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Emission patterns and risk assessment of polybrominated diphenyl ethers and bromophenols in water and sediments from the Beijiang River, South China

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ABSTRACT

To reveal the emission patterns of brominated flame retardants (BFRs) in the Beijiang River, South China, concentrations of polybrominated diphenyl ethers (PBDEs) and phenolic BFRs (2,4,6-tribromophenol (TBP), pentabromophenol (PeBP), tetrabromobisphenol A (TBBPA)), and bisphenol A (BPA) in water and sediments were simultaneously measured, and the geographic information system (GIS) were applied to analyse their emission patterns. Results showed that PBDEs, TBP, PeBP, TBBPA and BPA were ubiquitous in the water and sediment samples collected from the Beijiang River. However, most of the concentrations were very low or below the detection limits (DL). In water, Σ_{20}PBDEs (sum of all 20 PBDEs congeners) levels ranged from < DL to 232 pg L^{-1}, with the predominant congeners containing low bromine contents. The levels of TBP, PeBP, TBBPA and BPA in water were lower than 810 pg L^{-1}. In sediments, Σ_{20}PBDEs varied from 260 to 5640 pg g^{-1} dry weight (d.w.), with the predominant congeners containing high bromine contents. The levels of TBP, PeBP, TBBPA and BPA were lower than 600 pg g^{-1} d.w.. Risk assessments indicated that the water and sediments at the sampling locations imposed no estrogenic risk ($E_2EQ < 1.0$ ng E_2 L^{-1}), and the eco-toxicity assessment at three trophic levels also showed no risk at all sampling sites in water ($RQ_{Total} < 1.0$), but with a potential eco-toxicity at some sampling points in sediments ($1.0 < RQ_{Total} < 10.0$).

1. Introduction

Brominated flame retardants (BFRs) are organic chemicals that contain bromine, which are used to increase the fire resistance of consumer and industrial products. These compounds are ubiquitously found in a variety of materials including textiles, furniture and electronics and so on (WHO/ICPS, 1994, 1997). The most used BFRs are polybrominated diphenyl ethers (PBDEs), tetrabromobisphenol A (TBBPA), polybrominated biphenyls (PBBs) as well as hexabromocyclododecane (HBCD) (Covaci et al., 2003). Although some of BFRs have been banned recently (BSEF, 2014) or are restricted in use due to their persistence, toxicity and bioaccumulation, they are still often detected in various environmental matrices (An et al., 2011a; Chen et al., 2009; Xiong et al., 2015) and biota (Cruz et al., 2015; He et al., 2012; Sun et al., 2015), even in humans (Covaci et al., 2003; Wang et al., 2015a). Because of their continued presence in the environment, their emission patterns were monitored frequently. Such researches provide us with the evidence for the need of a better understanding of the current uses of these pollutants and their risks in the environment (Klecka et al., 2010).

PBDEs are an important group of BFRs that have been used extensively as additives in materials such as textiles, electronic appliances and other consumer products over recent decades (Li et al., 2015; Stiborova et al., 2015). The commercially available

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PBDEs mixtures divided into three products (PentaBDE, OctaBDE and DecaBDE), according to the average number of bromine atoms in the molecule, were produced globally in the past few decades. The PentaBDE and OctaBDE commercial products have been added into the list of emerging persistent organic pollutants (POPs) by the Stockholm Convention in May 2009 due to their high persistence, bioaccumulation and toxicity (PBT) (UNEP, 2009), while DecaBDE commercial products are banned in Europe and USA, but still used in China (Besis and Samara, 2012). With regard to PBDEs in China, it is important to monitor their emission patterns for a better understanding of their fate and environmental risks. As the largest electronic and telecommunication equipment manufacturing base, high levels of PBDEs pollution have been widely detected in the environments of the Pearl River Delta (PRD), including the atmosphere, water, sediments and organisms (Chen et al., 2013; He et al., 2012; Sun et al., 2014; Wang et al., 2014; Zhang et al., 2009). Several studies have been carried out on water and sediments in the Dongjiang River, the Pearl River, the Xijiang River, the PRD estuary and the coastal areas (Chen et al., 2009, 2013; Feng et al., 2012; Zhang et al., 2015). These studies mainly concerned on the levels, distribution and composition profiles of PBDEs. The information will be useful for a better understanding of the current uses of these chemicals and the risks imposed by their presence in the environments. However, the emission patterns and risk assessment of PBDE pollution were rarely attempted.

TBBPA, TBP and pentabromophenol (PeBP) are also widely used in a wide range of industries, such as textile, electronic and car producers (Polo et al., 2006). TBP may also be formed as a by-product of TBBPA, either in its photo-oxidation, chemical oxidation and biodegradation in water and sediments (An et al., 2011b; Wang et al., 2015b) or from the decomposition of plastics (Polo et al., 2006). In contrast to PBDEs, TBBPA is used primarily as a reactive flame retardant which is covalently bound to polymers and thus less easily released into the environment (de Wit et al., 2010). However, both additive and reactive TBBPA can be released into the environment from products which has been frequently detected in air, water, sediments, soil and human tissues (Nakao et al., 2015; Ni and Zeng, 2013; Wang et al., 2015a; Xiong et al., 2015). Several studies have demonstrated the toxic properties of TBBPA, including endocrine-disrupting activity, immunotoxicity, and neurotoxicity (Decherf et al., 2010; Hendriks et al., 2014; Nakajima et al., 2009).

