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Polybrominated Diphenyl Ethers in Seafood Products of South China

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South China is probably one of the heaviest polybrominated diphenyl ether (PBDE) polluted regions in the world, thanks to the presence of huge and rapidly growing electronics manufacturing industries, as well as several of the world's largest e-waste recycling sites in the region. In the present work, a wide variety of nonfish seafood products collected from South China was analyzed for PBDE residues. The concentrations of PBDEs in seafood products were highly species-specific, and the magnitude of PBDE pollution was moderate in South China compared to the global levels. Congener patterns of PBDEs in seafood samples suggested that seafood products are prone to accumulating low-brominated congeners, and possible metabolic debromination of BDE-99 to BDE-47 could occur in certain organisms, such as crabs and mantis shrimp. Generally, the congener profile was dominated by BDE-209, and to a lesser extent by BDE-47 and BDE-99, which was consistent with the fact that Deca-BDE is mass-produced in China and with previous sediment results from the same area. The occurrence of BDE-209 in aquatic species from South China suggests that BDE-209 appears to be more bioavailable than previously thought, and the environmental fate and safety of BDE-209 require further investigation and call for a thorough reassessment.

KEYWORDS: Polybrominated diphenyl ethers; shrimp; crab; shellfish; Pearl River Delta

INTRODUCTION

Polybrominated diphenyl ethers (PBDEs) are extensively utilized as additive flame retardants in resin and synthetic polymer materials and, consequently, are present in many commercial and household products (*1*). PBDEs may be released into the ambient environment as a result of manufacturing, usage, and disposal of PBDE-containing products. Greater research efforts have been directed toward PBDEs in recent years because of concerns about their ubiquity in the environment; bioaccumulative potentials in wildlife and human tissues (*2*, *3*); and continuously rising concentrations with a doubling time of ~5 years in human blood, milk, and tissues during the past 30 years (*4*). In addition, PBDEs are likely to disrupt thyroid hormones and cause neurobehavioral deficits and possibly cancer (*3*, *5*). Worse yet, PBDEs can be transformed into more poisonous products, polybrominated dibenzodioxins and dibenzofurans, under pyrolytic conditions that often occur during recycling of PBDE-containing plastic materials or during uncontrolled or insufficient combustion such as accidental fires or landfill fires (*6*, *7*).

Although there is no detailed information available about the production and usage of PBDEs in China, the enormous electronics, plastics, and textile manufacturing plants in the Pearl River Delta (PRD) of South China (e.g., the gross output of the electronics and information industry in the PRD exceeded $125 billion in 2005, http://www.southcn.com/news/gdnews) are expected to generate large amounts of PBDE residues. Furthermore, within the PRD, Shantou houses perhaps the world's largest electronics-waste (e-waste) recycling site, and another e-waste recycling site of considerably large scale is located in the suburb of Guangzhou. These establishments strongly point to the likelihood of PBDE inputs to the PRD and adjacent regions. A recent study suggested that China and its adjacent developing countries have probably become the "hot spot" of PBDEs (*8*). Therefore, there is an urgent need to examine the occurrence of PBDEs in the PRD and adjacent regions, as strongly recommended by Martin et al. (*9*).

Nonfish seafood products, such as shrimp, crabs, and shellfish, are extensively farmed in the coastal areas of South China and are favorite foods for local residents. These species are mostly sediment-dwelling animals capable of accumulating contaminants from the sediment. In addition, these sedentary organisms

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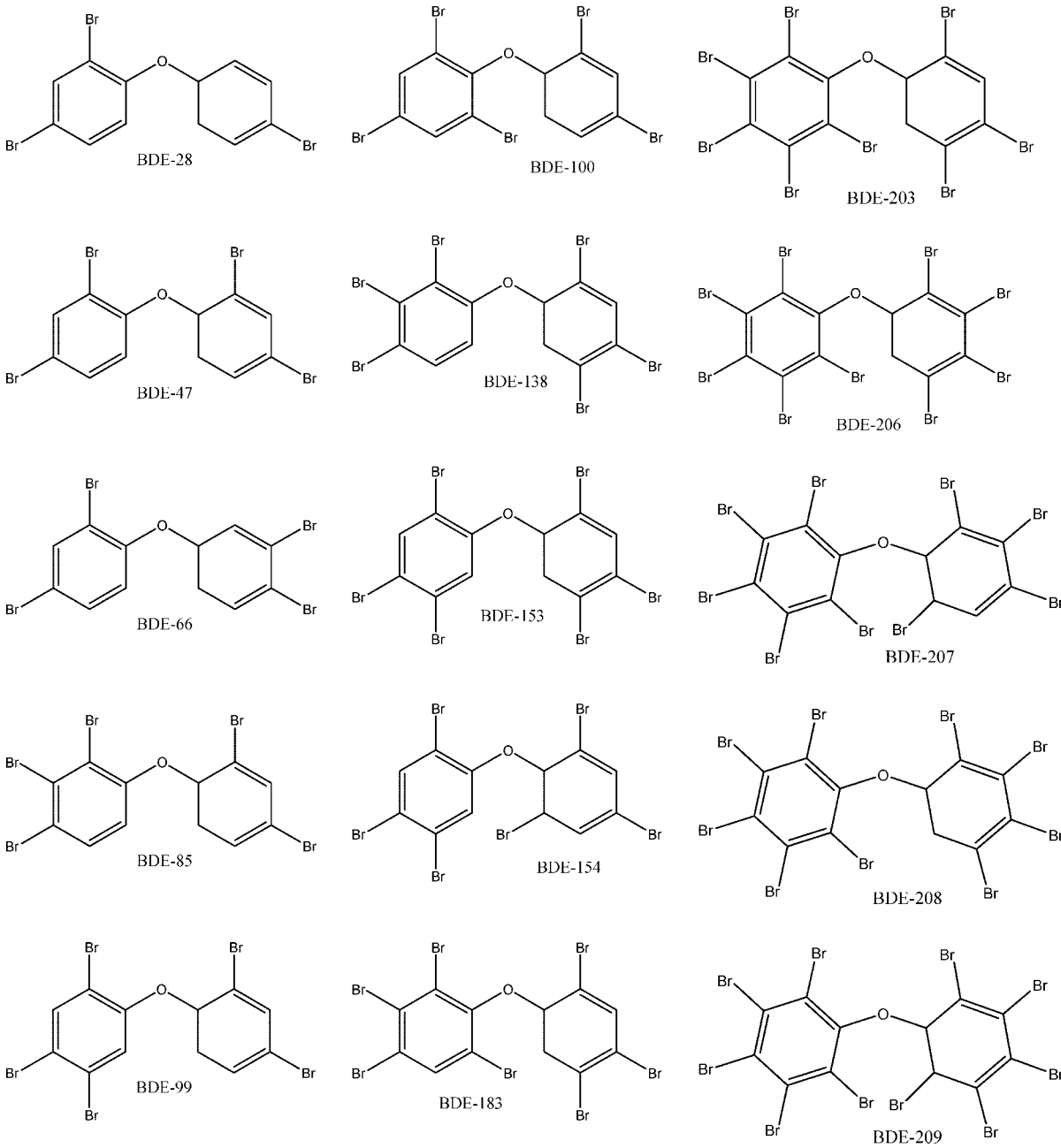

