Environ. Sci. Technol. **2007**, *41,* 6007–6013

Riverine Inputs of Polybrominated Diphenyl Ethers from the Pearl River Delta (China) to the Coastal Ocean

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Riverine runoff is an important mode to transport anthropogenic pollutants from terrestrial sources to oceans. Polybrominated diphenyl ethers (PBDEs) were measured in riverine runoff samples from the eight major outlets within the Pearl River Delta (PRD), China, an economically fast developing region housing a vast number of electronics manufacturing and assembling plants. The $\sum_{17}$PBDEs (sum of 17 BDE congeners, i.e., BDE-28, -47, -66, -85, -99, -100, -138, -153, -154, -183, -196, -197, -203, -206, -207, -208, and -209) concentrations varied from 344 to 68 000 pg/L, with those of BDE-209, BDE-47, and BDE-99 being 335–65 200, 3–143, and <1–200 pg/L, respectively. These levels were in the high end of the global PBDEs concentrations in the aquatic environments. The monthly inputs of $\sum_{17}$PBDEs ranged from 0.21 to 215 kg at individual outlets, and the annual input of $\sum_{17}$PBDEs from all the outlets was estimated at 2140 kg/year. Of the target BDE congeners, BDE-209 was the most predominant component with an annual input of 1960 kg/year, followed by BDE-47 (13.3 kg/year) and BDE-99 (11.7 kg/year). An extrapolation of the past use of PBDEs in the region concluded that 23 metric tons of $\sum_{17}$PBDEs have been discharged into the coastal ocean from the PRD in the last 20 years. The amount of PBDEs imported to China in the form of e-waste was estimated at 35 000 metric tons/year, higher than the annual domestic production of brominated fire retardants (∼10 000 metric tons/year) and the annual riverine input of total PBDEs from the PRD, suggesting that the majority of PBDEs inventory has been accumulated from importation of e-wastes. Because of the continuous importation of e-wastes and strong demand for brominated fire retardants, the impact of PBDEs on China's and the world's environments is expected to persist for many years to come.

Introduction

Polybrominated diphenyl ethers (PBDEs), constituents of three commercial mixtures designated as penta-BDE, octa-BDE, and deca-BDE, have been widely used as flame retardants embedded in plastics, paints, electrical components, textiles, foam, rubber, and other casing materials (*1–4*). Penta-BDE and octa-BDE have been banned in Europe, and they will be banned in the state of California in the United States in 2008. In Asia, the market demand for PBDEs was 24 650 metric tons in 2001, accounting for 37% of the world figure. Within this figure, 23 000 metric tons were deca-BDE, and 150 and 1500 metric tons were penta-BDE and octa-BDE, respectively (*4*). In China, the domestic production and demand of PBDEs are enormous and have increased yearly (*1*). In addition, a portion of PBDEs currently used in China is expected to be imported from other countries (*5*). An emerging issue is that China has become the largest recipient of electronics wastes (e-wastes) in the world. Although the exact volume of e-waste imported to China has remained unknown, China's Environmental Protection Administration estimated that 80% of the global e-wastes is imported to Asia, 90% of which enters China, and around 50–80% of e-waste generated in the United States (U.S.) is destined for China (*6*). It was reported that four large warehouses in the port of Nansha, adjacent to the Pearl River Estuary (Figure 1), received most of the imported e-wastes transported by shipping containers; these wastes were in turn trucked to recycling sites (e.g., Guiyu town) (*7*). Recycling of e-wastes is expected to mobilize a large portion of PBDEs from electronic components into the environment.

PBDEs have been widely detected in air, water, soil, fish, birds, marine mammals, and humans in recent years, and in many cases, the concentrations of PBDEs have been increasing over time (*8–16*). The levels, distributions, and trends of PBDEs in the environment and humans have been well documented in North America, Europe, and the Arctic over the past few years. In Asia, most data regarding the PBDEs contamination have been acquired from Japan and Singapore (*5*). Several reports of PBDEs in environmental samples from the Pearl River Delta (PRD), China, were published (*1*, *17–19*). Overall, much more information is still needed to understand the fate of these pollutants which is critical for risk assessment as the PRD is one of the largest users of brominated fire retardants and recipients of global e-waste in the world. In addition, the PRD is located in a subtropical and East Asian monsoon zone adjacent to the South China Sea. The annual mean temperature is 14–22 °C and annual precipitation is 1200–2200 mm. As a result, riverine runoff is an important route to transport contaminants to global oceans. So far, no study has been conducted to address this issue.