Bisphenol A (BPA), another environmental estrogen and an endocrine disruptor, is a synthetic chemical primarily used to produce polycarbonate plastics and epoxy resins (Cooper et al., 2008; EC, 2003; Melnick et al., 2002). Due to the diverse uses of BPA in consumer products, it has been regularly detected in a wide range of environmental matrices, including air, water, sewage sludge and sediments (Huang et al., 2012; Lee et al., 2013; Xiong et al., 2015), even human blood and tissues (Vandenberg et al., 2010; Zhang et al., 2013). Several studies have reported that BPA is a potential endocrine disruptor (Rogers et al., 2013; Vandenberg et al., 2010).

This study aims to examine the emission patterns of PBDEs, TBBPA, TBP, PeBP and BPA in water and sediment samples from the Beijiang River, and to assess the associated risks of these pollutants to the ecosystems. These data, which have been previously unavailable, will be useful for a better understanding of the current uses of these chemicals and the risks imposed by their presence in the environments.

2. Materials and methods

2.1. Materials

Standards of 20 PBDEs, TBP, PeBP, TBBPA and BPA were obtained from AccuStandard Inc. (New Haven, CT). Surrogates, including ^{13}C-PCB141, ^{13}C-TBP, ^{13}C-TBBPA and ^{13}C-BPA were purchased from Cambridge Isotope Laboratories, Inc. (Andover, MA).

All solvents were high-performance liquid chromatography grade from CNW technologies (ANPEL Scientific Instrument Co., Ltd, Shanghai, China). LC-C_{18} (40–63 μm) and SAX sorbents were also supplied by CNW technologies. Oasis MAX (150 mg, 6 cc) cartridges were purchased from Waters Corp. (Milford, MA). LC-Florisil cartridges (1 g, 6 cc) and silylating reagent bis(-trimethylsilyl)trifluoroacetamide/trimethychlorosilane (BSTFA:TMCS, 99:1, v/v, Supelco-33148) were from Sigma-Aldrich (Louis, MO). Neutral alumina (mesh size 100–200) and silica sorbents (mesh size 300–400) were provided by Sinopharm Chemical Reagent Co., Ltd (Shanghai, China) and used after Soxhlet extraction, activated (450 °C for 4 h) and deactivated (1.5% of distilled water deactivated).

2.2. Study area and sample collection

The Beijiang River, with a runoff volume of 4.82×10^{10} m^3 year^{-1}, is the second largest branch of the Pearl River (Chen et al., 2009). There are two electronic waste dismantling regions located in the upstream area of the Beijiang River. In addition, the rivers run through the urban, rural, industrialized and less-industrialized areas. Thus this river was likely subject to pollution of PBDEs, TBP, PeBP, TBBPA and BPA. A total of fifteen water samples were collected using pre-cleaned brown glass containers from the River in April 2014, and thirteen surface sediments were collected using pre-cleaned stainless steel containers and the stainless steel static gravity corer (8 cm ID) was employed to ensure the undisturbance of the surface sediment layer (Fig. S1 and Table S1; "S" indicates tables and figures in the Supplementary Material (SM) afterwards).

2.3. Pretreatment procedure and instrument analysis

2.3.1. Pretreatment

Water samples were filtered within 24 h with pre-baked (450 °C, 4 h) GF/F filters (142 mm, ø). Then a volume of 0.5 L of sample filtrate was used to determine target pollutant concentrations. Filtrate for further experiments was first spiked with recovery surrogates (^{13}C-PCB141 (20 ng), ^{13}C-TBP (40 ng), ^{13}C-BPA (40 ng), and ^{13}C-TBBPA (160 ng)) and left overnight for the equilibration. Then, the sample was extracted using the solid phase extraction (SPE) method according to our previous publication (Li et al., 2016; Xiong et al., 2015). A brief description of the SPE is provided in the SM. Mixed extracts were then dried under a gentle nitrogen stream and derivatized using 100 μL of BSTFA:TMCS at 60 °C for 1 h just before the analysis. This derivation step was formatted with bis-trimethylsilyl (TMS_2). For sediment, five gram sieved sample (200 mesh) was spiked with recovery surrogates and then ultrasonically extracted with 20 mL of hexane/acetone (1:1, v/v) for 40 min. During the extraction, HCl-activated copper granules were added to the sample to remove elemental sulfur. The sample was centrifuged (1000 rpm, 5 min) and the supernatant was collected. This extraction process was repeated twice. All the three extracts were then combined and concentrated to 1 mL under a gentle nitrogen stream, and then cleaned up (Xiong et al., 2015).

2.3.2. GC/MS analysis

Sample analysis of PBDEs was performed as our previous publication (Xiong et al., 2015). A brief description of the instrumental method is provided in the SM. Analysis of the derivatized TBP, PeBP and TBBPA was performed using Agilent 7890A gas chromatograph (GC) coupled with an Agilent 5975C mass spectrometer (MS) using

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