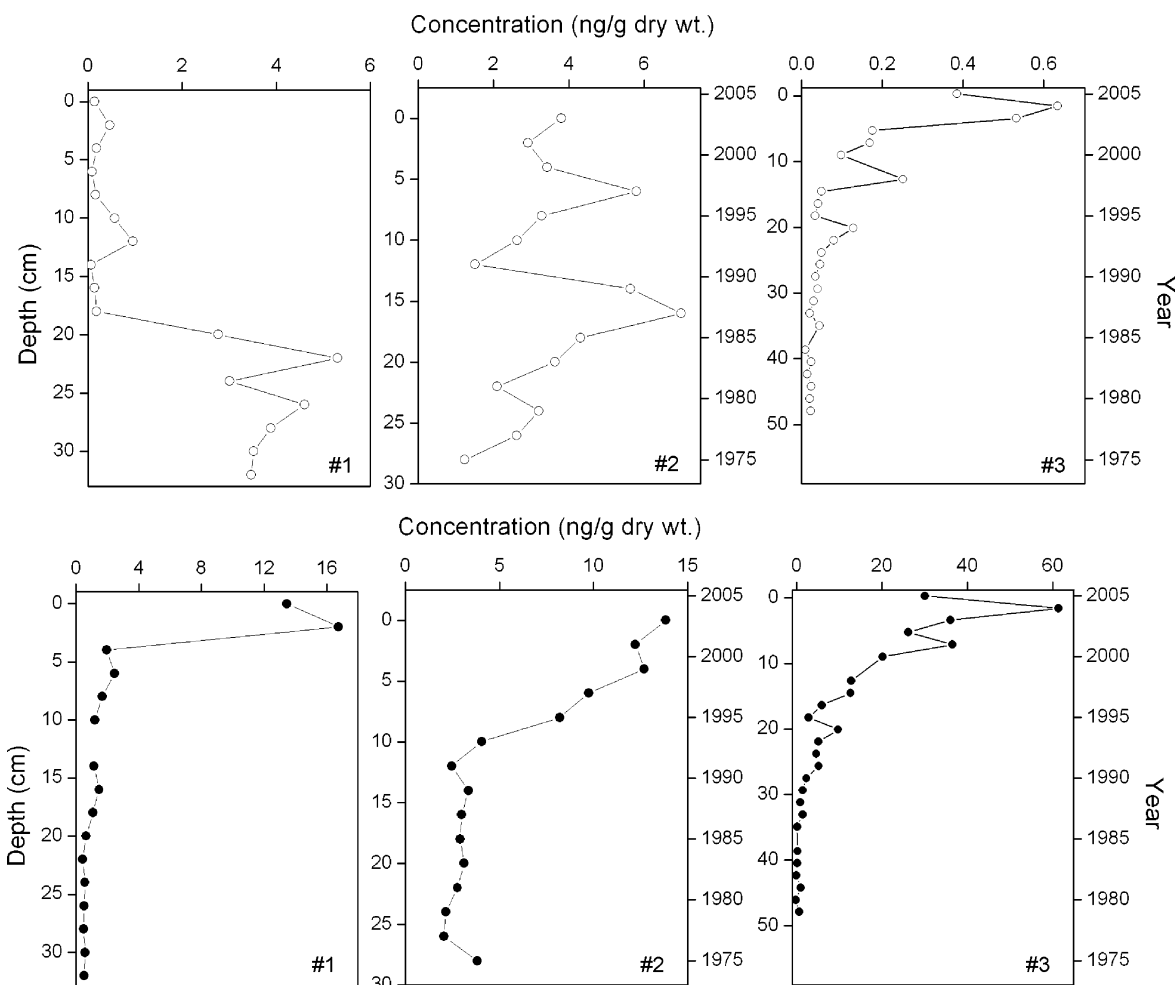


FIGURE 2. Temporal trends of Σ PBDEs (tri- through hepta- BDEs, ○) and BDE 209 (●) concentrations in the three sediment cores of the Pear River Estuary.

of the historical consumption and production of penta-mixture in China are not available presently. Despite the fluctuations throughout core no. 2, Σ PBDEs concentrations in sediments deposited after 1989 are comparable to those before 1989 as shown in Table 1, indicating the continuous inputs of Σ PBDEs to the PRE in recent years. Finally, there is a continuous and obvious increase of Σ PBDEs concentrations toward the surface sediments in core no. 3 after 1994, suggesting the continuously increasing Σ PBDEs inputs in

the western part of the PRE over the past decade. Σ PBDEs concentrations have a faster t_2 (~2.2 years) in sediments deposited after 1994 than those in pre-1994 sediments (Table 1).

