Polybrominated diphenyl ethers in combusted residues and soils from an open burning site of electronic wastes

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Abstract Polybrominated diphenyl ethers (PBDEs) are ubiquitous environmental contaminants due to their extensive use. Combusted residue from electronic waste (e-waste) combustion is one of the contamination sources because PBDEs may be deposited in the soil and transported to remote locations. The transport and deposition behaviors of PBDEs released from burning were evaluated by analyzing their concentrations and congener distributions. Total PBDE concentrations were detected in the range from 2379 to 6238 ng/g (dry weight) in the combusted residue samples collected from a large open burning site and from 247.4 to 1422.3 ng/g in soil samples collected from different locations close to the open burning site. BDE-209, 183, 153, 99, and 47 were detected in relative high concentrations in both combusted residue and soil samples. The interpretation of the PBDEs concentrations and congener patterns in the combusted residue and soil samples indicated that PBDEs contamination in soil might be a result of e-waste burning and transportation, and deposit of the combusted residue. The total PBDE concentrations decreased significantly with increasing distance from the burned site, suggesting that the

combusted activities were the major source of PBDEs in the region and the transportation behavior of lower brominated congeners might not differ from that of higher brominated congeners for short distances.

Keywords Brominated flame retardants (BFRs) · BDE-209 · Open burning · Combusted residue · Soil · GC–MS

Introduction

Polybrominated diphenyl ethers (PBDEs) are used in large quantities as brominated flame retardants (BFRs) that are added to a variety of consumer and electronic products (Alaee et al. 2003). There are three different PBDEs technical products that are the mixtures of diphenyl ethers with various numbers of bromine atoms on the two rings. Penta-BDE technical products such as Bromkal 70-5DE or Great Lake DE-71, which contains primarily tetra-, penta- and some hexa-BDEs (Sjodin et al. 1998), while the octa-BDE product contains hexa- to nona-brominated congeners and the deca-BDE product is almost entirely composed of BDE-209 (Alaee et al. 2003). Penta-BDE mixtures are considered generally more toxic than Octa-BDE, whereas BDE-209 is essentially non-toxic to invertebrates. Penta-BDE and Octa-BDE have been listed in Stockholm Convention in 2009. However, BDE-209 remains legal in most countries and is starting to be banned in some countries (Betts 2008; BSEF 2003). The PBDEs technical products are commonly used in printed circuit boards, components such as connectors, cables, plastic covers and parts of keyboards and monitors in computers (Martin et al. 2004). PBDEs have caused considerable concerns not only because they have been found in the environmental matrices (air, water, sediment, and soil) (de Wit

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2002), biota (fish, birds, marine mammals) (Hites 2004) as well as human blood, milk and adipose (Gill et al. 2004), but also because their concentrations have exponentially increased and some PBDEs congeners possess persistent, bioaccumulative and toxicological properties (Law et al. 2003; Hites 2004).

Soils represent a major sink for these compounds released to the environment (Zou et al. 2007). PBDEs may be bound strongly to soil particles and thus may remain in soil for several years (Palm et al. 2002; Gouin and Harner 2003). Possible degradation of PBDE, particularly the high brominated congeners, in soil has become a concern. Little degradation, however, was reported during atmospheric transport or within the soil because the PBDEs congener composition and distribution measured in background soils closely matched those reported in the technical penta-BDE product (Hassanin et al. 2004; Hale et al. 2006). Airborne congeners of the PBDEs mixture are likely to accumulate in soil as a result of atmospheric deposition. Most of the degradation and metabolism of PBDEs occur in the plant from soils (Mueller et al. 2006; Huang et al. 2010). A recent study has shown that plants could enhance the degradation of PBDEs in soils (Wang et al. 2011).

Obsolete computers and electronic components have been imported into the developing countries of Asia such as China (Terazono et al. 2006). The town of Guiyu located in Guangdong Province has become one of the main centers of e-waste recycling in China. The traditionally rice-growing community has been turned into an intensive e-waste recycling center since 1995. Humans are exposed to PBDEs from the uncontrolled dismantling, acid treatment, and open burning of this material in the field. The open burning of computer casings and circuit boards stripped of metal parts may produce toxic fumes and combusted residues that contain organic pollutants. Concentrations of PBDEs detected in the Guiyu air were high when compared with those from other cities, which were primarily due to the incomplete combustion of e-wastes (Wong et al. 2007). The uncontrolled recycling activities of e-wastes were found to result in PBDEs entering to the environment (Cai and Jiang 2006; Leung et al. 2007; Luo et al. 2009; Tang et al. 2010). In addition, soils are the main retention for disposal and landfill of e-wastes (Hassanin et al. 2004). Therefore, PBDEs released from e-waste recycling activities may have contaminated nearby rice fields and posed potential risk to human health.

