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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 negative chemical ionization (NCI) in selective ion-monitoring mode, equipped with a HP-5 ms (30 m × 0.32 mm, 0.5 μm film thickness) column. Ion fragments *m/z* 329.7 and 331.8 were monitored for TBP, *m/z* 335.7 and 337.8 for ^{13}C-TBP, *m/z* 607 and 609 for TBBPA, and *m/z* 619 and 621 for ^{13}C-TBBPA. The analysis of the derivatized BPA was performed according to our previous study (An et al., 2011b). Ion fragments *m/z* 357.2 and 372.2 were monitored for BPA, and *m/z* 369.2 and 384.2 for ^{13}C-BPA.

2.4. QA/QC

The method limits of detection (LOD) were in the range of 10 to 70 pg L^{-1} water using a sample size of 0.5 L for all compounds, while varied from 1 to 7 pg g^{-1} sediment using a sample size of 5 g. A detailed description of the method limits of detection is provided in the SM (Table S2). No objective analytes were detected in the procedural blanks. Surrogate recoveries in all samples were 82.53 ± 9.27% for ^{13}C-PCB141, 86.65 ± 18.51% for ^{13}C-TBP, 81.86 ± 12.89% for ^{13}C-TBBPA and 91.00 ± 7.67% for ^{13}C-BPA, respectively. Recoveries of 20 PBDEs congeners ranged from 83.14 to 115.30% (relative standard deviations <15.5%) in three spiked blank samples and from 85.47 to 109.21% (relative standard deviations <11.6%) in three spiked matrix samples. TBP, PeBP, TBBPA and BPA recoveries varied from 83.21 to 104.91% (relative standard deviations <9.2%) in three spiked blank samples and from 74.65 to 121.32% (relative standard deviations <13.7%) in three spiked matrix samples. Reported concentrations were not corrected by the surrogate recovery.

2.5. Data analysis

Statistical analysis was performed using Microsoft Excel 2010 and the Statistical Package for Social Sciences v18.0 software (SPSS In., IL, USA). The emission pattern map of BFRs in each river sub-basin was performed using software ArcGIS ver. 10.2 based on the concentrations of BFRs. The study area was divided into 15 sub-basins.

2.6. Risk assessment

2.6.1. Estrogenic activity assessment

Endocrine-disrupting activity of TBBPA and BPA in water was calculated using Eq. (1) (Sun et al., 2013).

$$E_2EQ = E_2EF \times MEC \tag{1}$$

where E_2EQ represents 17β-estradiol equivalency; E_2EF represents the estrogenic equivalency factor of TBBPA (0.45×10^{-6}) and BPA (13.7×10^{-6}) (Kitamura et al., 2005); MEC is the measured environmental concentration (ng L^{-1}) of each organics. For sediments, it was assumed that pore water is the primary exposure route for organisms. MEC was based on pore water concentration, calculated using the equilibrium partitioning approach in Eq. (2) (Ditoro et al., 1991):

$$C_{pw} = \frac{C_s}{f_{oc}K_{oc}} \tag{2}$$

where C_{pw} is the estimated pore water concentration (ng L^{-1}); C_s is the measured sediment concentration (ng g^{-1}); f_{oc} (=0.1) is the fraction of organic carbon in sediment (Cristale et al., 2013a); and K_{oc} is the partition coefficient for sediment organic carbon, predicted using Advanced Chemistry Development (ACD/Labs) Software.