Figure 1. Chemical structures of 15 target analytes: brominated diphenyl ether (BDE)-28, -47, -66, -85, -99, -100, -138, -153, -154, -183, -203, -206, -207, -208, and -209.

are the best representatives of their habitats. Therefore, monitoring the occurrence of PBDEs in seafood products is an important step toward a thorough understanding of the levels of PBDE contamination in the environment and potential health effects for local residents of the study region.

Currently, information on the occurrence of PBDEs in nonfish seafood products from China is scarce. In the present work, 21 aquatic species collected from southern China were analyzed to comprehensively examine the levels, distribution, and bioaccumulation of PBDEs in these sediment-dwelling organisms.

MATERIALS AND METHODS

Sampling. A variety of seafood products, including six species of shrimp, two species of crab, and 13 species of shellfish, were collected from local fishery markets in 11 coastal cities of south China from June to October of 2005 (*10*). The sampling locations were representative of the main fishery production zone and the possibly heavy PBDE-polluted area. Selection of the seafood products was based on the geographic distribution of farming areas, commercial availability, and potentials to accumulate organic pollutants. Upon collection, samples were stored in polyethylene bags, kept in ice, and transported immediately to the laboratory where they were stored at –20 °C until being analyzed.

Materials. A total of 15 PBDE congeners, including BDE-28, -47, -66, -85, -99, -100, -138, -153, -154, -183, -203, -206, -207, -208, and -209, were included for measurements (**Figure 1**). Individual BDE standards used for identification and quantitation were acquired from Accustandards (New Haven, CT). The standard solution of decachlorobiphenyl (PCB 209) was obtained from Ultra Scientific (North Kingstown, RI). Standard solutions of ^{13}C-PCB 141 and ^{13}C-PCB 208 were purchased from Cambridge Isotope Laboratories (Andover, MA). All organic solvents were redistilled in a glass system, and silica (80–100 mesh) and alumina (100–200 mesh) were extracted with 50% methanol in dichloromethane (v/v) for 72 h before use. Sodium sulfate was baked at 450 °C and stored in sealed containers.

Sample Preparation and Extraction. Frozen samples were thawed and rinsed individually with purified water to remove possible impurities. The edible parts from about 20–30 specimens of the same species collected from each location were pooled and homogenized. Upon freeze-drying for 48 h, all samples were ground into powders and stored at –20 °C until chemical analysis was performed.

An aliquot (~5 g dry weight) of each sample was spiked with surrogate standards ^{13}C-PCB 141 and PCB 209 and Soxhlet-extracted for 48 h with 200 mL of 50% acetone in *n*-hexane (v/v). The extract was concentrated to about 5 mL with a Zymark TurboVap II (Hopkinton, MA) at 30 °C. A portion of the concentrated extract was split for lipid content determination, and the rest was subject to gel permeation chromatography based on a 50 cm × 2.5 cm i.d. glass column packed with 40 g of Bio-Beads SX-3 (Bio-Rad Laboratories, Hercules, CA). The column, loaded with the extract, was eluted with 50% dichloromethane in *n*-hexane (v/v) for lipid removal. The fraction from 110 to 280 mL containing PBDEs was collected and concentrated. The subsequent cleanup and fractionation were performed on a 10 mm i.d. multilayer alumina/silica column packed, from 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 column was prewashed with 5 mL of *n*-hexane, and as the solvent reached the top layer, the defatted sample was added and slowly eluted with 70 mL of 50% dichloromethane in *n*-hexane (v/v). The effluent was concentrated, quantitatively transferred into a 2 mL vial, and further concentrated to the final volume of 100 μL under a gentle nitrogen stream. An internal standard (^{13}C-PCB 208) was added prior to instrumental analysis.

Instrumental Analysis. The analysis of PBDE was performed following the procedure described by Mai et al. (*11*). Briefly, quantification was performed with a Shimadzu Model 2010 gas chromatograph (GC) coupled with a Model QP 2010 spectrometer (MS) (Shimadzu, Japan) using the negative chemical ionization and the selective ion monitoring mode. GC columns used for quantification were a DB-XLB (30 m × 0.25 mm i.d., 0.25 μm film thickness) capillary column for low-brominated congeners (BDE-28 to BDE-183) and a CP-Sil 13 CB (12.5 m × 0.25 mm i.d., 0.2 μm film thickness) capillary column for the highly brominated congeners (including BDE 203, 206, 207, 208, and 209). Manual injection was conducted in the splitless mode with a split time of 1 min. The temperatures of the ion source and interface were 200 and 280 °C, respectively.

