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Temporal trends in concentrations of brominated flame retardants in UK foodstuffs suggest active impacts of global phase-out of PBDEs and HBCDD

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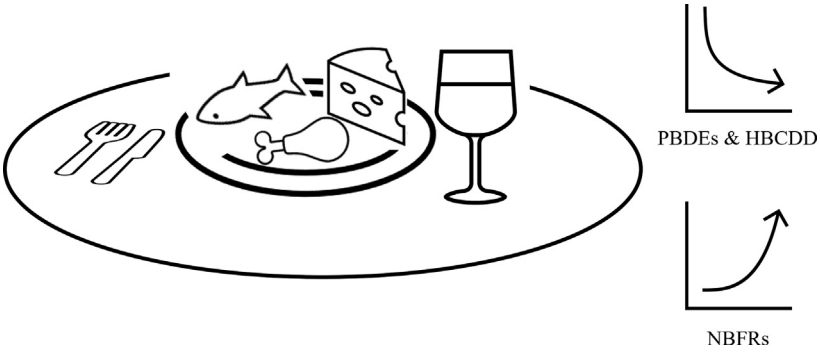
HIGHLIGHTS

- NBFRs were the predominant BFRs in UK foodstuffs.
- Levels of legacy BFRs dropped significantly in UK foodstuffs.
- Levels of BTBPE and BEH-TEBP increased considerably in UK foodstuffs.
- Significant decrease in DBDPE levels was observed in UK foodstuffs.
- Dietary exposure to BFRs decreased significantly for children with increasing age.

GRAPHICAL ABSTRACT



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ABSTRACT

Global restrictions on use of legacy brominated flame retardants (BFRs) such as polybrominated diphenyl ethers (PBDEs) and hexabromocyclododecane (HBCDD) have generated demand for novel BFRs (NBFRs) as substitutes. Our research group has previously reported decreased concentrations of PBDEs and HBCDD and increased concentrations of NBFRs in UK indoor environments, suggesting that restrictions on PBDEs and HBCDD are exerting an impact. In this study, we analysed UK foodstuffs collected in 2020–21 and compared the BFR concentrations found with those found in similar samples collected in 2015 to investigate whether similar trends in BFR concentrations would be observed. Concentrations of PBDEs and HBCDD isomers detected in our samples had declined by 78–92 % and 59–97 % since the 2015 study, respectively. Moreover, concentrations of NBFRs (dominated by 1,2-bis(2,4,6-tribromophenoxy) ethane (BTBPE or TBE), and bis(2-ethyl hexyl) tetrabromophthalate (BEH-TEBP or TBPH)) in UK foodstuffs increased significantly (28–1400 %) between 2015 and 2020–21. Combined, these findings suggest that restrictions on use of PBDEs and HBCDD have had a discernible impact on concentrations of these legacy BFRs and their NBFR replacements in UK foodstuffs. Interestingly, given recent reports of a significant increase in concentrations of decabromodiphenyl ethane (DBDPE) in UK house dust between 2014 and 2019, a significant decline (70–84 %) in concentrations of DBDPE was observed in UK foodstuffs.

1. Introduction

Brominated flame retardants (BFRs) have been widely used in commercial products to help meet fire safety regulations. Owing to their extensive use, polybrominated diphenyl ethers (PBDEs) and hexabromocyclododecanes (HBCDDs) have been detected in all aspects of the environment and biotas including humans (Jiang et al., 2019; Klincic et al., 2020; Ma et al., 2021; Ma et al., 2022). This ubiquitous presence is compounded by concerns about their adverse effects on humans and the environment, including genetic toxicity, endocrine disruption, neurotoxicity, behavioural disorders, cancer, etc. (McDonald, 2002; Schrenk et al., 2021; Yu et al., 2015). Combined with

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their persistence in the environment and capacity for bioaccumulation (Fernandes et al., 2016; Łabunska et al., 2015; Tao et al., 2017; Wang et al., 2019; Zacs et al., 2021), such evidence has led to restrictions on their production and use. In Europe, commercial penta- and octa-BDE were banned in 2004, with deca-BDE products heavily restricted in 2008 (Ma et al., 2022). These actions were followed by their listing under the Stockholm Convention on Persistent Organic Pollutants (POPs) of the United Nations Environment Programme (UNEP) in 2009 and 2017, respectively, resulting in a global phase-out of PBDEs (Sharkey et al., 2020). HBCDD was also listed under the Stockholm Convention in 2014, leading to global phase-out of their production and applications (Sharkey et al., 2020) – albeit with some exemptions. As a result of these restrictions, global demand for alternative FRs has increased sharply, with novel BFRs (NBFRs) being an important option (Ma et al., 2022).

Current understanding is that continuous consumption of BFRs should generate higher BFR concentrations in the environment, while environmental contamination with and human exposure to BFRs should decline in response to measures designed to restrict/prohibit their use. This is supported by temporal changes in concentrations of BFRs in indoor and outdoor environments (Drage et al., 2020; Hale et al., 2006; Li et al., 2015; Tanabe, 2008; Tao et al., 2016), biota (Johansson et al., 2011; Shi et al., 2018; Tanabe, 2008), and humans (Fangstrom et al., 2008; Koizumi et al., 2005; Ma et al., 2013; Ma et al., 2017; Shi et al., 2018; Toms et al., 2012). Following restrictions on use of PBDEs and HBCDD in Europe, we reported contaminations of legacy and novel BFRs in UK foodstuffs and indoor environments (Drage et al., 2020; Tao et al., 2016; Tao et al., 2017). Interestingly, while temporal changes in concentrations of BFRs in UK indoor environments appeared consistent with the restrictions in Europe (Drage et al., 2020; Tao et al., 2016), we did not observe any significant changes in BFR concentrations in UK foodstuffs, suggesting slow response of UK foodstuffs to restrictions on use of PBDEs and HBCDD (Tao et al., 2017).

Therefore, following the same sampling, extraction, and clean-up protocols as those employed by Tao et al. (2017), UK foodstuffs were collected and analysed in the present study. Our target BFRs were: 8 PBDE congeners (BDE-28, -47, -99, -100, -153, -154, -183, -209), 9 NBFRs (pentabromobenzene (PBBz), pentabromotoluene (PBT), pentabromoethylbenzene (PBEB), 2,3-dibromopropyl-2,4,6-tribromophenyl ether (DPTE), hexabromobenzene (HBBz), 2-ethyl hexyl-2,3,4,5-tetrabromobenzoate (EH-TBB or TBB), 1,2-bis(2,4,6-tribromophenoxy) ethane (BTBPE or TBE), bis(2-ethyl hexyl) tetrabromophthalate (BEH-TEBP or TBPH), decabromodiphenyl ethane (DBDPE)), and 3 HBCDD isomers (α-, β-, γ-HBCDD). The aims of the current study were to: 1) characterise current concentrations and relative abundance of legacy and novel BFRs in UK foodstuffs; 2) establish whether there have been any significant temporal changes in concentrations of these BFRs in UK foodstuffs since the study of Tao et al. (2017); and 3) estimate dietary exposure to these BFRs for UK citizens and evaluate any potential health risks.

