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RESEARCH ARTICLE

Exposure evaluation and risk assessment of polybrominated diphenyl ethers in dust from microenvironments in Nsukka, Nigeria

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Abstract

The health risks of polybrominated diphenyl ethers (PBDEs) to toddlers, children, and adults in creches, nursery schools, cars, and offices in Nsukka, Nigeria, via inhalation, ingestion, and dermal exposure pathways were evaluated. Eight PBDEs congeners (BDE-28, BDE-47, BDE-100, BDE-99, BDE-154, BDE-153, BDE-183, and BDE-209) were determined using gas chromatography-mass spectrometry. This is the first study on PBDEs in creches and nursery schools in Africa. The mean (median) $\sum_8$PBDEs (ng/g) in creches, nursery schools, offices, and cars were 4355 (1850), 2095 (1130), and 37741 (2620) respectively. The concentrations of PBDEs between the three microenvironments were significantly different ($p < 0.05$), and the highest concentration was found in cars. Ingestion of dust was the predominant pathway of exposure to PBDEs for toddlers and children, while dermal absorption was the dominant pathway for adults. Dermal absorption and ingestion in cars, creches, and nursery schools were of the same magnitude. Toddlers with the highest ingestion rate of PBDEs in creches, nursery schools, and cars are at risk especially from prolonged exposure.

Keywords Creches · Dust · Exposure pathways · PBDEs · Pollution · Toddlers

Introduction

Globally, environmental pollution due to increasing levels of persistent organic pollutants (POPs) is a problem which was intensified by urbanization and industrialization (Ibeto et al. 2019). Polybrominated diphenyl ethers (PBDEs) are POPs which are brominated flame retardants mainly used to reduce flammability of commercial products, e.g., electronics, furniture, expanded and extruded plastic, and textiles (Jans 2016; Niu et al. 2019). They are recalcitrant, lipophilic, mostly stored in body fat, and readily migrate from one phase to another. They are potentially mobile between water, air, and soil (O'Driscoll et al. 2016). For instance, they are released from the recycling process of PBDE-containing waste printed circuit board (Guo et al. 2020), and hexabromocyclododecane (HBCD) is found at very high levels in water near e-waste dismantling sites (Xiang et al. 2018). Dust from indoor environs is a significant route from which humans are exposed to PBDEs as a result of its large surface area that is a depository for contaminants over a prolonged exposure time (Civan and Kara 2016).

Globally, decabrominated diphenyl ethers (decaBDE), pentabrominated diphenyl ethers (pentaBDE), and octabrominated diphenyl ethers (octaBDE) are the three major formulations of polybrominated diphenyl ethers. PentaBDE are used in production of printed circuit boards, furniture, carpet underlay, mattresses, cable sheets, paper laminates, electrical wire coatings, paints, etc. (USEPA 2010). OctaBDE are used in high impact plastics such as ABS (acrylonitrile butadiene styrene) polymers in plastic casing production for electronic objects like cathode rays, TVs and computer monitors, kitchen items, telephone, photocopying machines and printers (UNEP 2010). DecaBDE are essential for production of electronics, automotive vehicles, textile and furniture, cable/wire insulation, etc. Due to their nature as additives, they are possibly released throughout a product's lifetime (Lucas et al. 2018) and into the environment. Commercial PBDEs found mostly in the environment are somewhat resilient to degradation (Akortia et al. 2016).

Polybrominated diphenyl ethers persist in the environment due to slow degradation and have the ability to accumulate

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and pose adverse health effects (Zhong et al. 2018). PentaBDE which mainly affects the nervous system, causing memory weakness, is the most toxic and produces biotoxic effects even at low concentrations (Xie et al. 2012). OctaBDE is teratogenic and negatively affects the embryonic development. Although decaBDE has the least toxicity, in large doses, it is carcinogenic and causes liver and mild thyroid toxicity (Jin et al. 2019). Concentrations of some PBDEs have been linked with the threat of acute lymphoblastic leukemia in children (Ward et al. 2014). Due to the deleterious effects of several congeners, production and utilization of commercial penta-, octa-, and decaBDE categorized as persistent organic pollutants were restricted (Vuong et al. 2018).

Irrespective of the restriction enforced on the three commercial technical PBDEs mixture, they are still found in various products, furnishing, and building materials (La Guardia et al. 2006). Nigerians being great importers of second hand goods such as cars, clothes, electronics, baby toys, household utensils, and computers unknowingly import products treated with PBDEs which have been banned in other countries. This is due to the belief that they are of higher durability than newly manufactured ones and have become a source of PBDEs in the country. These imported goods are used in microenvironments including creches, nursery schools, homes, and offices.

The amount of time spent by humans daily indoors in offices, creches, nursery schools, homes, and computer rooms gives ample opportunity to be exposed to PBDEs. Exposure routes of human beings to PBDEs include diets (Martellini et al. 2016), inhalation, and indoor dust ingestion (Li et al. 2015b). Kang et al. (2011) revealed that exposure of children to PBDEs from indoor dust were significantly higher than dietary intake. Also, PBDEs were found in human breast milk, and these pose a concern as these congeners, specifically BDE-47, BDE-99, BDE-100, BDE-154, and BDE-153, are passed from mother to child (Hassan and Shoeib 2015).

