



Organohalogen pollutants in surface particulates from workshop floors of four major e-waste recycling sites in China and implications for emission lists



Yan-Hong Zeng^a, Bin Tang^{a,b}, Xiao-Jun Luo^a, Xiao-Bo Zheng^c, Ping-An Peng^a, Bi-Xian Mai^{a,*}

^a 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, China

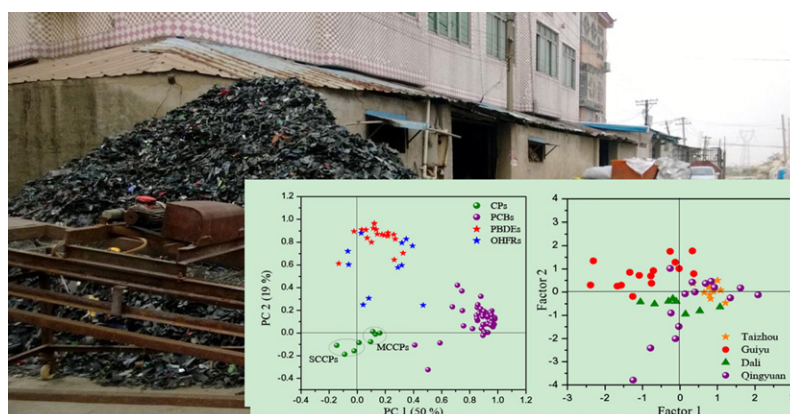
^b Graduate University of Chinese Academy of Sciences, Beijing 100049, China

^c College of Natural Resources and Environment, South China Agricultural University, Guangzhou 510642, China

HIGHLIGHTS

- Report of characterizing the types and possible sources of OHPs in e-waste sites
- Guiyu was a typical site contaminated by HFRs, while Dali was dominated by CPs.
- Qingyuan and Taizhou were representative PCB-polluted regions.
- Electronic devices and plastics may account for the high content of HFRs.
- Metal products are likely the major source of CPs.

GRAPHICAL ABSTRACT



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ABSTRACT

To examine the environmental pollution associated with e-waste recycling activities, the concentrations of organohalogenated pollutants (OHPs), i.e., short- and medium-chain chlorinated paraffins (SCCPs and MCCPs), polychlorinated biphenyls (PCBs), polybrominated diphenyl ethers (PBDEs), and several other halogenated flame retardants (OHFRs), were investigated in surface particulates from the workshop floors of four major e-waste recycling sites (Taizhou, Guiyu, Dali and Qingyuan) in China. The mean levels of SCCPs, MCCPs, PCBs, PBDEs and OHFRs in surface particulates ranged from 30,000–61,000, 170,000–890,000, 2700–27,000, 52,000–240,000, and 62,000–140,000 ng/g dry weight (dw), respectively. OHFRs, including decabromodiphenyl ethane, dechlorane plus, 1,2-bis(2,4,6-tribromophenoxy)ethane, tetrabromobisphenol A, hexabromocyclododecanes, polybrominated biphenyls, hexabromobenzene, pentabromotoluene, and pentabromoethylbenzene, were frequently (>50% detection frequency) detected in surface particulates with mean concentration ranges of 39,000–63,000, 310–2700, 98–16,000, 21,000–56,000, 55–5700, 1700–27,000, 42–1600, 3.2–220, and 5.8–12 ng/g dw, respectively. The composition of OHPs varied depend on the e-waste items processing in different regions. Guiyu and Dali were typical sites contaminated by halogenated flame retardants (HFRs) and CPs, respectively, while Qingyuan, and Taizhou were representative PCB-polluted regions. The evidence produced by this preliminary study indicated that

* Corresponding author.

E-mail address: nancymai@gig.ac.cn (B.-X. Mai).

electronic devices and plastics may account for the high content of HFRs and the metal products are likely the major source of CPs in these e-waste sites.

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1. Introduction

With the rapid growth of economies and the development of new technologies, global e-waste production is increasing. According to the United Nations Environment Programme (UNEP) (2006) (UNEP, 2006), the world's production of e-waste is estimated at 20–50 million tons per year and is expected to increase by at least 3–5% annually (Communities, 2000). However, approximately 70% of the global exported e-waste is designated for China (Liu et al., 2006). Another UNEP report estimates that China will become the world's second largest producer of e-waste (2.3 million tons per year) by 2020 (Schlupe et al.). Therefore, China appears to be the largest dumping site for e-waste because of the dual pressure illegally imported and domestically generated e-waste.

Because of the primitiveness of e-waste recycling activities, including peeling and melting plastic, combusting or roasting circuit boards, and extracting metals with strong acids (Li et al., 2007; Wong et al., 2007), the environmental effects of e-waste disposal are attracting increasing attention. Concerns focus not only on the volume of e-waste generated but also on the list of e-waste-associated contaminants. Organohalogen pollutants (OHPs) are one of the most concerning classes because of their significant levels in e-waste (Robinson, 2009). Some OHPs, such as short- and medium-chain chlorinated paraffins (SCCPs and MCCPs), polychlorinated biphenyls (PCBs), polybrominated diphenyl ethers (PBDEs), and polybrominated biphenyls (PBBs), have been banned or restricted in some regions of the world because of their persistence and hazardous properties (Arnot et al., 2009; Betts, 2008). Nevertheless, more non-regulated OHPs, e.g., decabromodiphenyl ethane (DBDPE), tetrabromobisphenol A (TBBPA), hexabromocyclododecanes (HBCDs), dechlorane plus (DP), hexabromobenzene (HBB), pentabromoethylbenzene (PBEB), 1,2-bis(2,4,6-tribromophenoxy)ethane (BTBPE), and pentabromotoluene (PBT), continue to be produced, and some are considered as alternatives for conventional OHPs, such as PBDEs (Covaci et al., 2011; Sverko et al., 2011). To date, the available data on these alternative OHPs indicate that these chemicals might also be persistent, bioaccumulative and toxic (Covaci et al., 2011). Thus, the pollution status of OHPs in these hot spots (e-waste recycling sites) is particularly concerning.

