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Estimated PBDE and PBB Congeners in Soil from an Electronics Waste Disposal Site

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Abstract This study estimated PBDE and PBB congener emissions into the environment from three different e-waste disposal sites that consisted of rude broilers (RB), acid baths (AB) and end-up dumps (ED). Different PBDE and PBB congener profiles were analyzed, and some of their emission sources were discussed. For the examined sites, the levels of ΣPBB and ΣPBDE were highest at ED (ΣPBB 1943.86 ng/g, dw; ΣPBDE 990.87 ng/g, dw), followed by RB (ΣPBB 704.58 ng/g, dw; ΣPBDE 799.27 ng/g, dw) and finally AB (ΣPBB 108.78 ng/g, dw; ΣPBDE 171.18 ng/g, dw). PBE-209 (AB 48.67 ng/g, 28.43%; RB 160.23 ng/g, 20.05%; ED 234.12 ng/g, 23.63%) and PBE-203 (AB 51.23 ng/g, 29.93%; RB 130.34 ng/g, 16.31%; ED 93.41 ng/g, 9.43%) exhibited the highest concentrations when compared to the other congeners. Furthermore, high levels of deca-BDE (BDE-209) were observed in AB (48.67 ng/g, 28.43%) and RB sites (160.23 ng/g, 20.05%), which was in accordance with the large amount of these materials in electronics products in China.

Keywords Electronic waste (e-waste) · Different disposal sites · Polybrominated biphenyls ether (PBDEs) · Polybrominated biphenyls (PBBs)

Electronic waste (e-waste) is a rapidly growing environmental problem throughout the world. Expansion of the global market for electrical and electronic products continues to accelerate, while the lifespan of products is dropping. These results in an explosion in the amount of electronic scrap produced (Electronics 2001). These rapidly growing "e-waste" streams present additional difficulties because a wide range of hazardous chemicals are (or have been) used in electrical and electronic devices; these subsequently create substantial problems in the handling, recycling and disposal of obsolete products (Luo et al. 2009). E-waste follows a number of different pathways into the environment: first, most e-waste directly enters the second-hand market for reuse after simple repairs; second, totally useless e-products are generally dismantled by hand to recover the raw materials such as plastics, copper, aluminum and ferrous metal; and third, e-waste that cannot be dismantled by hand (such as printed circuit boards and fine wires) is processed with destructive technologies, such as open burning, broilers and acid baths, which cause organic pollutant release and bring potential risk to the local environments (Deng et al. 2007).

Brominated flame retardants, such as PBB and PBDEs, are used in a variety of consumer electronic products, and several of these flame retardants are produced in large quantities. They are added to plastics used in products such as home electrical appliances, textiles, plastic foams etc. to make them difficult to burn. They are sometimes added in concentrations up to 30% by weight (WHO 1994). The presence of brominated flame retardants in environmental samples can be directly attributed to the anthropogenic use of these e-wastes (Wang et al. 2005). PBDEs have been reported in soil as well as sewage sludge and water, and clear evidence has been shown that their levels in the environment are increasing. This is especially true around

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e-waste disposal sites (Wang et al. 2005). It has been reported that the air in Guiyu, one such e-waste disposal site, contains PBDEs at levels 100 times higher than other sites in the world. These elevated concentrations in Guiyu were due to e-waste burning, since PBDEs are released when plastics containing brominated flame retardants are heated (welding of mats, melting of polymers) (Wit 2002).

Brominated flame retardants (BFRs), such as polybrominated diphenyl ethers (PBDEs) or polybrominated biphenyls (PBBs), are in a class of POPs for which the body burden is increasing. Exposure to these materials might be more harmful than previously thought. Some PBDE congeners have dioxin-like effects, interfering with the aryl hydrocarbon (Ah)-receptor (Meerts et al. 1998). BDE-99 has been shown to induce learning disabilities in mice (Eriksson et al. 1998). Other PBDE congeners have hepatotoxic and mutagen effects. Still others may act as estrogen receptor agonists in vitro (Meerts et al. 2001). It is not definitively known whether or not PBBs can cause cancer in human beings, although it has been observed that they can cause cancer in lab mice exposed to very high concentrations. Based on such animal tests, the United States Department of Health and Human Services has concluded that PBBs might reasonably be characterized as carcinogens. The International Agency for Research on Cancer also suggested PBBs may be carcinogenic to humans. Studies in animals exposed to large amounts of PBBs for a short period or to smaller amounts over a longer period showed that PBBs could lead to weight loss, skin disorders, nervous and immune systems effects, as well as effects on the liver, kidneys, and thyroid gland (Nakari and Huhtala 2008; Sweeney and Symanski 2007).