Children especially toddlers vary from adults in their vulnerability to harmful chemicals as a result of their reduced capability to excrete xenobiotic toxic chemicals, lesser body weight, speedy growth, and structural development of functional vital organs (Chen et al. 2009). In most countries, children within the age of 0.5 to 6 years spend the majority of their daytime indoors in daycare facilities such as creches and nursery schools which leaves them with ample time to be exposed to PBDEs. Inhalation and dermal absorption are believed to be an important means of exposure to PBDEs for kids as a result of their playing activities near the floor. The discharge of PBDEs in dust could occur indoor via exposure from toys, electronic items, and foams, rather than from outdoor environs (Ding et al. 2016).

PBDE levels in humans in North Carolina have been reported (Leonetti et al. 2016). There are also studies on concentrations of PBDEs in the environment including electronic dumpsites (Iwegbue et al. 2019; Ohajinwa et al. 2019) and homes (Olukunle et al. 2015a; Harrad et al. 2016) in Nigeria. PBDE levels have been reported for offices in China (Li et al. 2015a) and Egypt (Hassan and Shoeib 2015). However, there are no information on PBDE levels in offices and cars in South East Nigeria and in creches and nursery schools in the whole of Africa. Hence, this study was aimed at the evaluation of the levels, exposure pathways, source, and health risks of PBDEs in dust from creches, nursery schools, offices, and private cars in Nsukka, and the contribution of each microenvironment to the general human exposure was assessed.

Materials and method

Chemicals

Acetone, n-hexane, and activated sodium sulfate from Merck, USA, and activated silica (silica gel 60/200 mesh size) from Loba Chemie, India, were purchased. All the reagents and chemicals were of analytical grade. Standard PBDE mixture of 2,2′,3,3′,4,4′,5,5′,6,6′-decabromodiphenyl ether (BDE-209), 2,2′,3,4,4′,5′,6-heptabromodiphenyl ether (BDE-183), 2,2′,4,4′,5,6′-hexabromodiphenyl ether (BDE-154), 2,2′,4,4′,5,5′-hexabromodiphenyl ether (BDE-153), 2,2′,4,4′,6-pentabromodiphenyl ethers (BDE-100), 2,2′,4,4′,5,-penabromodiphenyl ether (BDE-99), 2,2′,4,4′-tetrabromodiphenyl ether (BDE-47), and 2,4,4′-tribromodiphenyl ether (BDE-28) was acquired from AccuStandard (New Haven, CT).

Sample collection

Forty-five (45) composite dust samples were collected from creches and nursery schools (N = 15 i.e. 5 creches and 10 nursery schools), offices (N = 15), and private cars (N = 15) from Nsukka, Nigeria, in August 2019 on a weekly basis using a handheld vacuum cleaner. A composite sample comprised of three samples. The map of the study area and other details are presented in Fig. 1 and Table S1. Before sampling, the detachable parts of the vacuum cleaner which contained the dust unit was washed with soapy water, dried, and rinsed with n-hexane. In between each sampling location, the detachable parts were cleaned and rinsed with n-hexane. The samples were collected from products surface and floor in creches, nursery schools, and offices, while for cars, the samples were collected from seats, floor, and trunk. Sampling was done for 10 min. Information on potential PBDEs contaminants were recorded during sampling, which was achieved with the use of questionnaires. This included number of teachers and children in the creches and nursery schools, chairs and tables used, electronics and mattresses used, type of flooring, ventilation,