The objectives of this study were to determine the total annual input of 17 BDE congeners, including BDE-28, -47, -66, -85, -99, -100, -138, -153, -154, -183, -196, -197, -203, -206, -207, -208, and -209 (designated as $\sum_{17}$PBDEs thereafter), from the PRD to the coastal ocean and to estimate the inflows of PBDEs to China via e-waste importation. In addition, the riverine runoff concentrations of PBDEs were compared to those in water bodies in other regions of the world.

Methods and Materials

Sample Collection and Filtration. The locality of the sampling sites is displayed in Figure 1. The eight riverine runoff outlets include four eastern outlets, Humen, Jiaomen, Honqilimen, and Hengmen, and four western outlets, Modaomen, Jitimen, Hutiaomen, and Yamen. Sample collection was carried out monthly, from March 2005 to February 2006, approximately 1 h before the intraday lower tides. The volume of each sample was 40 L, composed of subsamples collected at various points along a river cross section (details presented in the Supporting Information). Water was taken with stainless-steel submersible pumps into 10 L brown glass

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10.1021/es070782x CCC: $37.00 © 2007 American Chemical Society
Published on Web 07/24/2007

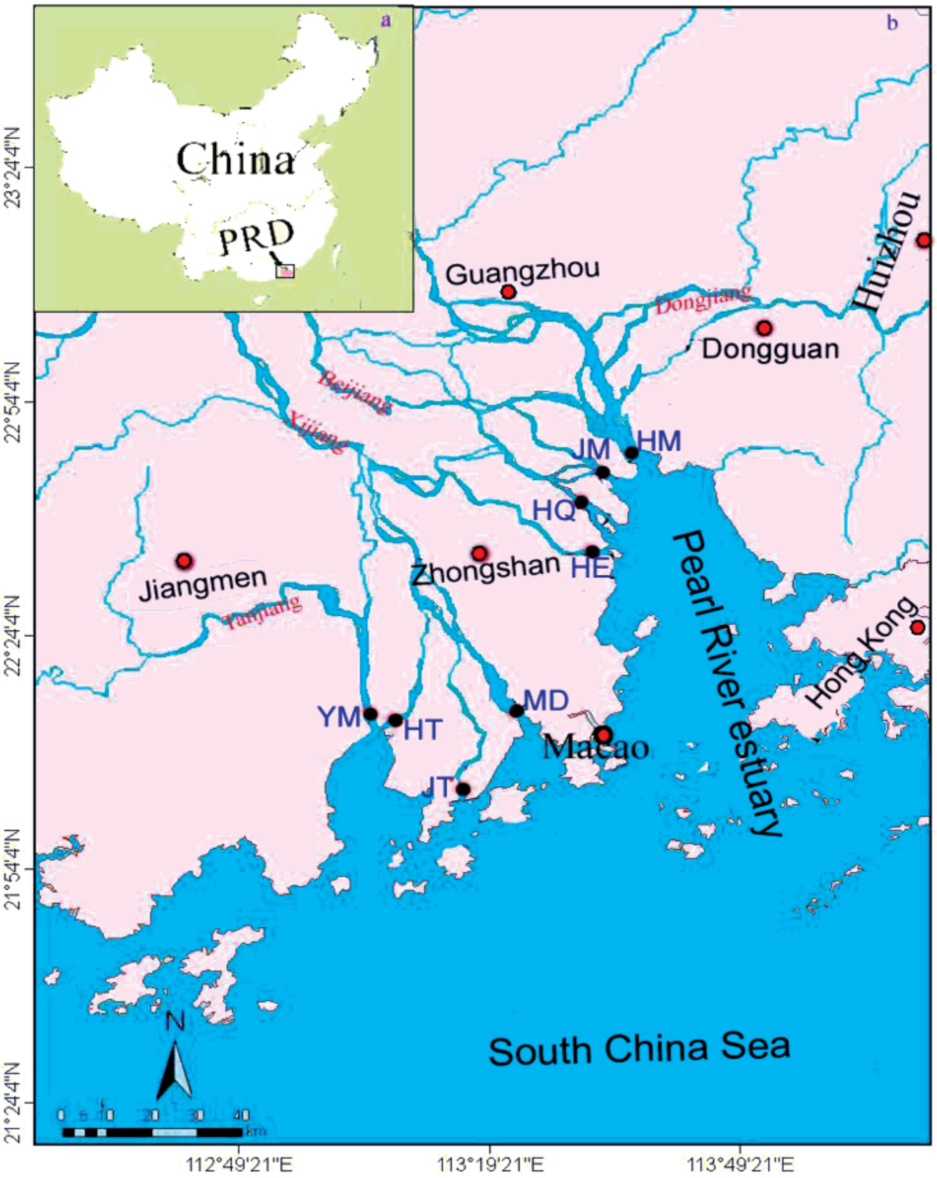

FIGURE 1. (a) The geographical locality of the Pearl River Delta (PRD). (b) The sampling sites at the eight major riverine runoff outlets within the Pearl River Delta, China: Humen (HM); Jiaomen (JM); Honqilimen (HQ); Hengmen (HE); Modaomen (MD); Jitimen (JT); Hutiaomen (HT); and Yamen (YM).

bottles that were cooled with ice during transport to the laboratory. In the laboratory, water samples were filtered using a vermicular system (precleaned with acetone). Suspended particulate matter (SPM) was collected with glass fiber filters (GF/F, 0.7 μm nominal pore size, 142 mm diameter, Whatman International, Maidstone, England) which were kiln dried at 450 °C for 4 h prior to use. SPM-loaded filters were wrapped in precleaned aluminum foil and immediately stored at −20 °C until analyzed. Filtrates were processed immediately upon filtration using the procedures described below.