2. Materials and methods

2.1. Sampling methodology

UK food samples were collected and processed in accordance with a previously reported strategy (Tao et al., 2017). This enables temporal changes in BFR concentrations in UK food items to be characterised. During December 2020 and October 2021, a total of 108 individual food samples (covering 15 food categories) were collected from 3 supermarkets in Birmingham representing national retail chains. Specifically, only animal-derived foodstuffs were sampled and analysed because BFRs are lipophilic and bioaccumulative compounds. Three samples of each food category were purchased from each supermarket (except for cheese and chicken eggs, for which more samples were collected and analysed), and homogenised into a composite sample. Detailed information on the food samples collected is summarised in Table S6. All composite samples (n = 36) were freeze-dried and then stored at −20 °C prior to analysis.

2.2. Analytical protocols

Information on the chemicals and reagents used in this study was given in Section 1.1 in Supplementary Materials. Extraction and clean-up of food samples and determination of lipid content were conducted following a previously reported protocol (Tao et al., 2017), with detailed information given in Section 1.2 in Supplementary Materials. Briefly, approximately 0.5 g of freeze-dried food samples were accurately weighed and spiked with internal (or surrogate) standards (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) before extraction. Hexane/acetone (3:1, *v*/v) was used to extract the samples in an accelerated solvent extractor (Dionex ASE 350). The ASE cells (34 mL) were filled from bottom to top with: pre-cleaned hydromatrix, 2 g florisil, 3 g alumina, samples, and pre-cleaned hydromatrix. The extracts were collected and concentrated to 5 mL before shaking with 5 mL sulfuric acid (95 %) to remove lipids and proteins. The purified extracts were then reconstituted into 50 μL toluene containing 200 pg/μL ^{13}C-BDE-100 and d_{18}-γ-HBCDD as recovery determination (or syringe) standards before GC–MS and LC-MS/MS analysis.

Analysis of PBDEs and NBFRs was conducted on a Trace 1310 GC coupled to an ISQ™ single quadrupole mass spectrometer (Thermo Scientific, TX, USA) operated in EI mode. Analysis of HBCDD diastereomers was conducted on a Shimadzu LC-20AB HPLC (Shimadzu, Kyoto, Japan) coupled to a Sciex API 2000 triple quadrupole mass spectrometer (Applied Biosystems, Foster City, CA, USA) operated in electrospray negative ionisation (ESI^-) mode. Detailed information was given in Section 1.3 in Supplementary Materials.

2.3. Estimation of daily dietary intake of BFRs

The equation below was adopted to estimate daily dietary intake of BFRs in this study:

$$DI = \sum_{i=1}^{n} \frac{C_i \times CR_i}{BW}$$

where C_i is the concentration (ng/g ww) of BFRs in a particular food item i (Tables S6-S9); CR_i is the daily food consumption (g/day) of a particular food item i (Tables S14-S16); BW is the average body weight (kg) of UK citizens from all age groups (Table S13).

2.4. QA/QC

A full 5-point calibration was conducted for all the target compounds. The relative standard deviation (RSD) of relative response factors (RRFs) for each analyte was below 10 %, with the corresponding R^2 values of 0.9890–0.9999, indicating excellent linearity of the calibration plots. The limit of detection (LOD) and limit of quantification (LOQ) for each analyte were calculated based on signal/noise ratios of 3 and 10, respectively. One method blank was processed for each batch of 5 samples. None of the target compounds were detected in the method blanks except for BDE-47, which was detected at concentrations below the LOQ. As a result, concentrations were not blank-corrected. Five replicates of an egg sample were conducted to evaluate the precision of the method. The RSD of the concentrations of each analyte was below 10 % except for BDE-99, for which the RSD was 12 %. More information on QA/QC is provided in Section 1.4 and Tables S1-S5 in Supplementary Materials.

2.5. Statistical analysis

Statistical analysis was conducted using Microsoft Office 365 and IBM SPSS Statistics 28.0 (Chicago, IL, USA). Paired samples *t*-test was used to identify any changes in BFR concentrations in UK foodstuffs between 2015 and 2020–21. For statistical purposes, concentrations below LOD (or LOQ) were assumed to be 0.5 × LOD (or 0.5 × LOQ) when the detection frequency (DF) exceeded 50 % for a specific analyte, while

concentrations below LOD (or LOQ) were assumed to be DF × LOD (or DF × LOQ) when DF < 50 % (Tao et al., 2017).

3. Results and discussion

3.1. Concentrations and relative abundance of BFRs in UK foodstuffs

Table 1 presents descriptive statistics for all the target BFRs in UK foodstuffs. Mean concentrations of BFRs in different food items are shown in Fig. 1, with detailed data provided in Tables S6 – S9. The relative contributions of NBFRs, PBDEs, and HBCDD isomers to total BFRs are shown in Fig. 2 and Fig. S2.

3.1.1. Concentrations and relative abundance of NBFRs in UK foodstuffs

Concentrations of Σ_9NBFRs ranged from <0.42 ng/g lw (<110 pg/g ww) to 170 ng/g lw (5600 pg/g ww) in UK foodstuffs, with mean and median concentrations of 29 ng/g lw (910 pg/g ww) and 9.9 ng/g lw (460 pg/g ww), respectively. BTBPE (mean: 15 ng/g lw or 480 pg/g ww) and BEH-TEBP (mean: 11 ng/g lw or 360 pg/g ww) were the most abundant and most frequently detected NBFRs, contributing 52 % and 38 % of ΣNBFRs, respectively. EH-TBB, DBDPE, and DPTE were detected in <50 % of samples. Mean concentrations of these three NBFRs were 1.5 ng/g lw (21 pg/g ww), 0.63 ng/g lw (26 pg/g ww), and 0.97 ng/g lw (27 pg/g ww), respectively. PBBz was only detected in one composite food sample at 0.29 ng/g lw (14 pg/g ww), while concentrations of PBT, PBEB, and HBBz were below LOD in all samples.

Table S10 summarises literature data on concentrations of NBFRs in foodstuffs from different countries. Surprisingly, BTBPE and BEH-TEBP concentrations reported in this study were broadly comparable to the concentrations reported in foodstuffs collected from several e-waste recycling sites in China (Labunska et al., 2015; Zeng et al., 2016; Zheng et al., 2016), and were generally one order of magnitude higher than the concentrations reported in foodstuffs collected from France (Venisseau et al., 2018), Belgium (Poma et al., 2018), Tanzania (Polder et al., 2016), and China (non-e-waste recycling areas) (Shi et al., 2016). Comparable concentrations to this study were reported for DPTE in foodstuffs from China (Shi et al., 2016), as well as for DBDPE in foodstuffs from China (Labunska et al., 2015; Shi et al., 2018) and Spain (Trabalon et al., 2017). EH-TBB was detected in UK foodstuffs at concentrations broadly comparable to those in French food samples (Venisseau et al., 2018), but concentrations in our study were 1–2 orders of magnitude lower than the concentrations reported in foodstuffs collected from an e-waste recycling site in China (Labunska et al., 2015).

