DISTRIBUTION OF POLYBROMODIPHENYL ETHERS IN INDOOR DUST AND HUMAN EXPOSURE IN PRETORIA, SOUTH AFRICA

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Introduction

Polybromodiphenyl ethers (PBDEs) have been used for more than three decades as flame retardants. As they are additive flame retardants, under suitable condition, they are likely to migrate from the product materials into the environment[1]. Furthermore, due to their wide use in different consumer products; their detection in various environmental samples has also increased. The widespread production and use of PBDEs and strong evidence of increasing contamination of the environment by these chemicals have attracted worldwide scientific attention. Thus, many researchers have shown their presence in humans[2-4], indoor dust[5-10], in human hair[11, 12], sediment[13]. To date, their adverse effects on humans and the environments triggered the banning of production and use of Penta- and Octa- BDE commercial mixtures in electronic and electrical applications[14].

Indoor dust has been identified as a potentials source of human exposure to PBDEs[12, 15]. In general, suspended dust particles in the air over time settle to form settled indoor dust. Consequently, the composition of settled indoor dust is partially a reflection of indoor air contamination[16]. Hence, estimation of human exposure through the concentration of contaminants detected in settled indoor dust can provide the degree of pollutants inhaled or ingested in indoor environment. Despite many research reports on PBDEs, there is very scarce report from Africa. Therefore, the main objectives of this study were to: (1) estimate daily human exposure rate to PBDEs congener and sources in homes in Pretoria, South Africa and (2) determine the distribution of PBDEs indifferent dust particle size ranges.

Materials and Methods

For congener identification, sixteen certified standard solutions of PBDEs (each 1.2 mL of 50 mg L^{-1}) were purchased from Wellington Laboratories (Guelph, Ontario, Canada). For method validation, house dust standard reference material-2585 was purchased from NIST (Gaithersburg, MD, USA). Isotopic labelled internal standards (1.2 mL of 50 mg L^{-1} of ^{13}C12-BDE-139 and $^{13}C_{12}$-BDE-209) were purchased from Cambridge isotope laboratories (CIL, Andover, MA, USA). Copper powder (purity 99.98% from Saarchem (Pty) Ltd., Muldersdrift, South Africa), silicagel (100 - 200 mesh), sodium sulphate (purity 99.9%), glass wool, HPLC grade solvents: acetone, hexane, and dichloromethane products of Sigma Aldrich (Chemie GmbH, Steinheim, Germany), 50 ml of nonane (Purity 99.8%, Sigma Aldrich, product of Switzerland) were purchased from Industrial Analytical Pty. Ltd. (Midrand, Gauteng, South Africa).

Dust samples were collected using 1000 watts portable standard vacuum cleaner (Model: 601SA, made in China) equipped with a dust collection bag. Dust samples were collected from floor of living rooms of 31 homes. In order to investigate the relationship between dust particle size and PBDEs distribution, 12 dust samples were collected from offices and homes using the same equipment. For source characterization, based on the previous results[9, 10], samples were collected from five homes and four offices. Office dust samples were collected from the inside of computer monitors, and printers while home dusts were obtained using vacuum cleaner from the inner parts of television and surface parts of DVD and VCDs. In addition, Polyurethane foams (PUFs), which had been degenerated into fine particles, were collected from inside old cushioning and chairs that were used in the offices. Old and used carpets were also collected from one home and office.

The extraction of all dust samples was carried out on Soxhlet extractor using a mixture of *n*- hexane: acetone (2:1, v/v). The sample cleanup was carried out using Pasture pipette column chromatography which was packed with silica gel (neutral, basic and acidic) and sodium sulphate. The detail of extraction and clean up has been described elsewhere[10]. For particle size characterization Microtrac S3500 Particle Size Analyzer and stainless steel sieves were used. Before analysis on Microtrac S3500, all 12 dust samples were first sieved using 250 µm and, thereafter, using 150 µm stainless steel sieves was used. The analyses of PBDEs were conducted on HRGC-EI-LRMS and quantified using five level calibration and internal standards: BDE-77 used for quantification of BDE-3, 17, 28, 47, 66, 85, 99, 100 and 126, $^{13}C_{12}$ –BDE-139 used for quantification of BDE-138, 153, 154, and 183, and $^{13}C_{12}$ –BDE-209 for BDE-209.