The surface particulates on workshop floors can provide information about the concentration and distribution of contaminants in e-waste because a large number of OHPs may end up concentrated in the surface environment, although recycling may remove some contaminants. Therefore, the primary objective of the present study was to gain an overview of the levels, compositions and congener group profiles of OHPs in surface particulates from four major e-waste recycling areas (Taizhou, Guiyu, Qingyuan and Dali) in China. In addition, an effort was made to determine the potential emission list for OHPs associated with e-waste, as the levels and patterns of OHPs found in e-waste largely depend on the type of items being dismantled (Robinson, 2009). The present study is one of very few papers investigating the levels of a wide variety of environmental pollutants in surface particulates at four representative e-waste recycling areas in China. We hope that this work will be useful to the government, as it develops a strategy to guide future e-waste disposal.

2. Experimental section

2.1. Study area

The study areas—Taizhou in Zhejiang Province (East China) and Guiyu, Qingyuan and Dali in Guangdong Province (South China)—are

the four regions with the most intensive e-waste recycling activity in China. Taizhou has been involved in e-waste recycling for at least 30 years, and >2 million tons of e-waste are dismantled annually (Han et al., 2009; Tang et al., 2014). In these areas, electrical and electronic apparatuses, including refrigerators, washing machines and televisions, are recycled to recover useful materials. Guiyu is an established e-waste recycling town where over 6000 small-scale, family-run workshops participate in this industry, dismantling and recycling over 1 million tons of e-waste annually (Fu et al., 2011; Wang et al., 2005). Electronic devices and plastic products, such as displays, capacitors, and plastic pipes, are dismantled here. The recycling activities in Guiyu include dismantling e-waste and renovating e-waste components and are called “industrial chain extension” by the local government. Qingyuan was relatively recently reported to be an e-waste recycling city and houses >1300 dismantling and recycling workshops that dismantle approximately 1 million tons of e-waste annually (Wang et al., 2014; Wu et al., 2008). In this region, light e-waste (mobile cellphones, video recorders, and circuit boards) and heavy e-waste (electrical machines and transformers) are manually dismantled in small family-run workshops aiming to recycle metal materials. In addition, over the years, enormous quantities of capacitors and transformers have been dismantled in Qingyuan. Compared to Taizhou, Guiyu and Qingyuan, the e-waste recycling activities in Dali are less intensive, and most of the area is used as temporary e-waste warehouses. The e-waste storage facilities located in the front parts of houses or near residential areas usually house steel and non-ferrous metals, such as iron wire, aluminum products, and scrap metal.

2.2. Sampling

Sampling campaigns were conducted between July 2013 and December 2013. A total of 48 particulate samples were collected from the workshop floors at Qingyuan (N 23.42° E 113.01°), Guiyu (N 23.30° E 116.33°), Dali (N 23.02° E 113.06°) and Taizhou (N 28.50° E 121.30°) (Fig. 1). Briefly, 10 of 48 samples were collected in three regions in Taizhou, mainly from a typical e-waste recycling park at Fengjiang town, family-run workshops at Tongshan village and a freight terminal at Jiaojiang. Eight samples were collected at family-run workshops at Dali town in Foushan city. Fifteen samples from Guiyu were collected in three regions, mainly from typical e-waste recycling villages including: Meizhou, Beilin, and Huamei. As for Qingyuan, fifteen samples were collected from typical e-waste recycling regions, including Baihetang, Dongjiapu, Banchong. For each sample, three to six subsamples from a workshop were pooled, to yield representative composite samples. Only one representative sample was obtained for each e-waste workshop. Different types of e-wastes were recycled at the different sites, and detailed information about each is included in Table S1. Surface particulates were collected using a straw brush with a gentle sweeping motion to collect fine particulates inside the workshops. The particulates were then wrapped in aluminum foil and transported to the laboratory. All the samples were air-dried and sieved through 80-mesh screens. Finally, samples were stored in brown glass bottles at -20°C until chemical analysis.

In order to check the compositions of the particulates, one out of every four samples for each e-waste region was randomly selected to analyze with scanning electron microscope (SEM). The pictures of these samples indicated that the particulates sampled in the present study was mainly consisted of irregular tiny particles. Moreover, the energy dispersive X-ray spectrometric microanalysis (EDX) with SEM suggested that silicon was the most abundant ingredient of these irregular

