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# Distribution of Polybrominated Diphenyl Ethers in Sediments of the Pearl River Delta and Adjacent South China Sea

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Spatial and temporal distributions of polybrominated diphenyl ethers (PBDEs) in sediments of the Pearl River Delta (PRD) and adjacent South China Sea (SCS) of southern China were examined. A total of 66 surface sediment samples were collected and analyzed to determine the concentrations of 10 PBDE congeners (BDE-28, -47, -66, -100, -99, -154, -153, -138, -183, and -209). The concentrations of BDE-209 and $\sum$PBDEs (defined as the sum of all targeted PBDE congeners except for BDE-209) ranged from 0.4 to 7340 and from 0.04 to 94.7 ng/g, respectively. The $\sum$PBDEs concentrations were mostly $<$50 ng/g, within the range for riverine and coastal sediments around the world, whereas the BDE-209 concentrations at the most contaminated sites were at the high end of the worldwide figures. Congener compositions were dominated by BDE-209 (72.6–99.7%), with minor contributions from penta- and octa-BDEs. Slightly different PBDE compositions were observed among samples collected from different locations, attributable to possible decomposition of highly brominated congeners and/or redistribution between particles of various sizes during atmospheric or fluvial transportation. The PBDE patterns in the SCS and Pearl River Estuary sediments were similar to those in sediments of the Zhujiang and Dongjiang Rivers, reflecting the widespread influence from local inputs. Analyses of two short sediment cores collected from the Pearl River Estuary showed that concentrations of BDE-209 rapidly increased in the upper layers of both cores, coincident with the growth of the electronics manufacturing capacities in the PRD region. The major sources of PBDEs were probably waste discharges from the cities of Guangzhou, Dongguan, and Shenzhen, the three fastest growing urban centers in the PRD.

## Introduction

Polybrominated diphenyl ethers (PBDEs) are widely utilized fire retardants embedded in plastics, paints, electrical components, textiles, foam, rubber, and other casing materials. As a result, they can be found in many commercial and household products, such as computers, televisions, furniture, and carpets (*1*). They are of environmental concern due to their persistence, potential for bioaccumulation and widespread distribution via atmospheric transport, and possible adverse effects in wildlife and humans (*2*). Major commercial products principally contain penta-, octa-, or deca-BDE mixtures. Annual worldwide consumption of PBDEs in 1999 was about 70 000 tons, of which 49% was used in North America, 37% in Asia, and 12% in Europe (*3*). In China, the domestic production of brominated flame retardants (BFRs) was 10 000 tons in 2000 and deca-BDE was one of the most produced BFRs. The domestic demand of BFRs has increased at a rate of 8% per year in China. In addition, a portion of BFRs currently used in China is expected to be imported from other countries (although the exact amount is unknown), because three of the largest BFR manufacturers in the world (i.e., Great Lakes Chemical, Indianapolis, IN; Albemarle Chemical, Richmond, VA; and Dead Sea Chemical, Beer-Sheva, Israel) all have distributors in China to sell BFRs.

PBDEs have been widely detected in air, water, fish, birds, marine mammals, and humans in recent years. The levels of PBDE contamination have increased over the last 20–25 years in the environment, concomitant with a decrease of concentrations for other halogenated chemicals, such as PCBs (*4*). A recent review showed that PBDE concentrations in human samples increased exponentially with a doubling time of ~5 yr (*5*). The concentrations and distribution of PBDEs in the environment and humans have been well documented in North America, Europe, and the Arctic, and a vast number of publications are available in the literature. In the Asian Pacific region, most data regarding the PBDE contamination have been acquired from Japan (*6*–*13*). Only two reports of PBDEs in environmental samples from China are published (*14*, *15*), and the numbers 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.

The present study aimed to comprehensively examine the status of PBDE contamination in the aquatic environment of the Pearl River Delta (PRD) and adjacent South China Sea (SCS) (Figure 1) via a large survey of surface sediments. The sampling plan was so designed to allow a thorough assessment of the spatial distribution of PBDEs in three major river systems within the PRD, representative of different levels of industrial and agricultural activities, as well as the coastal and estuarine regions and nearby open ocean. In addition, two short sediment cores were collected from the Pearl River Estuary (PRE) and used to assess the recent trend of PBDE contamination in the study area.

A comprehensive survey of PBDE contamination like this study was urgently needed, given the encouraged growth of electronics, plastics, and textile manufacturing activities in the PRD region. For example, it is estimated that one out of three computers manufactured in the world is assembled in Dongguan (Figure 1), the largest manufacturing base of electronic products in the PRD region. Because the PRD region is in the northern subtropical zone, the mild temperatures and frequent year-round rainfall facilitate the transportation of contaminants to the aquatic environments. Ultimately, PBDEs originated from the PRD region may be transported to the oceans via the SCS.