Sample Extraction and Analysis. The procedures of extraction and chromatographic separation were described in detail elsewhere (*20*) and only a brief description is given herein. Dissolved organics retained on a glass column (25 mm i.d. × 400 mm length) containing XAD-2:XAD-4 resin (1:1 in length) were eluted three times with 50 mL of methanol, followed by three extractions with 50 mL of dichloromethane (DCM) and methanol (1:1 in volume) in an ultrasonic bath. The extracts were combined and spiked with known amounts of surrogate standards. Liquid−liquid back extraction was carried out five times with 100 mL of DCM upon addition of 500 mL distilled water and appropriate amount of NaCl for removal of methanol. The DCM phase was further extracted with 10 mL of distilled water three times to remove residual methanol. The SPM-loaded filters were freeze-dried, weighed, and spiked with surrogate standards prior to Soxhlet extraction for 72 h with 400 mL of DCM:acetone (1:1 in volume). Active copper was added for desulphurization. All extracts were condensed and solvent-exchanged to hexane and further reduced to 1 mL by a Zymark TurboVap500 (Zymark Corporation, Hopkinton, MA). The extracts were cleaned up with a 10 mm i.d. glass column containing a series of silica and alumina (*20*), and the eluent were concentrated with the Zymark TurboVap 500 to 0.5 mL. Final volume was reduced to 100 μL under a gentle N_2 stream. The internal standard, $^{13}C-PCB$ 208, was added into all extracts before instrumental analysis.

Sample analysis was performed with a Shimadzu model 2010 GC-MS equipped with AOC-20i auto injector (Shimadzu, Japan), using negative chemical ionization in the selected ion monitoring model, with helium as the carrier gas at a

TABLE 1. Average Concentrations (ng/L) and Total Inputs (kg) of Σ_{17}PBDEs, BDE-47, BDE-99, and BDE-209, as well as Yearly Water Discharge Q_i, for the Eight Major Riverine Outlets of the Pearl River Delta, China

	average concentration				Q_i	total inputs			
outlet	Σ_{17}PBDEs	BDE-47	BDE-99	BDE-209	(10^9 m^3)	Σ_{17}PBDEs	BDE-47	BDE-99	BDE-209
Humen	8.13	0.050	0.041	7.54	45.5	649	3.26	2.90	604
Jiaomen	4.39	0.051	0.054	3.84	49.8	321	3.06	2.89	284
Honqilimen	3.59	0.034	0.023	3.20	30.9	143	1.13	0.77	129
Hengmen	8.72	0.057	0.049	7.95	39.4	373	2.30	1.92	337
Modaomen	3.47	0.032	0.029	3.12	73.2	219	1.96	1.83	197
Jitimen	5.24	0.035	0.022	4.80	9.86	29.9	0.31	0.19	27.3
Hutiaomen	2.69	0.028	0.022	2.44	10.6	42.4	0.36	0.30	38.2
Yamen	19.1	0.047	0.044	18.0	17.2	362	0.90	0.87	340
Total						2140	13.3	11.7	1960

flow rate of 1 mL/min. A DB-XLB (30 m × 0.25 mm i.d., 0.25 μm film thickness) capillary column was used for separation of BDE-28, -47, -66, -85, -99, -100, -138, -153, -154, and -183. For BDE-196, -197, -203, -206, -207, -208, and -209, a CP-Sil 13 CB (12.5 m × 0.25 mm i.d., 0.2 μm film thickness) capillary column was used. The temperature programs and quantitation ions employed were detailed elsewhere (*19*).