Several quality control methods were assessed in order to obtain reliable data. For instance, following the injection of three samples, one solvent blank and standard were run to ensure that the samples and the analysis process were free of contamination as well as to control deviation of the retention time. For each congener, the linearity of the calibration curve was also evaluated. Accordingly, good linearity has been achieved with r^2 value of greater than 0.989. The recovery of the spiked internal standards BDE-77, $^{13}C_{12}$- BDE-139 and $^{13}C_{12}$-BDE-209 were varied in between 84-112%, 76-96% and 72-84%, respectively, and corresponded to the average recovery of 95%, 86% and 78% in the same order. The validation of the method was done through analysis of SRM-2585 in triplicate. A good recovery was achieved for the lower congeners than higher once, which is > 95%, for BDE-183 (85%) and BDE-209 (78%).

Results and discussion

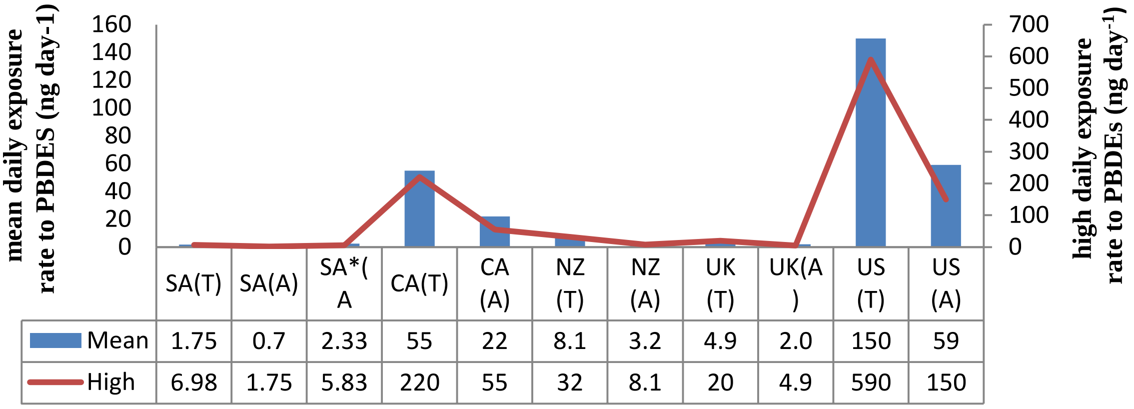
Of the 15 PBDEs congeners considered for identification, only BDE-47 and BDE-99 exhibited median value and BDE-17, 28, 126, 138 and 183 were not detected. The corresponding mean concentrations for BDE-3, 15, 47, 66, 100, 99, 85, 154, 153 and 209 were 0.35, 0.58, 11.89, 0.91, 1.06, 15.18, 2.71, 1.21, 0.98 and 16.22 ng g^{-1}, respectively. Similar to the results observed in our previous work of office dust[10], the number and type of congeners detected in each sample was non-uniform. Such non-uniform distribution of congeners of PBDEs in research of landfill sites of the same area was also reported[17].

Estimation of human exposure to PBDEs was calculated. The calculation was based on the assumption of 100% absorption of intake, and mean adult and toddler ingestion of 20 and 50 mg day^{-1} and high dust ingestion rate of 50 and 100 mg day^{-1}, respectively[5, 18]. Using the median and mean concentration of BDE-209 and ΣPBDEs in home dust, the mean and high dust ingestion rate for adults and toddles were calculated. The summaries of daily human exposure estimation of the present and previous study (determined from the analysis result data of office dust) are presented in Table 1. The comparison of adult exposure rate to PBDEs in both microenvironments using mean and high dust ingestion rate showed human exposure to PBDEs in office, was about 9 and 2 times greater than home, respectively (irrespective of median or mean used for calculation). The comparison of mean values of this study using both mean and high dust ingestion rates with the other studies are given in Fig. 1.