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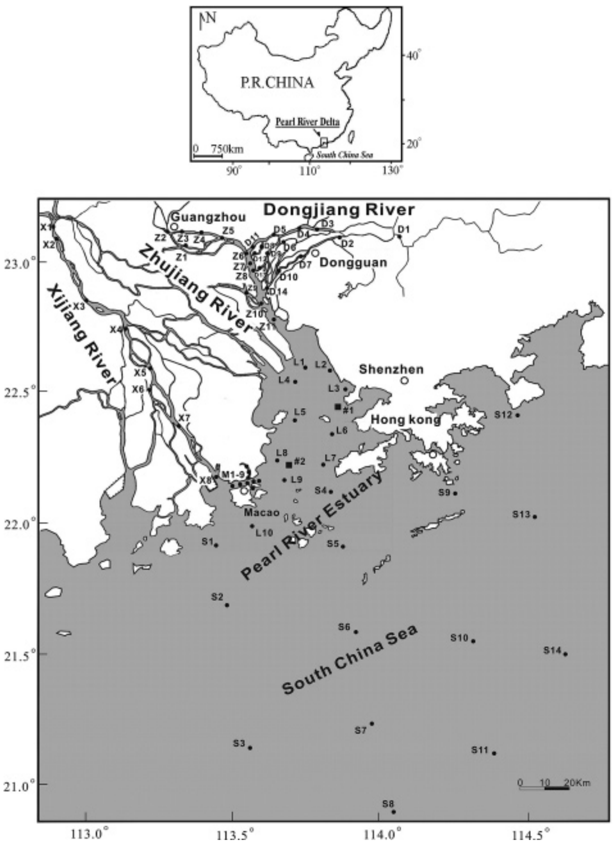

**FIGURE 1. (a) Schematic showing the geographical locality of the Pearl River Delta in China. (b) Map of the general study area and sampling sites (dots for surface sediments and darkened square for core sediments) around the Pearl River Delta, Pearl River Estuary, and northern South China Sea. Sample numbers correspond to data provided in Table S1 of Supporting Information. Z, Zhjiang River; D, Dongjiang River; X, Xijiang River; M, Macao Coast; L, Pearl River Estuary; S, South China Sea.**

## Experimental Section

**Sample Collection.** A detailed description of the sampling area within the PRD (Figure 1) was given elsewhere (*16*). Thirty-three sediments were collected from the three major rivers of the PRD in August, September, and October 2002. The locations were selected to cover the whole region with various levels and types of exposure, including both rural (Xijiang River) and urbanized (Zhujiang River and Dongjiang River) areas. Nine sediment samples were collected around the coast of Macao, which was a known depositional zone (*16*), in September 2002. Ten estuarine sediments were collected along the PRE in April 2004. Fourteen offshore sediment samples were collected in the northern SCS in July 2002 (Figure 1). Sediments were collected using a Van Veen stainless steel grab sampler. The top 5-cm layer of sediments was scooped using a precleaned stainless steel scoop into solvent-rinsed aluminum containers. Because the sediment accumulation rates ranged from 1.2 to 1.5 cm/yr in the Zhujiang River and from 0.9 to 3.9 cm/yr in the PRE (*17*), the top 5-cm layer of sediments was expected to represent modern inputs. All the samples were transported on ice to the laboratory, where they were stored at −20 °C until analyzed.

In addition, two sediment cores of approximately 30-cm long were obtained from the eastern and southwestern sides of the PRE (labeled #1 and #2 in Figure 1). A previous study obtained average sedimentation rates of 0.86 and 1.52 cm/yr at the eastern and southwestern sides, respectively, of the PRE (*17*). Therefore, the top 30 cm of sediments was expected to encompass at least 20−30 years of depositional records. The sediment cores were collected in October 2003 using a Plexiglas gravity corer (10 cm i.d.) with automatic clutch and reverse catcher. Prior to use, the Plexiglas barrels were washed thoroughly with detergent and rinsed with Milli-Q water. Care was taken not to disturb the sediment surface by maintaining approximately 10−20 cm of clean bottom water above the core. Immediately upon collection, the cores were extruded aboard ship using a precleaned push plunger and sectioned into 2-cm slices using a stainless steel blade. Sectioned sediment samples were packed into solvent-rinsed glass jars and immediately stored at −20 °C until analyzed.

**Materials.** A standard mixture containing BDE-28, -47, -66, -85, -99, -100, -138, -153, and -154 at 10 $\mu$g/mL each and individual standards of BDE-183 and -209 at 50 $\mu$g/mL were purchased from AccuStandards (New Haven, CT). A standard solution of 2,4,5,6-tetrachloro-*m*-xylene and decachlorobiphenyl (PCB 209) at 500 $\mu$g/mL each was obtained from Ultra Scientific (North Kingstown, RI). Individual standard solutions of $^{13}$C-labeled PCB 141 and PCB 208 (40 ± 2 $\mu$g/mL) each were purchased from Cambridge Isotope Laboratories (Andover, MA). All organic solvents were redistilled using a glass system. Neutral silica gel (80−100 mesh) and alumina (100−200 mesh) were Soxhlet extracted with a mixture of 1:1 methylene chloride:methanol for 72 h prior to use. Sodium sulfate was baked at 450 °C and stored in sealed containers.