This paper estimated PBDE and PBB congener concentrations in the environment around three different e-waste disposal sites that consisted of rude broilers (RB), acid baths (AB) and an end-up dump (ED). The levels of different PBDE and PBB congeners were analyzed, and some of their sources are discussed here.

Materials and Methods

A total of 48 soil samples were taken in March 2008 with a 2 cm diameter gravity corer from three locations in Zhejiang Province (in east China), near three different e-waste disposal sites–a rude broiler (RB, N28.35558 E121.25313), an acid bath site for printed circuit boards (AB, N40.04081 E116.41003) and an end-up dump (ED, N28.40590 E121.31020). According to the multispot collection principle (Xi et al. 1996), samples were collected at different depths and different points at the same sampling site from a tank. The three locations were geographically distant from each other. Samples were taken from a reservoir approximately 50 m from the central e-waste processing area, and all other samples were collected from each of the sites using a stainless steel shovel at a uniform depth of 0–10 cm. The samples were freeze-dried and sieved (<2 mm).

The following authentic reference substances were used in the analysis (abbreviations and origins are given): PBDEs: 4,4′-Dibromodiphenyl ether (BDE-015), 2,4,4′-Tribromodiphenyl ether (BDE-028), 3,3′4-Tribromodiphenyl ether (BDE-035), 3,3′,4,4′-Tetrabromodiphenyl ether (BDE-077), 2,2′,3,4,4′-Pentabromodiphenyl ether (BDE-085), 3,3′,4,4′5-Pentabromodiphenyl ether (BDE-126), 2,2′,3,3′,4,4′ -Hexabromodiphenyl ether (BDE-128), 2,2′3,4,4′5,5′,6-Octabromodiphenyl ether (BDE-203), 2,3,3′,4,4′,5,5′,6-Octabromodiphenyl ether (BDE-205), 2,2′,3,3′,4,4′,5,5′,6,6′-decabromodiphenyl ether (BDE-209). PBBs: 4-Bromodiphenyl (B-003), 2-Bromodiphenyl (B-001), 4,4′-Bromodiphenyl (B-015), 2,5-Diromodiphenyl (B-009), 2,4,6-Tribromodiphenyl (B-030), 3,3′,4,4′-Tetrabromodiphenyl (B-077), 2,2′,4,5′,6 -Pentabromodiphenyl (B-103), 3,3′,4,4′,5,5′-Hexabromodiphenyl (B-169), Decabromodiphenyl (B-209), all bought from AccuStandard, Inc. (USA). All solvents used for the analyses (n-hexane, acetone, dichloromethane and iso-octane) were of SupraSolv grade (Beijing, Refine Chemistry and Industry Company, China).

During extraction, a soil sample (around 10 g) was placed into an extraction thimble that had been pre-washed with hexane. A small amount (0.5 g) of copper powder (Merck) was added and mixed with the sample, followed by the addition of internal standards. Samples were extracted using a Soxhlet extractor operated in hot extraction mode. Several solvent mixtures (250 mL), such as $CH_3OH/CH_3–C_6H_5$ (9:1, v/v), hexane/acetone (1:1, v/v) and hexane/dichloromethane (1:9, v/v) were tested using different extraction conditions and extraction times (2, 3 and 4 h). In each case, the extract was concentrated and transferred onto a hand-packed HPLC chromatography column. Columns were prepared by placing 10 g of activated silica gel (Qiangdao Chemical andf Industry Company, 600 C activation 200/300 meshes) in the bottom of a 40 mm column fitted with glass wool. On top of this were placed 30 cm (50 g) of silica gel (Qiangdao Chemical and Industry Company, special for column chromatography) and 2.5 cm (12 g) of anhydrous Na_2SO_4. The column packing materials were stored in an oven at 110°C until use. The prepared columns were prewashed with 300 mL of $CH_3OH/CH_3–C_6H_5$ (9:1, v/v). The eluted fractions were concentrated to near dryness by a rotary evaporator, and further dried under a gentle nitrogen stream. The final extract was re-solubilized in 2 mL iso-octane.