Quality Assurance/Quality Control. Quality assurance and quality control procedures have been described in detail elsewhere (*1*, *18*). Procedure blanks ($n = 3$), laboratory blanks ($n = 4$), and duplicate samples (three for every outlet) were processed alternately throughout the sampling analysis. Only considerably low concentrations of BDE-47 (a mean of 3 pg/L) and BDE-99 (a mean of 4 pg/L) were found in procedural blank, and BDE-209 (124 pg/L) was found in only one procedural blank of SPM with the concentration close to the lowest level of the calibration curve. The lowest concentration level from the calibration curve was defined as the reporting limit for a specific analyte. The reporting limit was 1.25 pg/L for BDE congeners (except for BDE-209), and 125 pg/L for BDE-209. The relative standard deviations (RSD; %) for the concentrations of 17 BDE congeners in duplicate samples, were 2.6−29.3% and 1.2−31.3% for filtrate and SPM samples, respectively. Detailed RSD data are presented in Table S4. The surrogate recoveries in all filtrate samples were 79.8 ± 18.9% for ^{13}C−PCB-141 and 69.8 ± 15.4% for PCB-209, and in all SPM phase they were 63.3 ± 13.5% for ^{13}C−PCB-141 and 70.8 ± 18.2% for PCB-209, respectively. In addition, the mean blank values of BDE-47 and BDE-99 were subtracted from the sample measurements, and all data were reported without surrogate recovery correction

Data Analysis. The monthly inputs of Σ_{17}PBDEs from the eight runoff outlets from March 2005 to February 2006 were calculated by

$$F_{i,j} = C_{i,j} \times Q_{i,j} \times 10^{-9} \qquad (1)$$

where $F_{i,j}$ (kg/month) is the input of Σ_{17}PBDEs from the ith outlet during period j; $C_{i,j}$ (ng/L) is the total concentrations of Σ_{17}PBDEs in both the aqueous and SPM phases (Table S 2); and $Q_{i,j}$ (m^3) is the total discharge amount from the ith outlet during time period j and was estimated using the procedures detailed in the Supporting Information. The total annual input (F_i) from the ith outlet was then estimated by

$$F_i = \sum_{j=1}^{12} F_{i,j} \qquad (2)$$

For any concentration below the reporting limit, zero and half the reporting limit were employed for the concentration and input calculations, respectively.

Results and Discussion

Occurrence and Levels of PBDEs. Higher than 90% of total Σ_{17}PBDEs concentrations in the water samples were due to BDE-47, -99, and -209 (Table 1). BDE-47 and -99 are the major constituents of the penta-BDE formula and are known to bioaccumulate and biomagnify in the food chain (*21*). Therefore, only BDE-47, -99, and -209 are discussed in detail along with Σ_{17}PBDEs. While detailed concentration data are presented in Table S2, the average concentrations of Σ_{17}PBDEs, BDE-47, BDE-99, and BDE-209 are summarized in Table 1. The levels of Σ_{17}PBDEs were 0.34−68.0 ng/L, whereas those of BDE-209, -99, and -47 were 0.33−65.2, <0.001−0.200, and 0.003−0.143 ng/L, respectively. The monthly Σ_{17}PBDEs concentrations varied widely in the eight sampling locations (Figure 2). In addition, the mean concentrations of Σ_{17}PBDEs in water samples collected from Humen and Hengmen Outlets were twice as much as those from the other outlets except for Yamen Outlet, although the difference was not statistically significant. This was probably due to the fact that the water courses draining into Humen Outlet run through several large urban areas including Guangzhou, Huizhou, and Dongguan that have housed important electronics/electrical manufacturing capacities and water courses draining into Hengmen Outlet run through the City of Zhongshan that is an emerging electronics manufacturing center. In particular, Dongguan is the world's largest manufacturing center for a large number of industries that intensively use brominated fire retardants (*1*). At the same time, the water discharge amounts through the two outlets are about 20% and 14% of the total through the eight outlets, respectively. Therefore, waste discharge from these urban centers to the water systems is likely the main reason for high PBDEs contamination. However, the mean Σ_{17}PBDEs concentration in water samples collected from Yamen was the highest among all the outlets (Figure 2). This seemingly unusual result may have been due to waste discharge from the City of Jiangmen, an emerging electronics manufacturing base. As a result, the amount of Σ_{17}PBDEs transported through the Yamen outlet is enormous (Table 1) although the water discharge through this outlet only makes up ∼4.7% of the total amount among the eight outlets.