**Extraction and Analytical Procedures.** Sediment samples were freeze-dried, ground, and homogenized by sieving through a stainless steel 75-mesh (0.5-mm) sieve and stored in glass containers at −20 °C until extraction. Samples of various sizes (10, 15, and 30 g for river, estuary, and offshore sediments, respectively) were spiked with PCB 209 and $^{13}$C-PCB 141 and extracted with a mixture of acetone and hexane (1:1) for 72 h with a Soxhlet extractor. Activated copper granules were added to the extraction flasks during the extraction to remove elemental sulfur. Concentrated extracts were cleaned and fractionated on a 10-mm i.d. silica/alumina column packed, from the bottom to top, 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 200 $\mu$L under a gentle $N_2$ stream. A known amount of internal standard ($^{13}$C-PCB 208) was added to all extracts prior to instrumental analysis.

Sample analysis was performed with a Shimadzu Model 2010 gas chromatograph (GC) coupled with a Model QP2010 mass spectrometer (MS) (Shimadzu, Japan) using negative chemical ionization (NCI) in the selected ion monitoring (SIM) mode. A DB-XLB (30 m × 0.25 mm i.d., 0.25 $\mu$m film thickness) capillary column was used for the determination of PBDE congeners except for BDE-209. The column temperature was initiated at 110 °C (held for 1 min) and increased to 180 °C at 8 °C/min (held for 1 min), 240 °C at 2 °C/min (held for 5 min), 280 °C at 2 °C/min (held for 25 min), and 290 °C at 5 °C/min (held for 13 min). Manual injection of the 1-$\mu$L samples was conducted at the splitless mode and the split mode was turned on after 1 min. Methane was used as a chemical ionization moderating gas at an ion source pressure of $2.4 \times 10^{-3}$ Pa and helium as the carrier gas at a flow rate of 1 mL/min. The ion source and interface temperatures were set to 200 and 280 °C, respectively. For BDE-209, a CP-Sil 13 CB (12.5 m × 0.25 mm i.d., 0.2 $\mu$m film thickness) capillary column was used. The oven temperature was programmed from 110 to 300 °C at a rate of 8 °C/min (held for 20 min) and the high-pressure splitless injection mode was used with a split time of 1 min.

Ion fragments $m/z$ 79 and 81 ($[\mathrm{Br}]^-$) were monitored for tri- to hepta-BDEs, and $m/z$ 79, 81, 486.7, and 488.7 for BDE-209. For surrogate standards, $m/z$ 372, 374, and 376 were monitored for $^{13}$C-PCB 141 and $m/z$ 496, 498, and 500 for PCB 209. In addition, $m/z$ 474, 476, and 478 were used for the internal standard ($^{13}$C-PCB 208). Quantification of tri- to hepta-BDEs was carried out with the internal calibration procedure, whereas BDE-209 was quantified with the external standard method. A previous study showed that the use of $^{13}$C-PCB 208 as the internal standard for determination of BDE-209 by NCI resulted in higher relative standard deviations than those obtained with external standard calibration (*18*). Peaks were quantified only if the signal/noise ≥ 3 and the ratio between two monitored ions was within 15% of the standard value. BDE-85 was not quantified due to chromatographic interference in some of the samples. The limit of detection (LOD), defined as a signal of 3 times the noise level, ranged from 0.01 to 0.04 ng/g for all congeners except for BDE-209, when 10 g of dry sediment was extracted. The LOD for BDE-209 was 1 ng/g.

**QA/QC.** For each batch of 20 field samples, a procedural blank (solvent with a filter paper identical to that used to wrap the sediment), a spiked blank (11 PBDE congeners spiked into solvent with the filter paper), a spiked matrix sample (11 PBDE congeners spiked into pre-extracted sediment), a spiked matrix duplicate, and a sample duplicate were processed. Only small concentrations of BDE-47 and -99 were found in procedural blanks, and they were appropriately subtracted from those in the sample extracts. The surrogate recoveries in 99 samples (both field collected and laboratory prepared) were 102.1 ± 15.2% for $^{13}$C-PCB 141 and 104 ± 19.5% for PCB 209, respectively. The relative percent difference for individual PBDE congeners identified in paired duplicate samples ($n = 4$) was all <15%. Recoveries of 11 PBDEs congeners (BDE-28, -47, -66, -100, -99, -85, -154, -153, -138, -183, and -209) ranged from 67.8 to 114.2% (relative standard deviations <13%) in five spiked blank samples and from 65.4 to 103.6% (relative standard deviations <18%) in five spiked matrix samples. Reported concentrations were not surrogate recovery corrected.

**Organic Carbon Determination.** Sediment organic carbon was determined with an elemental analyzer (CHNS Vario Ei III, Elementar) after removal of carbonates with HCl.

## Results and Discussion

**Sediment Concentration and Geographical Distribution.** Detailed concentration data from the present study are given in Table S1 of Supporting Information (where "S" designates tables or figures in the Supporting Information). In the rest of the paper, $\sum$PBDEs refers to the sum of all targeted PBDE congeners except for BDE-209. All 66 field samples contained detectable concentrations of PBDEs, indicating that these pollutants are widespread in river, estuarine, and marine sediments of southern China. The concentrations of $\sum$PBDEs and BDE-209 ranged from 0.04 to 94.7 ng/g with an average of 9.9 ng/g and from 0.4 to 7341 ng/g with an average of 465 ng/g, respectively. In general, the concentrations of BDE-209 were 1−2 orders of magnitude higher than those of $\sum$PBDEs (Figures 2 and 3).

