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PBDD/Fs in Surface Sediments from the East River, China

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Abstract The contamination status of polybrominated dibenzo-*p*-dioxins and dibenzofurans (PBDD/Fs) was preliminarily investigated in surface sediments from the East River. The concentrations of eight 2,3,7,8-substituted tetra- to hexa- PBDD/Fs were found to be in the range of 0.32–110 (mean 13) pg g^{-1} and the corresponding TEQ concentrations were 0.087–18 (mean 2) pg I-TEQ g^{-1}. All sediments were characterized by the dominant PBDFs. 2,3,4,7,8-PeBDF was the most important TEQ contributor, accounting for 47%–77% of the total I-TEQ of PBDD/Fs. PCDD/Fs contributed dominantly to the total TEQs of PCDD/Fs, PBDD/Fs and dioxin-like PCBs in most samples except of the sediment from the Shima River. The higher PBDD/F concentrations in the Shima River may be attributed to the use of BFRs in the electrical and electronics industries, which posed a potential risk of dioxins on ecological system.

Keywords PBDD/F · East River · Sediment · Source

Polybrominated dibenzo-*p*-dioxins and dibenzofurans (PBDD/Fs) are considered as a group of toxic environmental contaminants. The physicochemical properties and toxicity of PBDD/Fs are similar to those of PCDD/Fs (WHO 1998). They are mainly released from the processes of usage, manufacturing and recycling of brominated flame retardants (BFRs) and the products containing BFRs (Weber and Kuch 2003; Ren et al. 2008). Concerns of PBDD/Fs have increased because BFRs are extensively added in polymers, paints, textiles and other materials in electrical equipments, furnishings and vehicles. Yet few studies of the PBDD/Fs in environment were reported.

The East River is the major tributary of the Pearl River, which is the third largest river in China. It originates in Jiangxi Province; flows through several cities in Guangdong Province, including Heyuan, Huizhou and Shenzhen, Dongguan and Guangzhou; and finally enters into the South China Sea. In Guangdong Province, the East River is 435 km long, with a basin of 31,840 km^2. It is an important source of water for drinking, agricultural and industrial uses. Most drinking water for Hong Kong and Shenzhen are abstracted from the East River. Increased concerns have been raised by the Chinese public about water quality deterioration in the East River. The East River was heavily contaminated by polybrominated diphenyl ethers (PBDEs), and BDE209 was the predominant congener with an average concentration of 1,440 ng g^{-1}, one of the highest concentrations ever reported worldwide (Mai et al. 2005). Higher pollution levels of PAHs, PBDEs and PCDD/Fs were found in environment in Guangzhou and Dongguan (Fu et al. 2003; Mai et al. 2005; Ren et al. 2007a). In the East River basin, the main industries related to dioxins are electrical and electronics manufacture and waste incinerators. Dongguan has become the world's largest manufacturing base for electronics/electrical products. The electrical and electronics industry may pose a potential risk of PBDD/F pollution because of the wide usage of BFRs in electrical products (Hanari et al. 2006; Wichmann et al. 2002).

The present study aims to assess the contamination status of PBDD/Fs in surface sediments from the East River, the characteristics of PBDD/Fs, and preliminarily investigate the sources of PBDD/Fs.

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Materials and Methods

Sampling locations are shown in Fig. 1. Nine sediments were sampled along the East River in April 2007. Surface sediments (about 5 cm in depth) were collected with a grab sampler (Ekman grab, Wildlife Supply Company, Buffalo, USA) and placed in pre-cleaned glass bottles. The top 5 cm layer of sediments was expected to represent the modern inputs. The samples were stored at −20°C until analysis.