3.1.2. Concentrations and relative abundance of PBDEs in UK foodstuffs

Concentrations of Σ_8PBDEs ranged from 0.13 ng/g lw (13 pg/g ww) to 36 ng/g lw (760 pg/g ww) in UK foodstuffs, with mean and median concentrations of 4.2 ng/g lw (190 pg/g ww) and 2.3 ng/g lw (120 pg/g ww), respectively. BDE-183 and BDE-47 were the only PBDE congeners with detection frequencies higher than 50 %. This was followed by BDE-209, which was detected in 44 % of the samples. Compared to previous studies conducted in other countries (Table S11), PBDE concentrations reported in this study were generally at the same level with the concentrations reported in foodstuffs from Latvia (Zacs et al., 2021), Netherlands (Gebbink et al., 2019), France (Riviere et al., 2014; Venisseau et al., 2018), Belgium (Covaci et al., 2009; Poma et al., 2018), and Japan (Kakimoto et al., 2012), but were considerably lower than the concentrations reported in foodstuffs from Tanzania (Polder et al., 2016), Spain (Trabalon et al., 2017), Ireland (Garcia Lopez et al., 2018), China (Wang et al., 2019; Zeng et al., 2016), and the US (Hites et al., 2004; Schecter et al., 2010).

At least one PBDE congener was detected in all UK food samples. This could reflect the wide use of PBDEs. However, the average contribution of PBDEs to total BFRs was only 13 %, strongly outweighed by the average contribution of 86 % of NBFRs to total BFRs. Following global restrictions on PBDE production and consumption, our findings may provide evidence of the replacement of PBDEs by NBFRs in consumer products.

3.1.3. Concentrations and relative abundance of HBCDDs in UK foodstuffs

Σ_3HBCDDs made only a very small contribution (1.2 %) to total BFR concentrations in UK foodstuffs. Concentrations of Σ_3HBCDDs ranged from <0.056 ng/g lw (<4.0 pg/g ww) to 3.5 ng/g lw (420 pg/g ww), with mean and median concentrations of 0.41 ng/g lw (33 pg/g ww) and 0.13 ng/g lw (6.9 pg/g ww), respectively. All 3 diastereomers of HBCDDs targeted in this study were detected in <50 % of our samples. With an average contribution of 50 % to Σ_3HBCDDs concentrations, α-HBCDD was most abundant, followed by β-HBCDD and γ-HBCDD, which account for 37 % and 13 % of Σ_3HBCDDs concentrations, respectively.

Table S12 summarises concentrations of HBCDD in foodstuffs from different countries. HBCDD concentrations in chicken eggs reported in this study were comparable to those reported in Latvia (Zacs et al., 2021),

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

BFRs	DF [a]	Minimum	5th percentile	25th percentile	Median	75th percentile	95th percentile	Maximum	Mean
BDE-28	0 %	<0.019 (<1.6)	<0.020 (<2.2)	<0.026 (<2.6)	<0.044 (<3.2)	<0.096 (<4.2)	<0.75 (<6.6)	<1.1 (<7.1)	<0.16 (<3.7)
BDE-47	58 %	<0.0069 (<0.59)	<0.016 (<0.85)	<0.055 (<1.0)	0.13 (13)	0.37 (24)	2.3 (300)	3.3 (500)	0.48 (52)
BDE-99	28 %	<0.0050 (<0.42)	<0.0054 (<0.56)	<0.0082 (<0.73)	<0.026 (<1.0)	0.3 (47)	5.4 (340)	10 (490)	0.87 (62)
BDE-100	36 %	<0.0058 (<0.51)	<0.0063 (<0.68)	<0.0099 (<0.91)	<0.029 (<1.4)	0.19 (29)	1.0 (55)	2.9 (94)	0.26 (14)
BDE-153	25 %	<0.0038 (<0.33)	<0.0046 (<0.44)	<0.0065 (<0.54)	<0.017 (<0.78)	0.060 (2.5)	0.46 (23)	4.6 (24)	0.18 (4.5)
BDE-154	19 %	<0.0048 (<0.41)	<0.0056 (<0.55)	<0.0082 (<0.66)	<0.021 (<0.82)	<0.16 (<1.6)	0.36 (64)	13 (93)	0.41 (10)
BDE-183	61 %	<0.024 (<2.6)	<0.029 (<2.8)	<0.087 (<4.6)	0.16 (12)	0.45 (23)	2.2 (42)	2.7 (61)	0.42 (15)
BDE-209	44 %	<0.026 (<3.0)	<0.031 (<3.3)	<0.044 (<4.0)	<0.53 (<8.7)	0.85 (50)	6.7 (100)	23 (150)	1.6 (30)
Σ_8PBDEs	**–**	**0.13 (13)**	**0.27 (18)**	**1.0 (38)**	**2.3 (120)**	**3.8 (290)**	**16 (570)**	**36 (760)**	**4.2 (190)**
PBBz	3 %	<0.010 (<0.92)	<0.011 (<1.2)	<0.015 (<1.5)	<0.025 (<1.8)	<0.069 (<2.4)	<0.19 (<3.8)	0.29 (14)	0.010 (0.44)
PBT	0 %	<0.017 (<1.5)	<0.018 (<2.0)	<0.024 (<2.3)	<0.039 (<2.9)	<0.085 (<3.7)	<0.67 (<5.8)	<0.98 (<6.4)	<0.14 (<3.3)
PBEB	0 %	<0.0069 (<0.60)	<0.0074 (<0.80)	<0.0096 (<0.96)	<0.016 (<1.2)	<0.035 (<1.5)	<0.27 (<2.4)	<0.40 (<2.6)	<0.057 (<1.3)
DPTE	19 %	<0.061 (<5.3)	<0.065 (<7.6)	<0.092 (<9.1)	<0.18 (<13)	<2.4 (<21)	5.6 (180)	9.1 (190)	0.97 (27)
HBBz	0 %	<0.0076 (<0.66)	<0.0081 (<0.88)	<0.011 (<1.1)	<0.018 (<1.3)	<0.038 (<1.7)	<0.30 (<2.6)	<0.44 (<2.9)	<0.062 (<1.5)
EH-TBB	11 %	<0.051 (<4.4)	<0.057 (<6.2)	<0.077 (<7.3)	<0.12 (<9.5)	<0.52 (<15)	7.2 (150)	35 (290)	1.5 (21)
BTBPE	83 %	<0.29 (<44)	<0.44 (<70)	0.67 (72)	3.0 (120)	13 (390)	83 (1800)	110 (5500)	15 (480)
BEH-TEBP	61 %	<0.33 (<37)	<0.44 (<40)	<0.77 (<60)	1.1 (110)	9.8 (300)	56 (1100)	65 (4700)	11 (360)
DBDPE	22 %	<0.15 (<13)	<0.17 (<18)	<0.24 (<23)	<0.45 (<32)	<2.5 (<54)	2.8 (104)	4.8 (440)	0.63 (26)
Σ_9NBFRs	**–**	**<0.42 (<110)**	**0.58 (120)**	**2.3 (270)**	**9.9 (460)**	**29 (830)**	**120 (3800)**	**170 (5600)**	**29 (910)**
α-HBCDD	39 %	<0.029 (<2.5)	<0.035 (<3.3)	<0.055 (<4.1)	<0.13 (<5.2)	0.72 (9.6)	0.78 (160)	3.1 (370)	0.20 (25)
β-HBCDD	22 %	<0.054 (<4.7)	<0.067 (<5.3)	<0.093 (<5.9)	<0.21 (<6.5)	<0.49 (<9.1)	0.55 (9.4)	1.6 (50)	0.15 (4.7)
γ-HBCDD	31 %	<0.021 (<1.5)	<0.022 (<2.0)	<0.042 (<2.4)	<0.071 (<3.1)	0.076 (3.6)	0.21 (14)	0.30 (23)	0.055 (3.1)
Σ_3HBCDDs	**–**	**<0.056 (<4.0)**	**<0.063 (<5.3)**	**<0.12 (<6.8)**	**0.13 (6.9)**	**0.40 (15)**	**1.5 (170)**	**3.5 (420)**	**0.41 (33)**
Σ_{20}BFRs	**–**	**1.7 (90)**	**2.3 (140)**	**3.7 (460)**	**13 (620)**	**32 (1200)**	**130 (4000)**	**210 (5900)**	**33 (1100)**

