



## Research Paper

# Mixed bromine/chlorine transformation products of tetrabromobisphenol A: Potential specific molecular markers in e-waste dismantling areas

Xiang Ge<sup>a,b,1</sup>, Shengtao Ma<sup>a,b,c,1</sup>, Yanping Huo<sup>d</sup>, Yan Yang<sup>a,b,c</sup>, Xiaojun Luo<sup>e,f</sup>, Yingxin Yu<sup>a,b,\*</sup>, Taicheng An<sup>a,b</sup>

<sup>a</sup> Guangdong-Hong Kong-Macao Joint Laboratory for Contaminants Exposure and Health, Institute of Environmental Health and Pollution Control, Guangdong University of Technology, Guangzhou 510006, PR China

<sup>b</sup> Guangdong Key Laboratory of Environmental Catalysis and Health Risk Control, Key Laboratory for City Cluster Environmental Safety and Green Development of the Ministry of Education, School of Environmental Science and Engineering, Guangdong University of Technology, Guangzhou 510006, PR China

<sup>c</sup> Synergy Innovation Institute of GDUT, Shantou 515041, PR China

<sup>d</sup> School of Chemical Engineering and Light Industry, Guangdong University of Technology, Guangzhou 510006, PR China

<sup>e</sup> State Key Laboratory of Organic Geochemistry and Guangdong Key Laboratory of Environmental Protection and Resources Utilization, Guangzhou Institute of Geochemistry, Chinese Academy of Sciences, Guangzhou 510640, PR China

<sup>f</sup> Guangdong-Hong Kong-Macao Joint Laboratory for Environmental Pollution and Control, Guangzhou Institute of Geochemistry, Chinese Academy of Sciences, Guangzhou 510640, PR China



## ARTICLE INFO

Editor: Dr. B. Lee

## Keywords:

Electronic waste dismantling  
Specific molecular marker  
Tetrabromobisphenol A  
Transformation product

## ABSTRACT

Mixed bromine/chlorine transformation products ( $\text{Cl}_y\text{Br}_x\text{BPAs}$ ) of tetrabromobisphenol A (TBBPA) were recently identified for the first time in an electronic waste (e-waste) dismantling site. To determine whether these compounds can be used as specific molecular markers of e-waste dismantling activities, the environmental occurrences and distributions of TBBPA and its transformation products including debromination products ( $\text{Br}_x\text{BPAs}$ ) and  $\text{Cl}_y\text{Br}_x\text{BPAs}$  were analyzed in soil samples from three sites in China: Guiyu (an e-waste site), Qingyuan (a former e-waste site now mainly used for old wire and cable recycling), and Shouguang (a flame retardant production base). Levels of the target analytes in Guiyu were significantly higher than in Qingyuan and Shouguang.  $\text{Br}_x\text{BPAs}$  and  $\text{Cl}_y\text{Br}_x\text{BPAs}$  were widely detected in Guiyu at concentrations between 1 and 4 orders of magnitude lower than their parent compound TBBPA. The highest concentration was found in an e-waste dismantling park, with lower concentrations in surrounding area. The levels of  $\text{Cl}_y\text{Br}_x\text{BPAs}$  in Qingyuan were much lower, indicating that the  $\text{Cl}_y\text{Br}_x\text{BPAs}$  may come from the processing of wires and cables, but not rule out the incubation on their own in soils. None of  $\text{Cl}_y\text{Br}_x\text{BPAs}$  were detected in Shouguang.  $\text{Cl}_y\text{Br}_x\text{BPAs}$  may thus be useful as specific molecular markers for determining the intensity of e-waste dismantling activities.

## 1. Introduction

Electronic waste (e-waste) consists of obsolete household appliances, personal portable electronic devices, as well as other related components, and is commonly disposed of by dismantling. E-waste dismantling activities can release many different organic flame retardants including traditional halogenated compounds, emerging non-halogenated alternatives, and derivatives developed to enhance fire safety (Li et al., 2018, 2019a, 2019b; Zhan et al., 2019). Same organic flame retardants have been detected at several typical e-waste dismantling sites in China

(including sites in Guiyu town in Shantou, several subordinate towns of Qingyuan in South China, Taizhou in East China, and Tianjin in North China) (Gao et al., 2011; Tang et al., 2013; Wu et al., 2019; Yu et al., 2010; Zeng et al., 2016), despite the use of different e-waste categories and treatment processes at those sites.

For example, early days in Guiyu, e-waste dismantling was commonly performed in family-based workshops using primitive methods such as manual crushing and open burning. This caused severe pollution, prompting the establishment of an industry park in 2015 to manage e-waste dismantling activities uniformly. Similarly, Qingyuan

\* Corresponding author at: Guangdong-Hong Kong-Macao Joint Laboratory for Contaminants Exposure and Health, Institute of Environmental Health and Pollution Control, Guangdong University of Technology, Guangzhou 510006, PR China.

E-mail address: [yuyingxin@gdut.edu.cn](mailto:yuyingxin@gdut.edu.cn) (Y. Yu).

<sup>1</sup> The authors contributed equally to this work.

<https://doi.org/10.1016/j.jhazmat.2021.127126>

Received 6 June 2021; Received in revised form 1 September 2021; Accepted 1 September 2021

Available online 5 September 2021

0304-3894/© 2021 Elsevier B.V. All rights reserved.

organized some ones earlier, such as Huaqing, Jiali'an, and Xinghe industry parks (established in 2006, 2010, and 2011, respectively), to provide sites for individual enterprises to recover renewable resources. However, much more current activities in Guiyu park focus on dismantling printed circuit boards, whereas recycling copper from old wires and cables, as well as secondary plastic, are major in Qingyuan. Unfortunately, few studies on flame retardant pollution have taken these differences into account. Consequently, there is a need to identify new analytes from disposal processes of various e-waste, even as specific molecular markers to distinguish the e-waste dismantling from other industries.

We previously reported the detection of various transformation products of tetrabromobisphenol A (TBBPA), including both debromination products ( $\text{Br}_x\text{BPAs}$ ,  $x = 1-3$ ) and mixed bromine/chlorine transformation products ( $\text{Cl}_y\text{Br}_x\text{BPAs}$ ,  $x = 1-3$ ;  $y = 1-2$ ), in dust samples from different e-waste dismantling workshops in Guiyu, and showed that the abundance of these analytes was closely related to e-waste dismantling activities (Liu et al., 2020). TBBPA is a very widely used flame retardant that is produced in large quantities and is not currently banned. Despite its ubiquity in environments related to e-waste processing, little is known about the occurrence and distribution of its transformation products (Chen et al., 2021; Doumas et al., 2018; Liu et al., 2017, 2020). Interestingly, TBBPA is the main organic flame retardant used in printed circuit boards but is not used in wires and cables (Hall and Williams, 2007; U.S. EPA, 2015; Wei et al., 2010; Zhou et al., 2014). We therefore hypothesized that transformation products of TBBPA, especially  $\text{Cl}_y\text{Br}_x\text{BPAs}$ , might be generated during the processing of printed circuit boards and could serve as specific molecular markers. While several publications have reported the formation of mixed halogenated pollutants at e-waste dismantling sites (Tue et al., 2019; Yu et al., 2011), there is little information on the usefulness of these mixed halogenated pollutants as specific markers. Additionally, given the relatively higher abundance of these transformation products at e-waste recycling sites and their potential toxicity, there is an urgent need for further study of mixed halogenated pollutants (Akiyama et al., 2015; Kudo et al., 2006; Yu et al., 2019).

To address these needs, levels of TBBPA and its halogenated transformation products were investigated at three sites including two e-waste dismantling sites (Guiyu and Qingyuan in Guangdong Province) and a flame retardant production base (Shouguang, in Shandong Province). Both Guiyu and Qingyuan have subtropical monsoon climates, while Shouguang belongs to the temperate monsoon zone. Grid soil samples were collected at Guiyu to determine the occurrence and distribution of TBBPA and its transformation products. The composition profiles of the target chemicals were analyzed and some assumptions about the transformation pathways of TBBPA and BPA into  $\text{Br}_x\text{BPAs}$  and  $\text{Cl}_y\text{Br}_x\text{BPAs}$  were also proposed. The concentrations measured at Guiyu were compared to those at Qingyuan and Shouguang, and the potential of the targeted analytes to serve as specific markers of e-waste dismantling activities was evaluated. The results presented here provide new insights into the emission characteristics of these transformation products and the environmental footprint of the modern e-waste dismantling industry more generally.

