POLYBROMOBIPHENYLS AND POLYBROMODIPHENYL ETHERS IN INDOOR DUST FROM PRETORIA, SOUTH AFRICA.

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Introduction

Brominated flame retardants (BFRs) are chemicals which are added to consumer products such as plastics, textiles and electronics during production in order to meet fire safety regulations. Polybromobiphenyls (PBBs) and Polybromodiphenyl ethers (PBDEs) are among the BFRs categories that are used as additive brominated flame retardants. PBBs and PBDEs lack binding sites chemically to bond to the host materials[1] and consequently, they can easily be released from such materials into the environment during product use or disposal. Due to their widespread use, PBDEs are disseminated worldwide as an environmental contaminant and have been detected in dust[2-4], aquatic and terrestrial biota[5]. Their concentrations both in the environment and in humans have been found to be on the increase. As a result, the use of penta- and octa-BDE mixtures have been banned in all applications in the European Union Market since August 2004[6]. Recently, both penta- and octa-BDE mixtures have been listed as persistent organic pollutants (POPs) under Annex A of Stockholm Convention in order to stop its production and use[7]. Generally, dust has been identified as a potentially significant source of PBDEs[8-11], and indoor dust is one of the main exposure routes for both children and adults[12]. Since most people spend their time indoors; ingestion of indoor dust is unavoidable. The recognition of indoor dust as a significant source of BFRs has triggered research on the matrix. To date, there is no report on the presence and concentration of the above mentioned BFRs in South Africa indoor dust except recently published paper on BDE209 congener[13]. Therefore, the main objective of this study is to identify and quantify those congeners present among 16 major PBBs (BB 1, 2, 4, 10, 15, 26, 29, 30, 31, 38, 49, 80, 103, 153, 155 and 209) and 16 PBDEs (BDE 3, 15, 17, 28, 47, 66, 77, 85, 99, 100, 126, 138, 153, 154, 183, 209) in indoor dust from Pretoria, South Africa.

Materials and Methods

House dust standard reference material - 2585 purchased from NIST (Gaithersburg, MD, USA) was used in method validation. 1.2 mL of 50 mgL^{-1} of each certified standard solution of PBBs and PBDEs purchased from Wellington Laboratories (Guelph, Ontario, Canada) were used for instrumental calibration and identification of peaks. The chromatographic conditions used in our earlier study[13] are employed in the present study. The suitability of this method for the lower PBBs and PBDEs were checked on GC-ECD and HRGC-EI-LRMS on different type of column.

Dust samples were collected from floor carpets in the living rooms of the houses sampled using a portable vacuum cleaner of 1000 watts (Model: 601SA, made in China). Dust samples from hotel and department store were, however, collected from carpet and tiled floors using normal vacuum cleaners. At the time of dust collection, all available information on electronic and other materials was recorded. After collection, all dust samples were sieved separately using 250 µm sieves, homogenised thoroughly and stored in 50 mL pre-cleaned amber glass at room temperature until extraction. In each case, depending on the available amount of dust collected, dry sieved dust samples (2.2 - 6.5 g) were weighed, about 0.25g of pre-prepared activated copper powder added and homogenized. Thereafter, transferred to a cellulose extraction thimble (19 mm ID and 90 mm in length), covered with glass wool, placed inside Soxhlet apparatus and extracted with 270 mL of *n*-hexane:acetone (2:1 *v/v*) for 8 h. Evaporation, clean up and concentration methods were as described elsewhere[13]. BB209 and BDE209 were analysed separately on GC-ECD while the other congeners were analysed using HRGC-EI-LRMS. Concentration of each congener was determined using five level calibrations of external standards.

Results and discussion

Recoveries of house dust standard reference material (2585) for PBDEs ranged from 84±5.7 - 137±7.9%. High recoveries were obtained for lower congeners while the lowest recovery was for BDE209. The high recoveries obtained validated the method used in the present study. From a total of thirty two targeted congeners measured, only three PBBs (BB4, BB10, and BB209) and seven PBDEs (BDE3, BDE15, BDE47, BDE66, BDE85, BDE99 and BDE209) were detected in low concentrations that ranged from <dl - 98.6 ng g^{-1}. The summary of the analysis results for all ten detected individual congeners are given in Table 1.

