Characterization of brominated flame retardants from e-waste components in China

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ABSTRACT

Many studies show that high levels of many toxic metals and persistent and bio-accumulative chemicals have been found in electronic waste (e-waste) dismantling sites and their surrounding environmental media. Both flame-retardant plastic housing materials and printed circuit boards (PCBs) could be the major contributors. However, relatively little work has focused on the use or content of toxic substances and their changing in scrap housing materials and PCBs from home appliances. This study evaluated the existence of brominated flame retardants (BFRs, including polybrominated diphenyl ethers (PBDEs) and Tetrabromobisphenol-A (TBBPA)) in housing plastics and PCBs from home appliances collected from various e-waste recyclers in China. These were then analyzed for the potential migration of BFRs from the e-waste components into their recycled products. The results show that both PBDEs and TBBPA were found with high level in most of e-waste samples, indicating that the widespread use of BFRs in home appliances are entering into the end-of-life stage. For the plastics samples, CRT TVs and LCD monitors should be given priority for the control of BFRs. Regarding PBDEs, the dominant congeners of BDE-209 in the plastics samples contributed 90.72–93.54% to the total concentrations of PBDEs, yet there are large variations for PCBs samples: BDE-28, -47, -99, and -153 were also important congeners compositions, except for BDE-209. Compared with previous studies, the BFRs concentrations in current Chinese e-waste are trending to decline. This study also found that BFRs in housing plastics and PCBs will be transferred into the recycled products with other purpose use, and the new products could have highly enriched capacities for BFRs. The obtained results could be helpful to manage e-waste and their components properly in order to minimize associated environmental and health risks of BFRs, particularly for their further reuse.

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1. Introduction

Due to the rapid expansion of electronic inventions, manufacturing innovations, and ever-shortening product lifespans, large amounts of electronic waste (e-waste) are generated, posing a serious challenge to waste management in developed and developing countries (Li et al., 2013; Song et al., 2016). China, as one of the largest electronics manufacturing countries and one of the emerging economies in the world, has risen to become the second largest e-waste generator, next to USA (Duan et al., 2014; Li and Song, 2016).

E-waste is not only a crisis of quantity but also a crisis of toxic parts, such as heavy metals and brominated flame retardants (BFRs) (Song and Li, 2014a,b, 2015; Zeng et al., 2016). BFRs, as the most effective flame-retarding agents, have been extensively used to increase the fire resistance (Chen et al., 2012). Manufacturers of e-products consume a major portion of the global BFRs market, accounting for 56% of the total BFR products. Most of them are used for equipment housings and printed circuit boards (PCBs) (Herat, 2008; Ma et al., 2016). China has become one of the largest consumers of flame retardants with an expected annual growth rate of 7%, of which BFRs accounted for the majority of consumption (Ma et al., 2016; Zhu et al., 2013).
TBBPA and PBDEs, which historically were added to a plethora of e-products to impart flame retardancy, are two high-production-volume and current-use BFRs (Li et al., 2014b; Ren et al., 2013). As the additive BFR, PBDEs do not react chemically with the components of the polymer and, therefore, may easily leach out of the polymer matrix after incorporation, with important implications for human exposure (Li et al., 2016). TBBPA is the most widely used BFR worldwide, accounting for around 60% of the total BFRs market (Law et al., 2006; Liu et al., 2016). Total production of PBDEs has been estimated to have been between 1.3 million to 1.5 million tons from 1970 and 2005 (UNEP, 2010). Changes in the global demand for TBBPA and PBDEs will depend on the demand of Asian countries, especially China, due to the high volume of printed wiring boards (PCBs) and electronic components manufactured in this region (Song et al., 2012; Tan et al., 2017). At the global level, the Parties of the Stockholm Convention for Persistent Organic Pollutants (POPs) decided to list commercial penta-BDE and commercial octa-BDE as POP substances in 2009, and many manufacturers have already substituted for them, or will soon phase these out (Danon-Schaffer et al., 2013). While these toxic BFRs were gradually or planned to be phased out in new products worldwide in recent years, toxic BFRs that are already in service will continue to threaten our environment and health if they are not properly managed at end of life. Addressing such impacts of toxic BFRs requires an understanding of the containment of BFRs in e-waste.