## 2. Materials and methods

### 2.1. Chemicals and reagents

TBBPA and bisphenol A (BPA) were purchased from AccuStandard (New Haven, CT, USA). Isotopically labeled  $d_3$ -triclosan ( $d_3$ -TCS) was supplied by C/N/D Isotopes (Pointe Claire, Canada) and used as an internal standard. Four  $\text{Br}_x\text{BPAs}$  (2-BrBPA, 2,2'-Br<sub>2</sub>BPA, 2,6-Br<sub>2</sub>BPA, and 2,2',6-Br<sub>3</sub>BPA) and seven  $\text{Cl}_y\text{Br}_x\text{BPAs}$  (2-Cl-2'-BrBPA, 2-Cl-6-BrBPA, 2-Cl-2',6-Br<sub>2</sub>BPA, 2-Cl-2',6'-Br<sub>2</sub>BPA, 2-Cl-2',6,6'-Br<sub>3</sub>BPA, 2,2'-Cl<sub>2</sub>-6-BrBPA, and 2,2'-Cl<sub>2</sub>-6,6'-Br<sub>2</sub>BPA) were synthesized in our lab as described previously (Liu et al., 2020). All reagents including acetone,

dichloromethane, *n*-hexane, ethyl acetate, acetic acid, and acetonitrile were of high-performance liquid chromatography (HPLC) grade and were obtained from CNW Technologies (Düsseldorf, Germany).

Empty solid phase extraction (SPE) cartridges (12 mL) and Florisil (60–100 mesh) were purchased from Biocomma (Shenzhen, China) and CNW Technologies (Düsseldorf, Germany), respectively. Microporous membranes (0.22  $\mu\text{m}$ ) were purchased from Membrana (Wuppertal, Germany). Copper sheets for desulfurization were also purchased from CNW Technologies (Düsseldorf, Germany) and were activated with hydrochloric acid before use.

### 2.2. Sampling and sample preparation

Soil Samples were collected from Shantou (Guiyu town) and Qingyuan in Guangdong province, and Shouguang in Shandong province (Fig. S1A–C). A total of 107 soil samples were collected in Guiyu during November of 2018; we have previously reported an analysis of these samples (Ge et al., 2020). Of these samples, 24 were collected from an e-waste dismantling park, and the others ( $n = 83$ ) were from the park's surroundings. Sampling sites were initially selected based on the grid layout, with supplemental sampling of selected sites expected to be highly polluted. These samples were mainly used to investigate differences in the levels of the target analytes inside and outside the park, and to characterize their distributions. A further 37 soil samples were collected from several wire and cable recycling parks and their surrounding areas in Qingyuan during October of 2020. The main purpose of collecting these samples was to verify that the  $\text{Cl}_y\text{Br}_x\text{BPAs}$  detected in Guiyu originated from e-waste dismantling activities. Finally, 31 soil samples were collected from two chemical industry parks and reference sites in Shouguang in August, 2020. Shouguang is a flame retardant production base where no e-waste dismantling activities take place.

After collection, soil samples were wrapped in aluminum foil, sealed individually in bags, and immediately transported back to the laboratory in an ice-box. Samples were prepared for extraction by mixing five subsamples from the same sampling site, lyophilizing to remove water, grinding to fine particles, and then sieving through a 100-mesh screen. Finally, the prepared soil samples were stored in brown glass bottles at  $-20\text{ }^\circ\text{C}$  until use.

### 2.3. Analytical protocols

Extraction was typically performed using 0.5 g of soil prepared as described below. The soil was placed in a Teflon centrifuge tube and a 10 mL mixture of acetone, dichloromethane, and *n*-hexane (1:2:2, v/v) was added, after which the sample was vortexed for 1 min and subjected to ultrasonic extraction for 10 min. The solid and liquid phases were separated by centrifugation at 2000 rpm for 10 min. The extraction-centrifugation process was repeated three times and the supernatants were collected and combined. Copper scraps were then added and the resulting mixture was left to stand overnight to induce desulfurization. After concentrated to approximately 1 mL, the extract was passed through an SPE cartridge loaded with 2 g Florisil, eluting the target analytes using a 10 mL mixture of ethyl acetate and dichloromethane (1:1, v/v). Finally, the eluate was concentrated under a gentle nitrogen flow and then filtered through a microporous membrane. After adding  $d_3$ -TCS as an internal standard, the sample was stored at  $-20\text{ }^\circ\text{C}$  until instrumental analysis.

### 2.4. Instrumental analysis

Determination of target analytes was performed using an Agilent 1260 Infinity II HPLC system coupled with a 6470 triple quadrupole mass spectrometer (Agilent, USA). A C18 reversed-phase analytical column (100 mm  $\times$  2.1 mm, 1.7  $\mu\text{m}$ ) was used, and the column temperature was set to 40  $^\circ\text{C}$ . The mobile phases were acetonitrile and water mixed with 0.1% acetic acid (v/v), and the flow rate was 0.4 mL/min.

The gradient based on acetonitrile was as follows: 0–2 min, 95–85%; 2–2.1 min, 85–50%; 2.1–10 min, 50%; 10–15 min, 50–20%; 15–18 min, 20–5%; 18–19 min, 5%; 19–20 min, 5–1%; and 20–22 min, 1%. For mass spectrometry (MS), the source and sheath gas temperatures were 300 and 350 °C, and the flow rates were 5 and 12 L/min, respectively. The nebulizer pressure was 45 psi. The Agilent Jet Stream electrospray ionization was conducted in the negative ion mode with a capillary voltage of 3500 V, and a nozzle voltage of 500 V, respectively. More detailed information including MS/MS transitions and retention times is given in Table S1.

## 2.5. Quality assurance and quality controls

Each batch of 10 samples was analyzed alongside one matrix blank and one spiked matrix. The matrix blank samples contained anhydrous sodium sulfate; no target analytes were detected in any blank samples, indicating that no relevant contaminants were introduced during the analytical process. Analysis of the spiked matrix samples indicated that the recoveries of the target analytes were between 76.1% and 109.0%. The regression coefficients of the calibration curves used to quantify the target analytes were all > 0.999. The limit of detection (LOD) and limit of quantification (LOQ) of each analyte were defined as 3 and 10 times that analyte's signal-to-noise ratio; the LOD and LOQ values determined in this way are listed in Table S1. All concentrations are reported in ng/g dw (dry weight) unless otherwise specified.

## 2.6. Statistical analysis

Analytes whose concentration was below the LOD were reported as being not detected (n.d.). For analytes whose concentration were between the LOD and the LOQ, the concentration was recorded as being half the LOQ if the analyte's detection frequency was > 50% or one quarter of the LOQ otherwise (GB 17378.2-2007, 2007; Ge et al., 2020). All data analysis was performed using SPSS (IBM, USA). The significance of differences in analyte concentration between the e-waste dismantling park and the surrounding areas was evaluated using the Mann-Whitney *U* test, and the significance of relationships between the analytes was evaluated using Spearman's correlation coefficient. A principal component analysis (PCA) was used to perform dimensionality reduction to facilitate source analysis. The significance threshold was set at *p* < 0.05. Contour plots were drawn with Surfer (Golden Software, USA), using the Kriging method for interpolation.

Because 2-Cl-2',6-Br<sub>2</sub>BPA and 2-Cl-2',6'-Br<sub>2</sub>BPA co-eluted, we denote mixtures of these congeners as 2-Cl-2',6<sup>#</sup>-Br<sub>2</sub>BPA. Although other two isomers, 2,6-Cl<sub>2</sub>-2'-BrBPA and 2,6-Cl<sub>2</sub>-2',6'-Br<sub>2</sub>BPA were not

synthesized and detected, possible co-elution individually with 2,2'-Cl<sub>2</sub>-6-BrBPA and 2,2'-Cl<sub>2</sub>-6,6'-Br<sub>2</sub>BPA could not be excluded, in spite of relative low concentration in this study. Additionally, for the convenience of discussion, the analytes were divided into two groups, A and B. TBBPA, Br<sub>x</sub>BPAs, and BPA were placed in Group A because they represent the start and end points of debromination, while the Cl<sub>y</sub>Br<sub>x</sub>BPA isomers were placed in Group B because they are formed by "Br-to-Cl" exchange reactions and their levels are much lower than the Group A compounds.

