

UNIVERSITY OF BIRMINGHAM

TEMPORAL CHANGES IN HALOGENATED FLAME RETARDANT CONCENTRATIONS IN FOODSTUFFS AND INDOOR AND OUTDOOR ENVIRONMENTS: IMPLICATIONS FOR HUMAN EXPOSURE

by

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A thesis submitted to the University of Birmingham for the degree of

DOCTOR OF PHILOSOPHY

School of Geography, Earth, and Environmental Sciences

College of Life & Environmental Sciences

The University of Birmingham

August 2023

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ACKNOWLEDGEMENTS

Time flies! It seems like yesterday that me and my supervisors, Prof. Stuart Harrad and Dr. Reginald Cline-Cole, met at our first monthly meeting. Having had great experiences during my PhD study, I am working on this final task, my PhD thesis. Here, I would like to deliver my deepest gratitude to Stuart and Reg, because for so many years I have been convinced that a good supervisor is the biggest fortune for students. I learned optimism from my supervisors, and then I could get well along with my anxiety during COVID; I learned critical thinking from my supervisors, and then I could treat all the failures critically during my PhD study; I learned patience from my supervisors, and then I could take good care of everything that is important in my life.

Here I must convey my great respect to Dr. Marta Venier at Indiana University Bloomington, not only because of all the patience, encouragement, and support I received from her during my visit, but also because of her serious attitude towards scientific research. Working in this group with so many wonderful colleagues was a very memorable experience, and I look forward to any opportunities to work with her again.

Particularly, I would like to thank Dr. Mohamed Abou-Elwafa Abdallah, for all the patience and support that he offered to me, and for him being a perfect example for my PhD study. His professionalism gave me great confidence that any difficulties could finally be overcome.

I also want to deliver my special thanks to Dr. William A. Stubbings, who showed great patience and professionalism no matter what difficulties I encountered in my research. Words failed when I tried to express my gratitude, perhaps due to my poor English, lol~ but I want to say that I am so lucky to have a “third supervisor” during my entire PhD study!

And also Nicholas Davidson, the most important man in the world! The UK can lose its PM, but LES cannot lose Nick! I deeply appreciate all the efforts he has made to get not this research group but the whole college in motion!

It was so great to have met so many excellent colleagues in this group, and I have had a wonderful experience working with them during the past 4 years! I am so lucky to have another chance to work with you guys, and I look forward to meeting you all in the UK again!

最后，我想要感谢家人三十年来对我无穷无尽的理解与爱。正是这份理解与爱支撑我走出小农村，迈向更广更大的舞台。感谢你们为此所付出的一切，让我长成如今的模样。

ABSTRACT

Brominated flame retardants (BFRs) have been found to exert significant adverse impacts on environmental safety and human health. With global restrictions in use of legacy BFRs, demand for novel BFRs (NBFRs) is expected to rise. However, little is known about how global restrictions could impact on human exposure to legacy and emerging BFRs. Therefore, animal-derived food items were collected from Nigeria (n = 26), the US (n = 72), and the UK (n = 108) for BFR analysis. Comparison with previous dietary studies reveals high concentrations of polybrominated diphenyl ethers (PBDEs) in Nigerian foodstuffs in recent years with associated high dietary exposure, while PBDE concentrations in US foodstuffs seemed to be relatively constant with time. Concentrations of NBFRs, but not PBDEs, in US food items were significantly impacted by price, raising the issue of environmental justice. In UK foodstuffs, however, concentrations of PBDEs and hexabromocyclododecane (HBCDD) declined significantly between 2015 and 2020-21, while concentrations of NBFRs increased considerably. Reassuringly, comparison of our exposure estimates with health-based limit values suggests minimal adverse health effects of dietary intake of BFRs on residents of the three countries.

Impact of legislation on BFR concentrations in UK indoor and outdoor environments is also explored. Paired floor dust samples (n = 30) and indoor air samples (n = 30) from 8 UK homes, together with outdoor air samples (n = 16), were collected in Birmingham, UK between 2021 – 2022. These samples enable us to estimate human exposure to BFRs via dust ingestion and inhalation in the UK. BDE-209 and decabromodiphenyl ethane (DBDPE) were the main BFRs in UK indoor and outdoor environments. The maximum concentration of DBDPE (10,000 pg/m^3) in outdoor air is the highest reported anywhere to date, with DBDPE concentrations in UK indoor dust and indoor air also among the highest globally, likely due to its frequent use in construction materials and home appliances. For outdoor air, we observed significant correlations between concentrations of tri- to hepta-BDEs and HBCDD and temperature. These suggest primary emissions from active use of these BFRs have diminished and are now outweighed by secondary emissions (e.g., evaporation of BFRs from soil). Conversely, the lack of significant correlations between temperature and concentrations of BDE-209 and DBDPE, indicate ongoing primary emissions from indoor sources remain important for these BFRs. Comparison with earlier studies in Birmingham reveals significant declines in concentrations of legacy BFRs in UK indoor and outdoor environments over the last decade, but significant increases for concentrations of NBFRs. While there appears minimal health burdens from BFR exposure for UK adults, dust ingestion of BDE-209 may pose significant risk for UK toddlers.

We also analysed dust samples from inside (n = 6) and outside (n = 30) of five UK electrical and electronic waste (e-waste) recycling facilities for BFR concentrations.

One of the studied e-waste recycling facilities was identified as a likely source of BFR contamination to UK urban environments. Further, industrial activities were also identified as another potential source of NBFRs (but not PBDEs or HBCDD). This likely reflects the phase-out of PBDEs and HBCDD and the use of NBFRs as substitutes in industrial activities in the UK. To the best of our knowledge, this is the first study evaluating impacts of regulated e-waste recycling activities on environmental contamination with BFRs in Europe.

LIST OF PUBLICATIONS

Published papers:

Ma, Y., Stubbings, W.A., Cline-Cole, R., Harrad, S. (2021). Human exposure to halogenated and organophosphate flame retardants through informal e-waste handling activities - A critical review. *Environ. Pollut.* 268: 115727.

Ma, Y., Stubbings, W.A., Abdallah, M.A.E., Cline-Cole, R., Harrad, S. (2022). 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: 150747.

Ma, Y., Stubbings, W.A., Abdallah, M.A.E., Cline-Cole, R., Harrad, S. (2023). 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: 160956.

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Ma, Y., Stubbings, W.A., Cline-Cole, R., Abdallah, M.A.E., Harrad, S. (2024). Rising concentrations of polybrominated diphenyl ethers (PBDEs) in Nigerian foodstuffs despite global restrictions. *Emerg. Contam.* 10, 100264.

Submitted papers (currently under review):

Ma, Y., Stubbings, W.A., Jin, J., Cline-Cole, R., Abdallah, M.A.E., Harrad, S. Impact of legislation on brominated flame retardant (BFR) concentrations in UK indoor and outdoor environments: evidence for declining indoor emissions of some legacy BFRs. Submitted to *Environ. Sci. Technol.*

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ABBREVIATIONS

HFRs: halogenated flame retardants

BFRs: brominated flame retardants

PBDEs: polybrominated diphenyl ethers

HBCDD: hexabromocyclododecane

NBFRs: novel brominated flame retardants

pTBX: 2,3,5,6-tetrabromo-p-xylene

PBBz: pentabromobenzene

PBT: pentabromotoluene

PBEB: pentabromoethylbenzene

DPTE or TBP-DBPE: 2,3-dibromopropyl-2,4,6-tribromophenyl ether

HBBz: hexabromobenzene

EH-TBB or TBB: 2-ethyl hexyl-2,3,4,5-tetrabromobenzoate

BTBPE or TBE: bis(2,4,6-tribromophenoxy) ethane

BEH-TEBP or TBPH: bis(2-ethyl hexyl) tetrabromophthalate

DBDPE: decabromodiphenyl ethane

GC-MS: gas chromatography – mass spectrometer

HPLC-MS/MS: high performance liquid chromatography – triple quadrupole mass spectrometer

lw: lipid weight

dw: dry weight

ww: wet weight

e-waste: electrical and electronic waste

WEEE: waste electrical and electronic equipment

PUF: polyurethane foam

ABS: acrylonitrile butadiene styrene

HIPS: high impact polystyrene

BAF: bioaccumulation factor

BMF: biomagnification factor

RfD: reference dose

HQ: hazard quotient

HI: hazard index

Chapter One

General Introduction

This chapter contains material taken verbatim from the following two papers:

Ma, Y., Stubbings, W.A., Cline-Cole, R., Harrad, S. (2021). Human exposure to halogenated and organophosphate flame retardants through informal e-waste handling activities - A critical review. *Environmental Pollution,* 268: 115727.

Ma, Y., Stubbings, W.A., Abdallah, M.A.E., Cline-Cole, R., Harrad, S. (2022). 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. *Science of The Total Environment,* 807: 150747.

1.1 Physicochemical properties and global use of BFRs

A wide range of chemicals have been used extensively as flame retardants (FRs) in various commercial and household products such as electronic and electrical goods, textiles and fabrics, foam furnishing upholstery, and building insulation materials, to meet fire safety regulations (Liu et al., 2016; Stubbings and Harrad, 2014). It has been estimated that there are more than 175 different kinds of commercially used FRs, including halogenated FRs (HFRs), organophosphate FRs (OPFRs), nitrogen-containing FRs, and inorganic FRs (Birnbaum and Staskal, 2004; BSEF, 2000). Among these, brominated FRs (BFRs) are one of the most used FRs worldwide. Table 1-1 summarises literature data on global production / consumption of BFRs. Total global market demand for BFRs was estimated to be 204,300 tonnes in 1999 (BSEF, 2000). In 2005, total global demand reached 311,000 tonnes (Heimstad et al., 2009), increasing further to 410,000 tonnes in 2008 (Shaw et al., 2010). Notably, the demand for BFRs in Asia (~56% of global demand) exceeded greatly that in the Americas (~29%) and Europe (~15%) (Birnbaum and Staskal, 2004; BSEF, 2000).

1.1.1 Physicochemical properties and global use of PBDEs

Polybrominated diphenyl ethers (PBDEs) are a class of BFRs that have been used in a wide range of products since the 1970s (WHO, 1994). There are three different commercial PBDE mixtures, namely the penta-BDE mixture, the octa-BDE mixture, and the deca-BDE-mixture. PBDEs are highly hydrophobic chemicals and are typically semi-volatile (Ma et al., 2017b). They can be very persistent in the environment and can accumulate in biota including humans through food webs, and are thus classified as persistent organic pollutants (POPs) (Ma et al., 2017b). These properties enable PBDEs to be transported over long distances via volatilisation and dry or wet deposition (Li et al., 2018a). There are a total of 209 different PBDE congeners, with the most studied being BDE-28, -47, -99, -100, -153, -154, -183, and -209, primarily because these 8 PBDE congeners constitute the majority of commercial PBDE products (Al-Omran, 2016). Physicochemical properties of these 8 PBDE congeners are summarised

in Table 1-2.

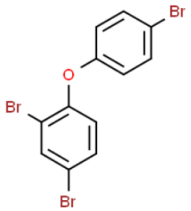
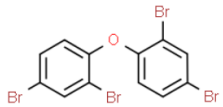
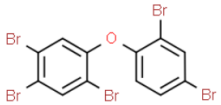
PBDEs were added into products typically at concentrations of 3-30% by weight (WHO, 1994). The Americas and Asia represented 50.6% and 37.2% of global PBDE consumption in 1999, respectively, with the remaining 12.2% consumed in Europe (BSEF, 2000). The major uses of PBDEs in the US and Europe were in flexible polyurethane foam (PUF), acrylonitrile butadiene styrene (ABS), textile coatings, wire and cable insulation, electrical and electronic connectors, and other interior parts (Rahman et al., 2001; UNEP, 2010). However, PBDEs were not added to PUF in household furniture and textiles in China, where their use was limited to polymers in electrical and electronic appliances such as monitors, television sets, computer cases, wire and cable insulation, and connectors (Chen et al., 2008; Ni et al., 2013). The extensive use of PBDEs, coupled with concerns about their negative environmental, ecological, and human health impacts, led to the cessation of the production and use of commercial penta- and octa-BDE mixtures in Europe and North America between 2004 and 2006, with the use of commercial deca-BDE mixtures restricted from 2008. China never produced octa-BDE commercially, and the production and consumption of commercial penta-BDE mixtures were prohibited in 2007. Meanwhile, the annual production of deca-BDE in China decreased considerably from 25,000 tonnes to 10,000 tonnes between 2009 and 2011 (Chen et al., 2012; Ma et al., 2017a). In 2009, commercial penta- and octa-BDE mixtures were phased out globally due to their listing under the Stockholm Convention on persistent organic pollutants (POPs) of the United Nations Environment Programme (UNEP), with deca-BDE listed in 2017 (Sharkey et al., 2020). However, global in-use and waste stocks of PBDEs (mainly deca-BDE) were estimated to be 425,000 and 113,000 tonnes in 2018, respectively, with an additional 45,000 tonnes of PBDEs (mainly deca-BDE) estimated to reappear in new products as a result of recycling of flame-retarded polymers (Abbasi et al., 2019).

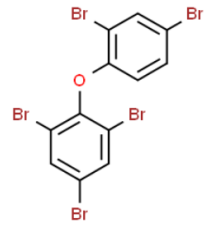
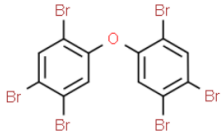
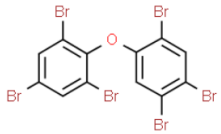
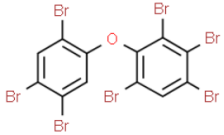
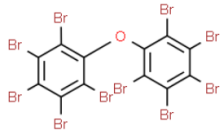
Table 1-1. Global production and consumption volumes (tonnes) of BFRs

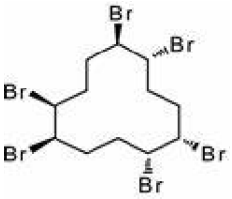
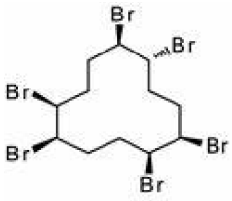
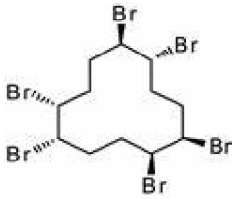
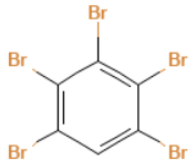
FRs	Volume (region, year)	Reference
∑BFRs	204,300 (global, 1999) [a]	(BSEF, 2000)
	311,000 (global, 2005) [b]	(Heimstad et al., 2009)
	410,000 (global, 2008) [c]	(Shaw et al., 2010)
∑PBDEs	67,100 (global, 1999) [a]	(BSEF, 2000)
	2,000 (global, 2018) [c]	(Abbasi et al., 2019)
deca-BDE	54,800 (global, 1999) [a]	(BSEF, 2000)
	25,000 (China, 2009) [c]	(Ma et al., 2017a)
	10,000 (China, 2011) [c]	(Ma et al., 2017a)
octa-BDE	3,825 (global, 1999) [a]	(BSEF, 2000)
penta-BDE	8,500 (global, 1999) [a]	(BSEF, 2000)
HBCDDs	15,900 (global, 1999) [a]	(BSEF, 2000)
	16,700 (global, 2001) [c]	(Cao et al., 2018)
	31,000 (global, 2011) [c]	(Cao et al., 2018)
	8,900 (Europe, 1999) [a]	(BSEF, 2000)
	9,500 (Europe, 2001) [a]	(Birnbaum and Staskal, 2004)
	11,000 (Europe, 2007) [b]	(Marvin et al., 2011)
	500 (China, 2001) [c]	(Cao et al., 2018)
	18,000 (China, 2011) [c]	(Cao et al., 2018)
∑NBFRs	100,000-180,000 (global, annual) [c]	(McGrath et al., 2017b; Papachlimitzou et al., 2012)
DBDPE	11,000 (China, 2006) [c]	(Wang et al., 2012; Wu et al., 2012)
BTBPE	16,710 (global, 2001) [c]	(Covaci et al., 2011)
BEH-TEBP	450-4,500 (US, 1990-2006) [c]	(Covaci et al., 2011)
EH-TBB	<450 (US, 2015) [c]	(Knudsen et al., 2016; Xiong et al., 2019)
PBT	1,000-5,000 (global, 1997) [c]	(Covaci et al., 2011)
	600 (China, 2011) [c]	(Covaci et al., 2011)
HBBz	350 (Japan, 2001) [b]	(Covaci et al., 2011)
	600 (China, 2011) [c]	(Covaci et al., 2011)

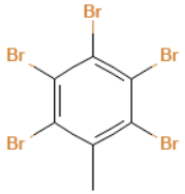
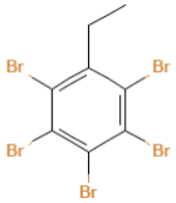
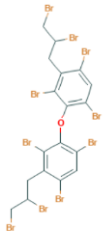
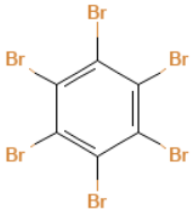
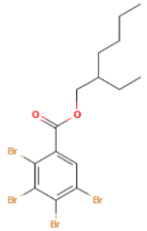
[a] estimated total market demand; [b] consumption volumes; [c] production volumes.

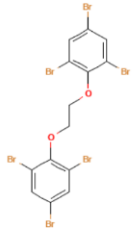
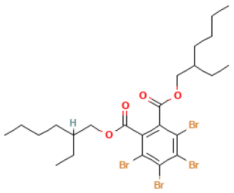
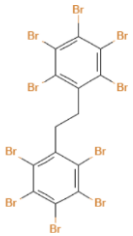
Table 1-2. Physicochemical properties of target BFRs

Abbreviation	Full name	Molecular Formula	2D Molecular Structure	Molecular Mass (g/mol)	Vapour pressure (Pa)	log K_{OA}	log K_{OW}	Water solubility (μg·L^{-1}, 25 ℃)
PBDEs	**Polybrominated diphenyl ethers**							
BDE-28	2,4,4′-tribromodiphenyl ether	$C_{12}H_7Br_3O$		407	2.19×10^{-3} (25 ℃) [a, *]	9.50 [b, *]	5.98 [a, *]	70 [a, *]
BDE-47	2,2′,4,4′-tetrabromodiphenyl Ether	$C_{12}H_6Br_4O$		486	1.86×10^{-4} (25 ℃) [a, *] 7.5×10^{-3} (60 ℃) [g, #]	10.53 [b, *]	6.55 [a, *]	15 [a, *]
BDE-99	2,2′,4,4′,5-pentabromodiphenyl ether	$C_{12}H_5Br_5O$		565	1.76×10^{-5} (25 ℃) [a, *] 9.77×10^{-4} (60 ℃) [g, #]	11.31 [b, *]	7.13 [a, *]	9 [a, *]

BDE-100	2,2′,4,4′,6-pentabromodiphenyl ether	$C_{12}H_5Br_5O$		565	2.86×10^{-5} (25 °C) [a, *] 1.94×10^{-3} (60 °C) [g, #]	11.13 [b, *]	6.86 [a, *]	40 [a, *]
BDE-153	2,2',4,4',5,5'-hexabromodiphenyl ether	$C_{12}H_4Br_6O$		644	2.09×10^{-6} (25 °C) [a, *] 1.29×10^{-4} (60 °C) [g, #]	11.82 [b, *]	7.62 [a, *]	1 [a, *]
BDE-154	2,2',4,4',5,6'-hexabromodiphenyl ether	$C_{12}H_4Br_6O$		644	3.80×10^{-6} (25 °C) [a, *] 2.34×10^{-4} (60 °C) [g, #]	11.92 [b, *]	7.39 [a, *]	1 [a, *]
BDE-183	2,2',3,4,4',5',6-heptabromodiphenyl ether	$C_{12}H_3Br_7O$		722	4.68×10^{-7} (25 °C) [a, *] 6.26×10^{-5} (60 °C) [g, #]	11.96 [b, *]	8.27 [j]	2 [a, *]
BDE-209	decabromodiphenyl ether	$C_{12}Br_{10}O$		959	9.02×10^{-13} (25 °C) [h, *]	15.27 [i, #]	8.70 [i, #]	<0.1 [j]

HBCDD	**Hexabromocyclododecane**							
α-HBCDD	α-hexabromocyclododecane	$C_{12}H_{18}Br_6$		642	1.05×10^{-8} (25 ℃) [e, *]	14.43 [f, #]	5.07 [d, *]	48.8 (20 ℃) [c, *]
β-HBCDD	β- hexabromocyclododecane	$C_{12}H_{18}Br_6$		642	5.82×10^{-9} (25 ℃) [e, *]	14.64 [f, #]	5.12 [d, *]	14.7 (20 ℃) [c, *]
γ-HBCDD	γ- hexabromocyclododecane	$C_{12}H_{18}Br_6$		642	8.39×10^{-11} (25 ℃) [e, *]	14.17 [f, #]	5.47 [d, *]	2.1 (20 ℃) [c, *]
NBFRs	**Novel brominated flame retardants**							
PBBz	pentabromobenzene	C_6HBr_5		473	-	9.10 [l, #]	6.44 [l, #]	-

PBT	pentabromotoluene	$C_7H_3Br_5$		487	1.22×10^{-3} (25 °C) [p]	9.66 [o, *]	5.87 [p]	780 [p]
PBEB	pentabromoethylbenzene	$C_8H_5Br_5$		501	3.2×10^{-4} (25 °C) [l, #]	9.9 [l, *]	6.40 [l, #]	350 [l, #]
DPTE	2,3-dibromopropyl-2,4,6-tribromophenyl ether	$C_{18}H_{12}Br_{10}O$		1043	1.86×10^{-5} (25 °C) [l]	-	5.82 [l]	-
HBBz	hexabromobenzene	C_6Br_6		551	1.14×10^{-4} (25 °C) [p]	10.26 [o, *]	5.85 [p]	770 [p]
EH-TBB	2-ethyl hexyl-2,3,4,5-tetrabromobenzoate	$C_{15}H_{18}Br_4O_2$		550	3.71×10^{-7} (25 °C) [l, *]	12.34 [n]	8.75 [l, #]	11.4 [l, #]

BTBPE	bis(2,4,6-tribromophenoxy) ethane	$C_{14}H_8Br_6O_2$		688	3.88×10^{-10} (25 °C) [l, #]	15 [m]	7.88 [l, #]	19 [l, #]
BEH-TEBP	bis(2-ethyl hexyl) tetrabromophthalate	$C_{24}H_{34}Br_4O_4$		706	1.55×10^{-11} (25 °C) [l, #]	17.7 [m]	10.08 [l, #]	1.6 [l, #]
DBDPE	decabromodiphenyl ethane	$C_{14}H_4Br_{10}$		971	6.0×10^{-15} (25 °C) [l, #]	18.8 [m]	11.1 [l, #]	0.21 [l, #]

* data obtained/calculated from experimental observations; # data estimated/modelled with equations/software.

a. Tittlemier et al. (2002); b. Harner and Shoeib (2002); c. Environment Canada and Health Canada (2010); d. Hayward et al. (2006), e. Kuramochi and Sakai (2010); f. Rauert (2014); g. Rauert et al. (2015); h. Fu and Suuberg (2011); i. Wania and Dugani (2003); j. Abdallah (2016); k. Sverko et al. (2011); l. Tao (2016); m. Harju et al. (2009); n. Stapleton et al. (2008); o. Stenzel et al. (2013); p. Covaci et al. (2011); q. Brommer et al. (2014); r. van der Veen and de Boer (2012); s. WHO (1998).

1.1.2 Physicochemical properties and global use of HBCDD

Hexabromocyclododecane (HBCDD) has been manufactured and used as a BFR since the 1960s (Koch et al., 2015). The global production of HBCDD almost doubled between 2001 and 2011, with an increase from 16,700 tonnes to 31,000 tonnes (Cao et al., 2018). In Europe, the demand for HBCDD was an estimated 8,900 and 9,500 tonnes in 1999 and 2001, respectively (Birnbaum and Staskal, 2004; BSEF, 2000); with EU consumption of HBCDD reaching 11,000 tonnes in 2007 (Marvin et al., 2011). HBCDD was mainly applied in polystyrene insulation foam in the EU, although a small proportion was also used in electrical and electronic products, household furniture, textiles, and fabrics (EuropeanCommission, 2011; Weil and Levchik, 2008). In China, the production of HBCDD increased sharply from 500 tonnes to 18,000 tonnes between 2001 and 2011, which could be attributed to the booming construction industry over the years (Cao et al., 2018).

Table 1-2 summarises physicochemical properties of different HBCDD isomers, namely α-, β-, and γ-HBCDD. γ-HBCDD is the dominant ingredient of commercial HBCDD mixtures. Like PBDEs, HBCDD is highly hydrophobic and semi-volatile, and can enter biota including humans via bioconcentration, bioaccumulation, and biomagnification (Koch et al., 2015; Waiyarat et al., 2023). It has also been regarded as a POP due to its persistence in the environment and biota and adverse effects on environmental safety (Koch et al., 2015; Li and Wania, 2018; Waiyarat et al., 2023). As a result, HBCDD was listed under the Stockholm Convention in 2014, leading to global phaseout of its production and application (Sharkey et al., 2020) - albeit with some exemptions.

1.1.3 Physicochemical properties and global use of NBFRs

The global phaseout of commercial PBDE and HBCDD products increased demand for novel BFRs (NBFRs) as substitutes. Generally, higher molecular mass and more complex chemical structure of NBFRs lead to higher values of physicochemical

properties like octanol-water partition coefficient (K_{OW}) and octanol-air partition coefficient (K_{OA}), but lower vapour pressure and water solubility. Table 1-2 summarises physicochemical properties of nine NBFRs included in this study, namely: pentabromobenzene (PBBz), pentabromotoluene (PBT), pentabromoethylbenzene (PBEB), 2,3-dibromopropyl-2,4,6-tribromophenyl ether (DPTE or TBP-DBPE), hexabromobenzene (HBBz), 2-ethyl hexyl-2,3,4,5-tetrabromobenzoate (EH-TBB or TBB), bis(2,4,6-tribromophenoxy) ethane (BTBPE or TBE), bis(2-ethyl hexyl) tetrabromophthalate (BEH-TEBP or TBPH), and decabromodiphenyl ethane (DBDPE). The similarities between molecular structure of NBFRs and that of PBDEs means NBFRs have similar physicochemical properties to PBDEs, i.e., NBFRs are hydrophobic and semi-volatile chemicals which are persistent and can bioaccumulate in biota (Covaci et al., 2011). For instance, PBBz, PBT, PBEB, and HBBz have similar K_{OW} and K_{OA} values to low-brominated PBDE congeners (Table 1-2). These NBFRs are environmentally persistent and are capable of long-distance transport (Gouteux et al., 2008; Kuramochi et al., 2014; Wu et al., 2011). DPTE is a bioaccumulative compound and likely shares similar physicochemical properties of POPs (Vetter et al., 2010). EH-TBB, BTBPE, and BEH-TEBP are more hydrophobic than are bromobenzenes, and can bioaccumulate and be very persistent in biota, with their half-lives in different biota ranging from months to years (Bearr et al., 2012; Ezechias et al., 2014; Hou et al., 2022; La Guardia et al., 2012; Lee et al., 2019; Wu et al., 2011; Zheng et al., 2018). Physicochemical properties of DBDPE are similar to those of BDE-209 due to their similar chemical structure, i.e., DBDPE has very low vapour pressure and water solubility but very high K_{OW} and K_{OA} values (Covaci et al., 2011). However, the bioaccumulation and biomagnification abilities of DBDPE seemed to be strongly species-dependent. For instance, DBDPE was found to be highly bioaccumulative in various aquatic organisms from different ecosystems (He et al., 2012; Hou et al., 2022; Law et al., 2006), while biomagnification factors below 1 were also reported for DBDPE in fish-kingfisher from Pearl River in China (Mo et al., 2012), an aquatic food web from Taihu Lake in China (Zheng et al., 2018), and white fish-emerald shiner from

Winnipeg Lake in Canada (Law et al., 2006). 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).

