

POLYBROMINATED DIPHENYL ETHERS (PBDEs) IN DUST SAMPLES FROM CZECH HOUSEHOLDS

Kalachová K, Pulkrabová J, Hrádková P, Poustka J, Hajšlová J

Institute of Chemical Technology, Prague, Department of Food Chemistry and Analysis, Technická 3, 166 28 Prague 6, Czech Republic

Abstract

Polybrominated diphenyl ethers (PBDEs), a wide group of additive flame retardants (BFRs), have been intensively used in many common products to accomplish the fire safety standards. Due to their release into the surrounding environment humans' exposure to these harmful chemicals may occur in various ways, inhalation of indoor dust with adsorbed PBDEs represents one of them. To assess the extent of contamination dust samples collected in 25 Czech households were analyzed for 16 PBDE most common congeners using pressurized liquid extraction (PLE) for their isolation and gas chromatography coupled to negative chemical ionization mass spectrometry (GC-MS-NCI) with quadrupole analyzer for identification and quantification. The concentrations of total PBDEs ranged between 81 and 3828 ng/g. Without any exception the dominating congener was no. 209. This deca-BDE contributed to the total amount of PBDEs by 73%, other relatively abundant congeners were BDE 99 (8%), BDE 206 (7%), BDE 207 (6%) and BDE 47 (4%). Based on these data, the estimated daily intake of sum of PBDEs ranged from 0.2 to 31.1 ng/day for adults and from 16.6 to 62.1 ng/day for toddlers. In addition to PBDEs, also representatives of other BFRs classes were identified in sample extracts. The most abundant were decabromodiphenyl ethane (DBDPE) and bis(2,4,6-tribromophenoxy)ethane (BTBPE). Occasionally, other four compounds, pentabromotoluene (PBT), pentabromoethylbenzene (PBEB), hexabromobenzene (HBB) and octabromo-1-phenyl-1,3,3-trimethylindane (Br Indane) were found in dust.

Introduction

Since the polybrominated diphenyl ethers (PBDEs) have been extensively used as flame retardants in a wide group of consumers products such as upholstered furniture, carpets, televisions, computers etc. to improve the fire resistance^{1,19} they have been found in various biotic and abiotic matrixes as fish, sediment, sewage sludge, air and dust also at places with no local sources^{2,3}. Due to their lipophilicity and stability PBDEs showed bioaccumulative potential and have also been determined in human plasma², human adipose tissue⁴ and human breast milk⁵.

Ingestion, inhalation and dermal absorption belong to the main human exposure pathways to PBDEs. Lipid rich food like fish can be a significant source of PBDEs and intake via indoor dust also seems to be an important way, mainly for toddlers who are exposed to PBDEs also through the breast milk⁶. According to Wilford *et al.* (2005) ingestion of dust particles can contribute to the total intake of PBDEs by 14-80% for adults and by 80-89% for toddlers⁷.

As lower brominated congeners are presented mainly in the air samples, dust is considered to be the main source of highly brominated less volatile congeners, like decabrominated BDE 209, that sorbs at the surface of dust particles⁷. BDE 209 formed approximately 97 % of technical deca-BDE mixture¹ which is contrary to penta- and octa-BDE mixture still permitted in some applications¹⁰ as BDE 209 is less bioavailable and more easily eliminated from the living organism probably due to its large molecule. However it might be degraded by light and during the ingestion in the gastrointestinal tract to more toxic lower brominated PBDEs that can be easily absorbed into the blood⁷. Although PBDEs started to be banned by law or optionally substituted by other classes of BFRs in 2004 they still remain both in indoor and outdoor environment as the products containing these BFRs remain in use for years¹. Widely used PBDEs are replaced, e.g. by pentabromotoluene (PBT), pentabromoethylbenzene (PBEB), hexabromobenzene (HBB), bis(2,4,6-tribromophenoxy)ethane (BTBPE), octabromo-1-phenyl-1,3,3-trimethylindane (Br Indane) and decabromodiphenyl ethane (DBDPE), that were determined till now mainly in abiotic matrixes¹¹.