## 3. Results and discussion

### 3.1. Occurrence of the chemicals in soil samples

TBBPA, Br<sub>x</sub>BPAs, and BPA were detectable with detection frequencies ranging from 8.3% to 100% in all samples from three regions (Table 1 and Table S2). Higher detection frequencies were observed in samples from the parks than surrounding areas in Guiyu and Qingyuan. Regarding Cl<sub>y</sub>Br<sub>x</sub>BPA, none of the chemicals was detected in samples from the Shouguan, a flame retardant production base. Three Cl<sub>y</sub>Br<sub>x</sub>BPAs (2-Cl-2',6,6'-Br<sub>3</sub>BPA, 2-Cl-2',6<sup>#</sup>-Br<sub>2</sub>BPA, and 2-Cl-2'-BrBPA) were detected with the detection frequencies between 32.0% and 68.0% in park samples in Qingyuan and only 2-Cl-2',6,6'-Br<sub>3</sub>BPA (16.7%) was detected in its surrounding soil samples. However, all seven Cl<sub>y</sub>Br<sub>x</sub>BPAs were detected in samples from Guiyu sites at the detection frequencies from 2.4% to 75.0%, indicating higher occurrence of these chemicals in the Guiyu sites.

### 3.2. Concentrations in soil samples from three sites

In Guiyu, the concentrations of all target analytes were significantly higher in the e-waste dismantling park than its surrounding area (*p* < 0.05). BPA was the most abundant chemical in Group A. Its median concentration was  $1.87 \times 10^4$  and 60.7 ng/g in the park and surrounding area soil samples, respectively (Table 1). 2-BrBPA had the second highest median concentration of  $2.77 \times 10^3$  ng/g in the e-waste dismantling park but was undetectable in the surrounding area. The analyte next to BPA in the surrounding area was TBBPA with a median concentration of 17.4 ng/g. In Qingyuan, as expected, BPA and TBBPA were the most abundant and secondary compounds in Group A, with a median of  $3.44 \times 10^3$  and 167 ng/g in the parks, while 174 and 6.38 ng/g in their surrounding areas (Table S2A). The median concentration of 2,2',6-Br<sub>3</sub>BPA (9.85 ng/g) was approximately twice that of 2-BrBPA (5.33 ng/g) in the parks, but the two congeners were almost undetectable in the surrounding area (0.06 ng/g vs. n.d.). In soil samples from the

**Table 1**

Concentrations (ng/g dw) of TBBPA, Br<sub>x</sub>BPAs, BPA, and Cl<sub>y</sub>Br<sub>x</sub>BPAs in soil samples from the e-waste dismantling park and its surrounding area in Guiyu.

Compounds	E-waste dismantling park				Surrounding area			
	Mean	Median	Range	DF <sup>b</sup>	Mean	Median	Range	DF
TBBPA	$1.08 \times 10^4 \pm 2.26 \times 10^4$	527	$82.6\text{--}9.83 \times 10^4$	100%	$293 \pm 1.05 \times 10^3$	17.4	n.d. <sup>c</sup> – $8.49 \times 10^3$	79.5%
2,2',6-Br <sub>3</sub> BPA	$1.62 \times 10^3 \pm 2.19 \times 10^3$	337	$29.4\text{--}6.91 \times 10^3$	100%	$53.9 \pm 278$	2.32	n.d.– $2.46 \times 10^3$	77.1%
2,2'-Br <sub>2</sub> BPA	$1.25 \times 10^3 \pm 1.25 \times 10^3$	850	$28.8\text{--}4.13 \times 10^3$	100%	$21.2 \pm 98.7$	n.d.	n.d.–834	36.1%
2,6-Br <sub>2</sub> BPA	$512 \pm 509$	262	$3.78\text{--}1.42 \times 10^3$	100%	$7.15 \pm 37.1$	n.d.	n.d.–324	28.9%
ΣBr <sub>2</sub> BPA	$1.76 \times 10^3 \pm 1.73 \times 10^3$	$1.11 \times 10^3$	$32.6\text{--}5.04 \times 10^3$	100%	$28.3 \pm 136$	n.d.	n.d.– $1.16 \times 10^3$	38.6%
2-BrBPA	$3.86 \times 10^3 \pm 4.49 \times 10^3$	$2.77 \times 10^3$	$69.2\text{--}1.99 \times 10^4$	100%	$39.1 \pm 120$	n.d.	n.d.–795	47.0%
Σ <sub>4</sub> Br <sub>x</sub> BPAs	$7.24 \times 10^3 \pm 7.12 \times 10^3$	$5.18 \times 10^3$	$131\text{--}2.49 \times 10^4$	100%	$121 \pm 515$	5.68	n.d.– $4.42 \times 10^3$	77.1%
BPA	$2.35 \times 10^4 \pm 2.28 \times 10^4$	$1.87 \times 10^4$	$366\text{--}1.08 \times 10^5$	100%	$491 \pm 914$	60.7	n.d.– $4.06 \times 10^3$	81.9%
2-Cl-2',6,6'-Br <sub>3</sub> BPA	$103 \pm 196$	n.d.	n.d.–676	37.5%	$2.75 \pm 13.7$	n.d.	n.d.–115	10.8%
2-Cl-2',6 <sup>#</sup> -Br <sub>2</sub> BPA <sup>a</sup>	$46.6 \pm 65.1$	3.35	n.d.–200	62.5%	$1.43 \pm 9.37$	n.d.	n.d.–85.1	9.6%
2-Cl-2'-BrBPA	$43.5 \pm 46.1$	26.8	n.d.–130	75.0%	$1.37 \pm 9.12$	n.d.	n.d.–80.2	6.0%
2-Cl-6-BrBPA	$6.16 \pm 9.23$	2.15	n.d.–27.0	50.0%	$0.11 \pm 0.81$	n.d.	n.d.–7.23	2.4%
2,2'-Cl <sub>2</sub> -6,6'-Br <sub>2</sub> BPA	$35.7 \pm 58.3$	n.d.	n.d.–233	45.8%	$0.78 \pm 4.03$	n.d.	n.d.–35.4	8.4%
2,2'-Cl <sub>2</sub> -6-BrBPA	$2.67 \pm 5.90$	n.d.	n.d.–21.1	25.0%	$0.05 \pm 0.27$	n.d.	n.d.–1.44	3.6%
Σ <sub>7</sub> Cl <sub>y</sub> Br <sub>x</sub> BPAs	$237 \pm 328$	79.0	n.d.– $1.18 \times 10^3$	79.2%	$6.48 \pm 32.8$	n.d.	n.d.–268	18.1%

a Because 2-Cl-2',6-Br<sub>2</sub>BPA and 2-Cl-2',6'-Br<sub>2</sub>BPA co-eluted, the mixture of these two compounds is denoted as 2-Cl-2',6<sup>#</sup>-Br<sub>2</sub>BPA. b detection frequency; c not detected.

Shouguang chemical industry parks, the median concentrations of TBBPA (5.99 ng/g), BPA (1.58 ng/g), and 2,2',6-Br<sub>3</sub>BPA (0.97 ng/g) were all orders of magnitude lower than in Guiyu and Qingyuan (Table S2B). The TBBPA, BPA, and total concentrations of four Br<sub>x</sub>BPA congeners (Σ<sub>4</sub>Br<sub>x</sub>BPA) in Guiyu were significantly higher than those in Qingyuan and Shouguang ( $p < 0.05$ ).

In contrast, the concentrations of Cl<sub>y</sub>Br<sub>x</sub>BPA were generally lower than those of the chemicals in Group A in Guiyu ( $p < 0.05$ ) (Table 1). The total concentrations of seven Cl<sub>y</sub>Br<sub>x</sub>BPA (Σ<sub>7</sub>Cl<sub>y</sub>Br<sub>x</sub>BPA) were n.d.–1.18 × 10<sup>3</sup> and n.d.–268 ng/g in the e-waste dismantling park and its surrounding area, respectively. Although the median concentrations of 2-Cl-2',6'-Br<sub>2</sub>BPA, 2-Cl-2'-BrBPA, and 2-Cl-6-BrBPA were 3.35, 26.8, and 2.15 ng/g, respectively, other congeners were not detected in the park. Except for the 2-Cl-2',6,6'-Br<sub>3</sub>BPA with a median of 0.93 ng/g in wire and cable recycling parks, Cl<sub>y</sub>Br<sub>x</sub>BPA were all undetectable in the surrounding areas of Guiyu and Qingyuan, as well as Shouguang at median level (Table S2).

