

New Mixed Bromine/Chlorine Transformation Products of Tetrabromobisphenol A: Synthesis and Identification in Dust Samples from an E-Waste Dismantling Site

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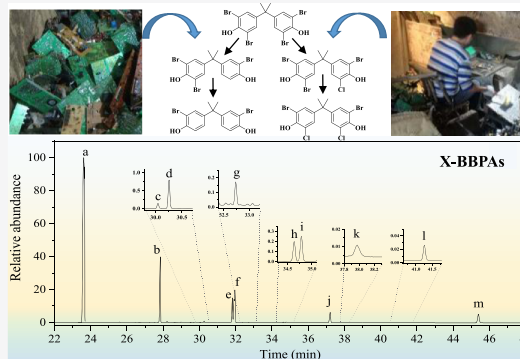


Article Recommendations



Supporting Information

ABSTRACT: The large-scale production and usage of tetrabromobisphenol A (TBBPA) and its analogues have caused widespread contamination, raising concern about their potential endocrine disruption effects on both humans and ecosystems. In the present study, debromination and unknown mixed bromine/chlorine transformation products of TBBPA (X-BBPA) were screened in dust samples from an e-waste dismantling site. Five monochloro products (2-chloro-2',6,6'-TriBBPA, 2-chloro-2',6-DiBBPA, 2-chloro-2',6'-DiBBPA, 2-chloro-2'-MoBBPA, and 2-chloro-6-MoBBPA) and two dichloro products (2,2'-dichloro-6,6'-DiBBPA and 2,2'-dichloro-6-MoBBPA) were successfully synthesized and structurally identified. TBBPA and its transformation products were detected by comparison of their mass spectra and retention times with those of synthetic standards. The mean concentration of X-BBPA was 1.63×10^4 ng/g in e-waste dismantling workshop dust samples based on dry weight, which was at a similar level to TBBPA. However, it was 1 order of magnitude lower than the concentrations of the debromination congeners. Thus, both debromination and chlorine–bromine exchange may be important reactions during the thermal processing of e-waste. The results on mixed chlorinated/brominated TBBPA transformation products provided new insights into TBBPA transformation. The elevated levels of the transformation products of TBBPA suggested that these products should be targeted to avoid underestimation of possible health risks.



INTRODUCTION

Tetrabromobisphenol A (TBBPA) is a commonly used brominated flame retardant (BFR) with a high production volume. It has been widely utilized as an additive BFR during the manufacture of printed circuit boards and plastic polymers to improve the insulation properties of electrical and electronic equipment.^{1,2} However, evidence from toxicological studies has shown that neurodevelopmental toxicity is associated with TBBPA exposure in zebrafish larvae via disruption on thyroid hormones.³ TBBPA has also been detected in the brains of mice after oral dosage, and several behavioral alterations have been observed.⁴ Alternatives to TBBPA, such as tetrachlorobisphenol A and tetrabromobisphenol S, can also affect the neural development in early stages at environmentally relevant doses.⁵ Their debrominated products, such as 2,2',6-tribromobisphenol A (2,2',6-TriBBPA) and 2,6-dibromobisphenol A (2,6-DiBBPA) (Table S1), can promote adipocyte differentiation in 3T3-L1 cells, similar to TBBPA.⁶ However, no restrictions have been placed on the usage of TBBPA, especially in the main production areas in Asia, that is, China and Japan.²

Unlike other additives, TBBPA is used mainly as a reactive BFR that covalently bonds to epoxy resins in circuit boards, and thus is not released as easily as nonchemically bonded BFRs. Nevertheless, TBBPA has been widely detected in global environmental matrices, such as air, dust,^{7–9} soil,¹⁰ water,^{11,12} sediment,^{13,14} wildlife,¹¹ and even the human body.^{15–17} Heavily polluted e-waste dismantling sites have been shown to have high TBBPA levels. For example, elevated concentrations of TBBPA in the air collected from the dismantling halls of a recycling plant were reported.⁸ Exceptionally high TBBPA concentrations at 2.72×10^3 – 4.12×10^4 ng/g dw (dry weight) have been reported in the sediments from a severely e-waste-polluted river in Guiyu.¹³ This is closely related to the large amounts and widespread usage of TBBPA, which is found to

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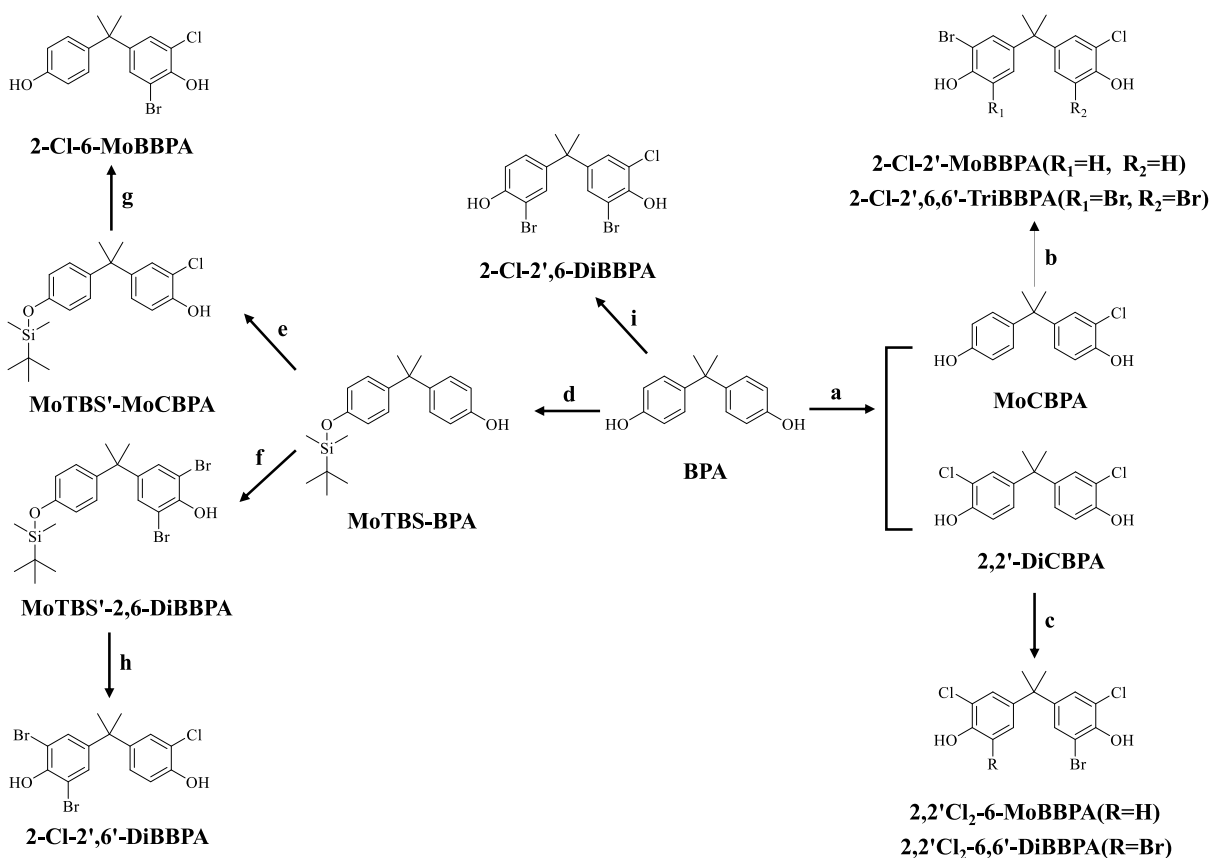


