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Polybrominated Diphenyl Ethers in Leaves and Soil from Typical Electronic Waste Polluted Area in South China

Z. Z. Yang · X. R. Zhao · Q. Zhao · Z. F. Qin · X. F. Qin · X. B. Xu · Z. X. Jin · C. X. Xu

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Abstract Polybrominated diphenyl ethers (PBDEs) in leaves and soil from typical e-waste polluted area in South China were investigated. The concentrations (ng/g dry weight) of PBDE congeners and ∑PBDE of five leaf samples were much lower than those in soil sample. The general patterns of ∑di-BDEs to ∑hepta-BDEs percentage distribution in leaf samples were similar to those of the soil sample, except the percentage of BDE209 which were lower than in soil. The percentages of ∑di-BDEs to ∑hepta-BDEs in soil were in the range of those in leaf samples. The results showed that the contamination of PBDEs in the leaf samples had good correlation with the soil around them.

Keywords PBDEs · Leaves · Soil · e-waste

Polybrominated diphenyl ethers (PBDEs) are a group of additive brominated flame retardants that have been used widely in commercial and household products for decades (Alaee et al. 2003; Watanabe and Sakai 2003). Similar in physicochemical properties to a number of other persistent organic pollutants (POPs), they are persistent in the environment, bioaccumulated in biota, and are atmospherically transported long distances from their sources (Ikonomou et al. 2002). Because of their ubiquity and potential toxicity, two of the three commercial PBDE mixtures ("penta-BDE" and "octa-BDE") have been banned by the European Union and by several US states.

Sources of environmental PBDEs contamination include leakage from consumer products and industrial facilities that manufacture PBDEs, but also from disposal sites of PBDE-containing products. To monitor the distribution of PBDEs in the environment, fish (Johnson and Olson 2001), birds (Voorspoels et al. 2006), bird eggs (Jonathan et al. 2006), and other biota have been used (Pettersson et al. 2004; Naert et al. 2006). On the assumption that their POPs concentrations broadly reflect ambient levels, herbage (Hassanin et al. 2005) and tree bark (Zhu and Hites 2006) have been used as 'environmental media' to investigate the long-range movement of PBDEs through the atmosphere. As facile samples, leaves should be researched in the distribution of PBDEs, but there are seldom reports on this point so far. We aimed the relationship between the PBDEs in plant leaves and those in soil around in an e-waste polluted area.

Materials and Methods

An EPA method 1614 standard solution of 39 PBDE congeners from Accustandard (New Haven, CT, USA) was used for the quantitation of the mono-through hepta-brominated BDEs which contained the following PBDE congeners: mono-BDEs 1, 2, and 3; di-BDEs 7, 8, 10, 11, 12, 13, and 15; tri-BDEs 17, 25, 28, 30, 32, 33, 35, and 37;

Z. Z. Yang · X. R. Zhao (✉) · Q. Zhao · Z. F. Qin · X. F. Qin · X. B. Xu
State Key Laboratory of Environmental Chemistry and Ecotoxicology, Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, PO Box 2871, 18 Shuangqing Road, Haidian District, Beijing 100085, People's Republic of China
e-mail: hhyyxxrr@163.com

Z. X. Jin
Taizhou University, Taizhou City 317000, Zhejiang Province, People's Republic of China

C. X. Xu
Yuanqiao Middle School, Taizhou City 318025, Zhejiang Province, People's Republic of China

tetra-BDEs 47, 49, 66, 71, 75, and 77; penta-BDEs 85, 99, 100, 116, 118, 119, and 126; hexa-BDEs 138, 153, 154, 155, and 166; and hepta-BDEs 181, 183, and 190. And, another PBDE analytical standard EO-5278 was purchased from Cambridge Isotope Laboratories, Inc. (MA, USA). EO-5278 was used for quantitation of BDE-209 which contained BDE-28, 47, 99, 100, 153, 154, 183, and 209. The internal surrogate standards used were decachlorobiphenyl (CB-209) from Supelco (Bellfonte, USA). Hexane, dichloromethane used for the extraction and cleanup procedures were pesticide grade (J. T. Baker, USA), and other solvents and reagents were of analytical grade.

Due to there lower labor cost and less stringent environmental regulations, electronic waste (e-waste) were imported and formed processing centers in some South China provinces such as Zhejiang and Guangdong. As the Chinese Government tightened up its regulations regarding e-waste, some e-waste recycling centers in South China were disappeared or secreted and many dump and disposal sites fell into desuetude. In this study, we collected the common plant leaves and surface soil near an abandoned dump which was said one of the earliest sites to dump and bury unsalvageable materials of e-waste.