The total E_2EQ of TBBPA and BPA was calculated using Eq. (3) based on E_2EQ of single estrogenic activity (Sun et al., 2013):

$$E_2EQ_{Total} = \Sigma E_2EQ_i = E_2EQ_{TBBPA} + E_2EQ_{BPA} \tag{3}$$

2.6.2. Eco-toxicity assessment

Eco-toxicity of target compounds in water and sediments was assessed using the risk quotient (RQ) on non-target organisms (Cristale et al., 2013b; Sánchez-Avila et al., 2012). At three trophic levels, LC_{50} or EC_{50} for fish, daphnia and green algae associated with PBDEs, TBP, PeBP, TBBPA and BPA were used for RQ calculation as Eq. (4) (Cristale et al., 2013b):

$$RQ = \frac{MEC}{PNEC} = \frac{MEC}{EC_{50} \text{ or } LC_{50}/f} \tag{4}$$

where PNEC is the predicted no effect concentration (mg L^{-1}), estimated as a quotient of toxicological relevant concentration (EC_{50} or LC_{50}) with a security factor ($f = 1000$). The software program ECOSAR (Ecological Structure Activity Relationships), recommended by U.S. EPA, was used to estimate the relative data, and the values of EC50 or LC50 for fish, daphnia and green algae for PNEC calculation were provided in the SM (Table S3), due to some EC_{50} and LC_{50} data are not found in the literature (Cristale et al., 2013a; Sánchez-Avila et al., 2012). For sediment, MEC was also estimated using Eq. (2) based on pore water. A sum of RQs was obtained from Eq. (5) (Cristale et al., 2013a).

$$RQ_{Total} = \Sigma RQ_i \tag{5}$$

3. Results and discussion

3.1. Emission patterns of PBDEs

Emission of PBDEs in water of the Beijiang River is summarized in Table S4. Σ_{20}PBDEs (defined as the sum of all targeted PBDE congeners) varied from < DL to 232 pg L^{-1} with a mean concentration of 96 pg L^{-1}. These levels were lower than those found in the other rivers from the Pearl River Delta (PRD), in which the Σ_{17}PBDEs concentrations, referring to the sum of BDE-28, -47, -66, -85, -99, -100, -138, -153, -154, -183, -196, -197, -203, -206, -207, -208 and -209, ranged from 0.34 to 68 ng L^{-1} (Guan et al., 2007), while they were in line with those in the Dongjiang River (He et al., 2012) and the Pearl River Estuary (Chen et al., 2011; Luo et al., 2008). The emission pattern map of this study is shown in Fig. 1a. It can be seen that there were large differences in Σ_{20}PBDEs emission among the sub-basins. The Qingyuan City (ID: S7) and Jiangkou Town (ID: S9) received the largest release of Σ_{20}PBDEs with the total up to 220 and 232 pg L^{-1}, respectively. By contrast, the Wangbu Town (ID: S14) received the lowest Σ_{20}PBDEs release of about < DL.

In sediments, the levels of PBDEs are summarized in Table S5. PBDEs were ubiquitous in all sediments collected from the Beijiang River, suggesting widespread influences across the studied region. Σ_{20}PBDEs in sediments varied from 0.26 to 5.64 ng g^{-1} dry weight (d.w.) with an average concentration of 2.90 ng g^{-1} d.w.. In contrast, Σ_{20}PBDEs measured in the Beijiang River sediments were much lower than those found in sediments from the other rivers of the PRD. Mai et al. collected 66 surface sediment samples from the PRD and adjacent South China Sea and analyzed 10 PBDEs congeners (BDE-28, -47, -66, -100, -99, -154, -153, -138, -183, and -209) (Mai et al., 2005), with the concentrations of BDE-209 and ΣPBDEs (defined as the sum of all targeted PBDE congeners except for BDE-

