



ELSEVIER

Contents lists available at ScienceDirect

Ecotoxicology and Environmental Safety

journal homepage: www.elsevier.com/locate/ecoenv

Levels of polybrominated diphenyl ethers in indoor dust and human exposure estimates from Makurdi, Nigeria

O.I. Olukunle^a, O.J. Okonkwo^{a,*}, R. Sha'ato^b, G. A Wase^b^a Environmental Chemistry Research Group, Department of Environmental, Water and Earth Sciences, Faculty of Science, Tshwane University of Technology, Private Bag X680, Pretoria, South Africa^b Department of Chemistry, University of Agriculture, PMB 102373 Makurdi, Benue State, Nigeria

ARTICLE INFO

Article history:

Received 15 April 2015

Received in revised form

11 June 2015

Accepted 13 June 2015

Available online 24 June 2015

Keywords:

Indoor dust

PBDEs

Human exposure

Nigeria

ABSTRACT

Information on polybrominated diphenyl ethers (PBDEs) in the indoor environment in developing countries is still relatively scarce. In this study, house ($n=10$) and office ($n=11$) dusts samples collected from Makurdi, Benue State Nigeria were extracted and analysed for most abundant PBDEs congeners in the environment. Soxhlet extraction followed by GC-EIMS was employed for the measurement of PBDEs (BDE-47, -100, -99, -154, -153, -183 and -209). The mean concentration of \sum_7 PBDEs ranged from 57 ng g^{-1} to 80 ng g^{-1} and a median value of 45 ng g^{-1} and 63 ng g^{-1} were obtained for house and office dust respectively. The daily exposure and ingestion dose estimates were calculated based on the assumption that 30 mg and 60 mg day^{-1} dust represent the ingestion rate. In addition, the corresponding time spent indoors was assumed to be 87.5% (adult) and 69% (children) in homes and 22% in offices and day care. The average value exposure rate of \sum_7 PBDEs for children and adults were 2 ng day^{-1} and 0.84 ng day^{-1} respectively. The results in the present study, showed higher exposure estimates for both children and adults' in house dust from Nigeria compared to South Africa.

© 2015 Elsevier Inc. All rights reserved.

1. Introduction

Polybrominated diphenyl ethers (PBDEs) are brominated organic compounds and an important member of the group of compounds known as brominated flame retardants (BFRs). Generally, flame retardants are chemicals reacted or incorporated into material goods such as polyurethane foams, textiles, wire insulation, automobiles, electronics, construction materials and other numerous plastic products. Primary use of BFRs is in the inhibition of ignition and to slow down propagation of flames thereby allowing enough time for people to escape. PBDEs are additive flame retardants used in a wide variety of consumer and industrial products because of their effectiveness. Three major commercial formulations of PBDEs were produced globally in the last few decades; the Penta-BDE, Octa-BDE and Deca-BDE. The Penta and Octa-BDE derivatives were banned by the European Union (EU) in August 2004 (BSEF, 2006) because they have the tendency to be more bioaccumulative and toxic than the Deca mixture. Since then, Penta and Octa-BDE derivatives have been recognised as persistent organic pollutants (POPs) and are now included in the list of new POPs under the Stockholm Convention (UNEP, 2009).

* Corresponding author. Fax: +27 12 382 6354
E-mail address: okonkwoj@tut.ac.za (O.J. Okonkwo).

According to the Bromine Science and Environmental Forum (BSEF, 2015), production and sales of Deca-BDE were voluntarily phased out in the US and Canada at the end of 2012 by BSEF members except for specific transportation and military applications, while voluntary phase out in all applications was slated for end of 2013. However, Deca-BDE is still being used with partial restrictions, especially in China. PBDEs have been shown to be persistent, bio-accumulative and endocrine disrupting; consequently, they have been implicated in several adverse effects on human health and are continually being detected in biotic and abiotic samples including human milk, serum and tissues (Jakobsson et al., 2002; Johnson-Restrepo et al., 2005; de Wit and Alae, 2006; Johnson et al., 2010; Darnerud et al., 2011; Kalantzi et al., 2011; Devanathan et al., 2012).

The release into the environment of brominated flame retardants occurs through a number of ways. Examples include; process of manufacture, incorporation into polymers or related finished products, disposal or recycling, leaching from products in use and disposed in landfills (de Wit et al., 2010; WHO/EHC-192, 1997). According to Alcock et al. (2003), six routes of exposure have been identified in which PBDEs could be released into the environment. These include combustion of the waste containing PBDEs; accidental burning of products containing PBDEs; emission from products in use containing PBDEs; blending of PBDEs within polymers; recycling of plastic products containing PBDEs and

formation during textile finishing with PBDEs.

