Rising concentrations of polybrominated diphenyl ethers (PBDEs) in Nigerian foodstuffs despite global restrictions

Ma, Yulong; Stubbings, William A.; Cline-Cole, Reginald; Abdallah, Mohamed Abou Elwafa; Harrad, Stuart

DOI:
10.1016/j.emcon.2023.100264

Document Version
Publisher's PDF, also known as Version of record

Citation for published version (Harvard):
Ma, Y, Stubbings, WA, Cline-Cole, R, Abdallah, MAE & Harrad, S 2024, 'Rising concentrations of polybrominated diphenyl ethers (PBDEs) in Nigerian foodstuffs despite global restrictions', *Emerging Contaminants*, vol. 10, no. 1, 100264. https://doi.org/10.1016/j.emcon.2023.100264

Emerging Contaminants 10 (2024) 100264

Contents lists available at ScienceDirect

Emerging Contaminants

journal homepage: www.keaipublishing.com/en/journals/emerging-contaminants

Rising concentrations of polybrominated diphenyl ethers (PBDEs) in Nigerian foodstuffs despite global restrictions

Yulong Ma [a, *], William A. Stubbings [a], Reginald Cline-Cole [b], Mohamed Abou-Elwafa Abdallah [a], Stuart Harrad [a]

[a] School of Geography, Earth, and Environmental Sciences, University of Birmingham, Birmingham, B15 2TT, UK
[b] Department of African Studies & Anthropology, School of History and Cultures, University of Birmingham, Birmingham, B15 2TT, UK

ARTICLE INFO

Article history:
Received 19 July 2023
Received in revised form
8 September 2023
Accepted 20 September 2023
Available online 21 September 2023

Keywords:
BFRs
Alternative flame retardants
Dietary exposure
Health risks
Food

ABSTRACT

The presence of brominated flame retardants (BFRs) in foodstuffs of African origin is poorly understood. To fill this gap, animal-derived food samples comprising 13 different items originally from Nigeria were obtained in 2021, and concentrations of novel brominated flame retardants (NBFRs), polybrominated diphenyl ethers (PBDEs), and hexabromocyclododecane (HBCDD) were measured. Arithmetic mean concentrations of NBFRs, PBDEs, and HBCDD in Nigerian foodstuffs were 2.1 ng/g (18 ng/g lipid weight (lw)), 1.3 ng/g (9.2 ng/g lw), and 0.42 ng/g (2.8 ng/g lw), with median concentrations of 1.7 ng/g (14 ng/g lw), 1.1 ng/g (8.2 ng/g lw), and <0.34 ng/g (<3.3 ng/g lw), respectively. Higher concentrations of NBFRs than of PBDEs and HBCDDs in Nigerian foodstuffs likely reflect use of NBFRs as substitutes for legacy BFRs in Nigeria. Comparison with previous dietary studies reveals rising concentrations of PBDEs in Nigerian foodstuffs in recent years with associated rises in dietary exposure, possibly due to active domestic use of PBDEs in Nigeria. Reassuringly, comparison of our exposure estimates with health-based limit values suggests adverse health effects of dietary intake of BFRs by Nigerians are unlikely to occur.

1. Introduction

Global production and use of polybrominated diphenyl ethers (PBDEs) and hexabromocyclododecane (HBCDD) has resulted in their ubiquitous presence in a wide range of abiotic environmental compartments, as well as biota including humans [1–4]. PBDEs and HBCDD are known as persistent and bioaccumulative compounds that can disrupt the human endocrine system, nervous system, and reproductive system, etc. [2,5,6]; thus their ubiquity has raised serious concerns about environmental safety and human health burdens. As a result, commercial penta-/octa-BDEs, HBCDD, and commercial deca-BDE were listed under the Stockholm Convention on persistent organic pollutants (POPs) in 2009, 2014, and 2017, respectively, leading to global phase-out of production and use of these legacy brominated flame retardants (BFRs) [1]. Despite such restrictions however, it is anticipated that global contamination of PBDEs and HBCDD will last for decades [7,8].

The restrictions on use of PBDEs and HBCDD have led to increasing demand for alternative products, with novel brominated flame retardants (NBFRs) being an important option [1]. Global production of NBFRs was estimated to be 100,000–180,000 tonnes annually, with decabromodiphenyl ethane (DBDPE), bis(2,4,6-tribromophenoxy) ethane (BTBPE or TBE), bis(2-ethyl hexyl) tetrabromophthalate (BEH-TEBP or TBPH), and 2-ethyl hexyl-2,3,4,5-tetrabromobenzoate (EH-TBB or TBB) being the most commonly used NBFRs [1]. To date, NBFRs are less studied than legacy BFRs, but previous studies have revealed similar or even stronger adverse human health effects of some NBFRs compared to PBDEs [2,9], raising the question of whether NBFRs are appropriate substitutes for legacy BFRs.

Dietary exposure is an important pathway of human exposure to BFRs, especially to low-to medium-brominated PBDEs and some NBFRs [10–12]. To the best of our knowledge, investigations on food contamination of BFRs are primarily conducted in Asia, Europe, and North America, with China being the most studied area [13,14]. Studies in Africa are comparatively rare. In Nigeria, for instance, very limited investigations have been conducted to report

* Corresponding author.
E-mail address: yxm901@bham.ac.uk (Y. Ma).
Peer review under responsibility of KeAi Communications Co., Ltd.

https://doi.org/10.1016/j.emcon.2023.100264

PBDE or HBCDD contaminations in food [15–17], and concentrations of NBFRs to our knowledge have never hitherto been investigated in foodstuffs of Nigerian origin.