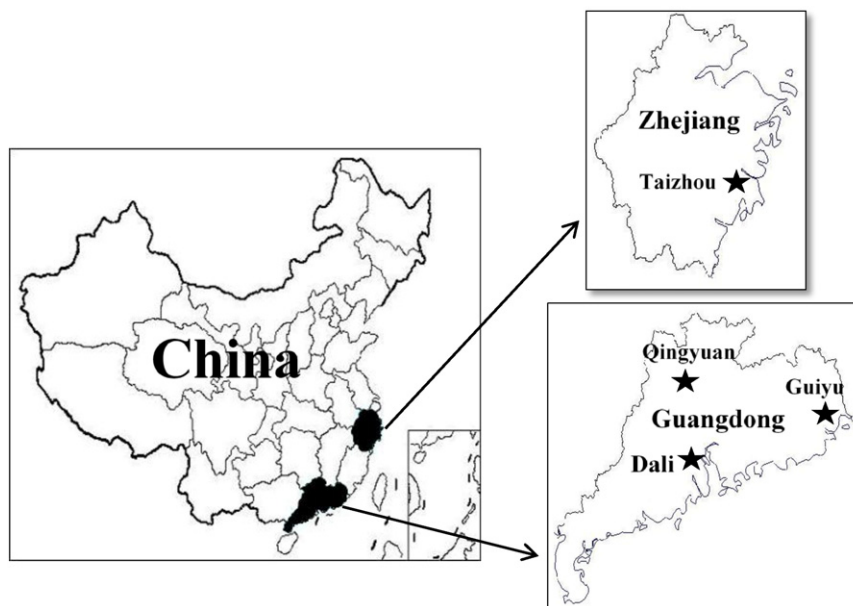


Fig. 1. Map of the four e-waste recycling sites in China: Qingyuan, Guiyu, Dali, and Taizhou.

particles, which indicated that dust was the predominant component of the particulates for all the studied samples.

2.3. Sample preparation

Homogenized dry samples of approximately 300 mg were weighed and then divided into three equal parts. The first equal part was used for CP analyses. This sub-sample was spiked with the surrogate standard ($^{13}\text{C}_{10}$ -*trans*-chlordane), subjected to ultrasonic extraction three times with 20 mL of dichloromethane, and then separated by centrifugation. The following procedures were used and were similar to those of our previous study (Chen et al., 2011), with some modifications. Details are provided in the Supporting Information (SI). The second equal part was spiked with the surrogate standard (PCB30, PCB65, PCB204, BDE77, BDE181, BDE205 and $^{13}\text{C}_{12}$ -BDE-209) and used for the determination of PCBs, PBDEs, PBBs, DBDPE, DP, BTBPE, PBT, HBB and PBEB. Detailed sample preparation procedures are described in the SI. The third equal part was spiked with the surrogate standard (^{13}C -labeled α -, β -, γ -HBCD and ^{13}C -labeled TBBPA) and used for the determination of TBBPA and HBCDs. Detailed sample preparation procedures are provided in the SI.

2.4. Instrumental analysis

The instrumental analyses of CPs (C_{10} – C_{17} with Cl_5 – Cl_{10}) were performed using a gas chromatograph/electron-capture negative ionization/low-resolution mass spectrometer (GC-ECNI-LRMS), as described by Chen et al. (Chen et al., 2011). Briefly, the samples were analyzed on an Agilent 6980 N gas chromatograph coupled to an Agilent 5975B mass spectrometer in ENCI mode. A DB-5HT (15 m \times 0.25 mm i.d., 0.10- μm film thickness) capillary column was used. The injector temperature was set to 250 $^{\circ}\text{C}$, the transfer line temperature was 280 $^{\circ}\text{C}$, and the ion source temperature was 200 $^{\circ}\text{C}$. The oven temperature programs are described in detail in the SI. To improve the instrument sensitivity, all monitored ions of SCCPs and MCCPs were divided into four groups: C_{10} and C_{11} , C_{12} and C_{13} , C_{14} and C_{15} , C_{16} and C_{17} . Therefore, for each sample, four individual injections were needed to analyze all the selected CP congeners. As described previously, congener groups were identified by their retention time range, signal shape, and isotope ratio. The quantification procedures for SCCP (C_{10} – C_{13} with Cl_5 – Cl_{10}) and MCCP (C_{14} – C_{17} with Cl_5 – Cl_{10}) were based on CP carbon

chain length and chlorination degree, as described previously (Reth et al., 2005).

The determination of PCBs was achieved using a GC/MS (Agilent 7890 A/5975C MSD; Agilent Technology, CA) in electron impact (EI) ionization mode. A DB-5 MS column (60 m \times 0.25 mm i.d. \times 0.25 μm film thickness) was used. The oven temperature program details are provided in the SI. PBDEs, PBBs, DBDPE, DP, BTBPE, PBT, HBB and PBEB were analyzed using a GC/MS (Agilent 6890 N/5975B MSD; Agilent Technology, CA) in ENCI mode. Di- to hepta-BDEs, PBB 153, DP, PBT, HBB and PBEB were separated with a DB-XLB (30 m \times 0.25 mm i.d., 0.25 μm film thickness) capillary column. For octa- through deca-BDEs, BTBPE, DBDPE and PBB 209, a DB-5HT (15 m \times 0.25 mm i.d., 0.10 μm film thickness) capillary column was used. The oven temperature program details are provided in the SI.

TBBPA and HBCDs were analyzed using an Agilent 1200 series liquid chromatography (LC) system coupled to an Agilent 6410 electrospray triple quadrupole mass spectrometer. A XDB- C_{18} column (50 mm \times 4.6 mm i.d., 1.8 μm , Agilent, CA) was used to separate the TBBPA and HBCD diastereoisomers. Details of the analytical methodology used for the separation and quantification of TBBPA and HBCDs were published previously (Feng et al., 2012).