The PRD houses a vast number of electronics, furniture, and appliance manufacturing plants that use large amounts of BFRs (mostly deca-BDE). It is, therefore, inevitable that considerably high levels of BDE-209 have been detected in sediments (*1*) and water (the present study) of the PRD. A number of recent studies have shown that BDE-209 was possibly debrominated by natural sunlight (*22*), bacteria (*23*), and metabolism (*24*). Therefore, it is possible for BDE-209 to transform into less brominated congeners that are probably more endocrine disrupting. In the present study, BDE-209 did not correlate very well with BDE-47, -99, and -183 ($r^2 < 0.2$, Figures S1a−c), but they showed good correlations with BDE-208, -207, and -206 ($r^2 = 0.6−0.9$, Figures S1d−f). Furthermore, the percentage of nona-BDEs contained in the commercial deca-BDE is ∼3%; however, the ratio of nona-BDEs to BDE-209 is ∼6% in the present study. This suggests that nona-BDEs may have originated from decomposition

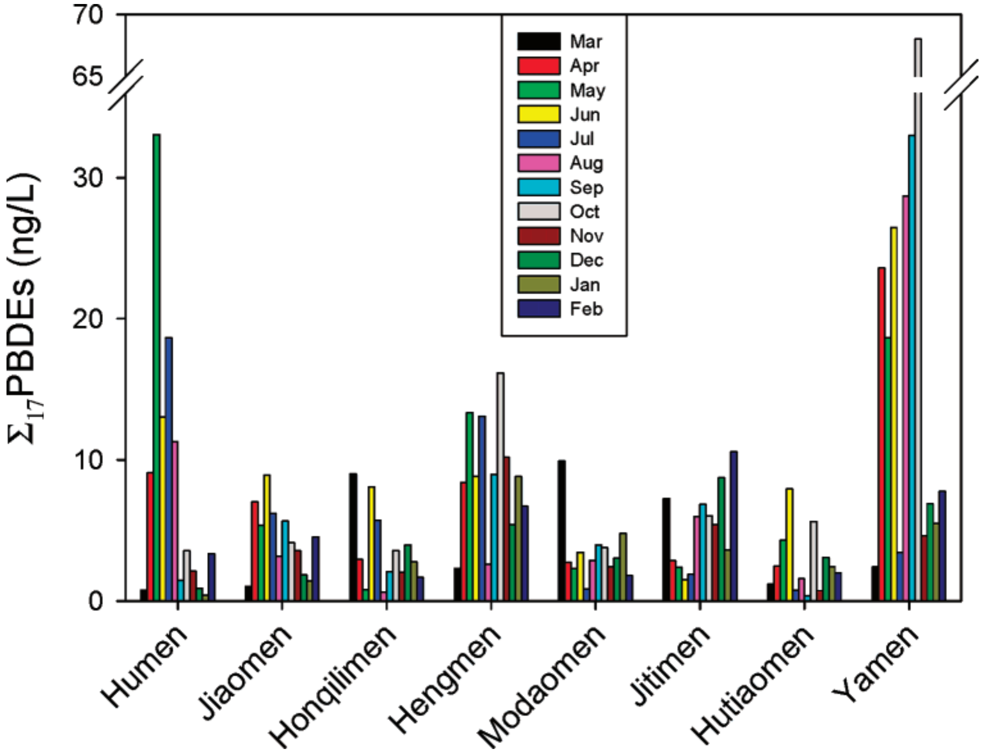

FIGURE 2. Concentrations of PBDEs in water samples collected from the eight major riverine runoff outlets within the Pearl River Delta, China.

TABLE 2. Comparison of Global Water Column Levels (pg/L) of Total PBDEs, BDE-47, BDE-99, and BDE-209

	∑PBDEs	BDE-47	BDE-99	BDE-209	year (ref)
Scheldt Estuary and North Sea, Dutch coast	<0.1–5.6[a]	1	0.5	<0.1–4	1999 (*25*)
Izmir Bay, Turkey	483[b], 566[c]	74, 20.5	110, 30	246, 497	2005 (*26*)
wastewater treatment plant effluent, California	29023[d]	10467	11200	1730	2004 (*34*)
Lake Ontario, North America	4–13[e]	0.11–3.83			1999 (*27*)
San Francisco Estuary, California	3–513[f]	<16.1–179.5	<13.1–90.7	12–191	2002 (*14*)
Lake Michigan, North America	31[g]				1997 (*14*)
	158[g]				1999 (*14*)
Japan[h]				<120–590	2003 (*28*)
Hong Kong, China					
seawater	56.8–151.2[i]	nd[j]–38.2	nd-25.3		2005 (*29*)
sea-surface microlayer	48.3–297.3[i]	nd-104.4	nd-2.6		2005 (*29*)
Pearl River, South China	344–68000[k]	3–143	<1–200	335–65237	2005–2006[l]

