



Identification and occurrence of TBBPA and its debromination and O-methylation transformation products in sediment, fish and whelks from a typical e-waste dismantling site

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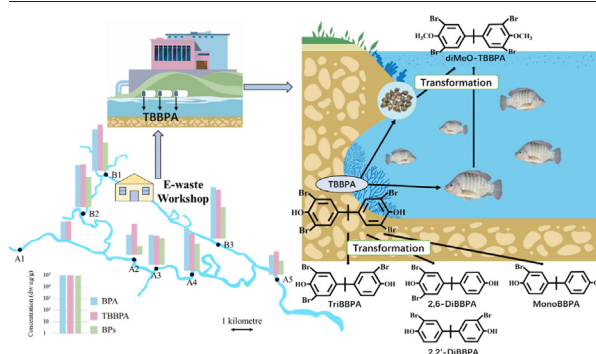
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HIGHLIGHTS

- TBBPA and its debromination and O-methylation products were identified.
- E-waste dismantling activities are major sources of TBBPA and its transformation products.
- Debromination products were the major transformation products found in sediment.
- O-methylation products in biotas were mainly derived from *in vivo* biotransformation.
- Transformation products should be included in future monitoring and risk assessment.

GRAPHICAL ABSTRACT



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ABSTRACT

Tetrabromobisphenol A (TBBPA) and its debromination (Σ BBPA) and O-methylation (Σ MeO-TBBPA) products were widely detected in matched sediments, fish, and whelks samples collected from a typical electronic waste (e-waste) dismantling site in Southern China, with concentrations ranging from 19.8 to 1.52×10^4 , 8.05 to 1.84×10^3 , and 0.08 to 11.9 ng/g dry weight in sediments, and 6.96 to 1.97×10^5 , 3.84 to 7.07×10^3 , and 3.42 to 472 ng/g lipid in biotas, for TBBPA, Σ BBPA, and Σ MeO-TBBPA, respectively. Significantly higher concentrations of these targets were found in samples collected close to the e-waste site, indicating their potential e-waste sources. Tri-BBPA was the most abundant debromination products in sediments, whereas diMeO-TBBPA was the dominant O-methylation product in biotas. Relatively higher levels of diMeO-TBBPA found in liver and kidneys, suggesting these chemicals might be mainly derived from the *in vivo* biotransformation. Furthermore, significantly higher biota-sediment accumulation factor values were found for diMeO-TBBPA than those of TBBPA, indicating that O-methylation would increase their accumulation in aquatic organisms. Our study provides insights into the accumulation and biotransformation of TBBPA in aquatic systems. Further studies should pay attention to the occurrence as well as potential health risks of these transformation products.

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1. Introduction

Tetrabromobisphenol A (TBBPA) is currently one of the most commonly used brominated flame retardants (BFRs) following the recent regulations on polybrominated diphenyl ethers (PBDEs) and hexabromocyclohexane (HBCD) under the Stockholm Convention on persistent organic pollutants (POPs). However, TBBPA may contaminate the environment via the release from consumer products, recovery of waste containing TBBPA, discharge from manufacturing and leaching from disposal sites (Liu et al., 2016a). It has been widely detected in environmental media, such as air (Ma et al., 2021), soil (Liu et al., 2017), dust (Deng et al., 2014; Liu et al., 2020), water (Chen et al., 2020) and sediments (Li et al., 2019; Zhu et al., 2020). Thus, it has become a pollutant of concern. Due to bioaccumulation (Lan et al., 2019), studies have indicated that TBBPA discharged into water may cause neurotoxicity and endocrine disruption to aquatic organisms (Wang et al., 2021; Yu et al., 2021). A great deal of work has been conducted on the occurrence and environmental fate of TBBPA. However, few studies have examined the transformation products, which may exhibit similar environmental behaviors to parental TBBPA, and some induce even more potential toxic effects than TBBPA (Liu et al., 2017; Ren et al., 2020).

In general, two major types of transformation products of TBBPA have been identified widely, i.e., debromination products (e.g., tribromobisphenol A (TriBBPA), dibromobisphenol A (DiBBPA), and monobromobisphenol A (MoBBPA) (Chu et al., 2005; Guerra et al., 2010)) and their corresponding O-methylation products (Kotthoff et al., 2017; Peng et al., 2014). These transformation products may be derived from microbial degradation in soil and sediment or biological metabolic transformation in biotas. It has been estimated that TriBBPA accounts for about 3% of TBBPA in industrial products (Howard and Muir, 2013). Nakao et al. (2015) found that levels of TriBBPA were three times higher than those of TBBPA in breast milk from Japan. In addition, the O-methylation products do not originate from industrial production and application, and thus are likely generated by transformation processes carried out by organisms and microorganisms in natural environment media, such as soil and sediment. High levels of the dimethyl product of TBBPA (diMeO-TBBPA) have been found in river sediments near plastic processing plants in Sweden (Peng et al., 2014), with concentrations comparable to levels of TBBPA. Even higher levels have been detected in bird eggs (Katrin et al., 2005). It has been demonstrated that about 10%–50% of TBBPA in sediments is transformed into monomethyl or dimethyl products under the action of microorganisms, which could promote their accumulation and enrichment in organisms due to the lipophilicity of the methyl substituent group (George and Häggblom, 2008). Methylation is also the main metabolic pathway of biotransformation in organisms (Chen et al., 2017). In the presence of earthworms *Metaphire guillelmi*, methylation products of TBBPA in the soil were shown to reach levels of up to 60% of the total metabolites (Gu et al., 2017). However, there have been few reports on the formation and accumulation of TBBPA and its transformation products in aquatic ecosystems.

Owing to the large amounts and widespread usage of TBBPA in electronic and electrical products, primitive electronic waste (e-waste) dismantling activities have become a significant source of TBBPA in China and other developing countries around the world (Liu et al., 2016b; Stubbings et al., 2021). During the disassembly process, especially the manual dismantling line (Deng et al., 2014), TBBPA may be released into the environment (Liu et al., 2016b) and can then accumulate in the biota (He et al., 2010). Elevated concentrations of TBBPA have been reported in river sediments (Li et al., 2019) and aquatic organisms (He et al., 2013) from typical e-waste dismantling sites. However, little is known about the occurrence and fate of transformation products at e-waste contaminated sites (Chen et al., 2021). It is also important to clarify their formation mechanism and bioaccumulation characteristics. In addition, bromophenols (BPs) and bisphenol (BPA) are also considered to be important transformation products of TBBPA owing to their usage as plastic additives in industrial products (Han et al., 2013). Thus, further studies are needed to identify their potential sources.

In the present study, we collected matched sediment, fish and whelk samples from a river flowing through a typical e-waste dismantling site in Southern China to investigate the occurrence and fate of TBBPA and its transformation products. A method for the simultaneous identification and quantification of TBBPA and its transformation products was developed based on trimethylsilyl derivatization followed by analysis with gas chromatography combined with triple quadrupole mass spectrometry (GC–MS/MS). The accumulation and tissue distribution of TBBPA and its transformation products in fish were also investigated to identify possible mechanisms of transformation and metabolism of TBBPA.