Due to the wide application of PBDEs and TBBPA in e-products, uncontrolled dismantling, acid treatment, and open burning of e-waste resulted in their being emitted into the ambient environment (Wang et al., 2015a; Wang et al., 2014; Zhu et al., 2013). TBBPA and PBDEs have been found in vegetables and in wetland plants (paddy rice plants and common reed plants) (Huang et al., 2011; Wang et al., 2016; Wang et al., 2011). This suggests that TBBPA and PBDEs may enter food networks by accumulating in plants and soil animals (e.g., earthworms) through the land application of TBBPA and PBDEs-containing biosolids and wastewater. TBBPA and PBDEs have been detected in the wildlife such as mussels and birds, and have also been detected in human adipose tissue, breast milk, and blood (Li et al., 2016; Wang et al., 2015b; Xu et al., 2014; Zhao et al., 2009). Therefore, the growth of the e-waste recycling industry, particularly in the developing countries, has drawn much attention to the sources of environmental contamination from PBDEs and TBBPA (Ma et al., 2016; Ni et al., 2013).

However, with regard to TBBPA and PBDEs, the origin of their potential environmental and health risks is far from clear. Only limited and rather uncertain data are available regarding the occurrence of PBDEs and TBBPA in e-waste (the emission source), and most relevant data were obtained prior to 2005 (Aldrian et al., 2015; Salhofer and Tesar, 2011; Schlummer et al., 2007). It is important to know how such chemicals in used e-products such as TVs and computer monitors are applied in the future because of their toxicity and persistence. In the e-products, the majority of PBDEs and TBBPA are used in equipment housings and PCBs, which are also the primary e-waste components. Thus, an investigation into the flows and stocks of PBDEs and TBBPA in plastics and PCB will assist in identifying the amounts of such chemicals in the devices and recycled products.

Therefore, this study aims to (i) quantify the contents of PBDEs and TBBPA from typical e-waste, like home appliances; (ii) compare the PBDEs and TBBPA concentrations between housing plastics and PCBs; (iii) reveal the source appointment and trends of these toxic substances; and (iv) understand the potential migration of PBDEs and TBBPA into new products. This study is intended to help manage e-waste and their components properly in order to minimize the associated environmental and health risks of PBDEs and TBBPA.

2. Materials and method

2.1. Sampling collection

Manufacturers of e-products consume a major portion of the global BFRs market by accounting for 56% of the product with most destined for equipment housings and PCBs (Ma et al., 2016). Therefore, housing plastics and PCBs were selected as the primary research objects for this study. The samples of housing plastics and PCBs from e-waste were collected in 2016 from two e-waste recycling enterprises in China. Table 1 presents the sample information of housing plastics and PCBs. For housing plastics, the CRT TV sets, washing machines, personal computers (PCs) (including LCD monitors and mainframes), and refrigerators were selected as the typical e-waste types; while the PCBs from the CRT TV sets and printers/copiers were considered in this study.

Most of the housing plastics and part of non-metallic fractions (NMFs) in PCBs will be reused in new products. Thus, it will be essential to know the potential level of BFRs in the new products for the development of effective e-waste management policies. To assess this, the obtained samples of new products from the e-waste recycling enterprises have been considered: plastic granulation from CRT TV housing plastics (NPI), and new products with NMFs as additional agents (RM1-3). Here, plastics types (such as PP, ABS, PS, and HIP), and plastics colors were also considered as influential factors as we sought to understand the differences between the different samples. Two potential BFRs (i.e. PBDEs and TBBPA) presented in the plastics and PCBs from e-waste were examined.

The sampling process followed procedures specified in the Technical Specifications on Sampling and Sample Preparation from Industry Solid Waste (HJ/T20-1998, In Chinese). Samples were collected manually from two e-waste recycling enterprises and then placed into the sampling bags. All samples were sent to the laboratory for further processing. For each sample, plastics and PCBs were collected from three sampling points in the sampling sites, and were consequently well mixed up to accomplish one sample preparation. All samples were air-dried at the room temperature and then cut into pieces in the laboratory. Consequently, the sample pieces were attired into particles of 100 meshes. To ensure the accuracy of testing results, every sample was analyzed twice where the mean value was adopted as the final result.

2.2. Analytical methods and data quality for PBDEs

2.2.1. Preparation and analysis of samples

Plastics and PCBs samples (around 2–5 g) were first spiked with 200 ng $^{13}$C$_{12}$-BDE-209 and 20 ng $^{13}$C$_{12}$-BDE-28, -47, -99, -100, -153, -154, -183) subjected to surrogate standards in order to analyze the recoveries. The samples preparation method has been well recognized in previous studies (Duan et al., 2016; Li et al., 2014a).

This study used a gas chromatography equipped with mass spectrometer (GC–MS, Agilent 7890B/5977) with Electron Ionization (EI) in selected ion monitoring (SIM) mode to determine the concentrations of BDE congeners (BDE-28, -47, -99, -100, -153, -154, -183). BDE-209 was monitored by negative chemical ionization (NCI) in selected ion monitoring (SIM) mode. In summary, all compounds were quantified according to the international standard (Duan et al., 2016).