Some of the possible indoor sources of BFRs include emission from electronic appliances such as television sets, computers and fabric products (Hirai et al., 2006; He et al., 2007; Chen et al., 2008; Takigami et al., 2008). Research also verified dependence of PBDE emission levels on the environmental conditions. For example, PBDEs concentration was found to be higher during warm months than in colder months and in addition, a decrease in PBDE concentrations was reported when old computers were replaced by new ones (Hazrati and Harrad, 2006). Similarly, Cheng et al. (2009) found higher PBDE concentrations in indoor dust collected when computers are working than when they are switched off. These findings indicate that an increase in temperature facilitates the release of volatile PBDEs and that old computers are a major emission source for indoor environments. Shih and Wang (2009) showed that photo-degradation is one of the means of conversion of higher PBDEs such as BDE-209 to lower congeners. On the other hand, after finding a positive relationship for the sum of PBDE concentrations in dust and blood plasma, it was concluded that inhalation of PBDEs from dust has been identified as a potentially significant source of PBDEs. High levels of PBDEs in an office with many computers have been reported and it was concluded that PBDE emission from computers play a very important role in the pollution of indoor environments (Karlsson et al., 2007; Lorber, 2008). Possible sources of PBDE emission to the outdoor environment may include leachates from waste disposal, ash and air emission from landfills and incineration of disposed products containing PBDEs. Exposure assessment of PBDEs and other persistent organic pollutants (POPs) in humans via different exposure pathways has been reported (Johnson-Restrepo and Kannan, 2009; Ni et al., 2013; Ma et al., 2014).

There are still very few reports on the presence and levels of PBDEs in indoor dust from developing countries (Gevao et al., 2006; Kefeni and Okonkwo, 2012; Ali et al., 2013) compared to those from developed countries. Nigeria and South Africa are developing countries with huge potentials for increasing economic and developmental growth. Consequently, it can be deduced that increased industrialisation may play a significant and similar role in the indoor environment of the two countries. Furthermore, the importation of finished products that may have been treated with PBDEs by the two countries because of high consumer demand is most likely to be high. The present study, therefore, focuses on the determination of most abundant PBDEs in indoor dust collected from homes and offices in Makurdi, Benue State in Nigeria and compares with similar studies conducted by our research group in Pretoria, South Africa. Furthermore, exposure estimates for children and adults in the two countries are also evaluated, and further compared to values from developed countries.

2. Materials and methods

2.1. Chemicals and reagents

Pure standards (1.2 mL of 50 mg L⁻¹) of each certified Standard solutions of PBDE (BDE-17, -47, -77, -99, -100, -118, -153, -154, -183, -209 and ¹³C-BDE-139 and -209) congeners were purchased from Wellington Laboratories (Guelph, Ontario, Canada). House dust reference material was purchased from National Institute of standards and Technology (Gaithersburg, MD, USA). Copper powder (purity 99.98% from Saarchem (Pty) Ltd., Muldersdrift, South Africa), silicagel (100–200 mesh), sodium sulphate (purity 99.9%), glass wool and HPLC grade solvents: acetone, hexane, dichloromethane and toluene (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. Pesticarb was purchased from Separations Pty, Pretoria South Africa.

All solvents used were of analytical grade and kept away from contamination. Other materials such as silica gel, sodium sulphate and copper powder were activated before use. Anhydrous sodium sulphate and silica gel at first use were heated in a muffle furnace at 450 °C for 16 h. Copper powder was activated by ultrasonication in 25% HCl for 15 min then rinsed thoroughly with Milli-Q water followed by acetone and kept under toluene until use (Cristale and Lacorte, 2013). Preparation of standards and serial dilution of working standards were done under fume hood.

2.2. Sampling

Dust samples were collected in 2012 from 10 homes and 11 offices in Makurdi, Benue State middle belt region of Nigeria in a procedure similar to one previously described by Kefeni (2012). The climate of the area is tropical sub humid. Samples were collected by surface swiping of all materials available in the homes such as televisions, computers, chairs, fans, air conditioners and chairs using glass wool pre-rinsed with acetone and dried @ 150 °C for 12 h. The glass wool was pre-weighed, after careful wiping of the surfaces, glass wool with dust was weighed to get the amount of dust collected. Swiped samples were pooled together where low mass was collected based on similarity of electronic items available in the office or home where sample was collected with the ones collected from the vacuum cleaner since the overall goal was to determine the occurrence and levels of PBDEs. Carpet dust was collected using a portable standard vacuum cleaner (Model: 601SA, made in China) of about 1000 W equipped with a dust collection bag. Details of the electronic items and characterisation of the interior of the homes were recorded. Samples were transferred from the vacuum cleaner into solvent rinsed foil, wrapped and taken to the laboratory where they were filtered and stored in amber glass bottles at a temperature of –10 °C prior to extraction and further analysis.