[a] Sum of BDE-47, BDE-99, and BDE-153. [b] Mean concentration of BDE-28, BDE-47, BDE-99, BDE-100, BDE-153, BDE-154, and BDE-209 in the dissolved and particle phases combined in summer. [c] Mean concentration in the dissolved and particle phases combined in winter. [d] Sum of BDE-7, -8, -15, -17, -25, -28, -35, -37, -47, -49, -66, -71, -75, -85, -99, -100, -119, -138, -140, -153, -154, -155, -183, -190, -206, -207, -208, and -209. [e] Sum of BDE-28, -47, -99, -153, -154, and -183. [f] Sum of BDE-17, -28, -47, -66, -85, -99, -100, -138, -153, -154, -183, -190, -206, -207, -208, and -209. [g] Sum of BDE-47, -99, -100, -153, -154, and -183. [h] Detected at one of thirty-eight stations at the detection limit of 120 ng/L. [i] Sum of BDE-28, -47, -99, -100, -153, -156, -183, and -209 in the dissolved and particle phases combined. [j] Not detected. [k] Sum of 17 BDE congeners in the dissolved and particle phases combined. [l] Present study.

of BDE-209 in addition to the contributions from deca-BDE. However, the present study was unable to draw definite conclusions about the debromination of BDE-209 due to insufficient data. Further investigations are worthwhile to better understand the mechanisms for debromination of BDE-209 in the environment.

Global Comparison of Water PBDEs Levels. Because very limited information is available on the occurrence of PBDEs in the world's water bodies, it is a challenge to compare the results from the present study to the global levels of water PBDEs. The concentrations of $\sum_{17}$PBDEs from the present study ranged from 344 to 68 000 pg/L with those of BDE-209 varying between 335 and 65 200 pg/L, whereas water total PBDEs concentrations reported in several regions around the world mostly ranged from below 0.1 to 500 pg/L except for effluent samples from wastewater treatment plants of California, which contained a total concentration of PBDEs at 29 023 pg/L (Table 2). For example, the total PBDEs (including BDE-47, -99, -153, and -209) concentrations in marine water collected from the Scheldt Estuary and the North Sea along the Dutch Coast in Europe ranged from 0.1 to 5.6 pg/L with the highest level in the Western Scheldt (*25*). Water samples (~55 L each) collected manually from the 30 cm depth in Izmir Bay, Turkey, contained total PBDEs (sum of BDE-28, -47, -99, -100, -154, -153, and -209) concentrations of 212 and 87 pg/L in the dissolved phase for summer and winter seasons, respectively, and of 271 and 479 pg/L in the particle phase (*26*).

In North America, PBDEs in Lake Ontario surface waters ranged from 4 to 13 pg/L (*27*), with BDE-47 and BDE-99 accounting for more than 70% of total PBDEs. The average total PBDEs (including BDE-47, -99, -100, -153, -154, and -183) concentrations in Lake Michigan water column were 31 pg/L in 1997 and 158 pg/L in 1999 (*14*). The total PBDEs (sum of BDE-17, -28, -47, -66, -85, -99, -100, -138-153, -154, -183, 190, -204, -206, -207, -208, and -209) concentrations in

TABLE 3. Values of K and n Estimated with Eq 3, as Well as Riverine Inputs (kg) of $\sum_{17}$ PBDEs and BDE-209 from Eight Major Outlets of the Pearl River Delta, China

	$\sum_{17}$PBDEs				BDE-209			
outlet	K	n	r^2	input	K	n	r^2	input
Humen	0.0004	2.03	0.86	763	0.00033	2.03	0.86	665
Jiaomen	0.020	1.42	0.93	299	0.021	1.39	0.92	267
Hongqilimen	0.028	1.33	0.65	96.3	0.025	1.33	0.58	85.4
Hengmen	0.195	1.19	0.73	340	0.184	1.17	0.70	290
Modaomen	1.76	0.81	0.68	293	0.93	0.80	0.65	156
Jitimen	2.88	0.60	0.78	26.7	2.81	0.58	0.76	23.2
Hutiaomen	0.16	1.44	0.60	26.4	0.015	1.43	0.59	23.3
Yamen	0.10	1.39	0.40	220	0.106	1.37	0.39	213
Total				2064				1723