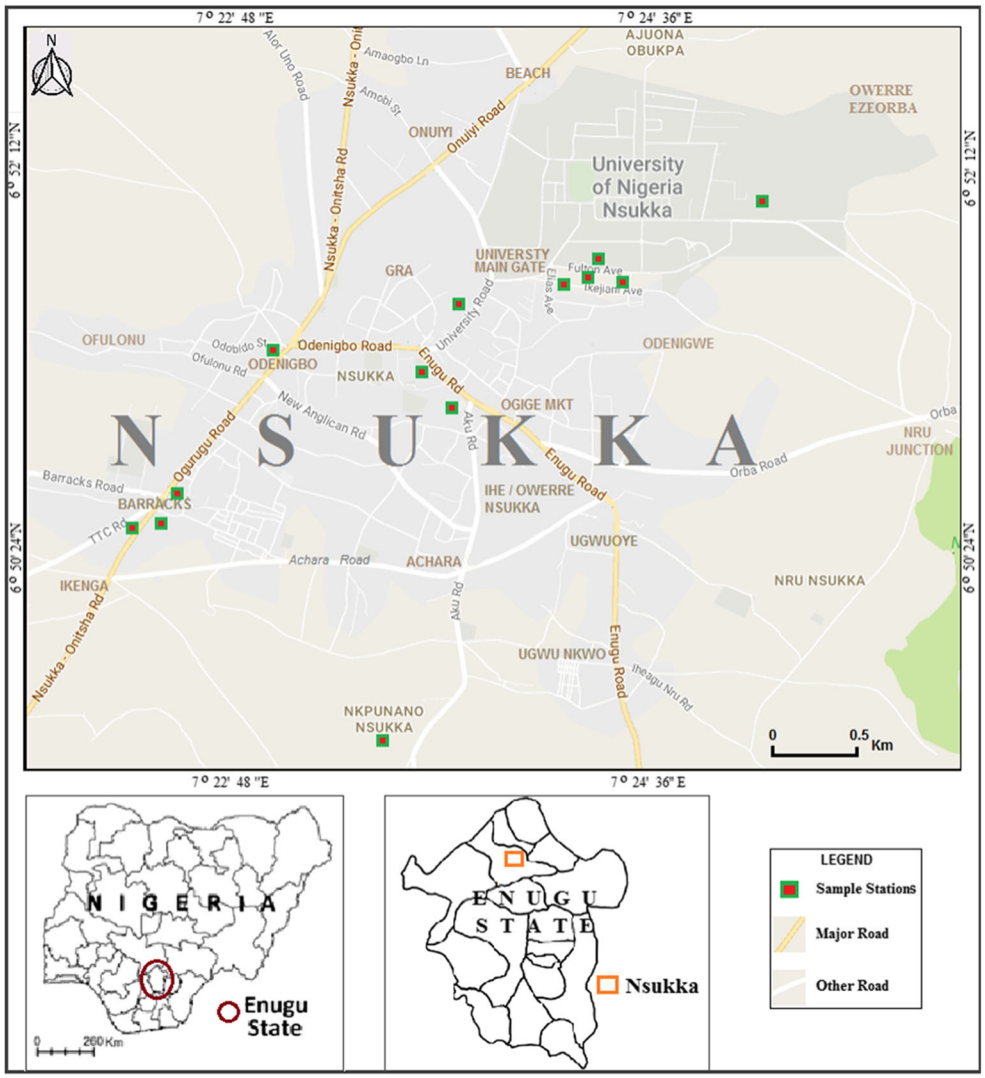

Fig. 1 Map of the study area

how often the classrooms were used, and approximate time spent by the children in the creches and nursery schools. In the office, the number and age of printers, computers, and other electronics were recorded. The type of chair and tables were also recorded. While for the cars, the model, age, and electronics were recorded. Preceding the analysis, the samples of dust were sieved using 52-mm mesh by shaking to get rid of any possible material that may interfere with the analysis. After sieving, the samples were stored in a pre-cleaned n-hexane bottle, covered with a lid and wrapped with aluminum foil. The bottles were stored at -4 °C until analysis.

Sample extraction and cleanup

Ten (10) ml hexane:acetone in the ratio of 1:1 was added to 3 g of dust, covered with aluminum foil to prevent evaporation and placed in ultrasonic bath for extraction at 40 °C for 20 min. It was allowed to settle and the solvent layer decanted. A rotary evaporator was used to concentrate the crude extracts to 2 ml (Akortia et al. 2019; Kofi et al. 2018).

The crude extracts obtained were passed through a column to remove any remaining impurities. The cleanup was done using a glass column packed with 4 g of silica gel (which has been previously activated for at least 6 h at 130 °C in a petri dish, loosely covered with foil) and topped with 2 g of anhydrous sodium sulphate. Ten (10) ml of hexane was added into the column to wet and rinse the sodium sulfate. The extract was eluted with 20 ml hexane from the column and concentrated to 2 ml (Niu et al. 2018; Śmiełowska and Zabiegała 2018). Samples extracts were analyzed after the calibration, and PBDE concentrations were obtained

Instrumental analysis

The levels of PBDEs in the dust samples were determined using Agilent 7820A GC coupled with 5975 Inert MSD (US), by operating MSD in scan mode and selective ion

monitoring (SIM) for low detection limits of the analytes of interest. The GC-MSD with triple-axis detector was equipped with an electron-impact source. HP-5 capillary column coated with 5% phenyl methyl siloxane (30 m length × 0.32 mm diameter × 0.25 μm film thickness) was the stationary phase. Helium was used as the carrier gas at a constant flow of 2.02 ml min^{-1} and initial pressure of 9.57 psi and an average velocity of 54.03 cm/sec. Samples (1 μL) were injected in split less mode at 300 °C. Purge flow to spilt vent was 50.0 ml min^{-1} at 2 min with a total flow of 16.67 ml/min; gas saver mode was turned off. The oven temperature was at first programmed at 150 °C (1 min) and then ramped at 17 °C min^{-1} to 315 °C (5 min). Run time was 15.71 min with a 3 min solvent delay.

The mass spectrometer was operated in an electron-impact ionization mode at 70 eV with ion source, quadrupole, and transfer line temperatures of 230 °C, 150 °C, and 300 °C, respectively. Acquisition of ion was via scan mode (scanning from m/z 200 to 1000 amu at 2.0 s/scan rate) and selective ion mode. Samples extracts were analyzed after the calibration and PBDEs concentrations were obtained.

Quality control/quality assurance

All glassware were properly washed with a soap solution, rinsed with deionized water, dried, and then rinsed again with a solvent. Sodium sulfate and silica gel were baked for 6 h at 130 °C in a petri dish, loosely covered with foil to remove moisture and impurities, and stored in a clean glass jar. The samples of dust were stored in a pre-cleaned n-hexane bottle and wrapped with aluminum foil to prevent photodegradation. Control samples were taken from an empty room. Serial dilution standards (0.10, 0.31, 0.62, 1.25, 2.50 ppm) of PBDE congeners of primary interest calibration mix (AccuStandard, USA) were used to calibrate the gas chromatography-mass spectrometry (GC-MS). A standard check (linearity of calibration curve) was done, and good linearity was achieved with regression coefficients of over 0.995. Preceding the calibration, the Mass-Spectrometer was auto-tuned to perfluorotributylamine using already proven criteria to check the abundance of m/z 69, 219, 502 and other instruments optimal and sensitivity conditions.