BDE 209 concentrations in sediments of the three cores followed a general increasing trend from the bottom to the surface, with maximum concentrations at the surface or subsurface segments of the sediment cores, except a sample at depth of 12–14 cm in core no. 1 with an unusually high

concentration. The cause of the extremely high concentration in this sample is unclear now and is to be investigated further. This value was not included in Figure 2 and the latter inventory calculation. A relatively constant or slowly increasing trend was observed from the bottom to depths of 20–22 cm in core no. 1, 12–14 cm in core no. 2 and 28–30 cm in core no. 3, corresponding to around 1990 for both core nos. 2 and 3 (Figure 2). The time period during which BDE 209 remained constant or slightly increasing corresponds to the time frame for deca- mixture application and production in the world, which began to increase in the late 1970s (24). After this period (approximately corresponding to 1990), BDE 209 concentrations showed a dramatic increase toward the surfaces in all the three sediment cores, with t_2 values of 6.4 ± 1.6 years at core #2 and 2.6 ± 0.5 years at core #3 (Table 1). This is consistent with the increasing demand for deca- mixture as a result of the encouraged growth of ETE manufacturing activities in the PRD region since the early 1990s, and will be further discussed in the following section. The t_2 for BDE 209 in dated sediment cores were estimated as 7.5 ± 1.2 years and 5.3 ± 0.7 years for Lakes Michigan and Erie, and as long as 45 ± 14 years for Lake Superior since the 1970s (2, 24). In another study, a sediment core collected from Drammenfjord, Norway showed a t_2 of 8.4 years from the mid-1980s for BDE 209 (9). The t_2 values for BDE 209 from the PRE are comparable to or slightly shorter than the results from Lakes Michigan and Erie and Drammenfjord, but much faster than those from Lake Superior. It is also noteworthy that the time at which BDE 209 concentrations started to obviously increase in the sediments of the PRD region seems to be 10–20 years later than those in North America and Europe where BDE 209 concentrations have continuously increased since the 1970s. This may reflect the difference in historical patterns of deca- mixture production and usage among these continents.

Inventory and Flux. The inventories of PBDEs at the two dated cores ranged from 5.8 to 106.2 ng cm⁻², with an average of 56.0 ng cm⁻² for ΣPBDEs, and from 172.8 to 563.6 ng cm⁻², with an average of 368.2 ng cm⁻² for BDE 209 (Table 1). Using the average inventories, we estimated the total burden of ΣPBDEs and BDE 209 would be 1.1 and 7.4 metric tons, respectively, in sediments of the PRE with a water surface area of 2016 km². However, the actual total inputs of PBDEs to the PRE were likely underestimated because a portion of PBDEs would be transported to the SCS from the estuary. Our previous study demonstrated that the burden of PAHs and OCPs in the northern SCS (with an area of 21 340 km²) accounts for about 40% of their total burden in the PRE and northern SCS (22). Therefore, assuming that 40% of the PBDEs are deposited in the northern SCS, the total burdens of ΣPBDEs and BDE 209 are about 1.9 and 12.4 metric tons, respectively, in the PRE and northern SCS area. The total PBDEs burden (14.3 metric tons) in the PRD and northern SCS were comparable to the PBDE burdens in Lake Erie (10.3 tons) with a similar area to that of our study, but lower than those in Lake Michigan (22.8 tons), adjacent to a highly urbanized area of the United States, with an area ~2.5 times that in the present study (24).