San Francisco Estuary water samples ranged from 3 to 513 pg/L with the highest concentration detected around the Lower South Bay of the estuary, which received effluents from a wastewater treatment plant (*14*). In Japan, no hexa-, octa-, or deca-BDE congeners were found in river, estuarine, or marine water samples collected nationwide in 1977, 1987, 1988, 1996, and 2002, whereas BDE-209 was detected in only two out of 114 samples with concentrations of 240 and 590 ng/L in 2003 (*28*). However, the detection limits in that study were 120 ng/L, which were 3 orders of magnitude greater than that employed in the present study. The dissolved and particulate concentrations of PBDEs (sum of BDE-28, -47, -99, -100, -153, -156, -183, and -209) were 31.1−118.7 pg/L and 25.7−32.5 pg/L, respectively, in coastal seawater of Hong Kong, with only trace amounts of BDE-209 detected at five sampling locations (*29*). Thus, the concentrations of BDE-47 and BDE-99 in the PRD were similar to those in the San Francisco Estuary and Izmir Bay, and higher than those in the water column of other regions. However, the BDE-209 concentrations the PRD were 1−3 orders of magnitude higher than those found in other water bodies in the world. Clearly, the concentrations of PBDEs obtained from the present study were generally at the high end of the global values.

Riverine Inputs of PBDEs. Riverine runoff is an important mode to transport anthropogenic pollutants from terrestrial sources to adjacent oceans. In an attempt to constrain such estimates, two different estimation methods were employed.

The first method employed eqs 1 and 2 (*30*) to estimate the monthly and annual inputs for the eight major outlets. Detailed concentration data are summarized in Table S2 and Table 1. The monthly inputs of $\sum_{17}$PBDEs discharged via the eight runoff outlets ranged from 0.21 to 215 kg (Table S2). As far as individual outlets concerned, the eastern outlets (Humen, Jiaomen, Hongqilimen, and Hengmen) in general discharge more PBDEs than the western outlets (Modaomen, Jitimen, Hutiaomen, and Yamen) (Table 1). This can be attributed to the same causes for the concentration pattern discussed previously. The annual input of $\sum_{17}$PBDEs from all the outlets (i.e., from the PRD to the coastal ocean) was estimated at 2140 kg. Among all contributing BDE congeners, BDE-209 was the dominant contributor with an annual input of 1960 kg, i.e., about 90% of the total, followed by BDE-47 and BDE-99 with annual inputs of 13.3 and 11.7 kg, respectively (Table 1).

The second method was based on the relationship between riverine input of PBDE and water flow such that

$$\text{input} = K\,(\text{water flow})^n \tag{3}$$

where K and n are constants (*31*). In the present study, the monthly inputs of PBDEs were regressed against water flows at each riverine outlet. The values of K and n (Table 3) were obtained from a regression analysis of the input and water flow data in Table S3. Because inputs of PBDEs were measured monthly in the present study, water flows available on a daily basis were averaged to obtain average monthly flows. The annual inputs (sum of 12 monthly inputs) of $\sum_{17}$PBDEs and BDE-209 from all the outlets combined were 2064 and 1723 kg, respectively (Table 3).

The annual inputs of $\sum_{17}$PBDEs and BDE-209 estimated by the second method (eq 3) were similar to or lower than those estimated by the first method (eqs 1 and 2). Theoretically, the second method would be more accurate than the first method in estimating annual riverine inputs. However, the parameters used in the second method probably carried large uncertainties, e.g., water flow was a monthly average instead of daily average (because each outlet was sampled monthly for 1 year), and there was a low correlation ($r^2 < 0.4$) for the Yamen Outlet. Consequently, estimation of riverine inputs by the first method should be more reasonable. Because no other measurements of PBDEs inputs from other parts of the world have been conducted, an assessment of global riverine inputs was deemed impossible.

