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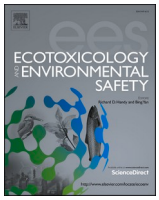

Organophosphate flame retardants, tetrabromobisphenol A, and their transformation products in sediment of e-waste dismantling areas and the flame-retardant production base

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ABSTRACT

Due to the prohibition of polybrominated diphenyl ethers, organophosphate flame retardants (OPFRs) and tetrabromobisphenol A (TBBPA) have become emerging flame retardants. However, knowledge about their occurrence, especially their transformation products, is still limited. This study collected sediment samples from two rivers, i.e., Lianjiang River (located at an e-waste dismantling area) and Xiaoqing River (situated at a flame retardant production base), to investigate the occurrence, composition, and spatiality distribution of OPFRs, TBBPA, and their transformation products. Both targets were detected in the Lianjiang River in the range of 220–1.4 $\times 10^4$ and 108–3.1 $\times 10^3$ ng/g dw (dry weight) for OPFRs and TBBPA, and 0.11–2.35 and 4.8–414 ng/g dw for their respective transformation products, respectively. The concentrations of OPFRs and TBBPA in the Xiaoqing River ranged from 4.15 to 31.5 and 0.76–2.51 ng/g dw, respectively, and no transformation products were detected. Different compositional characteristics of OPFRs and distinct spatial distribution from mainstream and tributary observed between the two rivers are attributed to the difference in the local industries. Spatial distribution and principal component analysis indicated that e-waste dismantling activities could be a vital source of local pollution. Besides, the confluence of tributaries seemed to determine the contaminant levels in the Xiaoqing River. Also, concentration ratios and Spearman's correlation between metabolites and parent chemicals were analyzed. Low concentration ratios (3.6 $\times 10^{-4}$ to 0.16) indicated a low transformation degree, and Spearman's correlation analysis suggested transformation products were partly stemming from commercial products. Considering the limited study of these transformation products, more studies on their sources, transform mechanism, and toxicity are required.

1. Introduction

Flame retardants are usually added to diverse materials (such as electronics, textiles, vehicles, and construction materials) to prevent combustion and fire spread (Van der Veen and de Boer, 2012). With the prohibition of polybrominated diphenyl ethers, organophosphate flame retardants (OPFRs) and tetrabromobisphenol A (TBBPA) are widely used as substitutes. However, several environmental and health adverse effects are attributed to these substitutes. For example, OPFRs have evidenced reproductive, developmental, corneal, and neuro toxicities (Dishaw et al., 2011; Li et al., 2015; Xiang et al., 2017; Yuan et al., 2016), while acute toxicity, endocrine disruption, and neurotoxicity have ascribed to TBBPA (Yu et al., 2019). Furthermore, the transformation products of OPFRs (mOPFRs) are associated with allergy,

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chronic kidney disease, and DNA oxidative stress (Kang et al., 2019; Lu et al., 2017; Sun et al., 2018), while the debrominated products of TBBPA (Br_xBPAs, x = 1–3) can promote adipocyte differentiation in 3T3-L1 cells (Akiyama et al., 2015). So, it is necessary to investigate the environmental behavior of OPFRs, TBBPA, and their transformation products in the environment.

However, investigation of these transformation products is still limited, especially compared to wide studies of their parent compounds. Currently, there were several studies have detected mOPFRs in water (Li et al., 2020), dust (Hu et al., 2020; Wang et al., 2020), municipal sludge (Fu et al., 2017a, 2017b; Wang et al., 2019), and in sediment (Xu et al., 2019). For example, Fu et al. (2017a, 2017b) studied OPFRs and mOPFRs in municipal sludge from China, and it showed that the total concentrations of OPFRs and mOPFRs were in the range of 43.9–2160 and 17.0–1300 ng/g, respectively. Nevertheless, Hu et al. (2020) investigated the co-occurrence of OPFRs and mOPFRs in indoor dust from Guangzhou, China. They observed higher concentrations of OPFRs and mOPFRs in indoor dust with the range of 726–39,312 and 68.8–14, 766 ng/g, respectively. The high levels of some mOPFRs could reflect their direct usage as an additive in their products. Comparatively, more studies have been conducted on the transformation products of TBBPA, especially Br_xBPA in sediment (Lan et al., 2019) and breast milk (Akiyama et al., 2015; Nakao et al., 2015). Recently, seven mixed bromine/chlorine transformation products of TBBPA (Cl_yBr_xBPA, $x + y \leq 4$) were identified in dust samples in workshops from an e-waste dismantling park (Liu et al., 2020). Although there was another report on the synthesis of Cl_yBr_xBPAs, the chemicals were undetected elsewhere (Doumas et al., 2018). Currently, the investigation on the presence of Cl_yBr_xBPA in the environment remains too limited, and it is necessary to investigate their occurrence and environmental behavior in various environmental matrices.