The main aims of the presented study were to establish the levels and profiles of 16 PBDEs congeners in dust from 25 Czech households compare them with data already published in other studies worldwide and identify representatives of other classes of BFRs.

Materials and Methods

Samples: Samples of dust analyzed in this study were collected between October and December 2008 in 25 Czech households from the floors and upholstered furniture by 20 minutes of vacuuming with home vacuum cleaner Selmer Solaris 5000 HT (Poland). Before analysis all samples were stored in vacuum paper bags deposit in plastic bags and kept in a dark and dry place.

Extraction and clean-up: 0.5 g of homogenized sample was extracted using pressurized liquid extraction (ASE300, Dionex, USA) with solvent mixture hexane:dichloromethane (1:1, v/v). 33 mL extraction cell was filled from the bottom with cellulose filter, 2 g of anhydrous magnesium sulphate, 2 g of Florisil[®], 0.5 g of sample and the rest of the cell was filled with sea sand. The PLE conditions were as follows: temperature 100 °C, pressure 1500 psi, heat time 5 min, static time 5 min, flush volume 60%, purge time 60 s and static cycles 3. Final extracts were reduced by rotary evaporation at 40 °C to the last drop and then completely dried by gentle stream of nitrogen. Pure extracts were finally dissolved in 0.5 mL of isooctane containing syringe standards BDE 37 and 77 (5 ng/ml) and ¹³C-BDE 209 (50 ng/ml).

Identification and quantification: Identification and quantification of 16 PBDEs congeners were performed on gas chromatograph (Agilent Technologies 6890N, USA) coupled to mass spectrometer with quadrupole analyzer (Agilent Technologies 5975 Inert XL, USA) operated in negative chemical ionization (NCI) and selected ion monitoring mode (SIM). Analytes were separated on a DB-XLB column (15 m × 0.18 mm i.d. × 0.07 μm; J&W Scientific, USA) using helium as a carrier gas. The oven temperature program was as follows: 80 °C (2 min) → 20 °C/min to 280 °C (1 min) → 5 °C/min to 315 °C (3 min). The inlet temperature was 280 °C; quadrupole was held at 150 °C, ion source at 150 °C and transfer line at 280 °C. Injected volume was 1 μL in pulsed splitless mode (50 psi, 1.5 min). The identification of target compounds was realized by comparison of their retention times with standards and quantification was done by calibration method with syringe standards using ion 79 for all congeners except for BDE 209 (ion 489) and ¹³C-BDE 209 (ion 494).

Quality assurance/Quality control: The analysis was performed in accredited testing laboratory (No. 1316.2) in the Czech Republic (current standard: EN ISO/IEC 17025). The quality control was realized on the house dust standard reference material (SRM 2585) provided by NIST (USA). Limits of quantification (LOQ) were: for PBDEs 28-154 (0.1-0.3 ng/g dust), PBDEs 183-207 (0.8-2.5 ng/g dust) and BDE 209 (5 ng/g dust). The average recovery range of PBDEs was 81-112%.

Results and Discussion

As documented in **Figure 1**, the levels and profiles of 16 PBDEs congeners determined in household dust samples varied considerably, the concentrations of total PBDEs ranged between 81 and 3828 ng/g of dust. In all examined samples, the dominating target analyte was BDE 209, which is the main component of technical deca-BDE mixture (> 97%) commonly used e.g. as a flame retardant in carpets and textiles⁹. This deca-BDE contributed to the total amount of PBDEs by approximately 73% followed by BDE 99 (8.1%), BDE 206 (7.2%), BDE 207 (5.7%) and BDE 47 (4.2%). Other congeners were represented by less than 1% (**Figure 2**).