Ion fragments used for monitoring were *m*/*z* 79 and 81 ($[Br]^-$) for tri- to hepta-BDEs; *m*/*z* 79, 81, 486.7, and 488.7 for the highly brominated BDE; *m*/*z* 372, 374, and 376 for ^{13}C-PCB 141; *m*/*z* 496, 498, and 500 for PCB 209; and *m*/*z* 474, 476, and 478 for the internal standard (^{13}C-PCB 208). Quantification of PBDEs was carried out with an internal calibration procedure. The limit of detection was determined as 10 times the signal-to-noise ratio, which was 2 ng/kg of wet weight (all concentrations are thereafter expressed in wet sample weight except where specified) for BDE-28, BDE-47, BDE-66, BDE-100, BDE-99, and BDE-153; 3 ng/kg for BDE-85, BDE-138, and BDE-154; 5 ng/kg for BDE-183; 50 ng/kg for BDE-203, BDE-208, BDE-207, and BDE-206; and 100 ng/kg for BDE-209.

Quality Control/Quality Assurance. A standard solution containing all the target analytes was analyzed every day to ensure that the calibration curves remained valid (variability < ±20%) before sample analysis. For each batch of 20 samples, a procedural blank (pure solvent) and a spiked blank (target analyte standards spiked into solvent) were processed. No quantifiable amounts of target compounds were found in the blanks. The surrogate recoveries were 77 ± 21% for ^{13}C-PCB 141 and 87 ± 18% for PCB 209. Recoveries of individual BDE congeners in spiked blank samples ($n = 6$) were 90 ± 21% for BDE-28, 88 ± 20% for BDE-47, 85 ± 20% for BDE-66, 84 ± 16% for BDE-100, 84 ± 19% for BDE-99, 83 ± 20% for BDE-85, 101 ± 8% for BDE-154, 84 ± 17% for BDE-153, 87 ± 16% for BDE-138, and 87 ± 24% for BDE-183. Reported concentrations were not corrected with surrogate recoveries.

RESULTS AND DISCUSSION

PBDE Concentrations in Seafood Products. The present work was based on a market basket survey. Samples were collected from 11 coastal cities of south China and were analyzed for the presence and concentrations of 15 BDE congeners. Overall, PBDEs were detected in 98.5% of the seafood samples. As for the specific BDE congener, most low-brominated congeners were detectable in >50% of the samples (except for BDE-138, which was detected in 15.7% of the samples), while highly brominated congeners, such as BDE-183, -203, -206, -207, and -208, were seldom detected. In addition, BDE-209 was also found in 44.4% of the total samples. Therefore, only BDE-28 to BDE-154 and BDE-209 are discussed below. The concentrations of BDE-28, BDE-47, BDE-66, BDE-85, BDE-99, BDE-100, BDE-138, BDE-153, and BDE-154, as well as BDE-209, in different species from South China are summarized in **Table 1**. The highest median concentration of $\sum PBDE_9$ (sum of BDE-28, BDE-47, BDE-66, BDE-85, BDE-99, BDE-100, BDE-138, BDE-153, and BDE-154) was found in oysters (966 ng/kg), while scallops contained the lowest median concentration of $\sum PBDE_9$ (21.3 ng/kg).

As far as individual species were concerned, the difference in $\sum PBDE_9$ concentration between different species suggests that bioaccumulation of PBDEs in seafood products was highly species-specific. The crab is a scavenger in benthic environments feeding on the carcasses of higher organisms, and the median concentration of $\sum PBDE_9$ (60.6 ng/kg) in crabs was approximately 2 times those in shrimp. Likewise, the mantis shrimp is also a ferocious sediment-dwelling predator with feeding habits similar to those of the crab, and their median concentration of $\sum PBDE_9$ (57.4 ng/kg) was also significantly higher than those in other shrimp and close to those in crabs. The different feeding habits may be, to a great extent, responsible for the large difference between the levels of $\sum PBDE_9$ in crabs, mantis shrimp, and other shrimp. In shellfish, a broad span of the levels of $\sum PBDE_9$ was obtained among different species. The highest level of $\sum PBDE_9$ occurred in oysters and was 1 or 2 orders of magnitude higher than those in other shellfish. Generally, the levels of $\sum PBDE_9$ in shellfish followed a descending order of oyster > razor clam > mussel > ark shell ~ clam ~ other shellfish > scallop. We postulated that the difference in the levels of $\sum PBDE_9$ between species is probably due to the different ecological characteristics of different species such as feeding habits and habitats. In addition, because the seafood samples were collected randomly from local markets, the different biological properties such as age, gender, weight, and lipid content of individual samples, as well as various environmental factors such as the proximity to local PBDE sources, may all potentially have influenced the levels of $\sum PBDE_9$ in individual samples.