Thus, it is important to investigate the urban emission sources of the three technical products of PBDEs and their relationship with applications in electronic products, as well as this subsequent disposal (Alcock et al. 2003). The combustion of e-waste in the presence of copper from printed circuit boards and computer wiring may lead to higher emissions of PBDEs into the environment (Leung

et al. 2007). Studies have confirmed human exposure to PBDEs via inhalation (Harrad et al. 2004) and oral pathways (Hites 2004; Sjödin et al. 2004) leading to health risks. Previous studies on PBDEs concentrations and congener patterns in soil from an e-waste sites indicated that a majority of PBDEs contamination came from disposal (Wang et al. 2005; Cai and Jiang 2006; Zou et al. 2007). Investigation on PBDEs transportability in short distances is needed because the transportation of higher brominated congeners in short distances may differ from that of lower brominated congeners (Zhao et al. 2009).

This study aims to apply developed GC–MS/MS methods for analyzing combusted residue and surface soil samples collected from an open e-waste burning site near a rice field to obtain environmental concentrations and to determine possible sources of contamination and mechanisms of transport and deposition of PBDEs between combusted residues and soils. It is hoped that the results obtained will provide a better understanding of the extent of pollution by e-waste and also contribute useful information for further research on the fate and transport of PBDEs, especially for BDE-209.

Materials and methods

Chemicals and reagents

Dichloromethane (DCM), hexane and acetone were purchased from Tedia Company Inc. (Fairfield, OH, USA) and nonane from Fluka (Milwaukee, USA) at pesticide grade. Granular anhydrous sodium sulfate was purchased from Tedia (Fairfield, USA), silica gel 60 (0.063–0.200 mm) from Merck (Whitehouse Station, USA), acid alumina (Brockmann I, Standard Grade, ~150 mesh) from Aldrich Chemical Co. (Milwaukee, USA), copper powder from UniChem (Surrey, UK) and concentrated sulfuric acid from BDH Laboratory Supplies (Dorset, UK) at analytical grade.

PBDEs standard solutions were purchased from Wellington Laboratories (Ontario, Canada) in 2004. A calibration solution BDE-CVS-E (5 ampoules in 1 kit) contained 19 PBDE congeners (BDE-3, 7, 15, 17, 28, 47, 66, 71, 77, 85, 99, 100, 119, 126, 138, 153, 154, 183, and 209). A native standard mix containing BDE-MXD (BDE-17, 47, 66, 100, 153, 183, and 209) and ¹³C-labeled PBDEs mix (MBDE-MXC) (¹³C-labeled BDE-15, 28, 47, 99, 153, 154, and 183) and ¹³C-BDE-209 was used to optimize extraction and clean-up procedure for good recovery.

Sample collection

Samples were collected from a large e-waste open burning site (N: 23.3204; E: 116.3688) in Guiyu, Guangdong

Province, Southeast China, in December 2004 (Fig. 1). Guiyu soils are Ferric Acrisols according to the Soil Map of the People's Republic of China. Guiyu belongs to the sub-tropical climate with an annual average temperature of 21.5 °C, relative humidity of 80 % and a mean annual rainfall of 1721 mm (Yu et al. 2006). In winter the most common wind is from the north or northeast. Dissolved organic carbon ranged from 73 to 200 mg/kg among the different sampling sites. Soil organic carbon ranged from 6.1 to 14.35 % and was generally higher at open burning and near open burning sites than that at a nearby rice field and reservoir site (Zhang et al. 2010). Triplicate residue and soil samples were collected at each sampling site. Six combusted residue (CR) samples were taken from different burning areas of a large open burning site. The combusted residue samples contained black and white combusted residues with incomplete combusted plastic particles and chips. The surface soil samples were collected at eight locations from south to north, 100 m apart, along an 800-m transect away from the open burning site to the Nanyang River (N: 23.3215; E: 116.3692). Soil sample #1 (S1) was collected from the location closest to the open burning site, while S8 sample was the farthest. The surface soil sampling depth was 0–15 cm after the removal of the litter layer. The sample was collected by a hand-held corer that was cleaned with distilled water before and after the sample collection. The collected samples were each wrapped in aluminum

foil, sealed in a double plastic bag and stored at 4 °C until analysis.