A procedural blank was included in every 5 samples. No PBDE was detected in the procedural blank. The limits of detection (LOD) and quantification (LOQ) were evaluated based on the standard deviation of the calibration curve. The LOD was determined using LOD = 3.3 × SD/b, where b is the slope of calibration curve and SD is a residual standard deviation of the calibration curve, while the limit of quantification was calculated as LOQ = 3 × LOD. All the PBDE congeners had LOD and LOQ (mg/kg) of 0.003 and 0.01 respectively except BDE-209 with 0.013 and 0.04 respectively.

Recovery analysis of the PBDEs was done by spiking 0.1 ml of 0.25 mg/L PBDE congeners of primary interest calibration mix (AccuStandard, USA) to the dust samples before extraction. Three replicate samples were analyzed to validate the method. The average recovery of the 8 PBDE congeners was 80–108%. Full details are shown in Table 1.

Human exposure assessment

Human exposure to PBDEs in dust was assessed using an exposure scenario: inhalation, ingestion, and dermal contact. The exposure parameters for children and adults are shown in Table 2.

The average daily dose (ADD) of PBDEs in dust via inhalation, ingestion, and dermal contact are shown in Eqs. 1, 2, and 3 (USEPA 2009; Civan and Kara 2016). ADD_{inh}, ADD_{ing}, and ADD_{der} are average daily dose (mg/kg/day) via inhalation, ingestion, and dermal contact, respectively.

$$ADD_{inh} = C_{dust} \times \frac{ET_i \times R_{inh} \times ED_i \times EF}{PEF \times BW \times T_{aveg}} \quad (1)$$

$$ADD_{ing} = C_{dust} \times \frac{ET_i \times R_{ing} \times ED_i \times EF}{BW \times T_{avg}} \times CF \quad (2)$$

$$ADD_{der} = C_{dust} \times \frac{EA_{skin} \times SAF \times DAF \times ET_i \times EF \times ED_i}{BW \times T_{aveg}} \times CF \quad (3)$$

The hazard quotient (HQ) and hazard index (HI) as shown in Eqs. 4 and 5 respectively are used to estimate the non-carcinogenic risk from the exposure to PBDEs. Values of HQ and HI less than 1 show that there are no adverse effects, while HQ and HI greater than 1 indicate the possibility of adverse effects (USEPA 2010; Ohajinwa et al. 2019). Currently, only four PBDE congeners have reference dose (mg/kg-day): BDE 47 (0.0001), BDE 99 (0.0001), BDE 153 (0.0002), and BDE 209 (0.007) (Civan and Kara 2016).

$$HQi = \frac{ADD_i}{RFD_i} \quad (4)$$

$$HI = \sum_{i=1}^{n} HQ_i \quad (5)$$

where HQ_i is the hazard quotient of the PBDEs via inhalation, ingestion, and dermal contact pathway; ADD_i is the average daily dose (mg/kg/day) of the PBDEs; and Rfd_i is the reference dose via the three exposure pathways.

Statistical analysis

Descriptive statistics was done using Excel 2013. Origen 8 pro was used for Spearman correlation analysis to determine the relationship between the PBDE congeners, and Kruskal-

Table 1 Results of recovery analysis of PBDEs in dust

PBDEs	Unspiked concentration (mg/kg)	Spiked concentration (mg/kg)	% Recovery
BDE-28	0.16	0.40 ± 0.01	96 ± 0.02
BDE-47	0.33	0.60 ± 0.01	107 ± 0.04
BDE-100	0.38	0.60 ± 0.02	88 ± 0.07
BDE-99	1.09	1.36 ± 0.00	108 ± 0.00
BDE-154	2.41	2.62 ± 0.01	83 ± 0.01
BDE-153	0.11	0.33 ± 0.01	87 ± 0.04
BDE-183	1.01	1.22 ± 0.01	83 ± 0.03
BDE-209	0.22	2.21 ± 0.02	80 ± 0.02

$n = 3$, mean ± standard error

Wallis analysis of variance to determine significant difference between the three microenvironments. Principal component analysis was applied to determine the major PBDE congeners that explains the variability of the dataset using R software version 3.6.1.

Results and discussion

PBDE levels in the microenvironments

The summary of the statistics of PBDEs concentrations in dust from the creches, nursery schools, offices, and cars are shown in Table 3, while the concentrations of PBDEs in each individual sample are presented in Tables S2a–c of the supplementary material.

BDE-99 and BDE-100 were detected in all the samples, while BDE-209 was not detected in majority of the samples. Mean concentrations (ng/g) of the PBDEs ranged from 69 to 1187 in creches and nursery schools, 39 to 441 in offices, and 45 to 16198 in cars. The mean (median) ∑PBDEs (ng/g) in creches and nursery schools, offices, and cars were 4355 (1850), 2095 (1130), and 37741 (2620), respectively. The mean concentrations of PBDEs in dust from the microenvironments were compared with those from other studies as shown in Table 4. The total highest concentration was found in car. This is due to the elevated concentrations (ng/g) of pentaBDE: 101,830 for BDE-47, 98,170 for BDE-100, 225,330 for BDE-99, and 66,690 for BDE-154 in one of the cars. The concentration of BDE-99 exceeded the maximum value (190,000 for BDE-209) reported by Harrad and Abdallah (2011) for the UK. At the time of sampling, the car has been used for 24 years, and the model is Toyota