2.2.2. QA/QC

In our study, proper handling was employed from sample collection to chemical analysis to ensure the good identification and quantification of targeted compounds. Specifically, all equipments were rinsed with acetone and hexane to avoid contamination. The
retention time of GC matched with those of the standard compounds very well, within ±0.1 min. Peaks were not integrated unless the signal-to-noise ratio was over 3. Otherwise, they were deemed as non-detected samples and a value of 0 was assigned. All samples were spiked with a surrogate recovery standard prior to the extraction, and recovery was set to fall in the range of 70–130%. The recovery of BDE-209 was set to fall in the range of 50–150%. The recoveries of the target compounds after flowing through the multi-layer silica gel column were 92–107% (standard deviations are below 16.4%). In addition, congeners in the procedural blank samples were undetectable or lower than the detection limits.

2.3. Analytical methods and data quality for TBBPA

2.3.1. Preparation and analysis of samples

Plastics and PCBs samples were extracted and analyzed by following the method described by Song et al., 2014. Briefly, 0.1 g of each sample was weighed and transferred into a 15 mL polypropylene (PP) conical tube. After spiking with 20 ng 13C12-TBBPA (internal standards, IS), the sample was extracted with a 5 mL solvent mixture of methanol and water (5:3, v/v) by shaking for 60 min. The mixture was centrifuged at 4500 g for 5 min, and the supernatant was transferred into a glass tube. The extraction step was repeated three times with same amount of solvent, and the extracts were combined and concentrated to ~4 mL under a gentle nitrogen stream. The solution was diluted to 10 mL with 0.2% formic acid (pH 2.5), and the extracts were loaded onto a Sep-Pak C18 cartridge preconditioned with 5 mL of methanol and 5 mL of water. After loading, the cartridge was washed with 5 mL of water and the analytes were diluted with 4 mL of methanol, 3 mL of tetrahydrofuran/methanol (4:6) and 3 mL of tetrahydrofuran, and finally concentrated to 1 mL.

The concentrations of TBBPA was determined with an Agilent 1260 HPLC (Agilent Technologies Inc., Santa Clara, CA) interfaced with an Applied Biosystems QTRAP 4500 mass spectrometer (ESI-MS/MS; Applied Biosystems, Foster City, CA).

2.3.2. QA/QC

The surrogate recoveries obtained from all samples were 103.8 ± 13.5% for TBBPA. Duplicate analysis of randomly selected samples showed a coefficient variation of <20% for TBBPA. The detection limits were 2 ng/g for TBBPA. A midpoint calibration standard (in methanol) was injected as a check for instrumental drift in sensitivity after every 10 samples, and a pure solvent (methanol) was injected as a check for carry-over from sample to sample.

3. Results and discussion

3.1. PBDEs in e-waste

3.1.1. PBDEs in housing plastics

The housing plastics samples were categorized into five types of e-waste, including CRT TVs (n = 3), washing machines (n = 6), LCD monitors (n = 6), PCs mainframes (n = 3), and refrigerators (Rf) (n = 1). All 19 samples were found to contain the PBDEs in these plastics. Previous studies also reported PBDEs were detected in 40% and
51% of all BFRs containing housing samples (Schlummer et al., 2007; Li et al., 2014a). The 100% detection rate in this study could be due to the relatively fewer samples.

Fig. 1(A) presents the mean concentrations of $\sum$PBDEs in five types of e-waste in China. Among all the plastic samples in this study, the concentrations of $\sum$PBDEs in CRT TV plastics were higher than others, up to 11.31 mg/kg, followed by refrigerators (6.63 mg/kg) and desktop mainframes (2.81 mg/kg). The housing plastics of LCD monitors were found to have the lowest concentrations of $\sum$PBDEs in this study.

As shown in Fig. 1(B), the detailed $\sum$PBDEs concentrations of all the samples are given. Regarding the CRT TV, the PS plastics had higher $\sum$PBDEs levels (15.20 mg/kg), followed by ABS plastics (9.63 mg/kg) and PP plastics (9.10 mg/kg). In the six samples of washing machines, the largest $\sum$PBDEs levels (5.54 mg/kg) were found in the MW2 (PP plastics, grayish white). On the whole, the average $\sum$PBDEs concentrations of PP plastics (WM2-6, 2.54 mg/kg) are a little higher than the ABS plastics (WM1). For the LCD monitors of PCs, the $\sum$PBDEs concentrations varied from 0.63 to 3.94 mg/kg. LM3 (HIDS plastics) were identified as having the highest $\sum$PBDEs concentrations. With respect to the desktop mainframe plastics, it can be found that the MF3 (unknown type of plastics) have higher $\sum$PBDEs concentrations than MF1 (HIDS plastics, 2.63 mg/kg) and MF2 (ABS plastics, 0.60 mg/kg). Overall, based on these research results, we know that the $\sum$PBDEs concentrations largely vary with the plastic types and e-waste categories.