The surface soil and five plant leaf samples were collected in May of 2006 including *Pteridium aquilinum* var. *latiusculum*,*Pteris multifida* Poir., *Sorghum bicolor* (L.) Moench, *Rumex japonicus* Houtt., and *Erigeron annuus* (L.) Pers. which were expressed as Pa, Pm, Sb, Rj, and Ea, respectively. The leaves were rinsed with distilled water carefully to remove the dust on the surface. After been freeze-dried, the soil was ground and sieved to 40 mesh completely, the leaf samples were crushed and well mixed respectively. Then they were preserved frozen at −20°C until analysis.

One gram of soil or leaf sample was ground with anhydrous sodium sulfate into free-flowing powder. The samples were extracted with 200 mL of hexane/dichloromethane (1:1, v/v) in Soxhlet extraction mode for 24 h. Before extraction, 1 mL of PCB209 solution at a concentration of 10 μg/L was added as a surrogate standard. Then the concentrated extracts were cleaned on a 15-mm i.d. column packed, from the bottom to top, with 2 g silver nitrate ($AgNO_3$) silica (10%, w/w), 1 g activated silica gel, 3 g basic silica gel (EPA Method 1614, Sect. 7.5.1.3), 1 g activated silica gel, 4 g acid silica gel (44% concentrated sulfuric acid, w/w), 4 g acid silica gel (22% concentrated sulfuric acid, w/w), 1 g activated silica gel, and 1 cm anhydrous sodium sulfate. The PBDE mixture were eluted with 70 mL of hexane:dichloromethane (1:1), and the final elutes volume were reduced to 1 mL for soil and to 50 μL for leaf samples under a gentle N2 stream. Throughout the extraction, cleanup and analysis procedure, the analytes were protected from light by wrapping the containers with aluminum foil or by using amber glassware.

The samples were analyzed on an Agilent 6890 series gas chromatograph coupled to an Agilent 5973 mass spectrometer using negative chemical ionization (NCI) in the selected ion monitoring mode. A DB-5MS (30 m × 0.25 mm i.d., 0.25 μm film thickness) capillary column was used for the determination of PBDE congeners except for BDE-209. Methane was used as a chemical ionization moderating gas and helium as the carrier gas at a flow rate of 1 mL/min. The ion source and interface temperatures were set to 150 and 300°C, respectively. The GC oven temperature program was carried out as follows: initial temperature 100°C held for 1 min, increased to 150°C at 10°C/min held 5 min, and then to 280°C at 5°C/min, to 290°C at 10°C/min, held for 15 min. For the determination of BDE-209, a DB-5 MS (15 m × 0.25 mm i.d., 0.25 μm film thickness) capillary column was used and the carrier gas at a flow rate of 1 mL/min. The temperature program was from 80°C (1 min) to 200°C at 10°C/min, and to 300°C (held 15 min) at 20°C/min. Both experiments were used the splitless injection mode during 1 min and injected 1 μL (injector temperature 265°C). The compounds were monitored at *m/z* 79 and 81 (for PBDE congeners), and *m/z* 486.7 and 488.7 (for BDE-209 only). The PCB CB-209 was detected at *m/z* 496 and 498.

Identifications of all compounds were confirmed, and concentrations were measured using an external quantification standard consisting of known amounts of all the target compounds. Three quality control criteria were used to ensure the correct identification of the target compounds: (a) the GC retention times matched those of the standard compounds within ±0.05 min. (b) The signal-to-noise ratio was greater than 3:1. (c) The isotopic ratios between the quantitative and confirmation ions were within ±15% of the theoretical values. For every set of six samples, a procedural blank were run in parallel to check the interference and cross-contamination. For the poor spiked recoveries (<50%) and low responded of mono-BDEs in NCI mode in this study, we did not analyze those compounds in the samples. All results of target analysis reported in the study were means of duplicate analyses, and the residue concentrations in samples below detection limits were regarded to be equal to zero in calculation of sum, means and so on. The detection limits, defined as a signal of three times the noise level, were in the range of 0.001 ng/g dry weight to 0.05 ng/g dry weight for di- to hepta-BDE, and 0.1 ng/g dry weight for deca-BDE. The matrix spike recoveries of the 37 PBDE congeners analyzed (the di- to hepta-BDEs of the 39 PBDE congeners standard solution and the BDE209) were between 75% and 115%. The recoveries of internal surrogate (CB209) in all samples tested were between 85% and 110%.