2. Materials and methods

2.1. Chemicals and reagents

Standards of 2,6,2'-tribromobisphenol (TriBBPA), 2,2'-dibromobisphenol (2,2'-DiBBPA), 2,6-dibromobisphenol (2,6-DiBBPA) and 2-monobromobisphenol (MoBBPA) with purities greater than 95% were synthesized in our laboratory (Liu et al., 2020). Their corresponding O-methylated ester derivatives were synthesized using diazomethane derivatization, including di-O-methyl-tetrabromobisphenol A (diMeO-TBBPA), di-O-methyl-2,6,2'-tribromobisphenol A (diMeO-TriBBPA), di-O-methyl-2,2'-dibromobisphenol A (diMeO-2,2'-DiBBPA), di-O-methyl-2,6-dibromobisphenol A (diMeO-2,6-DiBBPA) and di-O-methyl-monobromobisphenol A (diMeO-moBBPA). A full detail of the other chemicals and reagents is given in supporting information (SI, Text S1).

2.2. Sample collection

Eight surface sediment, seven whelk and seven fish samples were collected from tributaries and main streams of the Lianjiang River located in an e-waste dismantling area in Southern China in October 2019. The sample locations are shown in Fig. S1. Five surface sediments (A1, 2, 3, 4, 5), four *philippi* (whelk 1, 2, 3, 4), and four *tilapias* (fish 1, 2, 3, 4) samples were collected from the main streams. Three surface sediments (B1, 2, 3), three *philippi* (whelk 5, 6, 7) and three *tilapias* (fish 5, 6, 7) samples were collected from tributary streams. The A1 sampling site was located 5 km upstream of the Lianjiang River, and at this site, only sediment was collected. The *tilapias* with length of 15–20 cm and whelks with shell height of 40–60 mm were selected. Three *tilapias* and 3–5 whelk samples collected from the same site were combined and mixed with a homogenizer to produce a representative sample. A detailed description of the sampling methods was provided in Text S2 of SI.

2.3. Sample extraction and clean-up

The extraction and clean-up procedures for the biota samples are shown in Fig. S2. In brief, different tissue of biota sample was firstly freeze-dried, and then grind into a fine powder. Accurately weigh 2.0 g dried tissue powder from selected samples into an accelerated solvent extractor (ASE350, Thermo Fisher Scientific Inc., MA, USA) cell, then filled it with anhydrous sodium sulfate. For tissue samples of less than 2 g, all the samples were extracted. Next, the surrogate standards of ^{13}C -TBBPA and ^{13}C -PCB-141 (2 ng) were spiked into the samples after blending the contents of the extraction cell. Accelerated solvent extraction was repeated twice at 100 °C and 1500 psi with a mixture of n-hexane (n-Hex), dichloromethane (DCM) and ethyl acetate (EtAc) (1:2:2, v/v/v). The extracted organic phases were concentrated and the lipid content was determined by gravimetric analysis. Lipids in the extract were then removed by gel permeation chromatography (GPC) (column inner diameter 2.5 cm, filled with 20 g of Bio-Beads S-X3) with a mixture of DCM and Hex (1:1, v/v) as eluent solvent. A multi-layer gel column containing 6 g of florisil (1.5% H_2O , w/w), 5 g of neutral silica gel (1.5% H_2O , w/w) and 1.5 g anhydrous sodium sulfate from bottom to top was used for further purification (Fig. S2). Seventy-five milliliters of EtAc and Hex (1:1, v/v) mixture was used as the eluent after a 30 mL n-hexane pre-wash. A constant solvent flow rate of close to

2 mL·min⁻¹ was used to extract all target chemicals. The eluate was then concentrated and dried with a gentle flow of nitrogen. Finally, the sample extract was spiked with 10 µL isooctane, 10 µL internal standards ¹³C-PCB-208 (200 ng/mL in isooctane) and 30 µL BSTFA, then reacted in a drying oven at 65 °C for 2.5 h. The final sample was stored at -20 °C until instrumental analysis. For the sediments (0.5–1 g), the sample pretreatment procedure was nearly identical to that of the biological samples, except cop-powder was added before extraction to removed sulfur.

2.4. Instrumental analysis

Bisphenol A (BPA), bromophenols (BPs), TBBPA and its transformation products were quantified by GC-MS/MS (Shimadzu TQ8040 Kyoto, Japan) operated in the electron impact ionization mode. A DB-35 MS column (30 m × 0.25 mm × 0.25 µm, Agilent Technology, USA) was used for the chromatographic separation of target analytes. The injection temperature was kept at 280 °C, and 1 µL of sample extract was loaded by high-pressure splitless injection. The GC oven temperature was set as follow: held at 60 °C for 1 min, increased from 60 °C to 200 °C at 10 °C/min, then 200 °C to 280 °C at 5 °C/min, 280 °C to 300 °C at 10 °C/min and finally held at 300 °C for 10 min. The ion source and interface temperature for MS were set as 230 °C and 300 °C, respectively. The multiple reaction monitoring (MRM) transitions and chromatographic retention times are given in Table 1.

2.5. Calculation of biota-sediment accumulation factor (BSAF)

BSAF was calculated as

$$BSAF = C_{bio}/C_{sed}$$

where C_{bio} is the concentration of a given contaminant in the biota samples on a lipid basis (ng/g lipid weight (lw)), and C_{sed} is the concentration of the contaminant in sediment on an organic carbon basis (ng/g organic carbon). The organic carbon (OC) content of the sediment was determined by using an elemental analyzer (Elementar Vario EI, Germany) after acid-treatment (1 M HCl) to remove inorganic carbon from the samples.

2.6. Method validation and quality control

The recoveries of target analytes were evaluated by spiking the samples with a mixture of standards. The spiking levels was 5–100 ng/g corn oil for

biotas and 10–500 ng/g anhydrous sodium sulfate for sediments, respectively. The recoveries ranged from 57% to 105% for biotas and from 50% to 105% for sediments. The calculated matrix effects (ME) shown that phenolic compounds in the biological samples exhibited ion-enhancement (5% to 15%), and a matrix-matched calibration curve was applied to correct ME, full details are shown in Text S3.

A procedural blank and a matrix spike sample were run for each batch of ten samples during the pretreatment and instrumental analysis. One quality control standard was injected for each batch of 12 samples to monitor the stability and reproducibility of mass spectra. Only BPA and TBBPA were detected in the procedural blank at concentrations far below those in the samples (<5 ppb), which were blank-corrected. The recoveries of all target chemicals in the spiked matrix ranged from 61.4% to 99.5% for biotas, and from 55.2% to 103.4% for sediment, respectively, detail information is given in Table 1. The recoveries (average ± standard error) of the surrogate standards of ¹³C-TBBPA and ¹³C-PCB-141 in all samples ($n = 40$) were 76.7% ± 27.3% and 81.1% ± 19.4%, respectively. The concentrations of the target analytes were not recovery corrected. The method detection limits (MDL) for the biotas and sediments were also calculated (Text S3), as shown in Table 1.

2.7. Statistical analysis

Variance analysis was carried out on the concentration of pollutants in the fish samples to test the difference between each group. Compounds with measured concentrations below the MDL were recorded as undetected for calculations of mean and median values. Linear regression was performed among all compound concentrations to calculate the concentrations in different samples. All statistical analyses were performed using SPSS. A value of $P < 0.05$ was considered statistically significant.