According to “Restriction of the Use of Certain Hazardous Substances in Electrical and Electronic Equipment (RoHS)” directive by EU, there is an upper threshold limit (1000 mg/kg) for the concentration of $\sum$PBDEs. The $\sum$PBDEs concentrations of all plastics samples (LM1, LM2, and MF2) did not exceed the RoHS threshold limit in this study. Previous studies in China (Li et al., 2014a) reported that the $\sum$PBDEs concentrations in one-third of the

Fig. 1. PBDEs concentrations in five types of e-waste housing plastics in China (mg/kg): (A) Mean concentrations (including the maximum and minimum values); (B) Detailed concentrations for each sample.
samples exceeded the RoHS threshold limit, and the percentages exceeding the RoHS threshold limit were 28%, 54% and 9.1% for TVs, computer monitors, and printers, respectively. This indicates that as China’s policy for controlling PBDEs was implemented, the PBDEs levels in the current e-waste housing plastics continued to decrease. It also means that the potential PBDE risks were decreasing. It is worth noting that lower total amounts of PBDEs do not necessarily mean lower releases, and if these e-wastes are not treated properly, they will still cause serious environmental impacts.

Comparing with other studies: As summarized in Table 2, the concentration levels of total PBDEs in e-waste in ten countries (18 studies) varied from 0 to 172,000 mg/kg. More research focused on the PBDEs in TV plastics. Some studies investigated the trends of total PBDEs concentrations of TV housing plastics in different years. Li et al., 2014a found that the total PBDEs concentrations in China continued to increase from 1987 to 1998 by testing 102 TV samples, which were relatively lower than other research results (Tasaki et al., 2004; Danon-Schaffer et al., 2013; Korea NIER, 2011). In Li’s study (Li et al., 2014a), total PBDEs were not detected in the samples made in late 1980s (1985–1990), yet they were detected in the samples made after 1990. However, there were different trends in studies done in Japan and Korea.

In Japan, Tasaki et al., 2004 found that total PBDEs (90,883 mg/kg) in rear plastic covers of TVs made in 1990–1993 were the highest, followed by the results in the years 1987–1989 and 1994–1998. Sakai et al., 2001, Korea NIER, 2011, and Park et al., 2014 detected total PBDEs levels in all TV rear covers in Korea, and showed the similar trends with Japan. All research from Japan (Tasaki et al., 2004; Takigami et al., 2008), Korea (Sakai et al., 2001; Korea NIER, 2011; Park et al., 2014), and UK (Rauert and Harrad, 2015) suggest that the rear covers contained higher total PBDEs concentrations than the front covers in TV sets. For all kinds of e-waste plastics, the highest total PBDEs levels (172,000 mg/kg) were identified in the rear covers of TV sets in Korea in 1988 (Korea NIER, 2011).

Chen et al. (2012) and EMPA, 2010 found that total PBDEs levels of PCs’ plastics were higher than that of TV sets; however, Aldrian

### Table 2

PBDEs levels in e-waste plastics.

