Bull Environ Contam Toxicol (2010) 84:260–263
DOI 10.1007/s00128-009-9924-0

Vertical Distribution of Polybrominated Diphenyl Ethers (PBDEs) in Soil Cores Taken from a Typical Electronic Waste Polluted Area in South China

Z. Z. Yang · Y. F. Li · Y. X. Hou · H. Y. Liang · Z. F. Qin · S. Fu

Received: 30 July 2009 / Accepted: 8 December 2009 / Published online: 20 December 2009

Abstract 37 PBDE congeners were analyzed at six different depths in two soil cores taken from a typical electronic waste polluted area in South China. The PBDEs were congregated in the surface layer (0–5 cm) of soil cores and were 29 times in MK and 18 times in NW higher than the second lower layers (5–10 cm). As a whole, the concentrations of PBDEs were decreased with the soil depth increased in two cores. Lower brominated PBDE had higher penetrability than the deca-BDE in soil. The deca-BDE could be detected in deeper soil layers (15–20 cm in MK and 20–30 cm in NW) and the percentage of deca-BDE decreased with the increase of depth.

Keywords Polybrominated diphenyl ethers (PBDEs) · Soil core · Electronic waste · Vertical distribution

Polybrominated diphenyl ethers (PBDEs) are a group of additive brominated flame retardants (BFRs) that have been used widely in commercial and household products for decades (Alaee et al. 2003; Watanabe and Sakai 2003). PBDEs have been manufactured as three commercial formulations: PentaBDE composed mainly of tri- to hexa-BDEs, OctaBDE composed mainly of hexa- to octa-BDEs, and DecaBDE composed mainly of BDE-209. Due to their ubiquitous presence and persistence in the environment and potential toxicities such as thyroid hormone disrupting, neurotoxic, and developmental effects to wildlife and humans (Darnerud et al. 2001), two of the three commercial PBDE formulations (pentaBDE and octaBDE) have been banned by the European Union and by several U.S. states. DecaBDE remains in use and had a market demand of 56,100 metric tons in 2001 (Law et al. 2006). The estimated domestic production of predominant commercial deca-BDE mixture in China increased by 200% between 2000 and 2005, from 10,000 to about 30,000 tonnes (Chen et al. 2006). And due to lower labor cost and less stringent environmental regulations, China appears to be a large dumping site of e-wastes imported from overseas legally and illegally in recent years (Wang et al. 2005).

PBDEs are very hydrophobic (logKow 5-10) and resistant to environmental degradation processes. The temporal trends of the occurrence of PBDEs in the environment can also be derived from undisturbed and well-dated sediments in seas or lakes (Zegers et al. 2003). Soils represent an important reservoir for persistent organic pollutants (POPs) in the terrestrial environment and thus the fate of contaminants deposited to the surface soils is important to understand. Although describing the mass transport of chemicals in soils is important for understanding the overall environmental fate of multimedia contaminants, there are only a limited number of studies that have actually measured the vertical distribution of persistent organic pollutants (Armitage et al. 2006). In the present work, 37 PBDE congeners were analyzed at six different depths in two soil cores taken from a typical electronic waste

---

Z. Z. Yang (✉) · H. Y. Liang
Department of Public Health, Xinxiang Medical College,
453003 Xinxiang, Henan, China
e-mail: yzz4321@126.com

Y. F. Li · Y. X. Hou
College of Chemistry and Chemical Engineering,
Henan Institute of Science and Technology,
453003 Xinxiang, Henan, China

Z. Z. Yang · Z. F. Qin · S. Fu
State Key Laboratory of Environmental Chemistry
and Ecotoxicology, Research Center for Eco-Environmental
Sciences, Chinese Academy of Sciences, Post Office Box 2871,
18 Shuangqing Road, Haidian District, 100085 Beijing, China

polluted area in South China. The purpose of this study was to contribute to the available data in the scientific literature regarding the vertical distribution of PBDEs in soil profiles.

Materials and Methods

An EPA method 1614 standard solution of 39 PBDE congeners from Accustandard (New Haven, CT) was used for the quantification 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; 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). EO-5278 was used for quantitative analysis 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.