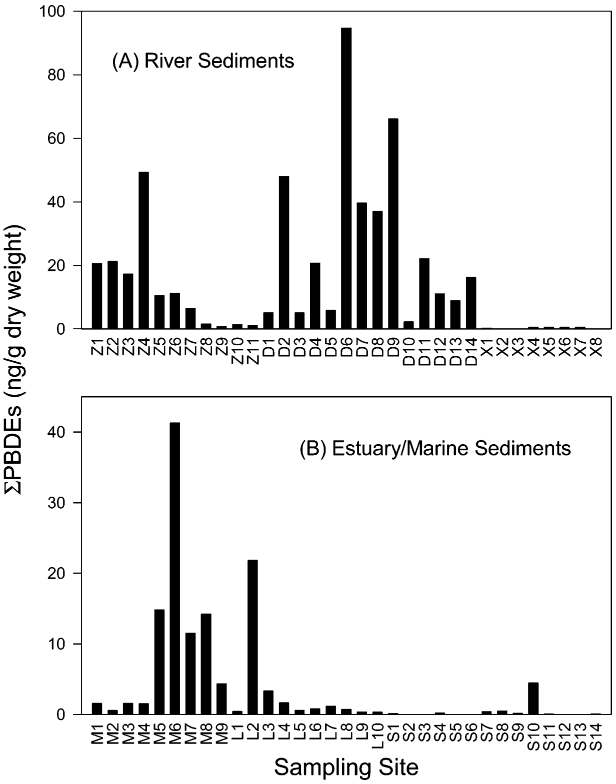

**FIGURE 2. Distribution of ∑PBDEs (except for BDE-209) in surface sediments from the Pearl River Delta and adjacent South China Sea: (A) river sediments and (B) estuary/marine sediments. Sampling locations are displayed in Figure 1.**

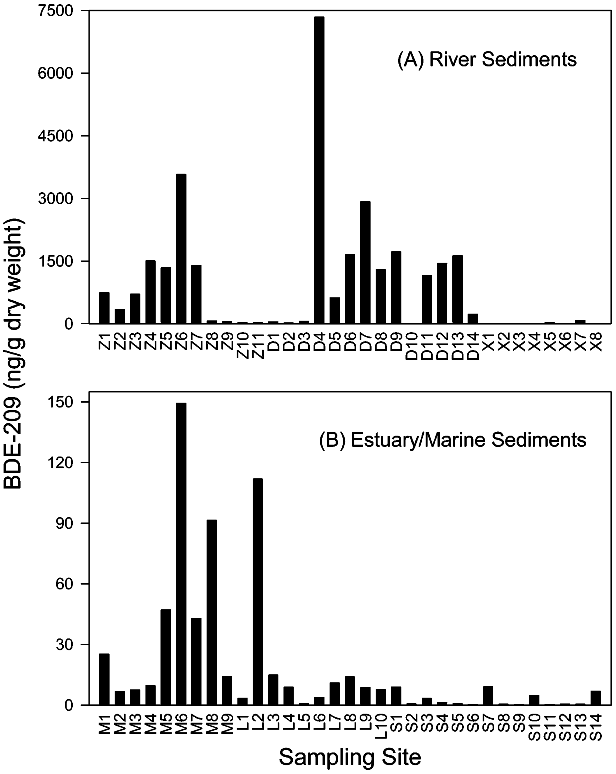

**FIGURE 3. Distribution of BDE-209 in surface sediments from the Pearl River Delta and adjacent South China Sea: (A) river sediments and (B) estuary/marine sediments. Sampling locations are displayed in Figure 1.**

The mean concentrations of $\sum$PBDEs decreased in the order of Dongjiang River > Zhujiang River > Macao coast > the PRE > the SCS > Xijiang River for $\sum$PBDEs, while those of BDE-209 decreased in the order of Dongjiang River > Zhujiang River > Macao coast > the PRE > Xijiang River > the SCS (Table 1). It is worthwhile to note that samples collected from the Dongjiang and Zhujiang Rivers had substantially higher concentrations of PBDEs than those collected from other geographical territories (Table 1). This was not unexpected, as Dongguan has become the world's largest manufacturing base for electronics/electrical products such as printed circuit boards, electroplates, textiles, and chemical, biochemical, and petrochemicals products. In

