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Polybrominated diphenyl ethers in e-waste: Level and transfer in a typical e-waste recycling site in Shanghai, Eastern China

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ABSTRACT

Very few data for polybrominated diphenyl ethers (PBDEs) were available in the electronic waste (e-waste) as one of the most PBDEs emission source. This study reported concentrations of PBDEs in e-waste including printer, rice cooker, computer monitor, TV, electric iron and water dispenser, as well as dust from e-waste, e-waste dismantling workshop and surface soil from inside and outside of an e-waste recycling plant in Shanghai, Eastern China. The results showed that PBDEs were detected in the majority of e-waste, and the concentrations of ΣPBDEs ranged from not detected to 175 g/kg, with a mean value of 10.8 g/kg. PBDEs were found in TVs made in China after 1990. The mean concentrations of ΣPBDEs in e-waste made in Korea, Japan, Singapore and China were 1.84 g/kg, 20.5 g/kg, 0.91 g/kg, 4.48 g/kg, respectively. The levels of ΣPBDEs in e-waste made in Japan far exceed the threshold limit of RoHS (1.00 g/kg). BDE-209 dominated in e-waste, accounting for over 93%. The compositional patterns of PBDEs congeners resembled the profile of Saytex 102E, indicating the source of deca-BDE. Among the samples of dust and surface soil from a typical e-waste recycling site, the highest concentrations of Σ_{18}PBDEs and BDE-209 were found in dust in e-waste, ranging from 1960 to 340,710 ng/g and from 910 to 320,400 ng/g, which were 1–2 orders of magnitude higher than other samples. It suggested that PBDEs released from e-waste via dust, and then transferred to surrounding environment.

1. Introduction

Along with the accelerating update of technology and continuous expansion of electronic industrial market, electronic waste (e-waste) becomes a serious global problem in 21st century. As estimated by the United Nations Environment Program, more than 50 million tonnes of E-waste are generated annually in the world (UNEP, 2005). Nevertheless, China is now facing dual pressure of e-waste from both domestic generation and illegal imports (Yang et al., 2008a). The percentage of e-waste amount from overseas was increased to 70% in 2010 and it is estimated that 1.5–3.3 million tons of e-waste are imported to China via illegal ways each year (Zhou and Xu, 2012).

It is not only a crisis of quantity but also a crisis of toxic parts (Ongondo et al., 2011; Pant et al., 2012; Xu et al., 2012). Driven by the profit, primitive handlings of e-waste, such as manual disassembling, open incineration and acid dipping, grew up and flourish in a few locations of China (Bi et al., 2007). The inappropriate e-waste recycling and disposal activities generate and release heavy metals and persistent organic pollutants (POPs) into the surrounding environment, which may be redistributed, bioaccumulated and biomagnified, with potentially adverse human health effects (Söderström et al., 2003; Wang et al., 2005; Wang et al., 2011). Polybrominated diphenyl ethers (PBDEs) are one class of the most concerns because the e-waste contain significant levels of PBDEs (Wang et al., 2005). PBDEs are anthropogenic chemical that have been extensively used as brominated flame retardants (BFRs) in furniture, building material and electronic components. Due to their toxicological effect, the production and use of PBDEs have been banned in Europe, meanwhile, penta- and octa-BDE formulations are now banned in North America (Kemmlein et al., 2009; Ward et al., 2008).

Uncontrolled e-waste recycling activities have become a new important source of PBDEs. High levels of ΣPBDEs were detected in soil from acid leaching site (2720–4250 ng/g, dry wt.), and from a printer roller dump site (593–2890 ng/g, dry wt.) at Guiyu, Southeast China (Leung et al., 2007). They were also found in soils (up to 25,479 ng/g, dry wt.), and sediments (up to 3526 ng/g, dey wt.) in Taizhou, Southeast China (Yang et al., 2008b, 2009). PBDEs were detected in various environmental samples in e-waste recycling areas in China indicating a severe risk to the local ecosystem and inhabitants' health (Bi et al., 2006; Luo et al., 2009a).

Yet, most of the previous researches were focused on the environmental media. Only limited and rather uncertain data are available regarding the occurrence of PBDEs in e-waste (the emission source). High concentrations were found in housings shredder residues (Schlummer et al., 2007). Average concentrations in small

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size e-waste amounted to 0.03 g/kg for penta-BDE, 0.53 g/kg for octa-BDE, and 0.51 g/kg for deca-BDE (Morf et al., 2005). Levels and patterns of PBDEs in e-waste may also be relevant to the component types, production time, producing region, however, researches in this area are still blank. So it is necessary to study the characterization of PBDEs in e-waste deeply and systematically, in order to provide rationalization proposals regarding proper handling of e-waste and the development of management policies.

Located in the Eastern China, Shanghai is the largest and most populous city of China. Meanwhile, technological innovation and intense market bring a rapid replacement process leading to increasing generation of waste electrical and electronic equipment (WEEE) in Shanghai. As shown in Fig. 1, part of electrical and electronic equipment enter the circulation in the secondary market. In addition, to enter the recycling link is the most important way for e-waste. There are several e-waste recycling sites in Shanghai, even though the handling capacity is limited. Many studies suggested that a major emission source of PBDEs is the low-tech e-waste recycling facilities (Ma et al., 2009b). Their impact on the surrounding environment can never be ignored.