The total global production volume of all NBFRs was estimated to be 100,000-180,000 tonnes annually (McGrath et al., 2017b; Papachlimitzou et al., 2012). Data on the production or consumption volumes of individual NBFRs is limited hitherto, but the most commonly used NBFRs are DBDPE, BTBPE, BEH-TEBP, and EH-TBB (Kuang et al., 2016; McGrath et al., 2017a; McGrath et al., 2017b; Olukunle and Okonkwo, 2015; Zheng et al., 2016). DBDPE was introduced in the mid-1980s, and is now primarily used as a replacement for deca-BDE (Covaci et al., 2011). In 2006, the production volume of DBDPE reached 11,000 tonnes in China, and this was estimated to increase at a rate of up to 85% per annum (Wang et al., 2012; Wu et al., 2012). DBDPE was mainly used in ABS, polycarbonate/ABS, high impact polystyrene (HIPS)/polyphenylene oxide and textiles (Covaci et al., 2011). BTBPE has been used in place of octa-BDE, while BEH-TEBP and EH-TBB constitute replacements of penta-BDE mixtures (Covaci et al., 2011; McGrath et al., 2017a; McGrath et al., 2017b). It was estimated that worldwide consumption of BTBPE reached 16,710 tonnes in 2001, while US production volumes of BEH-TEBP were 450 to 4,500 tonnes per year from 1990 to 2006 (Covaci et al., 2011). EH-TBB was listed as a high production volume chemical by the US Environmental Protection Agency (EPA) in 2006 (Ma et al., 2012), but 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). BTBPE was mainly used in ABS, HIPS, thermoplastics, thermoset resins, polycarbonates, and coatings (Covaci et al., 2011); BEH-TEBP was primarily applied into PUF applications, polyvinyl chloride (PVC) and neoprene, wire and cable insulation, film and sheeting, carpet backing, coated fabrics, wall coverings and adhesives (Covaci et al., 2011); while EH-TBB was predominantly consumed in PUF applications (Covaci et al., 2011).

Apart from these most extensively used NBFRs, some other NBFRs were also applied to various commercial products. For instance, the main applications of PBT were unsaturated polyesters, polyethylene, polypropylene, polystyrene, textile, rubbers, ABS, etc., with a production volume estimated at between 1000 and 5000 tonnes per year (Covaci et al., 2011). PBEB was mostly used in thermoset polyester resins, unsaturated polyesters, styrene butadiene copolymers, and textiles (Covaci et al., 2011; Wu et al., 2011). DPTE was produced by Chemische Fabrik Kalk (Germany) during 1972 and 1985 (Vetter et al., 2010). No other manufacturer has reported the production of DPTE, and its distribution remained unknown (Vetter et al., 2010). HBBz was used in paper, wood, textiles, electronic, and plastic goods, with an annual production volume of 600 tonnes in China (Covaci et al., 2011). The applications and consumption volumes of PBBz remain unclear to date.

1.1.4 Implications for environmental contamination and human exposure

The extensive use of legacy and emerging BFRs has resulted in their ubiquity in human tissue. Such internal exposure is the result of external exposure to BFRs via dietary intake, inhalation, dust ingestion, dermal contact with BFR-treated articles, etc. (see Fig. 1-1). Dietary intake and dust ingestion are generally the most studied and constitute important pathways of human exposure to BFRs, with inhalation of indoor air also frequently investigated (Tao, 2016). By comparison, ingestion of soil and inhalation of outdoor air are less important (Bruce-Vanderpuije et al., 2019; Jiang et al., 2019; Ma et al., 2021). Dermal uptake from BFR-treated materials is another significant pathway of human exposure to BFRs, with its contribution equivalent to or even greater than the contribution of dietary intake or dust ingestion (Abdallah and Harrad, 2018; Yadav et al., 2019; Yang et al., 2022). Therefore, contamination of BFRs in foodstuffs and in the environment is discussed in the following sections, with human exposure to BFRs and related adverse health effects highlighted.

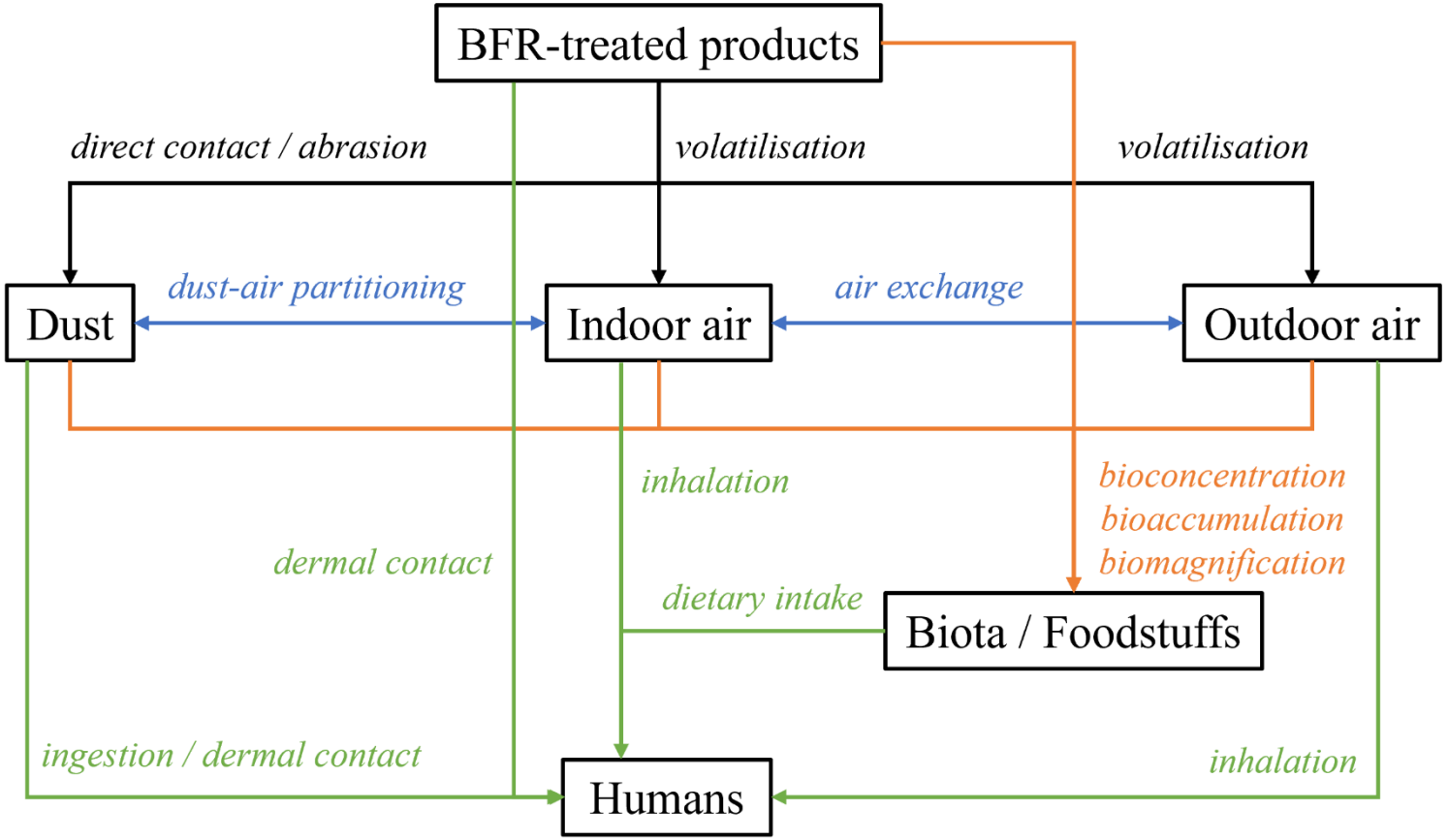


Fig. 1-1 Migration of BFRs from products to indoor and outdoor environments, biota, and humans

1.2 Occurrence of BFRs in foodstuffs

BFRs could migrate from products to the environment, and then accumulate in biota via inhalation and oral intake (see Fig. 1-1). BFRs are hydrophobic, lipophilic chemicals, and thus are assumed to accumulate in adipose tissues of animals (Hou et al., 2022; Li et al., 2023; Tao et al., 2016b; Zhao et al., 2023). Therefore, dietary investigations are mostly conducted to reveal BFR contamination in animal-derived food items. In this section, occurrence of legacy and emerging BFRs in animal-derived foodstuffs from different countries is discussed, with the literature data summarised in Tables 1-3, 1-4, and 1-5.

1.2.1 Occurrence of PBDEs in foodstuffs

Table 1-3 shows literature data on PBDE concentrations in animal-derived food items from different countries, including meat, aquatic food, eggs, and dairy products. PBDEs were generally at detectable levels in these food items globally. For instance, arithmetic mean concentrations of PBDEs in UK foodstuffs (sampling year: 2015) were 2.4 – 40 ng/g lw (250 – 2,800 pg/g ww) (Tao et al., 2017). These concentrations were comparable to or slightly higher than those from earlier observations of UK foodstuffs, suggesting slow response of UK foodstuffs to global restrictions on use of PBDEs (Tao et al., 2017). However, the different designs of previous studies made it unlikely to characterise temporal changes in PBDE concentrations in UK foodstuffs, and more recent updates are needed to better understand impacts of global restrictions on PBDE contamination in UK diet. PBDE concentrations reported in UK foodstuffs were generally higher than or at least comparable to those observed in foodstuffs from other parts of Europe, including Ireland (sampling year: 2015; range: 20 – 1,400 pg/g ww) (Garcia Lopez et al., 2018), France (sampling year: 2014-2016; arithmetic mean: 120 – 540 pg/g ww) (Venisseau et al., 2018), Belgium (sampling year: 2015-2016; arithmetic mean: 210 – 690 pg/g ww) (Poma et al., 2018), Latvia (sampling year: 2016-2019; arithmetic mean: 21 – 620 pg/g ww) (Zacs et al., 2021), etc.

Table 1-3. Literature data on concentrations of PBDEs (pg/g ww in parentheses) in foodstuffs from different countries (ng/g lw)

Country	Sampling time	Sample type	BDE-209	ΣPBDEs	References
UK	2015	meat	0.28-0.63 (21-32) [a]	2.4-21 (520-1,000) [a]	(Tao et al., 2017)
		fish	0.34-1.7 (32-150) [a]	14-40 (400-2,800) [a]	
		eggs	0.53 (56) [a]	2.4 (250) [a]	
		cheese	0.21 (37) [a]	5.3 (940) [a]	
UK	2013	meat		(40-590 [c])	(Fernandes et al., 2016)
		fish		(170-8,900 [c])	
		egg		(60-450 [c])	
		dairy products		(20-260 [c])	
Ireland	2015	fish	(<2.0-60 [c])	(20-1,400 [c])	(Garcia Lopez et al., 2018)
		eggs	(<190-800 [c])	(30-960 [c])	
Netherlands	2009-2014	meat		0.060-0.58 [a] / 0.040-0.34 [b]	(Gebbink et al., 2019)
		eggs		0.22 [a] / 0.14 [b]	
		fish		(2.5-1,300 [a])	
France	2014-2016	meat	(11 [b])	(170 [a])	(Venisseau et al., 2018)
		fish	(5.7 [b])	(540 [a])	
		egg	(22 [b])	(120 [a])	
France	2007-2009	meat	(52 [a])	(540 [a])	(Riviere et al., 2014)

		fish	(43 [a])	(79 [a])	
		eggs	(49 [a])	(68 [a])	
		cheese	(40 [a])	(65 [a])	
Belgium	2015-2016	meat		(690 [a])	(Poma et al., 2018)
		fish		(370 [a])	
		eggs		(210 [a])	
		dairy products		(600 [a])	
Belgium	2006-2007	egg	2.0-7.1 [a]	3.5-7.8 [a]	(Covaci et al., 2009)
Spain		fish/shellfish	(<20 [c])	(400-1,300 [c])	(Trabalon et al., 2017)
Latvia	2016-2019	meat	(12 [a] / 9.6 [b])	(34 [a] / 22 [b])	(Zacs et al., 2021)
		fish	(23 [a] / 7.5 [b])	(620 [a] / 390 [b])	
		eggs	(34 [a] / 24 [b])	(55 [a] / 36 [b])	
		cheese	(2.9 [a] / 2.9 [b])	(21 [a] / 8.5 [b])	
China	2016-2019	meat	0.64 (180) [a]		(Zhao et al., 2023)
		aquatic food	0.88 (84) [a]		
		eggs	2.1 (320) [a]		
		dairy products	0.48 (13) [a]		
China	2013	meat	20 (3,300) [a] / 13 (440) [b]	21 (3,400) [a] / 14 (460) [b]	(Wang et al., 2019)
		fish/seafood	13 (1,300) [a] / 5.5 (210) [b]	14 (1,400) [a] / 6.3 (270) [b]	

		eggs	13 (1,600) [a] / 11 (1,600) [b]	13 (1,700) [a] / 12 (1,800) [b]	
		dairy products	5.5 (90) [a] / 3.0 (58) [b]	5.9 (96) [a] / 3.2 (66) [b]	
China [d]	2013	eggs		620-46,000 [c]	(Zeng et al., 2016)
Japan	2011	fish		(2.0-880 [c])	(Kakimoto et al., 2012)
Tanzania	2012	eggs		1.1-350 [c]	(Polder et al., 2016)
Nigeria	2016-2017	meat		(16) [a]	(Babalola and Adeyi, 2018)
		aquatic food		(86) [a]	
		eggs		(5.2) [a]	
		dairy products		(7.2) [a]	
US	2001-2002	fish		(56-3,300 [a])	(Hites et al., 2004)
US	2009	meat		(14-210 [c])	(Schecter et al., 2010)
		fish		(25-1,500 [c])	
		eggs		(89 [c])	
		dairy products		(11-6,200 [c])	

a. mean concentrations; b. median concentrations; c. ranges; d. e-waste recycling sites.

Concentrations of PBDEs were also frequently reported in foodstuffs outside Europe, with China being the most studied area. For instance, arithmetic mean concentrations of PBDEs in meat, aquatic food, eggs, and dairy products from China were 21 ng/g lw (3,400 pg/g ww), 14 ng/g lw (1,400 pg/g ww), 13 ng/g lw (1,700 pg/g ww), and 5.9 ng/g lw (96 pg/g ww), with arithmetic mean concentrations of BDE-209 of 20 ng/g lw (3,300 pg/g ww), 13 ng/g lw (1,300 pg/g ww), 13 ng/g lw (1,600 pg/g ww), and 5.5 ng/g lw (90 pg/g ww), respectively, in 2013 (Wang et al., 2019). These concentrations of BDE-209 were considerably higher than those observed in a later study, which reported arithmetic mean concentrations of BDE-209 of 0.64 ng/g lw (180 pg/g ww), 0.88 ng/g lw (84 pg/g ww), 2.1 ng/g lw (320 pg/g ww), and 0.48 ng/g lw (13 pg/g ww), respectively, in meat, aquatic food, eggs, and dairy products collected between 2016 and 2019 (Zhao et al., 2023). These results likely suggest active impacts on food safety of regulatory efforts in China. PBDE concentrations were also reported in foodstuffs in Africa (e.g., Nigeria) and the US (see Table 1-3 for the concentrations) (Babalola and Adeyi, 2018; Hites et al., 2004; Schecter et al., 2010). However, it is hard to draw any reliable conclusions about the impacts of global restrictions on use of PBDEs on food contamination in these countries, due to the limited data available since the global phase-out of PBDEs. Therefore, updates on PBDE contamination in foodstuffs are needed urgently in these countries.

1.2.2 Occurrence of HBCDD in foodstuffs

HBCDD was also frequently detected in foodstuffs globally (Table 1-4). In the UK, arithmetic mean concentrations of HBCDD in various food items were between <0.24 ng/g lw (<43 pg/g ww) and 16 ng/g lw (830 pg/g ww) in 2015 (Tao et al., 2017), which was similar to those reported in UK foodstuffs in 2013 (arithmetic mean: <20 – 1,400 pg/g ww) (Fernandes et al., 2016). These concentrations were only slightly higher than observations on UK foodstuffs that were made ~10 years earlier (Driffield et al., 2008; UK-Food-Standards-Agency, 2006). Similar concentrations of HBCDD to those observed in the UK in 2015 were reported in foodstuffs from France (sampling year:

2014-2016; arithmetic mean: 130 – 140 pg/g ww) (Venisseau et al., 2018), Belgium (sampling year: 2015-2016; arithmetic mean: 0.10 – 970 pg/g ww) (Poma et al., 2018), Latvia (sampling year: 2016-2019; arithmetic mean: 24 – 730 pg/g ww) (Zacs et al., 2021), etc. Interestingly, HBCDD concentrations in foodstuffs seemed rather stable over time in these European countries (e.g., in the UK, France, and Belgium; see Table 1-4 for the concentrations), possibly because HBCDD was still in use or had just been phased out when these investigations were conducted. Therefore, impacts of global restrictions on HBCDD concentrations in foodstuffs need to be investigated in Europe years after these restrictions were implemented.

Similar findings can also be observed in China, where no major changes in HBCDD concentrations in foodstuffs were observed over time. For instance, arithmetic mean concentrations of HBCDD in different food items were 0.090 – 5.9 ng/g lw in 2011 (Labunska et al., 2015), 1.4 – 7.0 ng/g lw in 2013 (Wang et al., 2019), and 0.59 – 8.3 ng/g lw in 2019 (Zhao et al., 2023), respectively. Research investigating food contamination with HBCDD was less frequently conducted outside Europe and China. In the US, HBCDD concentrations in foodstuffs ranged between <11 pg/g ww and 590 pg/g ww in 2009 (Schecter et al., 2010), and recent updates on HBCDD concentrations in US foodstuffs are not available. HBCDD was barely detected in Nigerian foodstuffs (sampling year: 2017), with its concentrations ranging between <2.0 – 62 pg/g ww in animal-derived food items (Vaccher et al., 2020). Further investigations are needed to help understand current HBCDD concentrations in US and Nigerian foodstuffs.

Table 1-4. Literature data on concentrations of HBCDD (sum of α-, β-, and γ-HBCDD; pg/g ww in parentheses) in foodstuffs from different countries (ng/g lw)

Country	Sampling time	Sample type	HBCDD	References
UK	2015	meat	0.32-4.6 (26-200) [a]	(Tao et al., 2017)
		fish	3.6-16 (180-830) [a]	
		eggs	1.3 (300) [a]	
		cheese	<0.24 (<43) [a]	
UK	2013	meat	(40 [a])	(Fernandes et al., 2016)
		fish	(1,400 [a])	
		egg	(<20 [a])	
		dairy products	(40 [a])	
Ireland	2015	fish	(70-410 [c])	(Garcia Lopez et al., 2018)
		eggs	(10-20 [c])	
France	2014-2016	meat	(130 [a])	(Venisseau et al., 2018)
		fish	(140 [a])	
France	2007-2009	meat	(130 [a])	(Riviere et al., 2014)
		fish	(140 [a])	
		eggs	(26 [a])	
		cheese	(20 [a])	
Belgium	2015-2016	meat	(43 [a])	(Poma et al., 2018)
		fish	(130 [a])	
		eggs	(970 [a])	
		dairy products	(0.10 [a])	
Belgium	2006-2007	egg	6.5-8.5 [a]	(Covaci et al., 2009)
Sweden	1999	meat	<1.0-6.5 [a]	(Remberger et al., 2004)
		fish	48 [a]	
		egg	9.4 [a]	
Latvia	2016-2019	meat	(270 [a] / 160 [b])	(Zacs et al., 2021)
		fish	(730 [a] / 480 [b])	
		eggs	(24 [a] / 16 [b])	
		cheese	(330 [a] / 160 [b])	

China	2016-2019	meat	8.3 (1,800) [a]	(Zhao et al., 2023)
		aquatic food	5.2 (440) [a]	
		eggs	0.59 (94) [a]	
		dairy products	1.2 (42) [a]	
China	2013	meat	2.8 (570) [a] / 2.4 (180) [b]	(Wang et al., 2019)
		fish/seafood	7.0 (410) [a] / 5.6 (290) [b]	
		eggs	4.5 (600) [a] / 4.0 (500) [b]	
		dairy products	1.4 (140) [a] / 1.1 (44) [b]	
China [d]	2013	eggs	56-7,600 [c]	(Zeng et al., 2016)
China [d]	2011	fish	310 [a]	(Labunska et al., 2015)
		meat	<0.060-79 [a]	
		eggs	2.2-47 [a]	
China	2011	fish	5.9 [a]	(Labunska et al., 2015)
		meat	0.090-3.1 [a]	
		eggs	0.50-1.70 [a]	
Japan	2011	fish	(<LOD-22,000 [c])	(Kakimoto et al., 2012)
Tanzania	2012	eggs	<LOD-63 [c]	(Polder et al., 2016)
US	2009	meat	(23-190 [c])	(Schecter et al., 2010)
		fish	(<29-590 [c])	
		eggs	(<11 [c])	
		dairy products	(<64 [c])	

a. mean concentrations; b. median concentrations; c. ranges; d. e-waste recycling sites.

1.2.3 Occurrence of NBFRs in foodstuffs

Literature data on NBFR concentrations in foodstuffs from different countries is summarised in Table 1-5. NBFRs are less studied in foodstuffs compared to PBDEs and HBCDD, with China being the most studied area. DBDPE was not detected (<0.45 ng/g lw) in foodstuffs collected from non-e-waste impacted areas in China in 2011 (Labunska et al., 2015), but was detectable (arithmetic mean: 4.3 – 33 ng/g lw) in foodstuffs collected from non-e-waste impacted areas in 2016-2019 (Zhao et al., 2023). Despite the differences in the designs of these two studies, such results likely indicate elevating concentrations of DBDPE in foodstuffs in China in recent years. However, such increases in concentrations of other NBFRs cannot be observed in foodstuffs from China (see Table 1-5 for the concentrations). Investigations on food contamination with NBFRs outside China are relatively limited. In the UK, arithmetic mean concentrations of DBDPE, BEH-TEBP, BTBPE, and EH-TBB were <0.74 – 21 ng/g lw, <0.10 – 1.8 ng/g lw, <0.040 – 2.4 ng/g lw, and 0.10 – 1.4 ng/g lw, respectively, in foodstuffs collected in 2015; while PBBz, PBT, PBEB, DPTE, and HBBz were not detected in UK foodstuffs (Tao et al., 2017). As this was the first study reporting NBFR concentrations in UK foodstuffs, temporal changes in NBFR concentrations could not be discussed. NBFRs were also barely detected in foodstuffs from other European countries (e.g., France, Belgium, Spain, Latvia, etc.), with the concentrations only occasionally exceeding 100 pg/g ww (Poma et al., 2018; Trabalon et al., 2017; Venisseau et al., 2018; Zacs et al., 2021). In the US, only one study has reported concentrations of NBFRs (PBBz, HBBz, and DBDPE; see Table 1-5 for the concentrations) in US baby food (Liu et al., 2014), and concentrations of NBFRs have never been investigated in general animal-derived food items in the US. To the best of our knowledge, food contamination with NBFRs has never been studied in Nigeria. Overall, our knowledge about NBFR contamination in food is very limited in Europe, Africa, and the US, and future studies are favoured to fill this gap.