High levels of BDE 209 observed in this study are in accordance with almost all studies focused on PBDEs in dust^{1, 2, 7, 9, 13, 14, 15, 21, 23}. For instance *Santilo et al. (2001)* who analyzed PBDEs and OCPs in dust collected from parliament buildings in 8 countries worldwide, found the BDE 209 levels between 400 and 5750 ng/g¹⁵. The high contribution of BDE 209 to the total profile is in line with current high use rate of respective technical mixture that is, contrary to banned penta- and octa-BDE mixtures, still permitted in some applications (Directive 76/769/EEC)¹⁰. The accumulation of deca-BDE in dust corresponds to its lower volatility and stronger affinity to the solid particles' surface compared to lower brominated PBDEs⁷. It should be noted that nona-BDE 206 and 207 congeners detected in dust samples can penetrate into the environment not only due to uses of deca based technical mixtures in which they are minor components, but they may also be originated through

photodegradation of parent BDE 209, the mechanisms involved have been recently described by *Stapleton et al. (2008)*¹⁶. Relatively high occurrence of tetra-BDE 47 and penta-BDE 99 (compared to levels of other lower brominated PBDEs) is a consequence of earlier uses of penta-BDE technical mixture which used to be added mainly to polyurethane foam applied in upholstery, couches, chairs etc¹⁷. Worth to notice that contamination pattern of biotic samples is typically fairly different from dust, BDE 47 and 99 have been shown in several studies to be the most abundant congeners in human samples such as adipose tissue, breast milk and/or plasma¹⁸. Their levels in dust already published vary from 0.7 to 1120 ng/g for BDE 47 and from 1.0 to 1800 ng/g for BDE 99, what documents their lower accumulation potential in comparison with BDE 209^{1,2,7,9,12,13,14,21,22,23,24}. Regarding hepta-BDE 183 together with less often analysed octa-BDE 197 and 196 are dominant congeners of octa-BDE technical mixture mainly used in thermoplastics such as high-impact polystyrene¹⁷. The contribution of these congeners to the total amount of PBDEs found in this study was less than 1%, which is comparable e.g. with results published by *Stapleton et al. (2005)* who described contributions from <1 to 14%¹.

As mentioned above, ingestion and inhalation belong among the main pathways of human exposure to these compounds. According to United States Environmental Protection Agency (USEPA) protocol when estimating the daily exposure to PBDEs it is important to take into the consideration age, employment, other daily activities of particular individuals as well as the time spent in outdoor and indoor environment, in the later case exposure is assumed to be higher. *Wilford et al. (2005)* estimated that adult person spends approximately 90% indoor and inhales 4.16-100 mg of dust per one day and toddler (6 months to 2.5 year) spends indoor as adults and inhales 55-200 mg of dust per one day. 100% absorption efficiency for all congeners is taken into consideration^{7,8}. Based on these assumptions and considering the data generated in this study, the daily exposure (total PBDEs) due to contaminated dust was calculated, see **Table I**. The comparison of these results with studies conducted elsewhere is rather difficult as various estimation scenarios are employed, moreover, the spectrum of reported analytes is varying among the studies. Differences, as high as one order of magnitude, exist among the exposure estimates obtained by similar approach. For instance: British study 0.36-8.71 ng/day for adults and 4.8-17.4 ng/day for toddlers¹⁷; Canadian - 7.5-180 ng/day for adults and 99-360 ng/day for toddlers⁷; Singapore: 64-232 ng/day for adults and 4.8-116 ng/day for toddlers⁹.

In addition to target PBDEs also unknown signals of brominated compounds were detected, see **Figure 3**, and some of them also identified. The most abundant non-PBDE flame retardants were DBDPE and BTBPE. Other four new analytes occurred only in some dust samples. DBDPE has similar applications as BDE 209 including usage in thermoplastics and textiles^{2,11} and its presence in the air at electronic recycling facilities together with BTBPE has already been reported by *Pettersson-Julander et al. (2004)*²⁰ and in household air and dust by *Karlsson et al. (2007)*².

To conclude, the PBDEs levels and profiles in household dust established within this study are comparable with results reported worldwide. The differences among the reported contamination levels can be as attributed to existence of various emission sources e.g. the distribution of manufacture and usage of PBDEs has been more extensive in North America than in Europe and other continents^{2,12}. Moreover results are probably also influenced by sampling technique and by the year of construction, location and equipment of households as the materials prior to 2004 probably contained technical mixtures that are nowadays banned or less used^{1,10}.