Detailed descriptions of the sample extraction and fractionation procedures have been reported elsewhere (Li et al. 2008a). Briefly, sediment samples were freeze-dried and 10–30 g dry samples were spiked with ^{13}C-labeled surrogate standards (EDF-5071) prior to the 24 h Soxhlet extraction with toluene. All extracts were concentrated to 1 mL with a rotary evaporator. Sample cleanup was accomplished successively with acid silica gel slurry, multi-layer silica gel column and florisil column. Five grams of florisil was used for separating PCBs and interferences especially PBDEs from the analytes with 100 mL hexane, and then PBDD/Fs were collected with 80 mL 60:40 (v/v) dichloromethane (DCM): hexane and 80 mL DCM. Recovery standards (ED-5073) were added prior to GC injection.

Identification and quantification were performed with HRGC/HRMS (Trace GC 2000 and Finnigan MAT 95 XP) in positive electron impact (EI+) mode at the resolution >10,000. A DB-5 ms column (J&W Scientific, CA, 30 m, 0.25 mm ID, 0.1 mm film) was used. Oven temperature program was as follows: from 150°C (2 min) to 220°C at a rate of 40°C/min, then to 300°C (5 min) at a rate of 7.4°C/min. PCDD/Fs and dioxin-like PCB in the sediments were also determined according to the analytical method reported elsewhere (Ren et al. 2006, 2007b).

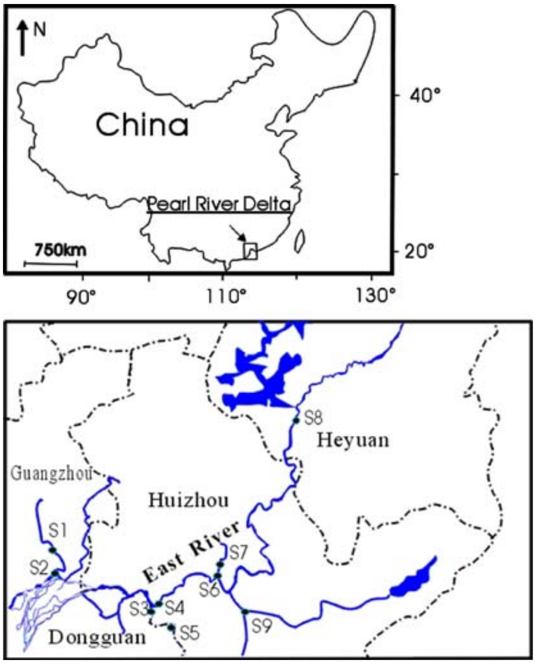

Fig. 1 Sampling stations in the East River, China

The recoveries of all the labeled compounds were 50%–110%. The detection limits were quantified as three times of the standard deviations for the mean concentration in the blanks, which were 0.05–0.3 pg g^{-1} for PBDD/Fs, 0.1–0.8 pg g^{-1} for PCDD/Fs and 0.05–0.6 pg g^{-1} for dioxin-like PCBs, respectively.

Results and Discussion

Because the toxic equivalency factors (TEFs) have not been determined for PBDD/Fs, the I-TEFs of PCDD/Fs were used for the corresponding congeners of PBDD/Fs to calculate their toxicity, which was suggested by WHO (WHO 1998). The concentrations of PBDD/Fs in sediments are shown in Table 1. The total concentrations of eight 2,3,7,8-substituted tetra- to hexa- PBDD/Fs in the surface sediments were found to range from 0.32 to 110 (mean 13) pg g^{-1} dw, while the corresponding TEQ concentrations were in the range of 0.087–18 (mean 2) pg g^{-1}. 1,2,3,7,8,9-HxBDD was not detectable in all samples in this study. Higher concentration of PBDD/Fs was found in the sediment at site 3 (S3) from the Shima River in Dongguan City.