Lianjiang River is the third largest river in the east of Guangdong province, South China. The 71 km river with a 1347 km^2 basin area flows into the South China Sea (Guo et al., 2009; Li et al., 2019). Additionally, the river passes through Guiyu town, one of China's largest e-waste dismantling areas. Between 1996 and 2015, the numerous electronics workshops in Guiyu town had handled electronic wastes up to 1.6×10^6 tons/year. With the local government's strict management of electronic wastes enacted in 2015, an industrial park was built, and the small workshops were closed. A considerable proportion of flame retardants used as additives added to electronic products can be quickly released to the environment during e-waste recycling, thus affecting the environment if the workshops do not pay attention to environmental protection. Xiaoqing River, a 240 km river channel with an 11,000 km^2 basin area, is the second-largest river in Shandong Province, second only to the Yellow River, North China. The river passes through Shouguang city, China's most prominent flame retardant production base (Zhuang and Gao, 2014). This region has large emissions of flame retardants (Wang et al., 2014; Zhen et al., 2018). Anthropogenic pollutants released into the environment can eventually accumulate into sediment through various environmental processes. Thus, sediment is a valuable matrix that can reflect long-term environmental pollution.

To understand the occurrence and fates of the chemicals, the two rivers were selected in the present study. We hypothesized that e-waste dismantling activities and flame retardant production were critical pollution sources. The composition characteristics between the two areas might vary significantly, especially for the transformation products of OPFRs and TBBPA. Therefore, surficial sediment samples in the Lianjiang River and Xiaoqing River were collected in the present study. The occurrence, spatial distribution, and transformation products of OPFRs and TBBPA in sediment samples were investigated. To the best of our knowledge, this study is the first report on Cl_yBr_xBPAs in sediment. The study provides abundant information to track pollution transport from flame retardant production and e-waste dismantling parks.

2. Materials and methods

2.1. Chemicals

Thirteen OPFR standards: tributyl phosphate (TBP), tripropyl phosphate (TPrP), tris(chloropropyl) phosphate (TCPP), tris(2-chloroethyl) phosphate (TCEP), tris(1-chloro-2-propyl) phosphate (TiCPP), triphenyl phosphate (TPHP), tris(2-butoxyethyl) phosphate (TBEP), tris (1,3-dichloro-2 propyl)phosphate (TDCP), 2-ethylhexyl diphenyl phosphate (EDP), tri-m-cresyl phosphate (*m*-TCP), tri-ocresyl phosphate (*o*-TCP), tri-p-cresyl phosphate (*p*-TCP), tris(2-isopropylphenyl) phosphate (TiPPP), and TBBPA were obtained from AccuStandard (New Haven, USA). Eight mOPFR standards viz. bis(2-chloroethyl) phosphate (BCEP), bis-(1-chloro-2-propyl) phosphate (BCIPP), diphenyl phosphate (DPHP), bis(1,3-dichloro-2-propyl) phosphate (BDCP), dibutyl phosphate (DBP), bis(butoxyethyl) phosphate (BBEP), two dicresyl phosphate (DCP) isomers, i.e., di-o-cresyl phosphate (DoCP), and di-p-cresyl phosphate (DpCP) were all obtained from Cambridge Isotope Laboratories, Inc. (MA, USA).

According to our previous study, the transformation products of TBBPA, i.e., BrxBPAs and ClyBrxBPAs, were synthesized in our laboratory (Liu et al., 2020). Isotopic-labeled standards d_{27}-PATE (phosphoric acid tributyl), d_{12}-TCEP, and d_{15}-TPhP were manufactured by AccuStandard (New Haven, USA). $^{13}C_{12}$-TBBPA was purchased from Wellington Laboratories (Guelph, ON, Canada). Also, d_{10}-BCEP, d_{12}-BCIPP, d_{10}-DPHP, d_{18}-DBP, d_{10}-BDCIPP, d_{14}-DoCP, d_{14}-DpCP, and d_8-BBEP were procured from Cambridge Isotope Laboratories, Inc. (MA, USA). All organic solvents were high-performance liquid chromatography (HPLC) grade and were supplied by ANPEL Laboratory Technologies Inc. (Shanghai, China).

2.2. Sample collection and pretreatment

The sediment samples were collected with a stainless steel sampler from 11 sites in the Lianjiang River (23°13′N–23°22′N, 116°20′E–116°20′E) in September 2020, and from 13 sites in the Xiaoqing River (37°15′N–37°30′N, 118°50′E–119°20′E) in August 2019 (Fig. 1). The samples were transported back to the laboratory within 24 h, and stored at −20 °C before further analysis. Sample pretreatment followed a procedure similar to our previous study, with some modifications (Ge et al., 2020). Briefly, the sediment samples were freeze-dried, ground, and sieved through a stainless steel screen (100 mesh). The samples (1 g for the Lianjiang River and 2 g for the Xiaoqing River) were spiked with surrogate standards (d_{27}-PATE, d_{12}-TCEP, d_{15}-TPhP, $^{13}C_{12}$-TBBPA, and deuterated mOPFRs), and extracted using accelerated solvent extraction with mixed solvents (ethyl acetate, dichloromethane, n-hexane = 2:2:1) under 100 par and at 100 °C. Activated copper powder was added to remove elemental sulfur before extraction. After accelerated solvent extraction, all the extracts were concentrated and passed through 2 g florisil SPE cartridges. The target compounds were eluted with 10 mL of ethyl acetate/dichloromethane (50:50, v/v). Finally, all elutes were further concentrated and dissolved in 50 μL isooctane for OPFRs or 200 μL methanol for TBBPA and related chemicals for instrumental analysis.