**TABLE 1. PBDE Concentrations (ng/g dry weight) in Sediments of the Pearl River Delta Region in Comparison with Those of the Reported Concentrations for World Rivers and Coastal Zones[a,b]**

| location | ∑PBDEs | BDE-209 |
|---|---|---|
| Pearl River Delta | | |
| Zhujiang River | 1.1−49.3 (12.9) | 26.3−3580 (890) |
| Dongjiang River | 2.2−94.7 (27.3) | 21.3−7340 (1440) |
| Xijiang River | 0.1−0.6 (0.36) | 1.9−77.4 (16.1) |
| Macao coast | 0.6−41.3 (10.2) | 6.7−149 (43.8) |
| Pear River Estuary | 0.3−21.8 (3.13) | 0.7−111.9 (18.5) |
| South China Sea | 0.04−4.5 (0.5) | 0.4−9.1 (2.8) |
| North America | | |
| U.S.A. | <0.5−52.3 | |
| Europe | | |
| U.K. | 1.3−1270.8 | 0.6−3190 |
| Netherlands | 0.6−17.6 | 4−510 |
| Sweden | 8−50 | 68−7100 |
| Portugal | 0.5−20 | |
| Spain | 0.4−34.1 | 2.1−132 |
| Danmark | 0.53 | 3.67−21.5 |
| Asia | | |
| Korea | 1.1−33.8 | |
| Japan | 8−352 | <25−11600 |
| China | | |
| Qingdao nearshore | 0.1−5.5 (1.4) | |

[a] Values in parentheses are mean concentrations. [b] Data for global sediments are derived from the references cited in Table S3.

addition, Guangzhou, the capital of Guangdong Province, is a highly populated urban center, housing heavy industrial and commercial activities. It can be concluded that waste discharges from the cities of Dongguan and Guangzhou are the likely sources of PBDEs to the PRD water system.

The PBDE concentrations varied substantially within the sampling locations at both the Dongjiang and Zhujiang Rivers (Figures 2 and 3), indicating that the PBDE contamination is probably derived from local discharge. As expected, the PBDE concentrations were also high in samples collected from the coast off Macao (Figures 2 and 3). This coastal region receives fluvial suspended particles from the PRD water network and effluents from Macao and Hong Kong, as the result of a southwestward coastal current (called the South China coastal current) originating from the counterclockwise Coriolis force in the Northern Hemisphere and the prevailing westward wind in the region (*16*, *19*). Among the samples collected from the PRE, two samples (L2 and L3) collected close to Shenzhen Bay contained relatively high concentrations of ∑PBDEs (3.3 and 21.8 ng/g, respectively) and BDE-209 (14.9 and 111.9 ng/g, respectively) as compared to other samples in the estuary (0.3−1.7 ng/g and 3.5−14.0 ng/g for ∑PBDEs and BDE-209, respectively). This area is influenced by waste discharges from the Shenzhen River that receives domestic sewage and industrial effluent from the city of Shenzhen, the second largest urbanized and industrialized center in the PRD.

Relatively low concentrations of PBDEs were found in samples from the Xijiang River than in those from other regions. Two explanations can be given. The first explanation is that the watershed of the Xijiang River is less urbanized and industrialized relative to the areas drained by the Zhujiang and Dongjiang Rivers. Another possible explanation is that the high flows of the Xijiang River reduce the magnitude of deposition for organic contaminants in the riverbed. The annual out-flow of freshwater through the Modaomen outlet is estimated to be $8.84 \times 10^{10}$ m$^3$/yr, the highest among the eight major outlets (*20*). Finally, all sediment samples (S1−S14) collected from the northern SCS contained measurable amounts of PBDEs (Table S1), and some samples had an even higher concentration of ∑PBDEs than those from the Xijiang River, indicating the influence of the coastal discharges from the PRD and/or atmospheric transport that led to deposition of PBDEs in the relatively remote sites (such as SCS).

**Global Comparison of Sediment PBDEs.** Sediment PBDE concentrations have been reported for various regions around the world, and most samples analyzed contained less than 50 ng/g of total ∑PBDEs (Tables 1 and S3). A number of European and Japanese samples had extremely high concentrations of PBDEs. For example, up to 368 and 898 ng/g for BDE-47 and BDE-99, respectively, were detected in the Tees Estuary, the downstream area of a manufacturing plant, in the United Kingdom (*21*), and up to 352 ng/g for ∑PBDEs was found in Osaka Bay, Japan (*22*). By comparison, most samples in our study had ∑PBDEs concentration less than 50 ng/g, consistent with reported data for river and estuary sediments in other parts of the world (Table 1). Notably, two sediment samples collected from the Dongjiang River contained high levels of ∑PBDEs (66.1 and 94.8 ng/g, respectively) (Table S1).

The highest sediment concentration of BDE-209 reported so far was 11 600 ng/g in a river sediment of Japan (*3*, *23*) and 7100 ng/g dry wt sample or 16 000 ng/g TOC in Sweden (*24*). Another relatively high value of BDE-209 concentration was 3190 ng/g in a river sediment of the United Kingdom (*21*). In the PRD, the highest BDE-209 concentration was 7340 ng/g, found in a sediment (D4, Figure 1) from the Dongjiang River. Generally, the concentrations of BDE-209 from the Dongjiang and Zhujiang Rivers were comparable to the highest concentrations reported in the literature (Tables 1 and S3).