Table 1-5. Literature data on concentrations of NBFRs (pg/g ww in parentheses) in foodstuffs from different countries (ng/g lw)

Country	Sampling time	Sample type	PBBz	PBT	PBEB	DPTE	HBBz	EH-TBB	BTBPE	BEH-TEBP	DBDPE	References
UK	2015	meat	<LOD [c]	<LOD [c]	<LOD [c]	<LOD [c]	<LOD [c]	0.19-1.4 [a]	<0.040-2.4 [a]	0.20-0.57 [a]	<1.1-4.6 [a]	(Tao et al., 2017)
		fish	<LOD [c]	<LOD [c]	<LOD [c]	<LOD [c]	<LOD [c]	0.22-0.43 [a]	<0.040-0.78 [a]	<0.10-1.1 [a]	<0.63-21 [a]	
		eggs	<LOD [c]	<LOD [c]	<LOD [c]	<LOD [c]	<LOD [c]	0.10 [a]	0.18 [a]	1.8 [a]	<1.2 [a]	
		cheese	<LOD [c]	<LOD [c]	<LOD [c]	<LOD [c]	<LOD [c]	0.11 [a]	0.20 [a]	0.22 [a]	<0.74 [a]	
France	2014-2016	meat	(<LOD-18 [c])	(<LOD-7.0 [c])	(<LOD-0.071 [c])		(<LOD-150 [c])	(<LOD-12 [c])	(<LOD-15 [c])			(Venisseau et al., 2018)
		fish	(<LOD-6.4 [c])	(<LOD-20 [c])	(<LOD-0.17 [c])		(<LOD-38 [c])	(<LOD-10 [c])	(<LOD-10 [c])			
		egg	(<LOD-4.0 [c])	(<LOD-12 [c])	(<LOD-0.13 [c])		(<LOD-16 [c])	(<LOD-1.3 [c])	(<LOD-12 [c])			
Belgium	2015-2016	meat								(6.0 [a])		(Poma et al., 2018)
		fish								(<LOD [c])		
		eggs								(<LOD [c])		
		dairy products								(<LOD [c])		
Spain		fish/shellfish			(<20 [c])		(<20-200 [c])				(<10 [c])	(Trabalon et al., 2017)
Latvia	2016-2019	meat			(0.34-5.7 [c])		(1.4-9.8 [c])					(Zacs et al., 2021)
		fish			(<0.96-3.1 [c])		(2.8-18 [c])					
		eggs			(<0.43-1.8 [c])		(0.93-5.7 [c])					
		cheese			(<0.30-2.9 [c])		(1.9-12 [c])					
China	2016-2019	meat		0.078 (21) [a]	0.0058 (1.4) [a]		0.012 (3.2) [a]		0.0098 (2.5) [a]		4.3 (1,200) [a]	(Zhao et al., 2023)

		aquatic food	0.061 (6.0) [a]	<LOD [a]		0.011 (0.98) [a]		0.049 (4.5) [a]	33 (3,000) [a]	
		eggs	0.041 (5.7) [a]	<LOD [a]		0.0054 (0.66) [a]		0.030 (4.2) [a]	10 (1,400) [a]	
		dairy products	0.037 (1.1) [a]	<LOD [a]		0.0067 (0.20) [a]		0.0025 [a]	9.0 (260) [a]	
China [d]	2010	eggs					(<LOD-100 [c])		(<LOD-1,800 [c])	(Zheng et al., 2016)
China	2010	eggs					(<LOD [c])		(<LOD-540 [c])	(Zheng et al., 2016)
China [d]	2013	eggs				2.0-6.8 [c]		0.40-78 [c]	4.5-190 [c]	(Zeng et al., 2016)
China	2011	meat	0.026-0.16 [c]		<LOD-0.081 [c]	<LOD-0.16 [c]		<LOD-0.067 [c]	<LOD-23 [c]	(Shi et al., 2016)
		fish	0.030-0.37 [c]		0.030-1.6 [c]	<LOD-2.2 [c]		<LOD-1.9 [c]	<LOD-70 [c]	
		eggs	0.0080-0.10 [c]		<LOD-0.057 [c]	<LOD-0.076 [c]		<LOD-4.1 [c]	<LOD-20 [c]	
China [d]	2011	fish		<0.17 [a]		6.5 [a]	62 [a]	6.8 [a]	15 [a]	<0.45 [a]	(Labunska et al., 2015)
		meat		<0.17-0.87 [a]		0.41-0.56 [a]	24-38 [a]	1.5-5.4 [a]	7.2-12 [a]	<0.45 [a]	
		eggs		<0.17 [a]		<0.15 [a]	3.1-5.4 [a]	<0.35-3.8 [a]	0.88-1.6 [a]	<0.45 [a]	
China	2011	fish		<0.17 [a]		<0.15 [a]	4.0 [a]	2.1 [a]	1.9 [a]	<0.45 [a]	(Labunska et al., 2015)
		meat		<0.17-1.2 [a]		<0.15 [a]	2.1-2.7 [a]	<0.35-2.7 [a]	<0.25-1.8 [a]	<0.45 [a]	
		eggs		<0.17 [a]		<0.15 [a]	1.2-1.7 [a]	<0.35 [a]	<0.25 [a]	<0.45 [a]	
Tanzania	2012	eggs						<LOD-9.8 [c]			(Polder et al., 2016)
US	2013	baby food	(<LOD-1.3 [a])			(2.4-6.2 [a])				(<LOD-19 [a])	(Liu et al., 2014)

a. mean concentrations; b. median concentrations; c. ranges; d. e-waste recycling sites.

1.3 Occurrence of BFRs in indoor and outdoor environments

BFRs have the tendency to accumulate in fine particles (Al-Omran and Harrad, 2016a, b; Muenhor and Harrad, 2012). Because BFRs are semi-volatile, emissions of BFRs from BFR-containing products to indoor and outdoor air are also ubiquitous (Poppendieck et al., 2017; Sun et al., 2018). In this section, mechanisms of BFR migration and emissions from BFR-containing products to dust and air are discussed, and recent investigations on BFR concentrations in house dust, home air, and outdoor air are summarised.

1.3.1 Migration of BFRs from commercial products to indoor dust

A significant number of BFR-containing products, such as electronic devices, furniture, and building materials, may make major contributions to the occurrence of BFRs in indoor dust (Al-Omran and Harrad, 2018; Keimowitz et al., 2016; Liagkouridis et al., 2017a; Stubbings and Harrad, 2014). A study conducted by Liagkouridis et al. (2017a) back-calculated emission rates of 19 BFRs to indoor dust by using previously reported data on concentrations of the 19 BFRs in floor dust in Norway, and the results indicated an median emission rate of 0.37 ng/h for BFRs. Although the results were likely to be underestimated since only floor dust rather than elevated surface dust was adopted (Liagkouridis et al., 2017a), this study could provide insights into the relation between BFR emissions and their levels in indoor dust. Generally, BFRs could migrate from products to dust via three pathways, i.e., direct contact between products and dust, abrasion of products, and deposition to dust after volatilisation of FRs from products (source-air-dust partitioning) (Rauert et al., 2014b).

1.3.1.1 Migration of BFRs to dust via direct contact

An HBCDD treated curtain with pre-characterized house dust spread evenly on the top was placed inside a cylindrical stainless steel test chamber (10 cm diameter × 20 cm height) to evaluate transfer of HBCDD via direct curtain-dust contact at room temperature (22±1 ℃) (Rauert et al., 2016). HBCDD concentrations increased

substantially after 24 h contact (from 110 ng/g to 1,500 – 14,000 ng/g) and 1 week contact (from 110 ng/g to 5,200 – 9,300 ng/g), suggesting rapid migration of HBCDD via direct curtain-dust contact. Rapid and substantial PBDE migration to dust was also observed in experiments where dust was placed in direct contact with a plastic TV casing, and the difference between PBDE congener profiles in pre-experiment dust and post-experiment dust, together with the similarity between congener profiles in post-experiment dust and the TV casing, provided further evidence of PBDE migration to dust (Rauert and Harrad, 2015).

Two hypotheses were adopted to explain the mechanism of migration of BFRs from products to dust (Liagkouridis et al., 2017a; Liagkouridis et al., 2017b; Rauert and Harrad, 2015; Rauert et al., 2016; Tokumura et al., 2019): (1) such transfer occurs as a result of contact between dust and gas phase BFRs present in the boundary layer directly above the source; and (2) direct product-dust contact allows dust particles to act as a sorbent accumulating BFRs directly from the surface of product. It is therefore reasonable to assume the vapour pressure of BFRs is likely to impact on transfer process (1), while K_{OW} values of BFRs will probably contribute more to transfer process (2). Interestingly, concentrations of α-HBCDD in post-experiment dust were significantly lower than γ-HBCDD after direct curtain-dust contact for 24 h and 1 week (paired t-test, $p=0.006$ for 24 h contact, and $p=0.018$ for 1 week contact) (Rauert et al., 2016), which was attributed to the higher K_{OW} value of γ-HBCDD. Therefore, despite the limited data hitherto, transfer process (2) seems more consistent with current experimental observations, i.e., K_{OW} is likely to be a more important factor influencing the direct migration of BFRs compared to vapour pressure. In addition, higher concentrations of BFRs in products could also contribute to direct transfer of FRs, which resulted in higher FR concentrations in post-experiment dust samples (Rauert and Harrad, 2015; Rauert et al., 2016).

1.3.1.2 Migration of BFRs to dust via abrasion of products

Abrasion of fine particles or fibres from products to dust is another significant contributor of high concentrations of FRs in indoor dust (Cao et al., 2014; Rauert and Harrad, 2015; Rauert et al., 2014a). A magnetic stirrer bar was introduced into an in-house designed test chamber (10 cm diameter × 20 cm height) to mimic abrasion of fibers from a piece of BFR-treated curtain to dust (Rauert et al., 2014a). HBCDD concentrations in the dust samples increased sharply from an original level of 110 ng/g to 52,500 ng/g after 48 hours of abrasion, and significant positive linear relationships were observed between abrasion time and HBCDD concentrations in dust (Rauert et al., 2014a). Applying forensic microscopy techniques to screen 3 archived UK dust samples, Rauert et al. (2014a) identified 2-10 bromine rich polymeric fragments per mg dust which were responsible for the elevated BFR levels in these dust samples (HBCDD: 490 – 88,600 ng/g, BDE-209: 24,000 – 1,440,000 ng/g). Similarly, a clear increase in concentrations of PBDEs (BDE-153, -154, -183, and -209) in post-experiment dust was also observed when a magnetic stirrer bar was used to mimic the process of abrasion of a plastic TV casing, and similar PBDE congener profiles observed in the TV casing and in post-experiment dust, which differed from congener profiles in pre-experiment dust, provided confirmed evidence of abrasion of fine particles from plastic TV casing to dust (Rauert and Harrad, 2015).

1.3.1.3 Migration of BFRs to dust via source-air-dust partitioning

Compared to direct product-dust contact and abrasion of products, source-air-dust partitioning seems to be less important, sometimes even neglectable, in contributing to high BFR levels in dust. For instance, source-air-dust partitioning yielded HBCDD concentrations in dust that were 1 to 2 orders of magnitude lower than dust HBCDD concentrations yielded from direct curtain-dust contact and abrasion of fibres from curtain to dust (Rauert et al., 2016). In the meantime, Rauert and Harrad (2015) also indicated that the migration of PBDEs from plastic TV casing to indoor dust was strongly influenced by abrasion of products and direct product-dust contact, while source-air-dust partitioning contributed no detectable transfer of PBDEs from TV

casing to dust.

1.3.2 Emissions of BFRs to air

Emission chamber tests have been conducted to study the emissions of BFRs from electronics, furnishings, and other commercial products via volatilisation (Kajiwara and Takigami, 2013; Kemmlein et al., 2003; Poppendieck et al., 2017; Rauert et al., 2014b; Sun et al., 2018). Generally, BFR physicochemical properties, chamber temperature, timescale of emission experiments, and concentrations of BFRs in the products or materials tested, are possible factors influencing emissions of BFRs to air.

1.3.2.1 Impact of physicochemical properties of BFRs on emissions to air

Significant correlations between the PBDE mass captured on a flexible polyurethane foam (PUF) cylinder (and deemed to have volatilised from curtains) and the vapour pressure of PBDE congeners were observed in a cylindrical test chamber (r^2=0.84, p=0.003) and a Micro-Chamber (r^2=0.67, p=0.024), which implied that the volatilisation emission behaviour of PBDEs was strongly influenced by their vapour pressure (Rauert et al., 2015). Sun et al. (2018) also observed higher emission rates of HBCDDs than of some NBFRs such as BTBPE and BEH-TEBP. Moreover, HBCDD had higher sensitivity to the rise of temperature (i.e., greater increase in emission rates per unit increase in temperature) than did NBFRs, which could possibly be attributed to the higher vapour pressure of HBCDD than the studied NBFRs (Sun et al., 2018).

1.3.2.2 Impact of temperature on emissions of BFRs to air

Previous studies have shown that increasing temperature is likely to increase emission rates of BFRs, including NBFRs (Sun et al., 2018), HBCDD (Kajiwara and Takigami, 2013; Sun et al., 2018), and PBDEs (Kajiwara and Takigami, 2013; Kemmlein et al., 2003). For instance, Kajiwara and Takigami (2013) adapted a small cylindrical stainless-steel chamber (7 cm diameter × 5.5 cm height) to conduct emission tests on three BFR-treated textile samples at temperature of 20-80 ℃. While the emission rates

of both HBCDDs and PBDEs remained stable over a temperature range of 20-60 ℃, a considerable increase in the emission rates of HBCDDs (~20 fold) and PBDEs (~6 fold) was observed at 80 ℃ (Kajiwara and Takigami, 2013). Notably, the relative abundance of α-HBCDD, which has the highest vapour pressure among the three HBCDD diastereomers, continued to increase as the temperature was raised, while that of γ-HBCDD (which has the lowest vapour pressure among the three HBCDD diastereomers) continued to decline (vapour pressure at 25 ℃: 1.05×10^{-8} Pa for α-HBCDD, 5.82×10^{-9} Pa for β-HBCDD, and 8.39×10^{-11} Pa for γ-HBCDD) (Kajiwara and Takigami, 2013). Moreover, the relative abundance of $\sum_{\text{di- to octa-}}$BDEs compared to $\sum_{\text{nona- to deca-}}$BDEs was noted to increase with temperature (Kajiwara and Takigami, 2013).

1.3.2.3 Impact on BFR emissions to air of timescale of experiments

It has been suggested that emission rates will be greatest at the beginning of an experiment when a material is tested in a ventilated chamber (Liang et al., 2015). This hypothesis is supported by Sun et al. (2018), who reported a continuous decline of emission rates of BEH-TEBP (from approximately 6.0 $pg\cdot g^{-1}\cdot h^{-1}$ to less than 1.0 $pg\cdot g^{-1}\cdot h^{-1}$) and HBCDD (from approximately 80 $pg\cdot g^{-1}\cdot h^{-1}$ to 10 $pg\cdot g^{-1}\cdot h^{-1}$) from new carpet during a 5-week experiment. A possible explanation for this temporal decline in emission rate is that volatilisation of BFRs present in the surface of the test material is more facile when the test material is initially placed into a chamber, leading to an initially high emission rate, whereas long-term emissions of BFRs are likely limited by the inefficient diffusion of BFRs from the inside of the test material to the surface (Poppendieck et al., 2017). Another study conducted by Kemmlein et al. (2003) evaluated emission behaviour of a wide range of BFRs from four product groups (insulating materials, assembly foam, upholstery/mattresses, and electronics/electrical equipment). Although some BFRs (i.e., HBCDDs and deca-BDE) were barely detected throughout the tests (therefore their emission rates were not discussed), emissions of other BFRs (i.e., tri- to penta-BDEs) increased considerably at relatively early stages

of the tests, and it is notable that equilibrium appeared to be attained for these BFRs after a test period of 60-160 days.

1.3.2.4 Impact of concentrations of BFRs in products on emissions to air

Sun et al. (2018) observed a significant positive linear relationship (r^2=0.65, p=0.003) between the emission rates of a range of BFRs (HBBz, HBCDD, BEH-TEBP, etc.) and their concentrations in 6 types of materials (new carpet, computer casing, sound insulation cotton, circuit board, decorative laminate, and PVC flooring). These results indicate BFR emissions from commercial products are likely influenced strongly by their concentrations in the materials. In addition, due to the lack of significant correlation between the physicochemical properties of BFRs and their emission rates, Sun et al. (2018) concluded that the concentration of BFRs in a product might have a more profound effect on BFR emission behaviour than either vapour pressure or K_{OA}.

1.3.2.5 Other factors influencing emissions of BFRs to air from products

Other factors influencing BFR emission behaviour include: the rate of air flow across the surface of a product, the surface area-to-volume ratio of a product, and the mode of BFR incorporation into the product (i.e., additive or reactive). For instance, using a filter paper spiked with PBDE standards, Rauert et al. (2015) identified detectable PBDE volatilisation in chamber experiments. However, this was not replicated when PBDE-containing TV casing was studied in the same chamber configuration, suggesting minimal volatilisation of PBDEs from the TV casing, even though the PBDE concentration in the TV casing was almost 10 times higher than in the filter paper (Rauert and Harrad, 2015). A likely explanation is that the PBDEs were bound strongly to the TV casing during the production process (melting and remoulding), with the greater surface area-to-volume ratio of the filter paper another contributory factor (Rauert and Harrad, 2015). In addition, the mode via which BFRs are incorporated into a polymer likely influences BFR emission behaviour. Specifically, emission rates of BFRs that are covalently (reactively) bound to materials are expected to be much lower

than if the BFRs are incorporated by physical mixing (additively) (Wolf et al., 2000). However, empirical evidence of this (especially from chamber tests) remains scarce, likely due to difficulties with experimental design.

1.3.3 Occurrence of BFRs in indoor dust

Literature data on BFR concentrations in house dust is given in Table 1-6. In the UK, arithmetic mean concentration of PBDEs in house dust dropped from 260,000 ng/g in 2007 (Stuart et al., 2008), through 34,000 ng/g in 2015 (Tao et al., 2016a), to 4,800 ng/g in 2019 (Drage et al., 2020). This likely reflected restrictions on use of PBDEs in the UK. However, little decline in concentrations of HBCDD was observed in UK house dust. Arithmetic mean and median concentrations of HBCDD were 8,300 ng/g and 610 ng/g in UK house dust in 2015 (Tao et al., 2016a), and were 46,000 ng/g and 280 ng/g in UK house dust in 2019, respectively (Drage et al., 2020). As the global phase-out of HBCDD began in 2014, it is likely that insufficient time had passed to enable significant declines in HBCDD concentrations in house dust when the studies were conducted. In terms of NBFRs, arithmetic mean concentrations of PBBz, PBT, PBEB, DPTE, HBBz, EH-TBB, BTBPE, BEH-TEBP, and DBDPE were 3.3 ng/g, 7.1 ng/g, 2.3 ng/g, 6.6 ng/g, 1.8 ng/g, 21 ng/g, 14 ng/g, 240 ng/g, and 240 ng/g, respectively, in UK house dust in 2015 (Tao et al., 2016a). Considerable increase in DBDPE concentrations was observed in UK house dust between 2015 and 2019 (arithmetic mean: 1,500 ng/g) (Drage et al., 2020), which was likely due to increasing use of DBDPE as a replacement for BDE-209 in the UK. However, no considerable changes in concentrations of BTBPE were observed (Drage et al., 2020), and our knowledge on temporal changes in concentrations of other NBFRs in UK house dust is very limited. Therefore, further research is needed to evaluate the impact of global restrictions on temporal changes in BFR contamination, especially NBFR contamination, in UK food items.

Table 1-6. Literature data on arithmetic mean concentrations of BFRs (medians in parentheses) in house dust (ng/g)

Country	Year	BDE-209	PBDEs [a]	PBBz	PBT	PBEB	DPTE	HBBz	EH-TBB	BTBPE	BEH-TEBP	DBDPE	HBCDD	References
UK	2019	4,800 (1,600)	4,800 (1,700)							11 (0.84)		1,500 (660)	46,000 (280)	(Drage et al., 2020)
UK	2015	34,000 (4,500)	34,000	3.3 (2.2)	7.1 (1.8)	2.3 (0.78)	6.6 (1.8)	1.8 (<0.030)	21 (10)	14 (5.6)	240 (65)	240 (41)	8,300 (610)	(Tao et al., 2016a)
UK	2007	260,000 (8,100)	260,000 (8,500)							120 (5.3)		270 (24)		(Stuart et al., 2008)
Ireland	2016	58,000 (13,000)	58,000									39,000 (4,200)	2,900 (490)	(Wemken et al., 2019)
Spain	2020	510	550			<LOD		<LOD	16		630	230	11,000	(Esplugas et al., 2022)
Spain	2016	(150)	(180)			(0.030)		(0.22)		(1.6)		(86)		(de la Torre et al., 2020)
Belgium	2016	(180)	(210)			(0.020)		(0.26)		(0.87)		(140)		(de la Torre et al., 2020)
Italy	2016	(230)	(280)			(0.060)		(0.36)		(1.7)		(120)		(de la Torre et al., 2020)

Czech Republic	2013	220	240	0.44		<LOD	2.1	17	5.8	60	20		(Venier et al., 2016)
China	2020	1,900	2,400									340	(Yan et al., 2022)
China	2013	2,200	2,200					86	13	2,500	650		(Bu et al., 2019)
Korea	2015	1,300	1,700						42		260		(Lee et al., 2020)
Nepal	2015	6.7	7.7			0.060	0.24	0.28	0.42	29	490		(Yadav et al., 2019)
Iraq	2013	960	1,000			0.28		7.1	17	110	150		(Al-Omran and Harrad, 2016b)
South Africa	2018	1,400	1,500					3,200		1,600			(Brits et al., 2019)
Nigeria	2019	290	310	0.10	0.96	27	0.93				480	11	(Akinrinade et al., 2021)
US	2013	2,800	4,000	2.6		1.4	13	920	22	2,500	370		(Venier et al., 2016)
Canada	2013	1,200	2,600	3.3		1.2	6.4	2,400	27	2,700	95		(Venier et al., 2016)
Australia	2019	1,400	2,000	<LOD	0.75	0.010		120	6.5	66	14,000		(Yang et al., 2022)

a. including BDE-209.

Concentrations of PBDEs and HBCDD in UK house dust were generally comparable to or higher than those reported elsewhere. For instance, arithmetic mean concentrations of PBDEs in house dust were 58,000 ng/g in Ireland (sampling year: 2016) (Wemken et al., 2019), 550 ng/g in Spain (sampling year: 2020) (Esplugas et al., 2022), 2,400 ng/g in China (sampling year: 2020) (Yan et al., 2022), 310 ng/g in Nigeria (sampling year: 2019) (Akinrinade et al., 2021), 4,000 ng/g in the US (sampling year: 2016) (Venier et al., 2016), etc. Arithmetic mean concentrations of HBCDD in house dust were 2,900 ng/g in Ireland (sampling year: 2016) (Wemken et al., 2019), 11,000 ng/g in Spain (sampling year: 2020) (Esplugas et al., 2022), 340 ng/g in China (sampling year: 2020) (Yan et al., 2022), 11 ng/g in Nigeria (sampling year: 2019) (Akinrinade et al., 2021), etc. With respect to NBFRs, however, investigations are relatively limited, with DBDPE, BEH-TEBP, and EH-TBB frequently detected as the main contributors to NBFRs in house dust (Akinrinade et al., 2021; Al-Omran and Harrad, 2016b; Bu et al., 2019; de la Torre et al., 2020; Esplugas et al., 2022; Lee et al., 2020; Venier et al., 2016; Wemken et al., 2019; Yadav et al., 2019; Yan et al., 2022; Yang et al., 2022). For instance, arithmetic mean concentrations of DBDPE were 39,000 ng/g and 14,000 ng/g, respectively, in house dust from Ireland (sampling year: 2016) (Wemken et al., 2019) and Australia (sampling year: 2019) (Yang et al., 2022). These concentrations were considerably higher than arithmetic mean concentrations of DBDPE in house dust from other parts of the world (arithmetic mean below 1,000 ng/g; see Table 1-6 for the concentrations).

1.3.4 Occurrence of BFRs in indoor air

Recent updates on BFR concentrations in home air in different countries are summarised in Table 1-7. Arithmetic mean concentrations of PBDEs and HBCDD in home air in the UK were 1,000 pg/m^3 and 320 pg/m^3, respectively, in 2015 (Tao et al., 2016a), which were comparable to arithmetic mean concentrations of PBDEs (930 pg/m^3) and HBCDD (110 pg/m^3) observed in home air in Ireland in 2016 (Wemken et al., 2019). Comparisons with earlier studies suggested no significant differences in

concentrations of PBDEs and HBCDD in home air in the UK between 2001 and 2015 (Tao et al., 2016a). Moreover, these concentrations were generally higher than or at least close to those observed in Spain, the Czech Republic, China, Japan, the US, and Canada (see Table 1-7 for the concentrations).

The 2015 study was the first record of NBFR concentrations in home air in the UK, and thus temporal changes in NBFR concentrations in UK indoor air remain unknown. Arithmetic mean concentrations of PBBz, PBT, PBEB, DPTE, HBBz, EH-TBB, BTBPE, BEH-TEBP, and DBDPE were 6.6 pg/m^3, 17 pg/m^3, 1.6 pg/m^3, 3.5 pg/m^3, 11 pg/m^3, 4.8 pg/m^3, 11 pg/m^3, 10 pg/m^3, and 26 pg/m^3, respectively, in UK home air in 2015 (Tao et al., 2016a). These concentrations were broadly comparable to those observed in home air in other parts of the world, with only a few exceptions, e.g., EH-TBB and BEH-TEBP in home air in Spain (Esplugas et al., 2022), DBDPE in home air in Ireland, Spain, and China (Cao et al., 2022; Ding et al., 2016; Esplugas et al., 2022; Wemken et al., 2019), etc. (see Table 1-7 for the concentrations).

1.3.5 Occurrence of BFRs in outdoor air

Table 1-7 summarises BFR concentrations in outdoor air globally. Arithmetic mean concentrations of PBDEs and HBCDD were 190 pg/m^3 and 100 pg/m^3, respectively, in UK ambient air in 2012 (Drage et al., 2016). These concentrations exceeded those observed in 2018 (n=1; PBDEs: 87 pg/m^3, HBCDD: 3.7 pg/m^3) (Saini et al., 2020). However, it is unlikely to pinpoint temporal changes in PBDE or HBCDD concentrations in UK ambient air, due to different designs and limited samples of the two studies. Saini et al. (2020) reported PBDE and HBCDD concentrations in outdoor air from 19 major cities globally, with the concentrations generally below 100 pg/m^3 (sampling year: 2018). However, relatively higher atmospheric concentrations of PBDEs were also reported in South Africa (sampling year: 2017; arithmetic mean: 770 pg/m^3) (Katima et al., 2018) and China (sampling year: 2013; median: 450 pg/m^3) (Ding et al., 2016).

Table 1-7. Literature data on arithmetic mean concentrations of BFRs (medians in parentheses) in indoor air (household) and outdoor air (pg/m^3)

Country	Year	BDE-209	PBDEs [a]	PBBz	PBT	PBEB	DPTE	HBBz	EH-TBB	BTBPE	BEH-TEBP	DBDPE	HBCDD	References
Indoor air														
UK [b]	2015	660 (170)	1,000	6.6 (5.3)	17 (11)	1.6 (1.3)	3.5 (2.0)	11 (4.2)	4.8 (2.0)	11 (5.0)	10 (2.1)	26 (<10)	320 (110)	(Tao et al., 2016a)
Ireland [b]	2016	880 (410)	930									390 (48)	110 (20)	(Wemken et al., 2019)
Spain [c]	2020	54	180			<LOD		<LOD	590		180	180	<LOD	(Esplugas et al., 2022)
Czech Republic [b]	2013	11	16	4.9		0.66		7.2	6.6	0.49	3.0	<LOD		(Venier et al., 2016)
China [b]	2013	(70)	(70)									(75)		(Ding et al., 2016)
China [c]	2017	(210)							(3.0)	(5.9)		(750)		(Cao et al., 2022)
Japan [c]	2006	19	36										110	(Takigami et al., 2009)
US [b]	2013	840	1,100	3.8		9.0		9.6	23	0.18	16	42		(Venier et al., 2016)
Canada [b]	2013	83	220	8.8		4.0		9.9	32	1.3	6.8	13		(Venier et al., 2016)
Outdoor air														

UK [b]	2012	150	190										100	(Drage et al., 2016)
UK [b]	2018	85	87	2.2	3.4	3.6	1.5	1.0	0.91		6.3		3.7	(Saini et al., 2020)
Spain [c]	2013		11			32		<LOD		<LOD		<LOD		(de la Torre et al., 2018)
China [c]	2008	57	69	0.46	6.1	0.34	0.30	4.8		1.1		11	150	(Qi et al., 2014)
China [b]	2013	(400)	(450)									(130)		(Ding et al., 2016)
China [c]	2017	(120)							(10)	(1.9)		(38)		(Cao et al., 2022)
China [b]	2018	48	53	7.9	8.7	0.32	2.3	0.95	1.5		1.2		53	(Saini et al., 2020)
Japan [c]	2006	14	22										14	(Takigami et al., 2009)
Nigeria [b]	2019	120	160	0.90	2.3	0.56		1.4				330	11	(Akinrinade et al., 2022)
South Africa [b]	2017	120	770						380	350	370		60	(Katima et al., 2018)
US [b]	2018	53	110	6.5	8.6	6.8	7.7	4.5	29		68		<LOD	(Saini et al., 2020)

a. including BDE-209; b. passive air samplers were used; c. active air samplers were used.