In the present study, 140 e-waste plastics samples were collected from e-waste recycling sites in Shanghai to investigate levels and compositional patterns of PBDEs in e-waste. Detailed information of PBDEs in e-waste such as time series was also discussed. Additionally, dust in e-waste, dust in dismantling workshop, surface soil inside and outside the e-waste recycling plant were collected to investigate the possible transfer during recycling process.

2. Materials and methods

2.1. Sample collection

Sampling campaigns were conducted between September 2008 and March 2009. A total of 157 samples were collected from e-waste recycling sites in Shanghai, including plastics, dust and surface soil. Briefly, plastics samples were cut from plastic housing of e-waste which were near the vents. As for the same types of plastic housing of e-waste, plastics were cut from the same position of the electronics with the same size was almost the same. Dust in e-waste was collected by vacuum-cleaning the inside of each e-waste until sufficient mass (>300 mg) was collected on a glass fiber filter. Dust in dismantling workshop were collected from the floor inside the dismantling workshop using a straw brush. Surface soil samples were collected outside the workshop in e-waste recycling plant and in a place at a distance of about 1 km from the e-waste recycling plant using a stainless steel shovel at a depth of 1–10 cm, respectively. All the samples were wrapped in aluminum foil and stored at -20 °C in the laboratory prior to analysis. Besides, the dust and surface soil samples were air-dried and sieved through 100 mesh screen before storing.

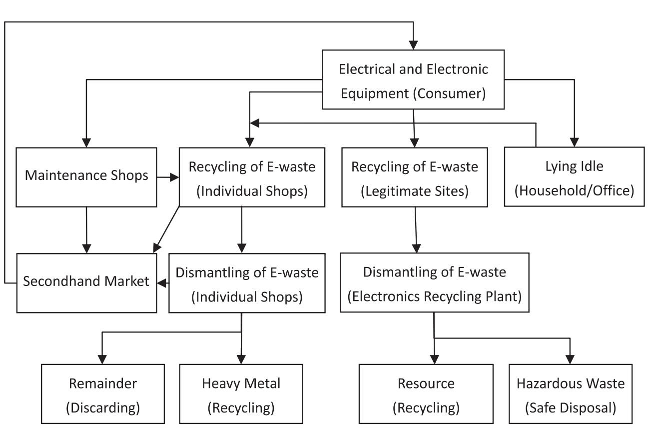

Fig. 1. The flow chart of electrical and electronic equipment in Shanghai.

2.2. Standard materials

The targets 19 PBDEs congeners were purchased from Accu Standards (New Haven, CT, USA), including three tri-BDEs (BDE-17, BDE-28, and BDE-33), three tetra-BDEs (BDE-47, BDE-49, and BDE-66), two penta-BDEs (BDE-99 and BDE-100), three hexa-BDEs (BDE-138, BDE-153, and BDE-154), four hepta-BDEs (BDE-183, BDE-190, BDE-196, and BDE-203), three nona-BDEs (BDE-206, BDE-207, and BDE-208), and deca-BDE (BDE-209). BDE-50 and BDE-172 used as surrogate standards and BDE-118 and BDE-128 used as internal standards were also purchased from AccuStandards.

2.3. Sample extraction and PBDEs analysis

The plastic samples of e-waste were firstly cleaned by distilled water, then cut into tiny fragments. These plastic fragments were prepared to "polymer film" to facilitate a complete extraction. Detailed extraction is provided in our previous study (Huang et al., 2010).

Dust and surface soil samples were weighed approximately 200 mg and 5 g respectively, and then extracted. The following procedures are the same as our previous study (Yang et al., 2011). PBDEs congeners were quantified with a Shimadzu GCMS-QP 2010 plus instrument with the selective ion monitoring (SIM) mode. A DB-5 column (15 m × 0.25 mm × 0.1 μm, J&W Scientific) was employed. For the analysis of tri- to hepta-BDE congeners, temperature program was 80 °C for 1 min, ramped at 12 °C/min to 140 °C, then 5 °C/min to 280 °C and held for 20 min. For octa- to deca-BDE congeners, the program was 110 °C for 1 min, ramped at 10 °C/min to 290 °C and hold for 20 min. Quantification of the target compounds was performed using an internal standard method. With a signal/noise ratio of better than 3, the limit of detection (LOD) for BDE-209 and other congeners were 2 ng/g and 0.1 ng/g based on dry weight, respectively.

2.4. Quality assurance and quality control

For each batch of e-waste plastic, dust and surface soil samples, a procedural blank, a spiked blank and a duplicate sample were processed. All targets were lower than the LOD in procedural blanks, so they were not subtracted from the sample measurement. The surrogate recovery of BDE-50 and BDE-172 was 99 ± 3.9% and 102 ± 3.5%, respectively. The relative standard deviation for individual PBDEs congener was less than 10% ($n = 5$). Recoveries of targets ranged from 82% to 119%, relative standard deviations ranged from 2.1% to 8.3% in spiked blank samples. Reported concentrations were not surrogate recovery corrected.

3. Results and discussion

3.1. Levels of PBDEs in e-waste

The e-waste plastics samples were categorized into six types according to the application of electrical and electronic products, including printer ($n = 11$), rice cooker ($n = 5$), computer monitor ($n = 13$), TV ($n = 102$), electric iron ($n = 2$), and water dispenser ($n = 7$). Fig. 2 presents detectable frequency and the concentrations of ΣPBDEs in different types of e-waste. PBDEs were detected in 71