Figure 1. Synthetic schemes for mixed halogenated products of TBBPA. Reaction conditions: (a) NaClO (available chlorine >5%), MeOH, 10 h, room temperature (RT); (b) pyridinium tribromide, EtOH, 2.5 h, RT; (c) pyridinium tribromide, EtOH, 2.5 h, RT; (d) 2.5 equiv imidazole, 1 equiv tBCDS, DMF, 1.0 h, RT; (e) NaClO (available chlorine >5%), THF, 5.0 h, RT; (f) 2.0 equiv pyridinium tribromide, THF, 2.0 h, RT; (g) (1) 1.0 equiv pyridinium tribromide, THF, 2.0 h, RT; (2) 2.5 equiv TBAF, THF, 1.0 h, 0 °C; (h) (1) 2.5 equiv TBAF, THF, 1.0 h, 0 °C; (2) 1.0 equiv *N*-chlorosuccinimide, 0.1 equiv AlCl₃, DCM, 2.0 h, RT; and (i) (1) 2.0 equiv pyridinium tribromide, EtOH, 2.5 h, RT; (2) 1.0 equiv *N*-chlorosuccinimide, 1.0 equiv AlCl₃, EtOH, 2.0 h, RT.

be the overwhelmingly dominant compound of nonpolybrominated diphenyl ether-halogenated flame retardants during thermal treatment of plastic casings and printed circuit boards.¹⁸ However, investigations of the environmental occurrence of TBBPA and the fates of its potential transformation products have been still limited.

Several debromination congeners, TriBBPA, DiBBPA, and MoBBPA (2-monobromobisphenol A), were found in sludge samples collected in Canada, with concentration ranges of 0.11–0.55, 0.18–0.52, and n.d. (not detected)–1.0 ng/g, respectively.¹⁴ These debromination products were also detected in sludge and sediment samples collected from the Ebro River in the northeast of Spain, with large variations from n.d. to 660 ng/g dw.¹⁹ Also, TriBBPA and DiBBPA were tentatively identified in soils collected near a manufacturing plant of BFRs based on the high-resolution mass spectrometric data.¹⁰ In addition, quantitative measurements showed that debrominated products of TriBBPA were the most abundant congeners in human breast milk from Japanese women, with an average concentration being 2.9 times higher than that of TBBPA.¹⁵ These results indicate that the transformation products of TBBPA should be simultaneously analyzed to improve the risk assessment.

Apart from the debrominated congeners, its anisole derivative, TBBPA-dimethyl ether (DM-TBBPA), has been detected in peregrine falcon eggs collected in South Greenland, with a concentration of 940 ng/g lipid weight, whereas TBBPA

was not detectable.²⁰ These results may be of great concern because the anisole metabolites of TBBPA are more lipophilic and environmentally persistent than the debrominated transformation products, and may favor the maternal transfer of contaminants to eggs.² Studies have also indicated that an etherified group at a position in the phenolic rings of TBBPA is crucial for the chemically induced adipogenic effects.²¹ Furthermore, several analogues of TBBPA, such as tetrabromobisphenol S bis(2,3-dibromopropyl ether) and TBBPA bis(2,3-dibromopropyl ether), have been introduced into markets.^{22,23} These analogues may be released into the environment during the lifetime of products, and thus may widely occur in the environment and biota together with their transformation products.^{1,2}

Apart from their debromination congeners and alternatives, the formation and occurrence of mixed halogenated reaction products have raised concern recently. For example, three monochloro-nona-bromo diphenyl ethers (Cl-nonaBDEs) in soil and air samples from south China were identified.²⁴ The occurrence of hexamix-chlorinated/brominated benzenes (HXBs) was determined in fly air, soil, and ash by Tang et al. using gas chromatography-high-resolution mass spectrometry.²⁵ The presence of brominated/chlorinated dibenzofurans (PXDFs) and diphenyl ethers (PXDEs) was also confirmed using two-dimensional gas chromatography-time-of-flight mass spectrometry. Furthermore, PXDFs and PXDEs were detected at concentrations of up to hundreds of nanograms per gram in

soils from e-waste recycling sites.²⁶ These results suggest that mixed chlorinated/brominated transformation products may be formed during thermal processing of solid waste or e-waste materials containing halogen-rich (Cl/Br) organic compounds. However, currently mixed chlorinated/brominated products of TBBPA (X-BBPA) have not been reported in environmental and biota matrices yet.

Therefore, in the present study, we proposed a hypothesis that X-BBPA was formed during primitive and informal e-waste dismantling processing, and may subsequently be released into the surrounding environment. To qualitatively and quantitatively analyze the possible debromination and mixed halogenated reaction products of TBBPA, dust samples were collected from a typical e-waste dismantling site in Guiyu, in South China, where extremely high TBBPA concentrations have been reported in river sediments.¹³ The target TBBPA transformation products were identified by comparing the mass spectra and retention times of the synthesized reference standards with those observed in the environmental samples. Furthermore, the composition characteristics of the transformation products of TBBPA in the dust samples collected from different e-waste dismantling workshops (EWs) were investigated to elucidate their possible formation mechanisms.