2.3. Sample treatment and analysis

About 100 mg fine sieved dust from each of the samples was weighed and extracted with Soxhlet. Prior to extraction, dust samples were spiked with 3 µl of labelled BDE-139 and BDE-209 standards to monitor recoveries. Extraction efficiencies of some selected solvents found in the literature such as *n*-hexane, toluene, acetone and dichloromethane were used individually and in some cases combined. A combination of *n*-hexane: acetone (2:1, v/v) gave the best recovery for most of the target analytes. Dust samples were sieved using a 150 µm sieve and shaken in a closed sifting pan. After each sieved sample, the sieve and pan were rinsed with acetone and wiped to avoid cross contamination. The weighed dust samples were transferred into a glass fibre thimble then spiked with ¹³C₁₂ BDE-139 and -209, 2 g activated copper added into the mixture and Soxhlet extracted with 180 mL hexane/acetone (2:1, v/v) for 8 h. Crude extract containing PBDEs was collected and concentrated to 1 mL by rotary evaporator (Buchi Rotavapor, R-210, supplied by Labotec, South Africa). Clean up followed the procedure earlier reported by Olukunle et al. (2015) using hexane for elution. The column for cleanup was prepared by packing in layers from bottom into Pasteur pipettes (230 mm) about 0.16 g of silica, 0.16 g basic silica, 0.16 g silica, 0.16 g acidic silica, 0.16 g silica and finally topped with 0.5 g sodium sulphate. The Pasteur pipette was plugged at the bottom with glass wool and also used to separate each layer of materials for enhanced cleaning. Before introduction of 1 mL reduced extract, the packed column was eluted to saturation with 12 mL *n*-hexane: dichloromethane (5:1, v/v). Sample was introduced into the column

before the solvent reached the bed of the sodium sulphate plugged with glass wool and was further eluted with 4 mL combined solvent. Thereafter, nitrogen gas was bubbled into the eluant and concentrate to 200 μL . About 10 μL of 2.5 $\text{ng } \mu\text{L}^{-1}$ surrogate standard (BDE-118) was added to check deviations in instrument conditions and thereafter, 1.0 μL of the extract was injected into the GC–MS under the optimised instrumental conditions.

The clean extracts were analysed by Shimadzu model 2010 plus gas chromatograph coupled with a model QP 2010 ultra, mass spectrometer (Shimadzu, Japan) using electron ionisation and injected by a Shimadzu AOC-20i auto sampler. Operation mode was in the selected ion-monitoring (SIM). A 15 m column of ZB 5 (0.25 mm ID, 0.25 $\mu\text{m } d_f$) was used for separation. The initial oven temperature was set at 90 $^{\circ}\text{C}$ (1 min), ramped at 30 $^{\circ}\text{C}/\text{min}$ –300 $^{\circ}\text{C}$ (5 min) and at 10 $^{\circ}\text{C}/\text{min}$ –310 (10 min). Helium with purity of 99.999% was used as the carrier gas at a constant flow of 1.5 mL min^{-1} . The injector, transfer line and ion source temperatures were set at 290 $^{\circ}\text{C}$, 300 $^{\circ}\text{C}$ and 250 $^{\circ}\text{C}$ respectively.

2.4. Quality assurance/quality control

Silica gel and sodium sulphate were stored in glass jar which was pre-cleaned and rinsed with n-hexane; acetone solvent and then sealed to avoid absorption of moisture and contamination. Glass wool was wrapped with aluminium foil and kept inside desiccators. To protect the analytes from degradation by UV-light, the samples were kept in amber glass bottles until extraction. Furthermore, the method performance and validation was evaluated by extracting organic contaminants in house dust “SRM-2585”. The recovery of surrogate standards $^{13}\text{C}_{12}$ -BDE-139 and $^{13}\text{C}_{12}$ -BDE-209 varied between 75–90% and 65–81% respectively. Prior to sample analysis and after, an initial solvent blank, a laboratory performance standard check (linearity of the calibration curve) was performed using individual and mixtures of the most common brominated flame retardants. Check standard was run after every five samples to monitor retention time deviation. The use of surrogate standards during extraction and after clean-up was done to ensure accuracy. The results of blank analysis were subtracted from those of the real samples, and check standards fall within acceptable concentration range. Retention times matched those of the standards and quantification was done by monitoring the molecular and reference ions using external methods. External calibration of the GCMS was done using seven level calibration standards. The instrument limit of detection was taken as $> 3 \times$ the signal to noise ratio of the lowest calibration standard and the observed range was between 0.01 and 0.24 $\text{ng } \mu\text{L}^{-1}$.

2.5. Data analysis

Statistical analysis was performed using STATISTICA software Version 2010. The differences between data were analysed using Analysis of Variance (ANOVA). Pearson correlation and students *T*-test was applied to test relationship between electronic items and PBDE concentrations. All statistical significance was set at alpha value of 0.05.

3. Results and discussion

A total of seven PBDEs (BDE-47, BDE-100, BDE-99, BDE-154, BDE-153, BDE-183 and BDE-209) were determined in dust samples and these seven were chosen because they have been found to be dominant congeners in most environmental samples including indoor and outdoor dust samples. They are representative of the Octa, Penta and Deca-BDE mixtures, therefore, are used to predict the potential sources of contamination. The results of analysis of

Table 1

Certified and measured concentrations of (ng g^{-1}) certified reference material (NIST SRM 2585–Organic contaminants in house dust).

Congener	Measured	Certified	Recovery (%)
BDE-17	104 \pm 4.1	115 \pm 1.2	90
BDE-28	40 \pm 1.0	47 \pm 4.4	85
BDE-47	463 \pm 9.0	497 \pm 46	93
BDE-100	146 \pm 3.5	145 \pm 11	101
BDE-99	628 \pm 0.08	892 \pm 53	70
BDE-154	73 \pm 0.7	84 \pm 2	88
BDE-153	85 \pm 0.8	119 \pm 1	72
BDE-183	48 \pm 4.5	43 \pm 3.5	111
BDE-209	2082 \pm 11	2510 \pm 190	83

house dust “SRM-2585” certified reference material is as shown in Table 1.