Concentrations of NBFRs are less frequently reported in outdoor air compared to legacy BFRs. Saini et al. (2020) reported concentrations of PBBz, PBT, PBEB, DPTE, HBBz, EH-TBB, and BEH-TEBP in outdoor air of 19 major cities in 19 countries. Atmospheric concentrations of PBBz, PBT, PBEB, DPTE, HBBz, and EH-TBB were generally below 100 pg/m^3 (sampling year: 2018), with only a few exceptions (Saini et al., 2020). Atmospheric concentrations of BEH-TEBP were slightly higher than those of other NBFRs, but were still below 100 pg/m^3 (sampling year: 2018) (Saini et al., 2020). It is noticeable that atmospheric concentrations of some NBFRs (EH-TBB, BTBPE, BEH-TEBP, and DBDPE) seemed particularly higher in Africa than in other regions. For instance, arithmetic mean concentrations of EH-TBB, BTBPE, and BEH-TEBP were 380 pg/m^3, 350 pg/m^3, and 370 pg/m^3, respectively, in outdoor air in South Africa (sampling year: 2017) (Katima et al., 2018); while the arithmetic mean concentration of DBDPE was 330 pg/m^3 in outdoor air in Nigeria (sampling year: 2019) (Akinrinade et al., 2022). Overall, our current knowledge about NBFR contamination in ambient air is very limited, and further studies are needed to narrow this gap.

1.4 Human exposure to BFRs

A comprehensive review of human exposure to BFRs via different pathways has been done previously (Tao, 2016). In this section, recent investigations on human exposure to BFRs are updated.

1.4.1 Recent updates on human exposure to BFRs: general populations

As shown in Table 1-8, mean (or median) estimates of human exposure to BFRs were generally below 100 ng/kg bw/day for the general public (adults and toddlers) in Europe. In the UK, for example, estimated mean dust ingestion of PBDEs, HBCDD, and NBFRs was 100 ng/kg bw/day, 34 ng/kg bw/day, and 3.7 ng/kg bw/day for toddlers, and 5.5 ng/kg bw/day, 1.8 ng/kg bw/day, and 0.72 ng/kg bw/day for adults, respectively, in 2015 (Tao et al., 2016a). Human exposure to BFRs (sum of PBDEs, HBCDD, and NBFRs) via dust ingestion was approximately one to two orders of magnitude higher than those

via dietary intake and indoor air inhalation in the UK in 2015 (Tao et al., 2016a; Tao et al., 2017). Similar findings were also reported in other European countries, including Ireland (Wemken et al., 2019), Spain (de la Torre et al., 2020; Esplugas et al., 2022; Trabalon et al., 2017), Belgium (de la Torre et al., 2020), and Italy (de la Torre et al., 2020), where dust ingestion of BFRs outweighed considerably human exposure to BFRs via other pathways both for adults and for toddlers (see Table 1-8 for detailed data). These results seem to indicate dust ingestion is the most important route of human exposure to BFRs for residents in Europe. However, it is also noticeable that investigations on human dermal uptake of BFRs are still limited. While a study conducted in Belgium, Italy, and Spain suggested dermal uptake of BFRs via dust-skin contact was almost neglectable compared to dust ingestion of BFRs (de la Torre et al., 2020), another study reported human dermal uptake of BFRs via fabric-skin contact exceeding considerably dust ingestion and dietary intake of BFRs (Abdallah and Harrad, 2018). It seems that fabric-skin contact, rather than dust-skin contact, is likely to contribute most to human dermal uptake of BFRs. A possible explanation is that BFR concentrations in treated fabrics are much higher than in dust, while it is also likely that duration of contact with fabrics (e.g., furniture, clothes) is longer than with dust and that the surface area with which dermal contact occurs is greater for fabrics than dust. Therefore, further investigations should pay serious attention to human dermal absorption of BFRs via fabric-skin contact.

Investigations conducted in Asia reported different findings, however, compared to the dominant contribution of dust ingestion to human exposure to BFRs in Europe. In China, for instance, adults' dietary intake of PBDEs (9.8 ng/kg bw/day) and NBFRs (2.7 ng/kg bw/day) exceeded dust ingestion of PBDEs (1.1 ng/kg bw/day) and NBFRs (0.87 ng/kg bw/day) in 2013, respectively (Bu et al., 2019; Wang et al., 2019). Another study also reported non-neglectable contribution of dermal uptake from dust and inhalation of indoor air to human exposure to BFRs (sum of PBDEs and NBFRs) in China compared to dust ingestion (Zhang et al., 2022b). Specifically, dermal uptake of BFRs was 2.3

ng/kg bw/day for toddlers and 1.0 ng/kg bw/day for adults, and inhalation exposure to BFRs was 0.85 ng/kg bw/day for toddlers and 0.35 ng/kg bw/day for adults, respectively, compared to dust ingestion of BFRs of 4.0 ng/kg bw/day for toddlers and 0.50 ng/kg bw/day for adults, in 2014 (Zhang et al., 2022b). Similarly, human dermal uptake of BFRs from dust that was equivalent to or greater than dust ingestion of BFRs was also reported for residents in Thailand (Waiyarat et al., 2023) and Nepal (Yadav et al., 2019). These results likely suggest variations in relative significance of different pathways of human exposure to BFRs between Europe and Asia.

Recent investigations on human exposure to BFRs outside Europe and Asia are limited. A study conducted in Australia revealed comparable contribution of dust ingestion and dermal uptake to human exposure to BFRs (Yang et al., 2022), while adult dust ingestion of PBDEs was outweighed by dietary intake of PBDEs in Nigeria (Akinrinade et al., 2021; Babalola and Adeyi, 2018).

1.4.2 Recent updates on human exposure to BFRs: e-waste related populations

E-waste related populations, including e-waste recycling workers and residents inhabiting the vicinity of e-waste recycling facilities, are generally more exposed to BFRs than general populations (see Table 1-8). A study conducted in an e-waste recycling site in China estimated a mean dietary intake of PBDEs of 520 ng/kg bw/day for toddlers and 120 ng/kg bw/day for adults in 2013, and a mean dietary intake of PBDEs of 560 ng/kg bw/day for toddlers and 130 ng/kg bw/day for adults in 2016, respectively (Huang et al., 2018), while another investigation reported a mean dust ingestion of PBDEs of 160 ng/kg bw/day for toddlers and 14 ng/kg bw/day for adults in an e-waste recycling site in China in 2014 (He et al., 2017). Dietary intake of HBCDD and NBFRs was estimated to be 1,500 ng/kg bw/day and 65 ng/kg bw/day for toddlers, and 480 ng/kg bw/day and 36 ng/kg bw/day for adults, respectively, in an e-waste recycling site in Vietnam in 2014 (Tao et al., 2016b). Similar findings could also be found elsewhere (Awasthi et al., 2018; Awasthi et al., 2016; Ma et al., 2021), and

likely indicate greater health burdens posed by BFRs to e-waste related populations than to other citizens.

To date, PBDEs are the most frequently reported BFRs globally in terms of human exposure through e-waste activities, especially via dietary intake and dust ingestion. Specifically, human exposure to PBDEs via dietary intake has been suggested to exceed other exposure pathways such as inhalation and dust ingestion. In two e-waste recycling sites in China, for instance, the median exposure to PBDEs through dietary intake was 5 times and 2 times higher than that via dust ingestion for adults and children, respectively, with high-end exposure via dietary intake approximately 10 and 30 times higher than that through dust ingestion for adults and children, respectively (Labunska et al., 2014). A higher contribution to human exposure to PBDEs via food consumption than dust ingestion was also identified for adults in two Vietnamese e-waste recycling facilities when a medium dust ingestion rate (20 mg/day for adults and 50 mg/day for children) was applied (Anh et al., 2017). Moreover, for children, exposure through food consumption was found roughly equivalent to that through dust ingestion (Anh et al., 2017). However, the contribution of food intake to PBDE exposure was very likely underestimated by Anh et al. (2017), since only fish consumption was included in that study. Furthermore, it is notable that the relative contribution of different pathways varies for different PBDE congeners. In a study conducted by Labunska et al. (2014), the relative contribution of dust ingestion to PBDE exposure compared to that of food consumption (defined as EDI_{dust} / (EDI_{food} + EDI_{dust}), using median exposure scenarios) was 1.0%, 2.1%, 0.2%, 0.2%, and 30.5% for BDE-47, -99, -153, -154, and -209, respectively, for adults, and 2.3%, 4.3%, 0.5%, 0.5%, and 49% for BDE-47, -99, -153, -154, and -209, respectively, for children. Compared to lower brominated PBDE congeners, the contribution of dust ingestion to overall exposure to BDE-209 is much higher.

Table 1-8. Literature data on human exposure to BFRs via dust ingestion, dietary intake, inhalation, and dermal uptake

Country	Population	Year	Exposure pathway	Exposure dose (ng/kg bw/day)	References
UK	General public	2015	Dietary intake	PBDEs average: 4.2 for toddlers and 1.8 for adults	(Tao et al., 2017)
				HBCDD average: 0.88 for toddlers and 0.44 for adults	
				NBFRs average: 2.6 for toddlers and 1.3 for adults	
			Dust ingestion	PBDEs: average: 100 for toddlers and 5.5 for adults	(Tao et al., 2016a)
				HBCDD average: 34 for toddlers and 1.8 for adults	
				NBFRs average: 3.7 for toddlers and 0.72 for adults	
			Inhalation	PBDEs average: 0.17 for toddlers and 0.12 for adults	
				HBCDD average: 0.027 for toddlers and 0.076 for adults	
				NBFRs average: 0.029 for toddlers and 0.026 for adults	
Ireland	General public	2017	Dust ingestion	PBDEs median: 64 for toddlers and 3.1 for adults	(Wemken et al., 2019)
				HBCDD median: 2.5 for toddlers and 0.14 for adults	
				DBDPE median: 21 for toddlers and 1.3 for adults	
			Inhalation	PBDEs median: 0.15 for toddlers and 0.14 for adults	
				HBCDD median: 0.0073 for toddlers and 0.0071 for adults	
				DBDPE median: 0.019 for toddlers and 0.016 for adults	
Spain	General public	2020	Dust ingestion	PBDEs average: 0.79 for toddlers and 0.27 for adults	(Esplugas et al., 2022)
				HBCDD average: 23 for toddlers and 9.1 for adults	
				NBFRs average: 1.3 for toddlers and 0.40 for adults	
			Inhalation	PBDEs average: 0.088 for toddlers and 0.040 for adults	
				HBCDD average: <0.23 for toddlers and <0.091 for adults	
				NBFRs average: 0.37 for toddlers and 0.20 for adults	

		n.a.	Dietary intake	PBDEs average: 0.40 for toddlers and 0.50 for adults	(Trabalon et al., 2017)
				NBFRs average: 0.14 for toddlers and 0.15 for adults	
Belgium & Italy & Spain	General public	2017	Dust ingestion	PBDEs average: 0.66 for toddlers and 0.034 for adults	(de la Torre et al., 2020)
				NBFRs average: 0.41 for toddlers and 0.021 for adults	
			Dermal uptake (dust)	PBDEs average: 0.0016 for toddlers and 0.0000923 for adults	
				NBFRs average: 0.00055 for toddlers and 0.000032 for adults	
Latvia	General public	2019	Dietary intake	PBDEs average: 1.2 for adults	(Zacs et al., 2021)
				HBCDD average: 2.9 for adults	
				NBFRs average: 0.47 for adults	
China	General public	2020	Dust ingestion	PBDEs average: 5.9 for toddlers and 0.95 for adults	(Yan et al., 2022)
				HBCDD average: 0.41 for toddlers and 0.066 for adults	
		2019	Dietary intake	BDE-209 average: 0.48 for adults	(Zhao et al., 2023)
				HBCDD average: 3.1 for adults	
				NBFRs average: 4.0 for adults	
		2018	Dietary intake	PBDEs average: 2.6 for adults	(Jian et al., 2020)
				NBFRs average: 0.93 for adults	
		2014	Dust ingestion	PBDEs average: 3.2 for toddlers and 0.40 for adults	(Zhang et al., 2022b)
				NBFRs average: 0.83 for toddlers and 0.10 for adults	
			Inhalation	PBDEs average: 0.80 for toddlers and 0.32 for adults	
				NBFRs average: 0.050 for toddlers and 0.030 for adults	
			Dermal uptake (dust)	PBDEs average: 2.2 for toddlers and 0.95 for adults	
				NBFRs average: 0.15 for toddlers and 0.090 for adults	
		2013	Dust ingestion	PBDEs average: 7.0 for toddlers and 1.1 for adults	(Bu et al., 2019)
				NBFRs average: 8.8 for toddlers and 0.87 for adults	

		2013	Dietary intake	PBDEs average: 9.8 for adults	(Wang et al., 2019)
				NBFRs average: 2.7 for adults	
	E-waste related	2017	Dust ingestion	HBCDD median: 0.040	(Shen et al., 2019)
				NBFRs median: 0.35	
			Dermal uptake (dust)	HBCDD median: 0.060	
				NBFRs median: 0.64	
		2016	Dietary intake	PBDEs average: 560 for toddlers and 130 for adults	(Huang et al., 2018)
				HBCDD average: 12 for toddlers and 2.7 for adults	
				NBFRs average: 5.6 for toddlers and 1.3 for adults	
		2014	Dust ingestion	PBDEs average: 160 for toddlers and 14 for adults	(He et al., 2017)
				DBDPE average: 16 for toddlers and 1.4 for adults	
		2013	Dietary intake	PBDEs average: 520 for toddlers and 120 for adults	(Huang et al., 2018)
				HBCDD average: 3.3 for toddlers and 0.80 for adults	
				NBFRs average: 4.0 for toddlers and 0.90 for adults	
		2013	Dust ingestion	PBDEs average: 16-350 for toddlers and 1.1-24 for adults	(Zheng et al., 2015)
				HBCDD average: 11-300 for toddlers and 0.73-20 for adults	
Korea	General public	2015	Dust ingestion	PBDEs average: 8.2 for toddlers and 0.56 for adults	(Lee et al., 2020)
				NBFRs average: 1.2 for toddlers and 0.15 for adults	
Thailand	General public	2020	Dust ingestion	HBCDD median: 0.052 for toddlers	(Waiyarat et al., 2023)
			Dermal uptake (dust)	HBCDD median: 0.049 for toddlers	
Vietnam	E-waste related	2014	Dietary intake	PBDEs median: 13 for toddlers and 15 for adults	(Anh et al., 2017)
				HBCDD average: 1,500 for toddlers and 480 for adults	(Tao et al., 2016b)
				NBFRs average: 65 for toddlers and 36 for adults	
			Dust ingestion	PBDEs median: 14 for toddlers and 1.3 for adults	(Anh et al., 2017)

Pakistan	E-waste related	2014	Inhalation	PBDEs average: 19	(Iqbal et al., 2017)
				NBFRs average: 14	
Nepal	General public	2015	Dust ingestion	PBDEs average: 0.0066 for toddlers and 0.00070 for adults	(Yadav et al., 2019)
				NBFRs average: 0.022 for toddlers and 0.022 for adults	
			Dermal uptake (dust)	PBDEs average: 0.092 for toddlers and 0.034 for adults	
				NBFRs average: 2.9 for toddlers and 1.1 for adults	
Australia	General public	2019	Dust ingestion	PBDEs average: 1.8 for toddlers and 0.040 for adults	(Yang et al., 2022)
				NBFRs average: 0.58 for toddlers and 0.010 for adults	
			Dermal uptake (dust)	PBDEs average: 0.88 for toddlers and 0.090 for adults	
				NBFRs average: 0.28 for toddlers and 0.030 for adults	
Nigeria	General public	2017	Dietary intake	PBDEs average: 0.13 for adults	(Babalola and Adeyi, 2018)
	General public	2019	Dust ingestion	PBDEs average: 1.4 for toddlers and 0.060 for adults	(Akinrinade et al., 2021)
				HBCDD average: 0.0052 for toddlers and 0.0021 for adults	
				NBFRs average: 2.5 for toddlers and 0.11 for adults	
n.a.	General public	n.a.	Dermal uptake (fabric)	penta-BDEs average: 6.1 for toddlers and 8.1 for adults in summer	(Abdallah and Harrad, 2018)
				penta-BDEs average: 1.3 for toddlers and 1.4 for adults in summer	
				HBCDD average: 77 for toddlers and 100 for adults in summer	
				HBCDD average: 16 for toddlers and 18 for adults in summer	

Food intake has also been reported as the dominant pathway of human exposure to NBFRs and HBCDD. In an e-waste recycling facility in Vietnam, for example, human exposure to DBDPE and BTBPE via dietary intake was 2 to 4 orders of magnitude higher than exposure via dermal absorption of soil and soil ingestion of DBDPE and BTBPE (Someya et al., 2016; Tao et al., 2016b). Similar results were also reported in an e-waste recycling facility in China, where the estimated dietary intake of DBDPE, as well as α-, β-, and γ-HBCDD, was about 1 to 2 orders of magnitude higher than dust ingestion for both adults and children (He et al., 2017; Huang et al., 2018; Shen et al., 2019).

It is notable that current investigations focused mainly on unregulated e-waste recycling and dismantling activities in Asia and Africa, and impacts of regulated e-waste activities on environmental contamination and human exposure to BFRs have been less studied, especially in Europe. Therefore, future studies are encouraged to fill this gap.

1.4.3 Recent updates on human exposure to BFRs: toddlers *vs* adults

It is notable that toddlers are generally exposed to BFRs more than adults do via dietary intake, dust ingestion, and dermal uptake (see Table 1-8). In the UK, for example, mean dietary intake of BFRs for toddlers almost doubled that for adults in 2015 (Tao et al., 2017), while mean dust ingestion of BFRs for toddlers was one order of magnitude higher than that for adults (Tao et al., 2016a). Greater exposure via dietary intake, dust ingestion, or dermal uptake of BFRs for toddlers than for adults was also reported in other parts of the world, including Ireland (Wemken et al., 2019), Spain (de la Torre et al., 2020; Esplugas et al., 2022; Trabalon et al., 2017), Italy (de la Torre et al., 2020), Belgium (de la Torre et al., 2020), China (Bu et al., 2019; He et al., 2017; Huang et al., 2018; Yan et al., 2022; Zhang et al., 2022b; Zheng et al., 2015), Korea (Lee et al., 2020), Vietnam (Anh et al., 2017; Tao et al., 2016b), Nepal (Yadav et al., 2019), Australia (Yang et al., 2022), Nigeria (Akinrinade et al., 2021), etc. These findings raised serious concerns about potential adverse health effects of BFRs on toddlers. In terms of

inhalation, however, previous studies mostly revealed comparable BFR exposure doses for toddlers and adults (Esplugas et al., 2022; Tao et al., 2016a; Wemken et al., 2019; Zhang et al., 2022b). For example, estimated median inhalation exposure to PBDEs, HBCDD, and NBFRs was 0.15 ng/kg bw/day, 0.0073 ng/kg bw/day, and 0.019 ng/kg bw/day for toddlers, respectively, in Ireland in 2017, which was very close to the estimates for adults (PBDEs median: 0.14 ng/kg bw/day; HBCDD median: 0.0071 ng/kg bw/day; NBFRs median: 0.016 ng/kg bw/day) (Wemken et al., 2019).

1.5 Adverse human health effects of BFRs

Studies investigating toxicity of BFRs have mostly been conducted by experimenting on animals (*in vivo*) and cells (*in vitro*) (Ezechias et al., 2014; Klincic et al., 2020; Koch et al., 2015; Xiong et al., 2019). Earlier *in vivo* and *in vitro* experiments have demonstrated that BFRs, including PBDEs, HBCDD, and NBFRs, are likely to have cytotoxicity, neurotoxicity, reproductive toxicity, hepatotoxicity, nephrotoxicity, carcinogenicity, etc., on test subjects (Ezechias et al., 2014; Gustafsson et al., 2023; Klincic et al., 2020; Koch et al., 2015; Leao-Buchir et al., 2023; Tanaka et al., 2023; Ullmann et al., 2022; Wang et al., 2023; Xiong et al., 2019; Zhang et al., 2023). However, investigations based on observations in humans are rather limited, likely due to ethical issues. As the pertinent animal and cell experiments have already been reviewed earlier in this chapter, this section focuses on studies investigating associations between BFR concentrations in the human body and related adverse health effects.

1.5.1 Adverse human health effects of PBDEs

PBDEs are reported thyroid hormone (TH) disruptors in humans (Eguchi et al., 2015; Guo et al., 2019; Zheng et al., 2017a; Zheng et al., 2017b). For instance, a preliminary study reported significantly negative correlations between PBDE concentrations in human serum and levels of THs in adults living along the Yangtze River in China (Hu et al., 2021). Specifically, free triiodothyronine (FT3), a free form of THs, was

significantly negatively associated with BDE-28 concentrations in human serum, while free thyroxine (FT4), also a free form of THs, was significantly negatively associated with concentrations of BDE-28, -47, -99, -100, -154, and -183 (Hu et al., 2021). PBDEs have strong binding affinity to thyroid-stimulating hormone (TSH), thyroglobulin (Tg), thyroxine-binding globulin (TBG), TH receptor α (TRα) and β (TRβ), and iodothyronine deiodinase 1 (ID1), and therefore could disrupt TH-regulated proteins and gene expression (Guo et al., 2019). It is also suggested that PBDEs could exert similar disrupting effects on female follicle-stimulating hormone (FSH) and male testosterone (Guo et al., 2018).

In addition to the disrupting effects on human hormones, epidemiological studies also revealed other potential adverse health effects of PBDEs on the human body. Xie et al. (2023) investigated associations between PBDE concentrations in human adipose tissues and prognostic biomarkers of breast cancer as well as progression-free survival of patients for the first time. The results suggested that exposure to PBDEs may contribute to the development, aggressiveness, and reoccurrence risk of breast cancer (Xie et al., 2023). Another study investigated the associations between PBDE concentrations in female adipose tissues and lipid profiles and found that some PBDE congeners showed a significant negative correlation with lipid levels, with BDE-138 being the most significant influencing factor of dyslipidemia (Zhang et al., 2022a). The authors indicated that exposure to certain PBDE congeners could be associated with liver injury, as PBDEs in the human body might accelerate lipid accumulation in the liver, consistent with a mechanism for the development of non-alcoholic fatty liver disease (Zhang et al., 2022a). In addition, female exposure to PBDEs was also found to be related to prolonged menstrual cycle and menstrual duration, which might influence reproductive health of women by altering menstrual status (Shi et al., 2022).

Specifically, health effects of PBDE exposure on the human reproductive system and thus on fetuses and infants are of particular concern due to the latter's substantially

weaker resistance and immunity. PBDEs were found to have adverse effects on human semen quality measured by sperm concentration and count, motility, and viability (Ermler and Kortenkamp, 2022; Yu et al., 2019; Yu et al., 2018). In another study exploring the effects of prenatal exposure to PBDEs on placental size and birth outcomes, PBDE concentrations in maternal serum were found to be related to decreased placental length, breadth, surface area, birth weight, birth length, gestational age, and Quetelet index (also known as body mass index or BMI, defined as body weight (kg) / body height ^{2} (m^2)) of newborns (Jin et al., 2020). PBDE concentrations in maternal serum were also significantly associated with an increased risk of fetal growth restriction (Jin et al., 2020). Similarly, Xu et al. (2015), along with Li et al. (2018b), Qian et al. (2023), and Reddam et al. (2023), reported that high prenatal exposure to PBDEs could lead to adverse physiological development in fetuses, in terms of reduced body-mass index, Apgar 1 score, and head circumference.

1.5.2 Adverse human health effects of HBCDD

Earlier animal experiments suggested HBCDD have similar effects compared to PBDEs, including cytotoxicity, thyroid toxicity, neurotoxicity, reproductive toxicity, hepatotoxicity, nephrotoxicity, etc. (Assar et al., 2023; Koch et al., 2015; Marvin et al., 2011). However, epidemiological studies focusing on HBCDD in human tissues are rather scarce, and to what extent the results obtained from animal experiments can be extrapolated to humans remains unclear.

To date, human toxicity of HBCDD is mostly investigated *in vitro* using human cells (Feiteiro et al., 2021). For example, HBCDD was observed to induce cytotoxicity in human liver cancer cell line (Hep G2) and neuroblastoma cell line (SH-SY5Y) (Al-Mousa and Michelangeli, 2012, 2014; Fery et al., 2010; Zhang et al., 2008). Experiments with human natural killer cells revealed the potential of HBCDD to decrease lytic function and adenosine triphosphate (ATP) levels and to increase risk of cancer development (Hinkson and Whalen, 2009). In addition to these cell experiments,

Johnson et al. (2013) measured serum hormone levels and HBCDD concentrations in house dust and found that increased concentrations of HBCDD in house dust were associated with an increased level of free androgen index and a decreased level of sex hormone-binding globulin in males.

1.5.3 Adverse human health effects of NBFRs

Observations on occurrence of NBFRs in human body and associated health effects are very limited, but previous studies suggested NBFRs are likely to exert similar disrupting effects on human hormones compared to PBDEs (Chen et al., 2019; Guo et al., 2019; Guo et al., 2020; Guo et al., 2018; Johnson et al., 2013). In an exploratory study conducted in the US, concentrations of BTBPE and BEH-TEBP in house dust were found to be positively correlated to levels of total T3 in male adults (Johnson et al., 2013). Although concentrations of BTBPE and BEH-TEBP in human tissues of these volunteers were not measured, this finding suggested human exposure to BTBPE and BEH-TEBP via house dust could lead to endocrine disruption in men (Johnson et al., 2013). Another study observed significantly higher levels of total T3 and total T4 in workers who were occupationally exposed to DBDPE compared to local residents with no occupational exposure (Chen et al., 2019). Further, decrease in levels of TBG, TSH, and expression of TRα, but increase in expression of ID1, was also observed in residents of an e-waste recycling region with high exposure to some NBFRs (Guo et al., 2019). For instance, concentrations of EH-TBB in serum of the residents were negatively associated with TBG levels, while concentrations of EH-TBB and BEH-TEBP were negatively associated with expression of TRα (Guo et al., 2019). Similar findings were reported in a follow-up study, where decreased levels of TSH and TRα expression but increased levels of ID1 expression along with more exposure to NBFRs were observed in children from an e-waste recycling site in China (Guo et al., 2020). The authors concluded that changed levels of TSH and gene expression of ID1 and TRα indicated adverse effects of NBFRs on peripheral metabolism of TH, which might disrupt the normal physiological function of TH (Guo et al., 2019; Guo et al., 2020).