In November 2006, two soil cores were collected at the undisturbed non-agricultural sites near an e-waste recycling village in Zhejiang province, China, which named MK and NW, respectively. Every soil core was collected by gently excavating a pit at the site location and then collecting soil at various depths from the side using a solvent-rinsed stainless steel spatula. Loose decaying litter was not included in the depth profile. Soil depths were carefully measured from the soil surface using a ruler. This sampling technique was preferred over taking soil cores as in previous studies (Cousins et al. 1999). Six different depth soil samples were collected in every soil core: 0–5, 5–10, 10–15, 15–20, 20–30 and 30–50 cm. The samples were transferred directly into pre-cleaned aluminium foil envelopes. After been freeze-dried, the soil samples were ground and sieved to 40 mesh, respectively. Then they were preserved frozen at −20°C until analysis.

Approximately 8 g of soil 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 0–5 cm soil samples and to 50 µL for other samples under 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. And the organic carbon (OC) of soil was estimated by weight loss-on-ignition (LOI).

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 (SIM) 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 6 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 0.01 ng/g dry weight for di- to hepta-BDE, and 0.05 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

As these sites were near an e-waste recycling village, the concentrations of ∑PBDEs (sum of the detected 37 PBDE congeners) in surface layers of two soil cores were much higher (284.5 ng/g dry weight in MK site and 2017.1 ng/g dry weight in NW site). Significantly different with PCBs vertical distribution in soil (Armitage et al. 2006; Gao et al. 2005), the PBDEs were congregated in the surface layer (0–5 cm) of soil cores and were 29 times in MK and 18 times in NW higher than the second lower layers (5–10 cm, Fig. 1). The dominate part of ∑PBDEs (sum of the detected 37 PBDE congeners) in surface layer of soil were deca-BDE, which indicated the main pollution source of DecaBDE commercial formulation in this area. As a whole, the concentrations of PBDEs were decreased with the soil depth increased in two cores. At the depth of 30–50 cm, the ∑PBDEs were 0.10 and 0.24 ng/g dry weight in MK and NW, respectively, and the deca-BDE was not detected in the soil of this layer in both cores.

There were two significant phenomena in PBDE percentage distribution in different depths of MK and NW soil cores (Fig. 2): (1) the deca-BDE could be detected in deeper soil layers (15–20 cm in MK and 20–30 cm in NW) and the percentage of deca-BDE decreased with the increase of depth; (2) the dramatic increase of the percentage of ∑di-BDE in the deepest layers of the two cores. Based on the halogenation of the phenyl rings, PBDE congeners are vary widely in physical–chemical properties such as octanol–water partition coefficients (logKow 5–10). On the basis of the physical–chemical properties of deca-BDE209 (e.g., a log subcooled liquid vapor pressure, VP, of −8.68 and an octanol–water partition coefficient, Kow, of 9.97), it was expected to be partitioned entirely to the particle phase in both air and rain (Tittlemier and Tomy 2001; Watanabe and Tatsukawa 1989). The higher brominated substitutes are less mobile in the environment, possibly because of their low volatility, water solubility and strong adsorption on solid samples (Watanabe and Sakai 2003). But recent studies (Gouin et al. 2006) implied that BDE-209 also have the same potential for long range transport if sorbed to aerosol particles. As the soil, Schrick et al. (2004) reported that nanoparticles could transport through some distance in soil by elution with water. So we could infer that the deca-BDE appeared in deeper layers of soil cores were mainly caused by the transport of suspension particles and the dissolvable organic matter in the soil eluted by rain water. The deca-BDE residue concentrations were below the detection limit under the depth of 20 cm in MK soil core and 30 cm in NW soil core. But there were detected di- to hepta-BDEs remained in the deepest layers of both cores, especially, the percentage of ∑di-BDE in the deepest layers of the two cores increased dramatically, which indicated the higher penetrability of lower brominated PBDE than the deca-BDE in soil. And it might contribute to the earlier appearance of lower brominated PBDE in sediment cores (Zegers et al. 2003).