**Correlation of Sediment PBDEs with Organic Carbon.** Because of their high hydrophobicities, PBDEs were expected to be associated mainly with organic carbon-rich particles. However, low correlation ($r^2 < 0.2$) was found between ∑PBDEs or BDE-209 and organic carbon in the PRE and riverine sediments that were expected to receive PBDE discharge from local sources (Figure S1). For the Macao coastal sediments, on the other hand, the correlation between ∑PBDEs or BDE-209 and organic carbon was moderate ($r^2 = 0.53$ and 0.52, respectively; Figure S1). The relatively high corrections between the PBDE concentrations and organic carbon in the Macao coastal sediments imply the role played by organic matter for transport and redistribution of PBDEs to the Macao coast, a depositional zone in the PRD region. A significant correlation ($r^2 = 0.67$) between the PCB concentrations and organic carbon was also observed in core sediments collected off the Macao coast (*25*). The poor correlation ($r^2 < 0.1$) between the PBDE concentration and TOC in the SCS sediments (Figure S1) may be attributed to the combined effect of transport, mixing, and depositional mechanisms associated with PBDEs and uncontaminated sediments of the SCS.

**Congener Patterns and Potential Sources.** The dominance of BDE-209 in the total PBDEs is apparent (Table S1). The contribution of BDE-209 ranged from 73 to 99.7% of the total PBDEs with the exception of four samples that had relatively low (31−53%) abundances of BDE-209. BDE-209 constituted more than 90% of the total PBDEs in 70% of the surface sediment samples. The ratio of BDE-209 to ∑PBDEs ranged from 2.7 to 317 with a median value of 43. This finding agrees with the fact that deca-BDE accounts for most of the total BFR production in China. The manufacture of electronics, where deca-BDE is heavily used, is the major industry in the PRD. Geometric means (and ranges) of the other BDE congeners, calculated as percent of total PBDEs, were as follows: BDE-99, 4.34% (0.1−25.5%); BDE-47, 2.87% (0.08−21.9%); BDE-153, 0.83% (0−4.2%); BDE-100, 0.60% (0−5.3%); BDE-154, 0.58% (0−2.7%); BDE-183, 0.52% (0−9.2%); BDE-

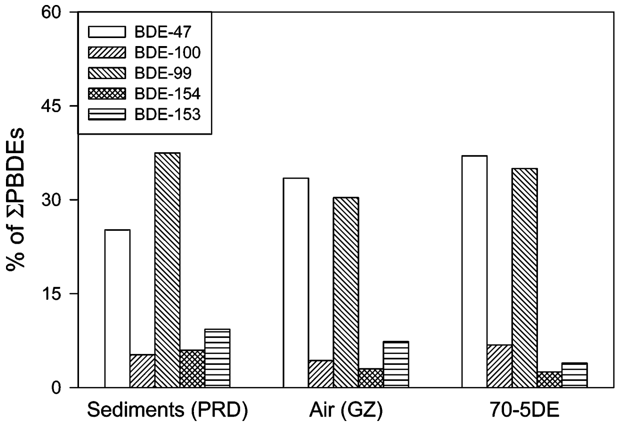

**FIGURE 4. Penta-BDE profiles in surface sediments from the PRD, air collected from Guangzhou, and Bromkal 70-5DE technical mixture (*26*). The order of the bars follows the eluting sequence on the GC column.**

66, 0.31% (0–3.9%); BDE-138, 0.30% (0–6.4%); and BDE-28, 0.26% (0–2.0%).

The correlations among the 10 PBDE congeners in all samples were examined to infer their potential sources. Good correlation was found among BDE-47, -99, -100, -153, and -154 ($r^2 > 0.9$) and between BDE-138 and BDE-183 ($r^2 = 0.86$). However, low correlation was found between BDE-209 and all other congeners ($r^2 < 0.2$) (Figure S2). This suggests that most of the tri- to hepta-BDEs were not originated from decomposition of deca-BDE, and the relatively unaltered present-day commercial penta-, octa-, and deca-BDE formulas are the likely sources of PBDEs to the PRD aquatic system. On the other hand, if these correlations were further examined within individual geographical territories (Figure S3), the BDE-209 concentrations were highly correlated with those of BDE-47, -99, -100, -138, and -183 ($r^2 > 0.7$, $n = 9$) in samples collected from the coast of Macao, but low correlations ($r^2 < 0.4$) were found in sediments from other territories. Although many factors were possible, the general correlations between BDE-209 and the penta- and octa-BDEs indicated that the mechanisms with which individual PBDEs were transported to the coast of Macao were similar.

Of the nine tri- to hepta-BDE congeners (∑PBDEs), BDE-47 and -99 were the predominant compounds. The relative abundances of BDE-47 and -99 were generally greater than 50% of ∑PBDEs, similar to the compositions of major penta-BDE commercial mixtures (*26*). These two congeners with BDE-100, -153, and -154, usually found in the technical penta-BDE mixture, comprised 64–100% of ∑PBDEs, with a mean value of 84% in the sediment samples. By comparison, BDE-183 and -138, two major components in octa-BDE mixture, accounted for only 0.0–29.9% of ∑PBDEs, with a mean value of 9.6%. Clearly, the penta-BDE commercial mixture is another major formula used in the PRD region in addition to the deca-BDE mixture. The PBDE pattern in air samples collected from the city of Guangzhou (Chen and Mai et al., unpublished data) was similar to that in the technical penta-BDE mixture (Bromkal 70–5DE) (*26*), i.e., BDE-47 is more abundant than BDE-99, but BDE-99 > BDE-47 was observed in all sediment samples from this study (Figure 4). This pattern has been observed previously in various sediments worldwide (*1*, *21*, *27*), except for two instances where BDE-47 was found to be more abundant than BDE-99 (*28*, *29*). The preferential accumulation of BDE-99 over BDE-47 in sediments can be attributed to the difference in hydrophobicity, i.e., log $K_{ow}$ of ~6.5 for BDE-99 and ~6.1 for BDE-47 (*29*).