In addition, another study analysed associations between NBFR concentrations in human serum and levels of human sex hormones (Guo et al., 2018). While EH-TBB and DBDPE were found negatively associated with female FSH levels, BTBPE could elevate male testosterone levels by interfering the conversion of testosterone to other intermediates, and the authors reported stronger disrupting effects of NBFRs on human sex hormones than PBDEs (Guo et al., 2018).

1.6 Objectives

1.6.1 Research gaps

PBDEs remain the most studied BFRs to date, with Asia and Europe, particularly China, being the most studied areas, while NBFRs are less studied compared to PBDEs. In the UK, the latest studies investigating BFR contamination in diet and indoor air were conducted in 2015 (Tao et al., 2016a; Tao et al., 2017), and the latest update on BFR concentrations in UK indoor dust and outdoor air was obtained in 2019 (Drage et al., 2020) and 2018 (Saini et al., 2020), respectively. These data are relatively recent and should reflect the current status of BFR contamination in the UK. However, each of these studies were "independent" investigations, which means they were very different from earlier studies in terms of study design, e.g., sampling, QA/QC, data interpretation, etc. This makes temporal changes in BFR concentrations, especially in NBFR concentrations, in the UK hard to characterise. In the meantime, the rapidly changing regulatory climate for BFRs means that very frequent updates are likely needed to properly evaluate environmental responses, i.e., how quickly restrictions on legacy BFRs result in lower legacy and higher replacement BFR concentrations in various matrices. Further, BFR concentrations inside and in the vicinity of UK e-waste recycling facilities have never been investigated, and thus occupational exposure to BFRs has not been studied for UK e-waste workers. In Nigeria and the US, recent updates on BFR contamination are very limited, especially in foodstuffs. The latest update on PBDE and HBCDD concentrations in US foodstuffs was obtained more than

10 years ago (Schecter et al., 2010), while contamination with NBFRs has never been reported in animal-derived foodstuffs in the US. Moreover, to the best of our knowledge, only three studies have reported concentrations of PBDEs in Nigerian foodstuffs (Babalola and Adeyi, 2018; Oloruntoba et al., 2019; Vaccher et al., 2020), while concentrations of NBFRs in Nigerian foodstuffs have never been reported previously.

1.6.2 Objectives of this study

Given the above background, this study analysed a wide range of BFRs in UK, US, and Nigerian foods as well as in air and dust from indoor and outdoor environments in the UK. Our target BFRs include: 8 PBDE congeners (BDE-28, -47, -99, -100, -153, -154, -183, and -209), 3 HBCDD isomers (α-, β-, and γ-HBCDD), and 9 NBFRs (PBBz, PBT, PBEB, DPTE (or TBP-DBPE), HBBz, EH-TBB (or TBB), BTBPE (or TBE), BEH-TEBP (or TBPH), and DBDPE). The overriding hypothesis of this study is that recent bans and restrictions on the manufacture and use of PBDEs and HBCDD have resulted in a reduction in their concentrations in air, dust, and food. Moreover, the same bans and restrictions have also driven a rise in concentrations of NBFRs as a result of their use as replacements for PBDEs and HBCDD. In light of this, the objectives of this study are to:

1) characterise temporal changes in BFR concentrations in UK foodstuffs, indoor dust, indoor air, and outdoor air;

2) understand how temporal changes in BFR concentrations in UK environments impact on human exposure to BFRs and evaluate related health risks;

3) investigate BFR contamination in UK e-waste recycling facilities and understand implications for occupational exposure;

4) update concentrations of BFRs, especially NBFRs, in foodstuffs in Nigeria and the US and evaluate associated health risks.

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Chapter Two

High Concentrations of Polybrominated Diphenyl Ethers (PBDEs) in Nigerian Foodstuffs Despite Global Restrictions

This chapter has been published in *Emerging Contaminants*:

Ma, Y., Stubbings, W.A., Cline-Cole, R., Abdallah, M.A.E., Harrad, S. (2024). Rising concentrations of polybrominated diphenyl ethers (PBDEs) in Nigerian foodstuffs despite global restrictions. *Emerging Contaminants,* 10, 100264.

Abstract

The presence of brominated flame retardants (BFRs) in foodstuffs of African origin is poorly understood. To fill this gap, 26 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 high concentrations of PBDEs in Nigerian foodstuffs in recent years with associated high 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.

Key words

BFRs; alternative flame retardants; dietary exposure; health risks; food.

2.1 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 (Jiang et al., 2019; Klincic et al., 2020; Ma et al., 2022; Ma et al., 2021). PBDEs and HBCDD are known as persistent and bioaccumulative compounds that can disrupt the human endocrine system, nervous system, and reproductive system, etc. (Chen et al., 2012; Ma et al., 2021; Mackintosh et al., 2015); 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) (Ma et al., 2022). Despite such restrictions however, it is anticipated that global contamination of PBDEs and HBCDD will last for decades (Abbasi et al., 2019; Li and Wania, 2018).

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 (Ma et al., 2022). 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 (Ma et al., 2022). 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 (Ma et al., 2021; Xiong et al., 2019), 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 (Ma et al., 2023a; Ma et al., 2023b; Tao et al., 2017). 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 (Li et al., 2023; Marques et al., 2022). Studies in Africa are comparatively rare. In Nigeria, for instance, very limited investigations have been conducted to report PBDE or HBCDD contaminations in food (Babalola and Adeyi, 2018; Oloruntoba et al., 2019; Vaccher et al., 2020), 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 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.

2.2 Materials and methods

2.2.1 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). Detailed information on the collected food samples can be found in Table S1 in

Supplementary Materials (Appendix. A). The samples were blended thoroughly with a stainless-steel hand blender once received at the University of Birmingham and stored at -20 ℃ until analysis.

2.2.2 Sample preparation

The sample preparation protocols have been published elsewhere (Ma et al., 2023b). Briefly, blended 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.

2.2.3 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℃, and the MS transfer line temperature was 300℃. 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 (Ma et al., 2023b).

2.2.4 Dietary exposure and health risk assessment

Human dietary exposure to BFRs was estimated using equation (1) (Ma et al., 2023b):

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

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) (Babalola and Adeyi, 2018):

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

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

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.

2.2.5 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.

2.2.6 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.

2.3 Results and discussion

2.3.1 BFR concentrations in Nigerian foodstuffs

A statistical summary of BFR concentrations in Nigerian foodstuffs is shown in Table 2-1, with arithmetic mean concentrations of BFRs in each food item given in Table S5 and S6.

2.3.1.1 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 2-1 for

concentrations).

We have recently reported concentrations of PBDEs in UK and US food items (Ma et al., 2023a; Ma et al., 2023b). 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 (Ma et al., 2023b), while those PBDEs containing two or three bromines were more abundant in US food (Ma et al., 2023a). PBDE concentrations in Nigerian foodstuffs were also broadly comparable to those in foodstuffs from non-e-waste impacted areas in China (Wang et al., 2019) and in Europe (Garcia Lopez et al., 2018; Poma et al., 2018; Trabalon et al., 2017; Venisseau et al., 2018), but were considerably lower than PBDE concentrations in food from an e-waste recycling site in China (Zeng et al., 2016).

2.3.1.2 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 (Ma et al., 2022), which could explain their occurrence in Nigerian food items. DPTE is a

bioaccumulative compound produced by Chemische Fabrik Kalk (Germany) during 1972 and 1985 (Vetter et al., 2010). No other manufacturer has reported production of DPTE, and its distribution is unknown (Vetter et al., 2010). 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 2-1 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 (Ma et al., 2023b), the US (Ma et al., 2023a), France (Venisseau et al., 2018), and a non-e-waste impacted area in China (Labunska et al., 2015), but were considerably lower than EH-TBB concentrations in foodstuffs from an e-waste recycling site in China (Labunska et al., 2015). 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 (Ma et al., 2023b) and an e-waste site in China (Labunska et al., 2015), comparable to those observed in foodstuffs from a non-e-waste impacted region in China (Labunska et al., 2015), but higher than those observed in foodstuffs from Belgium (Poma et al., 2018) and the US (Ma et al., 2023a). 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 (Ma et al., 2023b), but were slightly higher than those reported in foodstuffs from China (Shi et al., 2016).

Table 2-1. 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)**	**0.422.8)**

2.3.1.3 HBCDD concentrations in Nigerian foodstuffs

HBCDD was less frequently detected in Nigerian food items at lower concentrations compared to PBDEs and NBFRs. This is consistent with our recent observations about BFRs in UK and US foodstuffs (Ma et al., 2023a; Ma et al., 2023b), 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.

As shown in Table S9, HBCDD concentrations observed in this study generally exceeded our previous observations in the UK (Ma et al., 2023b) and the US (Ma et al., 2023a). Further, HBCDD concentrations in Nigerian food were at the same level as those observed in Latvia (Zacs et al., 2021), France (Venisseau et al., 2018), Belgium (Poma et al., 2018), Ireland (Garcia Lopez et al., 2018), and non-e-waste sites in China (Labunska et al., 2015; Wang et al., 2019), but were lower than HBCDD concentrations in food from Sweden (Remberger et al., 2004), Japan (Kakimoto et al., 2012), and e-waste impacted regions in China (Labunska et al., 2015; Zeng et al., 2016).

2.3.2 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. 2-1, with more detailed data given in Tables S5 and S6.

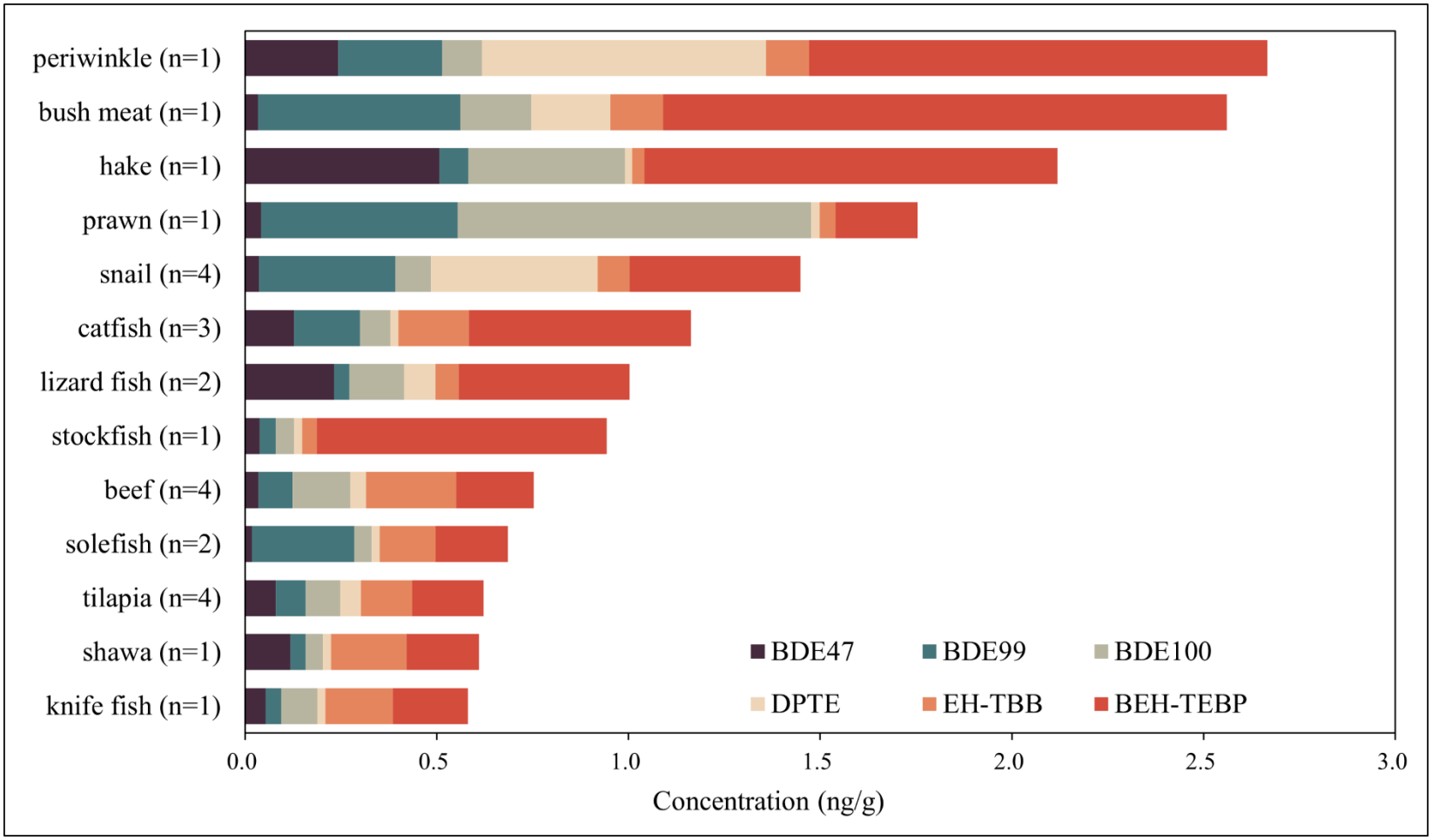


Fig. 2-1 Concentrations of selected BFRs (DF > 30%) in different Nigerian food items

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 (Ma et al., 2023a; Ma et al., 2023b; Tao et al., 2017). 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. Unfortunately, it is unlikely to evaluate the impact of food preparation (i.e., smoked, fried, or dried) on BFR concentrations due to the limited number of samples analysed in this study, and further investigations are encouraged to fill this gap.

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.

2.3.3 Comparisons with previous studies in Nigeria

Three previous studies have reported concentrations of PBDEs in Nigerian foodstuffs (Babalola and Adeyi, 2018; Oloruntoba et al., 2019; Vaccher et al., 2020). To the best of our knowledge, concentrations of NBFRs in Nigerian foodstuffs have never been reported previously.

Fig. 2-2 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 (Babalola and Adeyi, 2018; Vaccher et al., 2020). 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 high PBDE concentrations observed in this study. Water content of meat or aquatic produce normally lies between 50% and 90% (Ma et al., 2023a; Ma et al., 2023b; Tao et al., 2017; Vaccher et al., 2020), which makes dry weight concentrations of a compound in meat or fish approximately 2 to 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. 2-2). 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 (Babalola and Adeyi, 2018). Despite the different designs between our study and the two previous studies (Babalola and Adeyi, 2018; Vaccher et al., 2020), these results likely suggest high concentrations of PBDEs in Nigerian foodstuffs in recent years.

A recent study examined atmospheric concentrations of PBDEs in Lagos, Nigeria during 2019 and 2020, and found that the presence of PBDEs in Lagos atmosphere was significantly related to population density (Akinrinade et al., 2022). This likely indicates active domestic use of PBDEs in Nigeria, which may explain the high concentrations of PBDEs in Nigerian foodstuffs reported in this study. Although applications of PBDEs in new products are unlikely because of global restrictions, reuse and recycling of WEEE could contribute to PBDE contamination in Nigeria. Nigeria has been acting as an important receiver of used EEE. For instance, it was estimated that in 2015 and 2016 approximately 60-71 kt of used EEE were imported annually into

Nigeria through two main ports in Lagos (Forti et al., 2020). These used EEE were generally rich in PBDEs and were either reused or dismantled with very primitive techniques (Forti et al., 2020; Ma et al., 2021). Eventually PBDEs in these reused or dismantled EEE are likely to escape and finally contribute to high PBDE concentrations in Nigerian food items. It is also noticeable that the different food sampling design could be a contributing factor of high PBDE concentrations observed in this study. For instance, long-distance transport of food items from Nigeria to the UK and further preparation of food items in African stores in the UK might increase exposure of these food items to PBDEs.

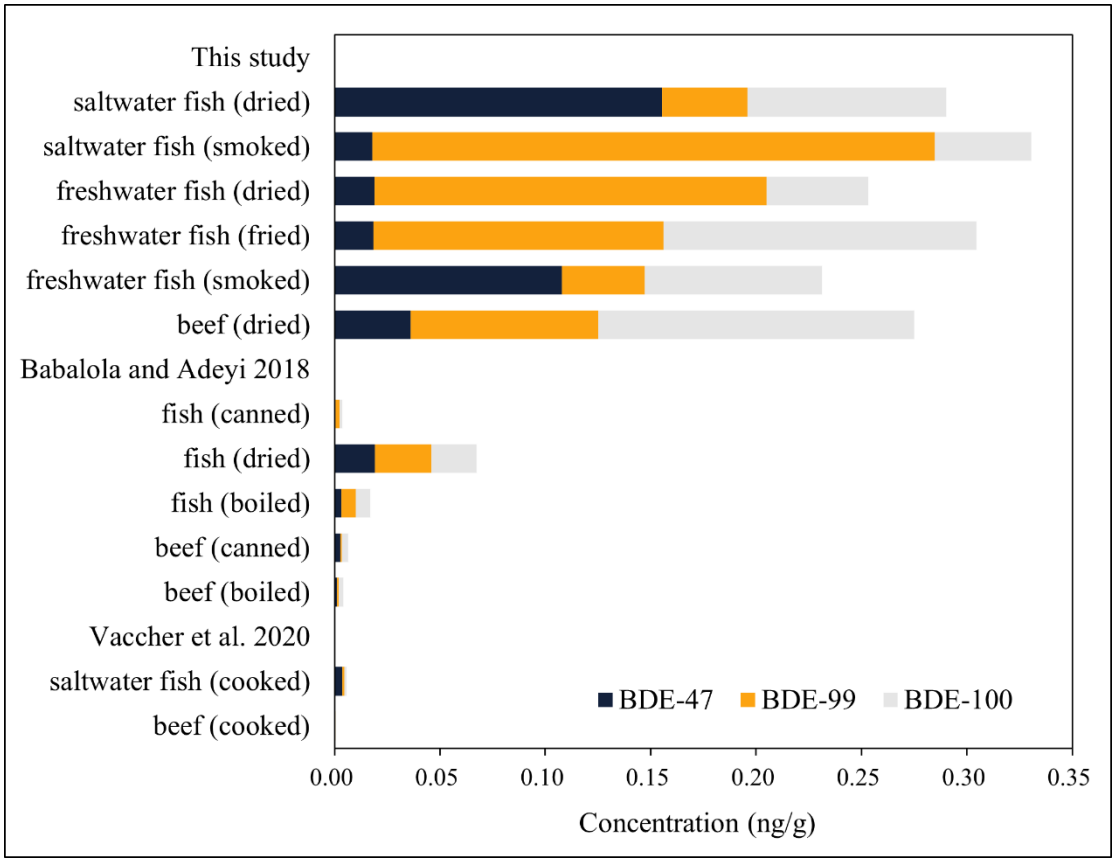


Fig. 2-2 PBDE concentrations in Nigerian food items: comparison with previous studies

2.3.4 Health risk assessment

2.3.4.1 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 (Bradley et al., 2020; Ingenbleek et al., 2017), and are summarised in Table S10. Body weights of Nigerian adults and toddlers were assumed to be 70 kg and 10 kg, respectively (USEPA, 2011). 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. It is notable that only a small number of food samples rather than a whole diet were analysed in this study, which might contribute to biased estimates. However, this study still constitutes a preliminary investigation which promotes our understanding of dietary exposure to BFRs for Nigerians.

Table 2-2 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 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. 2-3 compares mean estimates of dietary exposure to PBDEs of Nigerian adults in

2021 (this study) with those in 2017 (Babalola and Adeyi, 2018). 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 PBDEs of Nigerian adults in 2021 exceeded considerably those in 2017. This indicates greater 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.

2.3.4.2 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 (Akinrinade et al., 2021). 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 (Akinrinade et al., 2021). These results were consistent with an earlier study conducted in the UK (Tao et al., 2017), where dietary intake of tri-to-hexa-BDEs exceeded considerably intake from dust ingestion.

2.3.4.3 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 2-2. 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. In the meantime, we acknowledge that only a small number of food samples representing a very limited

types of food items are included in this study, which is likely to contribute to underestimation of dietary exposure to BFRs of Nigerians. Therefore, further investigations are encouraged to focus on a more representative diet.

Table 2-2. 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 USEPA (2017) and Ma et al. (2021);

[b] RfD for BDE-100 is not available, thus RfD for penta-BDE (2,000 ng/kg bw/day) was used as replacement;

[c] RfD for DPTE is not available, thus HQ cannot be calculated.

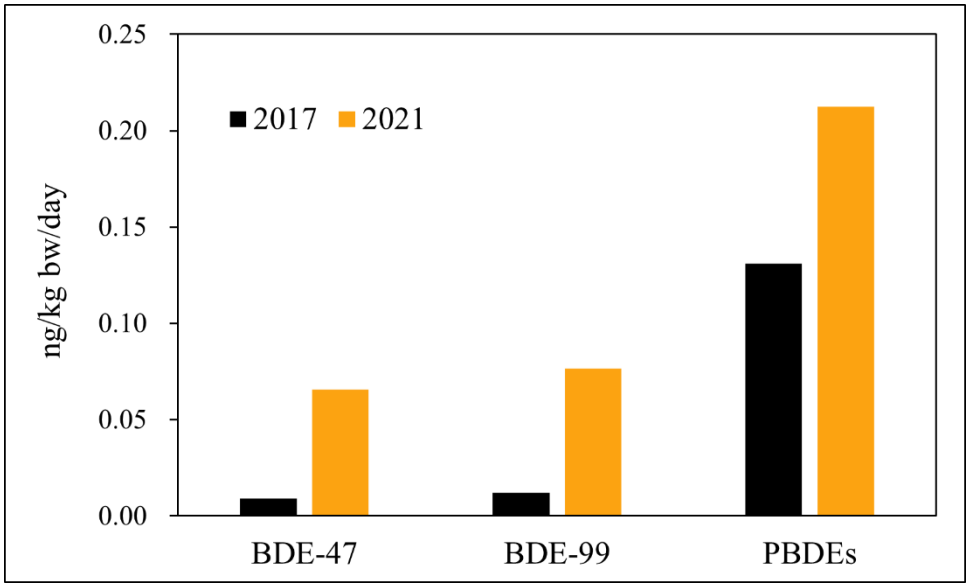


Fig. 2-3 Estimated mean dietary intake of PBDEs of Nigerian adults: comparisons between 2017 (Babalola and Adeyi, 2018) and 2021 (this study); PBDEs = sum of BDE-47, -99, and-100 in this study, while PBDEs = sum of BDE-17, -28, -47, -99, -100, -153, -154, and -183 in the 2017 study

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Chapter Three

Socio-Economic Factors Impact US Dietary Exposure to Halogenated Flame Retardants

This chapter has been published in *Environmental Science & Technology Letters*:

Ma, Y., Romanak, K.A., Capozzi, S.L., Xia, C., Lehman, D.C., Harrad, S., Cline-Cole, R., Venier, M. (2023). Socio-Economic Factors Impact US Dietary Exposure to Halogenated Flame Retardants. *Environmental Science & Technology Letters,* 10, 478−484.

Abstract

Although diet is an important route of exposure for BFRs, little is known of their presence in US food. Therefore, we purchased meat, fish, and dairy products samples (n = 72) in Bloomington, IN from 3 stores representing national retail chains at different price levels. Composite samples (n = 42) were analyzed for polybrominated diphenyl ethers (PBDEs), hexabromocyclododecane (HBCDD), NBFRs, and dechlorane plus (DP). Concentrations of total HFRs ranged between 54 - 1,400 pg/g ww, with PBDEs being the predominant compounds. Concentrations of NBFRs, but not PBDEs, in US food items were significantly impacted by price, raising the issue of environmental justice. Non-organic food generally had higher abundance of BDE-209 than organic food items. Estimates of dietary exposure revealed that meat and cheese consumption contribute most to the overall HFRs intake and that intakes are higher for children and for non-Hispanic Asians. Taking into account several caveats and limitations of this study, these results as a whole suggest that health burdens from dietary exposure to HFRs have become minimal for US citizens, highlighting the positive impact of regulatory efforts.

Keywords

PBDEs; NBFRs; deca-BDE; bromobenzene; dietary intake; health risk

3.1 Introduction

Halogenated flame retardants (HFRs) have been extensively used in commercial products, such as electronic and electrical goods, textiles and fabrics, foam for furnishings, and building insulation materials, to help meet fire safety regulations. Polybrominated diphenyl ethers (PBDEs) and hexabromocyclododecane (HBCDD) are two classes of brominated flame retardants (BFRs) which have been widely produced, with their global historical production volumes estimated to reach 1,900,000 tonnes and 600,000 tonnes, respectively (Abbasi et al., 2019; Li and Wania, 2018). Owing to their extensive use, PBDEs and HBCDD have become ubiquitous in the environment, in biota, and in humans (Jiang et al., 2019; Klincic et al., 2020; Ma et al., 2022; Ma et al., 2021). Because of concerns about their adverse impacts on environmental and ecological safety and human health (Chain et al., 2021; McDonald, 2002; Yu et al., 2015), combined with their persistence in the environment and capacity for bioaccumulation (Fernandes et al., 2016; Labunska et al., 2015; Tao et al., 2017; Wang et al., 2019; Zacs et al., 2021), restrictions on their production and use were introduced. In the US, commercial penta- and octa-BDE mixtures were banned by 2006, with deca-BDE restricted in 2008 (Ma et al., 2022); and these commercial mixtures were also listed under the Stockholm Convention on Persistent Organic Pollutants (POPs) in 2004 and 2019, respectively, resulting in a global phase-out of PBDEs (Sharkey et al., 2020). In the meantime, the global phase-out of these legacy BFRs generated an increased demand for alternative products such as novel BFRs (NBFRs) (Ma et al., 2022). Dechlorane plus (DP) was also introduced as a possible replacement for deca-BDE, resulting in a rise in global demand for DP (Chen et al., 2015). As a result of these replacement trends, several alternative HFRs have been frequently detected in the environment and biota in recent years (Feo et al., 2012; Ghelli et al., 2021; Hou et al., 2021; McGrath et al., 2017; Sverko et al., 2011).

Despite the extensive use of these legacy and emerging HFRs and their ubiquitous presence, limited information is available on their presence in US food items. An early

study investigated concentrations of 43 PBDEs in salmon samples collected throughout the US between September 2001 and December 2002, reporting mean concentrations of Σ_{43}PBDEs of 56 – 3,300 pg/g ww (Hites et al., 2004). Concentrations of PBDEs and HBCDDs were also observed in individual and composite food samples collected in Dallas, Texas between 2003 and 2010 (Schecter et al., 2010; Schecter et al., 2008; Schecter et al., 2006; Schecter et al., 2004; Schecter et al., 2012). Another study reported NBFR and DP concentrations in US baby food in 2013 (Liu et al., 2014). To the best of our knowledge, recent data on concentrations of these legacy and emerging HFRs in general food items is not available, and an update of the overall trends is needed 10 - 20 years after these levels were first investigated.