To fill this gap, food items of Nigerian origin were purchased from African food retail outlets online and in Birmingham, UK, and concentrations of selected BFRs were analysed, including: eight PBDE congeners (BDE-28, -47, −99, −100, −153, −154, −183, and −209), nine NBFRs (pentabromobenzene (PBBz), pentabromotoluene (PBT), pentabromoethylbenzene (PBEB), 2,3-dibromopropyl-2,4,6-tribromophenyl ether (DPTE or TBP-DBPE), hexabromobenzene (HBBz), EH-TBB (or TBB), BTBPE (or TBE), BEH-TEBP (or TBPH), and DBDPE), and three HBCDD isomers (α-, β-, and γ-HBCDD). The aims of this study are to: 1) characterise concentrations and the relative abundance of BFRs in Nigerian foodstuffs; 2) identify temporal changes in PBDE concentrations in Nigerian foodstuffs by comparing our observations with previous studies; and 3) estimate dietary intake of BFRs of Nigerians and evaluate any potential health risks.

2. Materials and methods

2.1. Sampling

Packaged food samples imported from Nigeria into the UK were acquired between May and December 2021. All items had been dried, smoked, or fried prior to packaging. A total of 26 food samples were collected and analysed in this study, including meat (n = 5), freshwater fish (n = 7), saltwater fish (n = 8), and other animal-derived food items (n = 6). The samples were blended thoroughly with a stainless-steel hand blender once received at the University of Birmingham and stored at −20 °C until analysis. Detailed information on the collected food samples can be found in Table S1 in Supplementary Materials.

2.2. Sample preparation

The sample preparation protocols have been published elsewhere [10]. Briefly, blended samples (individual samples) were sieved with a stainless-steel test sieve of 500 μm pore size. Approximately 500 mg of each food sample was accurately weighed and spiked with 15 ng of: BDE-77, BDE-128, ^{13}C-BDE-209, ^{13}C-HBBz, ^{13}C-EH-TBB, ^{13}C-BTBPE, ^{13}C-BEH-TEBP, ^{13}C-α-HBCDD, ^{13}C-β-HBCDD, and ^{13}C-γ-HBCDD as internal (surrogate) standards. The spiked samples were extracted using an accelerated solvent extractor (Dionex ASE 350) with hexane and acetone (3:1, v/v). The ASE cells (34 mL) were filled from bottom to top with 2 g of pre-cleaned hydromatrix, 2 g of florisil, 3 g of alumina, 0.5 g of food sample, and with pre-cleaned hydromatrix. About 10% of the crude extracts were used for gravimetric determination of sample lipid content, with the remaining ~90% of the extracts exchanged into 5 mL of hexane before shaking with 5 mL of sulfuric acid (95%). The purified extracts were collected, concentrated, and reconstituted into 100 μL of toluene containing 15 ng of ^{13}C-BDE-100 and d_{18}-γ-HBCDD as recovery determination (syringe) standards before GC-MS and LC-MS/MS analysis.

2.3. Analytical protocol

A Trace 1310 GC coupled to an ISQ™ single quadrupole mass spectrometer (Thermo Scientific, TX, USA) was used for analysis of PBDEs and NBFRs. The GC-MS was equipped with a capillary fused silica column (RESTEK, USA, 15 m × 0.25 mm inner diameter × 0.10 μm film thickness) and a programmable-temperature vaporiser (PTV) injector. The ion source was operated in EI SIM mode at 280 °C, and the MS transfer line temperature was 300 °C. Analysis of HBCDDs was performed on a Shimadzu LC-20AB HPLC (Shimadzu, Kyoto, Japan) with a Sciex API 2000 triple quadrupole mass spectrometer (Applied Biosystems, Foster City, CA, USA). The MS was operated in electrospray negative ionisation (ESI-) - multiple reaction monitoring (-MRM) mode. The HPLC was equipped with a Varian Pursuit XRS3 (Varian, Inc., Palo Alto, CA, USA) C18 reversed phase analytical column (150 mm × 2 mm i. d., 3 μm particle size). Deionized water and methanol were used as mobile phase A and mobile phase B, respectively. Detailed information can be found elsewhere [10].

2.4. Dietary exposure and health risk assessment

Human dietary exposure to BFRs was estimated using equation (1) [10]:

$$EDI = \sum_{i=1}^{n} \frac{C_i \times CR_i}{BW} \quad (1)$$

where *EDI* is the estimated daily intake of BFRs via food consumption (ng/kg bw/day); C_i is the concentrations of BFRs in a particular food item *i* (ng/g); CR_i is the consumption rate of a particular food item *i* (g/day); and *BW* is the average body weight (kg) of a Nigerian.

Non-carcinogenic risks from dietary exposure to BFRs were evaluated using equations (2) and (3) [17]:

$$HQ = EDI/RfD \quad (2)$$

$$HI = \Sigma HQ \quad (3)$$

where *HQ* is hazard quotient, defined as the ratio of estimated daily dietary intake of a particular BFR to its reference dose (RfD); and *HI* (hazard index) is the sum of *HQ* of all the target BFRs. An *HI* value exceeding 1 suggests likely adverse non-cancer effects on human health of dietary exposure to BFRs, while an *HI* value below 1 indicates negligible health risks.

2.5. QA/QC

Good linearity was obtained for all target BFRs from a 5-point calibration (Table S2). Limit of quantification (LOQs) for each analyte was calculated from a signal to noise ratio of 10 (Table S3). A method blank where food samples were replaced with 0.5 g of anhydrous sodium sulfate was analysed along with each batch of 5 samples. Recoveries of the internal standards in food sample analyses and blanks are summarised in Table S4. No target compounds were detected in the blanks, so sample data were not blank-corrected.