3.1. PBDE concentrations in indoor dust samples

Descriptive statistics of PBDE concentrations in the different microenvironments are as stated in Table 2. As can be seen in Table 2, detection frequency for target PBDEs was between 70% and 100% for Nigerian indoor dust samples. The observed high detection frequency suggests the prevalence of PBDEs in indoor environments as widely reported in the literature (Gevao et al., 2006; Allen et al., 2008; Batterman et al., 2010; Stasinska et al., 2013). The mean concentration of \sum_7 PBDE in all 10 house dust samples was observed to be 57 ng g^{-1} dry weight (d.w) and median of 50 ng g^{-1} d.w. This is consistent with the findings previously reported by our research group on home dust in Pretoria with a mean concentration of 51.1 ng g^{-1} d.w but a lower median of 15 ng g^{-1} (Kefeni, 2012). These observed mean concentrations were found to be about one order of magnitude lower (BDE-209 median: 622 ng g^{-1}) than was reported in house dust in Germany (Abb et al., 2011) and Australia (\sum_7 PBDE median: 571 ng g^{-1}) (Stasinska et al., 2013). A total \sum_7 PBDE of 3979 ng g^{-1} was determined in all 10 samples. Most of the target congeners were detected except BDE-154 and -153 in 3 of the house samples and BDE-100 and -99 in another two samples. Concentrations range from $< \text{dl}$ –201 ng g^{-1} , for BDE-209. As can be seen in Tables 2 and 3 congeners (BDE-47, BDE-183 and BDE-209) were detected in all the samples. The highest median concentrations were reported for BDE-209, while BDE-47, BDE-99 and BDE-153 exhibited relatively similar median values respectively. BDE-209 was the dominant congener in all samples with percentage contribution of about 42%, followed by BDE-47 (10.69%) and BDE-99 (9.87%) in the following order; BDE-183 (7.74%) $<$ BDE-154 (8.76%) $<$ BDE-100 (9.79%) $<$ BDE-153 (9.83%) $<$ BDE-99 (9.87%) $<$ BDE-47 (10.69%) $<$ BDE-209 (43.35%).

PBDE levels in office ($n=11$) dust samples for Nigeria were found slightly elevated than in house dust samples with an average of 79.8 ng g^{-1} d.w and median of 62.6 ng g^{-1} . A \sum_7 PBDE of 7008 ng g^{-1} was measured in all 11 samples. All target congeners were detected except BDE-183 in one office dust sample. Concentrations range from $< \text{dl}$ –429 ng g^{-1} (BDE-209). The highest median concentrations were reported for BDE-209, while BDE-100, BDE-99 and BDE-154 exhibited relatively similar median values respectively (Table 2). BDE-209 was the dominant congener in all samples with percentage contribution of about 41%, followed by BDE-153 (11.6%) and BDE-183 (11.4%) in the following order; BDE-47 (8.1%) $<$ BDE-100 (9%) $<$ BDE-99 (9.5%) $<$ BDE-154 (10.1%) $<$ BDE-183 (11.4%) $<$ BDE-153 (11.6%) $<$ BDE-209 (40.5%). Correlation tests of the number of electronic items found in both the office and house dust samples to \sum_7 PBDE concentrations were performed by applying Pearson correlation coefficients. A positive

Table 2
Summary of PBDE concentrations (ng g⁻¹) in house and office dust from Nigeria and South Africa.

Microenvironment	Analytes						
	BDE-47	BDE-100	BDE-99	BDE-154	BDE-153	BDE-183	BDE-209
Nigerian homes (n=10)							
Detection (%)	100	90	90	70	70	100	100
5th percentile	26.6	0.11	0.24	0.03	0.03	39.8	80.7
95th percentile	50.5	55.1	60.8	70.7	72.4	84	201
Mean	42.5	38.8	39.3	34.8	39.1	61.7	141
Std. dev.	7.8	15.8	22	25	27	14.2	40.2
Minimum	26	0.1	0.24	0.03	0.03	38.8	79
Maximum	51.1	55.6	62	72.1	73.6	85.3	202
Geometric mean	41.7	23.2	16.6	5.3	5.8	60	136
Nigerian offices (n=11)							
Detection (%)	100	100	100	100	100	90	100
5th percentile	37.4	41.6	44.7	48.2	59.3	57.6	116
95th percentile	81.3	85	96	95	110	111	261
Mean	51.6	56.1	60.6	64.7	74.3	72	180
Std. dev.	15.6	16.3	18.2	19	20	30	88.6
Minimum	35.8	38.1	43.1	46.7	51.7	1.0	112
Maximum	84.76	92.7	99.3	110	118	124	428
Geometric mean	49.7	54.1	58.4	62.4	72.1	52	165
South African homes (n=31*)							
Detection (%)	54.8	6.5	54.8	9.7	6.5	–	35.5
5th percentile	–	–	–	–	–	–	–
95th percentile	45.6	8.1	53.2	7.2	1.9	–	35.5
Mean	11.9	1.1	15.2	1.2	1.0	–	16.2
Std. dev.	–	–	–	–	–	–	–
Minimum	–	–	–	–	–	–	–
Maximum	48.2	16.6	71.1	23.1	26.6	–	78.9
Geometric mean	–	–	–	–	–	–	–
South African offices (n=16*)							
Detection (%)	62.5	–	81.3	–	6.3	–	31.3
5th percentile	–	–	–	–	–	–	–
95th percentile	–	–	–	–	–	–	–
Mean	35.3	–	64.	–	7–0.8	–	52.6
Std. dev.	32.4	–	44.	–	9–3.1	–	144
Minimum	< dl	–	< dl	–	< dl	–	< dl
Maximum	81.9	–	127	–	12.5	–	571
Geometric mean	–	–	–	–	–	–	–