Protocols from the literature were used during the quantification of the PBDE congers (Wang et al. 2007), and the analysis of BDE 209 was performed by reference to the literature (Covaci et al. 2005). The determination of PBB levels was performed via gas chromatography with electron capture detection (GC-ECD). An Agilent (Palo Alto, CA, USA) 7890 GC-ECD was equipped with a 30 m × 0.32 mm × 0.25 mm HP-5 19091 J-413 capillary column (Agilent, Shanghai, China). Nitrogen was used as a carrier gas at a constant flow of 3.0 mL/min (Miceli et al. 1985). Quantification of PBB was based on the size of the 2,4,5,2′,4′,5′ - hexabromobiphenyl peak (the most abundant component of Firemaster BP-6). A standard curve was constructed based on the PBB concentration (ng/mL) versus the area under the hexa-bromobiphenyl peak. The plot was linear from 0.5 to 1,000 ng/mL PBB. The data system integrated the area under the peaks and provided a print-out of the concentration of the PBB isomers. Samples that had a concentration initially determined to be higher than 1,000 ng/mL were appropriately diluted with iso-octane and re-analyzed, with the exception of BDE-209. A prepared control was also analyzed after every 10 samples for quality control.

The quality control method utilized for the PBDEs was based on the literature (Wang et al. 2007). The limit of quantification (LOQ) for PBB and PBDEs was based on GC/ECD and GC/MS performance and on laboratory background levels, which were determined by analyzing procedural blanks. Procedural blank levels were consistent (RSD 20%) and therefore, the median blank value was used for normalization via subtraction. The level of quantifications were defined as three times the standard deviation of the procedural blank, resulting in a certainty of more than 95% for results given for the samples.

Results and Discussion

The concentrations of PBDEs in soil samples collected near three different e-waste disposal sites are summarized in Table 1. ΣPBDE refers to the sum of all 10 examined BDE congeners. Figures 1 and 2 illustrate distributions of the levels of different congeners around AB, RB and ED. Relatively high concentrations of BDE congeners around RB were present in the form of BDE-85, BDE-126, BDE-203 and BDE-209. BDE-85, BDE-203 and BDE-209 were present at higher levels at ED than at AB (Fig. 1). The highest percentages of BDE-209, BDE-15 and BDE-28 in ΣPBDE were found in the samples collected from ED. All congeners were found at higher concentrations at ED than at AB or RB. The total PBB concentration (defined as the sum of different congeners) was as high as 1943.86 ng/g, with the mean concentration of individual congeners ranging from 0.21 to 330.99 ng/g (Table 2). The concentrations of most PBB congeners were relatively high at ED. The total PBB concentration was much higher around ED than at the other sites. Relatively high concentrations of PBB congeners B-169, B-103 and B-0209 were found at EB compared with AB and RB. Congeners concentrations around ED followed the order: B-169 > B-209 > B-103 > B-077 > B-003 (Fig. 2).

The concentrations of PBDEs and PBBs in soils from the three different e-waste disposal sites were found to be at high levels; this might be related to the amount they are used in electronics products and the disposal modes. It is known that brominated flame retardants (BFRs) are used in a variety of consumer electronics products, and several of those have been produced in large quantities (Alaee et al. 2003; Ou and Han 2005). PBDEs and PBBs have been the most popular BFRs over the past several decades. Their production and use has grown with increased use of synthetic polymers and the introduction of more rigorous safety requirements. This growth is reflected in their increasing levels in the environment (Zhang et al. 2007). To understand the reasons underlying the concentrations of various congener levels at different disposal sites, it is important to understand the disposal processes and techniques. The techniques used to recycle e-waste are often primitive, without facilities to safeguard individuals or the environment. The AB technique uses open-pit acid baths to recover gold and other metals. The RB technique removes electronic components from printed circuit boards by heating over a grill using honeycombed coal blocks (coal mixed with river sediment, which is contaminated) as fuel. The RB technique is also used to recover metal from cables. ED (8–10 years history), the end-up dump, is really an e-waste dump full of unsalvageable materials. In a previous study on organic pollutants, it was reported that high levels of PBDEs were present in the air around e-waste sites (Chen et al. 2009). This phenomenon was ascribed to heating or open burning during e-waste disposal, since PBDEs could be released when plastics containing brominated flame retardants were heated (Deng et al. 2007). Our results agree with these studies.