MATERIALS AND METHODS

Chemicals. Bisphenol A (BPA) and TBBPA were obtained from AccuStandard Inc (New Heaven, US). ¹³C₁₂-BPA and ¹³C₁₂-TBBPA were purchased from Cambridge Isotope Laboratories (Andover, MA, US) and Wellington Laboratories (Guelph, ON, Canada), respectively. Acetonitrile and methanol of high-performance liquid chromatograph (HPLC) grade were both purchased from Merck (Darmstadt, Germany), and acetic acid was obtained from CNW Technologies GmbH (Germany). *N,O*-bis(trimethylsilyl)trifluoroacetamide was obtained from Sigma-Aldrich (St. Louis, MO, US). Other reagents (guaranteed reagent grade) were used without further purification. Solid-phase extraction cartridges (2 g, 6 mL) were self made with florisil (300 °C overnight; once cooled, deactivated with 2% water).

The synthesis of seven unknown X-BBPAs, that is, 2-chloro-2',6,6'-tribromobisphenol A (2-Cl-2',6,6'-TriBBPA), 2-chloro-2',6-dibromobisphenol A (2-Cl-2',6-DiBBPA), 2-chloro-2',6'-dibromobisphenol A (2-Cl-2',6'-DiBBPA), 2-chloro-2'-monobromobisphenol A (2-Cl-2'-MoBBPA), 2-chloro-6-monobromobisphenol A (2-Cl-6-MoBBPA), 2,2'-dichloro-6,6'-dibromobisphenol A (2,2'-Cl₂-6,6'-DiBBPA), and 2,2'-dichloro-6-monobromobisphenol A (2,2'-Cl₂-6-MoBBPA), and four known debrominated metabolites MoBBPA, DiBBPA (2,2'-DiBBPA and 2,6-DiBBPA), and TriBBPA were described below. The chemical structures of these target analytes are given in the [Supporting Information](#) (Table S1).

Synthesis of TBBPA Transformation Products. As described by Nakao et al., MoBBPA, 2,2'-DiBBPA, and TriBBPA were synthesized by bromination of BPA with different amounts of bromine.¹⁵ The synthesis of 2,6-DiBBPA was according to the previous report by De Meulenaer et al.²⁷ The synthesis details are described in the [Supporting Information](#) (Figure S1). The synthesis of mixed bromine/chlorine transformation products of TBBPA is outlined in [Figure 1](#). All synthesis experiments were conducted at room temperature unless specified otherwise.

Synthesis of MoCBPA and 2,2'-DiCBPA. The parent compound BPA (6.85 g, 30 mmol) was dissolved in methanol

(50 mL). Sodium hypochlorite (30 mL, available chlorine >5%) was added dropwise and the mixture was stirred violently for 10 h.²⁸ Next, 25 mL of sodium sulfite (1 M) was added, and the reaction mixture was acidized with 10% HCl. The targets were extracted, washed, and dried. The product was eluted with petroleum ether-dichloromethane 1:5 (v/v) as the mobile phase on an open silica gel column, and 2,2'-DiCBPA and MoCBPA were collected sequentially. Finally, MoCBPA and 2,2'-DiCBPA were purified by recrystallization to obtain the single compounds.

Synthesis of 2-Cl-2'-MoBBPA and 2-Cl-2',6,6'-TriBBPA. Pyridinium tribromide was dissolved in ethanol (10 mL), which was added dropwise to a solution of MoCBPA (1.0 g, 3.8 mmol) in ethanol (20 mL). The molar ratio of pyridinium tribromide with MoCBPA was 0.8:1 and 2:1 for the synthesis of 2-Cl-2'-MoBBPA and 2-Cl-2',6,6'-TriBBPA, respectively. After reaction for 2.5 h and then adding water (50 mL), the targets were extracted, washed, and dried. The product was eluted with ethyl acetate-petroleum ether 1:25 (v/v) on an open silica gel column, and 2-Cl-2',6,6'-TriBBPA and 2-Cl-2'-MoBBPA were collected sequentially. Finally, the single 2-Cl-2'-MoBBPA and 2-Cl-2',6,6'-TriBBPA were purified by recrystallization.

Synthesis of 2-Cl-2',6-DiBBPA. 2,2'-DiBBPA (0.15 g, 0.388 mmol) was dissolved in ethanol (20 mL), *N*-chlorosuccinimide (51.8 mg, 0.388 mmol) and AlCl₃ (0.052 g, 0.388 mmol) were added, and the mixture was stirred vigorously for 2 h.²⁹ Afterward, sodium sulfite (1 M, 0.5 mL) was added and the reaction mixture was acidized with HCl (10%). The targets were extracted, washed, and dried. The compound 2-Cl-2',6-DiBBPA was isolated on a silica gel column with ethyl acetate-petroleum ether (1:15, v/v) and further purified by recrystallization.

Synthesis of 2,2'-Cl-6-MoBBPA and 2,2'-Cl-6,6'-DiBBPA. Pyridinium tribromide was dissolved in 10 mL of ethanol, which was added dropwise to a solution of 2,2'-DiCBPA (1.0 g, 3.36 mmol) in 20 mL of ethanol. For the synthesis of 2,2'-Cl-6-MoBBPA and 2,2'-Cl-6,6'-DiBBPA, the molar ratio of pyridinium tribromide with 2,2'-DiCBPA was 0.8:1 and 1.3:1, respectively. Following the reaction for 2.5 h, water (50 mL) was added, and the targets were extracted, washed, and dried. The product was eluted with ethyl acetate-petroleum ether 1:20 (v/v) on an open silica gel column, and 2,2'-Cl-6,6'-DiBBPA and 2,2'-Cl-6-MoBBPA were collected sequentially. Finally, 2,2'-Cl-6-MoBBPA and 2,2'-Cl-6,6'-DiBBPA were purified by recrystallization.