2.3. Instrumental analysis

The analyses of OPFRs (Ge et al., 2020) and TBBPA (and its transformation products) (Liu et al., 2020) were carried out as described in our previous studies. Those of mOPFRs were conducted by using an Agilent 1260 Infinity LC coupled with a 6470 Triple Quad mass spectrometry (Agilent Technologies, USA). Chemical separation occurred in an HPLCONE-5C8A analytical column (250 mm × 4.6 mm × 5 μm). The injection volume for the LC-MS/MS analysis was 10 μL·H_2O (containing 0.1% formic acid, v/v) and methanol were the mobile phases A and B, respectively. The gradient started at 35% phase B and was

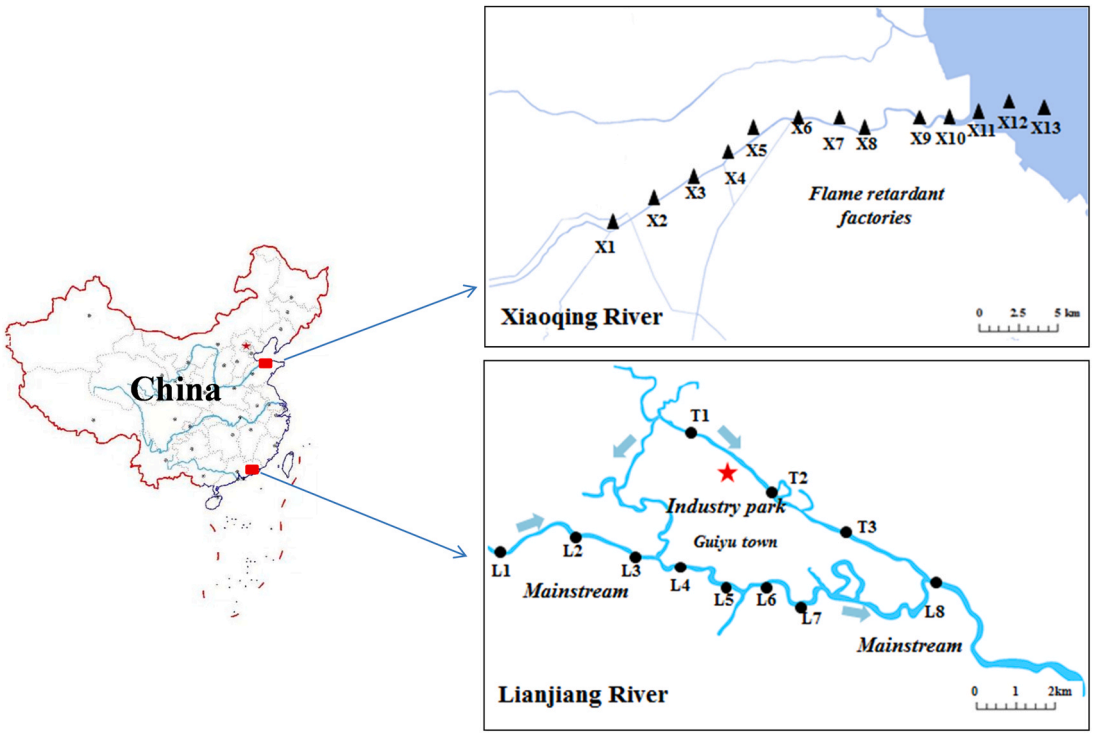

Fig. 1. Sampling sites at the Xiaoqing River and Lianjiang River.

ramped up to 75% phase B within 2 min, and to 95% phase B within 20 min. Here, it was held for 5 min before reverting back to 35% phase B at a flow rate of 0.400 mL/min. The source temperature and nebulizer pressure were set at 300 °C and 45 psi, respectively. Detailed information on MS/MS parameters are given in Table S1.

2.4. Quality assurance and quality control

In a batch experiment, we assessed ten sediment samples, one blank sample, and one spiked sample. The corrected recoveries of OPFRs and TBBPA, and their transformation products in the spiked samples were 74.0–93.1%. Seven-point calibration curves were established with regression coefficients (R^2) of >0.99 for all the chemicals. The limits of quantitation (LOQ) and limits of detection (LOD) are defined as ten-fold and three-fold of the signal-to-noise ratio, respectively (Table S2).

2.5. Statistical analysis

Statistical analyses were conducted using SPSS 13 (IBM, USA) software. Spearman's correlation analyses were used to analyze the correlations between transformation products and parent chemicals. The results were considered statistically significant when $p < 0.05$. The contaminant concentrations were expressed as ng/g dw (dry weight) unless otherwise specified. In the present study, the concentrations of 2-Cl-2′,6$^{\#}$-Br_2BPA represent those of 2-Cl-2′,6′-Br_2BBPA and 2-Cl-2′,6-Br_2BBPA, because they co-eluted in the chromatography.

3. Results and discussion

3.1. Identification of OPFRs, TBBPA, and their transformation products

The OPFRs and their transformation products in the sediment samples from the two rivers are listed in Table S3. Among the 13 OPFRs determined in the Lianjiang River samples, the concentrations of TPrP and TBEP were below the LODs. The detection frequencies of TCEP, EDP, TCP, TiPPP, and TDCP were 54.5%, 72.7%, 81.8%, 81.8%, and 90.9%, respectively. Other forms were found in all the sediment samples. In the Xiaoqing River, TBP, TPrP, TBEP, and TiPPP were below the LODs. Except for TCP (46.2%), the other congeners were present in all the samples. However, the mOPFRs were detected only in the Lianjiang River. Also, only DPHP, DBP, and DCP were detected at frequencies of 81.8–100%, while the other four mOPFR compounds were undetected.