Table 1: Summary of estimate of exposure (ng day^{-1}) of adult and toddler to PBDEs via office and home dust ingestion

			Mean dust ingestion rate		High dust ingestion rate		
Country	Exposure group	BFRs	median	mean	median	mean	References
SA home	Toddler	ΣPBDEs[a]	0.61	1.75	2.44	6.98	this study
		BDE-209	0.05	0.81	0.18	3.24	
	Adult	ΣPBDEs[a]	0.24	0.70	0.61	1.75	
		BDE-209	0.02	0.32	0.05	0.81	
SA office	Adult	ΣPBDEs[b]	2.19	2.33	5.48	5.83	[10]
		BDE-209	<dl	1.052	<dl	2.63	

[a] Σ (BDE-3, 15, 47, 66, 100, 99, 85, 154, & 153), [b] Σ (BDE-47, 66, 99, 66, 85, & 153)



	SA(T)	SA(A)	SA*(A	CA(T)	CA (A)	NZ (T)	NZ (A)	UK (T)	UK(A)	US (T)	US (A)
▬ Mean	1.75	0.7	2.33	55	22	8.1	3.2	4.9	2.0	150	59
— High	6.98	1.75	5.83	220	55	32	8.1	20	4.9	590	150

Fig. 1 Comparison of mean values of this study with the other studies using both mean and high dust ingestion rates (excluding BDE-209). (* = office, T = toddler, A = Adult, SA = South Africa, CA = Canada, NZ = New Zealand), (Source of data for Canada, New Zeland, UK, and US) [5]

With respect to tracing the sources of PBDEs, the corresponding percentage ratio of total concentrations of PBDEs detected from dust collected inside the electronic material to that found in the settled dust are presented in Fig. 2. The ratios were: 1.7(O1), 0.33(O2), 4.8(O3), 12.1(H1), 1.5(H2) and 0.66(H3). From Fig.2, electronic materials may have acted as the main emission sources of PBDEs to the indoor environments. No PBDEs were detected in carpets collected from both microenvironments and foams from offices, showing that they have not been treated with PBDEs. In one home, where previously PBDE congeners were absent in the settled dust, no PBDE congeners were also detected from the dust collected inside TV and DVD, confirming that these electronic materials were not treated with PBDEs.

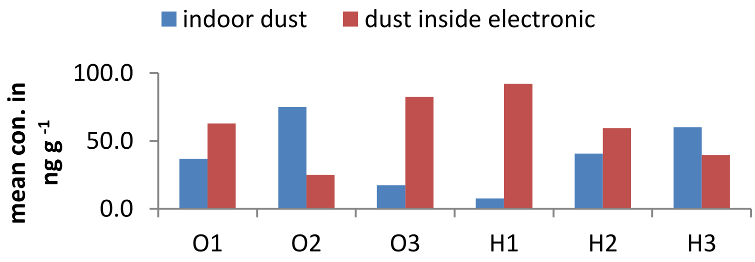


Fig. 2 Comparison of total concentrations of PBDEs obtained from dust collected inside the electronic materials and settled indoor dust of the same office or home, O1, O2* and O3 and H1, H2 and H3 represents office and home, respectively (*average PBDEs concentration from two offices)

The distribution of concentration of Polybromodiphenyl ethers (PBDEs) determined in different dust fractions, were found to be relatively higher in the order of dust particle size, 45-106 µm > (< 45 µm) > 106-150 µm. For the determination of dust particle size distribution, all 12 sieved dust samples were analysed on Microtrac S3500 Particle Size Analyzer. Accordingly, 97.0 and 99.5 mean volume percentage of dust collected from homes and offices were less than 105 µm, respectively. The result showed that almost all dust sieved by150 µm (in the offices and homes) were in the categories of total inhalable ranges, indicating that the presence of high concentrations of fine dust in indoor environment. Even in the absence of some other toxicants in indoor dust, inhalation or ingestion of fine dust particles can pose serious health risk. Generally, unlike stainless steel sieves, particle size analyser provided all ranges of distribution of dust particle size.

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