2.6. Statistical analysis

Microsoft Office 365 and IBM SPSS Statistics 29.0 (Chicago, IL, USA) were used for statistical analysis. Data were log-transformed and normality confirmed prior to any statistical tests, and only BFRs with a detection frequency (DF) exceeding 30% were tested. BFR concentrations below LOQ were designated as 0.5 × LOQ.

3. Results and discussion

3.1. BFR concentrations in Nigerian foodstuffs

A statistical summary of BFR concentrations in Nigerian foodstuffs is shown in Table 1, with arithmetic mean concentrations of

Table 1
Descriptive statistics for BFR concentrations (ng/g) in Nigerian foodstuffs (ng/g lw in parentheses).

BFRs	DF	Min	Median	Max	Arithmetic mean
BDE-28	0%	<0.081 (<0.27)	<0.095 (<0.81)	<0.11 (<1.7)	<0.095 (<0.78)
BDE-47	62%	<0.035 (<0.11)	0.043 (0.37)	0.51 (3.0)	0.097 (0.63)
BDE-99	65%	<0.078 (<0.36)	0.10 (0.47)	0.60 (8.7)	0.18 (1.6)
BDE-100	42%	<0.085 (<0.30)	<0.10 (<1.1)	0.92 (7.8)	0.14 (1.1)
BDE-153	4%	<0.040 (<0.13)	<0.045 (<0.40)	0.055 (0.40)	0.024 (0.19)
BDE-154	23%	<0.035 (<0.11)	<0.039 (<0.38)	0.27 (1.6)	0.053 (0.37)
BDE-183	12%	<0.097 (<0.32)	<0.11 (<1.0)	0.14 (1.5)	0.064 (0.51)
Σ_7PBDEs		**0.27 (1.3)**	**0.43 (3.5)**	**1.6 (14)**	**0.61 (4.8)**
BDE-209	8%	<0.76 (<2.5)	<0.89 (<8.0)	5.0 (18)	0.64 (4.4)
Σ_8PBDEs		**0.72 (2.6)**	**1.1 (8.2)**	**5.3 (20)**	**1.3 (9.2)**
PBBz	0%	<0.034 (<0.11)	<0.040 (<0.34)	<0.045 (<0.71)	<0.040 (<0.33)
PBT	0%	<0.074 (<0.25)	<0.086 (<0.74)	<0.096 (<1.5)	<0.086 (<0.71)
PBEB	0%	<0.054 (<0.18)	<0.063 (<0.54)	<0.071 (<1.1)	<0.063 (<0.52)
DPTE	42%	<0.035 (<0.13)	<0.045 (<0.43)	1.6 (23)	0.13 (1.5)
HBBz	12%	<0.052 (<0.18)	<0.062 (<0.52)	0.070 (0.75)	0.034 (0.29)
EH-TBB	62%	<0.064 (<0.33)	0.10 (0.71)	0.55 (2.4)	0.13 (0.88)
BTBPE	19%	<0.23 (<0.86)	<0.31 (<2.9)	0.91 (8.4)	0.22 (1.8)
BEH-TEBP	31%	<0.35 (<1.1)	<0.42 (<3.8)	1.5 (17)	0.44 (3.7)
DBDPE	4%	<1.5 (<5.1)	<1.8 (<15)	4.4 (54)	1.0 (8.9)
Σ_9NBFRs		**<2.8 (<9.2)**	**1.7 (14)**	**5.6 (69)**	**2.1 (18)**
α-HBCDD	19%	<0.073 (<0.26)	<0.086 (<0.83)	5.2 (26)	0.27 (1.5)
β-HBCDD	0%	<0.15 (<0.53)	<0.17 (<1.5)	<0.19 (<2.8)	<0.17 (<1.4)
γ-HBCDD	27%	<0.061 (<0.22)	<0.073 (<0.71)	0.33 (4.7)	0.067 (0.60)
Σ_3HBCDDs		**<0.28 (<1.0)**	**<0.34 (<3.3)**	**5.4 (27)**	**0.42 (2.8)**

BFRs in each food item given in Tables S5 and S6.

3.1.1. PBDE concentrations in Nigerian foodstuffs

Concentrations of Σ_8PBDEs ranged between 0.72 ng/g (2.6 ng/g lw) and 5.3 ng/g (20 ng/g lw) in Nigerian foodstuffs, with arithmetic mean and median concentrations of 1.3 ng/g (9.2 ng/g lw) and 1.1 ng/g (8.2 ng/g lw), respectively. BDE-99 and -47, with DFs of 65% and 62%, respectively, were the most detected PBDEs in Nigerian foodstuffs, followed by BDE-100, with a DF of 42%. Arithmetic mean concentrations of BDE-99, -47, and −100 were 0.18 ng/g (1.6 ng/g lw), 0.097 ng/g (0.63 ng/g lw), and 0.14 ng/g (1.1 ng/g lw) in Nigerian foodstuffs, with median concentrations of 0.10 ng/g (0.47 ng/g lw), 0.043 ng/g (0.37 ng/g lw), and <0.10 ng/g (<1.1 ng/g lw), respectively. In contrast, BDE-28 was not detected in Nigerian foodstuffs, while BDE-153, -154, −183, and −209 were only detected in less than 30% of the food samples (see Table 1 for concentrations).

We have recently reported concentrations of PBDEs in UK and US food items [10,11]. PBDE concentrations in Nigerian foodstuffs were only slightly higher than those in UK and US foodstuffs (see Table S7 for concentrations). However, PBDEs in food items from the three countries showed different patterns, i.e., PBDEs containing four or five bromines were generally more detected in Nigerian food (this study) and UK food [10], while those PBDEs containing two or three bromines were more abundant in US food [11]. While this could be explained by different formulas of commercial PBDE mixtures used in the three countries, such differences could also suggest more rapid disappearing of PBDEs in US foodstuffs than in Nigerian or UK foodstuffs, indicated by degradation of high-brominated PBDE congeners to low-brominated ones. PBDE concentrations in Nigerian foodstuffs were also broadly comparable to those in foodstuffs from non-e-waste impacted areas in China [18] and in Europe [19–22], but were considerably lower than PBDE concentrations in food from an e-waste recycling site in China [23].