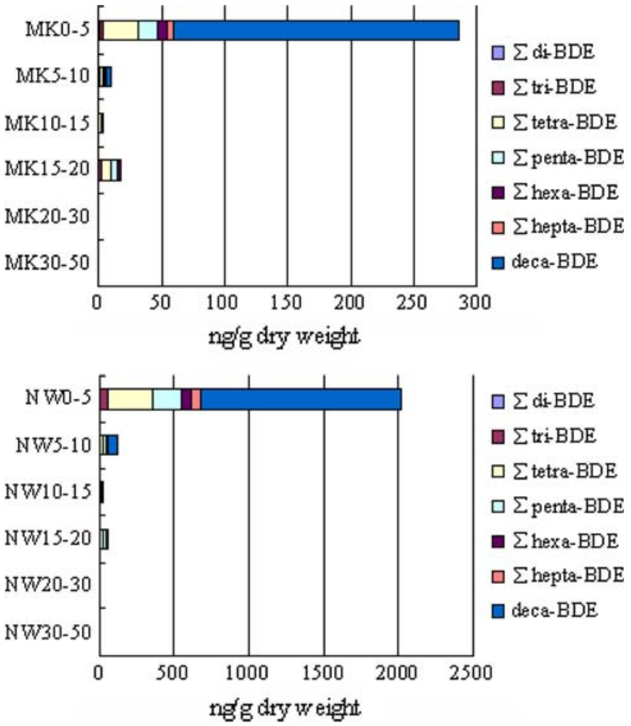

Fig. 1 PBDE concentration (ng/g dry weight) in different depths of MK and NW soil cores. ∑di-BDE: sum of di-BDEs 7, 8, 10, 11, 12, 13, and 15; ∑tri-BDE: sum of tri-BDEs 17, 25, 28, 30, 32, 33, 35, and 37; ∑tetra-BDE: sum of tetra-BDEs 47, 49, 66, 71, 75, and 77; ∑penta-BDE: sum of penta-BDEs 85, 99, 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

In both the soil cores, there was a same unexpected phenomenon of higher concentrations of PBDEs in 15–20 cm layer than the immediately upper layer (10–15 cm). We estimated the organic carbon (OC) of soil by weight loss-on-ignition (LOI) and calculated organic carbon percentage (OC%) distribution in different depths of MK and NW soil cores (Fig. 3). There was no significant difference of OC% distribution occurred in both soil cores, and the

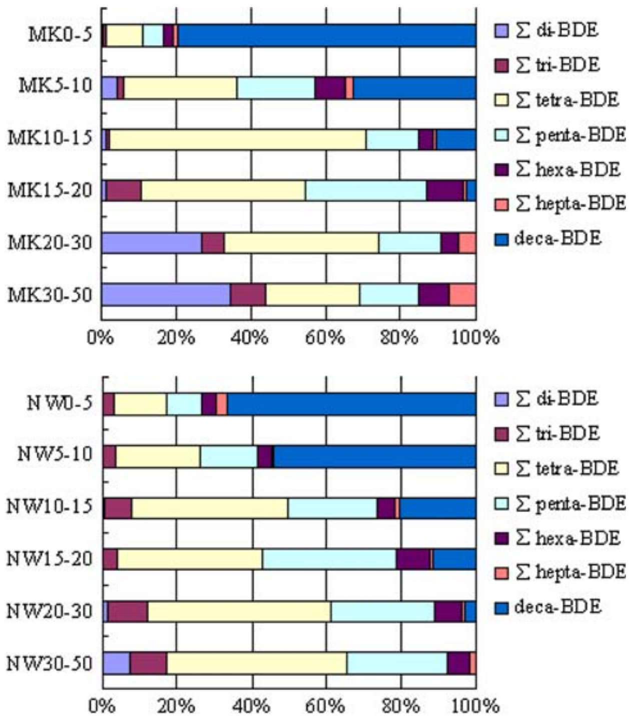

Fig. 2 PBDE percentage distribution in different depths of MK and NW soil cores. ∑di-BDE: sum of di-BDEs 7, 8, 10, 11, 12, 13, and 15; ∑tri-BDE: sum of tri-BDEs 17, 25, 28, 30, 32, 33, 35, and 37; ∑tetra-BDE: sum of tetra-BDEs 47, 49, 66, 71, 75, and 77; ∑penta-BDE: sum of penta-BDEs 85, 99, 100, 116, 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

