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AN EXPOSURE ASSESSMENT OF NIGERIANS TO POLYBROMINATED DIPHENYL ETHERS IN DUST SAMPLES COLLECTED FROM CARS AND THE INDOOR MICROENVIRONMENT

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INTRODUCTION

Polybrominated diphenyl ethers (PBDEs) are brominated organic compounds which belong to the group of compounds known as brominated flame retardants (BFRs). Generally, flame retardants are used in mobile phones, electronics, construction materials and other numerous plastic products. The primary function 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 2004¹ 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 Convention². The release into the environment of brominated flame retardants occurs through a number of routes. Examples include, but not limited to; process of manufacture, incorporation into polymers or related finished products, disposal or recycling, leaching from products in use and disposed in landfills^{3, 4}. According to Alcock et al.⁵, 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^{6, 7, 8, 9}. Research has also verified dependence of PBDE emission levels on the environmental conditions. For example, PBDEs concentration was found to be higher during warmer months than in colder months and in addition, a decrease in PBDE concentrations was reported when old computers were replaced by new ones¹⁰.

There is currently scarcity of information on the levels of PBDEs in cars and the indoor environment in most developing countries, particularly in the continent of Africa. The observed gap of information on PBDEs can be attributed to (1) lack of awareness on the health implications of PBDEs, (2) inadequate funding for research on emerging contaminants, and (3) low attention given to environmental issues. Considering the fact that Nigeria is the largest economy within the African continent and it imports a wide range of finished products which may be flame retarded with PBDEs from various parts of the world. PBDEs are, therefore, expected to be present within the Nigerian environment. Therefore, the main objective of this work was to determine the levels of common PBDE congeners in cars and indoor dust in selected parts of Nigeria and to assess the level of exposure.

MATERIALS AND METHODS

Dust samples were collected in the three major cities of Otukpo, Gboko and Makurdi in Benue state Nigeria. Details of dust sampling were as described by Olukunle et al.¹¹. Pure standard solutions (1.2 mL of 50 µg mL⁻¹ each) of 12 PBDE (BDE-47, -99, -100, -118, -153, -154, -128, -183, -209 and 13C-BDE-139, -77, and -209) congeners were purchased from Wellington Laboratories (Guelph, Ontario, Canada). 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 acetone, hexane, dichloromethane, methanol, isooctane, and toluene were purchased from Sigma Aldrich (Chemie GmbH, Steinheim, Germany). Pesticarb was supplied by Separations (Pty) Ltd., South Africa. Purification of materials such as silica gel, sodium sulphate, and copper powder were as described previously¹². Preparation of standards and serial dilution of working standards were carried out in the fume hood. About 100 mg of finely sieved (150 µm) dust sample was weighed and extracted by ultrasonication. Prior to extraction, dust samples were spiked with 3 µl of surrogate BDE-139 and BDE-209 standards to monitor recoveries. Briefly, 100 mg of dust was transferred into a 4 mL vial, spiked with surrogate standards and left overnight to equilibrate. Thereafter, samples were extracted with 3 mL solvent for 15

min at 55°C in an ultrasonic bath (Elmasonic S 40H, Germany) with maximum power of 340 watts. The extracts were centrifuged at 300 rpm for 3 min. Extraction was repeated three more times. Thereafter, 2 g of activated copper powder was added to the collected extracts and swirled to remove sulphur, and later transferred into clean tubes and reduced under a gentle flow of N₂ to about 1 mL before subjecting it to cleaning by column chromatography to remove unwanted co-eluent. The cleanup column used was a solvent-rinsed Pasteur pipette (230mm) plugged with glass wool at the bottom and thereafter packed in layers from bottom with about 0.16 g of silica, 0.06 g pestcarb, and 0.16 g silica and finally topped with 0.5 g sodium sulphate. Glass wool was used to separate each layer of materials to enhance the cleaning. Before introduction of 1.0 mL crude extract, the packed column was eluted to saturation with 12 mL toluene/dichloromethane (1:1, v/v). The Crude sample was introduced into the column before the solvent reached the bed of the sodium sulphate plugged with glass wool. The column was eluted with 4 mL of the mixed solvent. The extracts were concentrated to 200 µL under a gentle stream of nitrogen using a Reacti-Vap from Thermo Fisher Scientific (Bellefonte P.A, USA) supplied by Anatech Pty (Pretoria, South Africa). The purified extracts were analyzed by Shimadzu model 2010 plus gas chromatograph coupled with a model QP 2010 ultra-mass spectrometer (Shimadzu, Japan) equipped with EI and injected automatically by a Shimadzu A0C-20i auto sampler. Operation mode was in the selected ion-monitoring (SIM). A 15 m column; DB 5 (0.25 mm ID, 0.1 µm df) was used for separation. The oven temperature program was set at 90 °C (1 min), 30 °C/min to 300 °C (5 min) and 10 °C/min to 310 (10 min). Carrier gas was set at a constant flow of 1.5 mL min⁻¹. The injector, transfer line, and ion source temperatures were set at 290, 300, and 250 °C, respectively.

RESULTS AND DISCUSSION

Concentrations of PBDEs in the different microenvironment in some selected Nigerian cities have only recently been determined and exposure estimates calculated to generate the first set of scientific data. More information with respect to the coverage of the different geographical zone is still needed. Exposure estimates for PBDEs in the different microenvironment were calculated in house, office and car dust. Samples collected in Gboko, Otutkpo and Makurdi in Benue were analysed for PBDEs. The median, 5th percentile and 95th percentile concentrations (Table 1) of the most abundant congeners namely BDE-47, -99 and -209 were used for computation in this particular study to evaluate exposure to PBDE under the different scenarios. An assumption of 100 % absorption intake¹⁴ average dust ingestion of 20 and 50 mg day⁻¹ and 50 and 200 mg day⁻¹ for adults and children respectively¹⁵ were made.