PBDEs as fire retardants are widely utilized in plastics, electronic circuitry, television sets, textiles, and so on. Annual worldwide consumption of PBDEs exceeded 67 125 metric tons in 1999 (*3*). In China, the domestic production of BFRs was approximately 10 000 metric tons in 2000 with the domestic demand of BFRs rising at an annual rate of 8%, and deca-BDE has been one of the most produced BFRs (*1*). The magnitude of PBDEs contamination has substantially increased over the last 20−30 years in the PRD, as demonstrated by vertical profiles of PBDEs in short sediment cores from the Pearl River Estuary (*1*). Based on these considerations and assuming the year-over-year increase of PBDEs input was maintained at 8%, the total input of $\sum_{17}$PBDEs from the PRD to the coastal ocean over the last 20 years was estimated at 22.7 metric tons.

Inflows of PBDEs to China via e-Waste Importation. China has long been one of the significant dismantling and recycling grounds for global obsolete computers and electronic components, and Guangdong Province, where the PRD locates, is the center of imported e-wastes assemblage from which e-wastes are distributed to other provinces such as Hunan, Zhejiang, Shanghai, Tianjin, Fujian, and Shandong (*32*). The amount of wastes imported has maintained a fast-growing pace in recent years. It was reported that approximately 145 million electronic devices (including television sets, computers, and electric fans, etc.) were dismantled or disassembled in Guangdong Province, China, in 2002 (*5*).

A study conducted in 1999 by Stanford Resources projected that in 2001, more than 41 million personal computers would become obsolete in the U.S. (*7*). Experts estimated that more than 500 million obsolete computers in the U.S. would become obsolete between 1997 and 2007, which could result in 2.87 million tons of plastics wastes if every computer contains 6 kg plastic (*7*). It was estimated that BFRs constitute 5−30% of plastics (in weight) (*2*), 10% of BFRs are PBDEs (*7*), and the percentage of the obsolete computers generated in the U.S. that was imported to China was approximately 50−80% (*6*). If the PBDEs content in plastics is 1% and 70% of obsolete computers are assumed to import into China from the U.S., PBDEs imported into China from the U.S. would be approximately 20 000 tons between 1997 and 2007. Actually, computer wastes were estimated to make up only 4.4% of total e-wastes in the U.S. (*33*). If this is true, the total amount of PBDEs entering China via e-waste importation from the U.S. is enormous. In addition, as estimated by the United Nations Environment Program, more than 50 million tons of e-wastes (including mobile phones, TV sets, and computers etc.) were generated worldwide each year (*6*). Assuming that plastics make up 10% of total e-waste weight (plastics make up ∼23% of a computer weight (*33*)) and 70% of the global e-wastes is imported to China, the amount of PBDEs entering China is estimated at about 35 000 metric tons each year.

On the other hand, the annual amount of PBDEs demanded in the global market was estimated at about 67 000 metric tons/year in 1999 and 2001 (*4*). Therefore slightly more than 50% of the total amount of PBDEs generated worldwide may be imported to China in the form of e-waste. The estimated annual inflow (35 000 t/year) is also higher than the domestic production of BFRs (~10 000 metric tons in 2000). These comparisons suggest that the majority of PBDEs inventory in China appears to have been accumulated from the long-term importation of e-wastes and perhaps commercial BFRs products as well, and inflows of e-wastes have been an important source of PBDEs contamination to China's environments. It is worthwhile to note that the riverine input of total PBDEs from the PRD is ~2 metric tons/year, implying that a large portion of PBDEs has remained concentrated locally, e.g., near dismantling or disassembling sites. Nevertheless, PBDEs entering China may partially influence the global oceans' environment as a result of riverine discharge, as demonstrated in the present study, or bioaccumulated into aquatic species such as consumer fish and ultimately flown back to the world markets via fish exportation (*19*). Because importation of e-wastes is still ongoing, the demand for BRFs products in China has remained strong, and the release of PBDEs from electronic and other commercial products is gradual, the impact of PBDEs on China's and the world's environments as well as human health in general is expected to persist for many years to come.

Acknowledgments

This research was financially supported by the National Natural Science Foundation of China (40588001, U0633005, and 40532013) and the "One Hundred Talents" Program of the Chinese Academy of Sciences. We thank Mr. T. S. Xiang for assistance in the GC/MS analysis. We are also grateful to the sampling team consisted of mostly graduate students from the Guangzhou Institute of Geochemistry and Sun Yat-sen University for assistance in field work.

Note Added After ASAP Publication

This paper was published ASAP July 24, 2007 with an error in the first column of Table 2; the correction version was published ASAP July 25, 2007.

Supporting Information Available

Detailed description of sample protocols and estimation of water flows, tables of data, and an additional figure. This material is available free of charge via the Internet at http://pubs.acs.org.

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Received for review April 3, 2007. Revised manuscript received June 12, 2007. Accepted June 13, 2007.

ES070782X