<table>
<thead>
<tr>
<th>Location</th>
<th>Type</th>
<th>Year</th>
<th>Samples no.</th>
<th>(\sum)PBDEs (mg/kg)</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>China</td>
<td>PCs; TV; Mobile phone</td>
<td>–</td>
<td>4</td>
<td>3060; 1943; 0</td>
<td>Chen et al. (2012)</td>
</tr>
<tr>
<td>Austria</td>
<td>TV; PCs monitors</td>
<td>–</td>
<td>3000; 1600</td>
<td>TV: 85% &lt; 1000; 7% &gt; 50,000; PCs monitor: 53% &lt; 1000; 39% &gt; 50,000</td>
<td>Aldrian et al. (2015)</td>
</tr>
<tr>
<td></td>
<td>Small e-waste*</td>
<td>–</td>
<td>–</td>
<td>11.9; 12,400; 0.35; 0.10; 0.01</td>
<td>Salhofer and Tesar (2011)</td>
</tr>
<tr>
<td>Turkey</td>
<td>PCs; hair dryer; Toaster; Microwave oven; Carpet; Cable</td>
<td>–</td>
<td>–</td>
<td>317; 300; 308; 328.33; 323; 293</td>
<td>Bini et al. (2013)</td>
</tr>
<tr>
<td>Canada</td>
<td>60% PCs, 30% printers, 10% keyboards/mice</td>
<td>1980–1984; 1985–1989; 1990–1994; 1995–1999; 2000–2005</td>
<td>–</td>
<td>122,900; 172,000; 120,000; 118,000; 143,000; 144,000; 125,000; 400; 5700</td>
<td>Danon-Schaffer et al. (2013)</td>
</tr>
<tr>
<td></td>
<td>Front cabinet; Rear cabinet (CRT TV)</td>
<td>1989–1998</td>
<td>15</td>
<td>30,000; 48,000</td>
<td>Takigami et al. (2008)</td>
</tr>
<tr>
<td>Korea</td>
<td>TV rear cover</td>
<td>1990; 1991; 1992; 1994; 1996; 1997; 1998</td>
<td>–</td>
<td>89,000; 90,800; 100,000; 88,000; 91,000; 96,900; 979,000</td>
<td>Sakai et al. (2001)</td>
</tr>
<tr>
<td></td>
<td>Non-decaBromo flame retardant; Flame-retardant; Roughly-cut; Well-crushed TV housings</td>
<td>–</td>
<td>–</td>
<td>1; 25,000; 24,000; 25,000</td>
<td>Kim et al. (2006)</td>
</tr>
<tr>
<td></td>
<td>TV rear cover</td>
<td>1983; 1988; 1989; 1990; 1991; 1995; 1997; 1998; 2000; 2001</td>
<td>–</td>
<td>122,900; 172,000; 120,000; 118,000; 143,000; 144,000; 125,000; 400; 5700</td>
<td>Korea NIER (2011)</td>
</tr>
<tr>
<td></td>
<td>Front TV cover</td>
<td>1988; 1989; 1991; 1997; 2001</td>
<td>–</td>
<td>530; 2296; 243; 265; 70; 88</td>
<td>EMPA (2010)</td>
</tr>
<tr>
<td>Switzerland</td>
<td>Small e-waste*; TV housing rear covers; TV/PC housings (plastic)</td>
<td>2003</td>
<td>–</td>
<td>1074; 20,750; 12,350</td>
<td>Morf et al. (2005)</td>
</tr>
<tr>
<td></td>
<td>CRT TV plastics</td>
<td>–</td>
<td>5</td>
<td>2835</td>
<td>Stubbings and Harrad (2016)</td>
</tr>
<tr>
<td>Germany</td>
<td>Mixed shredder residues (9 TVs and 36 monitors)</td>
<td>–</td>
<td>7</td>
<td>800–7500</td>
<td>Schlummer et al. (2007)</td>
</tr>
<tr>
<td></td>
<td>Housing shredder residues (9 TVs and 36 monitors)</td>
<td>–</td>
<td>8</td>
<td>4,500–28,000</td>
<td></td>
</tr>
<tr>
<td>USA</td>
<td>VCRs; Telephone; Radio; PCs; Micro-wave; Printer; Mobile phone</td>
<td>–</td>
<td>7</td>
<td>10,200; 3050; 1300; 1100; 480; 440; 15</td>
<td>Petreas and Oros (2009)</td>
</tr>
</tbody>
</table>

* Refers to the small e-waste, e.g. vacuum cleaner, toaster, iron, kettle, electric fan, electric toothbrush, etc.
et al., 2015 showed opposite conclusions. In Turkey, Binici et al., 2013 indicated that there are similar total PBDEs levels for five kinds of e-waste plastics (PCs; hair dryers; toasters; microwave ovens; carpet; and cable) ranging from 293 to 328 mg/kg. In the USA, Petreas and Oros, 2009 found that mobile phone plastics and VCR plastics have the least and highest total PBDEs levels for the 7 types of e-waste, respectively. In Canada, Danon-Schaffer et al., 2013 studied mixed plastics (60% PCs, 30% printers, 10% keyboards/mice) from 1980 to 2005, and showed large variations: the total PBDEs level in 1985–1989 was 12,400 mg/kg, however, the highest total PBDEs level in other years was only 11.9 mg/kg. As shown in Table 2, the small size e-waste owned the relatively lower total PBDEs levels.

In comparison with other studies (Table 2), the total PBDEs concentrations of 5 types of e-waste in this study were at lower levels. On the whole, the total PBDEs concentrations in TV sets and PCs mainframes obtained in this study fell in the low-range of levels reported worldwide. No PBDEs levels in washing machines and LCD monitors were found in our reviews. The total PBDEs levels of the refrigerators in our study were much lower than that found in LCD monitors and mainframes have similar PBDEs dominant congener compositions, and the dominant congeners of BDE-209 contributed 90.72–93.54% to the total concentrations of PBDEs. Though BDE-209 was also an important congener (contributing to 35.58% of the total concentrations of PBDEs), BDE-183 and BDE-153 levels in refrigerator plastics were much higher than those of other four kinds of e-waste housing plastics, accounting for 39.35% and 18.09% of the total concentrations, respectively. Most studies showed that BDE-209 was the dominant congener (Takigami et al., 2008; Li et al., 2014; Park et al., 2014; Aldrian et al., 2015). However, Binici et al., 2013 indicated that other congeners (such as BDE-47, -183, and -206) for PCs, hair dryers, toasters, microwave ovens, carpet, and cable were also important compositions, and Danon-Schaffer et al., 2013 obtained the same results. Possible reasons are due to the different types of e-waste or different production dates.