[a] DF = detection frequency.

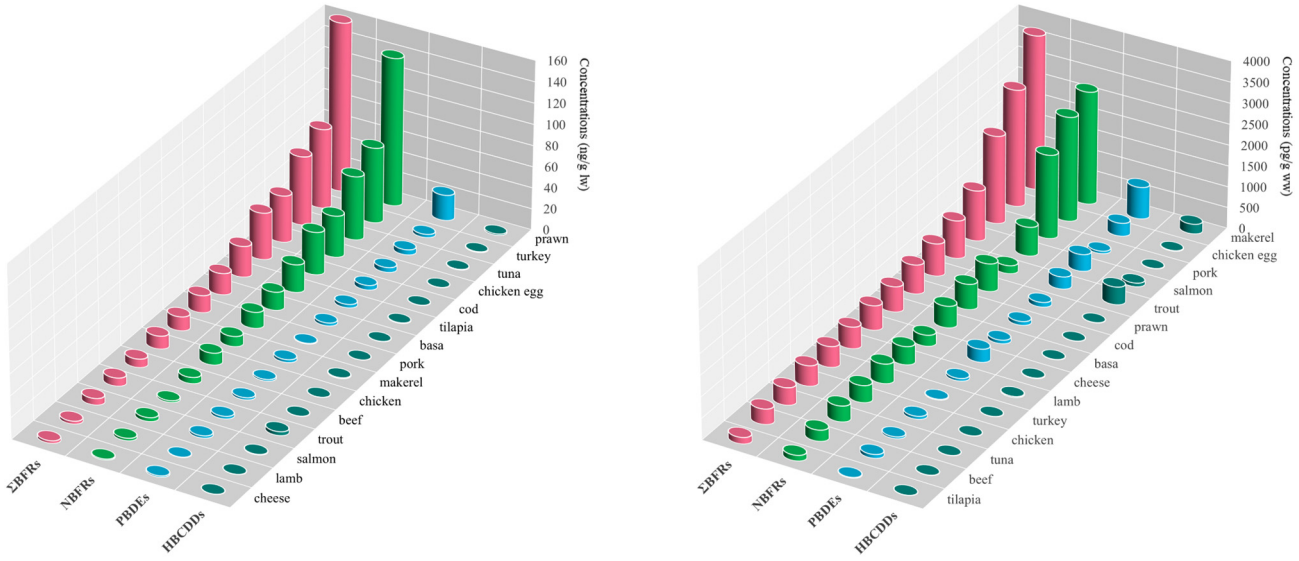

Fig. 1. Mean concentrations of BFRs in UK foodstuffs (left: data based on lipid weight; right: data based on wet weight).

France (Riviere et al., 2014), Ireland (Garcia Lopez et al., 2018), and the US (Schecter et al., 2010), but were considerably lower than HBCDD concentrations in chicken eggs from China (Labunska et al., 2015; Wang et al., 2019; Zeng et al., 2016), Belgium (Covaci et al., 2009; Poma et al., 2018), Sweden (Remberger et al., 2004), and Tanzania (Polder et al., 2016). In the meantime, HBCDD concentrations in meat, fish, and cheese samples collected from the UK were generally lower than reported previously elsewhere (Garcia Lopez et al., 2018; Kakimoto et al., 2012; Labunska et al., 2015; Poma et al., 2018; Remberger et al., 2004; Riviere et al., 2014; Schecter et al., 2010; Venisseau et al., 2018; Wang et al., 2019; Zacs et al., 2021). The extent to which the lower concentrations in our study reflect recent restrictions on use of HBCDD is unclear.

3.2. Temporal changes in BFR concentrations in UK foodstuffs between 2015 and 2020–21

We have previously reported concentrations of NBFRs, PBDEs, and HBCDD in UK foodstuff samples collected in 2015 (Tao et al., 2017). In the current study, we employed a similar sampling strategy as well as identical sample extraction and clean-up protocols for BFR analysis in UK foodstuffs. Combined, this facilitates assessment of temporal changes in BFR concentrations in UK foodstuffs. Specifically, the percentage changes in concentrations of 6 PBDE congeners (BDE-47, -99, -100, -153, -154, and -209), 4 NBFRs (EH-TBB, BTBPE, BEH-TEBP, and DBDPE), and 3 HBCDD diastereomers (α-, β-, and γ-HBCDD) in UK foodstuffs between 2015 and 2020–21 were calculated (Fig. 3 and Figs. S3a-S5b).