Table 1: PBBs and PBDEs level detected in house, hotel and department store

	House dust (n = 7)				Hotel (n = 1)	Dept. store (n = 1)
Congeners	median	Average	min	max	Average *	Average*
BB4	9.1	8.1	<dl	18.8	26	10.8
BB10	<dl	1.7	<dl	12	<dl	<dl
BB209	<dl	6.2	<dl	25.5	63	<dl
BDE3	<dl	1.9	<dl	13.6	<dl	<dl
BDE15	<dl	3.2	<dl	10.6	<dl	<dl
BDE47	34.6	27.6	<dl	60.3	28	17.7
BDE66	5.8	5.0	<dl	13.1	<dl	6.5
BDE85	9.6	9.9	<dl	24.6	17	12
BDE99	20.9	27.0	<dl	88.9	32	21.6
BDE209	<dl	27.3	<dl	98.6	78	<dl

*Triplicate analysis, <dl = less than detection limit, Dept = department

From the analysis results, BDE47 and BDE99 were the most frequently detected congeners followed by BDE85 and BB4 in 78% and 67% of the analysed samples, respectively. The maximum concentration detected was exhibited by BDE209 (98.6 ng g^{-1}) followed by BDE99 (88.9 ng g^{-1}) in house dust. On the other hand, the average detected concentrations for PBDEs ranged from 1.9 - 27.6, <dl - 78 and <dl - 21.6 ng g^{-1} while that for PBBs ranged from 1.7 - 8.1, <dl - 63, and <dl - 10.8 ng g^{-1} in house dust, hotel and department store, respectively. It was also observed that the type and the concentrations of congeners detected in house dust varied over a wide range. It has been suggested that the source of BFRs within a house-hold are furniture and electronic appliances from which BFRs are emitted [14]. The observed variation may, therefore, be attributed to the type and number of furniture and electronic appliances in the houses sampled and whether or not they are treated with these chemicals. However, the frequency of use of the electronic appliances, dusting and ventilation conditions in the houses are expected to contribute to the observed variation as well. In samples collected from a department store, few congeners were detected and this was probably because most of the electronic appliances and textile products available were not frequently used. The concentrations of PBBs detected were relatively very low probably due to less application on materials as a result of its production ban compared to that of PBDEs.

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To identify sources of PBBs and PBDEs detected from dust, Spearman rank correlation test was applied at statistical significance alpha value of 0.05.The Spearman rank correlation (r_s) has a value between $1 \geq r_s \geq -1$ and when $0 \leq r_s \leq 1$(positive correlation), $-1 \leq r_s \leq 0$ (negative correlation) and $r_s = 0$ (no correlation), with *P*-value set at statistically significant alpha values. The Spearman rank correlation test result between the summation of Σ_3PBBs and Σ_7PBDEs showed no common sources for both PBBs and PBDEs (r_s = -0.05, *P* = 0.05). The relationship between the number of electronic appliances in use (only for house dust) and the concentration of BFRs detected were also investigated. Similarly, no correlation was observed between the total number of electronic appliances in the house and the concentrations of BFRs detected, Σ_3PBBs (r_s = -0.21, *P* = 0.29), and Σ_7PBDEs (r_s = -0.13, *P* = 0.06). This might suggest that the current electronic appliances in use may have not been treated with BFRs or that the congeners detected may have originated from other sources. From this

preliminary investigation, the total concentrations of PBDEs detected in this study are lower than the concentrations reported from developed countries[4,15,16].

In order to get a better understanding of the sources and types of BFRs (PBBs and PBDEs) congeners present in indoor dust from South Africa, collection of more house and office dust samples from different possible sources are already in progress. Furthermore, the results from large sample size will be expected to be used to determine the exposure rate of South Africans via indoor dust ingestion.

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