Synthesis of 2-Cl-2',6'-DiBBPA. 2,6-DiBBPA (1.2 g, 3.1 mmol), obtained from BPA through intermediates mono-*tert*-butyldimethylsilyl-bisphenol A (MoTBS-BPA) and mono-*tert*-butyldimethylsilyl'-2,6-dibromobisphenol A (MoTBS'-2,6-DiBBPA), was dissolved in 25 mL of dichloromethane, and then *N*-chlorosuccinimide (0.415 g, 3.1 mmol) and AlCl₃ (0.041 g, 0.31 mmol) were added. After stirring violently for 2 h, sodium sulfite (1 M, 0.5 mL) was added and the reaction mixture was acidized with HCl (10%). The targets were extracted, washed, and dried. The product was eluted with ethyl acetate-petroleum ether 1:30 (v/v) on an open silica gel column and purified by recrystallization to obtain 2-Cl-2',6'-DiBBPA.

Synthesis of 2-Cl-6-MoBBPA. The *tert*-butyldimethylsilyl-protected brominated intermediate (MoTBS-BPA, 0.5 g, 1.46 mmol) from BPA ([Figure S1](#)) was dissolved in 15 mL of tetrahydrofuran (THF), and then sodium hypochlorite (about

Table 1. Optimized HPLC–MS/MS Parameters for the Target Analytes^a

analytes	retention time (min)	MRM transitions (<i>m/z</i>)	fragmentor (eV)	collision energy (eV)	IDL (pg)
BPA	11.72	227 → 133	110	30	0.6
		227 → 212	110	20	
¹³ C ₁₂ -BPA	17.72	239 → 139	110	30	0.6
		239 → 224	110	20	
MoBBPA	13.28	307 → 81	135	40	0.4
		305 → 79			
2-Cl-2'-MoBBPA	15.18	341 → 81	135	40	0.3
		339 → 79			
2-Cl-6-MoBBPA	15.35	341 → 81	135	40	0.3
		339 → 79			
2,2'-DiBBPA	15.70	385 → 79	135	40	0.4
		385 → 81			
2,6-DiBBPA	15.98	385 → 79	135	40	0.4
		385 → 81			
2,2'-Cl ₂ -6-MoBBPA	17.83	375 → 81	135	40	0.3
		373 → 79			
2-Cl-2',6-DiBBPA	18.34	421 → 81	135	40	0.3
		421 → 79			
2-Cl-2',6'-DiBBPA	18.34	421 → 81	135	40	0.3
		421 → 79			
2,2',6-TriBBPA	18.74	465 → 81	150	60	0.3
		463 → 79			
2,2'-Cl ₂ -6,6'-DiBBPA	19.87	455 → 81	150	40	0.3
		453 → 79			
2-Cl-2',6,6'-triBBPA	20.19	499 → 81	150	60	0.3
		497 → 79			
TBBPA	20.49	543 → 79	150	60	0.2
		543 → 81			
¹³ C ₁₂ -TBBPA	20.49	555 → 79	150	60	0.2
		555 → 81			

^aBPA: bisphenol A; TBBPA: tetrabromobisphenol A; BBPA: bromobisphenol A; and IDL: instrumental detection limit.

1 mL, available chlorine >5%) was added dropwise. After stirring violently for 5 h, sodium sulfite (1 M, 1 mL) was added and the reaction mixture was acidized with HCl (10%). Afterward, the targets were extracted, washed, and dried. The product was eluted with ethyl acetate-petroleum ether 1:50 (v/v) on an open silica gel column and purified by recrystallization to obtain the single compound mono-*tert*-butyldimethylsilyl'-2-monochlorobisphenol A (MoTBS'-MoCBPA). Subsequently, MoTBS'-MoCBPA was brominated with 1 equiv of pyridinium tribromide, and the product was eluted with ethyl acetate-petroleum ether 1:10 (v/v) on an open silica gel column, evaporated to dryness, and purified by recrystallization to obtain a mono-*tert*-butyldimethylsilyl-protected brominated intermediate. Afterward, a solution of tetrabutylammonium fluoride (TBAF) in THF was added and the reaction system was placed in an ice-water bath for 1 h to conduct deprotection of the brominated intermediate. Following the addition of water, the compound was acidized with HCl (10%), dried, and finally purified by recrystallization to obtain 2-Cl-6-MoBBPA.

Sampling and Treatment Protocols. A total of 15 dust samples were collected using a precleaned soft-bristled brush from the surfaces of tables, furniture, and windowsills in an e-waste dismantling industrial park in southern China. The residential area was about 1 km southwest of the industrial park, and the office building was located in the park and was close to the raw material-crushing workshop (RW) and the secondary copper blast furnace workshop (BW). Detailed

information on the sampling protocols was given in our previous report.³⁰ The samples were collected from five different functional areas of a typical e-waste workshop: three samples from RWs, five from EWs, three from secondary BWs, two from office building areas (OAs), and two from residential areas (RAs).

The dust samples (approximately 100 mg; 200 mg for OA and RA sites) were wrapped in cellulose filters. Soxhlet extraction was performed with a 200 mL mixture of acetone-dichloromethane-*n*-hexane (1:2:2, v/v/v) for 48 h after the recovery surrogate standard (¹³C₁₂-BPA, 10 ng) was spiked and copper sheets were added to remove sulfur. Subsequently, the extracts were concentrated and solvent exchanged with *n*-hexane, and reconcentrated to about 1 mL. The extracts were further cleaned up by passing through a florisil solid-phase extraction column (2 g, 6 mL). The target compounds were then eluted with 10 mL mixture of dichloromethane-ethyl acetate (1:1, v/v). The eluates were dried and then reconstituted in 200 μL of methanol with 10 ng of the internal standard. For structural identification of the target compounds by gas chromatography–mass spectrometry (GC–MS), the compounds were derivatized with *N,O*-bis-(trimethylsilyl)trifluoroacetamide to convert the phenols to their trimethylsilyl ether derivatives.