### 3.1.2. PBDE in PCBs

The compositional patterns of PBDEs in different e-waste housing plastics samples are illustrated in Fig. 2. It indicates that the housing plastics of CRT TVs, washing machines, LCD monitors and mainframes have similar PBDEs dominant congener compositions, and the dominant congeners of BDE-209 contributed 90.72–93.54% to the total concentrations of PBDEs. Though BDE-209 was also an important congener (contributing to 35.58% of the total concentrations of PBDEs), BDE-183 and BDE-153 levels in refrigerator plastics were much higher than those of other four kinds of e-waste housing plastics, accounting for 39.35% and 18.09% of the total concentrations, respectively. Most studies showed that BDE-209 was the dominant congener (Takigami et al., 2008; Li et al., 2014; Park et al., 2014; Aldrian et al., 2015). However, Binici et al., 2013 indicated that other congeners (such as BDE-47, -183, and -206) for PCs, hair dryers, toasters, microwave ovens, carpet, and cable were also important compositions, and Danon-Schaffer et al., 2013 obtained the same results. Possible reasons are due to the different types of e-waste or different production dates.

### 3.1.2. PBDE in PCBs

The concentrat`concentration patterns of PBDE congeners in housing plastics. PBDEs concentrations in PCBs (mg/kg).
3.2. TBBPA in e-waste

3.2.1. TBBPA in housing plastics

The 19 samples were analyzed to gain an understanding of the potential characteristics of TBBPA in housing plastics from five types of e-waste. The results are shown in Fig. 5. TBBPA was detected in fifteen samples of housing plastics, ranging from 0 to 34.00 mg/kg. The mean TBBPA concentrations of five kinds of e-waste followed the rank ordering: LCD monitors (10.96 mg/kg); CRT TVs (4.64 mg/kg); refrigerators (3.01 mg/kg); PCs mainframes (1.78 mg/kg); washing machines (0.11 mg/kg). This indicates that for the current e-waste housing plastics in China, LCD monitors have a relatively higher potential environmental risk of TBBPA.

### Table 3

<table>
<thead>
<tr>
<th>Location</th>
<th>Sources</th>
<th>Year</th>
<th>PBDEs (mg/kg)</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>China</td>
<td>TV</td>
<td>–</td>
<td>17285</td>
<td>Chen et al. (2012)</td>
</tr>
<tr>
<td>Austria</td>
<td>Small e-waste&lt;sup&gt;a&lt;/sup&gt;</td>
<td>–</td>
<td>92</td>
<td>Salhofer and Tesar (2011)</td>
</tr>
<tr>
<td>Switzerland</td>
<td>Small e-waste&lt;sup&gt;a&lt;/sup&gt;</td>
<td>–</td>
<td>54</td>
<td>Morf et al. (2005)</td>
</tr>
</tbody>
</table>

<sup>a</sup> Refers to the small e-waste, e.g. vacuum cleaner, toaster, iron, kettle, electric fan, electric toothbrush, etc.

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**Fig. 4.** Concentration patterns of PBDEs congeners in PCBs.

**Fig. 5.** TBBPA concentration in e-waste housing plastics (mg/kg).
With respect to CRT TVs, similar to the PBDEs concentrations, CT3 (PS plastics) contained higher TBBPA levels than CT1 (PP plastics) and CT2 (ABS plastics). For washing machines, only half (WM1, WM2, and WM5) of 6 samples contained detectable levels of TBBPA, and the highest TBBPA concentration in WM5 (mixed PP plastics) was only 0.60 mg/kg. TBBPA concentration (34.00 mg/kg) in LM4 samples from LCD monitors was highest of all the 19 e-waste samples, followed by LM2 samples (ABS plastics, 29.70 mg/kg). In the samples of desktop mainframes, the MF1 (HIPS plastics) had relatively higher TBBPA levels.

Comparing with other studies: Like PBDEs levels, most studies focused on the TBBPA concentrations in housing plastics of TV sets, as shown in Table 4. There are large differences of TBBPA levels in different studies. Chen et al. (2012) found that only PCs housing plastics contained TBBPA levels, much higher than that of the desktop mainframes in our study. Takigami et al. (2008) indicated that similar to PBDEs, the rear covers of CRT TVs had higher TBBPA levels (19,000 mg/kg), which was also higher than the results obtained in our study. According to the results of Morf et al. (2005), TV/PC mixed housing plastics contained higher TBBPA levels, up to 23,000 mg/kg, followed by TV rear covers, and small e-waste. The highest TBBPA levels were found from housing shredder residues of 9 TVs and 36 monitors from Schlummer et al. (2007), implying that the residues could own higher enrichment capacities of TBBPA.