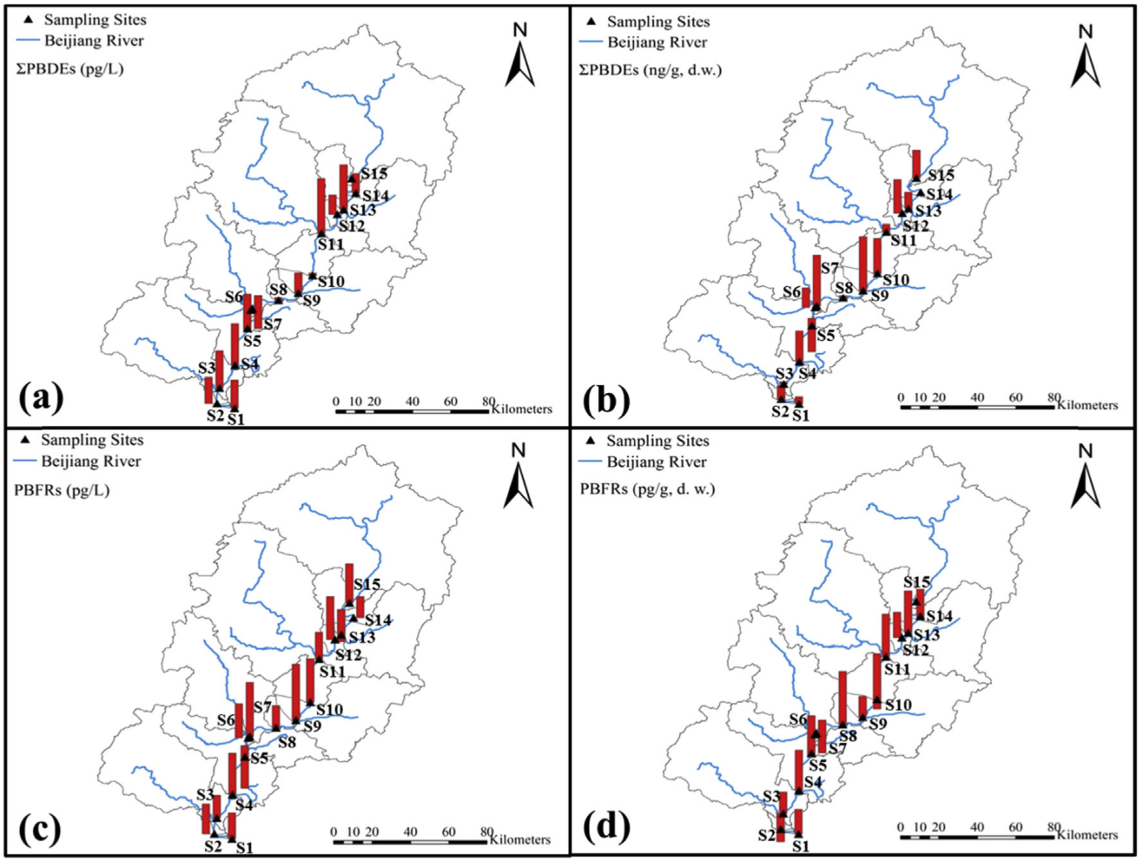

Fig. 1. Map of the study area showing the brominated flame retardants (BFRs) emission in each river sub-basin. (a) The environmental emission of Σ_{20}PBDEs (defined as the sum of all targeted PBDE congeners) in water for each sub-basin with the unit of pg L^{-1}; (b) The environmental emission of Σ_{20}PBDEs in sediments for each sub-basin with the unit of ng g^{-1}, d.w.; (c) The environmental emission of phenolic brominated flame retardants (PBFRs) (contained the sum of 2,4,6-tribromophenol, pentabromophenol, tetrabromobisphenol A and bisphenol A) in water for each sub-basin with the unit of pg L^{-1} and (d) The environmental emission of PBFRs in sediments for each sub-basin with the unit of pg g^{-1}, d.w.. Sub-basin IDs: S1. Sanshui District; S2. The confluence of the Xijiang River and the Beijiang River; S3. The confluence of the Suijiang River and the Beijiang River; S4. Lubao Town; S5. Shijiao Town; S6. The confluence of the Longtan River and the Beijiang River; S7. Qingyuan City; S8. The upstream of Qingyuan City; S9. Jiangkou Town; S10. Feilaixia scenic dam; S11. Lixi Town; S12. The confluence of the Lianjiang River and the Beijiang River; S13. Dazhan Town; S14. Wangbu Town; S15. The upstream of Whitehead hub.