3.2.1. Temporal changes in NBFR concentrations in UK foodstuffs

3.2.1.1. Σ_4NBFRs. Arithmetic mean concentrations of Σ_4NBFRs in meat, fish, cheese, and eggs have increased by 110 %, 320 %, 28 %, and 1400 % between 2015 and 2020–21, respectively. Paired-Samples *t*-test revealed such increases were statistically significant ($p = 0.047$). This suggests that increased use of NBFRs due to restrictions on PBDE and HBCDD production and consumption is now impacting food supplies in the UK. Although recent data on consumption volumes of NBFRs in Europe (especially in the UK) remains limited, global production of DBDPE was estimated to increase from 4540 to 22,700 t in 2006 to 22,700–45,400 t in 2012

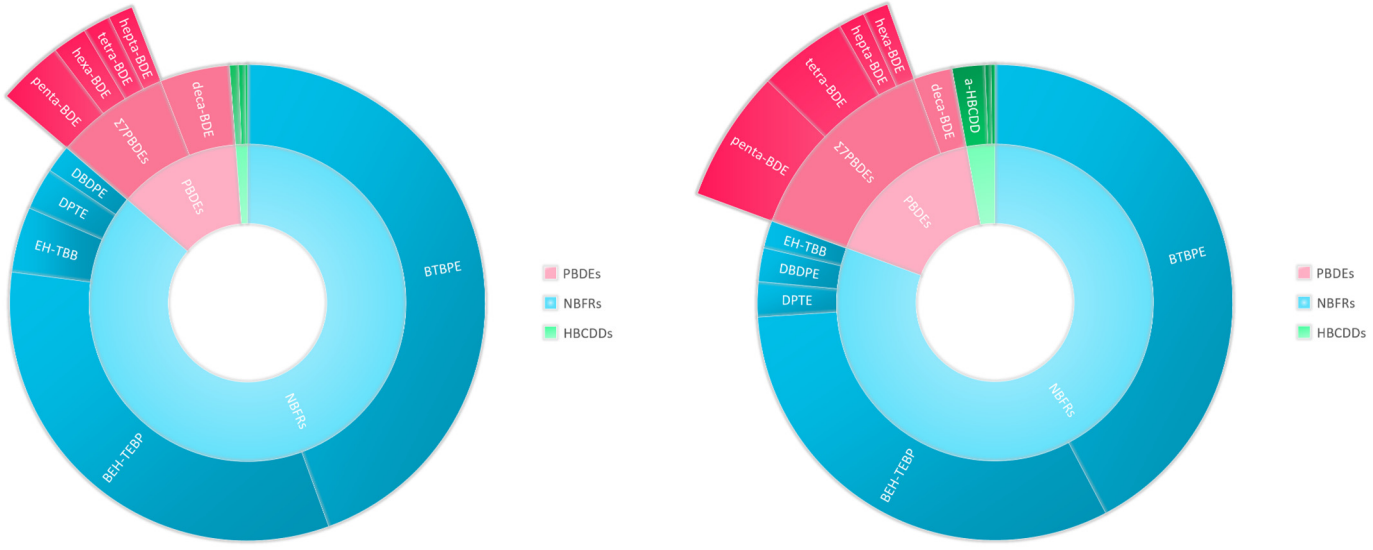

Fig. 2. Relative abundance of NBFRs, PBDEs, and HBCDDs in UK foodstuffs (left: data based on lipid weight; right: data based on wet weight).

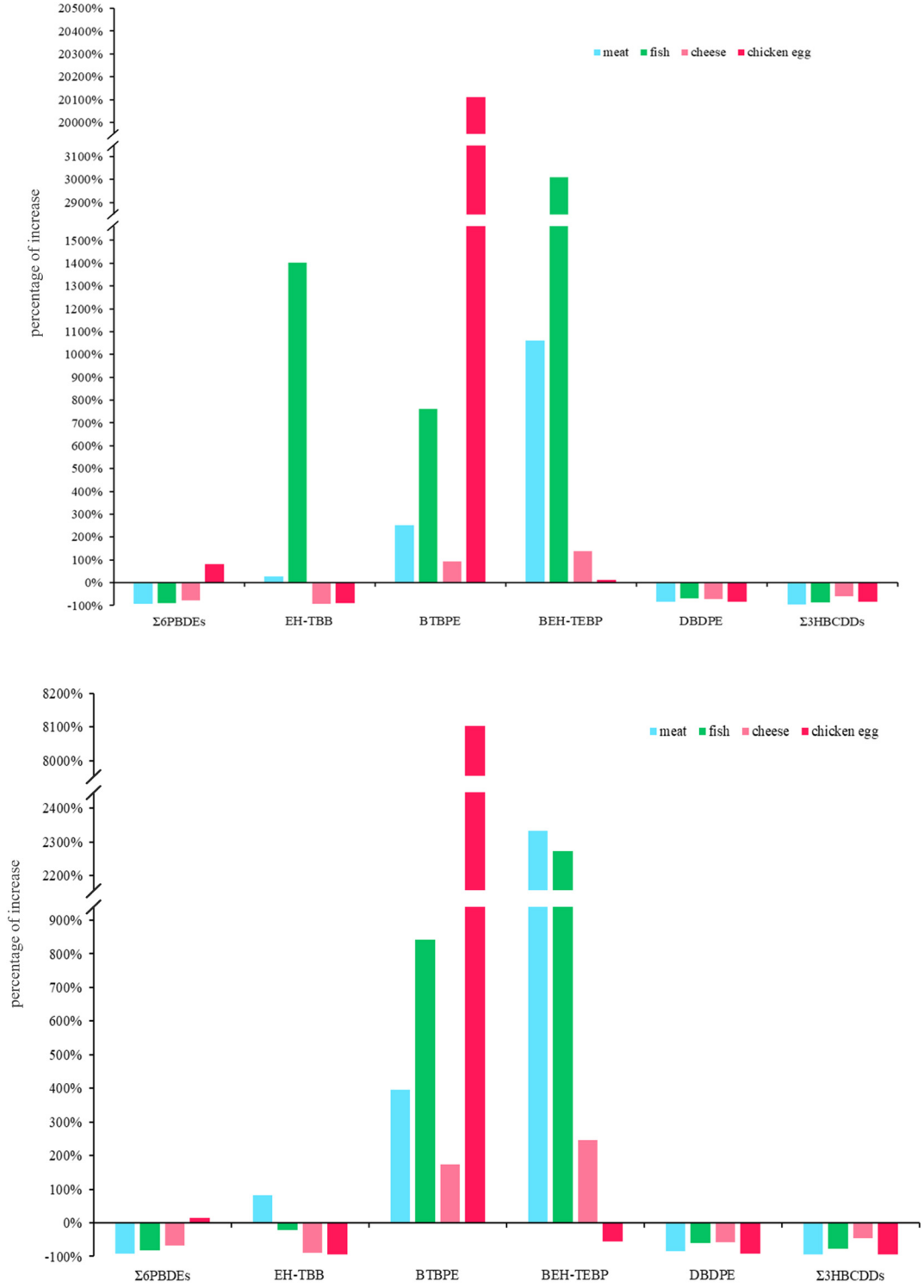

Fig. 3. Increase in BFR concentrations in UK foodstuffs between 2015 and 2020/2021 (up: data based on lipid-weight concentrations; down: data based on wet-weight concentrations).

(Hong et al., 2015), and global production of BTBPE also climbed sharply from ~5000 t to 16,710 t between 1997 and 2001 (Covaci et al., 2011; de Jourdan et al., 2013). BEH-TEBP was listed as a high production volume chemical by the US EPA (Xiong et al., 2019), and its annual production volumes in the US were 450–4500 t (Covaci et al., 2011). EH-TBB was also listed as a high production volume chemical by the US EPA in 2006 (Ma et al., 2012), but it was removed from the US EPA High Production Volume Information System in 2015, implying a production and import volume of <450 t in the US (Knudsen et al., 2016; Xiong et al., 2019).