Table 2 Exposure parameters for children and adults

Abbreviation	Exposure parameters	Age group			References
		Toddlers (0.5–2 years)	Children (2–6 years)	Adults	
C_{dust}	Concentration of the dust (ng/g)				
EA_{skin}	Exposure skin area (cm^2)	2564	2800	5700	USEPA 2001
R_{inh}	Rate of inhalation (m^3 day^{-1})	8	11.9	20	USEPA 1997
R_{ing}	Rate of dust ingestion (mg day^{-1})	80	60	30	USEPA 2001; Ohajinwa et al. 2019
SAF	Skin adherence factor (mg cm^{-2} h^{-1})	0.07	0.07	0.7	USEPA 2002
DAF	Dermal absorption factor (no unit)	0.1	0.1	0.1	USEPA 2001
T_{aveg}	Average lifetime days (ED × 365)	2 × 365	4 × 365	24 × 365	
BW	Body weight (kg)	12	20	70	Harrad et al. 2016
PEF	Particle emission factor (m^3 kg^{-1})	1.36×10^9	1.36×10^9	1.36×10^9	USEPA 2009
ED_i	Exposure duration in (years)	2	4	24	USEPA 2001
CF	Conversion factor	10^{-6}	10^{-6}	10^{-6}	USEPA 1997
ET_i	Exposure time per day (hours day^{-1})	8/24 (school), 1/24 (cars	8/24 (school), 1/24 (cars)	8/24 (offices), 3/24 (cars)	This study
EF	Exposure frequency days $year^{-1}$	350	350	350	This study

Camry manufactured in Japan. From the questionnaire, it was indicated that the car has not been vacuumed for over a year. Interiors of automobiles are most likely to contain PBDEs in nylon connectors, propylene molded parts and polyurethane forms in the interior upholstery and trim, and vehicle electronics (BSEF 2006). The concentrations of PBDEs in the microenvironments increased in the order of cars > schools > offices.

The most abundant PBDE in the microenvironments was BDE-99 which is surprising as it has been banned. This could be due to the use of older products of cars, electronics, and other materials treated with PBDEs in offices, creches, and nursery schools which were produced before the ban of penta- and octaPBDEs. PentaBDE mixture was formally used in the treatment of polyurethane foams in beddings, furniture, carpet underlays, vehicle interior, microprocessors packaging in computers, and printed circuit boards (Harrad et al. 2008). PentaBDE mixtures were reported to include six main congeners in this order BDE-99 > BDE-47 > BDE-100 > BDE-153 > BDE-154>BDE-85. The main congeners were BDE-99 and BDE-47 having about 49 and 38% respectively (La Guardia et al. 2006; Mandalakis et al. 2009). In this study, BDE-209 had the least concentration. This could be attributed to the debromination of BDE-209 by ultraviolet light. Nigeria with a tropical climate is known for its high temperatures. Higher PBDE congeners are prone to debromination in ultraviolet light, and higher temperatures can result to higher emission rates of PBDEs from materials including household items (Wang et al. 2018). Other studies have discovered that DecaBDE breaks down to lesser PBDEs congeners that is from nano- to hexaBDE in sediments, soil, and sand in laboratory condition of both natural and artificial sunlight (Soederstroem et al. 2004). Kruskal-Wallis ANOVA showed a significant difference in the concentrations of BDE-47, BDE-99, BDE-154, BDE-153, and BDE-209 in cars, offices, creches, and nursery schools, while BDE-28 and BDE-100 were not significantly different. Most likely BDE-28 and BDE-100 were used in products found in the three microenvironments.

Table 3 Concentrations (ng/g) of the PBDEs in dust from the microenvironments

PBDEs	Microenvironments	Mean	Median	Minimum	Maximum	Detection frequency (%)
BDE-28	Creches and nursery schools	451	180	10	2280	98
	Offices	268	140	< 0.01	1290	98
	Cars	219	50	< 0.01	1490	93
BDE-47	Creches and nursery schools	581	340	30	1530	98
	Offices	280	140	< 0.01	2140	87
	Cars	7222	320	< 0.01	101,830	91
BDE-100	Creches and nursery schools	543	370	100	2260	100
	Offices	437	240	80	1190	100
	Cars	6964	330	40	98,170	100
BDE-99	Creches and nursery schools	1187	270	50	8560	100
	Offices	441	350	40	1140	100
	Cars	16,198	970	150	225,330	100
BDE-154	Creches and nursery schools	627	240	20	2370	100
	Offices	201	40	< 0.01	1210	73
	Cars	5085	350	< 0.01	66,690	91
BDE-153	Creches and nursery schools	420	220	10	1240	100
	Offices	199	90	< 0.01	880	87
	Cars	1659	380	20	17,920	96
BDE-183	Creches and nursery schools	477	230	30	1840	100
	Offices	232	130	20	800	100
	Cars	379	220	< 0.01	1280	93
BDE-209	Creches and nursery schools	69	< 0.04	< 0.04	790	13
	Offices	39	110	< 0.04	410	18
	Cars	45	< 0.04	< 0.04	210	71
∑PBDEs	Creches and nursery schools	4355	1850	250	20,870	
	Offices	2095	1130	140	9060	
	Cars	37,741	2620	210	512,920	