3. Results and discussion

3.1. Target identification and method validation

To simultaneously identify TBBPA and its debromination products, phenolic compounds of TBBPA and its debromination products were derivatized with trimethylsilylation prior to instrumental analysis by GC-MS/MS. Identification of the target analytes was based on their retention times and MRM transitions. Typical chromatograms of the standard mixture and an actual fish sample are shown in Fig. S3. It can be seen that the target compounds were baseline separated by gas chromatography.

Table 1

Validation parameters for the determination of TBBPA and its transformation products by GC-EI-MS/MS.

Compound ^a	RT (min)	Quantifying transition <i>m/z</i> (eV)	Qualifying transition <i>m/z</i> (eV)	MDLs ^b (ng/g lw)	MDLs ^c (ng/g dw)	Recoveries for biotas ^d (mean ± SD, %)			Recoveries for sediment ^e (mean ± SD, %)		
						Low level (5 ng/g)	Medium level (50 ng/g)	High level (100 ng/g)	Low level (10 ng/g)	Medium level (100 ng/g)	High level (500 ng/g)
BPA	21.615	357 > 73 (CE25)	357 > 191 (CE20)	0.13	0.17	83.7 ± 2.1	86.2 ± 2.2	89.7 ± 1.9	97.6 ± 5.2	100.4 ± 3.0	103.4 ± 2.2
MonoBBPA	24.895	437 > 73 (CE25)	452 > 437 (CE15)	0.18	0.23	84.3 ± 2.9	89.7 ± 2.1	89.1 ± 2.0	86.2 ± 6.0	90.3 ± 2.2	83.6 ± 3.7
DiBBPA	28.090	515 > 73 (CE30)	515 > 191 (CE20)	0.22	0.24	79.1 ± 1.7	83.4 ± 3.5	87.5 ± 3.1	88.6 ± 6.8	93.3 ± 1.5	92.7 ± 3.0
TriBBPA	31.265	595 > 73 (CE25)	610 > 595 (CE15)	0.27	0.30	75.7 ± 4.0	73.1 ± 1.9	78.9 ± 1.8	77.4 ± 4.1	91.6 ± 4.8	85.9 ± 3.2
TBBPA	33.875	673 > 73 (CE25)	688 > 673 (CE20)	0.30	0.33	61.4 ± 4.2	62.0 ± 2.0	66.5 ± 1.7	55.2 ± 5.4	56.5 ± 4.3	71.4 ± 4.1
diMeO-MonoBBPA	23.555	336 > 321 (CE10)	334 > 319 (CE10)	0.12	0.11	90.3 ± 0.9	95.5 ± 2.0	96.0 ± 2.6	95.8 ± 4.6	102.3 ± 1.0	96.6 ± 6.4
diMeO-2,2'-DiBBPA	25.850	414 > 399 (CE10)	399 > 239 (CE25)	0.12	0.12	88.9 ± 7.2	99.6 ± 3.1	98.3 ± 7.1	93.9 ± 3.2	95.2 ± 3.0	75.9 ± 4.5
diMeO-2,6-DiBBPA	27.625	414 > 399 (CE10)	399 > 239 (CE25)	0.06	0.06	84.1 ± 10.6	86.4 ± 7.5	95.6 ± 2.2	93.5 ± 0.9	95.8 ± 5.7	94.3 ± 4.3
diMeO-TriBBPA	29.800	492 > 477 (CE10)	494 > 479 (CE10)	0.23	0.22	97.6 ± 2.2	88.8 ± 5.7	99.7 ± 5.4	90.1 ± 2.3	92.9 ± 4.2	87.2 ± 1.8
diMeO-TBBPA	31.750	572 > 557 (CE10)	557 > 382 (CE40)	0.22	0.23	84.1 ± 5.0	87.2 ± 1.1	87.9 ± 4.1	87.4 ± 3.7	92.9 ± 9.2	94.6 ± 4.7
2-MoBP	10.115	231 > 135 (CE20)	231 > 150 (CE10)	0.12	0.16	89.0 ± 2.4	88.6 ± 7.9	93.5 ± 5.5	99.2 ± 4.5	91.3 ± 5.2	98.7 ± 4.0
2,4-DiBP	12.908	309 > 137 (CE20)	309 > 148 (CE20)	0.13	0.14	98.0 ± 3.1	92.6 ± 4.4	927 ± 3.6	95.4 ± 4.2	93.0 ± 6.3	85.1 ± 4.1
2,4,6-TriBP	15.730	389 > 147 (CE25)	387 > 137 (CE30)	0.13	0.15	98.7 ± 1.6	88.7 ± 2.6	99.5 ± 5.1	83.0 ± 5.2	89.7 ± 0.9	89.0 ± 3.4
2,3,4,6-TetraBP	19.630	467 > 137 (CE25)	467 > 139 (CE15)	0.25	0.27	84.1 ± 7.5	91.1 ± 3.0	86.2 ± 4.7	76.0 ± 5.1	86.5 ± 0.3	81.8 ± 3.9
PBP	24.700	545 > 137 (CE30)	560 > 139 (CE30)	0.19	0.22	76.5 ± 5.1	81.0 ± 0.9	80.4 ± 3.2	75.3 ± 4.4	86.1 ± 5.1	77.7 ± 2.0

^a The phenolic compounds were quantified as their corresponding trimethylsilyl ether derivatives; CE: collision energy.

^b Method detection limit for biota samples.

^c Method detection limit for sediment samples.

^d Recoveries of target chemicals in biotas for low, medium and high spike concentrations ($n = 3$ for each spike levels).

^e Recoveries of target chemicals in sediment for low, medium and high spike concentration ($n = 3$ for each spike levels).

The mass spectrum analysis included MRM transitions, collision-induced dissociation (CID) energy voltages, retention times and MDLs, as listed in Table 1. The MDLs of biotas for TBBPA and BPA were 0.30 and 0.13 ng/g dw, and of sediments were 0.33 and 0.17 ng/g dw, respectively. In biotas, the MDLs of debromination products, O-methylation products and BPs were 0.18 to 0.27, 0.06 to 0.23 and 0.12 to 0.25 ng/g, respectively, compared to 0.23 to 0.30, 0.06 to 0.23 and 0.14 to 0.27 ng/g, respectively, in sediments. The MDLs in our study were lower than those reported by Guerra et al. (2010), whose LC-MS/MS analysis showed values of 0.6 to 2.7 ng/g for TBBPA and its debromination products in sediment. In addition, the sensitivity toward BPA was significantly improved by derivatization in our GC-MS/MS based method (0.17 ng/g), compared to the LC-MS/MS based method (3.7 ng/g) (Guerra et al., 2010). A few studies have reported the identification and occurrence of debromination products of TBBPA in the environment and biota (Chu et al., 2005; Guerra et al., 2010; Liu et al., 2017). However, most of them were unable to achieve baseline separation of the possible isomers of DiBBPA (2,2'-DiBBPA and 2,6-DiBBPA) because they used a HPLC-MS-MS method, except for the study by Liu et al. (2020). In our study, the target chemicals were separated unambiguously by GC (Fig. S3), enabling subsequent qualitative and quantitative analysis.

3.2. Occurrence of TBBPA and its transformation products in sediment

Concentrations of all target compounds in sediments are presented in Table 2. It can be seen that TBBPA and its debrominated products were widely detected in sediment, whereas relatively low detection frequencies (DFs) were found for methylated products, i.e., DFs of 87.5%, 50%, 62.5%, and 75% for diMeO-TBBPA, diMeO-TriBBPA, diMeO-DiBBPA, and diMeO-MoBBPA, respectively. This indicates that debromination might be easier than O-methylation during degradation of TBBPA.