Extraction and clean-up

The surface soil or combusted residue samples from each sampling site were thoroughly mixed and freeze-dried, ground and sieved through a 1 mm sieve. About 5–10 g of the dried sample was mixed with 4 g of anhydrous sodium sulfate (which was pre-cleaned with DCM and activated at 140 °C for 24 h), and 5 g of granular copper to remove elemental sulfur. After the spiking with 10–50 ng of MBDE-MXC (^{13}C -labeled PBDEs), the sample was extracted with 80 mL of acetone/hexane (1:1, v:v) for 16 h at 68 °C with Soxhlet extraction. The sample extract was concentrated with rotary evaporator and transferred to a glass bottle with 6 mL Hexane. The extract was loaded on a clean-up column containing, from top to bottom, 2 g of anhydrous sodium sulfate, 1 g of silica gel impregnated with sulfuric acid (44 %), 3 g of 30 % acid silica gel and 1 g active silica gel. *N*-hexane (30 mL) was used for the elution. The eluted solution was loaded onto another column containing 3 g anhydrous sodium sulfate and 4 g acid alumina. The column was eluted with 30 mL hexane/DCM (7:3, v:v), which was then concentrated under gentle nitrogen evaporation apparatus at room temperature. The sample was reconstituted in 50 μL nonane containing ^{13}C -BDE-139 at 100 pg/ μL .

GC/ion trap MS analysis

GC/ion trap MS analysis was performed on a Trace GC/PolariQ ion trap mass spectrometer (Thermo Quest, Austin, TX, USA) in MS/MS mode. A DB-5 ms column (30 m $\times$ 0.25 mm I.D., 0.25 μm film thickness) was used for the determination of congeners from mono- to hepta-BDEs. The temperature program was from 110 °C to 180 °C (held for 1 min) at 8 °C/min, then from 180 to 240 °C (held for 5 min) at 2 °C/min, and then from 240 to 265 °C (held for 6 min) at 2 °C/min. The GC injector temperature was maintained at 290 °C. The temperatures of the MS ion source and transfer line were kept at 250 °C and 300 °C, respectively. Sample extract or standard solution (1 μL) was injected with a solvent delay set at 6 min. The mass spectrometer was operated with electron impact ionization (EI) mode at source temperature of 250 °C and electron energy of 70 eV. Under the EI-MS conditions, the molecular ions ($[\text{M}]^+$ or $[\text{M}+2]^+$) and fragment ions resulting from the loss of Br_2 (i.e., $[\text{M}-\text{Br}_2+2]^+$ or $[\text{M}-\text{Br}_2+4]^+$) were selected as the precursor ions for tandem mass spectrometric analysis. The quantitative ions were selected based on the criteria of peak intensity and ion specificity as well as potential

Fig. 1 The sampling locations in Guiyu, Guangdong province, China

Fig. 2 Chromatograms of selected MS/MS quantification ions of mono to hepta-BDE (a) and the selected ion monitoring chromatogram of deca-BDE (b) from the analysis of a surface soil sample of S2

interference from other compounds. The important instrumental parameters, i.e., the “ q ” value, resonant excitation voltage (REV), excitation time (ET) and isolation time (IT) (Luo et al. 2007) were optimized to obtain the best selectivity and sensitivity. GC/MS analysis of BDE-209 was performed on Agilent 5975 GC/MSD with a DB-5 ms column (15 m $\times$ 0.25 mm I.D., 0.10 μ m film thickness), with the temperature program from 150 $^{\circ}$ C (held for 1 min) to 300 $^{\circ}$ C (held for 18 min) at 30 $^{\circ}$ C/min. The MS detector was operated with EI (70 eV) and selected ion monitoring (SIM) of the high abundance ion (m/z 799.3).

Quality assurance and quality control

The extraction recovery data were obtained with the surrogate standards added to the sample prior to the extraction. Recoveries of spiked control sample (surface soil from a field with no detectable PBDEs) ranged from 87 $\pm$ 3.2 % to 103 $\pm$ 4.5 %. Recoveries of the 13 C-labeled internal standards (MBDE-MXC: 8 13 C-labeled BDEs at 10 ng and 13 C-BDE-209 at 20 ng) in all samples ranged from 78 $\pm$ 3.8 % to 113 $\pm$ 4.2 % except BDE-3 which was 50 %. The poor recovery of BDE-3 was probably due to its relatively low boiling point, resulting in the loss during the concentration procedure.