3.3.2. TBBPA in PCBs

As shown in Fig. 6, no TBBTA were detected in PCBs samples from printer/copiers. TBBPA levels of CTP1 sample (PCBs with components from CRT TVs) reached to 8.38 mg/kg, about 32 times that of CTP2 samples, which implied that the components of PCBs could have higher TBBPA levels. Compared to CTP2, the CTP3 and CTP4 samples have larger enrichment capacities of TBBPA. Compared with the other studies’ results (Takigami et al., 2008; Morf et al., 2005) in Table 4, the TBBPA levels in our study were relatively lower, except in the samples where it was undetected (Chen et al., 2012).

### Table 4

<table>
<thead>
<tr>
<th>Location</th>
<th>Type</th>
<th>Year</th>
<th>Sample No.</th>
<th>TBBPA (mg/kg)</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>China</td>
<td>PCs; TV; Mobile phone; PCBs (TV)</td>
<td>1989–1998</td>
<td>15</td>
<td>15,804; 0; 0; 0</td>
<td>Chen et al. (2012)</td>
</tr>
<tr>
<td>Japan</td>
<td>Front cover; Rear cover; PCBs (CRT TV)</td>
<td>2003</td>
<td>7</td>
<td>3000–9600</td>
<td>Schlummer et al. (2007)</td>
</tr>
<tr>
<td>Switzerland</td>
<td>Small e-waste; TV housing rear covers; TV/PC housings (plastic);</td>
<td></td>
<td></td>
<td>2700–110,000</td>
<td>Morf et al. (2005)</td>
</tr>
<tr>
<td>Germany</td>
<td>Mixed shredded residues (9 TVs and 36 monitors)</td>
<td></td>
<td></td>
<td>3000–9600</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Housing shredded residues (9 TVs and 36 monitors)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

3.3. BFRs transfer into the new products

Currently, the reuse and recycling of e-waste plastics and PCBs NMFs are becoming the trend in the e-waste treatment industry, due to their potential environmental and economic benefits. Recent studies have revealed that plastic from e-waste containing PBDE is largely uncontrolled and is found in many recycled products (children’s toys, household goods, video tape casings and electronics) (UNEP, 2010). However, the potential pollutants (such as PBDEs and TBBPA) in them will not disappear, and may very possibly be transferred into the new products. Thus, it will be very necessary to understand the BRFs concentration in new products.

#### 3.3.1. PBDEs

Table 5 presents PBDE concentrations in new products reusing e-waste housing plastics and PCBs. It can be seen that except for in the RM1 sample, other samples (NP1, RM2, and RM3) had the similar PBDEs congeners with the raw housing plastics and PCBs materials: BDE209 were the dominant congeners, contributing to 93.44–96.09% of the total PBDEs levels. However, their Σ_PBDEs concentrations were higher than that of the raw housing plastics and PCBs materials, especially the RM2 and RM3. The results imply that the PBDEs in housing plastics and PCBs will be transferred into the new products, and the new products could have the high enrichment capacities on PBDEs, which means the higher potential environmental and health risk.

#### 3.3.2. TBBPA

Based on the detection results, the TBBPA concentrations of all four samples were less than the detection limit (0.002 mg/kg). This could be attributed to the low levels of TBBPA in the e-waste in this study. Further studies are needed to reveal the potential risk of TBBPA in reused products. The reduction of TBBPA in reused products implies a complete release of TBBPA into the environment of e-waste recycling workshops, translating to high occupational risks. Regulations on occupational safety and health are, therefore, necessary.

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**Fig. 6.** TBBPA concentration of e-waste PCBs (mg/kg).
Table 5
PBDEs concentrations in new products for reusing e-waste housing plastics and PCBs (mg/kg).