Furthermore, TBBPA was detected in the two rivers. The Br_xBPAs, i.e., mono-, bi-, and tri-BrBPA, were identified in the Lianjiang River, except for 2,6-Br_2BPA with a detection frequency of 90.9%. However, lower detection frequencies were observed for Cl_yBr_xBPAs. Among the seven Cl_yBr_xBPAs, only four products viz. 2-Cl-2′-BrBPA, 2,2′-Cl_2-6-BrBPA, 2-Cl-2′,6$^{\#}$-Br_2BPA, and 2-Cl-2′,6,6′-Br_3BPA were detected with the detection frequencies of 54.5%, 72.7%, 100%, and 72.7%, respectively. Except for TBBPA, all transformation products were undetected, despite using twice the sample size of the Xiaoqing River sample during the sample treatment and analysis.

3.2. Concentrations of OPFRs, TBBPA, and their transformation products

The OPFR concentrations in the Lianjiang River were 220–1.4 × 10^4 ng/g (Fig. 2 and Table S3A), with mean and median concentrations of 3.2 × 10^3 and 1.3 × 10^3 ng/g, respectively. These values indicated that the e-waste dismantling activities induced environmental contamination. Comparatively, lower concentrations of OPFRs were detected in the Xiaoqing River, ranging from 4.15 to 31.5 ng/g with a mean and median of 12.4 and 7.59 ng/g, respectively (Table S3B). Low levels of OPFRs in the Xiaoqing River could be attributed to the dredged sludge activities by the Shandong Provincial Government since 2018 (Wei, 2020). For the mOPFRs, their concentrations were much lower than their parent compounds, with no detectable mOPFRs in the Xiaoqing River. The concentrations of mOPFRs ranged from 0.11 to 2.35 ng/g, having respective mean and median concentrations of 0.63 and 0.22 ng/g in the Lianjiang River.

Similar high OPFR levels were also reported in pump pits at landfill sites and automobile destruction sites from Norway (Green et al., 2008). Li et al. (2019) reported an extremely high concentration of OPFR

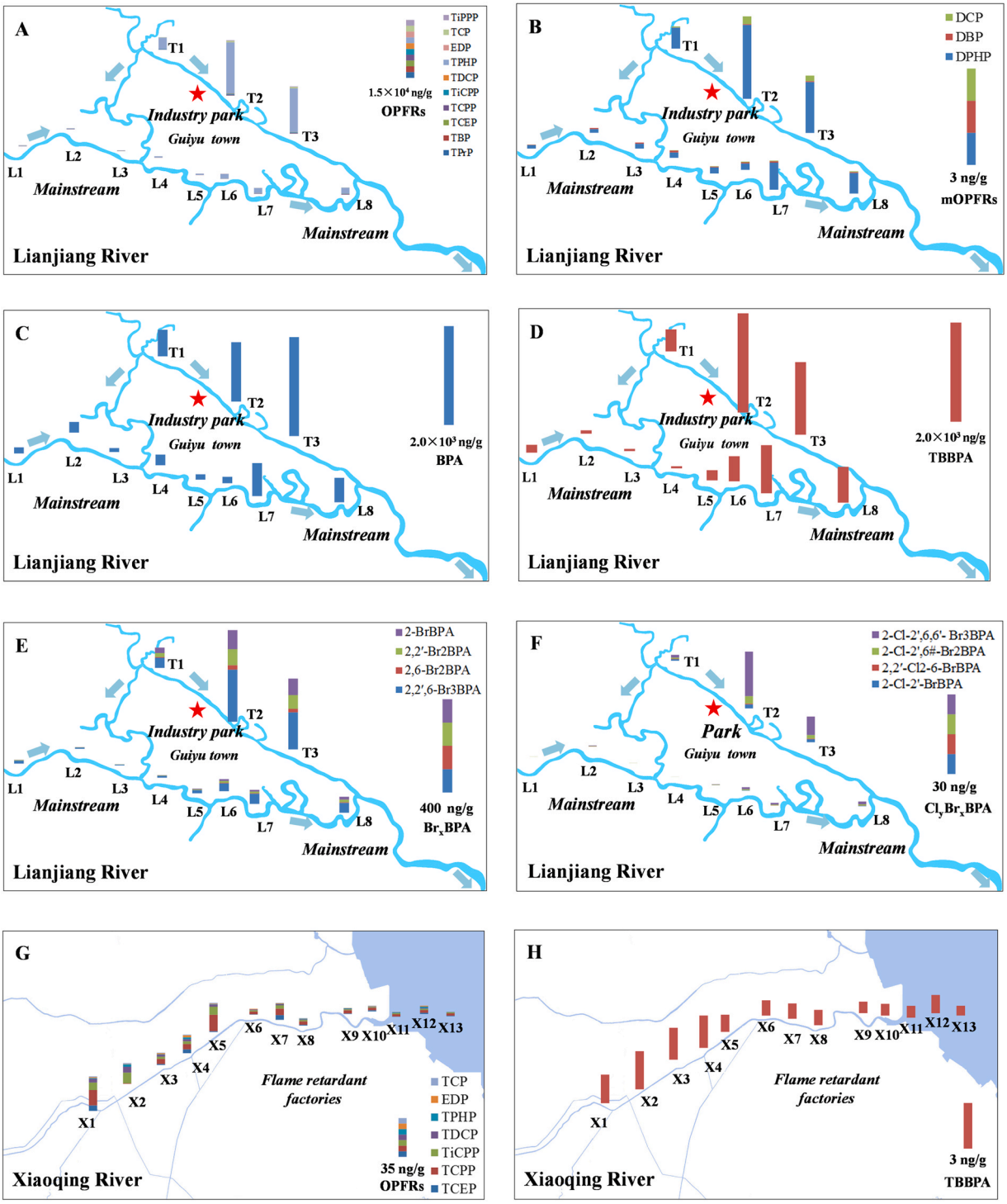

Fig. 2. Concentrations and spatial distributions of (A) OPFRs, (B) mOPFRs, (C) BPA, (D) TBBPA, (E) Br_xBPAs, (F) Cl_yBr_xBPAs in the Lianjiang River, and (G) OPFRs (H) TBBPA in the Xiaoqing River.