The analysis of calibration standards showed peak signal-to-noise ratio (S/N) of the selected ion better than three for all calibration points. The limits of detections (LOD) were 0.01–0.1 ng/g for the mono- to hepta-BDEs and 1 ng/g for deca-BDE. Calibration curve standards for mono- to hepta-BDE (from 1 to 1,000 μ g/g) and deca-BDE (from 100 to 10,000 μ g/g) at five concentration levels were subjected to the same extraction and clean-up steps described above. Linear responses with r^2 of 0.9993–0.9999 and 0.9991 were obtained for mono- to hepta-BDE and deca-BDE, respectively. The identification criteria were both the determination of correct retention time within <0.2 min of the expected retention time and the detection of the two confirmation ions at the area ratios within 10 % variation. Retention time shift in the chromatogram was corrected using the isotope internal standard. Quantification was based on isotope internal standard method.

Results and discussion

The typical chromatograms of PBDEs detected in S2 soil sample obtained from the GC/ion trap MS and GC/MSD analyses are shown in Fig. 2. All targeted PBDEs congeners were detected in the surface soil sample. Table 1 summarizes the concentrations (ng/g dry weight) of the PBDEs in the combusted residue and surface soil samples

Table 1 Concentrations of PBDEs congeners in the combusted residue and soil samples collected from the open burning site in Guiyu