<table>
<thead>
<tr>
<th>Types</th>
<th>BDE28</th>
<th>BDE47</th>
<th>BDE100</th>
<th>BDE99</th>
<th>BDE154</th>
<th>BDE153</th>
<th>BDE183</th>
<th>BDE209</th>
<th>Total</th>
</tr>
</thead>
<tbody>
<tr>
<td>Housing plastics (CRT TV)</td>
<td>NP1</td>
<td>0.01</td>
<td>0.01</td>
<td>0.00</td>
<td>0.01</td>
<td>0.08</td>
<td>0.28</td>
<td>0.61</td>
<td>14.20</td>
</tr>
<tr>
<td>PCBs (NMFs)</td>
<td>RM1</td>
<td>0.58</td>
<td>0.00</td>
<td>0.29</td>
<td>0.06</td>
<td>0.04</td>
<td>0.29</td>
<td>0.00</td>
<td>0.01</td>
</tr>
<tr>
<td></td>
<td>RM2</td>
<td>0.01</td>
<td>0.02</td>
<td>0.00</td>
<td>0.31</td>
<td>0.00</td>
<td>1.76</td>
<td>0.00</td>
<td>51.50</td>
</tr>
<tr>
<td></td>
<td>RM3</td>
<td>0.02</td>
<td>0.01</td>
<td>0.00</td>
<td>0.48</td>
<td>0.00</td>
<td>2.72</td>
<td>0.00</td>
<td>49.40</td>
</tr>
</tbody>
</table>

4. Discussion

The present study systematically examined the PBDEs and TBBPA concentrations in housing plastics and PCBs in e-waste from e-waste recycling enterprises in China, and discussed their potential transfer from raw materials to new products.

China has historically been one of the largest recipients of e-waste, and is also one of the countries faced with the most serious environmental pollution and human exposure of e-waste in the world. In the last ten years, the Chinese government has implemented some measures and policies to reduce informal recycling. For example, “The technical policy for the prevention and control of pollution by discarded appliances and electronic products”, issued in 2006, aimed to eliminate the use of PBDEs in e-products and to identify PBDEs as toxic and hazardous substances. “The ordinance on management of pollution and control of pollution from electronic information products” listed the responsibilities of designers, producers, and importers of e-products for potential environmental impacts. “Technical specifications of pollution control for processing waste electrical and electronic equipment” indicates that plastics containing PBDEs from e-wastes should be classified and treated. Landfilling of these plastics was banned, and the treatment of waste wire/cables containing PBDEs should be classified with other wire/cables. At the same time, about 109 formal e-waste recycling enterprises, which were included in the subsidy list of “Processing Fund for Electrical and Electronic Equipment”, have been established in China. According to research results obtained in this study, the PBDEs and TBBPA concentrations in the current e-waste have apparently declined in comparison with the previous studies. This suggests that the source eco-design has been carried out in the e-products, due to the implementation of China’s management policies.

In our study, most of the plastics and PCBs samples were found to contain the BFRs (especially the PBDEs) in different types of e-waste. In China, the production and usage of commercial penta-BDE was banned in 2006 (Hu et al., 2010). However, the congeners were still used, and the treatment of waste wire/cables containing PBDEs from e-wastes should be included in future research work.

Our study found that when the recovered plastics and NMFs were used to produce the new products, they contained BFRs, especially the PBDEs, which were transferred into the new products. Though the leaching properties of the products may meet national and industrial standards, some limits still need to be focused on: (1) in production processes, effective environmental monitoring and controls should be involved to avoid the secondary pollution; and (2) it should try to avoid being used to produce daily living products. In addition, some experts also thought that these hazardous substances, which have been prohibited in production and use worldwide, should be not reused and recycled, and should be treated for the final settlement. These plastics and NMFs, including high levels of PBDEs and TBBPA, are among these kinds of hazardous substances.

There are also several limitations in this study: (1) the samples did not include small size e-waste, e.g. mobile phones; (2) It only analyzed the potential PBDEs and TBBPA levels in e-waste, and did not refer to the new e-products. In addition, the production years were not considered in this study; (3) for new products from plastics and NMFs reuse, it only did a simple analysis - more samples should be included in future research work.

5. Conclusions

This study explores the characterization of extremely hazardous substances (PBDEs and TBBPA) in e-waste. Results show that most of the plastics and PCBs samples were found to contain the PBDEs and TBBPA in different types of e-waste, indicating a high frequent use of PBDEs and TBBPA in e-waste. However, the concentrations of PBDEs and TBBPA are trending down when compared with previous studies. It is worthy to note that low total amounts of BFRs do not necessarily mean low releases of these compounds. If these e-wastes are not treated properly, there is still a high potential for environmental and health risks. This study also found that the PBDEs in housing plastics and PCBs will be transferred into new products, and the new products could have higher enrichment capacities on PBDEs. Hence, further work should be directed toward a systematic examination of the release mechanism of PBDEs from e-waste to environmental medium, especially in informal sectors. Most importantly, plastics and PCBs materials with high PBDEs and TBBPA levels should be separated from other recycling materials before being sent for further recycling and treatment.

The results of this study help identify current and future flows of PBDEs and TBBPA in China. At the same time the results obtained from this study should help researchers in other countries understand important flows and stocks of PBDEs and TBBPA in plastics and PCBs from e-waste.

Acknowledgments

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References