Results and Discussion

The concentrations of 37 PBDEs and $\sum$PBDE (sum of the di- to hepta-BDEs of the 39 PBDE congeners standard

solution and the BDE209) in the soil and leave samples are given in Table 1. All the 37 PBDE congeners we analyzed were detected in the soil sample with a large range from 0.9 to 5,469 ng/g dry weight. The PBDE congener percentage profile of the soil sample is shown in Fig. 1, black bars. Different from the sediments of Pearl River Delta (Mai et al. 2005), the major PBDE congeners in soil were BDE99, BDE47 and BDE209 with the percentage of 21.47%, 21.00% and 12.90%, respectively. The PBDE congener profile of soil differed from that of the three major commercial PBDE products (Mark et al. 2006). Similar to the method of Linyan Zhu (Zhu and Hites 2006), we fitted the observed congener profile to a linear combination of the profiles of the commercial products (Fig. 1). We suggest that the main contamination were come from technical products penta-PBDE (DE-71) and deca-PBDE (102E) with the percentage of 85% and 13%, respectively. Since PBDEs were gradually degrade to lower brominated PBDE congeners or other compounds by chemical and biological processes (Catherine and Edwin 2007; Gunilla et al. 2004; Van den Steen et al. 2007), there should be more percentage of technical products deca-PBDE existed period of time ago. We could even conjecture that all the PBDEs in soil there were come from technical product deca-PBDE. Whatever, the lower percentage of BDE47 and BDE99, which were major components of technical product penta-PBDE, and the higher percentage in low brominated PBDE congeners in soil compared with the linear combination of the profiles of the commercial products (Fig. 1) indicated that it had been polluted by PBDEs for a long time which were consistent with the depiction of the dweller.

As shown in Table 1, the concentrations (ng/g dry weight) of PBDE congeners and ∑PBDE of the five leaf samples were much lower than those in the soil. Many controlled exposure experiments and field experiments had shown that the uptake of lipophilic organic pollutants through roots was not a significant pathway of accumulation (Staci and Ronald 1995). The PBDEs existed in those leaves should be mostly come from air. Similar to the soil, the major PBDE congeners in leaf simples were BDE47 (range from 17.21% to 28.75%) and BDE99 (range from 14.11% to 26.62%), but the percentage of BDE209 was much lower than that in soil with the range from 1.55% to 5.33%. Zhu and Hites (2006) had reported that BDE209 was the dominant congener of PBDEs deposited in tree bark with the percentage of 66%. As Hoh and Hites (2005) had shown, the less brominated PBDEs tend to partition to the gas phase, and deca-BDE tends to partition to the particle phase. And, Zhu also suggested that the less brominated compounds likely partitioned from the atmospheric vapor phase directly into the lipids of the tree bark, and the more brominated compounds likely accumulated by direct deposition of the particles onto the tree bark's surface. So the lower percentage of BDE209 in leaves compared with soil in our study maybe due to the rinse pre-experiment, and the relatively low bioaccumulation potential of BDE209 were similar to the biota from the North Sea (Jan et al. 2002).

The percentage distribution of the sum of the di-BDEs to the sum of hepta-BDEs and deca-BDE in soil and leaf samples are illustrated in Fig. 2. The general patterns of PBDEs percentage distribution in leaf samples were similar to those in soil sample. Due to the lower vapor pressure or relatively low bioaccumulation potential of BDE209, the

Table 1 The concentrations of 37 PBDEs and ∑PBDE (sum of the di- to hepta-BDEs of the 39 PBDE congeners standard solution and the BDE209) in soil and five leaf samples (ng/g dry weight)

Name	soil	Pa	Pm	Sb	Rj	Ea
BDE10	3.42	0.10	ND	ND	ND	1.00
BDE7	1.93	0.20	ND	ND	ND	ND
BDE11	217.84	4.30	4.40	2.00	1.20	31.00
BDE8	317.20	ND	ND	2.00	ND	ND
BDE12 + 13	18.96	ND	ND	ND	ND	2.00
BDE15	104.21	1.50	1.50	ND	0.90	10.00
BDE30	0.94	0.50	0.10	ND	ND	1.00
BDE32	53.54	0.90	2.00	ND	0.60	2.00
BDE17 + 25	374.55	ND	0.40	3.00	7.80	11.00
BDE28 + 33	1021.26	8.80	0.90	7.00	1.70	17.00
BDE35	54.47	0.80	1.00	ND	0.60	2.00
BDE37	188.13	3.00	3.60	2.00	2.20	5.00
BDE75	120.51	10.90	8.50	8.00	12.20	36.00
BDE49	1763.35	7.60	10.00	7.00	22.50	16.00
BDE71	138.15	ND	ND	ND	ND	ND
BDE47	5349.07	32.50	33.40	42.00	47.80	57.00
BDE66	2121.24	13.60	12.20	10.00	28.40	20.00
BDE77	112.55	3.80	0.90	1.00	2.40	2.00
BDE100	229.25	5.60	6.10	8.00	19.60	11.00
BDE119	176.45	1.80	0.70	ND	ND	ND
BDE99	5469.37	25.20	16.70	43.00	58.70	46.00
BDE116	1294.18	1.20	ND	ND	ND	ND
BDE118	947.20	3.30	3.60	3.00	15.20	7.00
BDE85	299.80	3.70	2.20	5.00	13.20	6.00
BDE126 + 155	267.45	ND	1.20	1.00	ND	1.00
BDE154	219.70	0.40	0.90	2.00	3.50	3.00
BDE153	849.96	0.30	0.80	6.00	17.60	11.00
BDE138	132.30	1.80	0.30	2.00	6.40	4.00
BDE166	147.25	0.40	ND	ND	ND	ND
BDE183	180.17	1.70	0.20	4.00	0.30	9.00
BDE181	7.62	5.60	0.70	1.00	ND	ND
BDE190	8.77	0.10	1.00	ND	0.10	ND
BDE209	3288.06	3.94	2.85	2.51	14.83	15.00
∑PBDEs	25478.84	143.54	116.15	161.51	277.73	326.00