In addition, the corresponding time spent at home, office and in cars was assumed to be 72%, 23.8% and 4.2 % for adults and for toddlers, 95.8% in homes, 23.8% at crèche/daycare and 4.2% in cars respectively. The reference daily dose (RfD) according to USEPA, (2011) for BDE-47 and -99 is 100 ng (kg body weight) day⁻¹ and 7000 ng (kg body weight) day⁻¹. These were converted to ng day⁻¹ assuming 70 kg and 20 kg for adults and toddlers respectively as shown in Table 2. The estimated mean daily exposure rates in Nigerian adults were, however, found to range between 0.01 and 1.82 ng day⁻¹, 0.01 and 5.25 ng day⁻¹ and 0.67 and 7.24 ng day⁻¹ for BDE-47, -99 and -209 respectively. Similarly for Nigerian toddlers a range of 0.01 and 9.68 ng day⁻¹, 0.01 and 21 ng day⁻¹ and 0.26 and 38.5 ng day⁻¹ for BDE-47, -99 and -209 were observed. These values when compared to a similar study by Harrad et al. (2016) in Lagos were observed to be slightly lower. (0.8 - 0.28 ng day⁻¹ and 1.3 - 180 ng day⁻¹ for BDE-99 and -209 in adults and the corresponding values for toddlers were 0.21 - 87 ng day⁻¹ and 4.3 - 600 ng day⁻¹ respectively). The observed difference in exposure could be attributed to a number of factors, for example Lagos which lies in the south west region is the most populous state (over 12 million inhabitants) and the economic hub of the country compared to Benue state, situated in the middle belt region and with a population of about 5 million inhabitants, has agriculture as its mainstay of the economy. The results thus represent the first set of exposure data to be generated for any known brominated flame retardants. More studies still need to be carried out to assess the contribution of other brominated flame retardants to health risks to which Nigerians are exposed. Recently exposure values of hexabromocyclododecane and tetrabromo bisphenol A was reported by Abdallah et al.¹⁶ in Lagos dust samples.

CONCLUSION

The study has shown that Nigerians are exposed to low levels of PBDEs via dust ingestion in cars and the indoor microenvironment. The observed level of exposure to BDE-99 and 209 in Benue State was however, lower than the levels reported in Lagos State. Factors such as temperature, population and other factors may be responsible for the observed difference. More study is needed to determine other

routes of exposure to brominated flame retardants which can also be extended to other legacy and novel brominated flame retardants.

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Table 1: The median, 5th percentile and 95th percentile (ng g⁻¹) of 3 congeners in different microenvironment

Congeners	Home			Office			Cars		
	5 th %	95 th %	Median	5 th %	95 th %	Median	5 th %	95 th %	Median
BDE-47	26.6	50.5	46.9	37.4	81.3	46	5.95	740	67.8
BDE-99	0.24	60.8	46.2	44.7	96	54.2	0.01	2500	13.9
BDE-209	80.7	201	139	116	261	140	0.01	346	122

TABLE 2: Estimated exposure (ng day⁻¹) of Nigerian adults and toddlers to BDE-47, -99 and 209 via ingestion of dust from cars and the indoor microenvironment.

Benue State	Adult						Toddler						References	
	5 th percentile		Median		95 th percentile		5 th percentile		Median		95 th percentile			RfD
	Mean	High	Mean	High	Mean	High	Mean	High	Mean	High	Mean	High		
Homes														
BDE-47	0.38	0.96	0.68	1.69	0.73	1.82	1.27	5.1	2.25	9.0	2.42	9.68	7000	This study
BDE-99	<0.01	0.01	2.0	5.0	0.89	2.19	0.01	0.05	2.21	8.85	2.91	11.65	7000	
BDE-209	1.16	2.91	0.67	1.66	2.9	7.24	3.87	15.46	6.66	26.63	9.63	38.51	490000	
Offices														
BDE-47	0.18	0.45	0.22	0.55	0.39	0.97	0.45	1.78	0.55	2.19	0.97	3.87	7000	Harrad et al., 2016
BDE-99	0.21	0.53	0.26	0.64	0.46	1.14	0.53	2.13	0.64	2.58	1.14	4.57	7000	
BDE-209	0.55	1.38	0.67	1.67	1.24	3.11	1.38	5.52	1.67	6.66	3.11	12.42	490000	
Cars														
BDE-47	0.01	0.13	0.06	0.14	0.06	1.55	0.01	0.05	0.14	0.57	1.56	6.22	7000	Harrad et al., 2016
BDE-99	<0.01	<0.01	0.012	0.03	2.1	5.25	<0.01	<0.01	0.03	0.12	5.25	21	7000	
BDE-209	<0.01	<0.01	0.1	0.26	0.29	0.72	<0.01	<0.01	0.26	1.03	0.73	2.91	490000	
Lagos State														
Homes														
BDE-99	0.06	0.15	0.2	0.5	1.5	3.7	0.2	0.8	0.67	2.67	4.9	20	7000	Harrad et al., 2016
BDE-209	1.29	3.2	5.6	14	13	32	4.3	17	19	75	43	170	490000	
Offices														
BDE-99	0.01	0.03	0.08	0.21	0.39	0.96	Na*	na	na	na	na	na	7000	Harrad et al., 2016
BDE-209	<0.01	<0.01	4.4	11	17	43	na	na	na	na	na	na	490000	
Cars														
BDE-99	0.01	0.01	0.04	0.1	6.7	17	0.01	0.05	0.1	0.41	17	87	7000	Harrad et al., 2016
BDE-209	<0.01	<0.01	0.66	1.7	43	110	<0.01	<0.01	1.7	6.6	110	150	490000	

na = not available