The average current fluxes of ΣPBDEs and BDE 209 to the PRE, as observed at the sediment surfaces of core nos. 2 and 3 (Table 1), are 2.1 and 29.7 ng cm⁻² yr⁻¹, respectively, which are considerably higher than the average surface fluxes of PBDEs to the Great Lakes (0.02–0.23 ng cm⁻² yr⁻¹ for ΣPBDEs and 0.14–6.92 ng cm⁻² yr⁻¹ for BDE 209) (2, 24–26). The relatively high fluxes in our study area may be attributed to the relatively high sedimentation rates in the PRE (0.59–2.35 g cm⁻² yr⁻¹), which are almost 1 order of magnitude higher than those observed in the Great Lakes (0.011–0.372 g cm⁻² yr⁻¹) (2, 24–26). Using the average surface fluxes at core nos. 2 and 3, representing the time period 2003–2005, the current

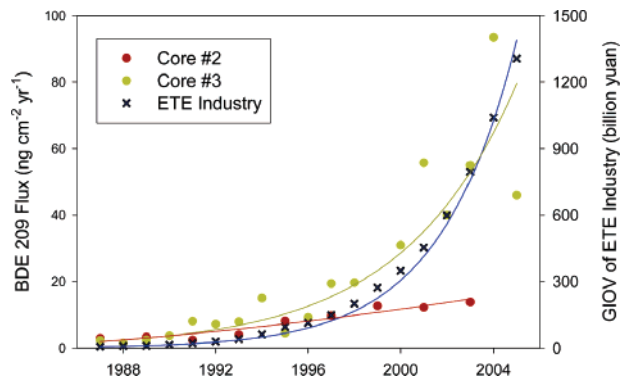


FIGURE 3. PBDEs fluxes to the Pearl River Estuary sediments compared to the gross industrial output values (GIOV) of electronic and telecommunication equipment (ETE) in the Pearl River Delta from 1987 to 2005.

loading rate of ΣPBDEs and BDE 209 to the PRE is estimated to be around 0.04 and 0.60 ton/yr, respectively.

As expected, the BDE 209 fluxes to the PRE showed an exponential increase in the past decade. This increase may be attributed to the increasing use of deca- mixture in the PRD region due to the rapid development of ETE manufacturing industries since the early 1990s. Relationship between the time-dependent fluxes of BDE 209 and the annual gross industrial output values (GIOV) of ETE manufacturing in the PRD region was examined for the period of 1987–2005. The increasing trend of BDE 209 fluxes to the PRE consistently accompanies the increasing profile of GIOV of ETE manufacturing (Figure 3). The exponential rise of BDE 209 fluxes started at depths corresponding to the early 1990s, fairly comparable to the initial stage of rapidly increasing GIOV at ~1990. The doubling time of GIOV of ETE manufacturing during the period 1987–2005, ~2.3 years, is close to the t_2 (2.6 ± 0.5 years) value of BDE 209 concentrations in core no. 3. The longer t_2 (6.4 ± 1.6 year) value observed in core no. 2 could stem from the recycling of chemicals due to sediment resuspension around this location (28), which diluted the concentrations and impeded the increase of chemicals. Comparatively, core no. 3 is located in relatively stable environment and could keep the PBDEs sedimentary record well (29). Furthermore, the large-scale process of e-waste recycling activities within the PRD in recent years may have liberated a large amount of PBDEs from the products to the PRE via surface runoff or atmospheric transport. This may contribute in part to the increase of PBDEs fluxes in the recent sediments of the PRE.

Potential Sources of PBDEs in Relation to Input Pathway and Environmental Degradation. PBDE concentrations and compositions in sediments are a complex function of emissions, transport pathways, and environmental transformations. The patterns of the seven frequently detected tri- to hepta-BDE congeners in the cores, compared with those in the surface sediments of three major rivers in the PRD, air of Guangzhou (19, 20), and two penta- mixtures (Bromkal 70-5DE and DE-71) (30), were illustrated in Figure 4. BDE 47 and 99 accounted for more than 50% of the ΣPBDEs over the three cores, similar to the results for surface sediments in the PRD region (19). The congener patterns in core nos. 1 and 2 fairly resemble those in the surface sediments collected in the Dongjiang and Zhujiang Rivers and DE-71. This suggests that the riverine input from local direct discharges is the most probably route of PBDEs transported to these locations. In core no. 3 the situation is different, where relatively high contribution of less brominated congeners (BDE 28, 47, and 66) compared to the other cores was observed. This site is close to Modaomen outlet, as a result mainly receives input from the Xijiang River that