ND: not detected

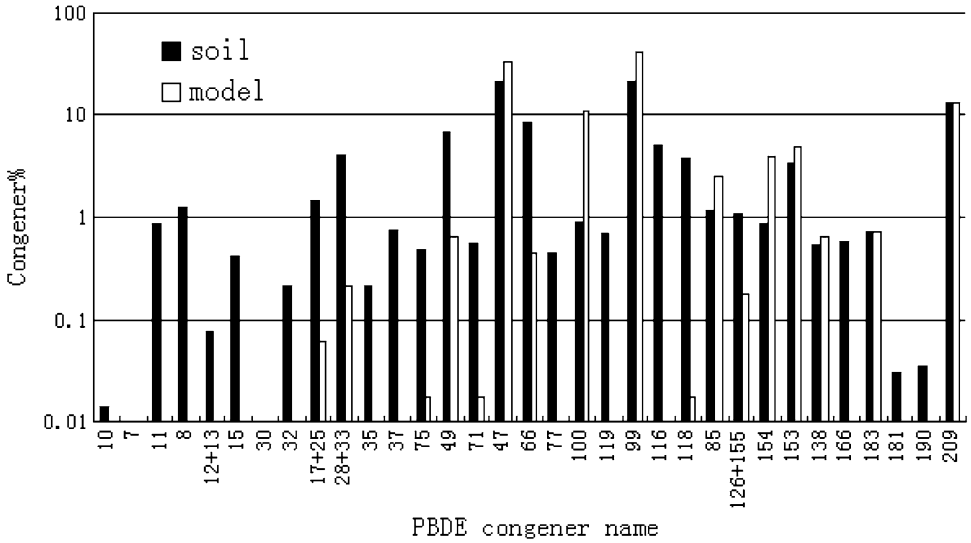

Fig. 1 PBDE congener profile for soil sample (black bars) and fitted congener profiles (white bars) based on a mixture of 85% penta-, 2% octa-, and 13% deca-BDE products

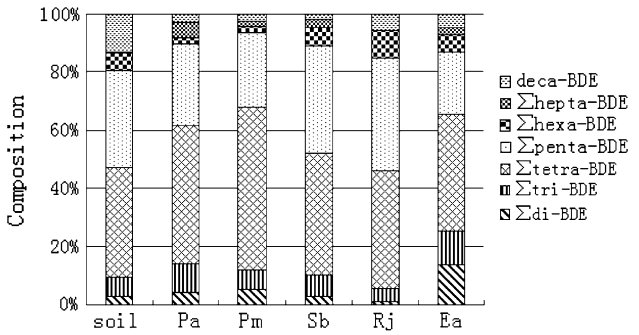

Fig. 2 The percentage distribution of the sum of the di-BDEs to the sum of hepta-BDEs and deca-BDE in soil and leaf samples. ∑di-BDE: sum of di-BDEs 7, 8, 10, 11, 12, 13, and 15; ∑tri-BDE: sum of tri-BDEs 17, 25, 28, 30, 32, 33, 35, and 37; ∑tetra-BDE: sum of tetra-BDEs 47, 49, 66, 71, 75, and 77; ∑penta-BDE: sum of penta-BDEs 85, 99, 100, 116, 118, 119, and 126; ∑hexa-BDE: sum of hexa-BDEs 138, 153, 154, 155, and 166; and∑hepta-BDE: sum of hepta-BDEs 181, 183, and 190

percentage of BDE209 in soil was higher than those in leaf samples. The percentages of ∑di-BDEs to ∑hepta-BDEs in soil were in the range of those in leaf samples. The results showed that the contamination of PBDEs in leaf samples had good correlation with the soil around them, and further investigation should be done to choose the fit vegetable species to detect the contamination levels in larger areas.

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