* South African house and office dust (Kefeni, 2012), < dl= below detection, (–)=not analysed/not available, Std. dev.=standard deviation

correlation was observed with a statistical significant difference (office; $r=0.83$, $p=0.001$, house; $r=0.53$, $p=0.002$). This means that emissions from computers and TVs might have contributed to PBDE concentrations in the dust samples. We found this to be

consistent with report by Yu et al. (2012), who found that PBDE concentrations in indoor dust were significantly higher than those in corresponding out-house (outside the same house) dust collected in Shanghai, China. Furthermore, Allen et al. (2008) found

Table 3
Comparison of median levels of PBDEs (ng g⁻¹) in indoor dust with other studies.

Study	Country	BDE-47	BDE-100	BDE-99	BDE-154	BDE-153	BDE-183	BDE-209	ΣPBDEs
This study	Nigeria (n=10)	46.9	42.6	46.2	44.9	50.4	30.4	139	50
		46*	51.1*	54.2*	58.6*	67.1*	71.9*	140*	80*
Kefeni (2012)	South Africa (n=31)	2.6	< dl	2.6	< dl	< dl	–	< dl	15.2
		44.0*	–	76.50*	–	< dl	–	< dl	162.2*
Stasinska et al. (2013)	Australia (n=30)	36.8	–	56.8	–	–	–	415	571
Abb et al. (2011)	Germany (n=24)	–	–	–	–	–	–	622	–
Ali et al. (2013)	Pakistan (n=15)	1.3	< 0.3	1.7	0.4	0.6	1.5	138	145
Sjodin et al. (2008)	Kuwait (n=15)	9.5	2.3	12	1.3	2.4	1.9	310	356
	Germany (n=10)	< 14	< 6	10	< 6	< 6	< 6	63	74
	Australia (n=10)	60	18	100	9	13	14	730	1200
	Great Britain (n=10)	22	4	28	3	5	5	10,000	10,000
Batterman et al. (2010)	United States (n=10)	430	150	880	80	140	70	2000	4200
	Michigan, USA, (n=18)	978	1200	1760	190	110	220	190	–
Harrad et al. (2008a)	Birmingham, UK, (n=18)	23	3.2	65	5.1	8.7	8.3	6,200	–
Suzuki et al. (2006)	Tokyo, Japan, (n=14)	30.5	–	38	–	15.	–	5–1100	–
Gevao et al. (2006)	Kuwait (n=17)	2.7	0.7	3.4	0.9	0.7	1.3	82.9	90

* Office, (–)=not available, and < dl=below detection

Table 4

Summary of estimated ingestion of BDE-47, -99 and -209 from settled indoor dust ($\times 10^{-5}$ $\mu\text{g}/\text{kg}$ bw/day) for adults and children from Nigeria compared to South Africa.

Congener	Adults		Children		References
	Median	Maximum	Median	Maximum	
South African home dust					
BDE-47	0.08	1.43	1.37	25.3	Kefeni et al. (2014)
BDE-99	0.08	2.1	1.37	37.3	
BDE-209	na	na	na	na	
Nigerian home dust					
BDE-47	1.4	1.51	24.6	26.8	This study
BDE-99	1.37	1.83	24.3	32.6	
BDE-209	4.12	6.0	73.2	106.1	
Nigerian office dust					
BDE-47	0.43	0.8	6.07	11.2	This study
BDE-99	0.51	0.94	7.5	13.1	
BDE-209	1.31	4.04	18.4	56.6	

significantly higher PBDE concentrations in the living area compared to the bedroom which indicated spatial variability within a home, thus confirming that the different microenvironments play an important role in the distribution of PBDEs in indoor dust. No correlation was, however, found between electronic items and PBDE concentrations in a previous study in Pretoria indoor dust by Kefeni et al. (2014).

A one way ANOVA was performed to test the level of significance in the different mean concentrations recorded for the seven congeners. A number of factors such as the presence of materials treated with flame retardants, smaller space, ventilation and climatic conditions may influence the overall concentrations of PBDEs obtained. According to Yu et al. (2009), higher temperatures can lead to higher emission rates of PBDEs from household products. The test results showed a positive correlation in the levels of PBDEs determined for most of the samples suggesting a common source of emission. Further analysis using Duncan test showed BDE-209 and BDE-47 to be significantly different ($p=0.02$) from the rest of the congeners while BDE-99, BDE-100 and BDE-153 concentrations are not significantly different ($p > 0.05$). The contribution to various commercial mixtures was found to be in the order; Penta-BDE (55%) > Deca-BDE (32%) > Octa-BDE (13%). Penta-BDE which comprise BDE-47, BDE-99, BDE-100, BDE-154 and BDE-153 is used in polyurethane foams which are found in most homes and in circuit boards while Deca-BDE, comprising mainly of BDE-209 is used in the hard casings of televisions and computers, electrical, electronic equipment and in plastics which are also common features in many homes.