209) varying from 0.4 to 7340 and from 0.04 to 94.70 ng g^{-1} d.w., respectively. During 2009–2010, Chen et al (Chen et al., 2013). also collected surface sediments from the PRD and analyzed 16 PBDEs congeners (BDE-28, -47, -66, -100, -99, -154, -153, -138, -183, -197, -203, -196, -208, -207, -206, and -209), with the Σ_{16}PBDEs (defined as the sum of all the 16 targeted PBDE congeners) in sediments from different water systems (Dongjiang River, Zhujing River, Beijiang River, Xijiang River, and Pearl River Estuary) ranging from 3.67 to 2520 ng g^{-1} d.w. (average of 17.1–588 ng g^{-1} d.w.). The emission pattern map for sediments of the study is shown in Fig. 1b. It can be seen that there were large differences in Σ_{20}PBDEs emission among the sub-basins. The Lixi Town (ID: S11) and Dazhan Town (ID: S13) received the largest release of Σ_{20}PBDEs with the total up to 5.64 and 4.62 ng g^{-1} d.w., respectively. By contrast, the Feilaixia scenic dam (ID: S10) received the lowest Σ_{20}PBDEs release of 0.26 ng g^{-1} d.w. (The sediment samples from the Qingyuan City (ID: S7) and the upstream of Whitehead hub (ID: S15) were not collected).

In addition, in water phase, the low bromine PBDEs congeners were the dominant species, and the high bromine PBDEs congeners were not detected (Fig. 2a). In contrast, it was just the opposite in sediments (Fig. 2b). In water, BDE-17, BDE-47 and BDE-99 were the dominant PBDE homologues, accounting for 64.6% to 100% of Σ_{20}PBDEs. In sediments, BDE-208 was the dominant PBDE congeners. The possible explanation may be that PBDE homologues have different hydrophobic characteristics ($\log K_{ow} = 5.48–8.70$ at 25 °C)

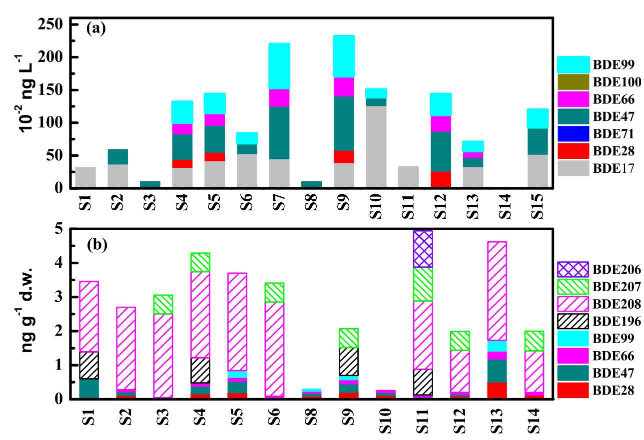

Fig. 2. The main PBDE congeners in water (a) and sediments (b) of the Beijiang River, South China.

(Parolini et al., 2013; Wania and Dugani, 2003). PBDEs with relatively low bromine contents are more hydrophilic than those with high bromine contents. In addition, BDE-209 was not detected in the river sediments. The reason for this may be as follows. Firstly, the runoff volume of the Beijiang River is very larger

(4.82×10^{10} m^3 $year^{-1}$), so the concentrations in the sediments are effectively diluted. Secondly, the method detection limit of BDE-209 (70 pg g^{-1} d.w.) was higher than that of other congeners (10–70 pg g^{-1} d.w.).