Global Comparison of PBDE Levels. Previous research on PBDEs has been conducted mainly in Europe, North America, and Japan (*4*). Information on the occurrence of PBDEs in the Asia-Pacific region other than Japan has also been gathered recently; for example, a series of PBDE surveys was conducted recently in Korea (*12, 13*), Hong Kong (*14, 15*), Singapore (*16, 17*), and coastal regions of China (*11, 18–20*). As an excellent bioindicator, mussels have been extensively investigated worldwide to assess the residual levels of organic contaminants (including PBDEs) in the global environment. This allows us to compare the state of PBDE pollution among different countries and regions. A congener-based comparison in which only the most abundant congeners observed in organisms are included is summarized in **Table 2**. The concentrations of BDE-47 and BDE-99 in mussels from the present work were not detected (nd)−0.063 ng/g and nd−0.059 ng/g, respectively, which were comparable with those in mussels from most

Table 1. PBDE Concentrations (ng/kg wet weight) in Seafood Products from South China

	shrimp[a]			mantis shrimp			crab[b]			other shellfish[c]			clam[d]		
	$n^e = 39$			$n = 11$			$n = 32$			$n = 19$			$n = 32$		
	range	average	median	range	average	median	range	average	median	range	average	median	range	average	median
BDE-28	nd[i]–45.4	5.9	3.9	2.7–68.1	14.4	4.5	nd–109	17.7	5.8	2.4–103	14	4.8	2.6–89.9	15.8	7.3
BDE-47	nd–267	31.1	15.6	17.0–749	148	37.8	nd–1139	131	28.2	4.6–117	27.4	12.3	nd–115	25.8	14.5
BDE-66	nd–71.3	3.8	0.0	nd–60.8	12.8	2.4	nd–115	12.1	3.0	nd–347	5.3	3.2	nd–180	17.4	4.7
BDE-100	nd–18.1	2.3	1.6	nd–16.7	4.8	2.5	nd–27.3	5.4	2.8	nd–39.5	4.4	1.7	nd–13.3	2.6	1.7
BDE-99	nd–133	14.2	6.7	3.0–21.2	8.3	5.4	nd–88.6	16.9	8.1	nd–64.5	13.4	6.2	3.1–83.0	14.2	9.0
BDE-85	nd–45.4	3.8	0.0	nd–12.3	5.3	4.8	nd–124	19.8	10.4	nd–130	17.8	7.4	nd–99.0	11.9	4.7
BDE-154	nd–25.5	2.5	0.7	nd–2.1	0.6	0.0	nd–45.2	5.4	2.3	nd–52.8	7.7	3.5	nd–74.1	10.6	5.5
BDE-153	nd–39.9	2.5	0.0	nd–2.7	0.5	0.0	nd–26.2	2.6	0.0	nd–7.2	1.8	1.6	nd–8.6	2.0	1.8
BDE-138	nd–9.0	0.4	0.0	nd	0.0	0.0	nd–8.7	0.5	0.0	nd	0.0	0.0	nd–32.5	1.9	0.0
$\sum PBDE_9$		66.5	28.5		195	57.4		211	60.6		91.8	40.7		102	49.2
BDE-209	nd–661	75.9	44.3	nd–289	93.2	99.3	nd–962	171	0.0	nd–579	127	117	nd–424	127	100

	scallop[f]			ark shell[g]			razor clam[h]			mussel			oyster		
	$n = 14$			$n = 15$			$n = 18$			$n = 109$			$n = 10$		
	range	average	median	range	average	median	range	average	median	range	average	median	range	average	median
BDE-28	2.2–21.5	6.0	4.1	nd–36.6	8.1	5.2	nd–98.3	36.3	26.7	nd–16.7	8.5	7.8	28.4–96.6	56.9	57.0
BDE-47	4.1–87.7	16.3	8.4	nd–43.6	42.0	9.6	nd–270	91.6	47.8	nd–62.5	27.3	25.5	53.3–694	397	439
BDE-66	nd–9.8	3.1	2.1	nd–93.9	11.1	5.2	nd–43.8	22.9	18.5	nd–13.7	5.8	3.8	31.7–216	118	113
BDE-100	nd–6.9	1.4	0.0	nd–44.9	4.4	0.0	nd–20.8	6.3	1.4	nd–14.6	3.7	2.7	nd–99.0	47.9	49.2
BDE-99	nd–35.9	7.7	3.7	nd–23.0	41.2	7.4	nd–139	50.3	32.3	nd–58.8	21.9	18.1	5.1–288	157	152
BDE-85	nd–5.8	1.5	0.0	nd–95.5	23.3	13.6	nd–164	81.3	68.4	nd–58.2	30.6	24.4	15.7–441	91.3	39.5
BDE-154	nd–5.4	1.6	1.1	nd–144	14.0	4.9	nd–270	86.5	37.2	5.1–55.2	25.1	24.6	4.4–393	120	60.6
BDE-153	nd–4.4	1.7	1.9	nd–30.7	3.1	0.0	nd–32.2	9.3	4.5	nd–3.8	1.3	1.3	2.3–60.5	27.8	27.2
BDE-138	nd–3.6	0.6	0.0	nd–58.5	5.0	0.0	nd–32.4	7.6	0.0	nd–8.9	0.9	0.0	3.6–95.6	39	28.8
$\sum PBDE_9$		39.9	21.3		152	45.9		392	237		125	108		1055	966
BDE-209	nd–446	122	108	nd–187	51.5	0.0	nd–583	165	45.7	nd–694	181	156	nd–205	126	156

[a] Includes *Penaeus monodon*, *Penaeus japonicus*, *Metapenaeus ensis*, *Macrobrachium rosenbergii*, and *Proambarus clarkia*. [b] Includes *Scylla serrata* and *Ovalipes punctatus*. [c] Includes *Haliotis diversicolor* and *Terebra maculata*. [d] Includes *Meretrix meretrix*, *Cyclina sinensis*, and *Venerupis variegata*. [e] n = number of samples. [f] Includes *Argopectens irradias* and *Patinopecten yessoensis*. [g] Includes *Tegillarca granosa* and *Scapharca subcrenata*. [h] Includes *Sinonovacula constricta* and *Solen grandis*. $\sum PBDE_9$: sum of BDE-28, BDE-47, BDE-66, BDE-85, BDE-99, BDE-100, BDE-138, BDE-153, and BDE-154.

