

# **Release of polybrominated diphenyl ethers from wastewater in China**

Xianzhi Peng, Caiming Tang, Yiyi Yu, Jianhua Tan, Qiuxin Huang, Shejun Chen,  
Bixian Mai

State Key Laboratory of Organic Geochemistry, Guangzhou Institute of Geochemistry,  
Chinese Academy of Sciences, Guangzhou 510640, China

## **Introduction**

Polybrominated diphenyl ethers (PBDEs) are a class of flame retardants that were added to thousands of consumer products, such as thermoplastics, electronic equipment, and textiles (Hale et al., 2001). Research has revealed that municipal sewage could be a significant source of PBDEs contamination that is ubiquitous throughout the environment (North, 2004; Song et al., 2006). The Pearl River Delta (PRD) is one of the largest manufacturing bases of electronic products and also one of the largest dumping sites of e-wastes in China. Previous reports have demonstrated significant PBDE pollution in air, sediment, water, biota, and soil in the PRD (Chen et al., 2006; Mai et al., 2005; Guan et al., 2007; Guo et al., 2007). In this study, a detailed investigation of PBDEs was conducted in municipal sewage from the PRD to estimate potential discharge of the PBDEs into the environment through sewage.

## **Materials and methods**

Sampling campaigns were conducted in two sewage treatment plants (GZSTP-A and GZSTP-B) located in Guangzhou, the biggest city in the PRD. Raw influent, effluents from outlets of major treatment steps, pretreatment solids, thickened sludge, and dewatered sludge were collected. The GZSTP-A has a designed capability of 30,000 m<sup>3</sup> d<sup>-1</sup> and serves a population of about 0.45 million. It treats a mixture (~6:4) of domestic and industrial wastewater mainly from chemical, food, automobile, and electronic manufacturers. The GZSTP-B serves a population of 2.5 million and handles wastewater from household (~90%) and business, with a total capacity of

330,000 m<sup>3</sup> d<sup>-1</sup>.

Sample treatment followed the procedures described in detail previously (Mai et al., 2005). Briefly, water samples were filtered through 0.7 µm glass fiber filters (Whatman, Maidstone, England), spiked with <sup>13</sup>C PCB 141, and passed through glass columns packed with XAD-2:XAD-4 resin (1:1 in volume). The resin was eluted three times with methanol, followed by three ultrasonic extractions with a mixture of dichloromethane (DCM) and methanol. The extracts were combined and then liquid–liquid extracted using DCM. The DCM extract was cleaned up on a complex acidic–basic–neutral silica/alumina column. The PBDEs were eluted with a mixture of hexane and DCM (1:1). The suspended particulate matter (SPM) collected on glass fiber filters and sludge samples were freeze-dried. The SPM and homogenized sludge samples were accurately weighed before being spiked with <sup>13</sup>C PCB 141 and soxhlet-extracted with a mixture of acetone and hexane. The extracts were cleaned up as described above. <sup>13</sup>C-PCB 208 was added as internal standard prior to instrumental analysis.

Seventeen congeners from tri- to deca-BDEs (including BDEs-28, -47, -66, -85, -99, -100, -153, -154, -183, -196, -197, -203, -205, -206, -207, -208, and -209) were analyzed by GC-MS using negative chemical ionization (NCI) in the selected ion monitoring (SIM) mode. Instrumental condition and analyte identification were detailed elsewhere (Mai et al., 2005).

The mass loading (ML) was calculated as:  $ML = Q \times C$ , where  $Q$  denotes the flow rate of wastewater (m<sup>3</sup> d<sup>-1</sup>) or daily production of sludge (kg d<sup>-1</sup>) and  $C$  refers to the PBDE concentration in wastewater (µg m<sup>-3</sup>) or sludge (µg kg<sup>-1</sup>), respectively.

## **Results and discussion**

The total concentrations of PBDEs (Σ17PBDEs) in raw sewage varied substantially from 13.3 to 2496.4 ng L<sup>-1</sup>, depending on the types and the SPM contents of the wastewater, in which the sum of BDEs-47, -99, and -209 represented 87.6 to 99.5%. The results were comparable to that of the Canadian wastewater ( Rayne and

Ikonomou, 2005). However, the concentrations of lower brominated congeners (i.e. BDEs-47, -99, and  $\Sigma 10$ PBDE) were generally less than 10% of those reported for the Canadian wastewaters, which may be ascribed to the much greater usage of penta-formulation PBDEs in North America (North, 2004; Song et al., 2006). The PBDE concentrations decreased sharply along the treatment in the STPs. The  $\Sigma 17$ PBDEs in the treated effluents ranged from 0.9 to 4.4 ng L<sup>-1</sup>, closely associated with the SPM contents, despite the size and treatment techniques of the STPs. BDE-209 was the predominant congener in wastewaters, accounting for 80.5% and 89.1% of the  $\Sigma 17$ PBDEs in the treated effluents and the influents respectively, followed by BDEs-47 and -99. The congener patterns agree well with the PBDE production pattern in Asia that deca-BDEs represent ~90% of the total PBDEs (Wang et al., 2007). However, they are quite different from those of wastewaters in North America, in which BDEs-47 (21.5 to 36.1%) and 99 (12.1 to 38.6%) were dominant congeners, while BDE-209 represented only 6.0 to 37.2% of the total PBDEs (North, 2004). This difference may be attributed to the different usage pattern.

The concentrations of  $\Sigma 17$ PBDEs in sludges were in the range of 158 to 23,750 ng g<sup>-1</sup> dry weight. BDE-209 was the most abundant congener and represented ~90% of the  $\Sigma 17$ PBDEs in the sludges of both STPs. These PBDE patterns appeared quite different from those reported for sludges in North America that BDE-209 accounted for only 27–35% of the total PBDEs (Hale et al., 2001; Knoth, 2004), but similar to reports for sludges in Europe (Eljarrat et al., 2008) and Kuwait (Gevao et al., 2008).

The estimated PBDEs releases were 0.1 and 1.74 (1.30–2.18) g d<sup>-1</sup> through the treated effluents from the two STPs respectively. This appears lower than those from the STPs with similar capacities in North America. The PBDEs releases through the dewatered sludge were estimated to be 0.9 and 213.2 (90.0–336.3) g d<sup>-1</sup> from the GZSTP-A and GZSTP-B, respectively. Furthermore, a certain amount of PBDEs might be removed with the pretreatment solids. A total of about 2280 kg of PBDEs per year might be released into the Pearl River with wastewater from the PRD, revealing that wastewater from the PRD is a significant contributor of PBDEs to the Pearl River and thus the Pearl River Estuary and the coastal South China Sea.

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