In addition, to verify whether debrominated and mixed halogenated transformation products of TBBPA were formed during the manufacturing and daily usage of electronic and electrical products, several waste-printed circuit board and

plastics from e-waste workshops were gathered and mechanically crushed. A portion (10 g) of cleaned e-waste material was ground into powder after freezing in liquid nitrogen. Then, the mixed e-waste powders (1 g) were extracted with a 10 mL mixture of acetone–dichloromethane (1:1, v/v). After centrifugation, the supernatants (~1 mL) were evaporated to near dryness. Finally, the residues were reconstituted in methanol for HPLC–MS/MS analyses.

Instrumental Analysis. Analyses were performed on an Agilent 6470 triple quadrupole MS coupled to an Agilent 1260 Infinity II HPLC (Agilent Technologies, USA). A Waters Acquity UPLC BEH C18 reversed-phase analytical column (100 mm × 2.1 mm, 1.7 μ m particle diameter, Waters, Milford, USA) was used. The temperature of the column was 40 °C. Water containing 0.1% acetic acid and acetonitrile was used as the mobile phase with a flow rate of 0.2 mL/min. The gradient program was as follows: 5%–15%, 2–2.1 min; 50%, 2.1–10 min; 50–80%, 10–15 min; 80–95%, 15–18 min; 95%, 18–19 min; 95–99%, 19–20 min; and 99%, 20–22 min. The temperatures of the source and the sheath gas were 300 and 350 °C with flow rates of 5 and 12 L/min, respectively. The nebulizer pressure was 45 psi. The capillary voltage was set at 3500 V and the nozzle voltage was set at 500 V for the negative AJS ESI mode. The MS/MS transitions, retention times, and collision energy settings are listed in Table 1.

GC–MS analyses of trimethylsilyl ether derivatives of the target compounds were performed using an Agilent 7890B GC coupled with a 5977B mass spectrometer. An Agilent DB-35MS capillary column (60 m × 0.25 mm × 0.25 μ m) was used. A 1 μ L sample was injected in a pulsed splitless mode with temperature of the injector being set at 260 °C. Helium (>99.999%) was used as the carrier gas at a constant flow rate of 1 mL/min. The temperature program of oven was as follows: 80 °C held for 1 min; 20 °C/min to 200 °C (held for 3 min); 5 °C/min to 300 °C; and then held at 300 °C for 30 min. The temperatures of the quadrupole, ion source, and transfer line of the mass spectrometer were set at 150, 230, and 300 °C, respectively. The instrument was operated in a mode of electron ionization (EI) and the mass spectra were recorded with m/z 50–700 in the full scan mode.

Quality Assurance and Quality Control. Two matrix-spiked samples and two blank samples were run. Anhydrous sodium sulfate spiked with target compounds was used as a fortified matrix instead of dust. The target analytes were not detected in the blank samples. The recovery of the surrogate standard ranged from 85 to 94%. The recovery of the target compounds ranged from 78 to 102% in the spiked samples. The instrumental detection limits (IDLs) with an S/N of 5 were 0.2–0.6 pg (Table S1) and the method detection limits were 0.04–0.12 ng/g. The data were expressed as ng/g dw unless specified otherwise.

RESULTS AND DISCUSSION

Synthesis of TBBPA Transformation Products. To study whether X-BBPAs could be formed during e-waste dismantling processes, seven X-BBPAs, including five mono-chlorine substitution products (2-chloro-2',6,6'-TriBBPA, 2-chloro-2',6-DiBBPA, 2-chloro-2',6'-DiBBPA, 2-chloro-2'-MoBBPA, and 2-chloro-6-MoBBPA) and two dichloro substitution products (2,2'-dichloro-6,6'-DiBBPA and 2,2'-dichloro-6-MoBBPA), were synthesized. In addition, to gain an insight into the possible formation mechanisms during e-waste

dismantling, four known debromination products (2-MoBBPA, 2,6-DiBBPA, 2,2'-DiBBPA, and 2,2',6-TriBBPA) were synthesized because they were not commercially available, although the presence of these compounds in breast milk, soil, sewage sludge, and sediments has been reported.^{6,11,18}

To obtain X-BBPAs with both chlorine and bromine atoms, the synthesis strategy involved chlorination and then bromination of BPA. In addition, *tert*-butyldimethylchlorosilane was used to protect the hydroxyl groups of the BPA transformation products. The structures of the synthesized products were characterized using ¹H NMR. The purity of all synthesized compounds was greater than 95% as measured by GC with a flame ionization detector. A typical chromatogram is shown in Figure S2.

Identification of TBBPA Transformation Products.

The transformation products of TBBPA in dust samples were identified using HPLC–MS/MS based on their retention times and mass spectra. A typical chromatogram is presented in Figure 2. The presence of 0.1% acetic acid in the mobile

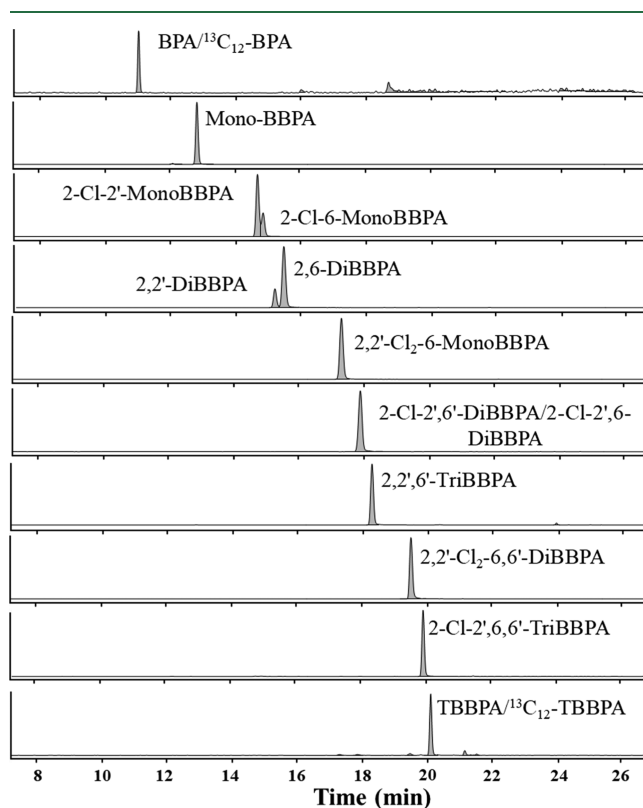


Figure 2. HPLC–MS/MS analysis of TBBPA and its transformation products.

phase was very important in achieving baseline resolution for these compounds, in particular, 2,2'-DiBBPA and 2,6-DiBBPA and 2-Cl-2'-MoBBPA and 2-Cl-6-MoBBPA, as shown in Table 1 and Figure 2. Several previous studies have reported the detection of debrominated congeners of TBBPA in the environment and biotas.^{10,14,19} However, the separation of DiBBPA has rarely been reported. In addition, the chromatographic conditions failed to achieve baseline separation of 2-chloro-2',6-DiBBPA and 2-chloro-2',6'-DiBBPA in the present study. Therefore, their concentrations in the dust samples were reported as the sum of the two isomers.