3.2. Emission patterns of TBP, PeBP, TBBPA and BPA

TBBPA were detected in almost all samples of the Beijiang River (Tables S6 and S7). However, the concentrations of TBBPA were very low. The concentrations in water samples ranged from 20 to 270 pg L^{-1} with an average of 197 pg L^{-1}. Comparatively, the concentrations of TBBPA in sediment samples varied from 20 to 600 pg g^{-1} d.w. with an average of 195 pg g^{-1} d.w.. TBP and PeBP are also used as BFRs in diverse industries. Thus the concentrations of TBP and PeBP were detected simultaneously (Tables S6 and S7). The concentrations of these pollutants were very low. The concentrations in water samples ranged from < DL to 810 pg L^{-1} (average of 399 pg L^{-1}) for TBP; from < DL to 190 pg L^{-1} (average of 148 pg L^{-1}) for PeBP. Comparatively, the concentrations of these compounds in sediment samples ranged from < DL to 410 pg g^{-1} d.w. with an average of 149 pg g^{-1} d.w. for TBP, while PeBP was not detected in all sediment samples.

The concentrations of BPA in water samples ranged from 60 to 720 pg L^{-1} with an average of 317 pg L^{-1}. Comparatively, the concentrations in sediment samples ranged from 80 to 400 pg g^{-1} d.w. with an average of 185 pg g^{-1} d.w. (Tables S6 and S7). Compared with TBBPA, BPA has greater water solubility (120–300 mg L^{-1} at pH 7) (Staples et al., 1998). Therefore, the concentrations of BPA in water were slightly higher than those of TBBPA. In addition, the degradation of TBBPA by microbes may be another possible source of BPA (An et al., 2011b; Liu et al., 2013), and BPA may also be adsorbed onto sediments (K_{oc} 314 to 1524) (Staples et al., 1998). Besides these two reasons, BPA is also widely used as an intermediate in the production of polycarbonate and epoxy resins, flame retardants, and other specialty products, and wastes created during the use of these products release considerable BPA, which may also be an important source of BPA.

The emission pattern map of phenolic brominated flame retardants (PBFRs) and BPA in water of the study is shown in Fig. 1c. There were large differences in emission pattern among the sub-basins. The Shijiao Town (ID: S5) and Qingyuan City (ID: S7) received the largest release of PBFRs with the total up to 1380 and 1450 pg L^{-1}, respectively. By contrast, the confluence of the Suijiang River and the Beijiang River (ID: S3) and Jiangkou Town (ID: S9) received the lowest PBFRs release of 300 pg L^{-1}. The PBFRs and BPA emission pattern map in sediments is also shown in Fig. 1d. Large differences were found in emission patterns among the sub-basins too. The Lixi Town (ID: S11) received the largest release of PBFRs with the total up to 830 pg g^{-1} d.w., and the Lubao Town (ID: S4) received the lowest PBFRs release of 210 pg g^{-1} d.w..

As a flame retardant, TBBPA is widely used as reactive flame retardant which is covalently bound to polymers and thus less easily released to the environment than non-bound PBDEs (de Wit et al., 2010). This might be one reason for low levels of TBBPA generally detected in the environment in comparison with PBDEs, which are additive flame retardants and blended with polymers. The degradation of TBBPA to other metabolites, such as 2,4-DBP, TBP and BPA, under aerobic or anaerobic conditions may be another possible factor affecting their concentrations (An et al., 2011b; Liu et al., 2013). The effluents of sewage treatment plants, municipal incinerators and factory flues of this surveyed region are also possible sources of TBBPA. TBP may be formed as by-products 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). So this compound could be detected in some water or sediment samples from the Beijiang River. Previous studies also reported that the concentrations of TBP and PeBP in water and sediments collected from an electronic waste recycling site in Guangdong Province, China, ranged from < DL to 320 ng L^{-1} (TBP) and from < DL to 37 ng L^{-1} (PeBP) in water, and from < DL to 47 ng g^{-1} d.w. (TBP) and from < DL to 25 ng g^{-1} d.w. (PeBP) in sediments (Xiong et al., 2015), and the riverine areas and the marine environments near a nuclear power plant in Korea, ranged from 0.378 to 20.2 ng L^{-1} (TBP) in seawater and from < DL to 3.34 ng L^{-1} (TBP) in riverine water, and ranged from < DL to 6.31 ng g^{-1} d.w. in sediments (Sim et al., 2009). These levels of concentrations were higher than those of this study.