(2.1×10^6 ng/g) in the Lianjiang River in 2013. Overall, OPFR concentrations in sediment samples from the Lianjiang River were higher than those reported elsewhere, such as Germany, Austria, Spain, and the UK (Cristale et al., 2013a, 2013b; Martinez-Carballo et al., 2007; Stachel et al., 2005). Similarly, the OPFR concentrations in the Xiaoqing River were lower than most areas globally, albeit similar to those from Taihu Lake and a Taiwan river (Cao et al., 2012; Chung and Ding, 2009). Moreover, the present concentrations of mOPFRs were much lower than those in municipal sludge and urban river sediment (Björnsdotter et al., 2018; Fu et al., 2017b; Liang et al., 2021). The plausible explanation is that domestic pollution could release more mOPFRs, although high population density could also contribute to high levels of pollution, more evidence is needed in the future.

Comparatively, TBBPA concentrations were 108–3.1×10^3 and 0.76–2.51 ng/g in the sediment samples from the Lianjiang River and Xiaoqing River, respectively, approximately an order of magnitude lower than those of OPFRs (Fig. 2, Table S4, and Table S5). Similarly, TBBPA concentrations in the Xiaoqing River were significantly lower than those in the Lianjiang River because of the dredging operation. The levels of TBBPA in the Lianjiang sediment samples were similar to those

of the Longtang River (China) and the rivers Skerne, Tees, and several others in England (Morris et al., 2004; Wang et al., 2015). Elsewhere, a review concluded that elevated TBBPA concentrations were present in e-waste dismantling and disposal sites (Malkoske et al., 2016). The TBBPA concentration from the Lianjiang River was higher than those in the riverine and estuarine sediment samples from China (Feng et al., 2012), manufacturing area sediment samples in Korea (Lee et al., 2015), and most polluted estuarine sediment samples in the Netherlands (Verslycke et al., 2005). Furthermore, the levels of TBBPA in the Xiaoqing River were lower than most rivers studied but slightly higher than a river in France (Verslycke et al., 2005). The much higher concentration was attributed to the areas being involved in e-waste dismantling activities, with limited mitigation actions taken. In contrast, the dredging operation in the Xiaoqing River might support contaminants' removal indirectly.

Regarding the transformation products, Br_xBPAs and Cl_yBr_xBPAs were 4.83–393 and 0.01–21.4 ng/g, respectively, in the Lianjiang River sediment samples and undetected in the Xiaoqing River (Fig. 2 and Table S4). Relative to TBBPA, limited research reports are available on its transformation products, especially for Cl_yBr_xBPAs. Only two reports on environmental Cl_yBr_xBPAs are available. One study observed the chemicals in the environment from dust samples in the e-waste dismantling site (Liu et al., 2021). The other study reported no traces in the water from kitchens and bathrooms (Doumas et al., 2018). Comparatively, several studies found Br_xBPAs in soil, sediment, milk samples (Akiyama et al., 2015; Lan et al., 2019; Liu et al., 2017; Nakao et al., 2015). Compared with Br_xBPA concentrations in the Bohai Sea adjacent area (not detected−5.45 $\times 10^6$ ng/g), the Br_xBPA concentrations in the Lianjiang River were much lower (Lan et al., 2019). In our previous study, the mean concentration of Br_xBPAs in dust samples was 1.63×10^4 ng/g (Liu et al., 2020), which was much higher than the present observations. Because transformation product data of TBBPA is still lacking, especially for Cl_yBr_xBPAs, more studies should be carried out to adequately understand TBBPA transformation in the environment.

3.3. Compositions of OPFRs and TBBPA, and their transformation products

The composition profiles of the chemicals are shown in Fig. 3(A–C). In the two rivers, OPFRs were the predominant compounds, accounting for about 90%. In the Lianjiang River, TPHP accounted for 90.7% of OPFRs, followed by TCP (2.6%), and TCPP (2.5%). TPHP is widely used as a plasticizer in polyester resins and polyvinyl chloride (Van der Veen and de Boer, 2012). Similar high TPHP composition was also observed in the e-waste dismantling areas, accounting for 86.9% and 87.4% in the industrial park and surrounding area soil samples, respectively (Ge et al., 2020). However, it was different from the Xiaoqing River sediment sample, which was predominated by TCPP (44.6%), and followed by TiCPP (21.5%), TCEP (12.5%), and TDCP (9.9%).