2.5. Quality assurance and quality control (QA/QC)

All equipment rinses were conducted with acetone, dichloromethane and hexane to avoid sample contamination. The sample preparation method was validated by analyzing spiked samples. During the sample analysis, method blank samples were measured for each extraction batch to monitor background interferences and contamination. Trace amounts of a few PCBs (PCB4 (10), PCB132(153), and PCB187) and PBDEs (BDE 47, BDE99 and BDE100) were detected in the procedure blanks, and the levels ranged between 12.1 and 33.4 ng/g dry weight (dw) for PCBs and between 2.2 and 2.6 ng/g dw for PBDEs. The average recoveries of the spiked surrogate standards ranged from 63 to 98%, 86–107%, 63–118%, 64–111%, and 67–105% for CPs ($^{13}\text{C}_{10}$ -*trans*-chlordane), PCBs (PCB30, PCB65, PCB204), PBDEs (BDE77, BDE181, BDE205 and $^{13}\text{C}_{12}$ -BDE-209), TBBPA (^{13}C -TBBPA), and HBCDs (^{13}C - α -, β -, γ -HBCD), respectively. Instrumental QC was performed with regular injections of solvent blanks and standard solutions. The method detection limit (MDL) was defined at a signal-to-noise (S/N) ratio of 10 in the solvent blanks. The MDLs were in the range of 0.2–2.4 ng/g dw for CPs,

0.1–1.4 ng/g dw for PCBs, 0.2–0.5 ng/g dw for PBDEs and other halogenated flame retardants, and 0.4–1.2 ng/g dw for HBCDs and TBBPA.

3. Results and discussion

3.1. Levels and sources of OHPs in the particulates

Descriptive statistics for the levels of SCCPs, MCCPs, PCBs, PBDEs, and OHFRs (including DBDPE, DP, BTBPE, TBBPA, HBCDs, PBBs, HBB, PBT, and PBEB) in the particulate samples are summarized in Table 1.

As presented in Table 1, SCCPs (C₁₀–C₁₃) and MCCPs (C₁₄–C₁₇) were analyzed. The SCCP concentrations in 48 samples ranged from 1800 to 240,000 ng/g dry weight (dw), with average values of 30,000 ng/g dw at Qingyuan, 33,000 ng/g dw at Guiyu, 38,000 ng/g dw at Taizhou, and 61,000 ng/g dw at Dali. Generally, the levels of MCCPs levels were much higher than those of SCCPs, and the concentrations of MCCPs exhibited the following order: Dali (mean of 890 µg/g, dw) > Taizhou (mean of 670 µg/g, dw) > Guiyu (mean of 340 µg/g, dw) > Qingyuan (mean of 170 µg/g, dw). The average MCCP/SCCP ratio (6.4 ± 1.8) of Qingyuan was comparable to that in Guiyu (7.0 ± 3.8) and that reported in a recent study (6.7 ± 0.98) conducted in the same region (Chen et al., 2011) but lower than those of the other sampling areas (11.9 ± 5.8 in Dali and 17.4 ± 10.7 in Taizhou) in the present study. This finding indicates that samples from Qingyuan and Guiyu contain fewer MCCPs than those from Dali, and Taizhou. The total CP concentrations (sum of SCCPs and MCCPs) differed significantly among the sampling locations (one-way ANOVA: $p < 0.05$). The CP levels in particulates collected from Dali were significantly higher than those from Guiyu ($p = 0.02$) and Qingyuan ($p < 0.01$) although the more intense e-waste activities conducted in these two area compared to Dali.

The concentrations of PCBs in particulates from the four e-waste sites were much lower than those of CPs and ranged from 300 ng/g dw–180,000 ng/g dw, with average values of 2700 ng/g dw in Guiyu, 6900 ng/g dw in Dali, 24,000 ng/g dw in Taizhou, and 27,000 ng/g dw in Qingyuan (Table 1). Unsurprisingly, lower levels of PCBs than CPs were detected at the e-waste sites because large quantities of CPs continue to be produced and used, whereas PCBs are being phased out globally. A one-way ANOVA revealed no significant differences in the total PCB concentrations between the four regions ($p > 0.05$), thus, there was less discrepancy in the PCB contents among e-waste sites in the sampled locations than expected.

The concentrations of PBDEs in particulates from the four e-waste sites ranged from 130 to 1,100,000 ng/g dw. The average concentrations of PBDEs were 61,000, 240,000, 52,000, and 130,000 ng/g dw in Taizhou, Guiyu, Dali, and Qingyuan, respectively (Table 1). The total PBDE concentrations in particulates from Guiyu were significantly higher than those from Taizhou and Dali (one-way ANOVA: $p = 0.05$), suggesting

heavier PBDE contamination in Guiyu than Taizhou and Dali, despite the greater e-waste-dismantling activities in Taizhou (2 million tons per year) compared to Guiyu (million tons per year).