The highest concentrations were found for TBBPA (19.8 to 1.52×10^4 ng/g dw; dry weight: dw), followed by the debromination products (8.10 to 1.82×10^3 ng/g dw). Among the detected transformation products, levels of TriBBPA were the highest (4.72 to 1.03×10^3 ng/g dw), followed by DiBBPA (2.15 to 412 ng/g dw, summed concentrations of 2,2'-DiBBPA and 2,6-DiBBPA) and MoBBPA (1.18 to 401 ng/g dw). The concentrations of O-methylation products ranged from 0.08 to 11.9 ng/g dw, and were 1–2 orders of magnitude lower than those of debromination products. This confirmed that debromination occurred more easily than O-methylation in

sediment from the Lianjiang River. This may be related to the preference of microbial debromination in sediments with an anaerobic environment. As reported by Sun et al. (2014), O-methylation of TBBPA takes place under aerobic conditions, whereas debromination is preferred under anaerobic conditions. In addition, debromination products of TBBPA can also originate from the direct emission from technical products of TBBPA (Howard and Muir, 2013).

Comparing the different sampling sites, high concentrations of TBBPA and transformation products were discovered in sediments from the tributary (B) sites close to the e-waste dismantling workshops, whereas lower concentrations were found at the main stream (A) sites far from the e-waste site (Fig. S4). Specifically, the concentrations of TBBPA in sediment from A sites ranged from 19.8 to 1.27×10^3 ng/g dw, which were about 1–3 orders of magnitudes lower than those reported for B sites. The lowest concentration of TBBPA was found at the background sampling site upstream of the Lianjiang River (A1). Although the larger volume of water flow in the mainstream could dilute these pollutants, the primitive e-waste dismantling activities might be a major source of these contaminants. In addition, due to the dilution effect of mainstream, relatively lower concentrations of TBBPA found in sediments downstream from the dismantling site (Fig. S4, sampling site A5).

The TBBPA concentrations found in our study were slightly lower than those reported for the same region by Li et al. (2019) (0.99 to 4.12×10^4 ng/g dw) in sediment collected in 2013. This may be ascribed to differences in the sampling time and variation in sampling sites away from the potential sources. In addition, the application of these more stringent environmental protection and remediation measures, such as sewage treatment facilities and pipeline network construction, have been carried out at e-waste polluted sites near the Lianjiang River since 2018, which may have reduced the emission of pollutants into the river. As shown in our previous research, low TBBPA concentrations (108 to 3.1×10^3 ng/g dw) were detected in sediment samples collected in 2020 from the same sampling sites of the Lianjiang River (Chen et al., 2021). However, the concentrations of TBBPA found in sediment in our study were higher than those reported by Wang et al. (2014) (24.7 to 914 ng/g dw) at an e-waste site in Qingyuan in 2012. The concentrations of TBBPA and its debrominated products in sediments from the Lianjiang River were also higher than those measured in the Xiaoqing River (2.08 to 1.35×10^3 ng/g dw, 1.16 to 253 ng/g dw, 0.15 to 97.1 ng/g dw, and n.d. to 52.3 ng/g dw for TBBPA, TriBBPA, DiBBPA, and MoBBPA, respectively), which flows through the major BFR factory zones of Eastern China (Lan et al., 2019). The concentrations of TBBPA in sediment from the e-waste contaminated sites were also notably higher than those near rivers without known sources of TBBPA, such as Lake Chaohu (n.d. to 518 ng/g dw) in China (Yang et al., 2012), the Dongjiang River (0.19 to 82.3 ng/g dw) in South China (He et al., 2013), and estuaries in the Netherlands and England (25 to 9.75×10^3 ng/g dw) (Morris et al., 2004). This suggests that primitive e-waste dismantling processes may be a major source of TBBPA contamination.

In addition, high levels of BPA were found in sediment from the tributary (3.46×10^3 to 2.57×10^4 ng/g dw), which were higher than those from the main river (35.9 to 4.68×10^3 ng/g dw). However, the occurrence of BPA is not only related to the direct release or debromination of TBBPA during primitive e-waste dismantling activities but also the wide utilization of BPA-based products in daily life. This was confirmed by the relatively high BPA concentrations found in the main stream compared to that of TBBPA, whereas in sediment from the tributary close to the e-waste dismantling site, the content of BPA in sediment was comparable to that of TBBPA, indicating that BPA in sediment of the main stream was influenced by a variety of anthropogenic activities since BPA was previously widely used in the manufacturing of polycarbonate and epoxy resins used in a variety of products, including baby bottles, plastic toys and protective coatings on metal food containers. However, the concentration of BPA in sediment in our study was higher than reported in other areas, such as the Bahe River in China (82 to 221 ng/g dw) (Wang et al., 2020), the Hyeongsan River in South Korea (5.5 to 88.5 ng/g dw) (Kim et al., 2014), and Iberian rivers in Spain (n.d. to -117 ng/g dw) (Gorga et al., 2015).

Table 2

Concentration of target compounds in river sediments (ng/g dry weight) from a typical e-waste dismantling site. (Sediment A was collected from the main stream, Sediment B was from the tributary at the e-waste dismantling site).

Compounds	A1	A2	A3	A4	A5	B1	B2	B3
BPA	35.9	50.1	3.65 $\times 10^3$	4.68 $\times 10^3$	52.0	3.46 $\times 10^3$	4.06 $\times 10^3$	2.57 $\times 10^4$
MonoBBPA	3.33	1.18	4.30	20.2	1.47	103	74.9	401
DiBBPA	9.58	2.26	6.78	36.6	2.15	151	57.6	412
TriBBPA	4.72	17.3	33.5	118	12.0	596	218	1.03×10^3
TBBPA	19.8	413	253	1.27×10^3	89.1	7.72×10^3	4.16 $\times 10^3$	1.52×10^4
diMeO-MonoBBPA	0.12	0.20	0.18	n.d.	n.d.	0.65	1.17	1.48
diMeO-2,2'-DiBBPA	n.d.	n.d.	0.17	1.92	n.d.	0.16	0.83	1.17
diMeO-2,6-DiBBPA	n.d.	0.12	0.31	n.d.	0.26	0.32	0.52	n.d.
diMeO-TriBBPA	n.d.	n.d.	0.31	n.d.	n.d.	0.89	1.70	2.80
diMeO-TBBPA	n.d.	0.40	0.48	0.82	0.25	5.92	3.95	3.11
2-MonoBP	0.10	0.40	5.22	3.32	1.70	36.6	12.0	41.0
2,4-DiBP	0.35	1.02	5.64	8.84	2.50	47.3	16.5	135
2,4,6-TriBP	0.56	4.19	167	171	12.2	162	357	348
TBP	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
PBP	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
ΣBBPA	37.4	434	297	1.44×10^3	105	8.57×10^3	4.51 $\times 10^3$	1.71×10^4
ΣdiMeO-BBPA	0.30	0.76	1.77	2.75	0.54	8.82	9.87	11.4
ΣBPs	1.01	5.62	178	183	16.6	246	386	524

The total concentration of all BPs in sediment ranged from 1.01 to 533 ng/g dw. Only low brominated BPs containing 1–3 bromine atoms were detected, with decreasing order of concentration 2,4,6-TriBP > 2,4-DiBP > 2-MonoBP. TBP and PBP was undetectable in all the sediment samples collected. Similarly, significantly higher concentrations of BPs were found in sediment from the tributary than from the main stream, indicating these BPs were also mainly derived from e-waste dismantling activities. 2,4,6-TriBP is also used as a flame retardant, while low brominated BPs may originate via diphenyl ether bond cleavage of PBDEs (Cao et al., 2017). Relatively high concentrations of PBDEs have been reported in sediment in a previous study (Li et al., 2019).