3.2. Comparison to other studies

The results from the present study were compared to PBDE levels reported in literature from other regions. Table 3 shows the comparison of median PBDE levels in indoor dust. These were observed to be higher than the median of 50 ng g^{-1} and 62.6 ng g^{-1} for house and office dust in this study except for the German house dust. Higher median values were, however, observed for most of the lower congeners compared to the other studies, except for the samples from the United States.

3.2.1. Exposure assessment via dust ingestion

There is presently no available report on the occurrence and possible exposure risks to which Nigerians are prone to from brominated flame retardants. According to Nnorom and Osibanjo (2008), there is high level trans-boundary movement of waste

electrical electronic equipment (WEEE) which may contain BFRs into the developing countries. It is assumed that based on this realisation, Nigerians are exposed to certain amounts of BFRs in the indoor environment. Therefore, exposure estimates (Table 4) of Nigerians to household and office dust was calculated and compared to a similar study from Pretoria, South Africa, taking into consideration the general assumption of 100% absorption intake (Jones-Otazo et al., 2005; Harrad et al., 2008b) and average dust ingestion of 30 and 60 mg day^{-1} for adults and children between the ages of 1 and 6 years respectively (USEPA, 2011). In addition, the corresponding time spent at home and office/day-care according to de Wit et al. (2012) was assumed to be 87.5% (adult) and 69% (children) in homes and 22% in offices and day-care. Dust ingestion estimates were then determined based on the median values of $\sum_6 \text{PBDEs}$ (BDE-47, -100, -99, 153, -154, and BDE-183) and BDE-209 in the different microenvironments. The method used for calculating PBDEs intake (ng day^{-1}) followed that described by Kefeni et al. (2014). The estimated mean daily exposure rates were, however, found to be 2 and 0.84 ng g^{-1} for children 1 < 6 years and adult respectively. These values were slightly higher than the 0.96 and 0.38 ng g^{-1} reported in Pretoria, South Africa. Higher mean exposure values in this case suggest higher exposure for Nigerians.

Furthermore, derived exposure values were then used to calculate dose estimates assuming an average body weight (bw) of 10 and 70 kg for children and adults respectively (Table 4). As can be seen in Table 4, the estimated daily ingestion doses of PBDEs were relatively higher compared to South Africa but by far lower than EPA, 2008 reference doses (RfDs) of $0.1 \mu\text{g kg}^{-1}$ for BDE-47 and -99.

4. Conclusion

Dust is a heterogeneous mixture of biologically derived materials including brominated flame retardants and has been recognised as an important pathway of human exposure to PBDEs. To this end, PBDE concentrations in household and office dust samples collected from Makurdi, Benue State, Nigeria were measured. The results show a significant difference among the samples. BDE-209 and BDE-47 were significantly different among seven target congeners. A positive correlation, however, was found between PBDE concentrations and number of electronic items in the homes and offices suggesting a likelihood of PBDE release from materials in the microenvironment. PBDE concentrations were higher than our previous studies in South African indoor dust. Consequently, the estimated daily ingestion doses of PBDEs were relatively higher compared to South Africa, but by far lower than EPA reference doses. This study provided the base line data on levels of PBDEs in Nigeria indoor environment.

Practical implications

This study confirms the ubiquitous nature of PBDEs in the indoor microenvironment dust samples in Nigeria and provides the exposure estimates for adults and children. Observed levels were higher than in previous study carried out in South Africa. This then means that Nigerians are more exposed to relatively higher doses of PBDEs compared to South Africans, but lower than in developed countries.

Acknowledgements

The authors are highly indebted to the Organisation for the

Prohibition of Chemical Weapons (OPCW) for financing this project and Tshwane University of Technology for providing the enabling environment.