Table 2. Comparison of PBDE Concentrations (ng/g) in Mussels Obtained from the Present Study with Those Reported from Different Countries and Areas

location	year	BDE-47	BDE-99	BDE-100	BDE-153	BDE-154	reference
U. K.[a]	1996	3.5	3.9	na[b]	na	na	*42*
Denmark[a]	2000	0.045–0.049	0.019–0.250	0.004–0.045	0.005–0.027	na	*43*
Greenland[a]	2000	0.1	0.02	0.02	0.05	na	*21*
France[a]	2001–2002	0.110–1.489	0.016–0.624	0.003–0.413	0.003–0.094	0.003–0.124	*44*
Norway[a]	2003	0.03–0.12	0.01–0.07	0.01–0.04	0.01–0.03	0.01–0.04	*22*
U. S. A.[a]	2002	nd[c]−3.7	nd−2.0	nd–0.7	na	na	*26*
Korean[a]	2004	0.332	0.236	0.096	0.015	0.025	*13*
Netherlands[d]	1999	0.9–4.3	0.3–1.6	na	0.1	na	*28*
Singapore[d]	2002	0.72–11	0.62–18	0.17–5.3	nd–0.64	0.05–0.45	*29*
Hong Kong[d]	2004	0.62–9.12	1.34–25.9	0–1.76	0–23.0	0–2.14	*14*
South China[a]	2005	nd–0.063	nd–0.059	nd–0.015	nd–0.004	0.006–0.055	this study

[a] On a wet weight basis. [b] na = not available. [c] nd = not detected. [d] On a dry weight basis.

European countries, such as Greenland (*21*), Norway (*22*), and Belgium (*23, 24*), but much lower than those in mussels from the United States (*25, 26*). The high levels of BDE-47 and BDE-99 in mussels from the United States were probably due to penta-BDE mixtures that have been substantively produced and used in North America (*27*). Concentrations of PBDE in mussels from the Netherlands (*28*), Singapore (*29*), and Hong Kong (*14*) (*13*) are normalized to dry sample weight. Even if a conversion factor of ∼10 (the water content of mussels measured in the present study was approximately 85–90%) was used to compare these data, the PBDE levels obtained from the present study were still lower than those from the Netherlands, Singapore, and Hong Kong.

It is worthwhile to note that the occurrence of BDE-209 observed in the present study was clearly different from those observed in several previous studies (*30–32*). The absence of BDE-209 in many previous studies does not necessarily exclude the occurrence of BDE-209 in the samples analyzed. One of the plausible explanations is that BDE-209 was not even included in the list of target analytes or some analytical procedures failed to detect BDE-209 because it can degrade easily during chromatographic analysis (*33, 34*). The present study detected BDE-209 in mussels at concentrations ranging from nd to 3.21 ng/g of dry weight, which were relatively low compared with those from South Korea (0.23–14.8 ng/g dry weight) (*13*), Hong Kong (0–14.3 ng/g dry weight) (*14*), and the Netherlands (4.9 ng/g dry weight) (*28*). This finding is quite significant, as BDE-209 is often assumed not to be bioavailable (*35*) because of its high molecular weight, thus posing no harm to biological species and humans. Recent studies have reported

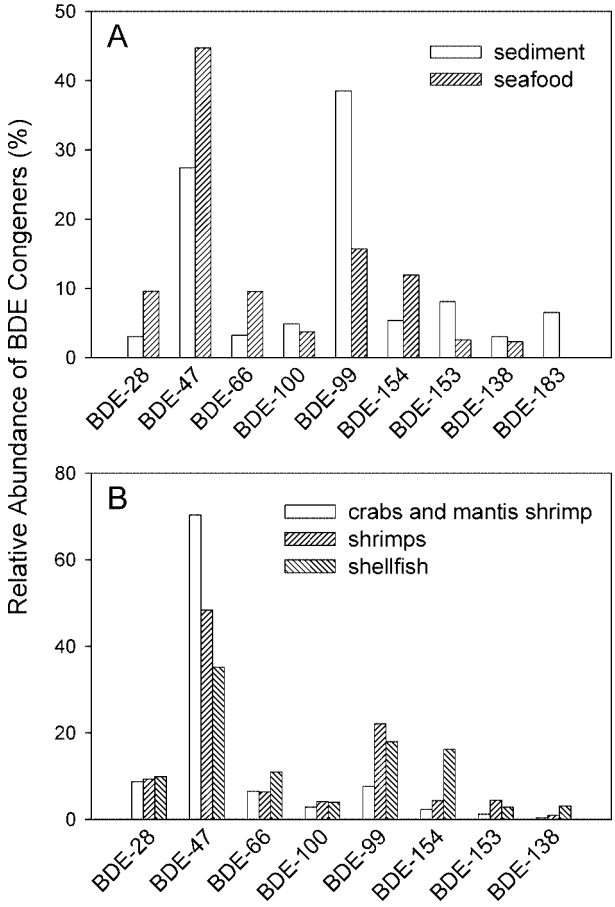

Figure 2. Relative abundances (%) of brominated diphenyl ether (BDE) congeners (excluding BDE-209): (a) BDE congeners in seafood products and local sediment (*39*) and (b) BDE congeners in different species (shrimp: *Penaeus monodon*, *Penaeus japonicus*, *Metapenaeus ensis*, *Macrobrachium rosenbergii*, and *Proambarus clarkia*; crabs and mantis shrimp: *Scylla serrata*, *Ovalipes punctatus*, and *Squilla oraloria*; shellfish: *Haliotis diversicolor*, *Terebra maculate*, *Meretrix meretrix*, *Cyclina sinensis*, *Venerupis variegate*, *Argopectens irradias*, *Patinopecten yessoensis*, *Tegillarca granosa*, *Scapharca subcrenata*, *Sinonovacula constrict*, *Solen grandis*, *Perna uiridis*, and *Crassostrea gigas*.