3.3. Occurrence of TBBPA and its transformation products in biotas

3.3.1. Fish

The concentrations of TBBPA, debromination and *O*-methylation products in fish ranged from 26.3 to 749 ng/g lw, 12.2 to 180 ng/g lw and 14.4 to 89.3 ng/g lw, respectively (Table 3). Similarly, the concentrations of TBBPA and its transformation products in fish samples (fish 5, 6, and 7) collected from close to the e-waste dismantling site ranged from 253 to 749 ng/g lw, which were apparently higher than levels in fish from the other sites (fish 1, 2, 3, and 4, 26.3 to 468 ng/g lw) (Fig. 1 and Fig. S4). In general, the TBBPA concentrations in tilapias in the present study are among the highest found around the world and were higher than levels found in aquatic birds from an e-waste region in Southern China (28–173 ng/g lw) (He et al., 2010). High levels of TBBPA (but lower than our study) were also detected in marine biological samples (n.d. to 207 ng/g lw) from the Chinese Bohai sea near a BFR production area (Liu et al., 2016a). In addition, concentrations of TBBPA in fish from the e-waste site in our study were one order of magnitude higher than biota species (0.56 to 22.1 ng/g lw) in mangrove wetlands of South China (Li et al., 2021), bull sharks (0.035 to 35.6 ng/g lw) and bottlenose dolphins (0.056 to 8.48 ng/g lw) in Florida (Johnson-Restrepo et al., 2008), and sardines (n.d. to 0.11 ng/g wet weight (ww)) from Japan (Ashizuka et al., 2010). However, relatively high levels of TBBPA in four fish species (28.5 to 39.4 ng/g ww) were reported in Lake Chaohu, China (Yang et al., 2012).

Regarding the tissue distribution characteristics, the concentrations of TBBPA in the gills, viscera and intestine (including intestinal contents) were 6.96 to 126 ng/g lw, 127 to 1.47×10^5 ng/g lw and 1.50×10^3 to 1.97×10^5 ng/g lw, respectively, the total concentrations of debromination products were 3.79 to 50.0 ng/g lw, 25.2 to 4.27×10^3 ng/g lw and 190 to 7.70×10^3 ng/g lw, respectively, and the concentrations of all *O*-methylation products were 1.63 to 148 ng/g lw, 6.62 to 256 ng/g lw and 11.5 to 221 ng/g lw, respectively (Fig. S5). The high

concentrations in the intestine may be due to undigested food or ingestion of other sediment residues. This suggests that dietary ingestion may be an important source of TBBPA and its transformation products in fish. For TBBPA and its debromination products with known external sources, the concentrations in the intestine were significantly higher than those in other tissues. However, for *O*-methylated products with no clear environmental sources, the concentrations in the viscera were higher than those in the intestine, and other tissues. This may be because the liver and kidneys are the main metabolic organs in the viscera, which contribute to the formation of *O*-methylated products.

A high concentration of TBBPA was also detected in the kidneys of four different fish species from Lake Chaohu (Yang et al., 2012). Tan et al. (2019) showed that TBBPA and its debrominated metabolites were mainly distributed in the livers and kidneys of adult zebrafish after exposure to water containing different TBBPA levels. The highest concentrations of TBBPA and its metabolites were found in liver of zebrafish, followed by kidney, which were significantly higher than those found in gill and muscle. However, the same study found that in zebrafish, the concentration in muscle was lower than in gill tissue (Tan et al., 2019), contrary to our study. This difference may be related to the different types of fish species studied or their different lifestyles. Yang et al. (2012) also detected higher concentrations of TBBPA in muscle than gill tissue in four different fish. In addition, the distribution ratio of diMeO-TBBPA in gill and muscle (0.78) was higher than that of TBBPA (0.23), indicating that the *O*-methylation products of TBBPA accumulated more easily in the gills, consistent with the higher lipid content extracted from the gill than muscle tissue. After substitution of phenolic hydroxyl groups with methyl, the resulting *O*-methylation products are more lipophilic, increasing the possibility of bioaccumulation in the gills with a higher lipid content (George and Hågblom, 2008).

We also investigated the relationship between the concentrations of the target analytes and fish size (Table S1). No significant correlation was found for TBBPA or its transformation products in relation to fish size. The highest concentration of TBBPA (746 ng/g lw) and *O*-methylation products (89.3 ng/g lw) were found in the smaller fish (159 g), but this was not the case for debromination products. However, Yang et al. (2012) reported a significant positive correlation between TBBPA accumulation and fish size. Since there may be chemical- and species-specific differences in the metabolism and accumulation of TBBPA and its transformation products, further research is needed to clarify the possible mechanism.

BPA and BPs were also identified in fish, with concentrations ranging from 259 to 1.26×10^3 ng/g lw and 50.6 to 787 ng/g lw, respectively. The BPA concentrations reported in our study (2.51 to 18.3 ng/g ww,

Table 3

Median concentration (range) of target compounds in biotas (ng/g lipid weight) from a river flowing through a typical e-waste dismantling site.