Compared with other locations, the Beijiang River showed relatively low levels of TBBPA contamination. He et al. reported the concentrations of TBBPA in water and sediments of the Dongjiang River in July 2009 (He et al., 2013), which is also located in east of the PRD in South China, ranged from 1.11 to 2.83 ng L^{-1} (average of 1.75 ng L^{-1}) and < DL to 82.3 ng g^{-1} d.w. (average of 15.2 ng g^{-1} d.w.), respectively. Feng et al. investigated the distribution of TBBPA in the sediments collected within in the PRD region from July 2009 to October 2010 (Feng et al., 2012), and the concentration of TBBPA ranged from 0.06 to 304 ng g^{-1} d.w..

The concentrations of BPA in the samples from the Beijiang River were lower than those from most other locations such as Tokyo Bay (Japan, 100 to 48×10^3 ng g^{-1} d.w.; 1998) (Hashimoto et al., 2005) and The Netherlands (<1.1 $\times 10^3$ to 43×10^3 ng g^{-1} d.w.; 1999) (Vethaak et al., 2005). Stuart et al. reported the concentrations of BPA in sediments of Massachusetts Bay, Boston, USA, ranging from 1.5 to 5 ng g^{-1} d.w. (Stuart et al., 2005), and Zhe et al. reported the levels from < DL to 6.1 ng g^{-1} d.w. in the sediment samples from the basin of Lake Erie (Lu et al., 2015). In our previous study, high levels of BPA in water and sediment samples were obtained for an electronic waste recycling site ranged from < DL to 860×10^3 ng L^{-1} and from < DL to 560×10^3 ng g^{-1} d.w. (Xiong et al., 2015).

3.3. Risk assessment

3.3.1. Estrogenic activity assessment

In order to estimate the estrogenic activity of TBBPA and BPA in water and sediments on the aquatic organisms in the Beijiang River, the 17β-estradiol equivalency quantity (E_2EQ) approach was employed (Sun et al., 2013; Xiong et al., 2015), where $E_2EQ > 1.0$ ng E_2 L^{-1} (the threshold of endocrine disrupting effects) indicates that contaminants may affect the endocrine systems of aquatic organisms in the receiving water environments (Commission, 1996). E_2EQ for TBBPA and BPA at each sampling point was calculated, and the estrogenic equivalency factors were calculated as 0.45×10^{-6} for TBBPA and 13.7×10^{-6} for BPA, respectively, as recommended method from reference (Kitamura et al., 2005). Since previous findings showed that TBBPA and BPA have additive toxic effects on aquatic organisms, a sum of E_2EQ was also performed for each sampling point. Fig. 3 presents E_2EQ obtained for TBBPA and BPA in water (Fig. 3a) and in sediments (Fig. 3b). For the Beijiang River, E_2EQ_{Total} in water and sediments ranged from 9.3×10^{-7} to 1.0×10^{-5} ng E_2 L^{-1} and 1.5×10^{-7} to 7.3×10^{-7} ng E_2 L^{-1}, respectively. These E_2EQ_{Total} were far less than the threshold of endocrine disrupting effects (1.0 ng E_2 L^{-1}) as compared with the reference (Commission, 1996), indicating no estrogenic risk was observed from these pollutants in the Beijiang River. In fact, BPA was a principal contributor of the total estrogenic activities as BPA is a widely accepted endocrine disruptor and possesses higher estrogenic equivalency factor (13.7×10^{-6}) than that (0.45×10^{-6}) of TBBPA. This result is well in line with that of our previous study (Xiong et al., 2015).