Therefore, the aims of this study were to: 1) provide data on current concentrations and relative abundance of legacy and emerging HFRs in US food items; 2) identify impacts of food price on HFR concentrations in US food items; 3) investigate whether there are differences in contamination of these HFRs in organic and non-organic US food items; and 4) estimate dietary exposure to these HFRs and evaluate any potential health risks, especially in relation to socio-economic factors.

3.2 Materials and Methods

3.2.1 Sampling

US food samples were purchased in Bloomington, IN, USA from 3 grocery stores representing national retail and processed at Indiana University in Bloomington, IN, USA. The same type of food items were collected from 3 supermarkets representing low (11 composite samples), medium (17 composite samples), and high (14 composite samples) food prices (for example, samples of salmon at the three different price points were purchased). Briefly, a total of 72 individual food samples representing 11 food items, organic and non-organic, were purchased between March and May 2022. One to three individual samples of each food item were homogenized into one composite sample, generating 42 composite food samples. All composite samples were freeze-

dried and then stored at -80°C before analysis. Detailed information on the food samples is shown in Table S1 in Supporting Information (SI, see Appendix. B).

3.2.2 Analytical protocols

Chemicals and reagents used in this study are summarized in SI. The concentrations of 21 PBDEs, 8 NBFRs, HBCDD, and DP (*syn*-DP and *anti*-DP) were measured in these food samples. Sample extraction and clean-up followed a previously published protocol with minor modifications (Tao et al., 2017). Detailed information on sample extraction and clean-up as well as lipid content determination is given in SI. Analyses were performed on an Agilent 7890A gas chromatograph coupled with an Agilent 5975C mass spectrometer (GC/MS) operated in electron capture negative ionization (ENCI) mode. Detailed information has been previously published (Ma et al., 2013), and is summarized in Table S2.

3.2.3 QA/QC

Linearity was obtained from a 11-point calibration for all target compounds (Table S3). The limit of detection (LOD) for each analyte was calculated based on a signal to noise ratio of 3 (Table S4). Together with each batch of 8-12 samples, 2 method blanks and 2 matrix spikes (with a known amount of target compounds prepared in hexane) were included (Tables S5 and S6). More information on QA/QC is available in SI.

3.2.4 Estimation of daily dietary intake of HFRs

Daily dietary intake (DI) of HFRs was estimated with the equation below:

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

where C_i is the median concentration (ng/g ww) of HFRs in a particular food item i; CR_i is the average daily food consumption (g/day) of a particular food item i; BW is the average body weight (kg) of US children (< 20 years old) and adults (≥ 20 years old). Further details can be found in SI.

3.2.5 Statistical analysis

Statistical analysis was done with Excel (Microsoft Office 365) and SPSS Statistics 29.0 (IBM, Chicago, IL, USA). Only the target HFRs with a DF exceeding 30% were included in the analyses. Data were logarithmically transformed and normality was confirmed using a Shapiro-Wilk test. Blanks were subtracted from samples on a mass basis for each batch. For statistical analyses, concentrations below LOD were designated as DF × LOD when DF exceeded 50% for a specific analyte, while concentrations below LOD were designated as zero when 30% < DF < 50%. HFRs detected in less than 30% of our food samples were included in the calculation of totals but they were excluded from statistical analyses and human dietary exposure estimation.

3.3 Results and Discussion

3.3.1 Concentrations and relative abundance of HFRs in US food items

Table 3-1 summarizes median concentrations of target HFRs in US food items, and Fig. S1 depicts relative contribution of these HFRs in US food. Averages and ranges of HFR concentrations are given in Table S7.

PBDEs were the dominant and most detected HFRs in these samples, with an average contribution of 81% to $\sum_{32}$HFRs. Cheese had the highest median concentration of $\sum_{21}$PBDEs, followed closely by salmon. These high PBDE concentrations are likely due to the relatively high lipid contents of salmon (8.4%) and cheese (27%) compared to lean meats such as chicken or turkey (~4%).

Table 3-1. Median concentrations (pg/g ww) of HFRs in US food items (n.d. = not detected; only HFRs with a detection frequency (DF) exceeding 30% are included)

HFRs	DF (%)	Meat				Fish					Dairy		All
		beef	pork	chicken	turkey	salmon	cod	tilapia	tuna	catfish	cheese	egg	
BDE-15	83	51	110	20	75	130	11	75	42	97	210	10	78
BDE-17	71	13	3.9	4.3	2.7	120	n.d.	3.1	n.d.	11	120	4.0	4.3
BDE-28	79	2.9	9.8	10	6.3	92	2.6	13	65	1.6	11	2.8	6.0
BDE-49	52	n.d.	6.4	6.0	4.8	11	3.4	n.d.	12	3.7	13	n.d.	5.3
BDE-47	33	n.d.	n.d.	n.d.	5.1	44	n.d.	n.d.	7.2	13	1.4	n.d.	n.d.
BDE-100	76	3.4	5.4	7.6	3.1	7.7	5.1	0.75	10	7.8	9.3	2.7	5.1
BDE-99	45	n.d.	n.d.	0.29	9.7	1.5	n.d.	n.d.	1.1	6.2	2.7	22	n.d.
BDE-154	88	8.2	11	9.6	8.9	12	8.5	7.0	11	11	32	6.9	9.1
BDE-153	60	2.4	3.4	5.9	7.0	4.8	1.5	n.d.	1.8	5.5	4.8	n.d.	2.8
BDE-139	33	11	n.d.	16	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	4.5	n.d.
BDE-140	48	6.9	7.6	1.2	8.0	n.d.	8.9	n.d.	18	8.3	n.d.	n.d.	n.d.
BDE-183	36	n.d.	4.1	2.1	0.77	n.d.	1.0	n.d.	n.d.	5.6	n.d.	n.d.	n.d.
BDE-209	60	3.7	6.5	9.7	15	3.2	0.55	n.d.	3.1	22	n.d.	4.2	4.6
Σ_{13}PBDEs		**130**	**190**	**120**	**200**	**390**	**49**	**110**	**170**	**190**	**510**	**150**	**180**
pTBX	40	n.d.	n.d.	4.2	n.d.	21	2.1	2.6	41	n.d.	n.d.	0.65	n.d.
PBBz	79	2.9	1.5	1.9	n.d.	5.9	2.4	0.84	1.2	5.4	2.9	1.7	2.1
EH-TBB	36	n.d.	7.2	n.d.	n.d.	n.d.	2.4	3.4	n.d.	4.7	n.d.	n.d.	n.d.
BEH-TEBP	33	n.d.	n.d.	0.29	3.8	n.d.	n.d.	4.7	n.d.	1.4	n.d.	0.55	n.d.
Σ_4NBFRs		**4.4**	**8.7**	**21**	**17**	**44**	**9.5**	**19**	**43**	**12**	**6.6**	**4.5**	**14**
Σ_2DP		**n.d.**	**n.d.**	**2.1**	**1.0**	**n.d.**	**0.60**	**0.32**	**0.17**	**16.3**	**0.064**	**n.d.**	n.d.

BDE-15 was the most detected and predominant PBDE congener in US food items, with an average contribution of 35% to $\sum_{21}$PBDEs. BDE-17 and BDE-28 accounted on average for 10% and 9.8% to $\sum_{21}$PBDEs. In contrast, deca-BDE was only detected with an average abundance of 6.8%. The higher abundance of lower-brominated PBDE congeners is likely due to the debromination of high-brominated PBDEs either abiotically in the environment (i.e. photodebromination) or *in vivo* in the animals before they are sacrificed for the market. The pattern is also a reflection of the phase-out of commercial PBDE mixtures in the US.

PBDE concentrations observed in this study were generally similar to what was reported from another two US-based studies (Table S8) on supermarket-purchased salmon (sampling year: 2001 – 2002) (Hites et al., 2004) and composite US food samples (sampling year: 2009) (Schecter et al., 2010). The two studies mentioned above are 10+ years old; hence, concentrations seem to be relatively constant with time, despite PBDEs having been withdrawn from the market some 10-15 years ago. However, BDE-47 and BDE-99, containing 4 and 5 bromines respectively, were the most abundant PBDEs detected in US food in the two studies above (Hites et al., 2004; Schecter et al., 2010), while BDE-15, which contains only two bromines, was the predominant PBDE congener observed in this study. Such difference possibly indicates more advanced aging of PBDEs in US food during the last decade. A recent survey of the UK market using samples collected in 2021 showed that levels of PBDEs had fallen compared to 2015 (Ma et al., 2023), indicating a slower response in dietary products to restrictions on use of PBDEs in the US compared to the UK. Concentrations measured in our study were also broadly comparable to those in food items from Europe (Covaci et al., 2009; Garcia Lopez et al., 2018; Ma et al., 2023; Poma et al., 2018; Riviere et al., 2014; Trabalon et al., 2017; Venisseau et al., 2018) and Japan (Kakimoto et al., 2012), but they were considerably lower than the concentrations in food items from Tanzania (Polder et al., 2016) and China (Wang et al., 2019; Zeng et al., 2016).

Compared to PBDEs, NBFRs were less abundant in US food, contributing on average 16% to $\sum_{32}$HFRs. Median concentration of $\sum_{8}$NBFRs was 21 pg/g ww. The highest concentrations were observed in turkey samples, with a median $\sum_{8}$NBFRs of 110 pg/g ww. This was followed by salmon and pork, with median concentrations of $\sum_{8}$NBFRs of 78 pg/g ww and 70 pg/g ww, respectively.

In general, pentabromobenzene (PBBz) was the most detected and most abundant NBFR observed in US food, with an average contribution of 32% to $\sum_{8}$NBFRs. PBBz was particularly abundant in beef and cheese, contributing 48% and 44%, respectively, to $\sum_{8}$NBFRs. 2,3,5,6-tetrabromo-p-xylene (pTBX) was also frequently detected with an average contribution of 20% to $\sum_{8}$NBFRs, and it was particularly abundant in tuna, contributing about 85% to $\sum_{8}$NBFRs. It is hard to pinpoint sources of bromobenzenes as they were never used in commercial mixtures, but they could be by-products or degradation products of BDE-209 or decabromodiphenyl ethane (DBDPE) (Ma et al., 2012; Venier et al., 2012).

Data on NBFR concentrations in US food is rather scarce, with only one publication reporting similar levels of PBBz, hexabromobenzene (HBBz), and DBDPE in US baby food from 2013 including formula, cereal, and puree (Table S9) (Liu et al., 2014). Comparable concentrations of PBBz, pentabromoethylbenzene (PBEB), HBBz, 2-ethyl hexyl-2,3,4,5-tetrabromobenzoate (EH-TBB or TBB), and DBDPE were also reported in UK food items collected in 2020 – 2021, but concentrations of 1,2-bis(2,4,6-tribromophenoxy) ethane (BTBPE or TBE) and bis(2-ethyl hexyl) tetrabromophthalate (BEH-TEBP or TBPH) in UK samples were considerably higher (Ma et al., 2023). We speculated such differences could be due to differences in consumption of BTBPE and BEH-TEBP in the UK and the US. However, data is very scarce on production and consumption of these two NBFRs, and our speculations require further verification. Further, NBFR concentrations reported in the present study were similar to those observed in food items from France (Venisseau et al., 2018), Latvia (Zacs et al., 2021),

Belgium (Poma et al., 2018), China (Jian et al., 2020; Shi et al., 2016), and Tanzania (Polder et al., 2016), but they were significantly lower than those from e-waste sites in China (Labunska et al., 2015; Zeng et al., 2016; Zheng et al., 2016).

Concentrations of HBCDD in different food items were not shown in Table 3-1 due to its low detection frequency (17%). However, HBCDD seemed to be particularly abundant in salmon, with a median concentration of 57 pg/g ww.

DP (sum of *syn*- and *anti*-DP) was detected in US food samples with a median concentration of 0.18 pg/g ww. The relative contribution of DP to $\sum_{32}$HFRs was minimal (0.87% on average). Concentrations of DP observed in the present study were comparable to those determined in food items from Japan (Kakimoto et al., 2014; Kakimoto et al., 2012), but were lower than those from Lebanon (Abdel Malak et al., 2019), Latvia (Zacs et al., 2021), and Belgium (Table S11) (Poma et al., 2018).

The fraction of *anti*-DP (f_{anti}), defined as *anti*-DP/total DP, provides useful information about the degradation processes and sources as f_{anti} is approximately 0.75 in commercial mixtures (Feo et al., 2012). In the present study, the mean f_{anti} was 0.69 ± 0.24, which is slightly lower than the f_{anti} value of 0.75 for commercial DP mixtures (Feo et al., 2012). This was likely due to specific enrichment in *syn*-DP in biota (Abdel Malak et al., 2019), as *syn*-DP is more bioaccumulative than *anti*-DP, especially in aquatic species (Feo et al., 2012).

3.3.2 Impact of price on HFR concentrations

No statistically significant difference (p = 0.830) was shown for $\sum_{13}$PBDE concentrations in US food items from the three price groups (Table S12), which is possibly due to either a lack of impact of food price or a sample size too small to detect any differences. However, one-way ANOVA revealed a marginally statistically significant difference (p = 0.052) in $\sum_{4}$NBFR concentrations in US food items from the

three price groups. Specifically, $\sum_4$NBFR concentrations in food items from the low-price group significantly exceeded those from both the medium-price group ($p = 0.049$) and high-price group ($p = 0.021$), while the difference between medium-price group and high-price group ($p = 0.615$) was not statistically significant.

NBFRs were generally more abundant in low price than in food of medium and high price (Fig. 3-1). Interestingly, the ratios of BDE-209 to low brominated PBDEs (i.e., BDE-15, -17, and -28) were considerably higher in meat and dairy products of low price than in meat and dairy products of medium and high price. This implied that deca-BDE was phased out earlier in the mass production of higher cost meat and dairy products. Consistent with this hypothesis, the higher ratios of BDE-209 to low-brominated PBDEs were not observed in low-priced fish, possibly because farm raised fish does not involve as much machinery as the production of meat and dairy products.

These results suggest that food price has a minimal impact on supermarket-purchased food items in the US for PBDEs but a significant impact for NBFRs. We speculate that the phase-out of PBDEs in the US drastically reduced PBDE contamination during production, packaging, transportation, and storage of food. On the contrary, ongoing use of NBFRs continues to result in significant contamination in US food and still poses a potential risk for consumers, especially for those purchasing food at the low price point, which raises the issue of environmental justice.

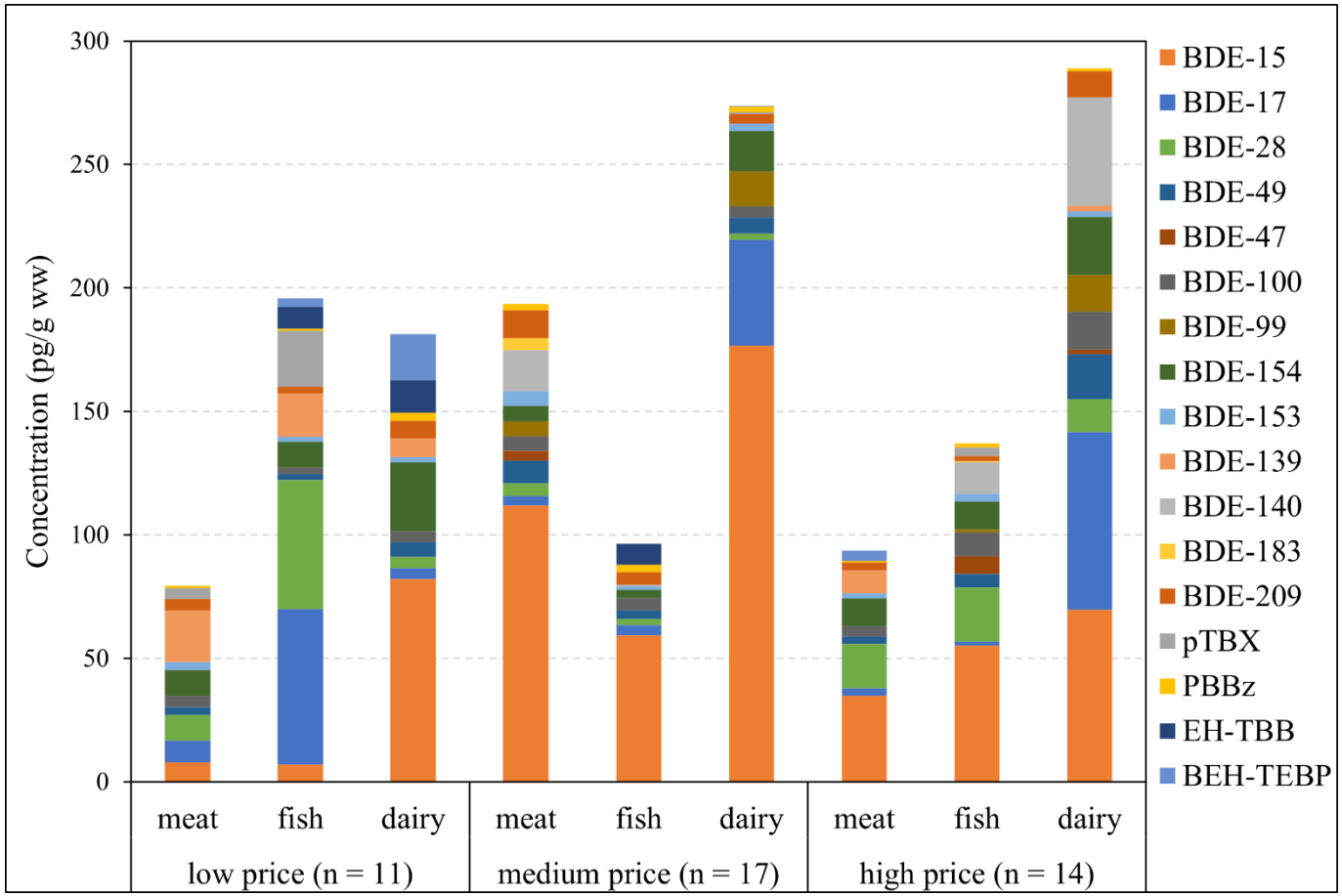


Fig. 3-1 Median concentrations of PBDEs and NBFRs in different US food items of low, medium, and high price. Only PBDEs and NBFRs with a DF exceeding 30% are included.

3.3.3 HFR concentrations in organic and non-organic food items

Median concentrations of $\sum_{13}$PBDEs and $\sum_{4}$NBFRs in organic food samples (14 composite samples) were very similar to the corresponding median concentrations in non-organic food items ((15 composite samples; Table S13), with no statistically significant differences observed using Paired-Samples t tests ($\sum_{13}$PBDEs: p = 0.941; $\sum_{4}$NBFRs: p = 0.735).

Relatively higher abundance of BDE-209 but lower abundance of low-brominated PBDEs to total PBDEs were observed in non-organic US food items than in organic US food (Figure S2). Such differences were similar to those observed in low-price versus medium- and high-price food, and again were likely due to differences between market sectors in the timing of the phase-out of deca-BDE in the US.

3.3.4 Estimation of daily dietary exposure to HFRs for the US population

Under a median-exposure scenario, daily dietary intake of HFRs was 0.77 ng/kg bw/day for US children and 0.47 ng/kg bw/day for US adults, respectively. PBDEs constituted 96% of dietary intake of HFRs, with the remaining 4% attributed to NBFRs and DP. Consumption of meat and cheese contributed most to dietary exposure to HFRs, accounting for 57% and 33%, respectively. This was followed by consumption of fish (6%) and chicken eggs (4%).

Daily dietary intake of HFRs was also estimated for US adults (≥ 20 years old) of different races (Fig. 3-2 and Table S19). Interestingly, non-Hispanic Asian adults had relatively higher dietary intake of HFRs than did other adult groups. Since non-Hispanic Asians consume a diet richer in fish than other groups, they are likely to ingest more HFRs via fish consumption. Similarly, due to a diet richer in cheese, non-Hispanic white adults were estimated to ingest more HFRs than other groups via cheese intake, which resulted in this group having the second highest dietary intake of HFRs. Due to limited sample size of this study and the availability of data on food consumption in the

US, a more in-depth analysis of the role of socio-economic factors in the overall exposure to HFRs was not possible, but it should be explored in follow-up studies.

Here, the estimated dietary intake of PBDEs for the US population was at least 3 orders of magnitude lower than the corresponding reference doses (RfDs) suggested by the US EPA for all routes of exposure (See Table S20 for a summary of RfDs for HFRs of interest) (USEPA, 2017) and 6 to 8 orders of magnitude lower than the corresponding RfDs suggested by European Chemicals Bureau (Pakalin et al., 2007) and by two other studies (Ali et al., 2012; Wang et al., 2013). It is therefore reasonable to speculate that health burdens posed by dietary intake of HFRs are minimal for the US population, although it should be noted that these oral RfDs refer to all possible routes of exposure to HFRs and diet is only one of them, with inhalation and dust ingestion playing a major role. Additionally, the RfD values are available for only a few compounds and do not consider the cumulative effect of complex mixtures containing up to a hundred individual chemicals. Therefore, the contribution of diet in the overall exposure to HFRs should be further evaluated in a broader context. Additionally, these results suggest that some groups of the US population might be exposed to higher levels of HFRs, in particular NBFRs, an observation that should be taken into account in exposure scenarios.

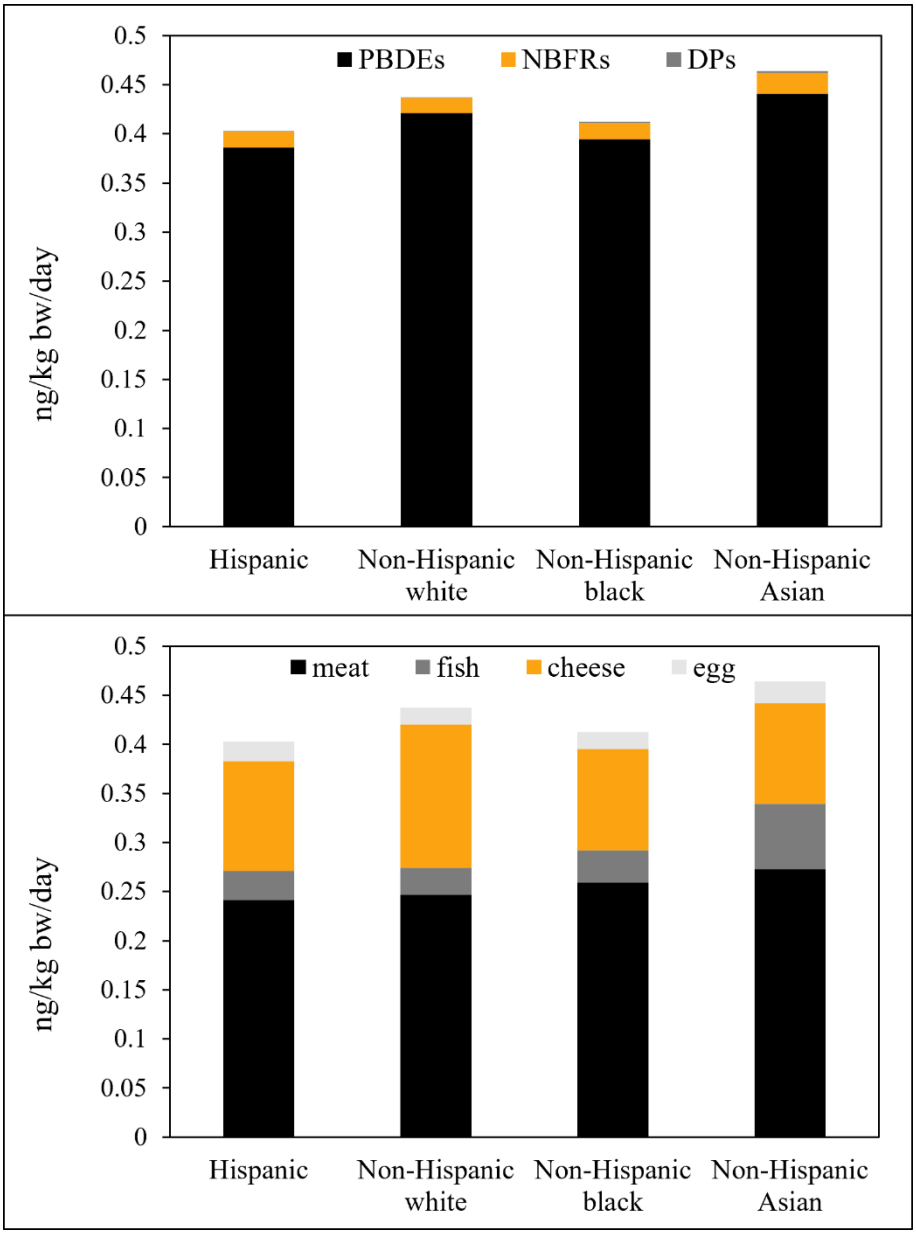


Fig. 3-2. Estimated median dietary intake of HFRs for US adults (≥ 20 years old) of different races: contribution of different FR classes (upper) and food categories (lower). See Table S19 for detailed data.

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Chapter Four

Temporal Trends in Concentrations of Brominated Flame Retardants in UK Foodstuffs Suggest Active Impacts of Global Phase-out of PBDEs and HBCDD

This chapter has been published in *Science of the Total Environment*:

Ma, Y., Stubbings, W.A., Abdallah, M.A.E., Cline-Cole, R., Harrad, S. (2023). Temporal trends in concentrations of brominated flame retardants in UK foodstuffs suggest active impacts of global phase-out of PBDEs and HBCDD. *Science of the Total Environment,* 863: 160956.

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 (28-1,400%) 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.

Keywords

dietary exposure; NBFRs; BTBPE; BEH-TEBP; DBDPE

4.1 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 their persistence in the environment and capacity for bioaccumulation (Fernandes et al., 2016; Labunska 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.

4.2 Materials and Methods

4.2.1 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℃ prior to analysis.

4.2.2 Analytical protocols

Information on the chemicals and reagents used in this study was given in Section 1.1 in Supplementary Materials (Appendix. C). 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.

4.2.3 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).

4.2.4 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.

4.2.5 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).

4.3 Results and Discussion

4.3.1 Concentrations and relative abundance of BFRs in UK foodstuffs

Table 4-1 presents descriptive statistics for all the target BFRs in UK foodstuffs. Mean concentrations of BFRs in different food items are shown in Fig. 4-1, with detailed data provided in Tables S6 – S9. The relative contributions of NBFRs, PBDEs, and HBCDD isomers to total BFRs are shown in Fig. 4-2 and Fig. S2.