OHFRs, including DBDPE, DP, BTBPE, TBBPA, HBCDs, PBBs, HBB, PBT, and PBEB, were frequently (>50% detection frequency) detected in the particulates from the four e-waste sites, with mean concentration ranges of 39,000–63,000, 310–2700, 98–16,000, 21,000–56,000, 55–5700, 1700–27,000, 42–1600, 3.2–220, and 5.8–12 ng/g dw, respectively (Table 1). DBDPE was the most dominant compound, accounting for >50% of the investigated OHFRs. TBBPA was the second most dominant pollutant, and the average levels of HBCDs, PBBs, DP, BTBPE, and HBB were much higher than those of PBT and PBEB. These results were expected as DBDPE is a replacement for deca-BDE, and the production and use of DBDPE are increasing at an estimated rate of 80% per year in China (Zhang et al., 2009). Similar to DBDPE, DP has been reported as a possible candidate to replace deca-BDE (Sverko et al., 2010), and BTBPE is used to replace technical octa-BDE mixtures (Hoh et al., 2005). TBBPA and HBCDs are the most widely used brominated flame retardants (HFRs) and accounted for 58.7% and 8.2%, respectively, of the total market demand for brominated flame retardants in 2001 (Morose, 2006). PBBs and HBB are two types of historically used HFRs. Decabromobiphenyl and possibly some other PBB mixtures are still produced commercially (de Boer et al., 2000), and HBB is being reintroduced into the market (Salamova and Hites, 2011). Compared to the other OHPs, the much lower concentrations of PBT and PBEB indicate that the e-wastes contained very small PBT and PBEB when compared other chemicals. Thus, these two chemicals cannot be considered as environmental concern in the e-waste recycling region. Moreover, the total OHFRs concentrations differed significantly among the four e-waste sites (one-way ANOVA: $p < 0.05$). The average ΣOHFR concentrations in particulates from Guiyu (140,000 ng/g, dw) were much higher than those from Taizhou (85,000 ng/g, dw), Dali (42,000 ng/g, dw), and Qingyuan (39,000 ng/g, dw).

As discussed above, the CP, PCB, PBDE, and OHFR concentrations differed among the e-waste sites. The total CP levels were significantly higher in particulate samples from Dali because of the metal product recycling that occurs in this area, whereas the highest PCB concentrations were found in samples collected from Qingyuan, where substantial recycling of capacitors and transformers has developed in the past few years. The highest concentrations of PBDEs and OHFRs were found in particulates sampled from Guiyu, a region known for the dismantling of electronic devices and plastics. These results were expected because CPs were mostly used as extreme pressure additives in metal working fluids and as secondary PVC plasticizers (Bayen et al., 2006); PCBs were used primarily as stable fluid insulators in high-voltage electric transformers, capacitors and hydraulic lubricants (Erickson, 1997); and PBDEs and OHFRs were mainly used in plastic products and as

Table 1
Summary of OHP concentrations in the particulates (ng/g dw) from four e-waste sites in China.

	Taizhou		Guiyu		Dali		Qingyuan	
	AV	Range	AV	Range	AV	Range	AV	Range
SCCPs	38,000	(7800–240,000)	33,000	(4900–110,000)	61,000	(41,000–98,000)	30,000	(1800–75,000)
MCCPs	670,000	(190,000–3,500,000)	340,000	(13,000–1,900,000)	890,000	(420,000–1,700,000)	170,000	(12,000–360,000)
PCBs	24,000	(12,000–47,000)	2700	(300–11,000)	6900	(1500–27,000)	27,000	(660–180,000)
PBDEs	61,000	(25,000–140,000)	240,000	(14,000–810,000)	52,000	(19,000–140,000)	130,000	(130–1,100,000)
ΣOHFRs ^a	85,000	(37,000–180,000)	140,000	(13,000–320,000)	75,000	(19,000–240,000)	62,000	(160–300,000)
DBDPE	48,000	(18,000–140,000)	63,000	(11,000–160,000)	42,000	(18,000–94,000)	39,000	(140–170,000)
DP	1600	(1000–3000)	2700	(210–16,000)	310	(190–420)	1300	(15–4500)
BTBPE	540	(220–1100)	16,000	(180–140,000)	98	(12–330)	700	(nd–6100)
TBBPA	33,000	(8100–87,000)	56,000	(nd–200,000)	33,000	(nd–2,100,000)	21,000	(nd–200,000)
HBCDs	1200	(200–3100)	5700	(210–57,000)	55	(nd–440)	460	(ng–2400)
PBBs	7400	(820–29,000)	27,000	(nd–170,000)	1700	(59–8700)	2800	(nd–12,000)
HBB	1100	(180–5700)	1600	(26–13,000)	42	(10–160)	390	(3–1600)
PBT	220	(26–590)	62	(3–510)	3.2	(0.8–13.5)	18	(0.1–160)
PBEB	8.4	(4–19)	5.8	(1–25)	10	(1.3–28)	12	(1–92)

ΣOHFRs^a: sum of DBDPE, DP, BTBPE, TBBPA, HBCDs, PBBs, HBB, PBT, and PBEB.

additives in various polymeric materials (Covaci et al., 2011). Therefore, the differing applications of these OHPs may account for the observed discrepancies in OHP occurrence among the four e-waste sites. However, detailed analyses to determine possible relationships between the type of e-waste recycled and the level and pattern of OHP contamination revealed no discernible trends (Fig. S1), likely because of the complex nature of the types of e-wastes dismantled in these recycling sites and to the fact that a specific e-waste type (e.g., electric wire) is not limited to one particular OHP formulation. In addition, correlation analysis was conducted among the different contaminants (SCCPs, MCCPs, PCBs, PBDEs, and OHFRs). Significant and positive correlations were only found between the total concentrations of OHFRs and PBDEs (Pearson correlation: $n = 48$, $r = 0.43$, $p = 0.002$). This suggests that PBDEs and OHFRs have similar emission sources and that the sources of SCCPs, MCCPs and PCBs are different.