Compound	Fish				Whelks (n = 7)
	Muscle (n = 7)	Gills (n = 7)	Visceral (n = 5)	Intestine and contents (n = 6)	
BPA	482 (259– 1.26×10^3)	328 (68.8– 2.31×10^3)	3.26×10^4 (481– 1.07×10^5)	2.96×10^4 (1.69×10^3 – 7.70×10^4)	259 (98.4–694)
MonoBBPA	8.61 (1.17–32.8)	3.03 (0.74–11.0)	173 (2.10–811)	209 (10.8– 1.45×10^3)	5.52 (4.06–11.5)
DiBBPA	10.5 (3.60–24.0)	2.72 (1.12–12.7)	356 (6.02–728)	232 (38.2– 1.4×10^3)	9.82 (3.96–11.4)
TriBBPA	23.8 (7.45–124)	6.77 (1.94–27.3)	748 (17.1– 2.74×10^3)	614 (140– 4.85×10^3)	22.6 (5.41–27.5)
TBBPA	253 (26.3–749)	57.0 (6.96–126)	8.34×10^3 (1.27 – 1.47×10^5)	1.78×10^4 (1.50×10^3 – 1.97×10^5)	82.6 (39.4–212)
diMeO-MonoBBPA	5.38 (0.55–7.46)	2.15 (0.60–5.71)	16.9 (0.79–38.0)	6.94 (1.82–18.7)	6.43 (1.04–9.86)
diMeO-2,2'-DiBBPA	3.42 (1.22–9.16)	1.20 (0.21–7.37)	8.50 (0.74–13.0)	8.15 (1.04–22.6)	5.85 (2.71–17.2)
diMeO-2,6-DiBBPA	9.14 (1.89–13.5)	2.37 (0.40–16.1)	21.3 (1.81–31.0)	33.7 (1.70–45.2)	6.61 (1.80–8.20)
diMeO-TriBBPA	10.1 (2.37–13.0)	2.42 (0.58–5.19)	14.6 (1.73–90.6)	8.63 (3.51–60.2)	14.6 (7.43–26.3)
diMeO-TBBPA	20.5 (8.41–46.2)	15.9 (1.63–114)	43.3 (1.55–83.0)	32.7 (3.78–73.8)	29.6 (8.86–41.0)
2-MoBP	21.6 (2.96–35.2)	14.7 (1.06–34.6)	66.3 (6.41–109)	32.0 (7.20–65.9)	50.7 (29.5–71.2)
2,4-DiBP	59.3 (7.53–140)	48.7 (5.57–74.7)	351 (9.07–935)	93.0 (51.6–787)	31.3 (9.26–72.0)
2,4,6-TriBP	107 (40.1–612)	41.0 (23.1–126)	2.08×10^3 (95.4– 3.85×10^3)	2.19×10^3 (412– 3.86×10^3)	88.1 (36.7–228)
2,3,4,6-TetraBP	n.d.	n.d.	10.3 (n.d.–16.1)	3.45 (n.d.–9.21)	n.d.
PBP	n.d.	n.d.	n.d.	n.d.	n.d.
ΣBBPA	396 (38.5–930)	69.6 (10.8–177)	9.62×10^3 (152– 151×10^5)	2.83×10^4 (1.69×10^3 – 205×10^5)	121 (52.8–262)
ΣdiMeO-ΣBBPA	48.5 (14.4–89.3)	24.0 (3.42–148)	104 (6.62–256)	90.2 (70.7–221)	63.1 (21.8–472)
ΣBPs	188 (50.6–787)	104 (29.7–235)	2.51×10^3 (111– 4.91×10^3)	2.31×10^3 (471– 4.72×10^3)	170 (75.5–371)

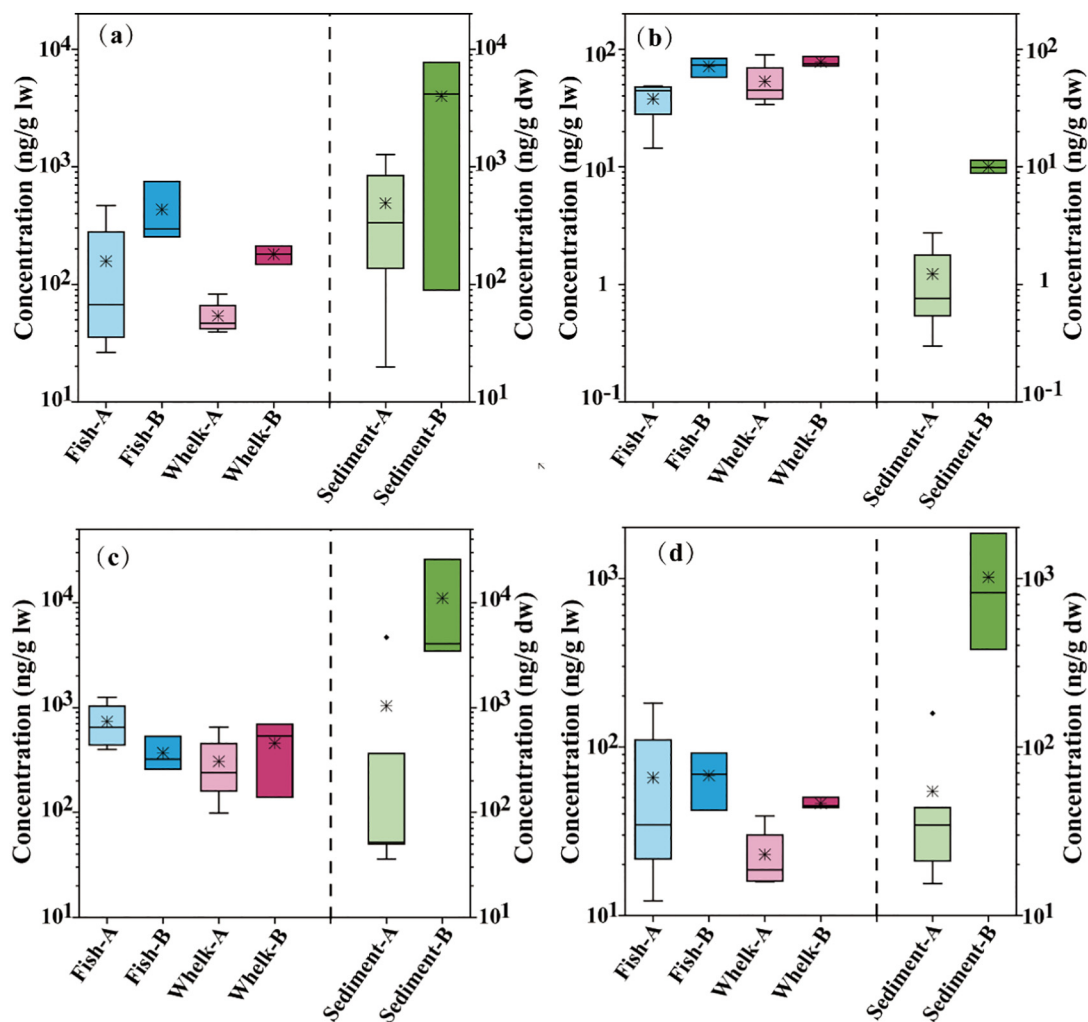


Fig. 1. Box and whisker plots of the concentration of TBBPA (a), diMeO-TBBPA (b), BPA (c), and bromophenols (d). (Sample-A was collected from the main stream, Sample-B was from the tributary at the e-waste dismantling site).

Table S2) were slightly lower than those found in fish muscle from the Pearl River Estuary (PRE) (3.73 to 65.5 ng/g ww) (Lv et al., 2019). This suggests that BPA levels are mainly influenced by anthropogenic activities. The developed economy and large population density in the PRE have resulted in extensive BPA pollution of the aquatic ecosystem. In addition, low brominated BPs have been widely detected, with similar composition profiles as in sediment. However, in our study 2,3,4,6-TetraBP was detected in the viscera and intestine and contents from fish samples collected from near the e-waste site, indicating that it may have originated from biotransformation since there was no known industrial source. 2,3,4,6-TetraBP has been confirmed as a biomarker of exposure to e-waste pollutants and has been detected in the serum of e-waste dismantling workers in India (Eguchi et al., 2012).

3.3.2. Whelks

The total concentrations of TBBPA, debromination and *O*-methylation products in whelks ranged from 39.4 to 212, 13.4 to 50, and 21.8 to 472 ng/g lw, respectively. Higher concentrations of *O*-methylation products were found in the muscle of whelks, which almost exceeded the levels of the parental TBBPA. Only a few previous studies have examined TBBPA and transformation products in whelks. The concentration of TBBPA found in whelks (45 ng/g ww) from the North Sea was higher than in our study (0.72 to 2.54 ng/g ww) (Morris et al., 2004). Watanabe et al. (1983) found that diMeO-TBBPA was exclusively detected in mussels collected in Osaka,

Japan. Although up to 940 ng/g lw of diMeO-TBBPA was found in peregrine falcon eggs from South Greenland, TBBPA was not detected in any of the eggs (Vorkamp et al., 2005). These studies indicate that *O*-methylation products may be the major metabolites of TBBPA in some organisms. Since in our study, the *O*-methylation products in matched sediment samples made little contribution to the total TBBPA content, as mentioned above, we suggest that *O*-methylation products may be mainly formed by *in vivo* biotransformation of TBBPA in whelks. However, it is still possible that *O*-methylation products were formed from TBBPA by chemical or microbial transformation in the environment and subsequently accumulated in the whelks. Furthermore, there is evidence that *O*-methylation products are more persistent, lipophilic and bio-accumulative in biotas than the parent compound (Balmer et al., 2004). Thus, they may cause more lasting toxic effects, which should be included in future routine analysis.

