

Levels of polybrominated diphenyl ethers in soils from an e-waste recycling site

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Introduction

Polybrominated diphenyl ethers (PBDEs) are anthropogenic chemicals that have been extensively used as flame retardants electronic components. PBDEs can be released into the environment, persistent with a high bioaccumulation potential and thus affect human health. The flame retardant have been detected with significant levels in environmental¹⁻² and biological³⁻⁴ samples. Recent toxicological studies suggested that several PBDEs and/or their metabolites might have disrupted the endocrine system⁵⁻⁶. Thus, trace analysis of PBDEs is important.

Illegal recycling operations of electronic wastes (e-wastes) have been reported to cause severe environmental pollution of PBDEs⁷. However, little information on the PBDE congener profiles and concentrations in the environment around the e-waste recycling site has been reported. This study aims to apply a capillary gas chromatography/ion-trap mass spectrometry method for analyzing PBDEs in soil samples collected from an e-waste disposal site. Various contamination sources of PBDEs were discussed based on the obtained analytical results.

Materials and Methods

PBDE standard solutions (CS-1 to CS-5) contained 19 native PBDEs and 10 ¹³C-labeled PBDEs were purchased from Wellington Laboratories (Ontario, Canada). The concentrations of mono- to heptabrominated diphenyl ethers ranged from 1 pg/μL to 400 pg/μL while the ¹³C-labeled standards were maintained constantly at 100 pg/μL. Matrix blank was spiked with known levels of PBDE standards prior to the sample preparation for evaluating method accuracy and precision. Environmental soil samples were collected from six sampling points around an approximate 30-m² disposal site of e-wastes. The samples were thoroughly mixed and ground prior to the sample preparation. One gram of each soil sample was mixed with 10 g anhydrous sodium sulphate and 5 g of acid washed copper powder. The sample was then spiked with 1 ng ¹³C-labeled PBDE internal standards and Soxhlet extracted with a solvent containing hexane and acetone (1:1, v/v) for 12 hours. The extract was cleaned-up with columns of acidic silica gel and activated neutral alumina. 1 mL of the sample extract was analyzed by using a GC/ion trap MS method described previously⁸.

Results and discussion

Recoveries of more than 65% were achieved for the Soxhlet extraction and column chromatographic clean-up for the targeted PBDEs except for the mono-BDE congener (BDE-3) which had an average recovery of 40%. The relative errors and relative standard deviations obtained from the analysis of spiked matrix blank were less than 30% (n=8) when the added PBDE levels were 1 ppb. Calibration standards were analyzed under the optimized MS/MS parameters. Linear calibration was obtained within the range of 1-400 pg for the PBDE congeners. For the ion trap MS/MS analysis, the most intensive ion peak of each PBDE congener was selected as the parent ion. The selected parent ions were isolated in the ion trap and fragmented by using CID mass spectrometry. MS/MS spectra of all analytes were recorded, from which a characteristic ion was selected as quantitative ion. The quantitative ions were selected based on the criteria of peak intensity and ion specificity as well as potential interference from other compounds. The [M-COBr]⁺ fragment ion was observed as the base peak for PBDEs with ortho-substituted bromine, while the fragmentation ion with the loss of Br₂ ([M-Br₂]⁺ ion) was the base ion for non-ortho substituted congeners.

Identification of the PBDEs in soil samples was performed with the criteria of chromatographic retention time,

selected characteristic ion and bromine isotope ratio. Isotope dilution MS technique was applied for the PBDE quantitation. Relative response factors of the native PBDEs to the corresponding ^{13}C -labeled internal standards were measured and used to quantify the PBDE levels in the samples. Only the PBDEs, whose ^{13}C -labelled internal standards were available, were quantitatively analyzed. The recoveries of the ^{13}C -labeled internal standards were better 60% with relative standard deviation ranging from 8 to 26%. Table 1 lists the quantitative results of the detected PBDE congeners. Both individual and averaged concentrations of the PBDEs are presented for the soil samples. Because the soil samples were collected from the sampling points around the same e-wastes disposal site, the detected PBDE levels were similar with a standard deviation of less than 30%. The data indicated that the PBDEs existed in the soil samples with concentrations ranging from sub-ppb to about 600 ppb (dry weight). Mono-BDE (BDE-3) was not detected in the collected soil samples. BDE-15 (di-BDE) was detected at concentrations from 0.60 to 0.92 ppb in the soil samples. The average concentration of the tri-BDE (BDE-28) was 5.01 ppb with a standard deviation of 0.62. Other PBDE congeners detected in the soils were BDE-47, BDE-99, BDE-139, BDE-153, BDE-154, and BDE-183, whose averaged levels varied from 12.3 to 552 ppb. 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 formulation⁹. Thus, the high levels of the PBDE congeners 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. Uncontrolled disposal and recycling have apparently resulted in the soil contamination with the PBDEs.

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References

1. Strandberg B., Dodder N. G., Basu I. and Hites R. A. (2001) *Environ. Sci. Technol.* 35: 1078-1083
2. Lacorte S., Guillamon M., Martinez E., Viana P. and Barcelo D. (2003) *Environ. Sci. Technol.* 37: 892-898.
3. Alaei M., Sergeant D. B., Ikononou M. G. and Luross J. M. (2001) *Chemosphere*, 44: 1489-1495.
4. Choi J. W., Fujimaki T. S., Kitamura K., Hashimoto S., Ito H., Suzuki N., Sakai S. and Morita, M. (2003) *Environ. Sci. Technol.* 37: 817-821.
5. Fowles J. R., Fairbrother A., Baecher-Steppan L. and Kerkvliet N. I. (1994) *Toxicology*, 86: 49-61.
6. Meerts I., van Zanden J. J., Luijckx E., van Leewen-Bol I., Marsh G., Jakobsson E., Bergman A. A. and Brouwer A. (2000) *Toxicol. Sci.* 56: 95-104.
7. Soderstrom G. and Marklund S. (2002) *Environ. Sci. Technol.* 36: 1959-1964.
8. Wang D., Cai Z., and Jiang G. (2005) *Rapid Comm. Mass Spec.* 19: 83-89.
9. de Wit, C. (2002) *Chemosphere*, 46: 583-624.

Table 1. Levels (ppb) of PBDEs detected in the soil samples (dried weight).

Congener	Soil 1	Soil 2	Soil 3	Soil 4	Soil 5	Soil 6	Ave +- SD ^b
BDE-3	nd ^a	nd	nd	nd	nd	nd	nd
BDE-15	0.60	0.69	0.81	0.76	0.78	0.92	0.76 +- 0.11
BDE-28	4.10	5.22	5.37	5.18	4.41	5.78	5.01 +- 0.62
BDE-47	206	195	264	220	213	204	217 +- 24.5
BDE-99	520	502	534	578	599	579	552 +- 38.6
BDE-139	26.1	32.4	41.8	30.7	33.0	46.0	35.0 +- 7.43

EMG - Brominated Flame Retardants

BDE-153	68.0	70.3	82.4	69.8	76.9	77.2	74.1 +- 5.59
BDE-154	42.0	39.2	48.5	54.9	52.3	57.1	49.0 +- 7.16
BDE-183	10.4	12.7	14.3	13.0	11.2	12.2	12.3 +- 1.38

^a: nd = not detected.

^b: Ave +- SD = averaged +- standard division.