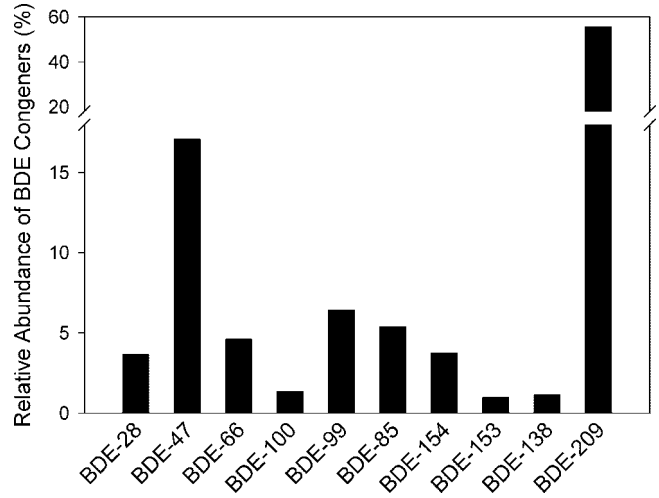

Figure 3. Relative abundances (%) of brominated diphenyl ether (BDE) congeners (including BDE-209) in seafood products (only the samples containing BDE-209 at levels above the limit of detection were included).

the presence of BDE-209 in several organisms, such as roaches (*35*), red foxes (*36*), gray seals (*37*), and sharks (*38*). The occurrence of BDE-209 in our samples further confirms the bioavailability of BDE-209 to certain organisms and suggests the need to reassess the bioavailability issues for BDE-209. It should be noted that this comparison is somewhat compromised, because the number of congeners varied greatly among different studies, which was probably reflective of the various patterns of BDE compositions in local BDE sources or the availability of BDE congener standards for the analytical laboratories involved. Overall, this assessment indicates that PBDE pollution in South China is moderate on the global scale.

Congener Profiles of PBDEs. The congener profiles of PBDE in seafood are schematically shown in **Figure 2**. For a consistent comparison with the profiles in local sediment (*39*), BDE-85 and BDE-209 are not included. Generally, BDE-47 and BDE-99 were the most abundant congeners in all samples, accounting for 44.7% and 15.7% of the total concentrations, respectively, which included BDE-28, BDE-47, BDE-66, BDE-99, BDE-100, BDE-138, BDE-153, and BDE-154. When compared to the local sediment (**Figure 2A**), the relative abundances of BDE-28, BDE-47, and BDE-66 were higher and the relative abundances of BDE-99, BDE-100, BDE-138, and BDE-153 were lower than those in the sediment (*39*), which suggests that seafood samples are prone to accumulating low-brominated congeners. Moreover, the congener profiles of PBDE were also species-dependent (**Figure 2B**). The remarkable dissimilarity is related to the relative abundances of BDE-47 and BDE-99 among different species. The relative abundances of BDE-47 and BDE-99 were relatively lower in shellfish compared to those in shrimp. In mantis shrimp and crabs, the congener profiles of PBDE were somewhat special, characterized by the relatively higher abundance of BDE-47 and lower abundance of BDE-99 compared to those in other species. The congener profiles of PBDEs in mantis shrimp and crabs could be partially explained by possible metabolic debromination of BDE-99 to BDE-47, which was shown to occur in common carp (*40*). In addition, different feeding habits could also be a plausible cause for the congener profiles in different species. Another interesting aspect is that the proportion of BDE-28 in the seafood products was much higher than that in the penta-BDE technical mixture (*41*). This may be explained by the possible biodegradation of higher brominated congeners in sediment and the higher bioaccumulation potential of BDE-28 compared to higher brominated congeners.

As mentioned above, BDE-209 was detected in more than one-third of the seafood samples. If only the samples with detectable BDE-209 are taken into account, the congener profile suggests that BDE-209 was the most abundant congener, followed by BDE-47 and BDE-99 (**Figure 3**). This pattern is quite similar to the BDE congener profile in mussels from the Korean coast, which was also predominated by BDE-209 (*13*). As for BDE-183, a major component of the octa-BDE technical mixture (*41*), it was seldom detected. Consequently, it can be concluded that the deca-BDE mixture is the most extensively used PBDE technical mixture in South China, and penta-BDE (characterized by BDE-47 and BDE-99) is also an important technical mixture used in the study area. This was consistent with the fact that deca-BDE has been mass-produced in China (the output of deca-BDE in 2006 in China was about 15000 tons; http://www.chinainfo.gov.cn/data) and with the sediment PBDE results (*11*). It should be noted that the assessment of PBDE sources was qualitative, at best, based on the BDE congener profiles in different species from the present study and other previous studies. A more quantitative apportionment would require a detailed understanding of the type of BDE

technical mixtures heavily used in the study area, the bioaccumulation of individual BDE congeners in aquatic species, and the mechanisms governing the transformation of PBDEs in the ambient environment.

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LITERATURE CITED

(1) Rahman, F.; Langford, K. H.; Scrimshaw, M. D.; Lester, J. N. Polybrominated diphenyl ethers (PBDE) flame retardants. *Sci. Total Environ.* **2001**, *275*, 1–17.

(2) de Wit, C. A. An overview of brominated flame retardants in the environment. *Chemosphere* **2002**, *46*, 583–624.

(3) McDonald, T. A. A perspective on the potential health risks of PBDEs. *Chemosphere* **2002**, *46*, 745–755.

(4) Hites, R. A. Polybrominated diphenyl ethers in the environment and in people: A meta-analysis of concentrations. *Environ. Sci. Technol.* **2004**, *38*, 945–956.

(5) Darnerud, P. O. Toxic effects of brominated flame retardants in man and in wildlife. *Environ. Int.* **2003**, *29*, 841–853.

(6) Rupp, S.; Metzger, J. W. Brominated-chlorinated diphenyl ethers formed by thermolysis of polybrominated diphenyl ethers at low temperatures. *Chemosphere* **2005**, *60*, 1644–1651.