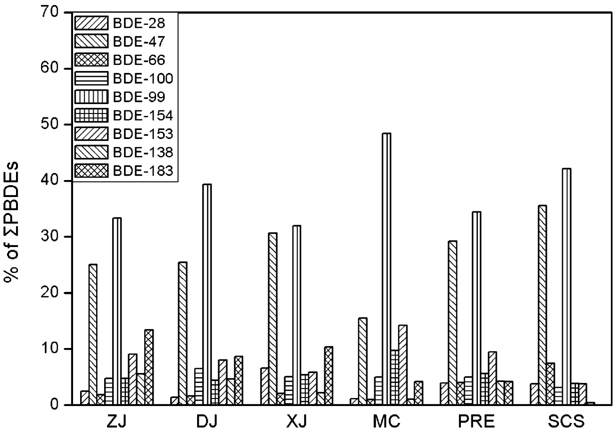

**FIGURE 5. Percent of individual BDE congeners to the sum of the nine tri- to hepta-BDEs (∑PBDEs) in sediments from different locations in the PRD and SCS. The order of the bars follows the eluting sequence on the GC column. ZJ, Zhujinag River; DJ, Dongjiang River; XJ, Xijiang River; MC, Macao Coast; PRE, Pearl River Estuary; SCS, South China Sea.**

The PBDE composition (excluding BDE-209) in sediments from the Zhujiang and Dongjiang Rivers was similar (Figure 5), with the relative abundance of PBDE congeners decreasing in the order of BDE-99 > -47 > -183 > -153 > -154 ~ -100 ~ -138 > -28 ~ -66 (Figure 5), suggesting that a uniform commercial formula was used in the PRD region. By comparison, distorted PBDE patterns were displayed in sediments collected from other locations (Figure 5) and are discussed in detail below.

The relative abundances of PBDEs in the Xijiang River sediments were as follows: BDE-99 > -47 > -183 > -28 ~ -153 ~ -154 ~ -100 > -138 ~ -66 (Figure 5). The contribution of BDE-28 (3.5–12.6%) and BDE-47 (14.6–44.4%) in the Xijiang River were higher than in the Zhujiang River (1.4–3.8% for BDE-28 and 21.3–29.1% for BDE-47, respectively) and in the Dongjiang River (0.5–2.4% for BDE-28 and 18.9–32.5% for BDE-47, respectively). A previous study suggested that the Xijiang River might receive atmospherically transported contaminants from other highly industrialized and urbanized regions around the PRD (*16*). Because both BDE-28 and -47 are more volatile than the heavier congeners, their relatively high abundances in the rural Xijiang area may stem from their long-range transport and the possible photodegradation of highly brominated congeners during atmospheric transportation. The photolytic debromination of PBDEs under experimental and natural conditions has been demonstrated in previous studies (*30*–*34*).

The PRE sediments displayed PBDE compositional distribution similar to those in the sediments of the Zhujiang and Dongjiang Rivers, but with a relatively low abundance of BDE-183 (Figure 5). Decomposition of BDE-183 may have occurred during hydrologic or atmospheric transport from sites near the sources of discharge to the sampling locations. The relative abundances of the highly brominated congeners (BDE-154, -153, -138, and -183) were even lower in the SCS samples (but with a higher abundance of BDE-66) as compared to the pattern in the PRE sediments. Alternatively, the relatively low abundance of heavier congeners found at the relatively remote sites (SCS) may be due to the fact that the heavier congeners are less mobile in aquatic environments. The similar PBDE patterns in the sediments of the Zhujiang River, Dongjiang River, PRE, and SCS suggest that discharges from the two major industrialized regions (Guangzhou and Dongguan) are the major sources of PBDEs to the northern part of the SCS.