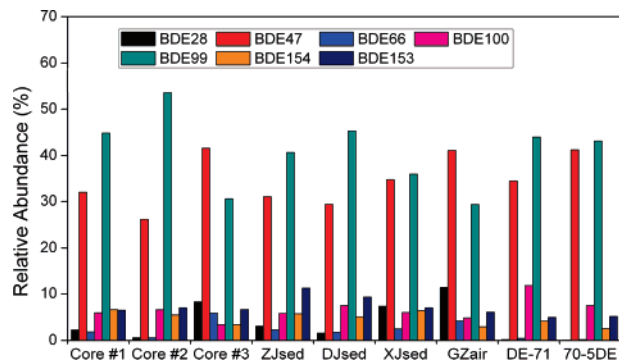


FIGURE 4. Comparison of PBDE congener profiles in the three sediment cores of the Pearl River Estuary, surface sediments in the Pearl River Delta (19), air in Guangzhou (20), and technical penta-BDEs mixtures (30). ZJ, Zhujiang River; DJ, Dongjiang River; XJ, Xijiang Rivers; GZ, Guangzhou.

runs through the west part of the PRD including less urbanized and industrialized (around the upstream river) and new developing areas (such as Fushan, Jiangmen around the downstream). Our previous study indicated that Xijiang River receives atmospherically transported pollutants such as PAHs and PBDEs from highly industrialized and urbanized areas of the PRD (19, 31). The PBDE compositions, coupled with the low Σ PBDEs concentrations, seem to support the atmospheric transport of these PBDEs because these congeners are more volatile than heavier ones and have the ability to transport long range in atmosphere (32). Core no. 3 displayed a similar congener pattern to the Xijiang River (19) but with an enhanced contribution of BDE 47, which has been proved to be more recalcitrant to photodegradation due to the lower number and substitution position of bromine atoms (33). Alternatively, debromination of highly brominated congeners during atmospheric and water current transport could result in the formation of BDE 47 and accordingly its high contribution in core no. 3 (34). However, the higher levels of BDE 209 in the upper sediments of core no. 3 were unlikely from atmospherically transported input. Industrial activities in the southwestern part of the PRD (new developing areas) may be the important source of BDE 209 in this core because high BDE 209 concentrations were also observed in the surface sediments in the downstream Xijiang River (19).

It was worthwhile to note that significant amounts of octa- and nona-BDEs (BDE 196, 197, 206, 207, and 208) were detected in the core sediments (only core no. 3 was analyzed for octa- and nona-BDEs, Table 1). To explore the initial origination of these congeners, two domestic deca-formulations purchased from chemical market in Guangzhou were analyzed. The results indicated that these formulations contain 8.2–10.4% (w/w) of octa- and nona-BDEs. Another recent study also reported that two deca-formulations from Europe (Bromkal 82-0DE) and North America (Saytex 102E) contained octa- and nona-BDEs with contributions of 2.5 and 9.9% (w/w), respectively (30). Octa- and nona-BDEs accounted for 0.0–16.3%, with a mean value of 10.3%, of the total octa- to deca-BDEs concentrations, and a very close correlation between BDE 209 and sum of octa- and nona-BDEs concentrations was found ($r = 0.98$, $p < 0.01$). This indicated that the deca- mixture could be the original source material for the octa- and nona-BDE congeners in the present study. However, the debromination of BDE 209 could not be ruled out as a potential source of less brominated congeners including octa- and nona-BDEs in the environment because some studies have observed the formation of lower brominated (tetra- through nona-) BDEs from degradation of BDE 209 under UV light and anaerobic conditions (34, 35). The significantly ($p = 0.02$) higher abundances of octa- and nona-

BDEs in the deep segments (9.3–16.3%, 16–32 cm) than those in the shallow sediments (6.6–10.1%, 0–16 cm) may suggest the higher degree of BDE 209 debromination in the longer buried sediments.

Acknowledgments

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