Con.	CR1	CR2	CR3	CR4	CR5	CR6	S1	S2	S3	S4	S5	S6	S7	S8
BDE-3	3.0 $\pm$ 0.2	4.2 $\pm$ 1.1	7.7 $\pm$ 2.2	5.0 $\pm$ 1.2	3.1 $\pm$ 0.8	9.0 $\pm$ 0.5	1.1 $\pm$ 0.1	0.9 $\pm$ 0.1	1.2 $\pm$ 0.1	0.8 $\pm$ 0.2	0.8 $\pm$ 0.1	0.7 $\pm$ 0.2	n.d.	0.1 $\pm$ 0.1
BDE-7	10 $\pm$ 0.9	24 $\pm$ 3.8	17 $\pm$ 3.4	29 $\pm$ 4.4	18 $\pm$ 2.3	20 $\pm$ 4.4	1 $\pm$ 0.1	1.9 $\pm$ 0.3	1.8 $\pm$ 0.3	2.8 $\pm$ 1.2	3.4 $\pm$ 1.4	1.1 $\pm$ 0.5	0.1 $\pm$ 0.1	0.2 $\pm$ 0.1
BDE-15	13 $\pm$ 2.3	25 $\pm$ 3.5	19 $\pm$ 3.6	16 $\pm$ 5.3	24 $\pm$ 3.1	17 $\pm$ 2.2	7.6 $\pm$ 1.6	4.3 $\pm$ 1.3	3.4 $\pm$ 0.2	3.3 $\pm$ 1.5	1.8 $\pm$ 0.9	0.9 $\pm$ 0.3	0.6 $\pm$ 0.2	1.2 $\pm$ 0.2
BDE-17	38 $\pm$ 3.5	38 $\pm$ 4.3	40 $\pm$ 5.6	34 $\pm$ 3.4	51 $\pm$ 4.3	23 $\pm$ 3.2	5.7 $\pm$ 1.4	4.3 $\pm$ 1.4	3.5 $\pm$ 0.4	3.3 $\pm$ 1.5	2.5 $\pm$ 1.1	1.2 $\pm$ 0.6	0.4 $\pm$ 0.1	0.9 $\pm$ 0.1
BDE-28	86 $\pm$ 7.1	78 $\pm$ 6.2	58 $\pm$ 4.7	132 $\pm$ 6.8	61 $\pm$ 5.2	135 $\pm$ 9.8	19.8 $\pm$ 1.9	14.5 $\pm$ 5.8	18.4 $\pm$ 5.3	26.6 $\pm$ 5.1	6.8 $\pm$ 2.7	4.9 $\pm$ 1.87	2.4 $\pm$ 0.5	4.8 $\pm$ 0.3
BDE-47	925 $\pm$ 23	450 $\pm$ 19	452 $\pm$ 24	1,099 $\pm$ 35	850 $\pm$ 67	682 $\pm$ 13	158 $\pm$ 10.4	99.5 $\pm$ 14.8	85.2 $\pm$ 13.7	62 $\pm$ 12.9	15.9 $\pm$ 4.2	14 $\pm$ 2.1	23.4 $\pm$ 6.8	33.9 $\pm$ 9.8
BDE-66	157 $\pm$ 13	87 $\pm$ 5.9	51 $\pm$ 5.9	154 $\pm$ 4.8	295 $\pm$ 9.8	210 $\pm$ 12	26.2 $\pm$ 1.4	10.3 $\pm$ 1.41	6.5 $\pm$ 1.3	11.3 $\pm$ 3.2	3.9 $\pm$ 1.1	1.2 $\pm$ 0.7	4.0 $\pm$ 0.4	9.6 $\pm$ 2.8
BDE-100	247 $\pm$ 3	46 $\pm$ 4.3	36 $\pm$ 3.2	17 $\pm$ 9.4	145 $\pm$ 19	152 $\pm$ 12	11.6 $\pm$ 1.4	10 $\pm$ 1.21	8.8 $\pm$ 3.6	7 $\pm$ 1.34	2.6 $\pm$ 0.9	1.2 $\pm$ 1.1	3.6 $\pm$ 0.2	2.8 $\pm$ 0.9
BDE-99	578 $\pm$ 13	615 $\pm$ 46	595 $\pm$ 10	758 $\pm$ 98	1,270 $\pm$ 95	621 $\pm$ 33	375 $\pm$ 21.9	150 $\pm$ 22.1	100 $\pm$ 19.8	66 $\pm$ 19.8	18 $\pm$ 5.45	19 $\pm$ 2.8	25.5 $\pm$ 3.8	21.9 $\pm$ 1.28
BDE-154	361 $\pm$ 28	44 $\pm$ 2.9	16 $\pm$ 2.8	152 $\pm$ 5.0	63 $\pm$ 8.8	178 $\pm$ 12	138 $\pm$ 10.8	146 $\pm$ 31.7	112 $\pm$ 24.3	11 $\pm$ 2.8	3.6 $\pm$ 1.87	4.5 $\pm$ 1.8	6.2 $\pm$ 0.5	18.3 $\pm$ 2.8
BDE-153	470 $\pm$ 68	308 $\pm$ 23	109 $\pm$ 10	377 $\pm$ 24	412 $\pm$ 33	629 $\pm$ 43	116 $\pm$ 17.8	131 $\pm$ 20.8	108 $\pm$ 19.5	15 $\pm$ 2.1	16.7 $\pm$ 3.9	23.5 $\pm$ 4.9	24.8 $\pm$ 1.8	14.1 $\pm$ 1.7
BDE-183	93 $\pm$ 18	682 $\pm$ 24	449 $\pm$ 67	409 $\pm$ 76	1,336 $\pm$ 23	1,206 $\pm$ 56	162 $\pm$ 18.1	159 $\pm$ 21.9	138 $\pm$ 14.8	119 $\pm$ 40.7	56 $\pm$ 12.6	54.7 $\pm$ 8.2	46.4 $\pm$ 0.5	50.2 $\pm$ 12.7
BDE-209	67 $\pm$ 3.3	280 $\pm$ 14	530 $\pm$ 87	498 $\pm$ 24	1,910 $\pm$ 68	1200 $\pm$ 45	400.3 $\pm$ 35.5	230.5 $\pm$ 32.4	280.3 $\pm$ 35.8	329.4 $\pm$ 32.8	130.9 $\pm$ 23	120.5 $\pm$ 15.2	81.1 $\pm$ 9.2	71.1 $\pm$ 14.8
Σ PBDEs	3,048	2,682	2,379	3,681	6,238	5,082	1,422.3	1,052.2	867.1	657.5	262.9	247.4	218.5	229.1

The values represent standard deviation; $n = 3$, concentration unit: ng/g dry weight

Con. concentration, Σ PBDEs total PBDEs concentration, CR combusted residue, S soil sample, n.d. not detected