3.2. Profiles of SCCPs, MCCPs, PCBs, PBDEs, DP, and HBCDs

The profiles of SCCPs and MCCPs from all the investigated sites appear similar, irrespective of the CP levels, except for the smaller contribution (38.2%) of C₁₃ homologues in particulates from Dali (Fig. 2). The most abundant SCCP in the particulate samples was the C₁₃ homologue (average contribution up to 45.4%), followed by the C₁₂ homologue (average contribution up to 33.6%) and C₁₁ homologue (average contribution up to 22.3%) (Fig. 2), unlike the commercial SCCP mixtures used in developed countries (dominant by C₁₁ homologues, 38–45%) (Reth et al., 2006) and China (dominant by C₁₀ homologues, 59–72%) (Gao

et al., 2012). The vapor pressure and subcooled-liquid water solubility tend to decrease with increasing carbon chain length (Glüge et al., 2013). Thus, shorter carbon chain groups are more prone to migrate away from the emission sources than longer carbon chain homologue groups. Additionally, these e-waste recycling areas not only dismantle domestic e-waste but also handle the e-waste imported from overseas (Zhang et al., 2012). Therefore, the different SCCP homologue group profiles between the particulate samples and commercial mixtures likely result from the various e-waste sources and complex environmental processes, such as volatilization and photochemical degradation. Regarding MCCPs, C₁₄ homologues predominated, with average proportions of 54%, 58%, 61%, and 57% in Taizhou, Guiyu, Qingyuan, and Dali, respectively (Fig. 2). The MCCP congener profile in the four e-waste areas was generally similar to those of the commercial MCCP mixtures used in both developed countries (Tomy and Stern, 1999) and China (Chen et al., 2011). However, the relative contents of C₉-MCCPs and C₁₀-MCCPs in the particulate samples were lower than those in commercial products, possibly because of the presence of high-chlorinated homologues (C₉-C₁₀), which could dechlorinate to produce low-chlorinated homologues (C₅-C₈) after production (Chen et al., 2011). CB 28(31), CB 110, CB 118, CB 132(153), and CB 138 were dominant PCB congeners (Fig. S2). No significant differences in PCB congener profiles were found among the four sampling areas.

The main congeners of PBDEs in samples from the four e-waste sites were nona-BDEs (BDE206, 207, and 208) and BDE209, with average fractions of 7.2–13.1% and 81.4–90.7%, respectively (Fig. S3). The high

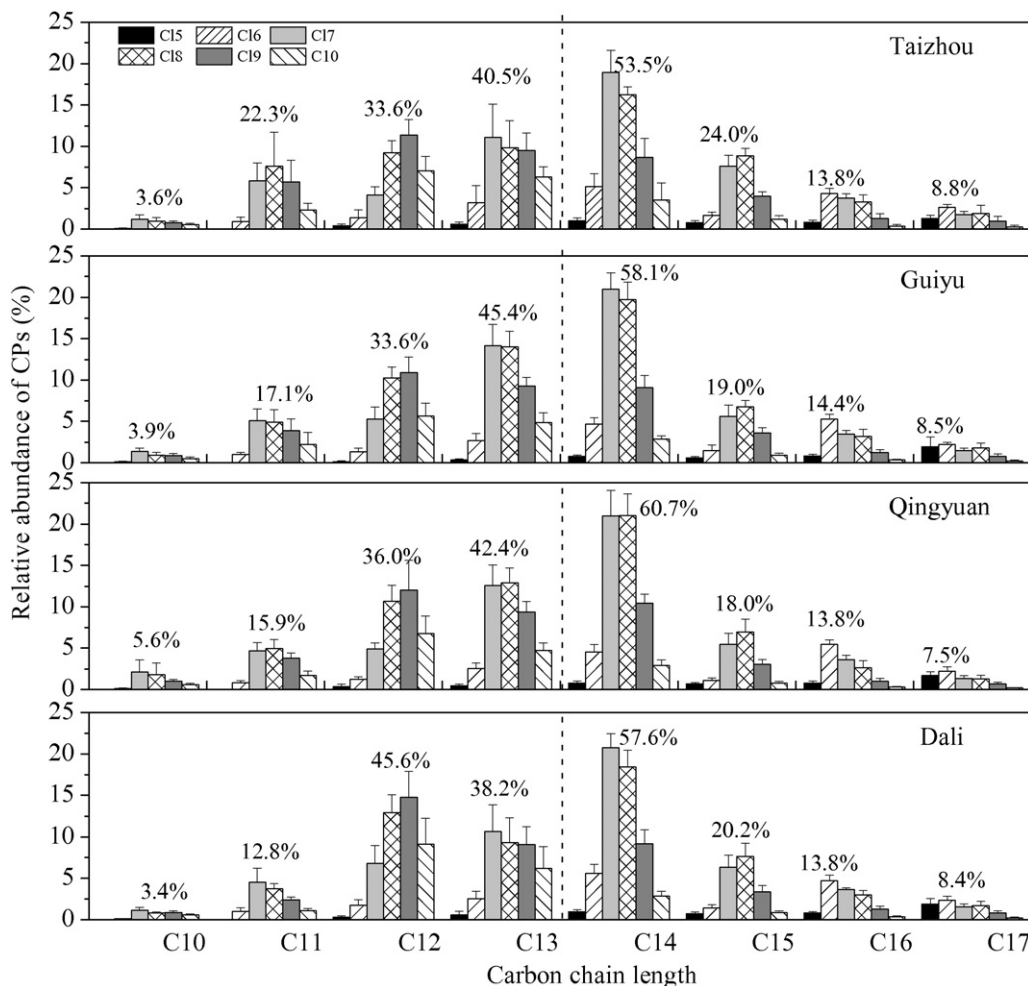


Fig. 2. Average individual SCCP (C₁₀–C₁₃) and MCCP (C₁₄–C₁₇) congener group profiles in different sampling areas: Taizhou, Guiyu, Qingyuan, and Dali. The values above the bar represent the contributions of each homologue group to the total SCCP or MCCP concentration.