3.1.2. NBFR concentrations in Nigerian foodstuffs

NBFRs were detected in Nigerian foodstuffs at concentrations ranging from <2.8 ng/g (<9.2 ng/g lw) to 5.6 ng/g (69 ng/g lw), with arithmetic mean and median concentrations of 2.1 ng/g (18 ng/g lw) and 1.7 ng/g (14 ng/g lw), respectively. These concentrations exceeded concentrations of PBDEs in Nigerian foodstuffs, possibly suggesting replacement of PBDEs with NBFRs in Nigeria. EH-TBB (DF = 62%) was the most detected NBFR in Nigerian food items, with arithmetic mean and median concentrations of 0.13 ng/g (0.88 ng/g lw) and 0.10 ng/g (0.71 ng/g lw), respectively. This was followed by DPTE (DF = 42%) and BEH-TEBP (DF = 31%), which had arithmetic mean concentrations of 0.13 ng/g (1.5 ng/g lw) and 0.44 ng/g (3.7 ng/g lw), respectively, in Nigerian foodstuffs. Consumption volumes of EH-TBB and BEH-TEBP in West Africa are unclear, but these two chemicals have been produced and used as substitutes for commercial penta- and octa-BDE mixtures globally [1], which could explain their occurrence in Nigerian food items. DPTE is a bioaccumulative compound produced by Chemische Fabrik Kalk (Germany) during 1972 and 1985 [24]. No other manufacturer has reported production of DPTE, and its distribution is unknown [24]. Therefore, further investigations are needed to understand the occurrence of DPTE in Nigerian foodstuffs. HBBz, BTBPE, and DBDPE were less frequently detected in Nigerian food, with their DFs below 30% (see Table 1 for concentrations); while PBBz, PBT, and PBEB were not detected in any food sample in this study.

Table S8 summarises literature data on NBFR concentrations in foodstuffs from different countries. Concentrations of EH-TBB in Nigerian foodstuffs were generally comparable to or slightly higher than the concentrations observed in foodstuffs from the UK [10], the US [11], France [19], and a non-e-waste impacted area in China [25], but were considerably lower than EH-TBB concentrations in foodstuffs from an e-waste recycling site in China [25]. BEH-TEBP concentrations observed in this study are in the middle of global observations, i.e., lower than those observed in foodstuffs from the UK [10] and an e-waste site in China [25], comparable to those observed in foodstuffs from a non-e-waste impacted region in China [25], but higher than those observed in foodstuffs from Belgium [22] and the US [11]. With respect to DPTE, literature data on its occurrence in food is limited. Our observations of DPTE concentrations in Nigerian foodstuffs were close to what was

reported in UK foodstuffs [10], but were slightly higher than those reported in foodstuffs from China [26].

3.1.3. HBCDD concentrations in Nigerian foodstuffs

HBCDD was less frequently detected in Nigerian food items and was present at lower concentrations compared to PBDEs and NBFRs. This is consistent with our recent observations about BFRs in UK and US foodstuffs [10,11], and likely reflects global restrictions on use of HBCDD. Concentrations of HBCDD were in the range between <0.28 ng/g (<1.0 ng/g lw) and 5.4 ng/g (27 ng/g lw), with arithmetic mean and median concentrations of 0.42 ng/g (2.8 ng/g lw) and <0.34 ng/g (<3.3 ng/g lw), respectively. γ-HBCDD (DF = 27%) was the most detected HBCDD isomer in Nigerian food, followed by α-HBCDD (DF = 19%). Arithmetic mean concentrations of γ-HBCDD and α-HBCDD were 0.067 ng/g (0.60 ng/g lw) and 0.27 ng/g (1.5 ng/g lw), respectively. β-HBCDD was not detected in Nigerian foodstuffs.

Literature data on HBCDD concentrations in foodstuffs from different countries is summarised in Table S9. HBCDD concentrations observed in this study generally exceeded our previous observations in the UK [10] and the US [11]. Further, HBCDD concentrations in Nigerian food were at the same level as those observed in Latvia [27], France [19], Belgium [22], Ireland [20], and non-e-waste sites in China [18,25], but were lower than HBCDD concentrations in food from Sweden [28], Japan [29], and e-waste impacted regions in China [23,25].

3.2. Variations in BFR concentrations in Nigerian food items

Nigerian food samples analysed in this study were classified into four groups (Table S1), namely meat (n = 5), freshwater fish (n = 7), saltwater fish (n = 8), and other animal-derived foodstuffs (n = 6). Concentrations of selected BFRs for which DF > 30%, including BDE-47, BDE-99, BDE-100, DPTE, EH-TBB, and BEH-TEBP, in different Nigerian food items are depicted in Fig. 1, with more detailed data given in Tables S5 and S6.

Arithmetic mean concentrations of Σ_6BFRs (sum of BDE-47, BDE-99, BDE-100, DPTE, EH-TBB, and BEH-TEBP) in freshwater fish (0.85 ng/g) and saltwater fish (0.96 ng/g) were lower than those in meat (1.1 ng/g) and other food items (1.7 ng/g). One-way analysis of variation (ANOVA) revealed no significant differences in concentrations of Σ_6BFRs among the four food groups ($p = 0.292$). This is similar to our previous observations of BFRs in UK and US food samples, where no significant differences were found in BFR concentrations among different food categories [10–12]. When considering each food item, the highest concentration of Σ_6BFRs was found in periwinkle (2.7 ng/g), followed closely by bush meat (2.6 ng/g) and hake (2.1 ng/g); while knife fish (0.58 ng/g), shawa (0.61 ng/g), and tilapia (0.62 ng/g) had relatively lower concentrations of Σ_6BFRs than other food items.

