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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.

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).

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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 electronics 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/copies 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 (NP1), and new products with NMFs as additional agents (RM1-3). Here, plastics types (such as PP, ABS, PS, and HIPS), 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

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