3.2.1.2. BTBPE. Mean concentrations of BTBPE (the predominant NBFR) in meat, fish, and cheese have increased by 250 %, 760 %, and 94 % between 2015 and 2020–21, respectively, with another surprising 200-fold increase in chicken eggs. Paired samples *t*-test suggested that the increase in BTBPE concentrations in UK foodstuffs was close to statistical significance ($p = 0.070$). As inter alia a replacement for Octa-BDE, use of BTBPE is projected to rise (Covaci et al., 2011; Ezechias et al., 2014; Hou et al., 2021; Ma et al., 2022), which might explain the considerable increase in BTBPE concentrations in UK foodstuffs. Additionally, lab-based and

field-based studies have identified strong bioaccumulation and biomagnification abilities of BTBPE in a variety of species, evidenced by calculated bioaccumulation factors (BAFs) of 57–1,200,000 (La Guardia et al., 2012; Lee et al., 2019; Wu et al., 2011) and biomagnification factors (BMFs) of 1.9–3.6 (Mo et al., 2012; Tomy et al., 2007), respectively. Such propensity for bioaccumulation/biomagnification is a plausible contributory factor to the increased concentrations of BTBPE observed in the current study, coupled with the relatively long half-life (43–1900 days) of BTBPE in biota (Lee et al., 2019; Tomy et al., 2007; Zheng et al., 2018). However, the relatively small sample sizes in the two studies are a limitation, as only 5 composite egg samples were analysed in the current study and only one composite egg sample was analysed in our previous study (Tao et al., 2017). Further investigation is recommended to evaluate temporal changes in BTBPE concentrations in chicken eggs from the UK.

3.2.1.3. BEH-TEBP. A statistically significant increase ($p = 0.049$) in BEH-TEBP concentrations (the second most predominant NBFR in this study) was also identified in UK foodstuffs. Between 2015 and 2020–21, increases of 1100 %, 3000 %, 140 %, and 11 % were determined for BEH-TEBP concentrations in meat, fish, cheese, and chicken eggs, respectively. Unfortunately, there is no information on the production of BEH-TEBP in recent years, but restrictions on use of the penta-BDE formulation are likely to increase global demand for BEH-TEBP. The significant increase in concentrations of BEH-TEBP in UK foodstuffs could also be explained by its strong ability to bioaccumulate in various species (BAFs = 510–100,000) (Ezechias et al., 2014; Hou et al., 2022; La Guardia et al., 2012), as well as its long half-life in biota (36–690 days) (Bearr et al., 2012; Zheng et al., 2018).

3.2.1.4. EH-TBB. Despite the significant increase observed in concentrations of BTBPE and BEH-TEBP, concentrations of EH-TBB reported in this study were not significantly different ($p = 0.25$) from those reported previously (Tao et al., 2017). Arithmetic mean concentrations in meat of EH-TBB have increased by 26 % between 2015 and 2020–21, while those in cheese and eggs dropped by 93 % and 88 % respectively. Interestingly, while a 14-fold increase in lipid-based concentrations of EH-TBB was observed in fish samples, the corresponding wet-weight concentrations dropped by 22 %. Such a seeming contradiction stems from a lower lipid content (0.36 %) and thus a much higher lipid-based concentration of EH-TBB (35 ng/g lw) in one tuna sample. Exclusion of this sample as an outlier resulted in a 94 % decrease in concentrations of EH-TBB in fish samples. However, previous studies reported BAFs (16–8900) (Hou et al., 2022; La Guardia et al., 2012; Lee et al., 2019) and half-lives (29–1000 days) (Bearr et al., 2012; Lee et al., 2019) of EH-TBB to be similar to those of BTBPE and BEH-TEBP, suggesting similar bioaccumulation abilities. Hence, our observed discrepancy between temporal trends in these 3 NBFRs in UK foods may instead reflect reduced use of EH-TBB.

3.2.1.5. DBDPE. A decline in DBDPE concentrations was also identified in UK foodstuffs between 2015 and 2020–21. Arithmetic mean concentrations of DBDPE have decreased by 84 %, 70 %, 71 %, and 83 %, respectively, in meat, fish, cheese, and egg samples. A paired samples *t*-test suggested such changes in DBDPE concentrations were statistically significant ($p = 0.0078$). DBDPE is now primarily used as a replacement for Deca-BDE (Covaci et al., 2011), and has been frequently detected in UK and Irish indoor dust and indoor air samples at elevated concentrations, suggesting its increased use over the last few years (Drage et al., 2020; Tao et al., 2016; Wemken et al., 2019). However, DBDPE was barely detected in human breast milk from UK and Ireland (Tao et al., 2017; Wemken et al., 2020). Together with the decline in DBDPE concentrations in UK foodstuffs observed in this study, these results probably reflect very low bioavailability of DBDPE. Although high BAFs (77–13,000,000) and BMFs (1.6–9.2) were reported for DBDPE in various aquatic organisms from different ecosystems (He et al., 2012; Hou et al., 2022; Law et al., 2006), BMFs <1 were also reported for fish-kingfisher from Pearl River (China) (Mo et al., 2012), an aquatic food web from Taihu Lake (China) (Zheng et al., 2018), and white fish-emerald shiner from Winnipeg Lake (Canada) (Law et al., 2006). These results indicated that bioaccumulation and biomagnification abilities of DBDPE were strongly species-dependent. Moreover, much shorter half-lives have been reported for DBDPE (2.5–17 days) than for other NBFRs (Hou et al., 2021; McKinney et al., 2011; Wang et al., 2020; Zheng et al., 2018), which could provide a rationale for the different temporal trends in DBDPE concentrations in UK foodstuffs compared to indoor dust.

3.2.2. Temporal changes in PBDE concentrations in UK foodstuffs

Significantly lower concentrations were observed in UK foodstuffs for both Σ_6PBDEs ($p < 0.001$) and individual PBDE congeners ($p = 0.0011$–0.065). Concentrations of Σ_6PBDEs have decreased by 92 %, 90 %, and 78 %, respectively, in meat, fish, and cheese samples during 2015 and 2020–21. This is very likely due to the global phase-out of PBDEs. In contrast however, concentrations of Σ_6PBDEs showed an unexpected increase by 81 % in chicken eggs over the same period, due to increased concentrations of lower-brominated BDEs, as concentrations of BDE-209 declined in egg samples (Figs. S4a and S4b). A possible explanation for this was debromination of BDE-209 to lower-brominated BDEs, as chicken eggs had higher ratios of $\Sigma_{\text{tri-hepta}}$PBDEs/BDE-209 (12) than did meat (1.6), fish (1.2), and cheese (7.0) in the current study.