As for the transformation products of OPFRs and TBBPA in the Lianjiang River, DPHP was the predominant mOPFR congener, contributing to 91.5% of the total concentrations, followed by DCP (9.4%) and DBP (4.1%). The identified and quantified DPHP agreed with the high portion of TPHP, the parent chemical that is environmentally transformed. Moreover, among the debrominated products of TBBPA, 2,2′,6-Br_3BPA was the most abundant congener, accounting for 57.5% of the total debromination products. Br_2BPA (including 2,6-Br_2BPA and 2,2′-Br_2BPA) and 2-BrBPA accounted for 22.1% and 20.4% of the Br_xBPAs, respectively. For the Cl_yBr_xBPAs, 2-Cl-2′,6,6′-Br_3BPA was the predominant product which accounted for 72.8% of the Cl_yBr_xBPAs, followed by 2-Cl-Br_2BPA (15.7%) and 2-Cl-2′-BrBPA (9.0%). The predominance of 2-Cl-2′,6,6′-Br_3BPA was consistent with our previous study in dust from the same e-waste dismantling area (Liu et al., 2020). On the contrary, the composition of Br_xBPAs in the present study was dissimilar to those in the previous study, where 2-BrBPA was the most abundant debromination product (Liu et al., 2020). Nevertheless, our results agreed with the analysis of sediment from the Zhangseng River, a tributary of the Xiaoqing River, i.e., MoBBPA <Di-BBPA <Tri-BBPA <TBBPA (Lan et al., 2019). One possible explanation is that the environmental matrix might influence the degradation mechanism of TBBPA, and the sampling sites could also affect TBBPA degradation.

3.4. Spatial distribution and sources of target chemicals

To understand the sources of the target compounds more clearly, spatial distribution and principal component analysis were combined to discuss the possible sources. For the Lianjiang River, the sampling sites L1–L8 were the main streams, and T1–T3 were the tributaries (Fig. 2A–F). From L1 to L3, OPFRs and TBBPA decreased slightly in concentration, indicating that Puning City upstream was a potential contamination source. Puning city, covering about 1620 km^2, is a country-level city located in the southeast Guangdong Province, China. It has nearly 2 million population. At L4–L7, the Lianjiang River flows through Guiyu town. The concentration of the chemicals increased gradually from L4 to L7, suggesting that the dense population and human activities in Guiyu could be responsible for the Lianjiang River pollution. At the downstream of Guiyu town (L8), the levels of most chemicals decreased, attributable to the dilution of downstream water. In the tributary samples from T1 to T3, the contaminant levels were much higher than the mainstream, mainly ascribed to e-waste dismantling activities. We observed that the river passes by the e-waste dismantling park, located between T1 and T2. In comparison, the contaminant levels in the tributary were about an order of magnitude

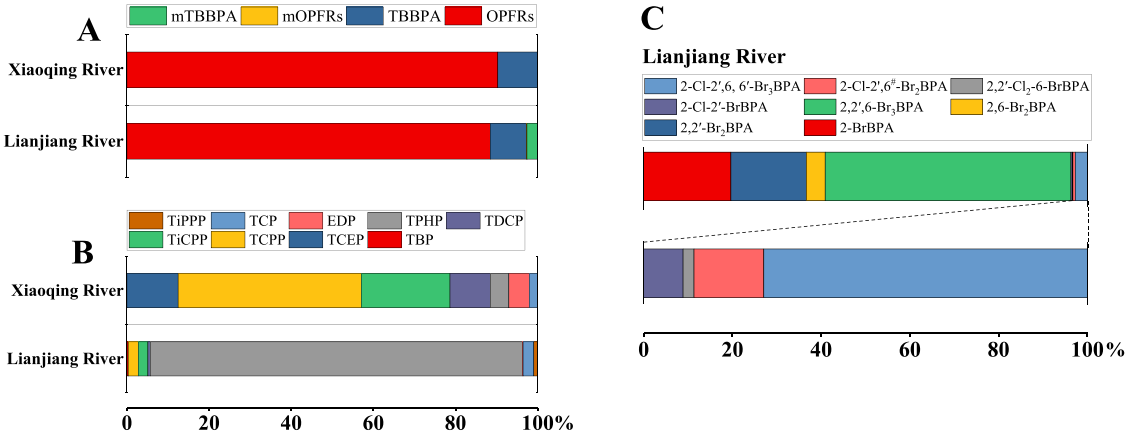

Fig. 3. Composition profiles of (A) all chemicals, (B) OPFRs, (C) mTBBPAs, and Cl_yBr_xBPAs in sediment in the Lianjiang River and Xiaoqing River.

higher than those in the mainstream, except for BPA. BPA is a plasticizer that can stem from domestic sewage (Chen et al., 2016). Here, the BPA levels did not show a significant difference between the mainstream and the tributary. These results indicated that e-waste dismantling activities from parks in Guiyu town had been a crucial source of contaminants to the local water system.

Different from the Lianjiang River, from upstream to downstream in the Xiaoqing River, the concentrations of OPFRs were decreased first, then increased, and finally reduced again from sites X1 to X13 (Fig. 2G–H). Such trends seem to be influenced by the river tributaries. We believe that pollutants from flame retardant manufacturing activities enter the Xiaoqing River through its tributaries. The highest concentration of OPFRs was detected at X1, located in the confluence of several tributaries. At X1–X3, the OPFR levels decreased, whereas, with the confluence of a tributary (Xinta River) at X6, the OPFRs increased. At the flame retardant manufacturing sites, the levels of OPFRs in X7 increased slightly. The levels of OPFRs at sites X11 and X12 also increased slightly after the confluence of the Zhangseng River. As for TBBPA, the highest concentration was detected at X2, ascribable to the confluence of several tributaries. Also, the levels of TBBPA gradually decrease until the confluence of the Zhangseng River, where the concentrations increased slightly. The different spatial distributions of OPFRs and TBBPA could be affected by the distinct products from local flame retardants factories. The contaminants in sediments from the Xiaoqing River were affected by the confluence of tributaries, as some tributaries were closer to the flame retardant manufacturers than the mainstream. Therefore, to better understand the source of pollution, it is necessary to investigate the spatial distribution of tributaries in the future.