With respect to BFR patterns, Σ_3NBFRs (sum of DPTE, EH-TBB, and BEH-TEBP) outweighed Σ_3PBDEs (sum of BDE-47, -99, and −100) in the majority of Nigerian food items. Arithmetic mean contribution of Σ_3NBFRs to Σ_6BFRs was 63%, compared to the contribution of Σ_3PBDEs of 37%. This may reflect use of NBFRs as substitutes for PBDEs involved in the processing and packaging of food in Nigeria.

3.3. Comparisons with previous studies in Nigeria

Three previous studies have reported concentrations of PBDEs in Nigerian foodstuffs [15–17]. To the best of our knowledge, concentrations of NBFRs in Nigerian foodstuffs have never been reported previously.

Fig. 2 compares concentrations of BDE-47, -99, and −100 in meat and fish samples of this study with those earlier observations. Concentrations of Σ_3PBDEs (sum of BDE-47, -99, and −100) in meat and fish in this study exceeded considerably those reported in samples collected in 2017 [15,17]. It is noticeable that food samples analysed in this study were dried, smoked, or fried prior to packaging; while the majority of food items analysed in the two earlier studies were wet samples and thus PBDE concentrations were reported based on wet weight of each food item. This likely contributes to the elevated PBDE concentrations observed in this study. Water content of meat or aquatic produce normally lies between 50% and 90% [10–12,15], which makes dry weight concentrations of a compound in meat or fish approximately 2–10 times higher than the corresponding wet weight concentrations. However, our observations of concentrations of Σ_3PBDEs in dried beef were more than 40 times higher than wet weight concentrations of Σ_3PBDEs reported in beef previously, and our observations of concentrations of Σ_3PBDEs in dried/smoked/fried fish were at least 20 times higher than wet weight concentrations of Σ_3PBDEs reported in fish previously (Fig. 2). Further, Σ_3PBDE concentrations in dried fish collected in 2021 (this study) were also approximately 4 times higher than those in dried fish collected in 2017 [17]. Despite the different designs between our study and the two previous studies [15,17], these results likely suggest rising concentrations of PBDEs in Nigerian foodstuffs in recent years.

A recent study examined atmospheric concentrations of PBDEs

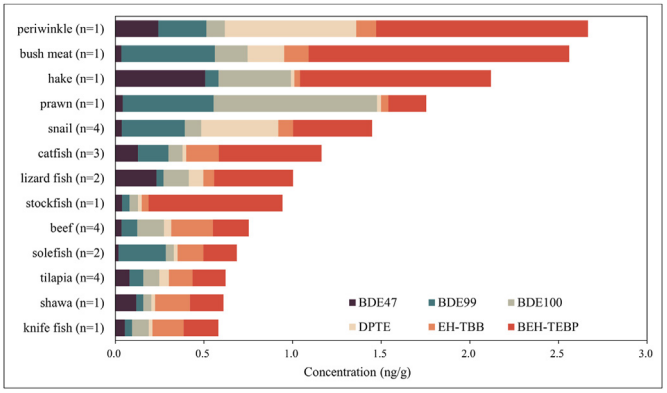

Fig. 1. Concentrations of selected BFRs (DF > 30%) in different Nigerian food items.

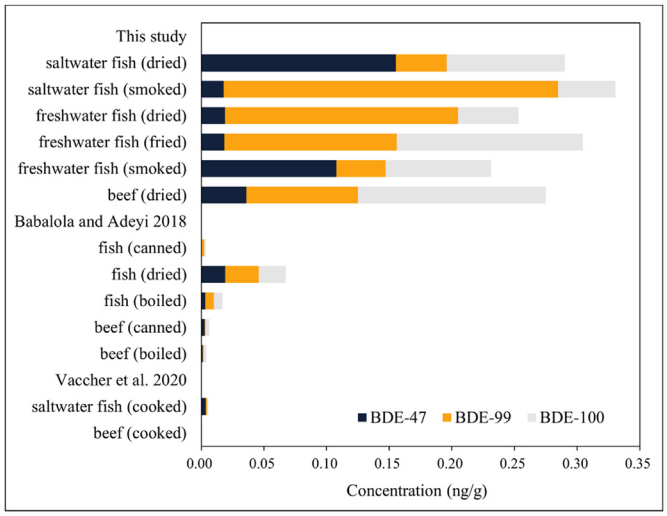

Fig. 2. PBDE concentrations in Nigerian food items: comparison with previous studies.

in Lagos, Nigeria during 2019 and 2020, and found that the presence of PBDEs in Lagos atmosphere was significantly related to population density [30]. This likely indicates active domestic use of PBDEs in Nigeria and therefore may explain the rising concentrations of PBDEs in Nigerian foodstuffs.

3.4. Health risk assessment

3.4.1. Estimates of human dietary exposure to BFRs in Nigeria

Dietary exposure to BFRs of Nigerian adults and toddlers was estimated by using equation (1). Food consumption rates (g/day) of Nigerian adults and toddlers were obtained elsewhere [31,32], and are summarised in Table S10. Body weights of Nigerian adults and toddlers were assumed to be 70 kg and 10 kg, respectively [33]. Arithmetic mean concentrations of BFRs in Nigerian food items and mean food consumption rates were assumed in our mean exposure scenario, while 95th percentile BFR concentrations and 95th percentile food consumption rates were used to generate upper-bound exposure estimates.