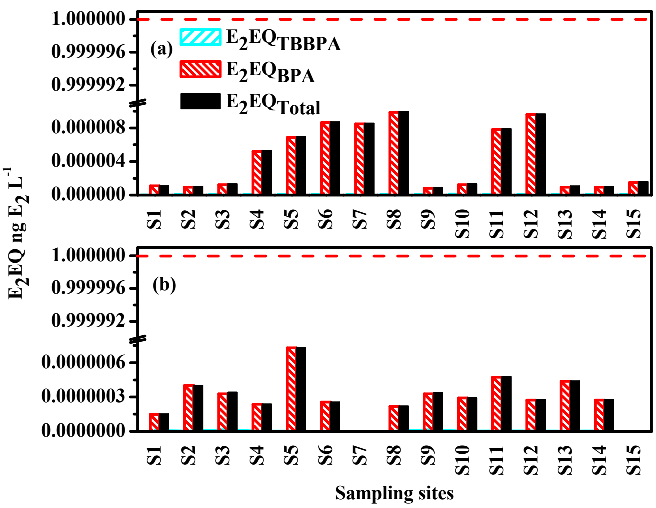

Fig. 3. The estimated 17β-estradiol equivalency quantity (E_2EQ) of TBBPA and BPA in water samples (a) and sediment samples (b) from the Beijiang River, South China.

3.3.2. Eco-toxicity assessment

Except estrogenic activity, the eco-toxicity of BFRs and BPA in water and sediments at three trophic levels (green algae, daphnia, and fish) were also investigated, using the risk quotient (RQ) approach as recommended (Commission, 2003). Considering the possible joint effects of these pollutants with a similar mode of action (Ginebreda et al., 2010), a summed RQ of each individually detected pollutant was calculated at each sampling point. Fig. 4 presents the RQ_{Total} obtained for all BFRs and BPA in water. For the Beijiang River, the RQ_{Total} ranged from 0.00126 to 0.04404 for green algae, from 0.00579 to 0.24057 for daphnia and from 0.00594 to 0.23228 for fish, respectively. These results indicated that no eco-toxicity ($RQ_{Total} < 1.0$) is expected at all three trophic levels at all sampling points of the studied river. Fig. 5 presents the RQ_{Total} obtained for all BFRs and BPA in sediments from the Beijiang River. The RQ_{Total} ranged from 0.00094 to 0.11698 for green algae, from 0.00397 to 2.77385 for daphnia and from 0.00340 to 3.65686 for fish, respectively. These results also indicated that no eco-toxicity ($RQ_{Total} < 1.0$) is expected for green algae at all sampling points of the studied river, while a potential eco-toxicity ($1.0 \leq RQ_{Total} < 10$) is expected for daphnia at sampling location S3 ($RQ_{Total} = 1.15$), S4 ($RQ_{Total} = 1.43$), S6 ($RQ_{Total} = 1.18$) and S11 ($RQ_{Total} = 2.77$), and a potential eco-toxicity ($1.0 \leq RQ_{Total} < 10$) is expected for fish at sampling locations S3 ($RQ_{Total} = 1.53$), S4 ($RQ_{Total} = 1.87$), S6 ($RQ_{Total} = 1.57$), S9 ($RQ_{Total} = 1.24$), S11 ($RQ_{Total} = 3.65$), S12 ($RQ_{Total} = 1.16$), and S14 ($RQ_{Total} = 1.20$).