To further understand the source of the targets, a principal component analysis (PCA) was carried out (Fig. 4A). For the Lianjiang River, the first principal component (PC1) explained 81.2% of the total variance, with high loadings of 2,2′,6-Br_3BPA (0.995), 2,6-Br_2BPA (0.992), 2,2′-Br_2BPA (0.991), and TPHP (0.988). However, only 9.38% of the total variance with loadings of EDP (0.934), DBP (0.710), and BPA (0.523) was explained by the second principal component (PC2). Most of the chemicals loaded on PC1 are flame retardants and plasticizers in polyester resins and polyvinyl chloride products. Consequently, e-waste dismantling activities in the Guiyu park could be a main pollutant source to the local water system, as the spatial distribution analysis supposed.

For PC2, EDP is applied in food packaging and paints, and BPA is utilized as a plasticizer in daily products (Chen et al., 2016; Yang et al., 2021). Thus, domestic sewage from Guiyu town could be another source of the chemicals. Therefore, e-waste dismantling activities could be the primary source of toxic chemicals in the Lianjiang River.

In the Xiaoqing River (Fig. 4B), PC1′ explained 56.0% of the variance with loadings of TiCPP (0.981), TCPP (0.980), and TDCP (0.887), while PC2′ explained 24.3% of the variance with loadings of EDP (0.915), TPHP (0.843), and TCP (0.826). For example, the OPFRs in PC1′, TiCPP, TCPP, and TDCP are used as additive flame retardants (Van der Veen and de Boer, 2012). Therefore, PC1′ indicated that those chemicals could be released from nearby flame retardant manufacturing sites. For PC2′, EDP is used in food packaging, while TPHP and TCP are applied in polyvinylchloride and hydraulic fluids (Van der Veen and de Boer, 2012). Thus, PC2′suggests that pollutants may stem from domestic sewage and industrial pollution. However, considering the high PC2′, we did not exclude the contribution of flame retardant manufacturers to the contamination.

3.5. Transformation of OPFRs and TBBPA

Owing to the detection of transformation products of OPFRs and TBBPA in the Lianjiang River only, further discussion will be solely on the River. To determine the relationship between the transformation products and parent chemicals, concentration ratios were calculated, and the analyte concentrations' associations were determined using

Table 1
Concentration ratios and correlation values of metabolite to their respective parent compounds in sediment of Lianjiang River.

Products/parents pairs	Concentration ratio min-max (average)	Correlation value
DPHP/TPHP	1.3×10^{-4}–1.1×10^{-3} (4.1×10^{-4})	$r = 0.936$, $p < 0.01$
DBP/TBP	7.8×10^{-4}–5.9×10^{-3} (2.8×10^{-3})	$r = 0.014$, $p > 0.05$
DCP/TCP	0–8.4×10^{-4} (3.6×10^{-4})	$r = 0.767$, $p < 0.01$
2,2′,6-Br_3BPA /TBBPA	0.08–0.33 (0.16)	$r = 0.964$, $p < 0.01$
2,6-Br_2BPA /TBBPA	0–0.018 (0.007)	$r = 0.882$, $p < 0.01$
2,2′-Br_2BPA /TBBPA	0.01–0.07 (0.04)	$r = 0.909$, $p < 0.01$
2-BrBPA /TBBPA	0.01–0.09 (0.04)	$r = 0.891$, $p < 0.01$
2-Cl-2′-BrBPA/TBBPA	0–2.4×10^{-3} (5.8×10^{-4})	$r = 0.753$, $p < 0.01$
2,2′-Cl_2-6-BrBPA/ TBBPA	0–7.3×10^{-4} (2.3×10^{-4})	$r = 0.874$, $p < 0.01$
2-Cl-2′,6#-Br_2BPA/ TBBPA	4.0×10^{-4}–5.0×10^{-3} (1.6×10^{-3})	$r = 0.907$, $p < 0.01$
2-Cl-2′,6,6′- Br_3BPA/ TBBPA	0–0.015 (0.004)	$r = 0.872$, $p < 0.01$

DPHP: diphenyl phosphate; TPHP: triphenyl phosphate; DBP: dibutyl phosphate; TBP: tributyl phosphate; DCP: dicresyl phosphate; TCP: tricresyl phosphate; TBBPA: Tetrabromobisphenol A.