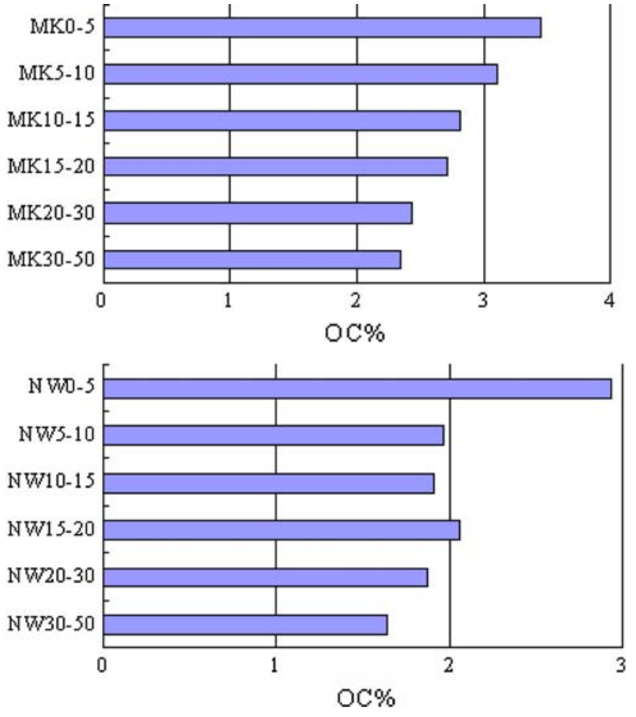

Fig. 3 Organic carbon percentage (OC%) distribution in different depths of MK and NW soil cores

further studies are needed to describing the mass transport of PBDEs in soils.

Acknowledgments This study was financially supported by the National Natural Scientific Foundation of China (No. 20707031), the National Basic Research Program of China (973 Program) (2003CB415005) and the Knowledge Innovation Program of Chinese Academy of Sciences (KZCX2-YW-420-3).

References

Alaee M, Arias P, SjÖdin A, Bergman A (2003) An overview of commercially used brominated flame-retardants, their applications, their use patterns in different countries/regions and possible modes of release. Environ Int 29:683–689

Armitage JM, Hanson M, Axelman J, Cousins IT (2006) Levels and vertical distribution of PCBs in agricultural and natural soils from Sweden. Sci Total Environ 371:344–352

Chen LG, Mai BX, Bi XH, Chen SJ, Wang XM, Ran Y, Luo XJ, Sheng GY, Fu JM, Zeng EY (2006) Concentration levels, compositional profiles, and gas-particle partitioning of polybrominated diphenyl ethers in the atmosphere of an urban city in South China. Environ Sci Technol 40:1190–1196

Cousins IT, Gevao B, Jones KC (1999) Measuring and modelling the vertical distribution of semi-volatile organic compounds in soils. I: PCB and PAH soil core data. Chemosphere 39:2507–2518

Darnerud PO, Eriksen GS, Johannesson T, Larsen PB, Viluksela M (2001) Polybrominated diphenyl ethers: occurrence, dietary exposure, and toxicology. Environ Health Perspect 109(Suppl. 1):49–68

Gao L, Zhao X, Zheng M, Zhang B, Liu W (2005) Distribution of Polychlorinated Biphenyls in Different Depths of Soil from a Polluted Area in the People's Republic of China. Bull Environ Contam Toxicol 74:962–967

Gouin T, Thomas GO, Chaemfa C, Harner T, Mackay D, Jones KC (2006) Concentrations of decabromodiphenyl ether in air from Southern Ontario: implications for particle-bound transport. Chemosphere 64:256–261

Law RJ, Allchin CR, de Boer J, Covaci A, Herzke D, Lepom P, Morris S, Tronczynski J, de Wit CA (2006) Levels and trends of brominated flame retardants in the European environment. Chemosphere 64:187–208

Schrick B, Hydutsky BW, Blough JL, Mallouk TE (2004) Delivery vehicles for zerovalent metal nanoparticles in soil and groundwater. Chem Mater 16:2187–2193

Tittlemier AS, Tomy G (2001) Vapor pressures of six brominated diphenyl ether congeners. Environ Toxicol Chem 20:146–148

Wang DL, Cai ZW, Jiang GB, Leung A, Wong MH, Wong WK (2005) Determination of polybrominated diphenyl ethers in soil and sediment from an electronic waste recycling facility. Chemosphere 60:810–816

Watanabe I, Sakai SI (2003) Environmental release and behavior of brominated flame retardants. Environ Int 29:665–682

Watanabe I, Tatsukawa R (1989) Proceedings, workshop on brominated aromatic flame retardants. Swedish National Chemical Inspectorate, Solna, Sweden (pp 63–71)

Zegers BN, Lewis WE, Booij K, Smittenberg RH, Boer W, de Bore J, Boon J (2003) Levels of polybrominated diphenyl ether flame retardants in sediment cores from Western Europe. Environ Sci Technol 37:3803–3807