We have previously reported temporal declines in PBDE concentrations in UK indoor environments (Tao et al., 2016), but did not identify any temporal declines in PBDE concentrations in UK foodstuffs, concluding that food responded relatively slowly to global restrictions on PBDE production and consumption (Tao et al., 2017). In the current study, however, we observed significantly declined concentrations of PBDEs in UK foodstuffs between 2015 and 2020–21. Combined with our observation of higher contributions of NBFRs than PBDEs to BFRs (Section 3.1.2), this study suggests restrictions on PBDEs are now reducing their presence in UK foodstuffs.

3.2.3. Temporal changes in HBCDD concentrations in UK foodstuffs

Similar to PBDEs, concentrations of Σ_3HBCDDs in UK foodstuffs also declined significantly ($p = 0.003$). Σ_3HBCDD concentrations in meat, fish, cheese, and chicken eggs fell by 97 %, 87 %, 59 %, and 85 % between 2015 and 2020–21, respectively. Our previous study reported comparable HBCDD concentrations in UK foodstuffs in 2015 to those in 2004 (Driffield et al., 2008) and 2006 (Food Standards Agency, 2006), suggesting slow response of UK foodstuffs to restrictions on use of HBCDD. The significantly lower concentrations of HBCDD observed in the present study indicate restrictions on HBCDD use have had a discernible impact on UK dietary contamination.

3.3. Estimation of daily dietary intake of BFRs for UK citizens

Daily dietary intakes of BFRs for UK citizens were estimated using the equation described in Section 2.3. Body weight data for UK citizens was obtained from NHS Digital (2019) (Table S13). Daily consumption of various food items for UK citizens from different age groups was obtained from University of Cambridge, MRC Epidemiology Unit, NatCen Social Research (2022), and is summarised in Tables S14-S16.

Estimates of daily dietary intake of BFRs for UK citizens are shown in Table 2 and Figs. 4, S6a, and S6b. Both average intake (where average consumption of food contaminated at the average concentration was assumed) and high-end intake (assuming food contaminated at the average concentrations consumed at the mean rate + 2 standard deviations) were estimated for UK citizens from all age groups. Daily dietary intake of BFRs was estimated to range from 2.7 ng/kg bw/day to 9.9 ng/kg bw/day under an average food intake scenario, and from 18 ng/kg bw/day to 62 ng/kg bw/day under a high food intake scenario, respectively. NBFRs constituted 85 % of total BFR intake, with the remaining 13 % and 2 % attributed to PBDEs and HBCDD, respectively. Consumption of meat and chicken eggs contributed most to dietary intake of BFRs, accounting for 48 % and 31 %, respectively. This was followed by consumption of fish/prawns (17 %) and cheese (4 %).

Table 2
Estimated average and high-end[a] dietary intake of BFRs (ng/kg bw/day) for UK citizens.

BFRs	Dietary intake	0–1 years	2–4 years	5–7 years	8–10 years	11–12 years	13–15 years	16–24 years	25–34 years	35–44 years	45–54 years	55–64 years	65–74 years	75+ years
DPTE	Average	0.25	0.15	0.12	0.10	0.087	0.071	0.076	0.084	0.081	0.076	0.072	0.068	0.070
	High-end	1.5	0.94	0.76	0.62	0.50	0.45	0.45	0.50	0.47	0.46	0.45	0.40	0.44
EH-TBB	Average	0.19	0.12	0.092	0.078	0.067	0.055	0.059	0.065	0.063	0.059	0.056	0.053	0.054
	High-end	1.2	0.73	0.59	0.48	0.39	0.35	0.35	0.39	0.37	0.35	0.35	0.31	0.34
BTBPE	Average	4.4	2.7	2.1	1.8	1.5	1.3	1.4	1.5	1.4	1.3	1.3	1.2	1.2
	High-end	27	17	13	11	9.0	8.0	8.0	9.0	8.4	8.1	7.9	7.1	7.8
BEH-TEBP	Average	3.3	2.0	1.6	1.3	1.2	0.95	1.0	1.1	1.1	1.0	0.96	0.91	0.93
	High-end	20	13	10	8.3	6.7	6.0	6.0	6.7	6.3	6.1	6.0	5.3	5.9
DBDPE	Average	0.24	0.15	0.11	0.097	0.083	0.069	0.074	0.081	0.078	0.073	0.069	0.066	0.067
	High-end	1.5	0.91	0.73	0.60	0.49	0.43	0.44	0.49	0.45	0.44	0.43	0.39	0.42
ΣNBFRs	Average	8.4	5.1	4.0	3.4	2.9	2.4	2.6	2.8	2.7	2.6	2.4	2.3	2.3
	High-end	51	32	26	21	17	15	15	17	16	15	15	13	15
BDE-209	Average	0.20	0.11	0.089	0.071	0.061	0.046	0.046	0.062	0.058	0.056	0.058	0.059	0.059
	High-end	1.4	0.81	0.67	0.52	0.44	0.37	0.35	0.44	0.41	0.39	0.39	0.36	0.39
ΣPBDEs	Average	1.3	0.73	0.56	0.45	0.39	0.29	0.29	0.39	0.37	0.36	0.37	0.38	0.38
	High-end	8.8	5.1	4.3	3.3	2.8	2.3	2.2	2.8	2.6	2.5	2.5	2.3	2.4
α-HBCDD	Average	0.13	0.054	0.048	0.043	0.034	0.028	0.027	0.043	0.040	0.041	0.044	0.051	0.054
	High-end	1.2	0.58	0.57	0.45	0.35	0.34	0.29	0.41	0.37	0.35	0.37	0.36	0.39
β-HBCDD	Average	0.025	0.010	0.0091	0.0080	0.0064	0.0052	0.0050	0.0082	0.0075	0.0078	0.0083	0.0095	0.010
	High-end	0.23	0.11	0.11	0.085	0.066	0.064	0.055	0.076	0.069	0.066	0.069	0.067	0.074
γ-HBCDD	Average	0.017	0.0067	0.0060	0.0053	0.0042	0.0034	0.0033	0.0054	0.0050	0.0051	0.0055	0.0063	0.0067
	High-end	0.15	0.072	0.070	0.056	0.043	0.042	0.036	0.050	0.046	0.043	0.046	0.044	0.049
ΣHBCDDs	Average	0.18	0.071	0.064	0.056	0.045	0.037	0.035	0.057	0.053	0.055	0.058	0.067	0.071
	High-end	1.6	0.77	0.75	0.59	0.46	0.45	0.39	0.54	0.48	0.46	0.48	0.47	0.52

[a] High-end estimations were made assuming high-end food intakes of mean + 2SD (Table S14), because statistically this equals to 95th percentile values.