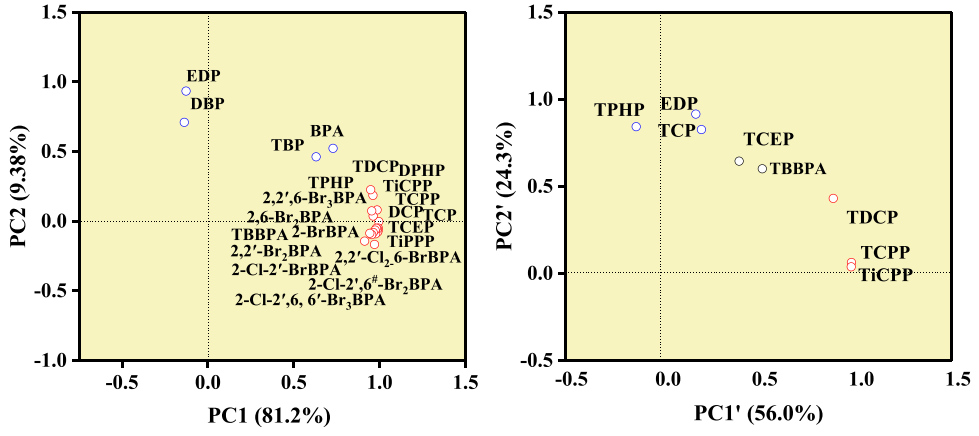

Fig. 4. Principle component analysis results of the target substances in (A) the Lianjiang River and (B) Xiaoqing River.

Spearman's correlation analysis (Table 1). As for mOPFRs, the mean concentration ratios of DPHP, DBP, and DCP to their parent compounds were 4.1×10^{-4}, 2.8×10^{-3}, and 3.6×10^{-4}, respectively. These values were much lower than those reported in other studies, which ranged from 0.22 to 17 for DPHP/TPHP and 0.18–6.7 for DBP/TBP (Hu et al., 2020; Liang et al., 2021; Wang et al., 2020; Xu et al., 2019). The different concentration ratios could be attributed to the different transformation rates in each environment. Therefore, multiple sources of mOPFRs may be reflected, especially when the concentration ratio is much larger than 1. The mOPFRs could arise from commercial usage leaching, impurities in OPFRs formula, and degradation from OPFRs (Liang et al., 2020). Due to the limited information, the source of mOPFRs remains vague. Thus, concentration ratios in the present study can provide a reference to future studies. However, it is worthy to note that the concentration ratios cannot quantify the contribution of mOPFRs from different sources, which need to clarify in the future study.

Furthermore, Spearman's correlation analysis showed that among the three ratios of mOPFRs/OPFRs, two (DPHP/TPHP and DCP/TCP) evinced positive correlations ($p < 0.01$), whereas DBP/TBP did not. The strong positive correlations suggested a close relationship between the levels of DPHP, DCP, and their parent compounds. Thus, DPHP and DCP would likely degrade from TPHP and TCP, respectively, although some of DPHP might stem from commercial products (Liang et al., 2020). Nevertheless, the information about the commercial application of mOPFRs is generally limited. Besides, the lack of correlation ($p > 0.05$) between DBP and TBP suggested that DBP was hardly possible degraded from TBP, as observed elsewhere (Hu et al., 2020). As reported in the literature, DBP can be industrially produced and used, partly explaining the no correlation between DBP and TBP (Quintana et al., 2006).

Among the TBBPA transformation products, the average concentration ratio of Br_xBPA to TBBPA ranged from 0.007 to 0.16 and from 2.3×10^{-4} to 4.0×10^{-3} for its ratio with Cl_yBr_xBPAs. Compared to Br_xBPA, low concentration ratios of Cl_yBr_xBPAs showed that it was difficult to be transformed/formed. All the chemicals exhibited strong positive correlations ($p < 0.01$) with TBBPA, indicating that these chemicals could be transformed from TBBPA.

The investigation on the transformation products is still limited, and the concentration ratios, which might reflect the transformation degree, are not available in the literature. In addition, the transformation mechanism of the TBBPA is not established yet, especially for Cl_yBr_xBPAs. Furthermore, the lack of toxicity data on Cl_yBr_xBPAs hinders understanding the potential ecological risk of those compounds in the aquatic environment. Thus, much more studies on these chemicals are imperative.

4. Conclusions

This study investigated OPFRs, TBBPA, and their transformation products in sediment samples from two typical rivers, i.e., the Lianjiang River and Xiaoqing River, located at e-waste dismantling area and flame retardant production base, respectively. The contaminants in the Lianjiang River were more concentrated than in the Xiaoqing River, showing that e-waste dismantling activities impact the environment more. The transformation products of OPFRs and TBBPA were detected in the Lianjiang River but not in the Xiaoqing River, suggesting that e-waste dismantling activities (such as burning circuit boards) may accelerate the transformation of OPFRs and TBBPA. These chemicals' different composition and spatial characteristics in the rivers may attribute to the various local environments and industries. Spatial distribution and principal component analysis in the Lianjiang River indicated that e-waste dismantling parks could be an essential source of the chemicals in the river. Also, the confluence of tributaries in the Xiaoqing River seems the main factor influencing the contaminants' levels. Except for industrial pollution, domestic sewage could also contribute to polluting the rivers. For the transformation products of OPFRs and TBBPA, Cl_yBr_xBPAs originate mainly from the parent TBBPA, while mOPFRs could arise from commercial products and degraded parent OPFRs. In a future study, it is desirable to focus on the transformation pathways, fate, and toxicity of the transformation products.

CRediT authorship contribution statement

Peng Chen: Sampling, Methodology, Data analysis, Draft preparation. **Shengtao Ma:** Sampling, Methodology. **Yan Yang:** Methodology, Data analysis. **Zenghua Qi:** Methodology, Data analysis. **Yujie Wang:** Methodology, Data analysis. **Guiying Li:** Design, Methodology. **Jianhui Tang:** Sampling, Methodology. **Yingxin Yu:** Design, Writing – review & editing.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.ecoenv.2021.112717.

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