contribution of BDE209 is consistent with that found in dust samples (BDE209 accounted for 76% of the Σ PBDEs) from another e-waste-dismantling workshop (Li et al., 2014). In fact, it was unsurprising to detect a high percentage of BDE209 in the workshop floor particulates because the commercial product deca-BDE remains commonly used, whereas penta-BDE and octa-BDE are being phased out globally. Examinations of differences in the fractions of BDE209 in the four e-waste sites indicate significant differences between the different e-waste sites (one-way ANOVA: $p = 0.003$). Specifically, the concentration of BDE209 in Dali was significantly higher than those in Taizhou (one-way ANOVA: $p = 0.002$), Guiyu (one-way ANOVA: $p < 0.001$), and Qingyuan (one-way ANOVA: $p = 0.009$). Dali's different PBDE profile compared to the other three e-waste sites was expected because of the different types of e-waste recycled at these sites. Moreover, the average concentration ratio of BDE183:BDE99 in samples from Dali (0.6) was much lower than those observed in samples from Taizhou (1.5), Guiyu (2.8), and Qingyuan (3.5) in the present study but was comparable to those observed in dust from previous studies (all < 1). This suggests that the octa-PBDE formulation in Taizhou, Guiyu, and Qingyuan contributes high quantities of pollution.

Few studies have monitored the value of f_{anti} (the ratio of the *anti*-DP concentration to the total concentration of *anti*-DP and *syn*-DP) in particulates from e-waste sites. The calculated f_{anti} values were 0.70 ± 0.06 , 0.72 ± 0.07 , 0.75 ± 0.06 , and 0.83 ± 0.03 in particulates from Taizhou, Guiyu, Dali, and Qingyuan, respectively (Fig. 3a). The f_{anti} in samples from Qingyuan was significantly higher than those from Taizhou ($p < 0.001$), Guiyu ($p < 0.001$), and Dali ($p = 0.001$), which indicated different DP contamination sources between Qingyuan and the other sites.

The HBCD diastereoisomer profiles in surface particulate samples in Taizhou, Guiyu, and Qingyuan are shown in Fig. 3b. The HBCD diastereoisomer profile in Dali was not available because of its low detection frequency ($< 50\%$) and concentration. As shown in Fig. 3b, the HBCD diastereoisomer profiles differed among the particulate samples studied here. α -HBCD was quite abundant in samples from Taizhou ($50 \pm 7\%$) and Qingyuan ($59 \pm 18\%$), whereas the mean proportion of α -HBCD ($41 \pm 21\%$) was comparable to that of γ -HBCD ($42 \pm 20\%$) in particulates from Guiyu but different from that of Chinese technical products (γ -HBCD: 81.6%). Variations in isomer profiles have also been reported in soil samples collected from the same e-waste recycling areas previously (Gao et al., 2011), and the variability in the diastereoisomer profiles of HBCDs in particulates may be attributable to a rapid photolytically mediated transformation of γ -HBCD into α -HBCD (Harrad et al., 2009) and likely a preferential degradation of γ -HBCD in dust (Abdallah et al., 2008).

3.3. Principal component analysis (PCA) of OHP levels

To further explore the pollution pattern and potential lists of OHPs associated with e-waste at the four e-waste sites, a PCA based on log₁₀-transformed data was conducted, and the result is shown in Fig. 4. The two dimensions explained most of the original variance with an accumulative contribution of 69%. As shown in Fig. 4a, PC1 explained 50% of the total variance and was characterized by a high loading of PCB congeners, indicating a PCB source in the e-waste, such as transformers and capacitors. PC2 accounted for 19% of the total variance and was highly associated with PBDEs and OHFRs, suggesting similar sources for these HFRs. SCCPs and MCCPs had low loadings in both factors, implying that CPs may arise from different sources than PCBs and HFRs.

Factor loadings revealed that particulate samples from Guiyu and Dali could be discriminated by factor 2 (Fig. 4b). Guiyu's factor scores were clustered at the top left of the plot and had a high score in factor 2 (the 1st group of Fig. 4b), corresponding to a high proportion of HFRs. In contrast, all samples from Dali had negative scores on factor 2, suggesting that particulate samples from Dali have relatively high CP contents. This clear partition in OHP occurrence between Guiyu and Dali is consistent with the fact that different types of e-waste are recycled in these areas; the major recycled e-waste items in Guiyu are electronic devices and plastics, whereas the e-waste dismantled in Dali primarily consists of metal devices (Table S1). Therefore, the results of the present study indicate that metal devices are the major source of CPs and that electronic devices and plastics may account for the high levels of HFRs, especially PBDEs.

Qingyuan's factor scores scattered over a wide range, reflecting the complex pollution status in this area. Generally, samples from Qingyuan were divided into two groups by factor 1. One group had negative scores on both factors (the 2nd group of Fig. 4b), probably resulting from the relatively high contents of SCCPs. The other group, similar to samples from Taizhou, had positive scores on factor 1 and were clustered into one group (the 3rd group of Fig. 4b) with high proportions of MCCPs and PCBs. Based on our field observations, the samples included in the 2nd group were collected from the residential stacking areas, where the major recycling e-waste items were heavy e-waste items, such as electrical machines and transformers (Table S1). In contrast, the samples included in the 3rd group were typically from e-waste workshop floors, where light e-waste items, including circuit boards, cellphones, and video recorders, were handled (Table S1). Clearly, the underlying reasons for the discrepancy in OHP occurrence between the two groups could be attributable to the different types of e-waste items recycled in these areas because the applications of OHPs differed. For example,