Noticeably, the mean concentration of each Cl<sub>y</sub>Br<sub>x</sub>BPA isomer is higher than the median concentration, and there are more not represented as n.d. at mean level (Table 1 and Table S2). In Guiyu, the mean concentration of each Cl<sub>y</sub>Br<sub>x</sub>BPA isomer ranged from a few ng/g to hundreds of ng/g in the soil samples. 2-Cl-2',6,6'-Br<sub>3</sub>BPA had the highest mean concentration in the park (103 ng/g), which was much higher than that in the surrounding area (2.75 ng/g). Similar results were observed for the other Cl<sub>y</sub>Br<sub>x</sub>BPA, whose concentrations had a declined trend in the order of 2-Cl-2',6,6'-Br<sub>3</sub>BPA > 2-Cl-2',6'-Br<sub>2</sub>BPA > 2-Cl-2'-BrBPA > 2,2'-Cl<sub>2</sub>-6,6'-Br<sub>2</sub>BPA > 2-Cl-6-BrBPA > 2,2'-Cl<sub>2</sub>-6-BrBPA in both the e-waste dismantling park and its surrounding area, although its statistical significance remains to be confirmed because of the abnormally distributed data. Conversely, Cl<sub>y</sub>Br<sub>x</sub>BPA were rarely detected in the soil samples from Qingyuan. Three Cl<sub>y</sub>Br<sub>x</sub>BPA congeners including 2-Cl-2',6,6'-Br<sub>3</sub>BPA (1.05 ng/g), 2-Cl-2',6'-Br<sub>2</sub>BPA (0.04 ng/g), and 2-Cl-2'-BrBPA (0.09 ng/g) were detectable in the cable and wire recycling parks, and only one, 2-Cl-2',6,6'-Br<sub>3</sub>BPA (0.41 ng/g), was detected in the surrounding areas, at a negligible concentration (Table S2A). Furthermore, no Cl<sub>y</sub>Br<sub>x</sub>BPA were detectable in Shouguang (Table S2B). This clearly shows that although Guiyu is currently a major e-waste dismantling site and Qingyuan is also used to engage in e-waste related works, the difference in waste-processing activities has caused a remarkable gap in the concentrations of Cl<sub>y</sub>Br<sub>x</sub>BPA between the two regions. Additionally, there were no Cl<sub>y</sub>Br<sub>x</sub>BPA in Shouguang, where flame retardants are produced, even though the region has abundant chlorine sources that could potentially contribute to the formation of Cl<sub>y</sub>Br<sub>x</sub>BPA from TBBPA.

### 3.3. Composition profiles and source implications

Much higher mean concentrations than the median ones, implies the potential existence of emission sources. Semi-volatile organic compounds in the soil transport through dry and wet deposition with small amount and low speed, resulting to the concentration decaying from the emission source to the surroundings suddenly. In the present study, the median levels of many compounds were lower than the LODs. The impact of emission sources on the surrounding areas was very important and should be considered. Therefore, the composition profiles is discussed based on the mean concentration of each compound.

The composition profiles of the target analytes in Guiyu are shown in Fig. 1. BPA dominated in Group A in both the e-waste dismantling park and its surrounding area, where its relative abundances were 56.6% and 54.2%, respectively. The second most abundant Group A analyte in both locations was TBBPA (25.9% and 32.3%, respectively). The high abundance of these compounds can be attributed to their large-scale production and use. As a high-production volume chemical, BPA was used as an intermediate in the production of epoxy resins and polycarbonate plastics to make various electronic equipments (Huang et al., 2012). Additionally, it can be formed reductively via the debromination of

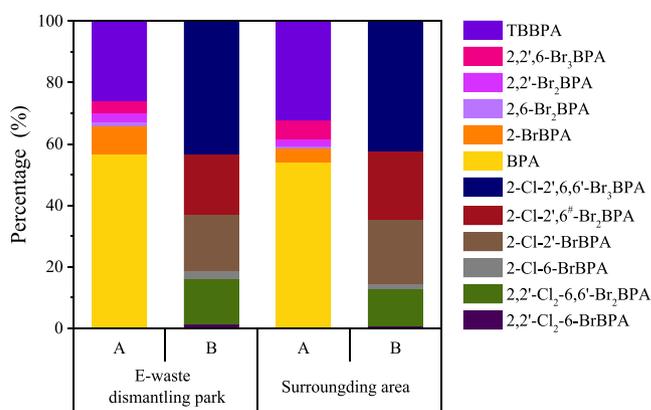


Fig. 1. Composition profiles of TBBPA, Br<sub>x</sub>BPA, and BPA (Group A) and Cl<sub>y</sub>Br<sub>x</sub>BPA (Group B) in soil samples from the e-waste dismantling park and its surrounding area in Guiyu. Because 2-Cl-2',6'-Br<sub>2</sub>BPA and 2-Cl-2',6'-Br<sub>2</sub>BPA co-eluted, the mixture of these two compounds is denoted as 2-Cl-2',6'-Br<sub>2</sub>BPA.

TBBPA during pyrolysis of printed circuit boards in e-waste dismantling processes or as a result of degradation induced by sunlight, microbes, and plants in soil (Grause et al., 2008; Liu et al., 2013, 2016a; Sun et al., 2014). As a reactive flame retardant, TBBPA is bound to other monomers in polymers. However, excessive addition leads to the presence of residual TBBPA in board substrate, which may be released during the usage or handling of the products (Zhou et al., 2014). Additionally, TBBPA has been used as an additive flame retardant to replace commercial penta- or octabromobisphenyl ethers, and is used in acrylonitrile-butadiene-styrene and high impact polystyrene resins, which could further contribute to its direct emissions into the environment during e-waste dismantling (Covaci et al., 2009; Liu et al., 2016b).

BPA was also the dominant group A analyte in Qingyuan: its relative abundance was 94.1% in soil samples from the wire and cable recycling parks, and 75.1% in samples from the surrounding areas (Fig. S2A). The relative abundance of TBBPA in Qingyuan was much lower than in Guiyu (5.3% in the parks, and 24.8% in the surrounding area). This may be because Qingyuan also recycled secondary plastics for pelletizing, piling up, and transportation, which could release a large amount of BPA. Additionally, wires and cables are flame-retarded by halogen-free chemicals with no TBBPA added (Wei et al., 2010), thus not contributing the stack of TBBPA composition. Interestingly, since there is no e-waste dismantling in Shouguang, the relative abundance of BPA in soil samples was only 6.8%, while that of TBBPA was 79.5% (Fig. S2B). This may be due to leakage of the flame retardant during transportation and its subsequent diffusion within the environment.

In Guiyu, Br<sub>x</sub>BPA accounted for 17.4% and 13.4% of Group A compounds in the e-waste dismantling park and the surrounding area, respectively. The relative abundance of individual Br<sub>x</sub>BPA congener decreased in the order of 2-BrBPA, ΣBr<sub>2</sub>BPA, and 2,2',6-Br<sub>3</sub>BPA in the e-waste dismantling park, and 2,2',6-Br<sub>3</sub>BPA, 2-BrBPA, and ΣBr<sub>2</sub>BPA in the surrounding area (Fig. 1). The dominance of 2-BrBPA among the Br<sub>x</sub>BPA in the e-waste dismantling park is probably because 2,2',6-Br<sub>3</sub>BPA, 2,2'-Br<sub>2</sub>BPA, and 2,6-Br<sub>2</sub>BPA are all debrominated, as well as BPA brominated to form 2-BrBPA considering a large BPA base and numerous bromine sources. Accordingly, we previously found that 2-BrBPA was the dominant Br<sub>x</sub>BPA in dust samples from an e-waste dismantling workshop, a raw material crushing workshop, and a secondary copper blast furnace workshop (Liu et al., 2020). In contrast, 2-BrBPA (0.2%) was not the predominant Br<sub>x</sub>BPA in the parks of Qingyuan, but its relative abundance was slightly lower than that of 2,2',6-Br<sub>3</sub>BPA (0.3%) (Fig. S2A). The relative abundance of the Br<sub>x</sub>BPA congeners in Shouguang decreased in the order of 2,2',6-Br<sub>3</sub>BPA, ΣBr<sub>2</sub>BPA, and 2-BrBPA (Fig. S2B), which is consistent with the order seen in soil samples collected by Lan et al. (2019) along the Xiaqing

river in Shouguang. Additionally, the ratio of 2,2'-Br<sub>2</sub>BPA to 2,6-Br<sub>2</sub>BPA observed in the Guiyu e-waste dismantling park was 2.4, which is slightly higher than the ratio of 2. This may be because alternative debromination from TBBPA play an important part where the remaining bromine atoms in two benzene rings would also be expected to be debrominated equally at all the three brominated positions (Fig. S3) (Von der Recke and Vetter, 2007).