Figure 2 showed the congener profile of PBDD/Fs in the sediments. PBDFs were found obviously in much higher concentrations than PBDDs, accounting for 87%–99% of the total 2,3,7,8-PBDD/Fs, in accordance with previously reported data of PBDD/Fs in the air (Li et al. 2007, 2008b; Wang et al. 2008). The correlation analysis reveals that PBDD/Fs concentrations were significantly correlated with PBDFs concentrations ($R = 0.99$). PBDFs were the main thermal reaction products and the main byproducts of BFRs such as tetrabromobisphenol A (TBBPA) and PBDEs (Gullett et al. 2007; Hanari et al. 2006; Wichmann et al. 2002).

2,3,4,7,8-PeBDF was the most important TEQ contributor, contributing 47%–77% of the total I-TEQ of PBDD/Fs, which was also found in air around electric waste dismantling area (Li et al. 2007) and in air of Shanghai, China (Li et al. 2008b). A significant correlation was found between the total TEQ concentrations of PBDD/Fs and the TEQ concentrations of 2,3,4,7,8-PeBDF ($R = 0.999$), showing 2,3,4,7,8-PeBDF could be possibly considered as an indicator isomer for faster evaluating the contamination status of PBDD/Fs in sediments from the East River ($y = 2.2359x - 0.0726$, where y is the TEQ concentration of PBDD/Fs and x is the TEQ concentration of 2,3,4,7,8-PeBDF).

Table 1 Concentrations (pg g^{-1}) of PBDD/Fs, PCDD/Fs and dioxin-like PCBs in the sediments from the East River, China

Sample locations	S1	S2	S3	S4	S5	S6	S7	S8	S9
2378-TBDF	0.55	0.17	82	0.21	0.063	0.89	1.0	0.26	0.80
12378-PeBDF	0.31	0.28	10	0.13	0.11	0.69	0.71	0.10	1.1
23478-PeBDF	0.25	0.17	16	0.13	0.13	0.60	0.60	0.16	0.65
2378-TBDD	0.074	0.029	1.0	0.027	0.0082	0.045	0.064	0.034	0.063
12378-PeBDD	0	0	0	0	0	0.10	0.13	0	0.085
123478/123678-HxBDD	0	0	0	0	0	0.17	0	0	0
123789-HxBDD	0	0	0	0	0	0	0	0	0
Σ8 PBDD/Fs	1.2	0.66	110	0.50	0.32	2.5	2.6	0.55	2.7
Σ17 PCDD/Fs	3,675	1,708	3,768	3,146	2,718	5,282	2,733	4,685	2,487
Σ12 Dioxin-like PCBs	140	240	270	48	87	63	100	81	150
Σ8 PBDD/Fs/Σ17 PCDD/Fs (%)	0.03	0.04	3	0.02	0.01	0.05	0.09	0.01	0.1
I-TEQ (PBDD/Fs)	0.27	0.15	18	0.12	0.087	0.54	0.57	0.15	0.56
I-TEQ (PCDD/Fs)	11	8.0	12	4.9	5.3	7.1	4.3	6.1	5.2
WHO_{98}-TEQ (PCB)	0.16	0.39	0.45	0.042	0.13	0.12	0.21	0.046	0.15
Total TEQ	11	8.5	30	5.1	5.5	7.8	5.1	6.3	6.0
TEQ (PBDD/Fs) (%)	2	2	58	2	2	7	11	2	9
TEQ (PCBs) (%)	1	5	1	1	2	2	4	1	3

Concentrations lower than the detection limits were set to zero

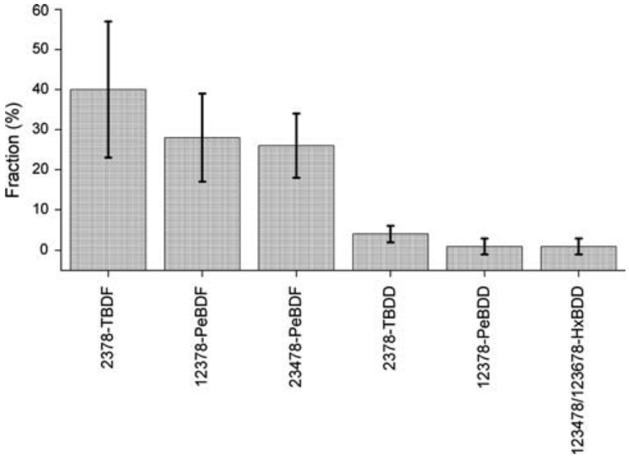

Fig. 2 Congener profile of PBDD/Fs in the sediments from the East River, China (1,2,3,7,8,9-HxBDD were undetectable)