Fig. 3 PBDEs concentrations and congener distributions in the combusted residue (CR) and soil samples from Guiyu. The combusted residue PBDEs data were averaged from the six combusted residue samples collected in the burning site

collected from the e-wastes burning site. Concentrations of total PBDEs (from the targeted mono- to hepta-BDEs and deca-BDE) ranged from 2,682 to 6,238 ng/g with a median of 3,071 ng/g for the six combusted residue samples from the open burning site where various dismantled and undismantled e-waste materials were combusted. Because the combusted residue samples were collected from different locations with diverse e-waste material, PBDEs were detected at various concentrations. It was found that total PBDEs concentrations in the combusted residue-5 (CR5) sample were greater than at the other sites (Table 1). The results might be explained from the different characteristics of the soil samples. While other combusted residue samples were gray in color, the CR5 sample was black with fine particle residues of plastic and circuit boards, probably due to incomplete combustion. Higher concentrations of PBDEs in CR5 might be attributed to the black particles. On the other hand, the total PBDEs concentrations in CR2 and CR3 were relatively low because some soil was found to be mixed into the combusted residue samples during the sampling. The median level of total PBDEs was similar to the published results of 2909 and 3230 ng/g in the e-waste recycling sites of Guiyu and Qingyuan, respectively (Gao et al. 2011).

The congener patterns of PBDEs detected in the six combusted residue samples were not the same. However, BDE-209, 183, 47, 99, and 153 were the dominant congeners in all combusted residue samples (Fig. 3), likely due to the same combustion source of commercial products. Concentrations of BDE-209 were 530, 1,910 and 1,200 ng/g in the samples of CR3, CR5 and CR6 with their respective percentage being 22.3, 30.6 and 23.6 % of total PBDEs. BDE-183 represented 18.9 to 25.4 % of the total PBDEs, with the concentrations at 449 ng/g in CR3, 682 ng/g in CR2, 1206 ng/g in CR5 and 1336 ng/g in CR6. The larger concentration of BDE-183 was probably because this

chemical is considered as a marker compound for the octamix PBDEs formulation (Law et al. 2003). Relatively low concentrations of BDE-209 and BDE-183 were detected in CR1, which also gave a different congener pattern compared to other combusted residue samples. The CR1 sample contained large concentrations of BDE-99, 47, and 153 indicating that this particular sample was probably associated with commercial penta-BDE products. In summary, the analytical results of combusted residue samples (Table 1) indicated that the major e-waste materials treated in the burn site contained the three technical fire-retardant products, with the deca-BDE as the dominant one. The results agree with the fact that deca-BDE is currently the major flame retardant product in use.

The total PBDEs concentrations in the eight soil samples ranged from 218.5 ng/g (S8) to 1,422.3 ng/g (S1). The concentrations of PBDEs in soil samples were significantly less than those in the burned combusted residue samples. The total PBDE concentrations in this study were similar to previous published results from a printer roller dump site (893–2,890 ng/g), duck pond (263–604 ng/g), and much higher than those from a rice field (34.7–70.9 ng/g) and reservoir (2.0–6.2 ng/g) (Leung et al. 2007). However, there were much higher concentrations of total PBDEs at 3230 and 2909 ng/g in surface soils from Qingyuan and Guiyu, respectively (Gao et al. 2011). The observed PBDE concentrations in the environmental samples indicated that the PBDEs contamination around the e-wastes open burning site in Guiyu was serious. The levels of PBDEs in environmental soil from Guiyu was about 1,000 times greater than those determined in the soil samples collected near the foam production facilities using the penta-BDE mixture as flame retardant in the UK and Norway (Wong et al. 2007).

The major concentration pattern of PBDEs in the soil samples was similar to the pattern of combusted residue

Fig. 4 Relationship between the total PBDEs concentrations and distance from e-wastes open burning site. The distance between samples was 100 m. The PBDEs data in combusted residue (CR) were averaged from the six combusted residue samples collected in the burning site

samples (Fig. 3). BDE-209, 183, 153, 154, 99, and 47 were also the major congeners detected in the soil samples. BDE-209 was the predominant congener consisting of 28.1 % of the total PBDEs in S1 (concentration of 400.3 ng/g) and 39 % in S8 (concentration of 91.1 ng/g). The percentage of BDE-209 was higher than 40 % in S5, S6 and S7. The averaged proportion of BDE-209 in total PBDEs in soils (average 38 %) was greater than that in the burned combusted residues (average 17.1 %). However, the average absolute concentration of BDE-209 in soils (216.8 ng/g) was less than those in combusted residues (747.5 ng/g). BDE-183 was also detected at larger

proportions (from 11.4 % in S1 and 21.9 % in S8), which was different from those detected in European background soils where BDE-183 was a minor contributor but BDE-47, 99, 100, 153, and 154 were most frequently detected (Hassanin et al. 2004).