4.3.1.1 Concentrations and relative abundance of NBFRs in UK foodstuffs

Concentrations of $\sum_9$NBFRs ranged from <0.42 ng/g lw (<110 pg/g ww) to 170 ng/g lw (5,600 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 less than 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).

4.3.1.2 Concentrations and relative abundance of PBDEs in UK foodstuffs

Concentrations of $\sum_8$PBDEs 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.

4.3.1.3 Concentrations and relative abundance of HBCDDs in UK foodstuffs

$\sum_3$HBCDDs made only a very small contribution (1.2%) to total BFR concentrations in UK foodstuffs. Concentrations of $\sum_3$HBCDDs 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 less than 50% of our samples. With an average contribution of 50% to $\sum_3$HBCDDs concentrations, α-HBCDD was most abundant, followed by β-HBCDD and γ-HBCDD, which account for 37% and 13% of $\sum_3$HBCDDs 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), 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.

Table 4-1. 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)
$\sum_9$NBFRs	**-**	**<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

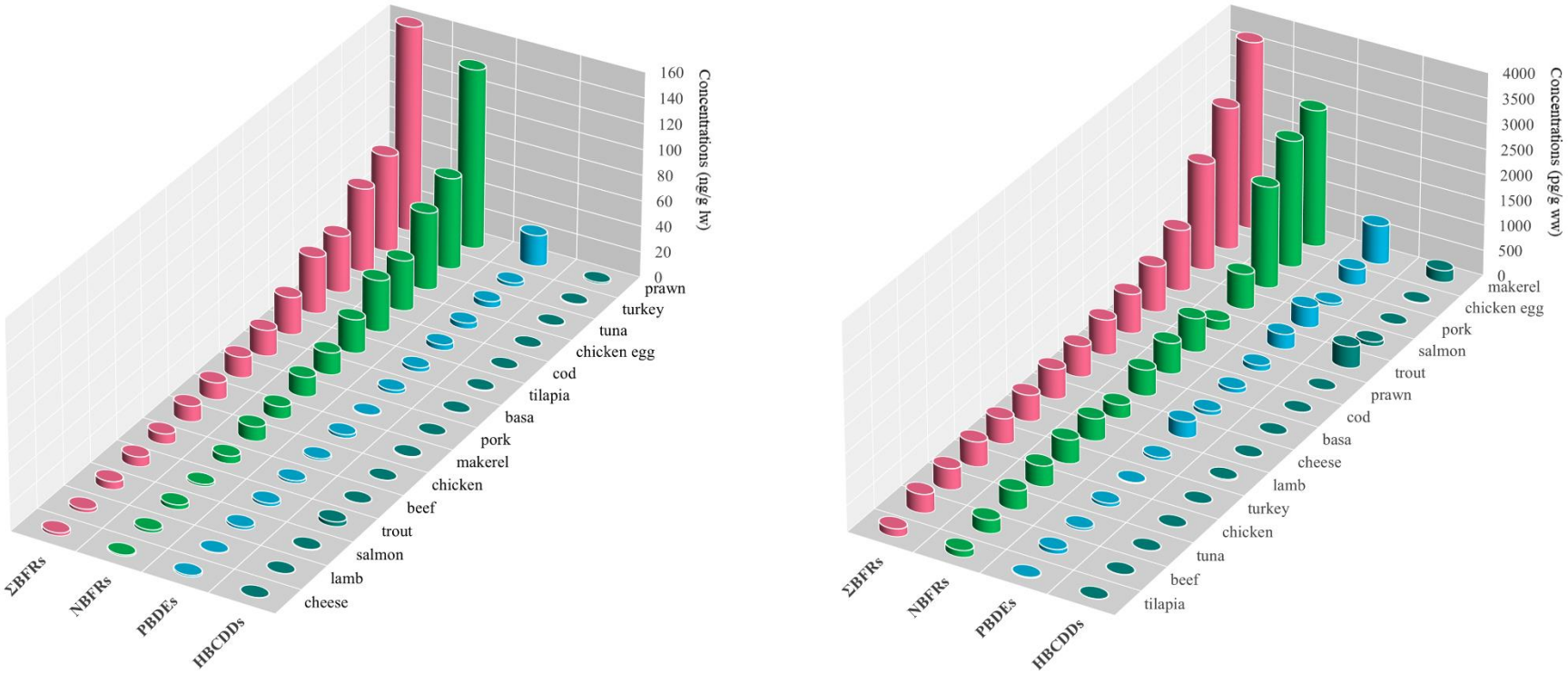


Fig. 4-1 Mean concentrations of BFRs in UK foodstuffs (left: data based on lipid weight; right: data based on wet weight)

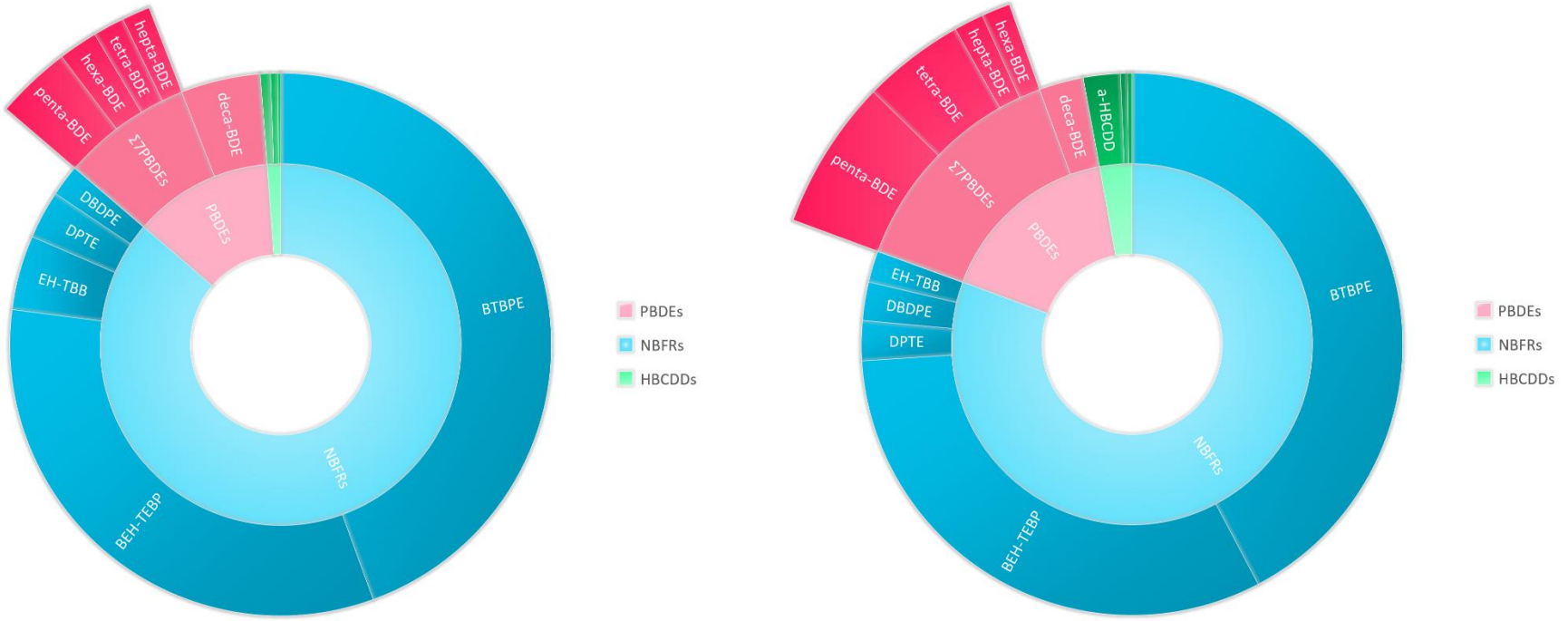


Fig. 4-2 Relative abundance of NBFRs, PBDEs, and HBCDDs in UK foodstuffs (left: data based on lipid weight; right: data based on wet weight)

4.3.2 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. 4-3 and Fig. S3a-S5b).

4.3.2.1 Temporal changes in NBFR concentrations in UK foodstuffs

$\sum_4$NBFRs: Arithmetic mean concentrations of $\sum_4$NBFRs in meat, fish, cheese, and eggs have increased by 110%, 320%, 28%, and 1,400% 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 4,540-22,700 tonnes in 2006 to 22,700-45,400 tonnes in 2012 (Hong et al., 2015), and global production of BTBPE also climbed sharply from ~5,000 tonnes to 16,710 tonnes 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 450-4,500 tonnes (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 less than 450 tonnes in the US (Knudsen et al., 2016; Xiong et al., 2019).

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 (43-1,900 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.

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 1,100%, 3,000%, 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).

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 (16-8,900) (Hou et al., 2022; La Guardia et al., 2012; Lee et al., 2019) and half-lives (29-1,000 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.

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.

4.3.2.2 Temporal changes in PBDE concentrations in UK foodstuffs

Significantly lower concentrations were observed in UK foodstuffs for both $\sum_6$PBDEs ($p < 0.001$) and individual PBDE congeners ($p = 0.0011$-0.065). Concentrations of $\sum_6$PBDEs 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 $\sum_6$PBDEs 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 (Fig. S4a and S4b). A possible explanation for this was debromination of BDE-209 to lower-brominated BDEs, as chicken eggs had higher ratios of $\sum_{\text{tri-hepta}}$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.

4.3.2.3 Temporal changes in HBCDD concentrations in UK foodstuffs

Similar to PBDEs, concentrations of $\sum_3$HBCDDs in UK foodstuffs also declined significantly ($p = 0.003$). $\sum_3$HBCDD concentrations in meat, fish, cheese, and chicken eggs fell by 97%, 87%, 59%, and 85% between 2015 to 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.

4.3.3 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 et al. (2022), and is summarised in Tables S14-S16.

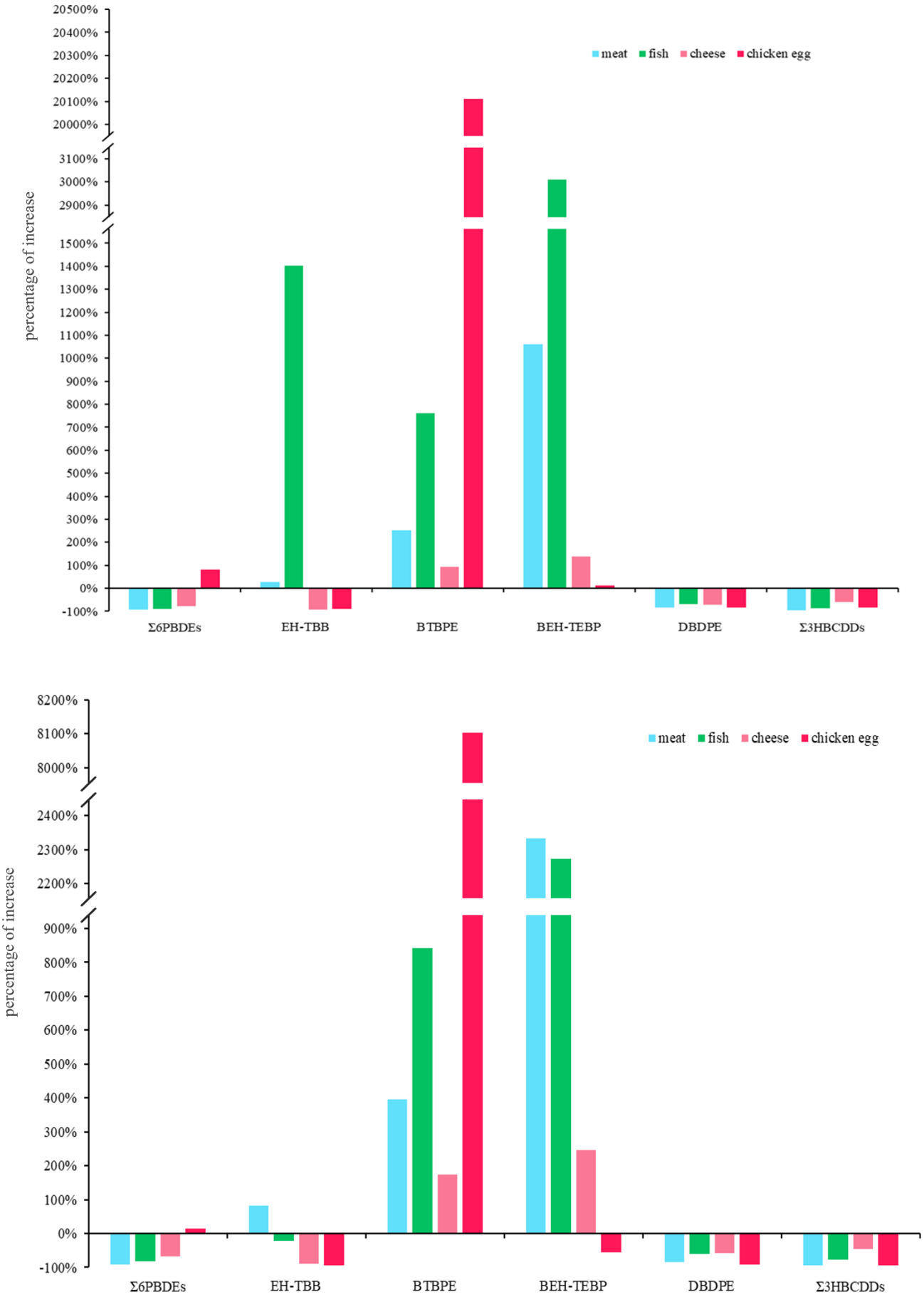


Fig. 4-3 Increase in BFR concentrations in UK foodstuffs between 2015 and 2020/2021 (up: data based on lipid-weight concentrations; down: data based on wet-weight concentrations)

Estimates of daily dietary intake of BFRs for UK citizens are shown in Table 4-2 and Fig. 4-4, 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%).

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 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).

Table 4-2. 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.

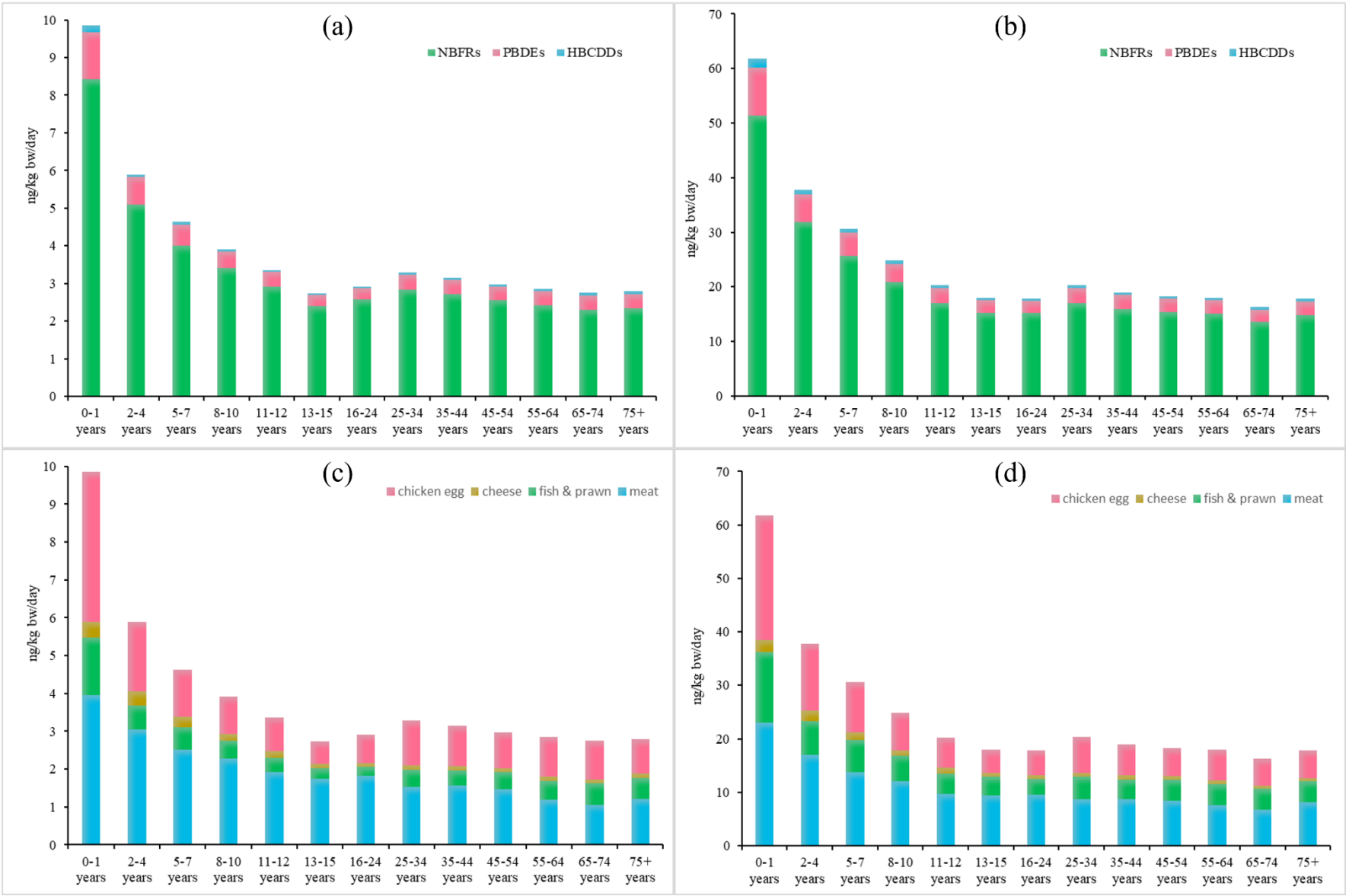


Fig. 4-4 Estimated dietary intake of BFRs for UK citizens from different age groups ((a) and (c): average estimations where average food intakes were assumed; (b) and (d): high-end estimations where high-end food intakes of average + 2SD were assumed)

As is shown in Fig. 4-4, 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.

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Chapter Five

Impact of Legislation on Brominated Flame Retardant (BFR) Concentrations in UK Indoor and Outdoor Environments: Evidence for Declining Indoor Emissions of Some Legacy BFRs

This chapter has been submitted to *Environmental Science & Technology* and is currently under review.

Abstract

Concentrations of polybrominated diphenyl ethers (PBDEs), hexabromocyclododecane (HBCDD), and novel brominated flame retardants (NBFRs) were measured in indoor dust, indoor air, and outdoor air in Birmingham, UK. Concentrations of ΣBFRs ranged from 490-89,000 ng/g, 46-14,000 pg/m^3, and 22-11,000 pg/m^3, respectively, in UK indoor dust, indoor air, and outdoor air. BDE-209 and decabromodiphenyl ethane (DBDPE) were the main contributors. The maximum concentration of DBDPE (10,000 pg/m^3) in outdoor air is the highest reported anywhere to date. For outdoor air, we observed significant correlations between concentrations of tri- to hepta-BDEs and HBCDD and temperature. These suggest primary emissions from active use of these BFRs have diminished and are now outweighed by secondary emissions (e.g., evaporation of BFRs from soil). Conversely, the lack of significant correlations between temperature and concentrations of BDE-209 and DBDPE, indicate ongoing primary emissions from indoor sources remain important for these BFRs. Comparison with earlier studies in Birmingham reveals significant ($p < 0.05$) declines in concentrations of legacy BFRs, but significant increases for NBFRs over the last decade. While there appears minimal health burdens from BFR exposure for UK adults, dust ingestion of BDE-209 may pose significant risk for UK toddlers.

Key words

house dust; ambient air; deca-BDE; NBFRs; human exposure; HBCDD.

5.1 Introduction

Polybrominated diphenyl ethers (PBDEs) and hexabromocyclododecane (HBCDD) are two classes of brominated flame retardants (BFRs) which have been ubiquitously used in commercial products. Following the frequent detection of these BFRs in environmental media (Al-Omran and Harrad, 2016a, b; Cao et al., 2022; de la Torre et al., 2018; Esplugas et al., 2022; Katima et al., 2018; Li et al., 2022; Tao et al., 2016a; Zhang et al., 2022; Zhou et al., 2022), biota samples (Bearr et al., 2012; He et al., 2012; Hou et al., 2022; Law et al., 2006; Ma et al., 2023; Tao et al., 2017; Tao et al., 2016b), and even human samples (Guo et al., 2018; Li et al., 2018; Li et al., 2017; Ma et al., 2017; Qiao et al., 2019; Shi et al., 2019; Tao et al., 2017), along with reports of adverse effects of these BFRs on the environment and human health (Guo et al., 2019; Hou et al., 2021; Ma et al., 2021; Zheng et al., 2017), commercial use of penta-/octa-BDEs and deca-BDE was banned in Europe in 2004 and 2008, respectively (Ma et al., 2022). Subsequently, penta-/octa-BDEs, HBCDD, and deca-BDE were listed under the Stockholm Convention in 2009, 2014, and 2017, respectively, leading to global phase-out of commercial production and use of these legacy BFRs (Ma et al., 2022). Nevertheless, environmental contamination with legacy BFRs is expected to last for decades due to their persistence, as well as global in-use and waste stocks of PBDEs and HBCDD (Abbasi et al., 2019; Li and Wania, 2018).

This has resulted in increasing demand for novel BFRs (NBFRs) as substitutes for legacy BFRs, with the most commonly used NBFRs being: decabromodiphenyl ethane (DBDPE), bis(2,4,6-tribromophenoxy) ethane (BTBPE), bis(2-ethyl hexyl) tetrabromophthalate (BEH-TEBP or TBPH), and 2-ethyl hexyl-2,3,4,5-tetrabromobenzoate (EH-TBB or TBB) (Ma et al., 2022). To date, NBFRs are less studied in terms of their adverse effects on human health compared to legacy BFRs, yet some previous reports suggested similar or even greater disrupting effects of NBFRs on human hormones compared to PBDEs (Ma et al., 2021).

Global restrictions on use of legacy BFRs and increased use of NBFRs should be

reflected by temporal changes in BFR concentrations in the environment and biota, a hypothesis suggested in previous studies (Drage et al., 2020; Lin et al., 2018; Ma et al., 2017; Ma et al., 2023; Tao et al., 2016a; Tao et al., 2017). This has been verified by our recent study reporting increasing NBFR concentrations but decreasing PBDE and HBCDD concentrations in UK foodstuffs (Ma et al., 2023). In terms of the UK indoor environment, a preliminary study compared concentrations of BFRs in UK indoor dust and indoor air in 2015 with earlier UK-based observations, and reported that concentrations of some legacy BFRs were decreasing in some microenvironments (e.g., BDE-47 and -99 in office air, BDE-209 in office dust), while concentrations of some NBFRs were increasing (e.g., DBDPE in house dust and office dust) (Tao et al., 2016a). Unfortunately, further comparisons were not possible (Tao et al., 2016a), partly due to differences in the designs of the earlier studies used for comparison (e.g., different sampling strategies), as well as limited historical data on NBFR concentrations available. A more recent study further identified a significant decline in BDE-47 and BDE-99 (but not BDE-209) concentrations that coincided with a significant increase in DBDPE concentrations in UK house dust (Drage et al., 2020). To the best of our knowledge, temporal changes in BFR concentrations in UK outdoor air have only been explored once hitherto (Drage et al., 2016). This earlier study reported slightly higher concentrations of tri- to hepta-BDEs and HBCDD in UK ambient air in 2012 than earlier observations, with no significant differences identified (Drage et al., 2016). Again, differences in study designs limited comparability and further exploration of temporal changes in atmospheric concentrations of legacy BFRs, while temporal changes in NBFR concentrations have to our knowledge, never been studied in UK ambient air.

To maximize comparability between studies from different years and sampling sites, for indoor dust and indoor air sampling, we adopted the same protocols as used in our 2015 study (Tao et al., 2016a), and used the outdoor air sampling protocols in an earlier UK-based study (Drage et al., 2016). A total of 8 PBDE congeners (BDE-28, -47, -99, -100, -153, -154, -183, and -209), 9 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, BEH-TEBP (or TBPH), and DBDPE), and 3 HBCDD isomers (α-, β-, and γ-HBCDD) were analyzed in this work. Our aims were to: 1) provide an update on BFR concentrations in UK indoor dust, indoor air, and outdoor air; 2) characterize seasonal variations in BFR concentrations in UK ambient air; 3) identify and explain temporal changes in BFR concentrations in UK indoor and outdoor environments in light of recent legislation; and 4) estimate potential health risks posed by BFR exposure to UK citizens.

5.2 Materials and Methods

5.2.1 Sampling

Floor dust samples (n = 30) were collected from living rooms, kitchens, and bedrooms from 8 UK homes in Birmingham during 2021. Dust samples were collected with a portable vacuum cleaner fitted with pre-cleaned nylon mesh filters of 25 μm pore size in the furniture attachment. A 1 m^2 square area of carpeted floors (or 4 m^2 for non-carpeted floors) was vacuumed for 2 min (or 4 min in case of non-carpeted floors), before the nylon mesh filters were carefully removed, properly sealed, and stored at -18 ℃. Detailed information on indoor dust sampling has been reported elsewhere (Tao et al., 2016a), and is given in the Supporting Information (SI, see Appendix. D).

Indoor air samples (n = 30) were collected from the same rooms as indoor dust samples. Passive air samplers (PAS, see Fig. S1) were deployed for 28 days in living rooms, kitchens, and bedrooms of 8 UK homes in Birmingham in 2021. Each PAS was equipped with a polyurethane foam disk (PUF, 140 mm diameter, 12 mm thickness, Leicester, UK; used for absorbing BFRs of gaseous phase) and a glass fiber filter (GFF, 12.5 cm diameter, 1 μm pore size, Whatman, UK; used for collecting total suspended particulates (TSP)). Harvested PUFs and GFFs were properly sealed and stored at 4 ℃ prior to analysis. Detailed protocols were reported in a previous study (Abdallah and Harrad, 2010), and are described in SI.

Outdoor air samples were collected in backyards of 4 UK homes in Birmingham in 2021 (n = 4), and at the Elms Road Observatory Site (EROS, University of Birmingham, Edgbaston, UK) during September 2021 and August 2022 (n = 12). The same configuration of PAS with a previous investigation (Drage et al., 2016) was used in this study so that observations from the two studies are comparable. Briefly, four PAS were deployed at each site for 28 days, and then were combined to provide one sample for analysis. Samples at EROS were taken monthly to enable seasonal changes in BFR concentrations to be observed. Harvested PUFs and GFFs were properly sealed and stored at 4 ℃ prior to analysis. Detailed information on outdoor air sampling is available in SI.