Table I: Estimation of human daily exposure to sum of PBDEs via indoor dust

	Dust intake [mg/day]		Intake of Σ PBDEs [ng/day]		
	Min.	5 % percentile	Average	Median	95 % percentile
Children	55	15.5	28.6	16.6	68.6
Adults	4.16	0.2	2.2	0.2	0.8
	Max.	5 % percentile	Average	Median	95 % percentile
Children	200	31.1	104.1	62.1	137.3
Adults	100	34.2	52.0	31.1	151.0

Acknowledgements

This research was supported by grants from the Ministry of Education, Youth and Sport of the Czech Republic – BIOBROM (2B06151) and MSM 6046137305. The authors acknowledge to Monika Stavělová from Earth Tech s.r.o. (Prague, Czech Republic) for organizing the samples' collection.

References

1. Stapleton H. M., Dodder N. G., Offenbergh J. H., Schantz M. M., Wise S. A. *Environ. Sci Technol.* 2005; 39:925.
2. Karlsson M., Julander A., van Bavel B., Hardell L. *Environ Inter* 2007; 33:62.
3. Law R. J., Allchin C. R., de Boer J., Covaci A., Herzke D., Lepom P., Morris S., Tronczynski J., Wit C. A. *Chemosphere* 2006; 64:187.
4. Pulkrabova J., Hradkova P., Hajslova J., Poustka J., Napravnikova M., Polacek V. *Environ Inter* 2009; 35:63.
5. Kazda R., Hajslova J., Poustka J., Cajka T. *Anal Chim Acta* 2004; 520:237.
6. Frederiksen M., Vorkamp K., Thomsen M., Knudsen L.E. *Int. J. Hyg. Environ. Health* 2009; 212:109.
7. Wilford B.H., Shoeib M., Harner T., Zhu J., Jones K.C. *Environ. Sci Technol.* 2005; 39: 7027.
8. USEPA available at www.epa.gov (April 24, 2009).
9. Tan J., Cheng S. M., Loganath A., Chong Y. S., Obbard J. P. *Chemosphere* 2007; 66:985.
10. BSEF 2009 available at www.bsef.com (April 21, 2009).
11. Kierkegaard A., Bjorklund J., Fridén U. *Environ. Sci. Technol* 2004; 38:3247.
12. Meeker J. D., Johnson P. I., Camann D., Hauser R. *Sci Total Environ* 2009; 407:3425.
13. Johnson-Restrepo B., Kannan K. *Chemosphere* 2009; doi: 10.1016/j.chemosphere.2009.02.068.
14. Harrad S., Ibarra C., Abdallah M., Boon R. *Environ Inter* 2008; 34:1170.
15. Santilo D., Johnston P., Brigden K. *Grennpeace Research Laboratories*, Report No. GRL-TN-03-2001.
16. Stapleton H. M., Dodder N. G. *Environ. Toxicol. Chem.* 2008; 27: 06.
17. Harrad S., Hazrati S., Ibarra C. *Environ. Sci. Technol.* 2006; 40:4633.
18. Hites R. A., *Environ. Sci. Technol* 2004; 38:945.
19. Sjödin A., Papke O., McGahee E., Focant J.F., Toms L. L., Herrmann T., Müller J., Needham L. L., Patterson D.G. *Chemosphere* 2008; 73:131.
20. Pettersson-Julander A., Bavel B., Engwall M., Westberg H. *The Royal Society of Chemistry* 2004; 6:874.
21. Toms L. L., Hearn I., Kennedy A., Harden F., Bartkow M., Temme Ch., Mueller J. F. *Environ Inter* 2009; doi: 10.1016/j.envint.2009.03.001
22. Wu N., Herrmann T., Paepke O., Tickner J., Hale R., Harvey J., La Guardia M., McClean M. D., Webster T. F., *Environ. Sci. Technol.* 2007; 41:1584.
23. Gevaio B., Al-Bahloul M., Al-Ghadban A. N., Al-Omair A., Ali L., Zafar J., Helaleh M. *Chemosphere* 2006; 64:603.
24. Julander A., Westberg H., Engwall M., van Bavel B. *Sci Total Environ* 2005; 350:151.