The most abundant Cl<sub>y</sub>Br<sub>x</sub>BPA congener was 2-Cl-2',6,6'-Br<sub>3</sub>BPA, whose relative abundance was 43.3% in the Guiyu e-waste dismantling park and 42.4% in the surrounding areas. The relative abundance of the congeners decreased in the order of 2-Cl-2',6,6'-Br<sub>3</sub>BPA, 2-Cl-2',6<sup>#</sup>-Br<sub>2</sub>BPA, 2-Cl-2'-BrBPA, 2,2'-Cl<sub>2</sub>-6,6'-Br<sub>2</sub>BPA, 2-Cl-6-BrBPA, and 2,2'-Cl<sub>2</sub>-6-BrBPA in both the park and the surrounding area (Fig. 1). This may imply that the more highly brominated mono-Cl-Br<sub>x</sub>BPA compounds formed more readily than their less brominated counterparts, and that both formed more readily than the doubly chlorinated derivatives. This inference is supported by the concentration ratios of these transformation products and their precursors. For example, the ratios of 2-Cl-2',6,6'-Br<sub>3</sub>BPA to TBBPA, 2-Cl-2',6<sup>#</sup>-Br<sub>2</sub>BPA to TBBPA, and 2,2'-Cl<sub>2</sub>-6,6'-Br<sub>2</sub>BPA to TBBPA were 0.0095, 0.0043, and 0.0033, respectively. Additionally, the ratio of 2,2',6-Br<sub>3</sub>BPA to TBBPA was approximately 0.15 in the e-waste dismantling park, which is much higher than the ratios of Cl<sub>y</sub>Br<sub>x</sub>BPA congeners to TBBPA. Therefore, it could be deduced that debromination may be much more likely to occur than "Br-to-Cl" exchange, only in terms of concentration ratio. Also, potential regular may be suitable for bromination when the ratios of 2-BrBPA (0.16), mono-Cl-BrBPA (0.0021), 2-Cl-2',6<sup>#</sup>-Br<sub>2</sub>BPA (0.0010), and 2,2'-Cl<sub>2</sub>-6-BrBPA (0.0001) to BPA were calculated. Moreover, 2,2'-Cl<sub>2</sub>-6,6'-Br<sub>2</sub>BPA may be formed by stepwise "Br-to-Cl" reaction from TBBPA (Fig. S3), considering that only 2-Cl-2',6,6'-Br<sub>3</sub>BPA and no 2,2'-Cl<sub>2</sub>-6,6'-Br<sub>2</sub>BPA was detected in Qingyuan. However, the process of replacing two bromine atoms with chlorine ones simultaneously may also occur, because the concentrations of 2-Cl-2',6,6'-Br<sub>3</sub>BPA and 2,2'-Cl<sub>2</sub>-6,6'-Br<sub>2</sub>BPA differ only by an order of magnitude, which is much closer compared the yield of the first "Br-to-Cl" reaction of parent compounds.

Analysis of the relationships between analytes can help reveal their possible sources. The correlations between the analyte concentrations in the soil samples from Guiyu are presented in Fig. 2. It is notable that the correlations between TBBPA and Br<sub>x</sub>BPA decays as *x* decreases from *x* = 3 to *x* = 0 (where the compound having *x* = 0 is BPA), as shown in Fig. 2A (Table S3A). This indicates that these debromination products have a common source (i.e., TBBPA), but there are other sources of BPA, which may be directly discharged during e-waste dismantling processes or formed by debromination of TBBPA. Additionally, Cl<sub>y</sub>Br<sub>x</sub>BPA showed stronger positive correlations with TBBPA, Br<sub>x</sub>BPA, and BPA, and with other Cl<sub>y</sub>Br<sub>x</sub>BPA, which may deduce that Cl<sub>y</sub>Br<sub>x</sub>BPA are formed by both "Br-to-Cl" exchange of Br<sub>x</sub>BPA and debromination of more heavily brominated Cl<sub>y</sub>Br<sub>x</sub>BPA congeners. However, further studies are needed to determine the mechanism of the "Br-to-Cl" exchange reaction.

To clarify the relationships between the analytes, separate PCA were conducted for the park and surrounding area in Guiyu. In the park PCA, analytes containing three or four halogen atoms were grouped together along PC1 (40.9%) while the other analytes grouped together on PC2 (40.5%) (Fig. 3A). PC1 and PC2 may represent different transformation pathways of Cl<sub>y</sub>Br<sub>x</sub>BPA, i.e., firstly debrominating from TBBPA or brominating from BPA, then the "Br-to-Cl" exchange reaction would occur (Fig. S3). Conversely, the PCA for the surrounding area showed that all analytes other than BPA were grouped on PC1' (49.3%), may indicate that these analytes were all transported to the surrounding area (Fig. 3B). This deduce was supported by the correlation heat map for the surrounding area (Fig. 2B). It is possible that the "Br-to-Cl" exchange does not occur during the transport of the analytes, and that only natural debromination is possible during this process. As a result, there were two distinct groups of highly correlated compounds, one consisting of TBBPA, BPA, and Br<sub>x</sub>BPA, and another consisting of Cl<sub>y</sub>Br<sub>x</sub>BPA.

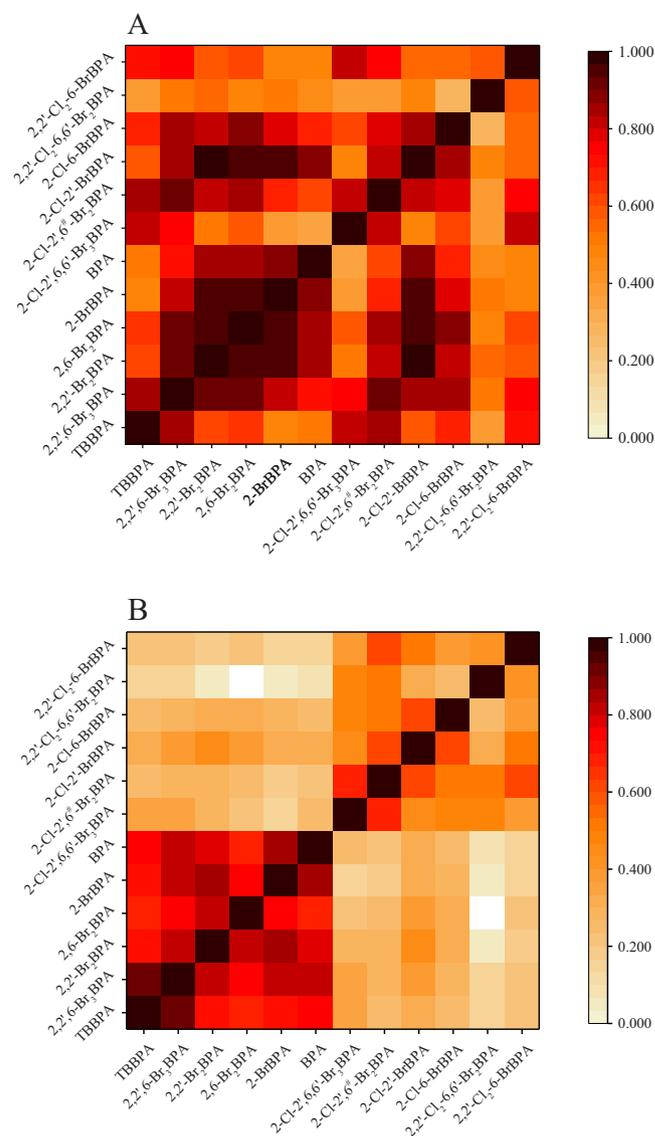
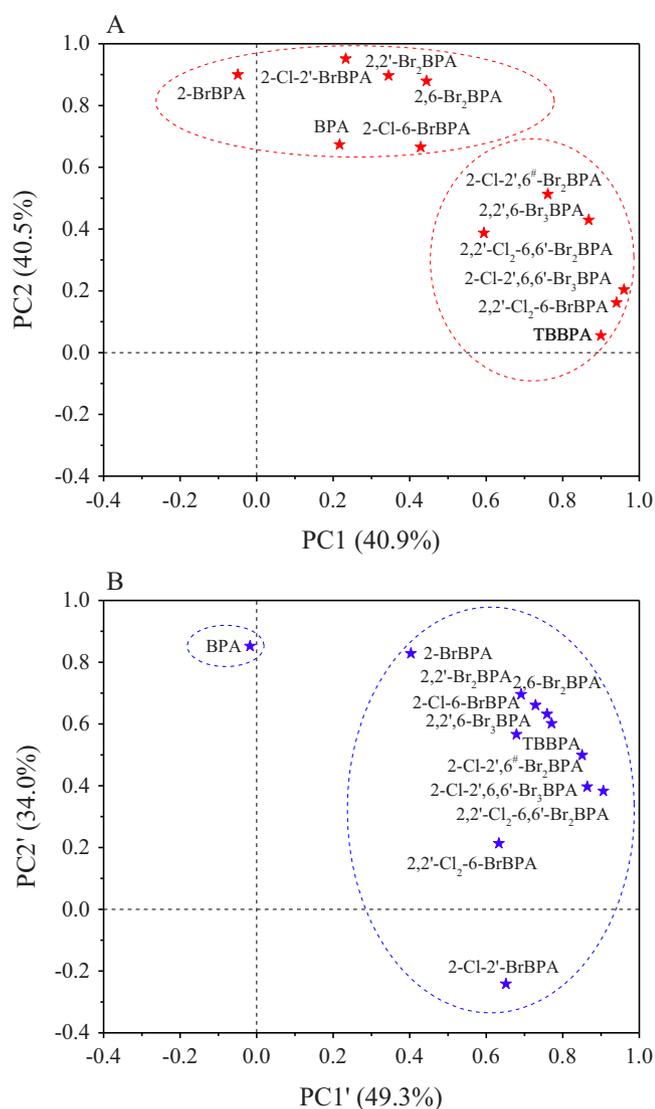