Regarding phenolic compounds, the concentrations of BPA and BPs ranged from 98.4 to 694 ng/g lw, and 75.5 to 371 ng/g lw, respectively, in whelks, which were comparable to or slightly lower than those found in muscle of fish samples. The composition of BPs in whelks was also similar to that found for fish, indicating that they may have similar sources derived from primitive e-waste dismantling activities. However, in contrast to fish samples, the content of bromophenols in whelks was higher than that of TBBPA and its transformation products, which might be related to the species-specific accumulation and enrichment of bromophenols in whelks (Liao and Kannan, 2019).

3.4. Composition profiles of TBBPA and its transformation products

The composition profiles of TBBPA and its transformation products in all the sediment and biota samples are shown in Fig. 2. There was little difference in the composition profiles between samples collected from the contaminated tributary and the main stream. TBBPA accounted for 69% to 90% of the total concentration, followed by TriBBPA (6% to 19%), while the other congeners contributed less than 5% to 12% of the total concentration. The composition profiles were similar between sediment and biotas, as well as among different types of tissue in fish, except a relatively higher contribution was found for TriBBPA in whelks (up to 19% of the total concentrations).

The composition profile of sediment in our study was similar to that reported previously for sediment samples collected from the Lianjiang River in 2020 (Chen et al., 2021), as well as from the Xiaoqing River, which showed concentrations in the order TBBPA > TriBBPA > DiBBPA > MoBBPA (Lan et al., 2019). The congener profile was also consistent with that of indoor dust collected from an office building at the same e-waste dismantling site (Liu et al., 2020), indicating that the pollutants in these sediments may be related to the disassembly of e-waste, which might undergo a continuous debromination process. However, different homologues have been observed in biotas. For example, TriBBPA was found to be the major debromination product of TBBPA in breast milk from Japan, with concentrations almost three times higher than that of TBBPA (Nakao et al., 2015).

In the case of *O*-methylation products, similar composition profiles were also found between sediment and biotas (Fig. 2). The compound showing the highest contribution to the total concentration of *O*-methylation products in sediment was diMeO-TBBPA (41% to 66%), followed by diMeO-TriBBPA (10% to 23%), whereas the contributions of other congeners diMeO-DiBBPA and diMeO-MoBBPA were similar among the different samples. The most likely source of diMeO-TBBPA was from biotransformation in biotas, since no specific anthropogenic sources of *O*-methylation products are known. diMeO-TriBBPA and lower brominated isomers might originate from the *O*-methylation of TriBBPA, or diMeO-TriBBPA may undergo debromination processes to generate diMeO-DiBBPA and diMeO-MoBBPA. The similar concentrations of diMeO-DiBBPA and diMeO-MoBBPA in fish and whelks, together with the relatively low levels of *O*-methylation products detected in sediment suggest the most likely source of *O*-methylation products was from biotransformation in biotas. However, further studies are needed to verify this.

3.5. Comparison of concentrations in sediments and biotas

Comparing the concentration of BPA, BPs, TBBPA and diMeO-TBBPA in all samples, higher concentrations of the target analytes were found in the tributary sediments (B1, 2, 3) and biotas (fish 5, 6, 7) (Fig. 1 and Fig. S4) than samples from the main stream, indicating that the primitive e-waste dismantling activities may be an important source of TBBPA and its transformation products. However, the concentration differences between the tributary and main stream in organisms were not as large as those in sediments. For example, the difference between TBBPA in sediments from A and B sites was 1–2 orders of magnitude, whereas the difference in TBBPA in organisms was within one order of magnitude. In the case of diMeO-TBBPA, the difference of TBBPA in sediments was more than one order of magnitude, whereas similar concentrations were found in biotas. This may be related to a variety of factors. In abiotic sediment samples, primitive e-waste disassembly activities were likely the main reason for the concentration difference of TBBPA, BPA and BPs between contaminated and background sites, whereas for transformation products with no specific anthropogenic source, such as diMeO-TBBPA, microbial transformation in sediment was probably the main source. Species-specific differences in absorption and enrichment of pollutants may partly explain the concentration difference.

In addition, the concentrations of diMeO-TBBPA in biotas were lower than their corresponding phenolic parental compounds. However, the concentration difference ranged from several times to tens of times, which was significantly lower than the three orders of magnitude difference observed in sediment. This further indicates that the diMeO-TBBPA in fish and whelks may have largely originated from the *in vivo* biotransformation of TBBPA and/or ease of accumulation and enrichment in biotas (Gu et al., 2017; Katrin et al., 2005; Kotthoff et al., 2017; Watanabe et al., 1983). However, there also studies indicated that TBBPA were easily metabolized by microorganisms in environmental media especially in complex soil and sediment (An et al., 2011; Li et al., 2016). Whelks belong to the benthos and may absorb more methylation products from sediment than fish. The contribution of diMeO-2,2'-DiBBPA was three times higher than that of diMeO-2,6-DiBBPA in sediment, whereas it made a comparable contribution in whelks. In contrast, the contribution of diMeO-2,2'-DiBBPA was lower than that of diMeO-2,6-DiBBPA in fish samples (Fig. 2), which may partly explain why fish had a lower concentration of methylation products than in whelks, which reside in sediment.

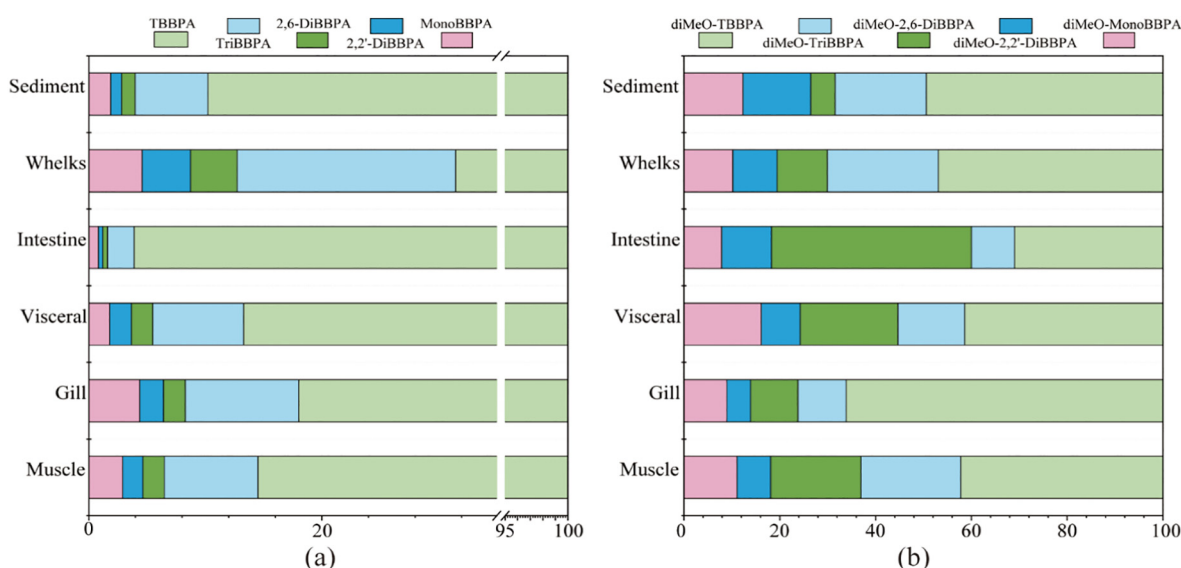


Fig. 2. Composition profiles of TBBPA and its transformation product in samples of sediment, whelks, and fish intestine, viscera, gill and muscle: (a) TBBPA and its debromination products; (b) *O*-methylation products.