(7) Barontinia, F.; Cozzani, V. Formation of hydrogen bromide and organobrominated compounds in the thermal degradation of electronic boards. *J. Anal. Appl. Pyrol.* **2006**, *77*, 41–55.

(8) Ueno, D.; Kajiwara, N.; Tanaka, H.; Subramanian, A.; Fillmann, G.; Lam, P. K. S.; Zheng, G. J.; Muchitar, M.; Razak, H.; Prudente, M.; Chung, K.-H.; Tanabe, S. Global pollution monitoring of polybrominated diphenyl ethers using Skipjack Tuna as a bioindicator. *Environ. Sci. Technol.* **2004**, *38*, 2312–2316.

(9) Martin, M.; Lam, P. K. S.; Richardson, B. J. An Asian quandary: where have all of the PBDEs gone. *Mar. Pollut. Bull.* **2004**, *49*, 375–382.

(10) Guo, J.-Y.; Zeng, E. Y.; Wu, F.-C.; Meng, X.-Z.; Mai, B.-X.; Luo, X.-J. Organochlorine pesticides in seafood products from southern China and health risk assessment. *Environ. Toxicol. Chem.* **2007**, *26*, 1109–1115.

(11) Mai, B. X.; Chen, S. J.; Luo, X. J.; Chen, L. G.; Yang, Q. S.; Sheng, G. Y.; Peng, P. A.; Fu, J. M.; Zeng, E. Y. Distribution of polybrominated diphenyl ethers in sediments of the Pearl River Delta and adjacent South China Sea. *Environ. Sci. Technol.* **2005**, *39*, 3521–3527.

(12) Kim, B. H.; Ikonomou, M. G.; Lee, S. J.; Kim, H. S.; Chang, Y. S. Concentrations of polybrominated diphenyl ethers, polychlorinated dibenzo-p-dioxins and dibenzofurans, and polychlorinated biphenyls in human blood samples from Korea. *Sci. Total Environ.* **2005**, *336*, 45–56.

(13) Moon, H.-B.; Kannan, K.; Lee, S.-J.; Choi, M. Polybrominated diphenyl ethers (PBDEs) in sediment and bivalves from Korean coastal waters. *Chemosphere* **2007**, *66*, 243–251.

(14) Liu, Y.; Zheng, G. J.; Yu, H.; Martin, M.; Richardson, B. J.; Lam, M. H. W.; Lam, P. K. S. Polybrominated diphenyl ethers (PBDEs) in sediments and mussel tissues from Hong Kong marine waters. *Mar. Pollut. Bull.* **2005**, *50*, 1173–1184.

(15) Ramu, K.; Kajiwara, N.; Tanabe, S.; Lam, P. K. S.; Jefferson, T. A. Polybrominated diphenyl ethers (PBDEs) and organochlorines in small cetaceans from Hong Kong waters: Levels, profiles and distribution. *Mar. Pollut. Bull.* **2005**, *51*, 669–676.

(16) Wurl, O.; Obbard, J. P. Organochlorine pesticides, polychlorinated biphenyls and polybrominated diphenyl ethers in Singapore's coastal marine sediments. *Chemosphere* **2005**, *58*, 925–933.

(17) Bayen, S.; Wurl, O.; Karuppiah, S.; Sivasothi, N.; Lee, H. K.; Obbard, J. P. Persistent organic pollutants in mangrove food webs in Singapore. *Chemosphere* **2005**, *61*, 303–313.

(18) Zheng, G. J.; Martin, M.; Richardson, B. J.; Yu, H.; Liu, Y.; Zhou, C.; Li, J.; Hu, G.; Lam, M. H. W.; Lam, P. K. S. Concentrations of polybrominated diphenyl ethers (PBDEs) in Pearl River Delta sediments. *Mar. Pollut. Bull.* **2004**, *49*, 514–524.

(19) Chen, S.-J.; Gao, X.-J.; Mai, B.-X.; Chen, Z.-M.; Luo, X.-J.; Sheng, G.-Y.; Fu, J.-M.; Zeng, E. Y. Polybrominated diphenyl ethers in surface sediments of the Yangtze River Delta: Levels, distribution and potential hydrodynamic influence. *Environ. Pollut.* **2006**, *144*, 951–957.

(20) Shen, M.; Yu, Y.; Zheng, G. J.; Yu, H.; Lam, P. K. S.; Feng, J.; Wei, Z. Polychlorinated biphenyls and polybrominated diphenyl ethers in surface sediments from the Yangtze River Delta. *Mar. Pollut. Bull.* **2006**, *52*, 1299–1304.

(21) Christensen, J. H.; Glasius, M.; Pecseli, M.; Platz, J.; Pritzl, G. Polybrominated diphenyl ethers (PBDEs) in marine fish and blue mussels from southern Greenland. *Chemosphere* **2002**, *47*, 631–638.

(22) Bethune, C.; Nielsen, J.; Julshamn, K. Current levels of primary polybrominated diphenyl ethers (PBDEs) in Norwegian seafood. *Organohalogen Compd.* **2004**, *66*, 3814–3819.

(23) Covaci, A.; Bervoets, L.; Hoff, P.; Voorspoels, S.; Voets, J.; van Campenhout, K.; Blust, R.; Schepens, P. PBDEs in freshwater mussels and fish from Flanders, Belgium. *Organohalogen Compd.* **2004**, *66*, 3801–3808.

(24) Voets, J.; Talloen, W.; de Tender, T.; van Dongen, S.; Covaci, A.; Blust, R.; Bervoets, L. Microcontaminant accumulation, physiological condition and bilateral asymmetry in zebra mussels (Dreissena polymorpha) from clean and contaminated surface waters. *Aquat. Toxicol.* **2006**, *79*, 213–225.