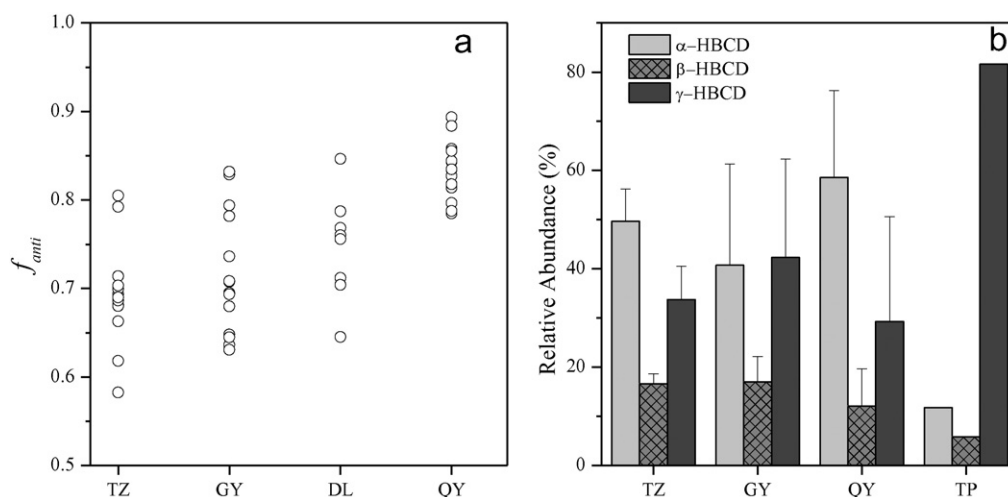


Fig. 3. a f_{anti} values of DP in particulate samples from e-waste recycling areas (TZ: Taizhou, GY: Guiyu, DL: Dali, and QY: Qingyuan). b HBCD diastereoisomer profiles in particulate samples from e-waste recycling areas and technical products (TP).

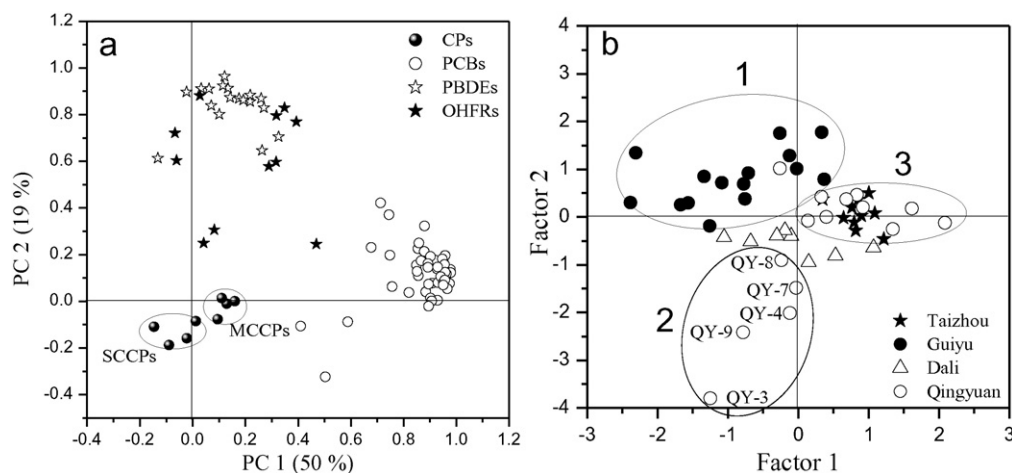


Fig. 4. PCA results based on the log₁₀-transformed concentrations of CP (including SCCPs and MCCPs), PBDE, PCB, and OHFR (including DBDPE, *syn*-DP, *anti*-DP, BTBPE, TBBPA, HBCDs, PBBs, HBB, PBT, PBEB) congeners (PC1, 50% variance; PC2, 19% variance). The figure legends present the factor loadings (a) and factor scores (b). QY: Qingyuan.

SCCPs are mainly used as extreme pressure additives in metal working fluids (Bayen et al., 2006), and PCBs are used as stable fluid insulators in high-voltage electric transformers, capacitors, and hydraulic lubricants and as plasticizer components (Erickson, 1997). However, in the present study, no conclusive evidence to support this conclusion was found. More studies are needed to identify the potential environmental contaminants arising from e-waste disposal.

4. Conclusions

This work provides an overview of the occurrence and potential emission lists of OHPs in surface particulates from areas that handle different types of e-waste. CPs were the predominant OHPs in all the particulate samples, followed by PBDEs, OHFRs, and PCBs. The total CP levels were significantly higher in particulate samples from Dali, whereas the highest PCB concentrations were found in samples collected from Qingyuan. The highest concentrations of PBDEs and OHFRs were found in particulates sampled from Guiyu. C₁₄ homologues and BDE209 were the most prevalent species of CPs and PBDEs, respectively. Higher f_{anti} values in samples from Qingyuan than from the other three e-waste sites suggested that the e-waste processed in Qingyuan was from a different source than that dismantled at the other sites. The variability in the diastereoisomer profiles of HBCDs in particulates may be attributable to a rapid photolytically mediated transformation of γ -HBCD into α -HBCD and likely a preferential degradation of γ -HBCD in dust. The evidence provided by this preliminary study indicates that electronic devices and plastics may account for the high levels of HFRs and that metal products are likely the major source of CPs in these e-waste sites.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <http://dx.doi.org/10.1016/j.scitotenv.2016.06.053>.

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