Fig. 2. Spearman correlation heat maps of TBBPA, Br<sub>x</sub>BPA, BPA, and Cl<sub>y</sub>Br<sub>x</sub>BPA in soil samples from the e-waste dismantling park (A) and its surrounding area (B) in Guiyu. Because 2-Cl-2',6-Br<sub>2</sub>BPA and 2-Cl-2',6<sup>#</sup>-Br<sub>2</sub>BPA co-eluted, the mixture of these two compounds is denoted as 2-Cl-2',6<sup>#</sup>-Br<sub>2</sub>BPA.

Interestingly, BPA was negatively correlated with PC1' and isolated on PC2' (34.0%), implying that some of the BPA in the surrounding area originates from other sources, in keeping with the results mentioned previously. However, another deduce could not be ruled out that these transformation products would be incubated spontaneously if there are enough TBBPA, BPA, bromine and chlorine sources. The sharp decay of relationship areas in Fig. 2B may be attributed to the possible low efficiency of "Br-to-Cl" exchange reaction. Therefore, more evidence was needed urgently to figure out the transformation pathways.

### 3.4. Spatial distribution based on grid soil samples

To understand the effect of the chemicals on the surrounding area, the distributions of BPA, TBBPA, and its transformation products in Guiyu were analyzed (Fig. 4A–D). The concentration contour plots showed that the most contaminated area was the e-waste dismantling park; the concentrations of all of the analytes in soil samples from the surrounding area were orders of magnitude lower than in the park. Noticeably, the southern part of the surrounding area (Guiyu town),



**Fig. 3.** Principal component analysis of TBBPA, Br<sub>x</sub>BPAs, BPA, and Cl<sub>y</sub>Br<sub>x</sub>BPAs in the e-waste dismantling park (A) and its surrounding area (B) in Guiyu. Because 2-Cl-2',6-Br<sub>2</sub>BPA and 2-Cl-2',6'-Br<sub>2</sub>BPA co-eluted, the mixture of these two compounds is denoted as 2-Cl-2',6<sup>#</sup>-Br<sub>2</sub>BPA.

which contained many family-based e-waste dismantling workshops before the park was built, had higher TBBPA and BPA concentrations than the northern part (Nanyang, a subordinate village of Guiyu) (Figs. 4A and 4B). This suggests that the TBBPA and BPA in soil samples originated from historical primitive e-waste dismantling activity. The area of BPA contamination seems larger than that of TBBPA, which may be because BPA is a widely used chemical with a high production volume and multiple possible sources unrelated to e-waste dismantling and TBBPA degradation.

The distribution of Br<sub>x</sub>BPAs was similar to that of TBBPA but their concentrations and contaminated area were somewhat lower (Fig. 4C). This was expected because Br<sub>x</sub>BPAs may be formed by debromination of TBBPA and thus have closely related sources. To better understand the spatial distribution of the Br<sub>x</sub>BPA congeners, their individual concentration contour plots are shown in Fig. S4A–D. The sizes of the contaminated areas for these congeners decreased in the order 2,2',6-Br<sub>3</sub>BPA > 2,2'-Br<sub>2</sub>BPA > 2,6-Br<sub>2</sub>BPA, strongly suggesting a point source of pollution centered on the e-waste dismantling park (Fig. S4A–C). Unexpectedly, 2-BrBPA did not follow this trend; its contaminated area was slightly smaller than that of 2,2',6-Br<sub>3</sub>BPA, but larger than those of

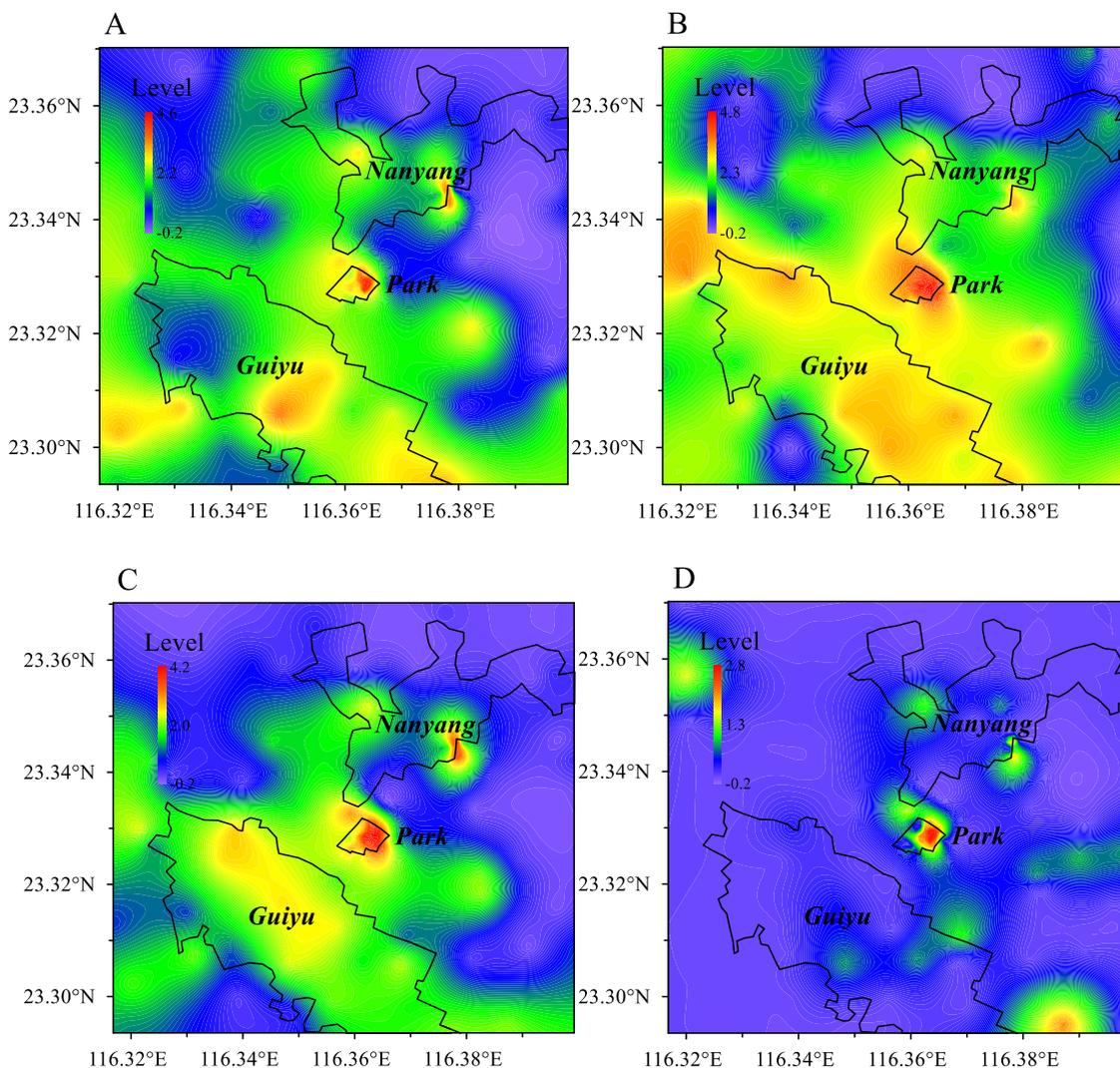
2,2'-Br<sub>2</sub>BPA and 2,6-Br<sub>2</sub>BPA (Fig. S4D). As noted previously, 2,2',6-Br<sub>3</sub>BPA, 2,2'-Br<sub>2</sub>BPA, and 2,6-Br<sub>2</sub>BPA may all be debrominated, as well as BPA brominate to form 2-BrBPA. Because, given the similar distributions of 2-BrBPA and BPA, their strong correlation coefficients (0.888 and 0.842, respectively,  $p < 0.05$ ) were found in the e-waste dismantling park and the surrounding area. Additionally, in spite of the concentration levels of the chemicals in Qingyuan were lower than Guiyu, the e-waste processed at Qingyuan has a high content of BPA and the content of brominated flame retardants is relatively low. This lack of bromine sources may prevent the formation of 2-BrBPA, explaining the low levels of this compound in the Qingyuan soil samples. More research is needed to test these hypotheses.