(25) Zhu, L. Y.; Hites, R. A. Determination of polybrominated diphenyl ethers in environmental standard reference materials. *Anal. Chem.* **2003**, *75*, 6696–6700.

(26) Oros, D. R.; Hoover, D.; Rodigari, F.; Crane, D.; Sericano, J. Levels and distribution of polybrominated diphenyl ethers in water, surface sediments, and bivalves from the San Francisco Estuary. *Environ. Sci. Technol.* **2005**, *39*, 33–41.

(27) Alaee, M.; Arias, P.; Sjödin, A.; Bergman, Å. An overview of commercially used brominated flame retardants, their applications, their use patterns in different countries/regions and possible modes of release. *Environ. Int.* **2003**, *29*, 683–689.

(28) de Boer, J.; Wester, P. G.; van der Horst, A.; Leonards, P. E. G. Polybrominated diphenyl ethers in influents, suspended particulate matter, sediments, sewage treatment plant and effluents and biota from the Netherlands. *Environ. Pollut.* **2003**, *122*, 63–74.

(29) Bayen, S.; Thomas, G. O.; Lee, H. K.; Obbard, J. P. Occurrence of polychlorinated biphenyls and polybrominated diphenyl ethers in green mussels (Perna viridis) from Singapore, Southeast Asia. *Environ. Toxicol. Chem.* **2003**, *22*, 2432–2437.

(30) Hale, R. C.; La Guardia, M. J.; Harvey, E. P.; Mainor, T. M.; Duff, W. H.; Gaylor, M. O. Polybrominated diphenyl ether flame retardants in Viginia freshwater fishes (USA). *Environ. Sci. Technol.* **2001**, *35*, 4585–4591.

(31) Dodder, N. G.; Strandberg, B.; Hites, R. A. Concentrations and spatial variations of polybrominated diphenyl ethers and several organochlorine compounds in fishes from the Northeastern United States. *Environ. Sci. Technol.* **2002**, *36*, 146–151.

(32) Eljarrat, E.; De La Cal, A.; Raldua, D.; Duran, C.; Barcelo, D. Occurrence and bioavailability of polybrominated diphenyl ethers and hexabromocyclododecane in sediment and fish from the Cinca River, a tributary of the Ebro River (Spain). *Environ. Sci. Technol.* **2004**, *38*, 2603–2608.

(33) Dirtu, A. C.; Ravindra, K.; Roosens, L.; van Grieken, R.; Neels, H.; Blust, R.; Covaci, A. Fast analysis of decabrominated diphenyl ether using low-pressure gas chromatography-electron-capture negative ionization mass spectrometry. *J. Chromatogr. A* **2007**, in press (available online July 22, 2007).

(34) Binelli, A.; Roscioli, C.; Guzzella, L. Improvements in the analysis of decabromodiphenyl ether using on-column injection and

electron-capture detection. *J. Chromatogr. A* **2006**, *1136*, 243–247.

(35) Burreau, S.; Zebühr, Y.; Broman, D.; Ishaq, R. Biomagnification of polychlorinated biphenyls (PCBs) and polybrominated diphenyl ethers (PBDEs) studied in pike (Esox lucius), perch (Perca fluviatilis) and roach (Rutilus rutilus) from the Baltic Sea. *Chemosphere* **2004**, *55*, 1043–1052.

(36) Voorspoels, S.; Covaci, A.; Lepom, P.; Escutenaire, S.; Schepens, P. Remarkable findings concerning PBDEs in the terrestrial top-predator red fox (Vulpes vulpes). *Environ. Sci. Technol.* **2006**, *40*, 2937–2943.

(37) Thomasa, G. O.; Moss, S. E. W.; Asplund, L.; Hall, A. J. Absorption of decabromodiphenyl ether and other organohalogen chemicals by grey seals (Halichoerus grypus). *Environ. Pollut.* **2005**, *133*, 581–586.

(38) Johnson-Restrepo, B.; Kannan, K.; Addink, R.; Adams, D. H. Polybrominated diphenyl ethers and polychlorinated biphenyls in a marine foodweb of coastal Florida. *Environ. Sci. Technol.* **2005**, *39*, 8243–8250.

(39) Chen, S.-J. Polybrominated diphenyl ethers in sediments in the aquatic environments of the Pearl River Delta and Yangtze River Delta. Ph.D. Thesis, State Key Laboratory of Organic Geochemistry, Guangzhou Institute of Geochemistry, Chinese Academy of Sciences, Guangzhou, China.

(40) Stapleton, H. M.; Letcher, R. J.; Li, J.; Baker, J. E. Dietary accumulation and metabolism of polybrominated diphenyl ethers by juvenile carp (*Cyprinus carpio*). *Environ. Toxicol. Chem.* **2004**, *23*, 1939–1946.

(41) Korytar, P.; Covaci, A.; de Boer, J.; Gelbin, A.; Brinkman, U. A. T. Retention-time database of 126 polybrominated diphenyl ether congeners and two Bromkal technical mixtures on seven capillary gas chromatographic columns. *J. Chromatogr., A* **2005**, *1065*, 239–249.

(42) Allchin, C. R.; Law, R. J.; Morris, S. Polybrominated diphenylethers in sediments and biota downstream of potential sources in the UK. *Environ. Pollut.* **1999**, *105*, 197–207.

(43) Christensen, J. H.; Platz, J. Screening of polybrominated diphenyl ethers in blue mussels, marine and freshwater sediments in Denmark. *J. Environ. Monit.* **2001**, *3*, 543–547.

(44) Johansson, I.; Héas-Moisan, K.; Guiot, N.; Munschy, C.; Tronczyński, J. Polybrominated diphenyl ethers (PBDEs) in mussels from selected French coastal sites: 1981–2003. *Chemosphere* **2006**, *64*, 296–305.

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