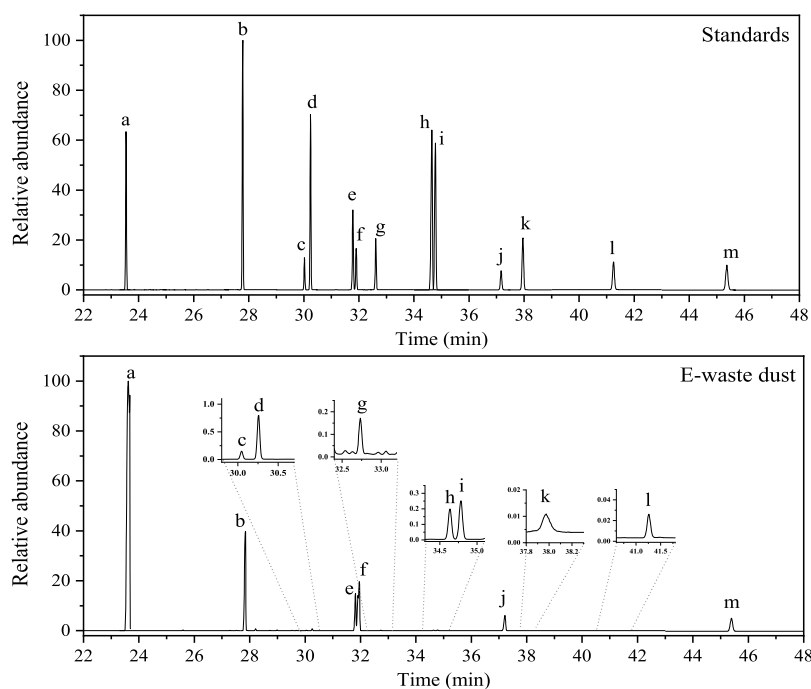


Figure 3. GC–MS total ion current (TIC) chromatogram of silylation derivatives of TBBPA and its transformation products in standards and e-waste dust in a dismantling workshop. (a) BPA and $^{13}\text{C}_{12}$ -BPA (23.548 min); (b) MoBBPA (27.782 min); (c) 2-Cl-6-MoBBPA (30.028 min); (d) 2-Cl-2'-MoBBPA (30.240 min); (e) 2,2'-DiBBPA (31.794 min); (f) 2,6-DiBBPA (31.911 min); (g) 2,2'-Cl₂-6-MoBBPA (32.624 min); (h) 2-Cl-2',6-DiBBPA (34.624 min); (i) 2-Cl-2',6'-DiBBPA (34.773 min); (j) 2,2',6-TriBBPA (37.178 min); (k) 2,2'-Cl₂-6,6'-DiBBPA (37.965 min); (l) 2-Cl-2',6,6'-triBBPA (41.253 min); and (m) TBBPA and $^{13}\text{C}_{12}$ -TBBPA (45.371 min).

Identification of the transformation products of TBBPA was further confirmed using GC. Their silylation derivatives were analyzed using GC–MS in the EI mode with a DB-35MS column with 60 m length. The retention times of the silylated isomers from the dust samples matched well with those of the synthesized standards (Figure 3). Typical mass spectra of the silylation derivatives of the TBBPA analogues are shown in Figure S3. The mass spectral characteristics of these derivatives were similar to those of TBBPA, with the major fragments formed by the loss of a trimethylsilyl group, generating phenyl ethers.

All these synthesized compounds were detected in the dust samples. For the debrominated compounds, the detection frequencies were 100%. The transformation products, 2-Cl-2',6,6'-TriBBPA, 2-Cl-2',6-DiBBPA, 2-Cl-2',6'-DiBBPA, and 2-Cl-2'-MoBBPA, were also detected in all samples. However, in half of the samples, the concentrations of 2-Cl-6-MoBBPA were below the method detection limit, while the transformation products with two chlorine substitutions, that is, 2,2'-Cl₂-6,6'-DiBBPA and 2,2'-Cl₂-6-MoBBPA, were detected only in three of 15 samples.

Levels of TBBPA and Its Transformation Products in the E-Waste Dust Samples. The total concentrations of TBBPA and its transformation products in the e-waste dust samples ranged from 1.13×10^4 to 2.06×10^5 ng/g (Table 2). The highest mean concentration was found in the EWs (2.06×10^5 ng/g), followed by the RWs (1.38×10^5 ng/g). These values were one order of magnitude higher than the mean concentrations in the BWs (3.24×10^4 ng/g) and nonrecycling sites. Our results indicated that informal e-waste dismantling activities might be the main source of TBBPA emission, however, relatively lower levels found in the dust samples of BWs might be related to the stronger decomposition of

reactive TBBPA at higher temperature applied in the secondary copper-smelting process.¹⁸ Among the compounds detected, MoBBPA had the highest concentration of 8.45×10^4 ng/g in the EWs, followed by 2,2'-DiBBPA (3.74×10^4 ng/g). The debrominated products generally had higher concentrations than TBBPA, whose concentrations were one or two orders of magnitude higher than those of the mixed chlorinated/brominated substitution products, except in the residential areas. The results suggested that e-waste dismantling activities were a major emission source of TBBPA and its transformation products.