References

- Abb, M., Stahl, B., Lorenz, W., 2011. Analysis of brominated flame retardants in house dust. *Chemosphere* 85 (11), 1657–1663.
- Alcock, R.A., Sweetman, A.J., Prevendouros, K., Jones, K.C., 2003. Understanding levels and trends of BDE-47 in the UK and North America: an assessment of principal reservoirs and source inputs. *Environ. Int.* 29 (6), 691–698.
- Ali, N., Ali, L., Mehdi, T., Dirtu, A.C., Al-Shammar, F., Neels, H., Covaci, A., 2013. Levels and profiles of organochlorines and flame retardants in car and house dust from Kuwait and Pakistan: Implication for human exposure via dust ingestion. *Environ. Int.* 55, 62–70.
- Allen, J.G., McClean, M.D., Stapleton, H.M., Webster, T.F., 2008. Critical factors in assessing exposure to PBDEs via house dust. *Environ. Int.* 34 (8), 1085–1091.
- Batterman, S., Godwin, C., Chernyak, S., Jia, C., Charles, S., 2010. Brominated flame retardants in offices in Michigan, U.S.A. *Environ. Int.* 36 (6), 548–556.
- BSEF, 2006. The European legislation on WEEE and ROHS February 2006 [Online]. Available from: (www.bsef.com). (accessed 11.04.09).
- BSEF, 2015. Our substances: Applications of Deca-BDE [Online]. Available from: (www.bsef.com/our-substances/deca-bde/applications). (accessed 09.04.15).
- Chen, D., Guardia, M.J.L., Harvey, E., Amaral, M., Wohlfort, K., Hale, R.C., 2008. Polybrominated diphenyl ethers in peregrine falcon (*Falco peregrinus*) eggs from the Northeastern U.S. *Environ. Sci. Technol.* 42 (20), 7594–7600.
- Cheng, C.C., Chiu, C.F., Chang, F.H., 2009. Characteristics of polybrominated diphenyl ethers in the indoor atmosphere of computer classrooms. *Sci. Res. Essay* 4 (10), 1117–1122.
- Cristale, J., Lacorte, S., 2013. Development and validation of a multiresidue method for the analysis of polybrominated diphenyl ethers, new brominated and organophosphorus flame retardants in sediment, sludge and dust. *J. Chromatogr. A* 1305 (2013), 267–275.
- Darnerud, P.O., Aune, M., Larsson, L., Lignell, S., Mutshatshi, T., Okonkwo, J., Botha, B., Agyei, N., 2011. Levels of brominated flame retardants and other persistent organic pollutants in breast milk samples from Limpopo province, South Africa. *Sci. Total Environ.* (409), 4048–4053.
- de Wit, C.A., Alaee, M., D.C.M., 2006. Levels and trends of brominated flame retardants in the Arctic. *Chemosphere* 64 (2), 209–233.
- de Wit, C.A., Hertzke, D., Vorkamp, K., 2010. Brominated flame retardants in the Arctic environment- trends and new candidates. *Sci. Tot. Environ.* 408, 2885–2918.
- de Wit, C.A., Bjorklund, J.A., Thureson, K., 2012. Tri-decabrominated diphenyl ethers and hexabromocyclododecane in indoor air and dust from Stockholm micro-environments 2: indoor sources and human exposure. *Environ. Int.* 39, 141–147.
- Devanathan, G., Subramanian, A., Sudaryanto, A., Takahashi, S., Isobe, T., Tanabe, S., 2012. Brominated flame retardants and polychlorinated biphenyls in human breast milk from several locations in India: potential contaminant sources in municipal dumping site. *Environ. Int.* 39 (1), 87–95.
- Gevao, B., Al-Bahloul, M., Al-Ghadban, A.N., Al-Omair, A., Ali, L., Zafar, J., Helaleh, M., 2006. House dust as a source of human exposure to polybrominated diphenyl ethers in Kuwait. *Chemosphere* 64 (4), 603–608.
- Harrad, S., Ibarra, Catalina, Abdallah, M.A.-E., Boon, R., Neels, H., Covaci, A., 2008a. Concentrations of brominated flame retardants in dust from United Kingdom cars, homes, and offices: Causes of variability and implications for human exposure. *Environ. Int.* 34 (8), 1170–1175.
- Harrad, S., Ibarra, C., Diamond, M., Melymuk, L., Robson, M., Douwes, J., Roosens, L., Dirtu, A.C., Covaci, A., 2008b. Polybrominated diphenyl ethers in domestic indoor dust from Canada, New Zealand, United Kingdom and United States. *Environ. Int.* 34 (2), 232–238.
- Hazrati, S., Harrad, S., 2006. Causes of variability in concentrations of polychlorinated biphenyls and polybrominated diphenyl ethers in indoor air. *Environ. Sci. Technol.* 40, 7584–7589.
- He, C., Morwaska, L., Taplin, L., 2007. Particle emission characteristics of office printers. *Environ. Sci. Technol.* 41, 6039–6045.
- Hirai, Y., Sakai, S., Sato, K., Hayakawa, K., Shiozaki, K., 2006. Emission of brominated flame retardants from TV sets. *Organohalogen Compd.* 68, 1772–1775.
- Jakobsson, K., Thureson, K., Rylander, L., Sjodin, A., Hagmar, L., Bergman, A., 2002. Exposure to polybrominated diphenyl ethers and tetrabromobisphenol A among computer technicians. *Chemosphere* 46, 709–716.
- Johnson-Restrepo, B., Kannan, K., Rapaport, D.P., Rodan, B.D., 2005. Polybrominated diphenyl ethers and polychlorinated biphenyls in human adipose tissue from New York. *Environ. Sci. Technol.* 39, 5177–5182.