The spatial distributions of the Cl<sub>y</sub>Br<sub>x</sub>BPAs differed strongly from those discussed above (Fig. 4D). These compounds were mainly detected in the e-waste dismantling park, i.e., the red area of the contour plot, suggesting that they are formed during e-waste dismantling activities. Although only one published report includes data on Cl<sub>y</sub>Br<sub>x</sub>BPAs levels in e-waste dismantling workshops, there have been several publications reporting the formation and detection of mixed halogenated dioxins, furans, and diphenyl ethers (Liu et al., 2020; Tue et al., 2019). The formation of these compounds is mainly attributed to “Br-to-Cl” exchange reactions. Previous studies have shown that polybrominated diphenyl ethers and hexabromobenzene can be transformed into mixed halogenated products during thermal treatment at 250–500 °C in the presence of chlorine sources (Rupp and Metzger, 2005). The distributions of all the Cl<sub>y</sub>Br<sub>x</sub>BPA congeners showed that their concentrations were highest in the park and gradually decreased as the distance from the park increased (Fig. S5A–F). The highest concentrations of the Cl<sub>y</sub>Br<sub>x</sub>BPA congeners occurred in the eastern part of the e-waste dismantling park, which is the main location at which thermal processes are performed during e-waste dismantling. Outside of the e-waste dismantling park, some relatively weak point sources were visible, which may be due to the scattered open burning of e-waste before the park was built. Overall, these results indicate that Cl<sub>y</sub>Br<sub>x</sub>BPAs are very common transformation products emitted during e-waste dismantling.

### 3.5. Potential specific molecular markers of e-waste dismantling activities

In both Guiyu and Qingyuan, there used to be many private workshops engaged in e-waste dismantling activities, and lots of printed circuit boards and plastic casings were burned in the open. After the establishment of industrial waste processing parks in the two locations, more environmentally friendly equipment and technologies for e-waste dismantling were introduced for processing printed circuit boards in Guiyu, while Qingyuan focused on recycling secondary plastics and second-hand copper from wires and cables. It is worth noting that the most common printed circuit boards on the market are the FR-4 type currently, which are made from glass fiber cloth impregnated with epoxy resin. Epoxy resins are often made of monomeric BPA doping with TBBPA to increase fire safety, while the plastic casings of printed circuit boards (which undergo high temperature treatment alongside printed circuit boards) are typically made from polyvinyl chloride (PVC), which are also the main stuff of wire and cable sheaths (Hall and Williams, 2007; U.S. EPA, 2015; Wei et al., 2010; Zhou et al., 2014).

The differing levels and distributions of TBBPA transformation products, and especially Cl<sub>y</sub>Br<sub>x</sub>BPAs, in Guiyu and Qingyuan can be explained based on the findings presented above. Firstly, we note that the formation of large quantities of Cl<sub>y</sub>Br<sub>x</sub>BPAs in Guiyu indicates that the parent compound (TBBPA and BPA), chlorine source, and high temperatures are present simultaneously. Secondly, in Qingyuan, other than that rare Cl<sub>y</sub>Br<sub>x</sub>BPAs in surrounding areas may be due to the previous open burning like Guiyu, levels of Cl<sub>y</sub>Br<sub>x</sub>BPAs in the parks are much lower than Guiyu. Field investigations revealed that some plastic casings (may contain TBBPA as additive flame retardant) and printed circuit boards are sometimes inadvertently mechanically crushed alongside wires and cables, and that the crushing process can generate



**Fig. 4.** Spatial distributions of TBBPA (A), BPA (B), Br<sub>x</sub>BPAs (C), and Cl<sub>7</sub>Br<sub>x</sub>BPAs (D) in Guiyu. The observed value at each sampling site was augmented by one before log-transformation (log10).

high temperatures (Fig. S6). However, on the one hand, the heating during crushing is sporadic; on the other hand, lower concentrations of TBBPA and BPA compared to Guiyu may limit the transformation to Cl<sub>7</sub>Br<sub>x</sub>BPAs due to the unknown yield of the halogen exchange reaction. Therefore, the parent compound and chlorine source are necessary and whether high temperature is necessary or positive for reaction needs further study. In addition, the concentration of the parent compound in Shouguang soil is far lower. In the case of sufficient chlorine source, maybe the low halogen exchange reaction yield would cause the Cl<sub>7</sub>Br<sub>x</sub>BPAs to fall below LODs.

We therefore believe that Cl<sub>7</sub>Br<sub>x</sub>BPAs might be a potential class of specific molecular markers of e-waste dismantling activities, and especially for the dismantling of printed circuit boards. However, somewhat to distinguish e-waste dismantling activity just relying on Cl<sub>7</sub>Br<sub>x</sub>BPAs has a certain of limitations. The results presented here suggest that mixed halogenated compounds could be formed in any process where a halogenated compound is mixed with some source of a different halogen in spite of high temperature treatment. Because Cl<sub>7</sub>Br<sub>x</sub>BPAs are relatively newly identified compounds in the environment, further researches on their transformation mechanisms and their potential as specific molecular markers of e-waste dismantling activities are urgently needed.

#### 4. Conclusions

TBBPA, BPA, Br<sub>x</sub>BPAs, and Cl<sub>7</sub>Br<sub>x</sub>BPAs were widely detected in grid soil samples from a typical e-waste dismantling site in Guiyu but their concentrations were low or not detectable in Qingyuan and Shouguang. In Guiyu, their distributions were centered on the e-waste dismantling park and extended into the surrounding area, indicating that e-waste dismantling activities are an important source of these chemicals. The concentrations of Br<sub>x</sub>BPAs were significantly higher than those of Cl<sub>7</sub>Br<sub>x</sub>BPAs, indicating that the formation of debrominated products may proceed more readily than “Br-to-Cl” exchange reactions. Based on the analyses of the waste processing sites at Guiyu and Qingyuan and the flame retardant production center at Shouguang, Cl<sub>7</sub>Br<sub>x</sub>BPAs were identified as potential specific molecular markers of e-waste dismantling activities, but there are still limitations. Although there is difference in the concentration of Cl<sub>7</sub>Br<sub>x</sub>BPAs in the three sites, we are not sure whether high temperature is required under the condition that the parent compounds (TBBPA and BPA) and a chlorine source are necessary. Also, Cl<sub>7</sub>Br<sub>x</sub>BPAs would be generated in other industries if the necessary conditions happen to be together. However, further researches are needed to determine the mechanisms by which Cl<sub>7</sub>Br<sub>x</sub>BPAs are formed, which could enable better control of pollutant emissions from e-waste dismantling activities.

## CRedit authorship contribution statement

**Xiang Ge**: Methodology, sampling, data analysis, and draft preparation. **Shengtao Ma**: Sampling, methodology, and draft preparation. **Yanping Huo**: Methodology. **Yan Yang**: Data analysis. **Xiaojun Luo**: Data analysis. **Yingxin Yu**: Design, data analysis, reviewing & editing. **Taicheng An**: Design.

## 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.

## Acknowledgments

The present study was supported by the National Natural Science Foundation of China (41991311, 41977303, 41703092, and 41731279), Guangdong-Hong Kong-Macao Joint Laboratory for Contaminants Exposure and Health (2020B1212030008), and 100 Talents Program of Guangdong University of Technology. We also thank Prof. Walter Vetter (University of Hohenheim, Germany) for his useful suggestions.

## Declaration of competing financial interests

There were no potential competing financial interests.

## Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at [doi:10.1016/j.jhazmat.2021.127126](https://doi.org/10.1016/j.jhazmat.2021.127126).