Currently, there are very limited information on the transformation products of TBBPA. For example, Wang et al. measured the concentrations of TBBPA and eight bisphenol analogues in indoor dust samples from 12 countries and reported the mean TBBPA concentration of 9.5 ng/g with a range of <1–3600 ng/g,³¹ which was significantly lower than the data reported in the present study. TBBPA was also reported in the dust samples from various indoor environments in Birmingham, UK, with the median concentrations of 2, 36, 62, and 230 ng/g in samples collected from cars, offices, homes, and public microenvironment, respectively.⁷ In Belgium, a median TBBPA concentration of 10 ng/g was reported in indoor samples.³² These results are significantly lower than the TBBPA concentrations in our e-waste dust samples, which ranged from 5.50×10^3 to 2.38×10^4 ng/g. A similar higher concentration of TBBPA was also reported in the indoor dust samples of residential houses in an e-waste recycling area in Southeast China, which ranged from 42.2 to 4.62×10^4 ng/g with a mean of 3.44×10^3 ng/g.³³ In another report, the concentrations of TBBPA in indoor dust (206–950 ng/g) emitted from waste TV recycling facility were apparently lower than those reported in our study.³⁴ Indeed, the

Table 2. Mean Concentrations and Standard Deviations (ng/g) of TBBPA and Its Transformation Products in Dust Samples

compounds	EW (<i>n</i> = 5)	RW (<i>n</i> = 3)	BW (<i>n</i> = 3)	OA (<i>n</i> = 2)	RA (<i>n</i> = 2)
BPA	1.67 × 10 ³ ± 1.15 × 10 ³	1.08 × 10 ³ ± 0.25 × 10 ³	229 ± 6.0	196 ± 26.0	48.8 ± 17.0
MoBBPA	8.45 × 10 ⁴ ± 6.35 × 10 ⁴	5.68 × 10 ⁴ ± 1.52 × 10 ⁴	1.25 × 10 ⁴ ± 0.47 × 10 ⁴	3.27 × 10 ³ ± 0.56 × 10 ³	454 ± 191
2-Cl-2'-MoBBPA	8.15 × 10 ³ ± 7.83 × 10 ³	1.67 × 10 ³ ± 0.4 × 10 ³	275 ± 162	38.7 ± 0.36	14.6 ± 3.4
2-Cl-6-MoBBPA	192 ± 429	1.29 × 10 ³ ± 0.27 × 10 ³	81.7 ± 71.8	36.4 ± 10.1	n.d. ^a
2,2'-DiBBPA	3.74 × 10 ⁴ ± 2.63 × 10 ⁴	2.41 × 10 ⁴ ± 0.55 × 10 ⁴	4.83 × 10 ³ ± 1.96 × 10 ³	897 ± 165	145 ± 23.8
2,6-DiBBPA	1.87 × 10 ⁴ ± 1.27 × 10 ⁴	1.24 × 10 ⁴ ± 0.30 × 10 ⁴	2.03 × 10 ³ ± 0.46 × 10 ³	752 ± 126	115 ± 41.6
2,2'-Cl ₂ -6-MoBBPA	5.3 ± 7.6	2.6 ± 4.5	n.d.	n.d.	n.d.
2-Cl-2',6-DiBBPA ^b	4.38 × 10 ³ ± 3.33 × 10 ³	2.18 × 10 ³ ± 0.31 × 10 ³	239 ± 15.8	53.9 ± 0.74	12.8 ± 0.04
2,2',6-TriBBPA	2.31 × 10 ⁴ ± 0.84 × 10 ⁴	1.75 × 10 ⁴ ± 0.16 × 10 ⁴	4.69 × 10 ³ ± 0.36 × 10 ³	1.92 × 10 ³ ± 0.18 × 10 ³	1.16 × 10 ³ ± 0.19 × 10 ³
2,2'-Cl ₂ -6,6'-DiBBPA	3.5 ± 4.9	0.9 ± 1.6	n.d.	n.d.	n.d.
2-Cl-2',6,6'-triBBPA	3.54 × 10 ³ ± 2.07 × 10 ³	1.53 × 10 ³ ± 0.38 × 10 ³	147 ± 50.1	44.5 ± 3.89	24.0 ± 6.26
TBBPA	2.38 × 10 ⁴ ± 0.39 × 10 ⁴	1.92 × 10 ⁴ ± 0.04 × 10 ⁴	7.40 × 10 ³ ± 2.55 × 10 ³	5.50 × 10 ³ ± 0.65 × 10 ³	9.35 × 10 ³ ± 0.98 × 10 ³
Σ ₇ -Cl-BBPA	1.63 × 10 ⁴ ± 1.30 × 10 ⁴	6.67 × 10 ³ ± 1.19 × 10 ³	743 ± 79.0	174 ± 6.65	51.4 ± 9.71
Σ ₄ -Br-BBPA	1.64 × 10 ⁵ ± 1.11 × 10 ⁵	1.12 × 10 ⁵ ± 0.25 × 10 ⁵	2.40 × 10 ⁴ ± 0.64 × 10 ⁴	6.83 × 10 ³ ± 1.03 × 10 ³	1.88 × 10 ³ ± 0.45 × 10 ³
Σ _{all} -BBPA	2.06 × 10 ⁵ ± 1.23 × 10 ⁵	1.38 × 10 ⁵ ± 0.26 × 10 ⁵	3.24 × 10 ⁴ ± 0.66 × 10 ⁴	1.27 × 10 ⁴ ± 0.17 × 10 ⁴	1.13 × 10 ⁴ ± 0.05 × 10 ⁴

^aNot detected. ^bCoelution of 2-Cl-2',6-DiBBPA and 2-Cl-2',6'-DiBBPA; *n*: number of samples; BPA: bisphenol A; TBBPA: tetrabromobisphenol A; BBPA: bromobisphenol A; RA: residential area; OA: office building area; EW: e-waste dismantling workshop; RW: raw material-crushing workshop; and BW: secondary copper blast furnace workshop.

concentrations of TBBPA and its transformation products in the present study were at the same levels as polybrominated diphenyl ethers reported previously,³⁵ indicating that extensive e-waste recycling activities may cause severe contamination by TBBPA analogues, with potential health consequences for exposed workers. However, we should note that the samples of the present study were limited. More research should be carried out.