Comparison with dietary intake estimates from our previous research (Tao et al., 2017) revealed a considerable decrease in the dietary intake of PBDEs and HBCDD of UK citizens between 2015 and 2020–21 (Table S17). Dietary intake of PBDEs decreased by 62 %–83 % and 65 %–84 % for UK toddlers (≤ 3 years old) and adults (≥ 18 years old) from 2015 to 2020–21, while intake of HBCDD decreased by 70 %–92 % and

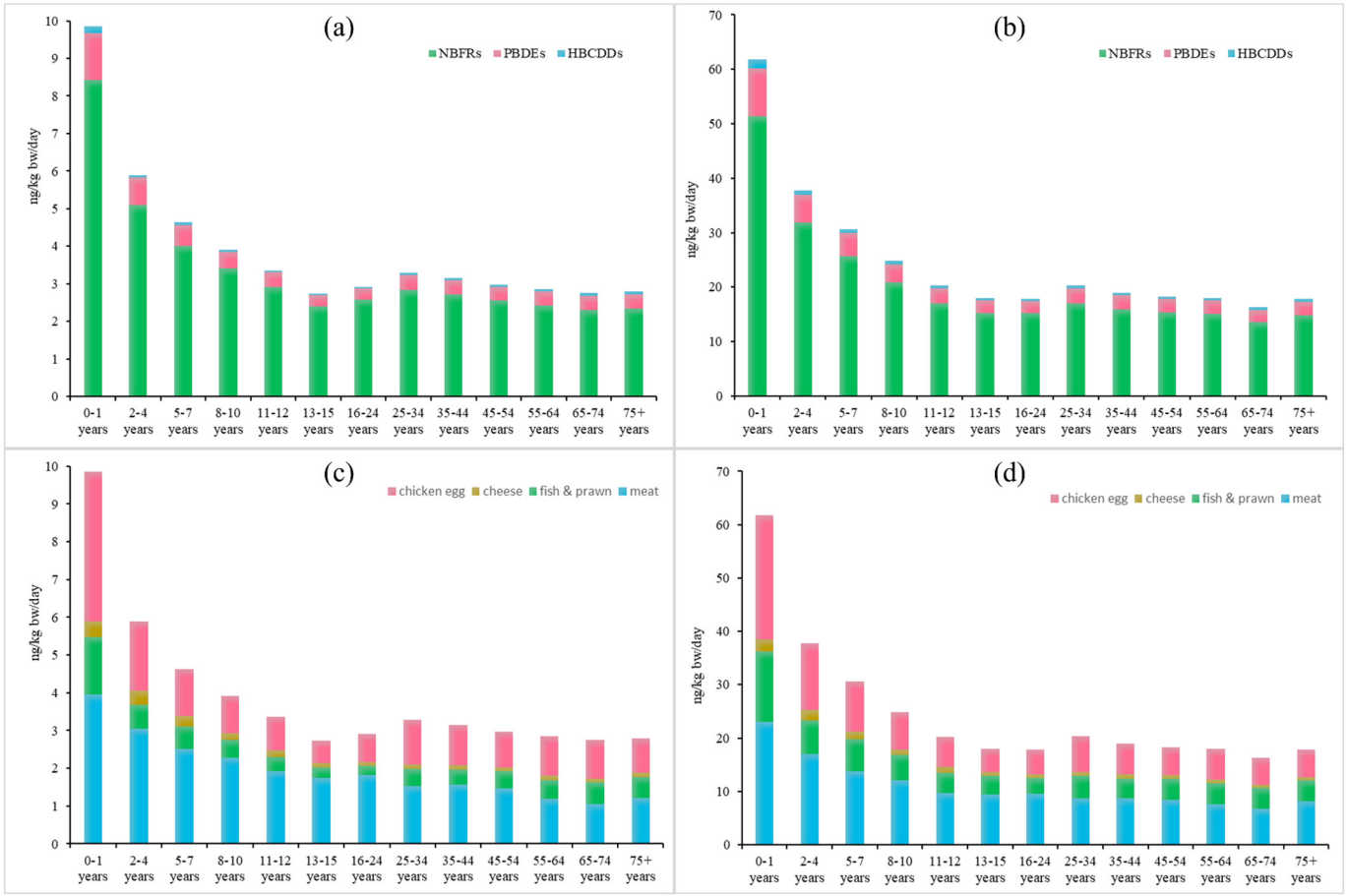

Fig. 4. Estimated dietary intake of BFRs for UK citizens from different age groups ((a) and (c): average estimations where average food intakes were assumed; (b) and (d): high-end estimations where high-end food intakes of average + 2SD were assumed).

74 %–92 %, respectively. Conversely, estimated UK dietary intake of NBFRs in this study was 2–3 times higher than our previous estimates. However, despite such increased intakes, it is noteworthy that dietary intake of NBFRs for UK citizens was generally 3 to 5 orders of magnitude lower than corresponding health-based reference doses (Table S18).

As is shown in Fig. 4, we observed significantly decreased dietary intake (body weight normalised) of BFRs with increasing age for children (p = 0.014), while for adults no considerable difference in intake of BFRs was observed between different age groups. These results raise concerns about possible adverse health effects of BFRs on toddlers because of their higher exposure doses and less developed immune system. Moreover, in addition to the relatively higher exposure doses estimated for toddlers than for other age groups based on our dietary data, this study still very likely underestimates dietary intake of BFRs for toddlers, as human milk and baby food (which were not sampled in this study) constitute important parts of their diet. Additionally, the margin of safety will be lower once other exposure pathways (e.g., dust ingestion, dermal uptake, etc.) are taken into account.

4. Conclusions

This study reported considerably increased concentrations of BTBPE and BEH-TEBP along with significantly lower concentrations of PBDEs and HBCDDs in UK foodstuffs from 2015 to 2020–21. Compared to our previous study where PBDEs were the predominant BFRs in UK foodstuffs in 2015 (Tao et al., 2017), the contribution of PBDEs to total BFRs was substantially outweighed by NBFRs in UK foodstuffs in 2020–21. These results likely reflect the global phase-out of use of PBDEs and HBCDD and their consequent replacement by NBFRs. In contrast, concentrations of EH-TBB and DBDPE in UK foodstuffs fell between 2015 and 2020–21. While reduced consumption of EH-TBB is a plausible explanation, the decrease in concentrations of DBDPE cannot be explained in the same way, and instead probably reflect the very low bioavailability of this high molecular weight chemical. Overall, estimates of UK dietary intake of BFRs show considerably decreased exposure to PBDEs and HBCDD but increased exposure to NBFRs. Significantly decreased dietary intakes of BFRs with increasing age was observed for children, while for adults no considerable difference in BFR exposure was observed between different age groups. This is of concern for toddlers, given their higher exposure and less developed immune system.

CRediT authorship contribution statement

Yulong Ma: Methodology, Validation, Formal analysis, Investigation, Visualization, Writing – original draft. **William A. Stubbings:** Writing – review & editing. **Mohamed Abou-Elwafa Abdallah:** Writing – review & editing. **Reginald Cline-Cole:** Supervision, Writing – review & editing. **Stuart Harrad:** Conceptualization, Supervision, Writing – review & editing, Project administration, Funding acquisition.

Data availability

Data will be made available on request.

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.

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Appendix A. Supplementary data

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