The corresponding data of PCDD/Fs and dioxin-like PCBs in these sites were also shown in Table 1. The sum of TEQs of PCDD/Fs, PBDD/Fs and dioxin-like PCBs were in the range of 5.1–30 (mean 10) pg g^{-1}. The American guidelines specified a value for dioxins in sediment, quoted as TCDD toxicity equivalents, was a ‘high risk to sensitive species’ of 25 pg TEQ g^{-1} (US EPA 1993). Using the American value, the site 3 with 30 pg TEQ g^{-1} was above the guideline and it can be predicted that adverse biological effects were likely to occur.

The concentrations of PBDD/Fs were much lower than those of PCDD/Fs, the former only accounted for 0.01%–0.1% of the later, and the TEQ concentrations of PBDD/Fs were only 2%–11% of the total TEQ, exception of the sample at site 3. Dioxin-like PCBs contributed only 1%–5% of the total TEQs. It can be concluded that PCDD/Fs contributed dominantly to the total TEQs at most sites in this study. Considering that the concentrations of PCDD/Fs were not high, we think that the concentrations of PBDD/Fs were also not high in sediments from most sites in this study.

The TEQ concentrations of PBDD/Fs were, respectively, 0.27 and 0.15 pg TEQ g^{-1}, accounting for only 2% of the total TEQ at site 1 and 2 in Guangzhou City. Differently, the average I-TEQ concentration of seventeen 2,3,7,8-PCDD/Fs and eight 2,3,7,8-PBDD/Fs was, respectively, 0.36 pg m^{-3} and 0.23 pg m^{-3}, PBDD/Fs contributed about 40% of the total TEQ in air from Tianhe district of Guangzhou City where is close to site 1 and site 2 (Li et al. 2007). Guangzhou, the capital of Guangdong Province, is a highly populated urban center, housing heavy industrial and commercial activities. The differences of the levels of PBDD/Fs in sediments and air from close sites may be partially attributed to the less stability of PBDD/Fs than PCDD/Fs (Chatkittikunwong and Creaser 1994; Lenoir et al. 1991). A significant correlation was not found between the concentrations of PBDD/Fs and PCDD/Fs, indicating that the main sources of PBDD/Fs were different from those of PCDD/Fs, exception of the sediment from site 3.

The concentration of PBDD/Fs in the sediment from the Shima River (S3) in Dongguan City was 110 pg g^{-1}, and the TEQ was 18 pg g^{-1}, accounting for 58% of the total TEQ. We speculated that the higher PBDD/F concentrations in the Shima River may be attributed to the use of BFRs in the electrical and electronics industries, which contributed to direct PBDD/F emission into the environment (Hanari et al. 2006; Wichmann et al. 2002). Municipal solid waste incinerators (MSWIs) and industrial waste incinerators (IWIs) were likely the minor sources because the TEQ ratios (in percentage) of the PBDD/F to the PCDD/F concentration were 0.72% and 5.4% in the stack flue gases of the MSWIs and the IWIs (Wang and Chang-Chien 2007). In addition, there were a yew MSWIs and IWIs in the studied areas. 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, the electrical industry posed a potential risk of PXDD/Fs on ecological system. A little dam with a height of 1 m has been built to make particles and hydrophobic pollutants deposit in the river. But the soluble hazardous substances can flow into the main steam of the East River because of the high content of total organic carbon in the Shima River. More concerns were suggested to the environmental safe of the Shima River.

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