Sediments collected from the Macao coast were enriched with BDE-99, -153 and -154 relative to other sediment samples (Figure 5). Because the coast of Macao receives organic matter discharged from the PRD, as well as from Hong Kong (*16*), the PBDE compositions in sediments from the coast of Macao

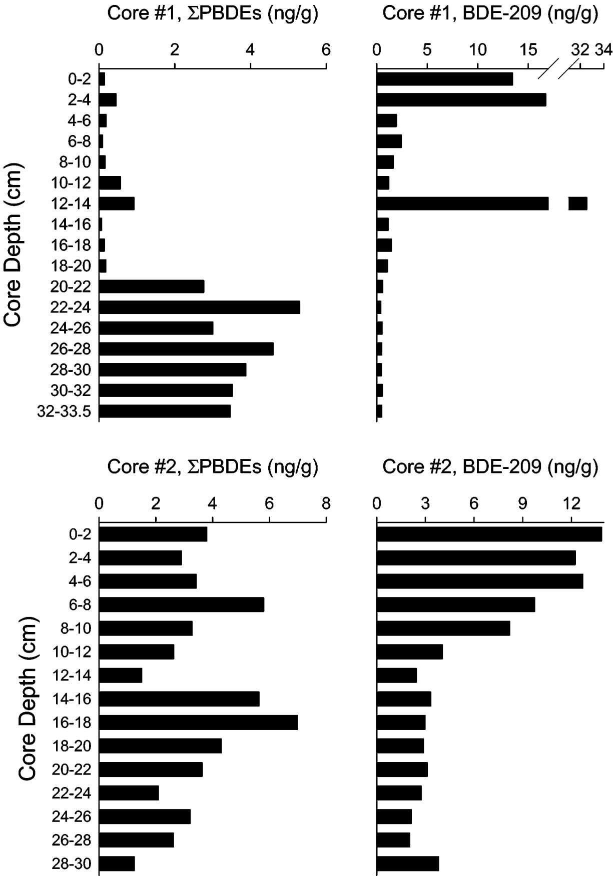

**FIGURE 6. Vertical profile of ∑PBDEs and BDE-209 concentrations in two short sediment cores collected from the Pearl River Estuary.**

may be reflective of inputs from Hong Kong. However, the PBDE compositions in sediments collected near Hong Kong (L7 and L8, Figure 1) were similar to those in sediments collected from the Zhujiang and Dongjiang Rivers. An alternative explanation is based on the notion that the coast of Macao is a depositional zone that captures fine suspended particles from the PRD and PRE. Because the higher brominated congeners such as BDE-99, -153, and -154 preferentially affiliate with small-sized particles, a hypothesis proposed by Rayne et al. (*29*) on the basis of the results of several studies examining the congener-specific partitioning of halogenated contaminants onto sediments of different sizes (*35*−*37*), the fine suspended particles deposited around the coast of Macao likely contained relatively high abundances of more hydrophobic PBDE congeners.

**Temporal Distribution of Sediment PBDEs.** The two short cores collected from the PRE (Figure 1) were analyzed to examine the temporal distribution of PBDEs in the study area. Detailed concentration data are presented in Table S2. The depth profiles of ∑PBDEs and BDE-209 (Figure 6) indicate that PBDEs have been used for the past 20−30 years in the PRD region. Most interestingly, the concentrations of BDE-209 in both cores rapidly increased in the upper layers of sediment, consistent with the fact that electronics manufacturing has become one of the major industries in the PRD since the mid-1990s. The highest BDE-209 concentration (32.6 ng/g) at the depth of 12−14 cm in core #1 might be the result of an accidental discharge of BDE-209 or other unidentified inputs. In core #1, the concentration of ∑PBDEs was much lower in the upper sediment layers (0.07−0.93 ng/g at 0−20 cm) than in the deeper sediment layers (2.8−5.3 ng/g at 20−33 cm depth). This may suggest that the use of penta- and octa-BDE mixtures in Shenzhen and Hong Kong was largely replaced by the deca-BDE formula. On the other hand, the concentrations of ∑PBDEs in the upper layers (1.5−5.8 ng/g at 0−14 cm) of core #2 was only slightly lower than those in the deeper sediments (1.2−7.0 ng/g at 16−31 cm). The different temporal trends of ∑PBDE concentrations indicate that penta- and octa-BDE mixtures may still be used in the major industrialized areas of the PRD region.

**Possible Debromination of BDE-209.** The high BDE-209 concentrations in sediments raised concerns about whether BDE-209 in sediments was transformed to less brominated congeners that are more likely to volatilize into the atmosphere and be taken up by organisms. The GC/NCI-MS chromatograms showed some peaks probably related to brominated compounds (Figure S4) that were not present in either the penta-BDE or octa-BDE formula but were identified as octa- and nona-BDEs on the basis of retention times found in the literature (*38*). Although traces of octa- and nona-BDEs (such as BDE-206, -207, and -208) are detectable in octa- and deca-BDE technical products (*39*, *40*), the relatively high abundances of octa- and nona-BDE congeners in our sediment samples (Figure S4) could not be entirely attributed to the technical mixtures. Deca-BDE technical mixtures purchased from the chemical market in Guangzhou were analyzed in the present study, and only BDE-209 was detectable. All these point to the possibility of debromination of BDE-209 in the aquatic environment. A number of recent studies have also shown that BDE-209 is fairly susceptible to breakdown under sunlight and in sediments and sludge (*30*, *32*, *41*, *42*). Clearly, further research should be conducted to thoroughly understand the degradation mechanism and fate of this compound in the PRD region, because transformation of even a small portion of BDE-209 into lower brominated PBDEs in sediments could result in serious environmental consequences for many years to come.

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## Supporting Information Available

Tables S1−S3, with associated references, and Figures S1−S4. This material is available free of charge via the Internet at http://pubs.acs.org.

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