Table 4 Concentrations (ng/g) of PBDEs in dust from selected reports

Microenvironments	Country	*n*	BDE-28	BDE-47	BDE-100	BDE-99	BDE-154	BDE-153	BDE-183	BDE-209	References
Offices											
	UK*	18	NA	67	NA	120	NA	16	NA	30,000	Harrad et al. 2008
	USA*	10	18	85	525	3310	182	126	1270	6930	Batterman et al. 2010
	South Africa*	11	17.3	135	461	25.2	83.5	52.8	70.2	678	Abafe and Martincigh 2015
	Nigeria*	11	NA	51.6	56.1	60.6	64.7	74.3	72	180	Olukunle et al. 2015a
	South Africa*	16	NA	35.3	NA	64.7	NA	0.8	NA	52.6	Kefeni and Okonkwo 2012
	Nigeria*	18	1.1	14	4.2	18	< 0.042	3.7	26	930	Harrad et al. 2016
	Egypt**	9	0.39	23	0.60	7.1	0.83	33	2.3	366	Hassan and Shoeib 2015
	Nigeria*	15	268	280	437	441	201	199	232	39	This study
Cars											
	USA*	12	45	5000	1600	9300	330	1000	2700	15,000,000	Batterman et al. 2009
	UK**	14	NA	100	17	130	10	14	6	190,000	Harrad and Abdallah 2011
	Egypt**	5	1.2	5.7	4.8	23	3.6	16	5.8	1540	Hassan and Shoeib 2015
	Nigeria*	12	NA	99.1	64.5	213	69.5	91.7	47.3	137	Olukunle et al. 2015b
	Greece*	30	14.2	375	55.8	476	76.9	71.5	150	7624	Besis et al. 2017
	Nigeria*	16	7.0	900	330	1700	450	720	83	10,000	Harrad et al. 2016
	Saudi Arabia*	15	LOQ	21	7	40	3	6	3	5900	Ali et al. 2016
	Nigeria	15	219	7222	6964	16,198	5085	1659	379	45	This study

N/B: NA not available; *mean; **median values

The mean concentrations of PBDEs in dust from cars and offices were higher than those previously reported in Makurdi and Lagos, Nigeria (Olukunle et al. 2015a, 2015b; Harrad et al. 2016). This could be due to the number, types, and age of materials in the microenvironments. For the creches and nursery schools, the median concentrations were higher than those reported in Australia and Sweden, with the exclusion of BDE-209. Kim et al. (2011) reported concentrations (ng/g) of eight PBDE congeners ranging from 0.82 to 7742.29 in daycare, 18 to 1307 in playroom, BDL to 5831.09 in kindergarten, and 26.15 to 16329.6 in indoor playground. The PBDE concentrations in daycare, kindergarten, and indoor playground were higher than those obtained in this study, while the concentrations in playroom were comparable to the PBDEs concentrations obtained from the studied creches and nursery schools. However, in this study, the median PBDE concentration (1850 ng/g) was higher than those obtained by de Wit et al. (2012) in daycare centers (1200 ng/g) in Stockholm, Sweden.

There was a strong positive correlation between BDE-28, BDE-47, BDE-99, BDE-100, BDE-154, BDE-153, and BDE-183 in the creches and nursery schools. In cars, there was a strong significant correlation between BDE-47, BDE-153, BDE-154, and BDE-99, while in offices, there were no significant correlations among the congeners. Results of the correlation are presented in Tables S3a–c.

As shown in Tables S4a–c, there was a correlation between the dust concentrations of PBDE and the parameters of the questionnaires for creches and nursery schools. There was a strong positive correlation ($r = 0.851$, $p = 0.007$) between the PBDEs concentrations and number of electronics. This is consistent with the observation made by Gou et al. (2016) in Taiwanese elementary schools. In addition, there was a positive correlation between the number of fridge ($r = 0.764$, $p = 0.027$), plastics ($r = 0.749$, $p = 0.003$), and floor type ($r = 0.766$, $p = 0.027$) and concentrations of PBDEs in offices. No positive correlation was observed in cars.

Principal component analysis

The concentrations of PBDEs in offices, creches, nursery schools, and cars were further examined using principal component analysis. Eigenvalues > 1 of the principal components (PCs) were extracted (Fig. 2). In offices, three principal components were extracted which accounted for 70.5% of the total variance. PC1 accounted for 39.6% and showed high loadings for BDE-28, BDE-47, BDE-100, and BDE-154 indicating similar commercial source. PC2 accounted for 17% and