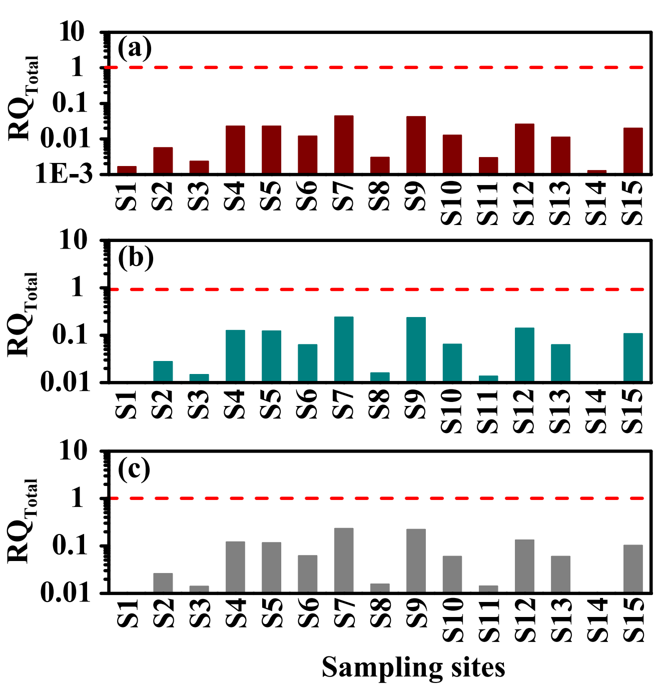

Fig. 4. Total risk quotient (RQ_{Total}) of PBDEs, PeBP, TBP, TBBPA and BPA for green algae (a), daphnia (b), and fish (c) in water from the Beijiang River, South China.

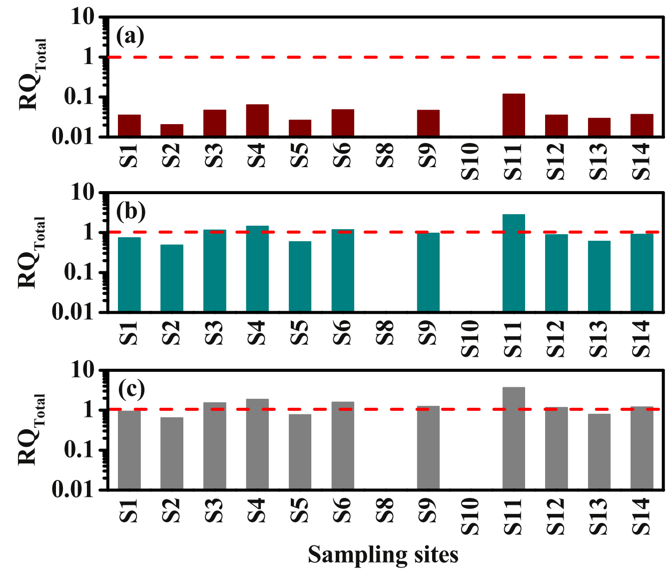

Fig. 5. Total risk quotient (RQ_{Total}) of PBDEs, PeBP, TBP, TBBPA and BPA for green algae (a), daphnia (b), and fish (c) in sediments from the Beijiang River, South China.

The eco-toxicity results across the three evaluated organisms indicated that green algae is the least affected by BFRs and BPA. This result is consistent with the results of our previous study (Xiong et al., 2015).

4. Conclusion

The concentrations of BFRs and BPA in water from the Beijiang River, South China, ranged from < DL to 810 pg L^{-1} for BFRs, and from 60 to 720 pg L^{-1} for BPA. Comparatively, the levels of these compounds in sediments varied from 260 to 5.64×10^6 pg g^{-1} d.w. for Σ_{20}PBDEs, from 20 to 600 pg g^{-1} d.w. for TBBPA, from < DL to 410 pg g^{-1} d.w. for TBP, and from 80 to 400 pg g^{-1} d.w for BPA. In addition, in water, low bromine PBDEs congeners were the dominant species, and high bromine PBDEs congeners were not found. No estrogenic risk ($E_2EQ < 1.0$ ng E_2 L^{-1}) was found for water and sediments from the Beijiang River, and no eco-toxicity risk ($RQ_{Total} < 1.0$) was obtained for green algae, daphnia and fish for water, while a potential eco-toxicity ($1.0 \leq RQ_{Total} < 10$) is expected for daphnia and fish from sediments at some sampling locations from the Beijiang River. Thus, for a more reliable eco-toxicity assessment, more short-term and long-term toxicological data are needed concerning the eco-toxicity of BFRs and BPA in water and sediments, under relevant environmental conditions.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.envpol.2016.06.021.

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