## References

- Akiyama, E., Kakutani, H., Nakao, T., Motomura, Y., Takano, Y., Sorakudo, R., Mizuno, A., Aozasa, O., Tachibana, K., Doi, T., Ohta, S., 2015. Facilitation of adipocyte differentiation of 3T3-L1 cells by debrominated tetrabromobisphenol A compounds detected in Japanese breast milk. *Environ. Res.* 140, 157–164.
- Chen, P., Ma, S.T., Yang, Y., Qi, Z.H., Wang, Y.J., Li, G.Y., Tang, J.H., Yu, Y.X., 2021. Organophosphate flame retardants, tetrabromobisphenol A, and their transformation products in sediment of e-waste dismantling areas and the flame-retardant production base. *Ecotoxicol. Environ. Saf.* 225, 112717.
- Covaci, A., Voorspoels, S., Abdallah, M., Geens, T., Harrad, S., Law, R., 2009. Analytical and environmental aspects of the flame retardant tetrabromobisphenol-A and its derivatives. *J. Chromatogr. A* 1216, 346–363.
- Doumas, M., Rouillon, S., Venisse, N., Nadeau, C., Eugene, P., Farce, A., Chavatte, P., Dupuis, A., Migeot, V., Carato, P., 2018. Chlorinated and brominated bisphenol A derivatives: synthesis, characterization and determination in water samples. *Chemosphere* 213, 434–442.
- Gao, S., Hong, J., Yu, Z., Wang, J., Yang, G., Sheng, G., Fu, J., 2011. Polybrominated diphenyl ethers in surface soils from e-waste recycling areas and industrial areas in South China: Concentration levels, congener profile, and inventory. *Environ. Toxicol. Chem.* 30, 2688–2696.
- GB 17378.2-2007, 2007. State standard of the People's Republic of China. The specification for marine monitoring. Part 2: Data Processing and Quality Control of Analysis.
- Ge, X., Ma, S., Zhang, X., Yang, Y., Li, G., Yu, Y., 2020. Halogenated and organophosphorous flame retardants in surface soils from an e-waste dismantling park and its surrounding area: Distributions, sources, and human health risks. *Environ. Int.* 139, 105741.
- Grause, G., Furusawa, M., Okuwaki, A., Yoshioka, T., 2008. Pyrolysis of tetrabromobisphenol-A containing paper laminated printed circuit boards. *Chemosphere* 71, 872–878.
- Hall, W.J., Williams, P.T., 2007. Separation and recovery of materials from scarp printed circuit boards. *Resour. Conserv. Recycl.* 51, 691–709.
- Huang, Y., Wong, C., Zheng, J., Bouwman, H., Barra, R., Wahlstrom, B., Neretin, L., Wong, M., 2012. Bisphenol A (BPA) in China: a review of sources, environmental levels, and potential human health impacts. *Environ. Int.* 42, 91–99.
- Kudo, Y., Yamauchi, K., Fukazawa, H., Terao, Y., 2006. In vitro and in vivo analysis of the thyroid system-disrupting activities of brominated phenolic and phenol compounds in *Xenopus laevis*. *Toxicol. Sci.* 92, 87–95.
- Lan, J., Shen, Z., Gao, W., Liu, A., 2019. Occurrence of bisphenol-A and its brominated derivatives in tributary and estuary of xiaoqing river adjacent to Bohai sea, China. *Mar. Pollut. Bull.* 149, 110551.
- Li, T., Bao, L., Wu, C., Liu, L., Wong, C., Zeng, E., 2019a. Organophosphate flame retardants emitted from thermal treatment and open burning of e-waste. *J. Hazard. Mater.* 367, 390–396.
- Li, T., Ge, J., Pei, J., Bao, L., Wu, C., Zeng, E., 2019b. Emissions and occupational exposure risk of halogenated flame retardants from primitive recycling of e-waste. *Environ. Sci. Technol.* 53, 12495–12505.
- Li, T., Zhou, J., Wu, C., Bao, L., Shi, L., Zeng, E., 2018. Characteristics of polybrominated diphenyl ethers released from thermal treatment and open burning of e-waste. *Environ. Sci. Technol.* 52, 4650–4657.
- Liu, A., Shi, J., Qu, G., Hu, L., Ma, Q., Song, M., Jing, C., Jiang, G., 2017. Identification of emerging brominated chemicals as the transformation products of tetrabromobisphenol A (TBBPA) derivatives in soil. *Environ. Sci. Technol.* 51, 5434–5444.
- Liu, C., Niu, X., Song, X., 2016a. A simulation research on the natural degradation process of tetrabromobisphenol A in soil under the atmospheric different environments. *Environ. Sci. Pollut. Res.* 23, 16406–16416.
- Liu, J., Ma, S., Lin, M., Tang, J., Yue, C., Zhang, Z., Yu, Y., An, T., 2020. New mixed bromine/chlorine transformation products of tetrabromobisphenol A: synthesis and identification in dust samples from an e-waste dismantling site. *Environ. Sci. Technol.* 54, 12235–12244.
- Liu, J., Wang, Y., Jiang, B., Wang, L., Chen, J., Guo, H., Ji, R., 2013. Degradation, metabolism, and bound-residue formation and release of tetrabromobisphenol A in soil during sequential anoxic-oxic incubation. *Environ. Sci. Technol.* 47, 8348–8354.
- Liu, K., Li, J., Yan, S., Zhang, W., Li, Y., Han, D., 2016b. A review of status of tetrabromobisphenol A (TBBPA) in China. *Chemosphere* 148, 8–20.
- Rupp, S., Metzger, J., 2005. Brominated-chlorinated diphenyl ethers formed by thermolysis of polybrominated diphenyl ethers at low temperatures. *Chemosphere* 60, 1644–1651.
- Sun, F., Kolvenbach, B., Nastold, P., Jiang, B., Ji, R., Corvini, P., 2014. Degradation and metabolism of tetrabromobisphenol A (TBBPA) in submerged soil and soil-plant systems. *Environ. Sci. Technol.* 48, 14291–14299.
- Tang, X., Zeng, B., Hashmi, M., Long, D., Yu, B., Ullah, N., Shen, C., Chen, Y., 2013. PBDEs and PCDD/Fs in surface soil taken from the Taizhou e-waste recycling area, China. *Chem. Ecol.* 30, 245–251.
- Tue, N., Matsushita, T., Goto, A., Itai, T., Asante, K., Obiri, S., Mohammed, S., Tanabe, S., Kunisue, T., 2019. Complex mixtures of brominated/chlorinated diphenyl ethers and dibenzofurans in soils from the Agbogbloshie e-waste site (Ghana): occurrence, formation, and exposure implications. *Environ. Sci. Technol.* 53, 3010–3017.
- U.S. EPA, 2015. Flame Retardants in Printed Circuit Boards. EPA Publication, 744-R-15-001.
- Von der Recke, R., Vetter, W., 2007. Photolytic transformation of polybrominated biphenyls leading to the structures of unknown hexa- to nonabromo-congeners. *J. Chromatogr. A* 1167, 184–194.
- Wei, M., Murphy, D., Barry, C., Mead, J., 2010. Halogen-free flame retardants for wire and cable applications. *Rubber Chem. Technol.* 83, 282–302.
- Wu, Z., Han, W., Xie, M., Han, M., Li, Y., Wang, Y., 2019. Occurrence and distribution of polybrominated diphenyl ethers in soils from an e-waste recycling area in northern China. *Ecotoxicol. Environ. Saf.* 167, 467–475.
- Yu, Y., Yu, Z., Chen, H., Han, Y., Xiang, M., Chen, X., Ma, R., Wang, Z., 2019. Tetrabromobisphenol A: Disposition, kinetics and toxicity in animals and humans. *Environ. Pollut.* 253, 909–917.
- Yu, Z., Lu, S., Gao, S., Wang, J., Li, H., Zeng, X., Sheng, G., Fu, J., 2010. Levels and isomer profiles of dechlorane plus in the surface soils from e-waste recycling areas and industrial areas in South China. *Environ. Pollut.* 158, 2920–2925.
- Yu, Z., Zheng, K., Ren, G., Wang, D., Ma, S., Peng, P., Wu, M., Sheng, G., Fu, J., 2011. Identification of monochloro-nonabromodiphenyl ethers in the air and soil samples from South China. *Environ. Sci. Technol.* 45, 2619–2625.
- Zeng, Y., Tang, B., Luo, X., Zheng, X., Peng, P., Mai, B., 2016. Organohalogen pollutants in surface particulates from workshop floors of four major e-waste recycling sites in China and implications for emission lists. *Sci. Total Environ.* 569–570, 982–989.
- Zhan, F., Zhang, H., Cao, R., Fan, Y., Xu, P., Chen, J., 2019. Release and transformation of BTBPE during the thermal treatment of flame retardant ABS plastics. *Environ. Sci. Technol.* 53, 185–193.
- Zhou, X., Guo, J., Zhang, W., Zhou, P., Deng, J., Lin, K., 2014. Tetrabromobisphenol A contamination and emission in printed circuit board production and implications for human exposure. *J. Hazard. Mater.* 273, 27–35.