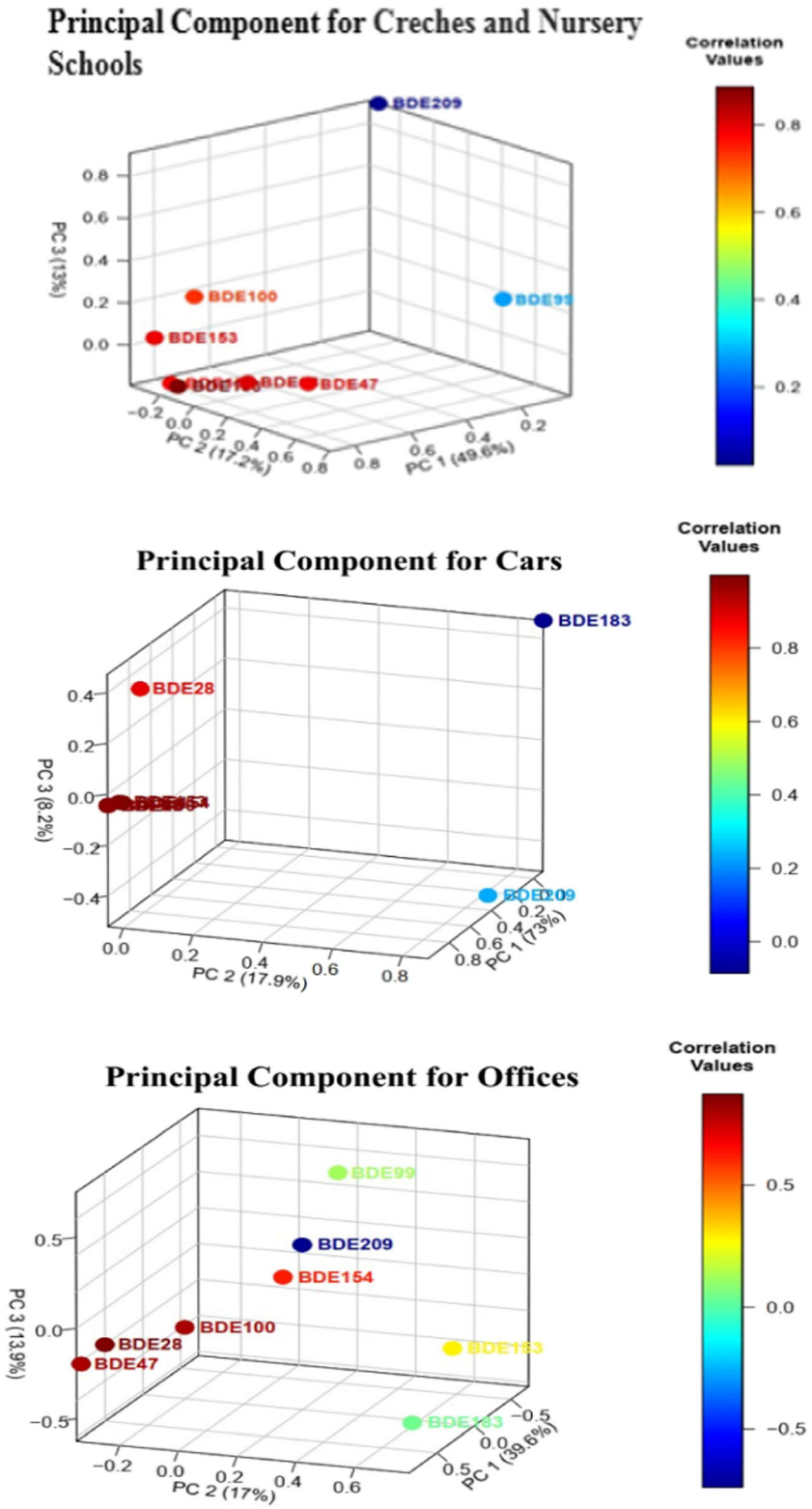

Fig. 2 Correlation plot of principal component analysis for the microenvironments

showed high loading for BDE-153, while PC3 accounted for 13.9% and showed high loading for BDE-99. The PCs in offices suggest the presence of products treated with commercial pentaBDE mixtures such as DE 71 and Bromkal 70-5DE. For creches and nursery schools, three PCs were extracted which accounted for 79.8% of the total variance. PC1 accounted for 49.6% and showed high loadings for BDE-183 and the major congeners of the commercial pentaBDE

Table 5 Average daily dose for toddlers, children, and adults in cars via inhalation, ingestion, and dermal absorption

PBDEs	Toddlers			Children			Adults		
	Inh ($\times10^{-9}$)	Ing ($\times10^{-8}$)	Der ($\times10^{-8}$)	Inh ($\times10^{-8}$)	Ing ($\times10^{-8}$)	Der ($\times10^{-8}$)	Inh ($\times10^{-8}$)	Ing ($\times10^{-8}$)	Der ($\times10^{-7}$)
BDE-28	1.4	6	1.6	0.10	2.5	0.8	0.2	1.6	2.1
BDE-47	50.4	149	43.6	3.81	89.7	29.3	7.3	41.7	55.5
BDE-100	45.8	136	39.8	3.47	81.8	26.7	6.7	38.1	50.6
BDE-99	103.0	312	91.1	7.83	187	61.2	15.1	87.2	116.0
BDE-154	34.8	102	29.9	2.46	61.4	20.1	5.1	28.6	38.0
BDE-153	10.6	34	9.8	0.81	20.2	6.6	1.6	9.4	12.5
BDE-183	1.7	7	2.1	0.13	4.3	1.4	0.3	2.0	2.6
BDE-209	0.3	2	0.6	0.02	1.1	0.4	0.04	0.9	1.9
$\sum_8$PBDEs	248	748	219	19	448	147	36	210	279

mixtures (except BDE-99). PC2 accounted for 17.2% of the total variance showing high loading for BDE-99, while PC3 had high loading for BDE-209 and accounted for 13% of the total variance. The differences in loadings for BDE- 99 in offices, creches, and nursery schools suggest that it may be from degradation of higher PBDEs. Rayne et al. (2006) observed that BDE-99 was the main product in the photodegradation of BDE-153 in acetonitrile and water. The result indicates the presence of products from commercial pentaBDE mixtures such as DE 71 and Bromkal 70-5DE in the creches and nursery schools. For cars, two PCs accounted for 90.9% of the total variance. PC1 explained 73% showing high loadings for major congeners of the commercial pentaBDE formulation. This suggests that the pentaBDE were from similar source such as DE 71 and Bromkal 70-5DE. PC2 accounted for 17.9% of the total variance and exhibited high loadings for BDE-183 and BDE-209 indicating similar source such as Bromkal 79-8DE an octaBDE commercial mixture. La Guardia et al. (2006) reported that Bromkal 79-8DE was composed of mainly BDE-209, BDE-183, BDE-207, BDE-203, BDE-197, and BDE-206. The PCs for car show that the parts were treated with commercial pentaBDE (DE 71 and Bromkal 70-5DE) and octaBDE (Bromkal 79-8DE) formulation.