- Johnson, P.I., Stapleton, H.M., Sjodin, A., Meeker, J.D., 2010. Relationships between polybrominated diphenyl ether concentrations in house dust and serum. *Environ. Sci. Technol.* 44, 5627–5632.
- Johnson-Restrepo, B., Kannan, K., 2009. An assessment of sources and pathways of human exposure to polybrominated diphenyl ethers in the United States. *Chemosphere* 76, 542–548.
- Jones-Otazo, H.A., Clarke, J.P., Diamond, M.L., Archbold, J.A., Ferguson, G., Harner, T., Richardson, G.M., Ryan, J.J., Wilford, B., 2005. Is house dust the missing exposure pathway for PBDEs? An analysis of the urban fate and human exposure to PBDEs. *Environ. Sci. Technol.* 39, 5121–5130.
- Kalantzi, O.I., Geens, T., Covaci, A., Siskos, P.A., 2011. Distribution of polybrominated diphenyl ethers (PBDEs) and other persistent organic pollutants in human serum from Greece. *Environ. Int.* 37, 349–353.
- Karlsson, M., Julander, A., Van Bavel, B., Hardell, L., 2007. Levels of brominated flame retardants in blood in relation to levels in household air and dust. *Environ. Int.* 33, 62–69.
- Kefeni, K.K., Okonkwo, O.J., 2012a. Analysis of major congeners of polybromobiphenyls and polybromodiphenyl ethers in office dust using high resolution gas chromatography-mass spectrometry. *Chemosphere* 87, 1070–1075.
- Kefeni, K.K., 2012b. Brominated Flame Retardant Concentrations in Office and Household Dust in South Africa (D. Tech). Tshwane University of Technology, Pretoria.
- Kefeni, K.K., Okonkwo, O.J., Botha, B.M., 2014. Polybromobiphenyls and polybromobiphenyl ethers in home dust: Relevance of socio-economic status and human exposure rate. *Sci. Tot. Environ.* 470–471, 1250–1256.
- Lorber, M., 2008. Exposure of Americans to polybrominated diphenyl ethers. *J. Expo. Sci. Environ. Epidemiol.* 18, 2–19.
- Ma, W.-L., Subedi, B., Kannan, K., 2014. The occurrence of bisphenol A, phthalates, parabens and other environmental phenolic compounds in house dust: a review. *Curr. Org. Chem.* 18, 2182–2199.
- Ni, K., Lu, Y., Wang, T., Kannan, K., Gosens, J., Xu, L., Li, Q., Wang, L., Liu, S., 2013. A review of human exposure to polybrominated diphenyl ethers (PBDEs) in China. *Int. J. Hyg. Environ. Health* 216, 607–623.
- Nnorom, I.C., Osibanjo, O., 2008. Sound management of brominated flame retarded (BFR) plastics from electronic wastes: State of the art options in Nigeria. *Resour. Conserv. Recycl.* 52, 1362–1372.
- Olukunle, O.I., Okonkwo, O.J., Wase, A.G., Sha'ato, R., 2015. Polybrominated diphenyl ethers in car dust in Nigeria: concentrations and implications for no-dietary human exposure. *Microchem. J.* 123, 99–104.
- Sjodin, A., Papke, O., McGahee, E., Focant, J.-F., Jones, R.S., Pless-Mullooli, T., et al., 2008. Concentration polybrominated diphenyl ethers (PBDEs) in household dust from various countries. *Chemosphere* 73 (1), S131–S136, Supplement.
- Shih, Y.-H., Wang, C.-K., 2009. Photolytic degradation of polybromobiphenyl ethers under UV lamp and solar irradiations. *J. Hazard. Mater.* 165 (1–3), 34.
- Stasinska, A., Reid, A., Hinwood, A., Stevenson, G., Callan, A., Odland, J.O., Heyworth, J., 2013. Concentrations of polybrominated diphenyl ethers (PBDEs) in residential dust samples from Western Australia. *Chemosphere* 91, 187–193.
- Suzuki, G., Nose, K., Takigami, H., Takahashi, S., Sakai, S., 2006. PBDEs and PBDD/Fs in house and office dust from Japan. *Organohalogen Compd.* 68, 1843–1846.
- Takigami, H., Suzuki, G., Hirai, Y., Sakai, S., 2008. Transfer of brominated flame retardants from components into dust inside television cabinets. *Chemosphere* 73 (2), 161–169.
- UNEP, 2009. The 9 new POPs under the Stockholm Convention [Online]. Available from: (www.chm.pops.int/programme/new). (accessed 09.04.11).
- USEPA, 2011. Exposure Factors Handbook (No. EPA/600/R-090/052F). National Center for Environmental Assessment, Office of Research and Development, Washington DC.
- WHO/EHC-192, 1997. Flame retardants: a general introduction. International Programme on Chemical Safety, World Health Organisation, Geneva.
- Yu, M., Luo, X.-J., Wu, J.-P., Chen, S.-J., Mai, B.-X., 2009. Bioaccumulation and trophic transfer of polybrominated diphenyl ethers (PBDEs) in biota from the Pearl River Estuary, South China. *Environ. Int.* 35, 1090–1095.
- Yu, Y.-X., Pang, Y.-P., Li, C., Li, J.-L., Zhang, X.-Y., Yu, Z.-Q., Feng, J.-L., Wu, M.-H., Sheng, G.-Y., Fu, J.-M., 2012. Concentrations and seasonal variations of polybrominated diphenyl ethers (PBDEs) in in- and out-house dust and human daily intake via dust ingestion corrected with bioaccessibility of PBDEs. *Environ. Int.* 42, 124–131.