We found far higher levels of ΣPBDE (990.87 ng/g, dw) and ΣPBB (1943.86 ng/g, dw) around ED than AB (ΣPBB108.78 ng/g; ΣPBDE 171.18 ng/g) and RB (ΣPBB 704.58 ng/g; ΣPBDE 799.27 ng/g, dw. We speculate that unsalvageable materials in e-waste dumps might release more persistent organic pollutants by degradation over time due to many environmental factors such as photodissociation, biodegradation etc. These sources of PBDEs and PBB have often been ignored because they are very slow processes. Figure 2 shows the different congener profiles of PBB, and reveals that congener patterns in the environmental samples do not match those of RB and AB. This finding indicates the existence of an environmental alteration, possibly a photochemical debromination, which has been previously discussed (Fang et al. 2008). The relatively

Table 1 BDE congeners in soil samples (ng/g, dry weight:dw)

	BDE-15	BDE-28	BDE-35	BDE-77	BDE-85	BDE-126	BDE-128	BDE-203	BDE-205	BDE-209	ΣPBDE
AB											
Mean	2.96	32.66	6.62	1.88	4.08	2.20	10.76	51.23	10.12	48.67	171.18
%	1.73	19.08	3.87	1.1	2.38	1.29	6.29	29.93	5.91	28.43	
Min.	0.10	26.63	3.60	1.30	1.56	1.65	1.40	12.21	4.6	1.20	
Max.	12.23	40.38	20.95	7.20	21.87	2.02	53.48	92.23	22.15	48.23	
RB											
Mean	4.42	16.27	2.19	80.46	234.13	150.03	16.65	130.34	4.55	160.23	799.27
%	0.55	2.04	0.27	10.07	29.29	18.77	2.08	16.31	0.57	20.05	
Min.	0.20	1.26	0.10	8.47	2.54	3.42	0.50	9.22	1.54	12.84	
Max.	6.23	23.45	4.55	167.94	324.45	211.34	13.43	235.72	18.32	330.45	
ED											
Mean	265.17	108.20	11.62	27.62	195.6	30.30	12.49	93.41	12.34	234.12	990.87
%	26.76	10.92	1.17	2.79	19.74	3.06	1.26	9.43	1.25	23.63	
Min.	7.54	0.45	7.23	2.11	0.33	4.32	0.65	4.68	1.75	3.32	
Max.	645.32	567.96	15.44	145.76	737.22	345.21	67.58	457.23	67.54	356.44	
LOD(pg/g)	12	8	4	18	7	7	6	6	12	30	