Health risk assessment of human exposure

The average daily dose (ADD) via inhalation, ingestion, and dermal absorption in the three microenvironments are shown in Tables 5 and 6. The ADD of $\sum_8$PBDEs via ingestion and dermal absorption for children and toddlers in creches, nursery schools, and cars were higher than exposure via inhalation. The same applies for the average daily dose of adults in offices and cars. The exposure via inhalation for adults in offices (1.8×10^{-10}), toddlers (9×10^{-10}), and children (7.25×10^{-10}) in creches and nursery schools were three order of magnitude lower than those of adults (3.62×10^{-7}), children (1.86×10^{-7}), and toddlers (2.48×10^{-7}) in cars. Furthermore, the exposure via ingestion and dermal absorption for children and toddlers in creches, nursery schools, and cars were of the same order of magnitude (10^{-6}, 10^{-6}). This suggests that the rates of exposure (1 h in cars and 8 h in school) via

Table 6 Average daily dose for toddlers, children, and adults in creches, nursery schools, and offices via inhalation, ingestion, and dermal absorption

PBDEs	Toddlers in creches and nursery schools			Children in creches and nursery schools			Adults in Offices		
	Inh ($\times10^{-11}$)	Ing ($\times10^{-7}$)	Der ($\times10^{-7}$)	Inh ($\times10^{-11}$)	Ing ($\times10^{-7}$)	Der ($\times10^{-7}$)	Inh ($\times10^{-11}$)	Ing ($\times10^{-8}$)	Der ($\times10^{-7}$)
BDE-28	3.4	3.5	1.0	7.3	5.6	1.8	2.0	2.6	3.5
BDE-47	9.6	9.8	2.9	8.9	5.8	1.8	2.4	3.1	4.1
BDE-100	7.1	7.2	2.1	10.3	5.8	1.9	3.1	4.4	5.8
BDE-99	32.9	33.6	9.8	11.5	7.3	2.3	3.3	4.9	6.5
BDE-154	13.2	13.5	3.9	7.7	5.2	1.7	1.9	2.6	3.5
BDE-153	11.8	12.0	3.5	7.2	5.0	1.5	1.7	2.4	3.2
BDE-183	8.4	8.6	2.5	8.9	5.6	1.8	1.9	2.5	3.3
BDE-209	3.6	3.6	1.1	10.8	8.7	2.9	1.8	2.4	3.2
$\sum_8$PBDEs	90	91.8	26.8	72.6	49	15.7	18	25	33

ingestion and dermal absorption for the toddlers and children in cars, creches, and nursery schools are likely equivalent. The ingestion rate especially for toddlers shows that they are at risk. Dust ingestion was the major exposure pathway for toddlers and children in cars (75%, 73%), creches, and nursery schools (77%, 76%), while dermal contact was the major exposure pathway for adults in offices (93%) and cars (92%).

The hazard index which is a summation of the hazard quotient was calculated for the three exposure pathways. HI < 1 shows no significant detrimental effects and vice versa (USEPA 2010). The HI via the exposure pathways for all the age groups in the three microenvironments (Supplementary Material; Table S5a&b) was below the crucial value of 1 showing that there was no present adverse effects. This finding is consistent with the study of Civan and Kara (2016).

Assessment of the contribution of each microenvironment to general human exposure to PBDEs via dust showed that cars (68%) contributed most to the exposure dose followed by the creches and nursery schools (27%), while offices (5%) had the lowest contribution. This suggested that in Nigeria, humans are generally exposed to the analyzed PBDEs mainly via cars.

Conclusion

This study affirmed that PBDEs are pervasive in Nigerian creches, nursery schools, offices, and cars. The levels of polybrominated diphenyl ethers in dust from creches and nursery schools in Nsukka have been determined, and it is also the first study in Africa. Health risk assessment showed that ingestion was the predominant pathway through which toddlers and children were exposed to PBDEs while dermal absorption was found to be the dominant pathway through which adults were exposed to PBDEs. There was a high correlation between the PBDEs and number of electronics in the creches and nursery schools. Principal component analysis indicated that PBDEs in dust from the microenvironments were from the commercial formulation of pentaBDE (Bromkal 70-5DE and DE 71) and octaBDE (Bromkal 79-8DE). PBDE pollution could arise from importation of old electronics and raw materials containing this contaminant. Although the hazard index in the microenvironments did not exceed the critical limit of 1, there is a possibility of long-term effects from prolonged exposure via continuous leaching of the PBDEs from several products in these facilities. Therefore, strict rules should be made in regulating importation by relevant agencies in Nigeria as is obtained in developed countries.

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Authors' contributions CNI designed the study, carried out statistical analysis, was involved in writing the manuscript, and supervised the project. EA carried out experimental studies and was also involved in writing of the manuscript. BI and DO were both involved in the experimental studies. All authors read and approved the final manuscript.

Data availability The datasets used and/or analyzed during the current study are available from the corresponding author on reasonable request.

Declarations

Ethics approval and consent to participate Not applicable.

Consent for publication Not applicable.

Competing interests The authors declare no competing interests.

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