Table 2 summarises estimates of dietary exposure to BFRs of Nigerian adults and toddlers. The estimated mean dietary intake of BFRs (sum of BDE-47, BDE-99, BDE-100, DPTE, EH-TBB, and BEH-TEBP) was 0.58 ng/kg bw/day and 1.8 ng/kg bw/day for Nigerian adults and toddlers, with upper-bound estimates of 9.9 ng/kg bw/day and 31 ng/kg bw/day, respectively. NBFRs (sum of DPTE, EH-TBB, and BEH-TEBP) contributed an average of 64% to dietary exposure to BFRs, with the remaining 36% attributed to PBDEs (sum of BDE-47, BDE-99, and BDE-100; Fig. S1). Under our mean exposure scenario, consumption of freshwater fish contributed most (54%) to dietary intake of BFRs, followed by saltwater fish (25%), meat (17%), and other animal-derived food (4%); while under our upper-bound exposure scenario, contributions of freshwater fish, saltwater fish, meat, and other animal-derived food to dietary intake of BFRs were 38%, 20%, 32%, and 9%, respectively (Fig. S2).

Fig. 3 compares mean estimates of dietary exposure to PBDEs of Nigerian adults in 2021 (this study) with those in 2017 [17]. Despite the differences in study designs (e.g., the 2017 study analysed a wider range of food items compared to this study), our estimates of mean dietary intake of BDE-47 and BDE-99 of Nigerian adults in 2021 were 7.3 and 6.4 times higher than those in 2017, respectively. This indicates increasing health burdens posed by dietary intake of PBDEs to Nigerians. Such comparisons cannot be made for NBFRs, unfortunately, due to limited data on food contamination with NBFRs in Nigeria. Follow-up studies are encouraged to fill this gap.

Table 2
Estimated dietary intake of BFRs (EDI; ng/kg bw/day) of Nigerian adults and toddlers and associated health risks.

BFRs	BDE-47	BDE-99	BDE-100[b]	DPTE[c]	EH-TBB	BEH-TEBP	Sum (HI)
RfD[a]	100	100	n.a.	n.a.	20,000	20,000	–
Mean exposure (adults)							
EDI	0.066	0.077	0.071	0.031	0.10	0.23	0.58
HQ	<0.001	<0.001	<0.001	n.a.	<0.001	<0.001	0.0015
Mean exposure (toddlers)							
EDI	0.21	0.24	0.22	0.098	0.32	0.74	1.8
HQ	0.0021	0.0024	<0.001	n.a.	<0.001	<0.001	0.0047
Upper-bound exposure (adults)							
EDI	1.0	1.4	1.2	0.75	1.3	4.3	9.9
HQ	0.010	0.014	<0.001	n.a.	<0.001	<0.001	0.025
Upper-bound exposure (toddlers)							
EDI	3.1	4.4	3.7	2.4	4.0	13	31
HQ	0.031	0.044	0.0019	n.a.	<0.001	<0.001	0.078

[a] RfD = reference doses (ng/kg bw/day), data obtained from Refs. [2,35].
[b] RfD for BDE-100 is not available, thus RfD for penta-BDE (2000 ng/kg bw/day) was used as replacement.
[c] RfD for DPTE is not available, thus HQ cannot be calculated.

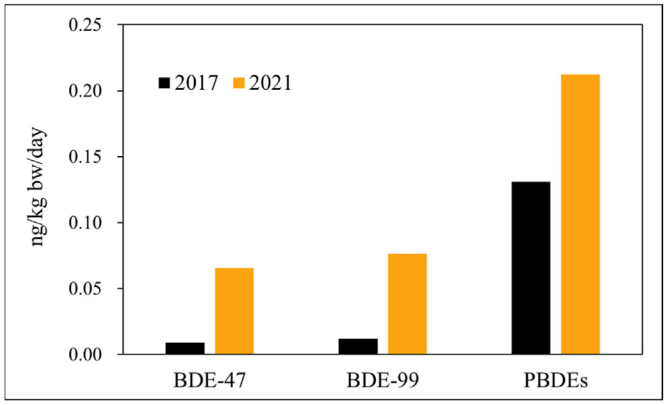

Fig. 3. Estimated mean dietary intake of PBDEs of Nigerian adults: comparisons between 2017 [17] and 2021 (this study); PBDEs = sum of BDE-47, -99, and-100 in this study, while PBDEs = sum of BDE-17, -28, –47, –99, –100, –153, –154, and –183 in the 2017 study.

3.4.2. Comparisons with dust ingestion of BFRs of Nigerians

Mean dust ingestion of PBDEs (sum of BDE-47, -99, –100, –153, –154, and –183) was 0.004 ng/kg bw/day and 0.1 ng/kg bw/day for adults and toddlers in Lagos, Nigeria, with high dust ingestion of PBDEs of 0.01 ng/kg bw/day and 0.4 ng/kg bw/day, respectively [34]. Our estimates of mean dietary exposure to PBDEs (sum of BDE-47, -99, and –100) were 53 and 6.7 times higher than mean dust ingestion of PBDEs (sum of BDE-47, -99, –100, –153, –154, and –183) for adults and toddlers, while our estimates of upper-bound dietary exposure to PBDEs were 360 and 28 times higher than high dust ingestion of PBDEs for adults and toddlers, respectively [34]. These results were consistent with an earlier study conducted in the UK [12], where dietary intake of tri-to-hexa-BDEs exceeded considerably intake from dust ingestion. Unfortunately, it is unlikely to compare the differences in patterns between dust ingestion and dietary intake of PBDEs for Nigerians, as dust ingestion of individual PBDE congeners was not specified in the previous study [34]. However, dust ingestion of BDE-209 contributed over 90% to dust ingestion of total PBDEs for Nigerians [34], while BDE-209 was only detected in 8% of Nigerian food samples analysed in this study, and therefore dietary intake of BDE-209 was not estimated. This likely indicates rapid biotic degradation of BDE-209 in foodstuffs of Nigerian origin.