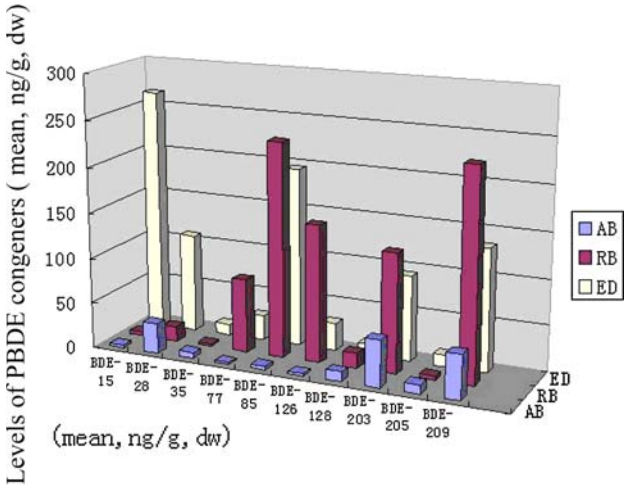

Fig. 1 Levels of PBDE congeners around three disposal sites

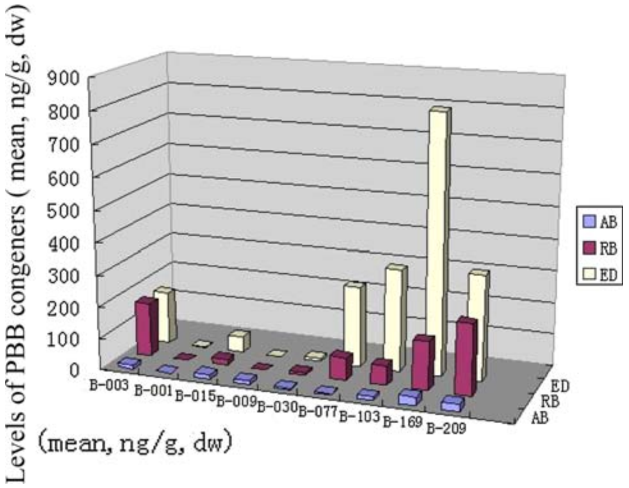

Fig. 2 Levels of PBB congeners around three disposal sites

long history of the ED site in our studies might help to explain the reason that PBDE profile in these samples differed from those at the RB and AB sites.

PBDE and PBB homolog analyses and component percentage analyses (Tables 1, 2) revealed that BDE 209 was present at a higher concentration than other congeners at RB. High concentrations of BDE 209 were also found at ED (330.99 ng/g dw) and RB (222.27 ng/g dw). The reason for this might be associated with the prevalence of their use as flame retardants in the past ten to twenty years in China. Even today, some printed circuit boards containing BDE 209 as a flame retardant are still used in China. This ongoing use may partially account for the BDE 209 residues in Chinese soil and sewage sludge (Ou et al. 2007). Further analysis was performed, and the results indicated that AB had lower levels of ΣPBDE and ΣPBB than RB and ED. Most electronic components from printed circuit boards are treated with strong acids, such as sulfuric and nitric acid, in the AB process, and we presume that few PBDEs and PBBs are released because the strong acid reacts with these compounds. Although we focused on brominated flame retardants, the importance of other pollutants resulting from the disposal of e-waste (such as heavy metals) should not be ignored. More attention should be paid to the RB process, which has the potential to produce more immediate, direct health risks than ED. The open burning of computer casings and circuit boards stripped of metal parts may produce toxic fumes and ashes containing organic pollutants.

Table 2 PBB congeners in soil samples (ng/g, dw)

	B-003	B-001	B-015	B-009	B-030	B-077	B-103	B-169	B-209	ΣPBB
AB										
Mean	12.58	2.06	14.94	10.71	3.51	4.01	10.68	26.71	23.58	108.78
	11.56	1.89	13.73	9.85	3.23	3.69	9.82	24.55	21.68	
Min.	0.20	0.10	0.20	0.10	0.20	0.20	3.00	7.50	19.60	
Max.	42.42	18.57	30.50	69.00	5.75	27.30	23.05	57.62	36.68	
RB										
Mean	170.34	0.02	19.71	0.01	7.01	70.58	61.33	153.31	222.27	704.58
	24.18	0	2.8	0	0.99	10.02	8.7	21.76	31.55	
Min.	0.01	0.00	1.44	0.00	0.12	0.24	1.89	1.89	78.49	
Max.	234.23	0.04	34.56	0.05	10.46	156.89	108.52	213.67	432.56	
ED										
Mean	166.41	0.21	50.33	0.15	10.43	252.96	321.68	810.70	330.99	1943.86
	8.56	0.01	2.59	0.01	0.54	13.01	16.55	41.71	17.03	
Min.	65.33	0.00	2.45	0.00	5.4	124.65	125.65	368.75	169.85	
Max.	456.34	0.89	76.44	1.43	23.43	464.23	568.34	956.43	467.31	
LOD(pg/g)	12	10	5	4	7	7	6	6	4	

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