Correlations between TBBPA and its transformation products, as well as their relations among sediment and biotas were also investigated. The most widely detected targets, TBBPA, TriBBPA and diMeO-BBPA, were included in the statistical analysis, and their correlation matrix heat map is presented in Fig. S6. The occurrence of TBBPA and its transformation products in sediment showed a close correlation ($R > 0.929$, $P < 0.01$). In fish samples, significant correlations were found between TBBPA and TriBBPA ($R = 0.857$, $P < 0.01$) and between TBBPA and diMeO-BBPA ($R = 0.879$, $P < 0.01$). However, no significant correlation was found between the debromination and *O*-methylated products. In addition, no significant correlation was found for the examined compounds in whelks, or among sediment and biotas. This indicates that these transformation products in fish were mainly derived from metabolism in biotas, whereas the transformation products in whelks originated from ingestion or *in vivo* biotransformation. In addition, the chemical- and species-specific differences in the metabolism and accumulation of TBBPA and its transformation products might also influence their correlation.

3.6. BSAF in biota

BSAF was calculated to evaluate the accumulation capacities of TBBPA and its transformation products in fish and whelks from sediment. A value of BSAF > 1.0 indicates the preferential partitioning of a compound of interest from sediment to biota (La Guardia et al., 2012). In our study, the BSAF values (mean $\pm$ SD) for TBBPA were 0.02 ± 0.03 in fish and 0.02 ± 0.02 in whelks, and for its debromination products BPs 0.09 ± 0.07 in fish and 0.03 ± 0.01 in whelks (Fig. 3). The BSAFs for TBBPA were lower than those reported for other species from the PRE, such as blue-spotted mudskipper, Chinese black sleeper, striped mullet, mud crab and red eelgoby, which had values ranging from 1.13 to 3.18 (Li et al., 2021). Variations in metabolic capacity may account for the difference in BSAF since tilapia have higher biotransformation capabilities than other species (González et al., 2009). However, in our study, diMeO-TBBPA showed a significantly higher BSAF value (1.69 ± 0.89 for fish and 2.09 ± 1.87 for whelks, respectively) than TBBPA (Fig. 3), indicating that bioaccumulation potential of the *O*-methylated products was higher than TBBPA, and the bioaccumulation of *O*-methylated TBBPA occurred in the biota. Few previous studies have investigated the bioaccumulation of diMeO-TBBPA in aquatic ecosystems, however, evidence from biotransformation of triclosan, a chemical with similar structure of TBBPA, indicates that methyl product has a higher bioaccumulation potential than triclosan, although they both do not seem to

bioaccumulate in a tropical marine environment (Zhang and Kelly, 2018). In addition, large variations in BSAF were observed for diMeO-TBBPA, which may be explained by the variation in bioavailability of organic contaminants in sediments. Nevertheless, our investigation indicates that the methylation of phenolic compounds may enhance their ability to accumulate in aquatic organisms.

There was no significant difference in BSAF between fish and whelks. This might be ascribed to the similar feeding habits of whelks and the omnivorous fish, since both tilapia and whelks ingest sediments as one of their food items.

4. Conclusion

The environmental occurrence and transformation of TBBPA and its transformation products in matched sediment, fish, and whelk samples collected from a typical e-waste dismantling site were investigated. The target chemicals were widely detected, especially in the sediment and biotas collected from close to the e-waste dismantling site, indicating that e-waste dismantling processes may be a major source of these pollutants. The debrominated products of TBBPA appeared to undergo a continuous debromination process and were observed in both sediment and biotas. In contrast, *O*-methylation products in biotas were mainly derived from *in vivo* biotransformation. Higher concentrations of diMeO-BBPA than debrominated products were observed in whelks, raising concerns that the *O*-methylation products may be more persistent, lipophilic and bioaccumulative in biota than the parent compound. Thus, *O*-methylation products may cause more lasting toxic effects, which should be included in future routine analysis.

CRediT authorship contribution statement

Yan Yang: Conceptualization, Writing - Reviewing and Editing.
Mengdi Zhang: Methodology, Data curation, Formal analysis, Writing - Original draft preparation.
Yuan Gao: Methodology, Validation.
Haojia Chen: Sample collection, Validation.
Juntao Cui: Methodology, Validation.
Yingxin Yu: Writing - Reviewing and Editing.
Shengtao Ma: Conceptualization, Writing - Review & Editing, Supervision.

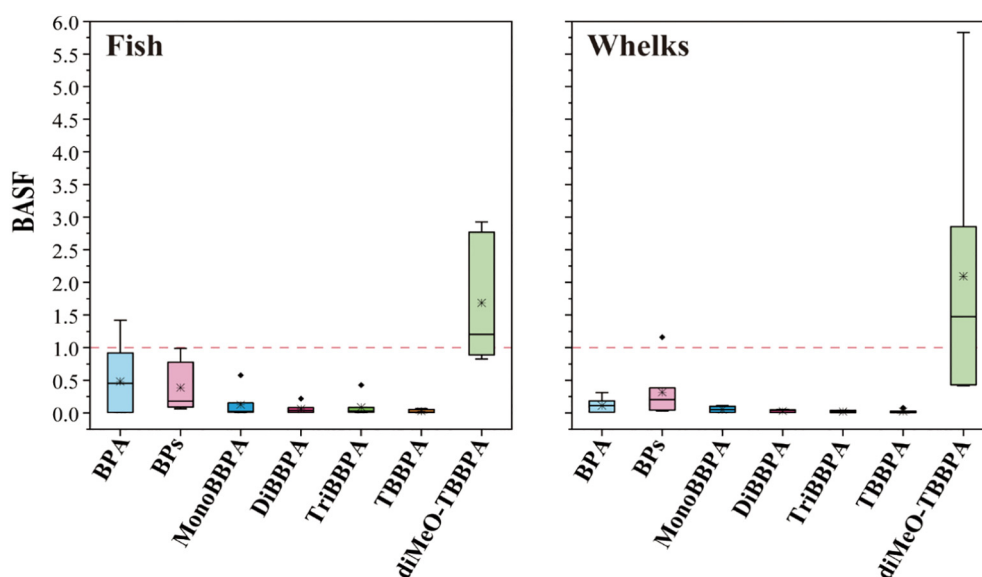


Fig. 3. Box-plot of the biota-sediment accumulation factor (BSAF) for TBBPA and its transformation products.

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. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.scitotenv.2022.155249>.

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