The concentrations of PBDEs and congener patterns in the samples collected from the open burning site were also different from those in soils collected from e-waste dumping sites (Wang et al. 2005; Cai and Jiang 2006). The open burning of computer casings and circuit boards stripped of metal parts may produce toxic fumes and ashes containing organic pollutants. 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 (Wong et al. 2007). The published data indicated that the PBDEs existed in the soil samples with concentrations up to 600 ng/g (dry weight) and tetra- (BDE-47), penta- (BDE-99) and hexa-BDE (BDE-139, BDE-153, BDE-154) were the predominant isomers and its congener pattern was similar to a commercial penta-BDE formulation which probably resulted from the commercial penta-BDE product used in the fire retardants because the soil samples were collected in the vicinity of a site for the e-wastes disposal in Taizhou, Zhejiang (Cai and Jiang 2006). Results are different from PBDEs congener distributions in surface soil of an electronic waste dismantling site from Shenzhen, of which BDE-209 was the predominant (up to 85–99 % of total PBDEs) (Qin et al. 2011). Uncontrolled disposal and recycling have apparently resulted in soil contamination with PBDEs. Higher brominated congeners (octa- and deca-BDEs) were also found with much greater concentrations in the samples from the open burning site in this study. This result is in line with other studies from the Pearl River Delta (PRD) where high BDE-209 concentrations were found in soils from the vicinity of PBDEs manufacturing sites (Luo et al. 2009; Qin et al. 2011).

The observed concentrations of PBDEs in the environmental samples indicated that the PBDEs contamination around the e-wastes open burning site in Guiyu is serious. The levels of PBDEs in environmental soil from Guiyu was about 1,000 times greater than those determined in soil samples collected near foam production facilities using the penta-BDE mixture as flame retardant in the UK and Norway (Harrad and Hunter 2006). Electronic wastes can cause major environmental contamination during the transportation, landfill, and incineration if not properly treated. Observations in soil samples from Guiyu indicated that uncontrolled open burning was one of the major sources of soil contamination of PBDEs.

As demonstrated in Fig. 4a, there was a general decline in concentrations of total PBDEs as a function of the distance from the combustion site (S1 to S8). The highest concentrations of PBDEs were detected in S1, collected from the site located closest to the open burning site and the soil with the lowest concentration was collected 800 m from the burning site. The total PBDE concentrations decreased dramatically with increasing distance from the burned site, suggesting that the combusted activities were the major source of PBDE contamination in the field. BDE-209 concentrations generally decreased from the open burning site to the remote areas (S1 to S8) (Fig. 4b). Although BDE-47, 153, 154 and 183 have a similar decreasing trend to BDE-209, their reduced concentration ratios were much lower than that of BDE-209 (Fig. 4b).

The obtained data showed that PBDEs transportability of higher brominated congeners for short distances could differ from that of lower brominated congeners.

The distributions of PBDE congeners in soils were similar to those in combusted residues, partly because PBDEs are relatively stable in the air and soil (Lee et al. 2004). The obtained data on PBDEs concentrations and congener patterns suggested that the major contamination of PBDEs in soil might come from the combusted residue transportation and deposit. The soil samples close to open burning of e-waste were influenced by the combusted residue which contained high levels of PBDEs possibly because some soil sample had been collected directly below shredded pieces of printed circuit board. The obtained data might also suggest that the PBDE contamination in the soils from areas surrounding e-waste facilities mainly came from the e-waste recycling sites via air transport (Gao et al. 2011). However, the adsorption capacity to particle were various for different PBDE congeners. The particle size and direction of wind could change the settlement rate. It was obvious that PBDEs diffusion from the point pollution source has made the dominant contribution to PBDEs contamination in the surrounding regions.

Conclusions

The concentrations of PBDEs in combusted residues collected from the e-waste open burning site in Guiyu were much greater than those in soil samples. BDE-209, 183, 153, 154, 99, and 47 that are the major components of commercial flame retardant products were detected in both combusted residue and soil samples in high concentrations. The total concentrations of PBDEs in the soil samples decreased with increasing distance from the e-wastes burning site. The results suggest that field soils might be contaminated by air transportation of combusted residues from e-waste incineration. The uncontrolled open burning of e-waste has resulted in serious environmental contamination of PBDEs.

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