To the best of our knowledge, the occurrence of X-BBPA in environmental media has not been reported previously. Only limited investigations reported detection of the debromination products of TBBPA in the environment or human body.^{10,14,19} For example, debrominated TriBBPA and DiBBPA in soils from sites around three plants of BFR production were reported by Liu and coauthors.¹⁰ Similar debrominated products, including MoBBPA, DiBBPA, and TriBBPA, have been detected in breast milk in Japan and sewage sludge from waste water treatment plants, as well as sediments in Cinca River (Spain), where there is an industrialized town with a chemical industry.^{11,18} High levels of BPA and TBBPA, as well as debromination from MoBBPA to TriBBPA, were also found in sediment, soil, and water samples collected from a typical river adjacent to Bohai Sea, with ranges of n.d.–5.45 × 10³ and n.d.–83.7 ng/g dw, and n.d.–559 ng/L, respectively.³⁶ Owing to the limited data available on environmental occurrence and relatively lower detection frequencies, such as in human milk samples, the effects of pollution by these transformation products remain unclear.

Composition Characteristics of TBBPA Analogues.

The chemical composition profiles of debrominated and X-BBPA in dust samples are shown in Figure 4. MoBBPA was the most abundant debromination product, with a contribution of 51% in the total debromination products, while 2-Cl-2',6,6'-TriBBPA was the predominant X-BBPA. The sum concentrations of the four debromination products (Σ₄Br-BBPA) were 8–42 times higher than those of the mixed chlorinated/brominated substitution products (Σ₇-Cl-BBPA). However, there were significant differences in homologue patterns of TBBPA and its transformation products in dust samples from different sampling sites. For example, the debrominated products, from MoBBPA to TriBBPA, were the most abundant homologues in the e-waste recycling workshops, whereas TBBPA (more than 80%) was the most abundant in dust samples from the nonrecycled residential sites (Figure 4). These results provided evidence for direct debrominated degradation of TBBPA caused by e-waste dismantling activities. Additionally, mechanochemical destruction during dismantling activities was demonstrated to be a potential source contributing to debromination of TBBPA.³⁷

For X-BBPAs, the contribution of Cl-MoBBPA was found to be relatively high in dust from dismantling workshops, while a high proportion of Cl-TriBBPA was found in dust from residential areas (Figure 4). Currently, there are no available data on mixed chlorinated/brominated products of TBBPA, although the formation of similar mixed halogenated products of other organic compounds in soils, such as Cl-NonaBDEs,²⁴ PXDFs, and PXDEs,²⁶ has been observed in e-waste recycling sites. HXBs in fly ash from municipal solid waste incineration have also been reported.²⁵ These studies indicated that thermal processes, such as open burning of e-waste materials and solid waste combustion, may result in exchange reactions of Br and Cl atoms when trace amounts of brominated and chlorinated organic compounds are present in materials. These observa-

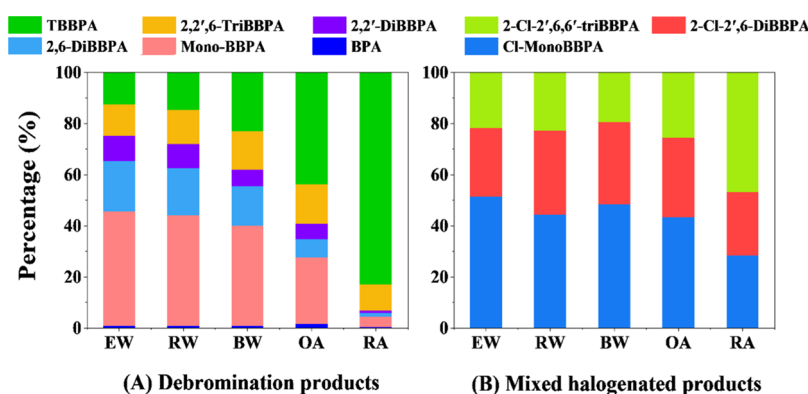


Figure 4. Composition profiles (%) of TBBPA and its transformation products in dust samples from e-waste sites (A: debromination products; B: mixed halogenated products; RW: raw material-crushing workshops, EW: e-waste dismantling workshops, BW: secondary copper blast furnace workshops, OA: office building areas, and RA: residential areas).

tions were also confirmed by bench-scale simulation studies. For example, PXDEs were predicted to be formed during thermolysis of BDE47 and BDE153 in the presence of tetrachloromethane.³⁸ Therefore, it is likely that mixed halogenated reaction products are formed during dismantling e-waste containing TBBPA as flame retardants.

However, there were also reports indicating that Tri-BBPA impurity accounted for less than 3% in commercial TBBPA products.³⁹ In the present study, only a small amount of TriBBPA (<3%) was found in the e-waste extract samples. A typical total ion chromatogram of the e-waste extract is given in Figure S4. This result further indicated that the presence of the debrominated products and X-BBPA was mainly derived from informal e-waste dismantling activities rather than the manufacturing and daily usage of electronic and electrical products. To better understand the mechanisms during e-waste dismantling processes, further investigations are urgently needed because of substantially high contamination levels in e-waste dismantling sites, as well as predominance of the transformation products observed.

The present results verified the occurrence of mixed bromine/chlorine transformation products of TBBPA in dust samples from an e-waste dismantling site, although the mechanisms were still unclear. The concentrations of these transformation products were apparently higher than that of TBBPA. Mixed bromine/chlorine transformation products of TBBPA were identified. Unlike polybrominated diphenyl ethers or other flame retardants, TBBPA is generally utilized as a single compound that covalently binds to polymer materials. Therefore, our findings suggest a new option of an ideal model compound for the investigation of bromine/chlorine exchange reactions of these halogenated compounds during thermal treatment processes. Nevertheless, more investigations are necessary to clarify the formation and emission of TBBPA transformation products, as well as their potential health consequences for e-waste-exposed dismantlers.

■ ASSOCIATED CONTENT

SI Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.est.0c04494>.

Syntheses of known debrominated TBBPA, transformation products, structural information of the synthesized TBBPA transformation products, synthetic schemes for debrominated products of TBBPA,

representative chromatogram of TriBBPA, mass spectra of silylation derivatives of TBBPA and its transformation products obtained by GC-EI-MS, HPLC-MS/MS chromatogram of TBBPA and its transformation products in an e-waste extract, and chemical information of TBBPA and its transformation products (PDF)

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Notes

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