3.4.3. Health risk assessment

Hazard quotient (HQ) and hazard index (HI) of dietary exposure to BFRs were calculated by using equations (2) and (3), respectively, and the results are given in Table 2. HI was estimated to be 0.0015 and 0.0047 for Nigerian adults and toddlers under mean dietary exposure scenario, with upper-bound estimates of HI of 0.025 and 0.078, respectively. These results suggest adverse health effects on Nigerian adults and toddlers of dietary intake of BFRs are unlikely to occur.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgments

This work is supported by the Global Challenges PhD Scholarship granted to Yulong Ma by the University of Birmingham.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.emcon.2023.100264.

References

[1] Y. Ma, W.A. Stubbings, M.A.E. Abdallah, R. Cline-Cole, S. Harrad, Formal waste treatment facilities as a source of halogenated flame retardants and organophosphate esters to the environment: a critical review with particular focus on outdoor air and soil, Sci. Total Environ. 807 (2022) 150747.
[2] Y. Ma, W.A. Stubbings, R. Cline-Cole, S. Harrad, Human exposure to halogenated and organophosphate flame retardants through informal e-waste handling activities - a critical review, Environ. Pollut. 268 (2021) 115727.
[3] D. Klincic, M. Dvorscak, K. Jagic, G. Mendas, S.H. Romanic, Levels and distribution of polybrominated diphenyl ethers in humans and environmental compartments: a comprehensive review of the last five years of research, Environ. Sci. Pollut. Res. 27 (2020) 5744–5758.
[4] Y. Jiang, L. Yuan, Q. Lin, S. Ma, Y. Yu, Polybrominated diphenyl ethers in the environment and human external and internal exposure in China: a review, Sci. Total Environ. 696 (2019) 133902.
[5] S.A. Mackintosh, J.S. Wallace, M.S. Gross, D.D. Navarro, A. Pérez-Fuentetaja, M. Alaee, D. Montecastro, D.S. Aga, Review on the occurrence and profiles of polybrominated diphenyl ethers in the Philippines, Environ. Int. 85 (2015) 314–326.
[6] Y. Chen, J. Li, L. Liu, N. Zhao, Polybrominated diphenyl ethers fate in China: a review with an emphasis on environmental contamination levels, human exposure and regulation, J. Environ. Manag. 113 (2012) 22–30.
[7] G. Abbasi, L. Li, K. Breivik, Global historical stocks and emissions of PBDEs, Environ. Sci. Technol. 53 (2019) 6330–6340.
[8] L. Li, F. Wania, Elucidating the variability in the hexabromocyclododecane diastereomer profile in the global environment, Environ. Sci. Technol. 52 (2018) 10532–10542.
[9] P. Xiong, X. Yan, Q. Zhu, G. Qu, J. Shi, C. Liao, G. Jiang, A review of environmental occurrence, fate, and toxicity of novel brominated flame retardants, Environ. Sci. Technol. 53 (2019) 13551–13569.
[10] Y. Ma, W.A. Stubbings, M.A.E. Abdallah, R. Cline-Cole, S. Harrad, Temporal trends in concentrations of brominated flame retardants in UK foodstuffs suggest active impacts of global phase-out of PBDEs and HBCDD, Sci. Total Environ. 863 (2023) 160956.
[11] Y. Ma, K.A. Romanak, S.L. Capozzi, C. Xia, D.C. Lehman, S. Harrad, R. Cline-Cole, M. Venier, Socio-economic factors impact US dietary exposure to halogenated flame retardants, Environ. Sci. Technol. Lett. 10 (2023) 478–484.
[12] F. Tao, M.A.E. Abdallah, D.C. Ashworth, P. Douglas, M.B. Toledano, S. Harrad, Emerging and legacy flame retardants in UK human milk and food suggest slow response to restrictions on use of PBDEs and HBCDD, Environ. Int. 105 (2017) 95–104.
[13] X. Li, Y. Liu, Y. Yin, P. Wang, X. Su, Occurrence of some legacy and emerging contaminants in feed and food and their ranking priorities for human exposure, Chemosphere 321 (2023) 138117.
[14] M. Marques, M. Nadal, J.L. Domingo, Human exposure to polybrominated diphenyl ethers (PBDEs) through the diet: an update of the scientific literature, Food Chem. Toxicol. 167 (2022) 113322.
[15] V. Vaccher, L. Ingenbleek, A. Adegboye, S.E. Hossou, A.Z. Kone, A.D. Oyedele, C. Kisito, Y.K. Dembele, R. Hu, I. Adbel Malak, R. Cariou, A. Venisseau, B. Veyrand, P. Marchand, S. Eyangoh, P. Verger, G. Dervilly-Pinel, J.C. Leblanc, B. Le Bizec, Levels of persistent organic pollutants (POPs) in foods from the first regional Sub-Saharan Africa Total Diet Study, Environ. Int. 135 (2020) 105413.
[16] K. Oloruntoba, O. Sindiku, O. Osibanjo, S. Balan, R. Weber, Polybrominated diphenyl ethers (PBDEs) in chicken eggs and cow milk around municipal dumpsites in Abuja, Nigeria, Ecotoxicol. Environ. Saf. 179 (2019) 282–289.
[17] B.A. Babalola, A.A. Adeyi, Levels, dietary intake and risk of polybrominated diphenyl ethers (PBDEs) in foods commonly consumed in Nigeria, Food Chem. 265 (2018) 78–84.
[18] J. Wang, X. Zhao, Y. Wang, Z. Shi, Tetrabromobisphenol A, hexabromocyclododecane isomers and polybrominated diphenyl ethers in foodstuffs from Beijing, China: contamination levels, dietary exposure and risk assessment, Sci. Total Environ. 666 (2019) 812–820.
[19] A. Venisseau, E. Bichon, A. Brosseaud, V. Vaccher, E. Lesquin, F. Larvor, S. Durand, G. Dervilly-Pinel, P. Marchand, B. Le Bizec, Occurrence of legacy and novel brominated flame retardants in food and feed in France for the period 2014 to 2016, Chemosphere 207 (2018) 497–506.
[20] M. Garcia Lopez, M. Driffield, A.R. Fernandes, F. Smith, J. Tarbin, A.S. Lloyd, J. Christy, M. Holland, Z. Steel, C. Tlustos, Occurrence of polybrominated diphenylethers, hexabromocyclododecanes, bromophenols and tetrabromobisphenols A and S in Irish foods, Chemosphere 197 (2018) 709–715.
[21] L. Trabalon, L. Vilavert, J.L. Domingo, E. Pocurull, F. Borrull, M. Nadal, Human exposure to brominated flame retardants through the consumption of fish and shellfish in Tarragona County (Catalonia, Spain), Food Chem. Toxicol. 104 (2017) 48–56.
[22] G. Poma, S.V. Malysheva, S. Goscinny, G. Malarvannan, S. Voorspoels, A. Covaci, J. Van Loco, Occurrence of selected halogenated flame retardants in Belgian foodstuff, Chemosphere 194 (2018) 256–265.
[23] Y.H. Zeng, X.J. Luo, B. Tang, B.X. Mai, Habitat- and species-dependent accumulation of organohalogen pollutants in home-produced eggs from an electronic waste recycling site in South China: levels, profiles, and human dietary exposure, Environ. Pollut. 216 (2016) 64–70.
[24] W. Vetter, R. Recke, P. Ostrowicz, N. Rosenfelder, Liquid chromatographic enantioseparation of the brominated flame retardant 2,3-dibromopropyl-2,4,6-tribromophenyl ether (DPTE) and enantiomer fractions in seal blubber, Chemosphere 78 (2010) 134–138.
[25] I. Labunska, M.A.E. Abdallah, I. Eulaers, A. Covaci, F. Tao, M. Wang, D. Santillo, P. Johnston, S. Harrad, Human dietary intake of organohalogen contaminants at e-waste recycling sites in Eastern China, Environ. Int. 74 (2015) 209–220.
[26] Z. Shi, L. Zhang, J. Li, Y. Zhao, Z. Sun, X. Zhou, Y. Wu, Novel brominated flame retardants in food composites and human milk from the Chinese Total Diet Study in 2011: concentrations and a dietary exposure assessment, Environ. Int. 96 (2016) 82–90.
[27] D. Zacs, I. Perkons, E. Abdulajeva, E. Pasecnaja, E. Bartkiene, V. Bartkevics, Polybrominated diphenyl ethers (PBDEs), hexabromocyclododecanes (HBCDD), dechlorane-related compounds (DRCs), and emerging brominated flame retardants (EBFRs) in foods: the levels, profiles, and dietary intake in Latvia, Sci. Total Environ. 752 (2021) 141996.
[28] M. Remberger, J. Sternbeck, A. Palm, L. Kaj, K. Strömberg, E. Brorström-Lundén, The environmental occurrence of hexabromocyclododecane in Sweden, Chemosphere 54 (2004) 9–21.
[29] K. Kakimoto, H. Nagayoshi, J. Yoshida, K. Akutsu, Y. Konishi, A. Toriba, K. Hayakawa, Detection of Dechlorane Plus and brominated flame retardants in marketed fish in Japan, Chemosphere 89 (2012) 416–419.
[30] O.E. Akinrinade, W.A. Stubbings, M.A. Abdallah, O. Ayejuyo, R. Alani, S. Harrad, Atmospheric concentrations of polychlorinated biphenyls, brominated flame retardants, and novel flame retardants in Lagos, Nigeria indicate substantial local sources, Environ. Res. 204 (2022) 112091.
[31] L. Ingenbleek, E. Jazet, A.D. Dzossa, S.B. Adebayo, J. Ogungbangbe, S. Dansou, Z.J. Diallo, C. Kouebou, A. Adegboye, E. Hossou, S. Coulibaly, S. Eyangoh, B. Le Bizec, P. Verger, J. Kamanzi, C. Merten, J.C. Leblanc, Methodology design of the regional sub-saharan Africa total diet study in Benin, Cameroon, Mali and Nigeria, Food Chem. Toxicol. 109 (2017) 155–169.
[32] B. Bradley, K.A. Byrd, M. Atkins, S. Isa, S.L. Akintola, K.A. Fakoya, H. Ene-Obong, S.H. Thilsted, Fish in food systems in Nigeria: A review. Penang, Malaysia: WorldFish. Program Report: 2020-06. https://fish.cgiar.org/publication/fish-in-food-systems-in-nigeria-a-review/, accessed 25th April 2023.
[33] U.S. Environmental Protection Agency, Exposure Factors Handbook 2011 Edition (Final Report), 2011. Washington, DC, EPA/600/R-09/052F.
[34] O.E. Akinrinade, W.A. Stubbings, M.A.E. Abdallah, O. Ayejuyo, R. Alani, S. Harrad, Concentrations of halogenated flame retardants and polychlorinated biphenyls in house dust from Lagos, Nigeria, Environ Sci Process Impacts 23 (2021) 1696–1705.
[35] U.S. Environmental Protection Agency, Technical Fact Sheet - Polybrominated Diphenyl Ethers (PBDEs), 2017 (EPA 505-F-17-015).