5.2.2 Analytical protocols

Chemicals and reagents used in this study are given in SI. Protocols for sample preparation and purification have been reported previously (Al-Omran and Harrad, 2016a, b; Drage et al., 2016; Tao et al., 2016a), and are summarized in SI. Briefly, dust samples were sieved and spiked with 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 prior to extraction with hexane and acetone (3:1, v/v). The crude extracts were cleaned with florisil, acid silica, and aminopropyl functionalized silica, and then were reconstituted into 100 μL of toluene containing ^{13}C-BDE-100 and d_{18}-γ-HBCDD as recovery determination (syringe) standards prior to GC-MS and LC-MS/MS analysis. Indoor and outdoor air samples (PUFs (gas phase) and GFFs (particle phase) were combined) were also spiked with internal (surrogate) standards and then were extracted on an accelerated solvent extractor (Dionex ASE 350) with hexane and acetone (3:1, v/v). The crude extracts were concentrated to 2 mL prior to purification with 4-6 mL sulfuric acid (95%), after which the extracts were reconstituted into 100 μL of toluene containing recovery determination (syringe) standards prior to instrumental 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 with a programmable-temperature vaporizer (PTV) injector. Separation of PBDEs and NBFRs was enabled by using a capillary fused silica column (RESTEK, USA, 15 m × 0.25 mm inner diameter, 0.10 μm film thickness). Analysis of HBCDD was conducted on a Shimadzu LC-20AB HPLC (Shimadzu, Kyoto, Japan) equipped with a Varian Pursuit XRS3 C18 (Varian, Inc., Palo Alto, CA, USA) reversed phase analytical column (150 mm × 2 mm i.d., 3 μm particle size), coupled to a Sciex API 2000 triple quadrupole mass spectrometer (Applied Biosystems, Foster City, CA, USA). The MS was operated in electrospray negative ionization (ESI^-) – multiple reaction monitoring (MRM) mode, and the HPLC was. Detailed protocols for GC-MS and HPLC-MS/MS analysis of BFRs have been reported elsewhere (Ma et al., 2023), and is available in SI.

5.2.3 QA/QC

Good linearity was obtained from a five-point calibration for all target BFRs (Table S1). Limits of quantification (LOQs) for the target BFRs were calculated based on a signal to noise ratio of 10 (Tables S2 and S3). A method blank (200 mg of anhydrous sodium sulfate) was analyzed along with each batch of 6 dust samples (Table S4). A field blank (a pre-cleaned PUF disk and a pre-conditioned GFF) was performed at each sampling site when indoor and outdoor PAS were deployed (Table S4). Ten replicate analyses of NIST SRM 2585 (organic contaminants in house dust) were performed prior to sample analyses (Tables S4 and S5). More information on QA/QC procedures can be found in SI.

5.2.4 Statistical analysis

All statistical analyses were conducted with Excel (Microsoft Office 365) and IBM SPSS Statistics 29.0 (Chicago, IL, USA). The data were logarithmically transformed, and normality confirmed prior to statistical analyses. Only BFRs with a detection frequency (DF) exceeding 50% were included in statistical analyses, with values where BFR concentrations were below LOQ designated as half of LOQ.

Table 5-1. Concentrations of BFRs in indoor dust, indoor air, and outdoor air collected from Birmingham, UK during 2021 and 2022. More detailed data can be found in SI.

BFRs	Indoor dust (ng/g; n = 30)			Indoor air (pg/m^3; n = 30)			Outdoor air (pg/m^3; n = 16)		
	DF	Median	Arithmetic mean	DF	Median	Arithmetic mean	DF	Median [a]	Arithmetic mean [a]
Σ_7PBDEs [b]	-	13	65	-	7.4	26	-	3.2 (3.1)	3.4 (3.4)
BDE-209	100%	2,300	9,900	80%	220	460	94%	17 (17)	40 (22)
PBBz	100%	1.9	3.3	100%	6.5	49	100%	0.64 (0.64)	0.61 (0.62)
PBT	100%	5.9	24	100%	51	150	100%	0.80 (0.74)	1.0 (1.1)
PBEB	47%	<0.12	0.18	93%	0.72	2.0	100%	0.44 (0.45)	0.52 (0.52)
DPTE	70%	1.1	3.0	20%	<0.17	19	81%	0.79 (0.79)	0.79 (0.76)
HBBz	100%	1.9	2.7	100%	3.5	6.0	100%	0.33 (0.32)	0.36 (0.34)
EH-TBB	90%	4.5	20	70%	3.8	10	63%	0.14 (0.10)	0.33 (0.34)
BTBPE	83%	15	17	33%	<3.2	19	69%	1.8 (1.5)	9.6 (9.0)
BEH-TEBP	100%	190	1,000	10%	<3.1	40	44%	<0.23 (<0.23)	4.8 (4.7)
DBDPE	100%	930	2,900	70%	46	490	94%	59 (46)	740 (98)
Σ_9NBFRs	-	2,200	4,000	-	140	780	-	81 (63)	760 (120)
Σ_3HBCDDs [c]	-	98	730	-	11	72	-	1.2 (1.2)	5.6 (5.1)

[a] median or arithmetic mean values in parentheses when the outlier (April 2022 EROS) is excluded.

[b] sum of BDE-28, -47, -99, -100, -153, -154, and -183.

[c] sum of α-, β-, and γ-HBCDD.

5.3 Results and Discussion

5.3.1 BFR concentrations in UK indoor and outdoor environments

Concentrations of BFRs in indoor dust, indoor air, and outdoor air collected from Birmingham, UK are summarized in Table 5-1, with more detailed data given in Tables S7-S10.

5.3.1.1 Indoor dust

Concentrations of BFRs (sum of PBDEs, NBFRs, and HBCDD) in house dust ranged from 490 ng/g to 89,000 ng/g, with arithmetic mean and median values of 15,000 ng/g and 7,100 ng/g, respectively. PBDEs were the most abundant BFRs detected in UK house dust, making an arithmetic mean contribution to BFRs of 68%. This was followed by NBFRs, which accounted for 27% on average of total BFRs, while HBCDD only contributed an average of 5%. Arithmetic mean concentrations of PBDEs (predominantly BDE-209), NBFRs (primarily DBDPE and BEH-TEBP), and HBCDD (mainly γ- and α-HBCDD) in UK house dust were: 9,900 ng/g, 4,000 ng/g, and 730 ng/g, with median concentrations of 2,300 ng/g, 2,200 ng/g, and 98 ng/g, respectively.

Table S11 summarizes literature data on BFR concentrations in house dust from different countries. PBDE concentrations reported in this study were considerably lower than those reported in Irish homes (arithmetic mean: 58,000 ng/g) (Wemken et al., 2019), but generally exceeded those reported elsewhere (arithmetic mean: 7.7-4,000 ng/g) (Al-Omran and Harrad, 2016b; Brits et al., 2019; Bu et al., 2019; de la Torre et al., 2020; Esplugas et al., 2022; Lee et al., 2020; Venier et al., 2016; Yadav et al., 2019; Yan et al., 2022; Yang et al., 2022). Our observations of DBDPE concentrations in UK house dust were lower than those reported in Australian homes (arithmetic mean: 14,000 ng/g) (Yang et al., 2022) and Irish homes (arithmetic mean: 39,000 ng/g) (Wemken et al., 2019), but were considerably higher than those reported in other parts of the world. NBFR concentrations in house dust from different countries vary greatly, with DBDPE, BEH-TEBP, and EH-TBB frequently detected as the predominant NBFRs (Al-Omran and Harrad, 2016b; Brits et al., 2019; Bu et al., 2019; de la Torre et

al., 2020; Esplugas et al., 2022; Lee et al., 2020; Venier et al., 2016; Yadav et al., 2019; Yan et al., 2022; Yang et al., 2022). This is consistent with our observations of NBFR profiles in UK house dust. Concentrations of HBCDD reported in this study were comparable to those reported in house dust collected from China (arithmetic mean: 340 ng/g) (Yan et al., 2022), but were considerably lower than the concentrations in house dust from Ireland (arithmetic mean: 2,900 ng/g) and Spain (arithmetic mean: 11,000 ng/g) (Esplugas et al., 2022; Wemken et al., 2019).

An independent samples *t*-test revealed significantly higher concentrations of PBDEs (arithmetic mean: 14,000 ng/g vs 940 ng/g) and HBCDD (arithmetic mean: 1,100 ng/g vs 65 ng/g) in floor dust collected from bedrooms than those from kitchens ($p < 0.01$). Likewise, concentrations of NBFRs in floor dust collected from bedrooms were considerably higher than those from kitchens (arithmetic mean: 4,600 ng/g vs 1,700 ng/g), although the difference was only marginally significant ($p = 0.061$). These observations were consistent with an earlier UK-based study (Kuang et al., 2016). A likely explanation for this could be the carpets frequently used in bedrooms (17 carpeted floors vs 1 non-carpeted floor in this study), i.e., the carpets could either be a source of BFRs or store BFR-containing dust, while carpeted floors were rare in kitchens (all 6 kitchen dust samples were taken from non-carpeted floors in this study). Concentrations of PBDEs (arithmetic mean: 6,200 ng/g), NBFRs (arithmetic mean: 4,300 ng/g), and HBCDD (arithmetic mean: 130 ng/g) in floor dust collected from living rooms, lay between those in bedrooms and kitchens, with no significant differences observed (ANOVA, $p > 0.05$), possibly because carpets were also used in living rooms (2 carpeted floors vs 4 non-carpeted floors in this study), although not as frequently as in bedrooms.

Floor dust samples from two types of residences were collected in this study, i.e., apartments and houses. Concentrations of PBDEs (arithmetic mean: 17,000 ng/g vs 3,500 ng/g) and HBCDD (arithmetic mean: 1,400 ng/g vs 120 ng/g) in dust collected from houses were significantly higher than those in dust from apartments (independent

samples *t*-test, $p < 0.05$). Mostly built in the first decade of the 21st century, the apartments examined in this study were constructed more recently than the houses examined. These results may reflect the phase-out of legacy BFRs, i.e., PBDEs and HBCDD, in construction materials in the UK in recent decades. In terms of NBFRs, however, concentrations of DBDPE (arithmetic mean: 3,900 ng/g in apartments vs 1,700 ng/g in houses) in floor dust from apartments were only marginally significantly higher than those from houses (independent samples *t*-test, $p = 0.098$), while no significant differences were observed for total NBFR concentrations (arithmetic mean: 4,200 ng/g in apartments vs 3,700 ng/g in houses). This suggested applications of NBFRs as substitutes for legacy BFRs in construction or refurbishment of both "newer" apartments and "older" houses in the UK.

5.3.1.2 Indoor air

Concentrations of total BFRs in indoor air were in the range 46-14,000 pg/m^3, with arithmetic mean and median concentrations of 1,300 pg/m^3 and 660 pg/m^3, respectively. Unlike indoor dust where PBDEs dominated BFR concentrations, NBFRs made an average contribution of 59% to total BFR concentrations in indoor air. Arithmetic mean and median concentrations of NBFRs (primarily DBDPE and PBT) were 780 pg/m^3 and 140 pg/m^3, respectively, in indoor air collected from UK homes. This was followed by PBDEs (mainly BDE-209), which had arithmetic mean and median levels of 480 pg/m^3 and 230 pg/m^3, respectively, contributing 36% on average to total BFRs. HBCDD, primarily α-HBCDD, accounted for 5% of total BFRs, with arithmetic mean and median concentrations in indoor air of 72 pg/m^3 and 11 pg/m^3, respectively.

As shown in Table S12, PBDE concentrations in indoor air from UK homes were generally comparable to those reported in Ireland (Wemken et al., 2019), Spain (Esplugas et al., 2022), the US (Venier et al., 2016), Canada (Venier et al., 2016), and China (Cao et al., 2022; Ding et al., 2016), but exceeded considerably those reported in the Czech Republic (Venier et al., 2016) and Japan (Takigami et al., 2009). With respect to indoor air concentrations of HBCDD, our observations of UK homes were

comparable to earlier observations in Ireland and Japan (Takigami et al., 2009; Wemken et al., 2019). Concentrations of DBDPE, the most abundant NBFR, in indoor air of UK homes were similar to previous observations in Ireland (Wemken et al., 2019), China (Ding et al., 2016), and Spain (Esplugas et al., 2022), and were one order of magnitude higher than DBDPE concentrations in indoor air collected from the US (Venier et al., 2016) and Canada (Venier et al., 2016). Importantly, we note that the highest concentration of DBDPE we observed in UK indoor air (10,000 pg/m^3) exceeded the maximum DBDPE concentration observed in indoor air of Irish homes (7,000 pg/m^3) (Wemken et al., 2019), and is exceeded only by the maximum reported in India of 15,400 pg/m^3 (Yadav et al., 2020).

ANOVA revealed no significant differences in BFR concentrations in indoor air from living rooms, kitchens, and bedrooms ($p > 0.05$). Arithmetic mean concentrations of total BFRs were 750 pg/m^3, 1,200 pg/m^3, and 1,600 pg/m^3 in indoor air of living rooms, kitchens, and bedrooms, respectively. This might indicate limited contributions of carpeted floors to BFR concentrations in indoor air, as other factors such as ventilation more likely pose an impact.

Concentrations of PBDEs (arithmetic mean: 650 pg/m^3 vs 340 pg/m^3) and HBCDD (arithmetic mean: 100 pg/m^3 vs 45 pg/m^3) observed in indoor air of "older" houses exceeded considerably those observed in indoor air from "newer" apartments, with such differences statistically significant for PBDEs (independent samples *t*-test, $p = 0.019$). By contrast, no significant differences were observed for NBFR concentrations in indoor air from houses and apartments (independent samples *t*-test, $p > 0.05$), despite the higher concentrations of total NBFRs in indoor air from apartments than from houses (arithmetic mean: 1,200 pg/m^3 in apartments vs 310 pg/m^3 in houses). These observations were consistent with what was observed in indoor dust, and again likely reflect the phase-out of legacy BFRs and increased use of NBFRs as substitutes in the construction industry in the UK.

5.3.1.3 Outdoor air

Concentrations of total BFRs in outdoor air ranged between 22 pg/m^3 and 11,000 pg/m^3, with arithmetic mean and median concentrations of 800 pg/m^3 and 100 pg/m^3, respectively. The highest BFR concentration, which is also an outlier, was observed at EROS at the University of Birmingham in April 2022, i.e., considerably higher concentrations of BDE-209 and DBDPE were identified (BDE-209: 300 pg/m^3 in April 2022 vs 5.1-52 pg/m^3 in other months; DBDPE: 10,000 pg/m^3 in April 2022 vs <0.33-370 pg/m^3 in other months; see Table S10). To our knowledge, this is at least 10 times higher than the highest DBDPE concentrations in outdoor air previously reported elsewhere (Cao et al., 2022; de la Torre et al., 2018; Ding et al., 2016; Qi et al., 2014). We speculate that extensive on-campus construction activities that were conducted to the southwest of EROS may be the source of the elevated concentrations of BDE-209 and DBDPE in outdoor air in this April 2022 sample, as southwest winds prevail across most of the UK. The extensive use of DBDPE in construction materials and the wide occurrence of BDE-209 in recycled materials could contribute to elevated concentrations of DBDPE and BDE-209 in ambient air. Interestingly, concentrations of Σ_7PBDEs (excluding BDE-209), Σ_8NBFRs (excluding DBDPE), and HBCDD in outdoor air in this April 2022 sample were comparable to concentrations observed in other months (Σ_7PBDEs: 4.5 pg/m^3 in April 2022 vs 2.2-5.6 pg/m^3 in other months; Σ_8NBFRs: 27 pg/m^3 in April 2022 vs 3.2-64 pg/m^3 in other months; HBCDD: 12 pg/m^3 in April 2022 vs 0.42-32 pg/m^3 in other months; see Table S10). These results suggest minimal impacts of new construction activities on atmospheric contamination of these BFRs. Further measurement of DBDPE in outdoor air at a wider range of locations would help evaluate whether such elevated concentrations exist elsewhere.

Table 5-1 compares arithmetic mean and median concentrations of BFRs in outdoor air before and after the April 2022 sample is excluded. With this sample included, NBFRs (mainly DBDPE) contributed an average of 94% to total BFRs in outdoor air, followed by PBDEs (predominantly BDE-209) and HBCDD (mainly α-HBCDD), which only

accounted for 5% and 1%, respectively, of total BFRs in outdoor air. When the April 2022 sample is excluded from consideration, however, average contributions of NBFRs, PBDEs, and HBCDD to atmospheric concentrations of BFRs were 79%, 18%, and 3%, respectively.

5.3.2 Correlations between BFR concentrations in indoor and outdoor environments

5.3.2.1 Indoor dust vs indoor air

Correlations between BFR concentrations in paired indoor dust (n = 30) and indoor air (n = 30) samples were examined using Spearman's rho, with test results given in Table S13. Interestingly, while no significant correlations were found for legacy BFRs (i.e., PBDEs and HBCDDs), significant positive correlations were obtained for concentrations of more volatile NBFRs (i.e., those with relatively lower octanol-air partition coefficient (K_{OA}), including PBBz, PBT, and HBBz) in paired indoor dust and indoor air samples ($p < 0.01$); while for less volatile NBFRs (EH-TBB and DBDPE) such significant correlations were not observed. These findings were consistent with an earlier UK-based study (Tao et al., 2016a), and were likely to indicate more rapid equilibrium of more volatile NBFRs in the indoor environment.

5.3.2.2 Indoor air vs outdoor air

A total of 4 outdoor air samples were collected from backyards of four UK homes, and correlations examined between BFR concentrations in the 4 outdoor air samples and arithmetic mean concentrations of BFRs in the corresponding indoor air samples (Table S13). No significant correlations between indoor air concentrations and outdoor air concentrations of most target BFRs were identified, suggesting a lack of clearly discernible impact of indoor environments on BFR contamination of the surrounding outdoor air near the studied homes. However, significant positive correlations were observed for PBT and PBEB concentrations in indoor air and outdoor air (Spearman's rho, $p < 0.001$), which may indicate a common source of PBT and PBEB in indoor and outdoor air, or suggest indoor air is the main source of PBT and PBEB in the

surrounding outdoor air. However, given the limited number of samples in this study, further investigation is needed to confirm this.

5.3.3 Seasonal variations in BFR concentrations in outdoor air

Fig. 5-1 depicts arithmetic mean atmospheric concentrations of BFRs observed at EROS in different seasons, with detailed data given in Table S14 and Fig. S2. Arithmetic mean atmospheric concentrations of total BFRs were 48 pg/m^3, 59 pg/m^3, 3,700 pg/m^3 (or 280 pg/m^3 when the April 2022 sample was excluded), and 260 pg/m^3 in autumn 2021, winter 2021, spring 2022, and summer 2022, respectively. With or without the April 2022 sample, an independent *t*-test revealed significantly higher concentrations of most of the target BFRs in spring and summer compared to autumn and winter ($p < 0.05$), including PBT, BTBPE, BEH-TEBP, DBDPE, Σ_9NBFRs (sum of all target NBFRs), Σ_7PBDEs (sum of BDE-28, -47, -99, -100, -153, -154, and -183), and HBCDD. Atmospheric concentrations of BDE-209 in spring and summer were also considerably higher than those in autumn and winter, although the difference was not statistically significant ($p = 0.13$). Similar findings to these results were reported elsewhere (Katima et al., 2018; Qi et al., 2014), possibly suggesting significant impacts of temperature on atmospheric concentrations of BFRs. To confirm this, an Excel template distributed by the Global Atmospheric Passive Sampling (GAPS) network was used to adjust air sampling rates of PAS in this study (Harner 2021). This enables impacts of ambient air temperature on air sampling rates of PAS to be evaluated, as higher temperature is likely to result in increased molecular diffusion and greater shifts to gas-particle partitioning in ambient air. Fig. S3 compares concentrations of tri-to-hepta-PBDEs and NBFRs before and after air sampling rates of PAS were adjusted with temperature (BDE-209 and HBCDD are not included in the template, and thus are not compared). The adjusted concentrations of PBDEs and NBFRs were very consistent with the pre-adjusted concentrations, with the variations below 1%. This confirms seasonal variations in atmospheric concentrations of BFRs were driven by variations in ambient air temperature and were not due to PAS calibration.

Further, we observed significant positive correlations between temperature and atmospheric concentrations of Σ_7PBDEs (excluding BDE-209; Spearman's rho, r = 0.588, p = 0.044), Σ_8NBFRs (excluding DBDPE; Spearman's rho, r = 0.680, p = 0.015), and HBCDD (Spearman's rho, r = 0.816, p = 0.001). This is interesting, as earlier UK studies failed to observe any significant correlations between atmospheric concentrations of BFRs and temperature (Drage et al., 2016; Harrad and Hunter, 2006), which was regarded as an indicator of ongoing primary emissions from indoor consumer products as an important source of atmospheric BFRs (Drage et al., 2016; Harrad and Hunter, 2006). Yet the significant correlations between concentrations of tri- to hepta-BDEs and HBCDD and temperature observed here suggest that primary emissions from active use of tri- to hepta-BDEs and HBCDD indoors have diminished to the point where they are outweighed by secondary emissions (e.g., evaporation of such BFRs from soil). The lack of significant correlations between BDE-209 and DBDPE concentrations and temperature, however, indicate that ongoing primary emissions from consumer products currently constitute a more important source of deca-BDE and DBDPE in the atmosphere compared to secondary emissions. These findings have important implications for policy development designed to reduce environmental contamination with BFRs. To illustrate, current and future actions to eliminate/minimize ongoing indoor sources of BDE-209 and DBDPE are likely to meet with greater success than similar policies aimed at tri-to-hepta-BDEs and HBCDD, for which the majority of emission sources are no longer indoor.

Other weather conditions apart from temperature were also investigated, including precipitation, air humidity, and wind speed (Table S15). Interestingly, while no significant correlations were obtained with Spearman's rho between the number of rainy days or wind speed and atmospheric concentrations of BFRs, significant negative correlations were found between air humidity and outdoor air concentrations of Σ_7PBDEs (excluding BDE-209; r = -0.678, p = 0.015), Σ_8NBFRs (excluding DBDPE; r = -0.907, p < 0.001), DBDPE (r = -0.745, p = 0.005) and HBCDD (r = -0.900, p < 0.001). Negative correlation was also identified between air humidity and atmospheric

BDE-209 concentrations, but the correlation was not significant (r = -0.316, p = 0.316). Atmospheric BFRs tend to accumulate in fine particles (Okonski et al., 2014), which are unlikely to be removed by dry or wet deposition (Katima et al., 2017). However, higher air humidity is known to promote the formation and growth of atmospheric aerosols (Ding et al., 2021). This is likely to explain the lack of impact of precipitation, yet the significant impact of air humidity, on BFR concentrations in the atmosphere.

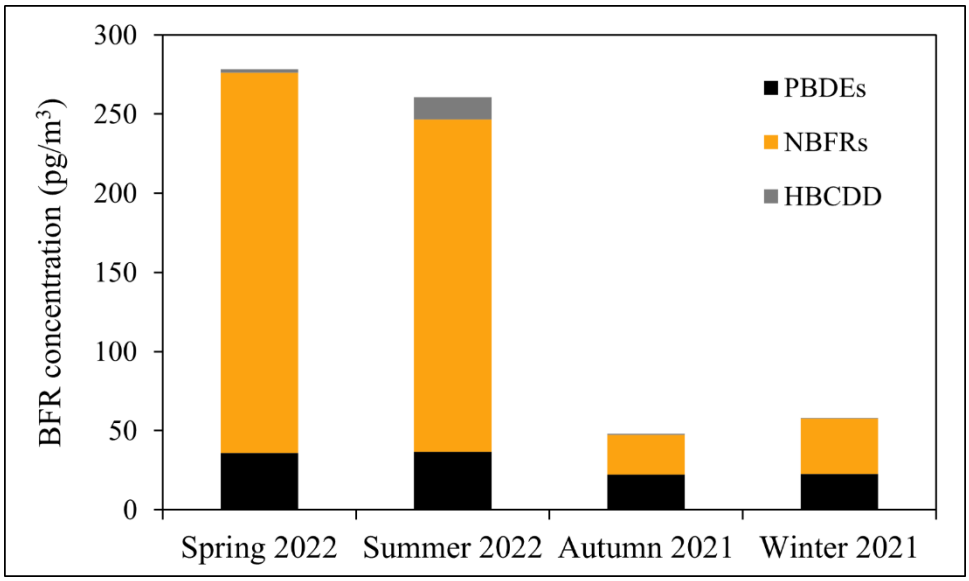


Fig. 5-1 Seasonal variations in atmospheric BFR concentrations observed at EROS (April 2022 excluded). Detailed data can be found in SI.

BFRs	Indoor dust (2015-2021)	Indoor air (2015-2021)	Outdoor air (2012-2021)
BDE-28	-89%	-98% **	-98% *
BDE-47	-59%	-95% **	-89% *
BDE-99	-80% **	-93% **	-93%
BDE-100	-74% **	-91%	-68%
BDE-153	+250%	-91%	-97%
BDE-154	+350%	-90%	-99% *
BDE-183	+280%	+26%	-75% **
BDE-209	-71%	-31%	-75%
ΣPBDEs	-71%	-52%	-78% **
PBBz	0%	+640% *	n.a.
PBT	+240% **	+760% **	n.a.
PBEB	-92%	+27%	n.a.
DPTE	-55%	+450%	n.a.
HBBz	+51% **	-45%	n.a.
EH-TBB	-5%	+110%	n.a.
BTBPE	+21%	+69%	n.a.
BEH-TEBP	+320% **	+300% *	n.a.
DBDPE	+1100% **	+1800% *	n.a.
ΣNBFRs	+640% **	+750% **	n.a.
α-HBCDD	-89% **	-13%	-92% *
β-HBCDD	-93% **	-8%	-95% **
γ-HBCDD	-92% **	-93% **	-95% **
ΣHBCDDs	-91% **	-78% **	-94% *

* significant difference at 0.05 level ($p < 0.05$)

** significant difference at 0.01 level ($p < 0.01$)

n.a. not available due to limited data on NBFR concentrations in 2012

Fig. 5-2 Percentage increase (red) / decrease (green) in arithmetic mean concentrations of BFRs in UK indoor dust, indoor air, and outdoor air (EROS). Detailed data can be found in SI.

5.3.4 Temporal changes in BFR concentrations in UK indoor and outdoor environments

Temporal changes in arithmetic mean concentrations of legacy and novel BFRs in UK indoor dust (2015-2021), indoor air (2015-2021), and outdoor air (2012-2021) are shown in Fig. 5-2. Detailed data can be found in Table S16. To clarify, we used identical passive air sampling rates (Table S6) to those used in the 2015 study for indoor air (Tao et al., 2016a), and the 2012 study for outdoor air (Drage et al., 2016).

5.3.4.1 Legacy BFRs

Considerable declines in concentrations of most of the target legacy BFRs (PBDEs and HBCDD) were observed in UK indoor and outdoor environments. Arithmetic mean concentrations of PBDEs (predominantly BDE-209) dropped by 71%, 52%, and 78% in UK indoor dust (2015-2021), indoor air (2015-2021), and outdoor air (2012-2021), respectively, and such changes in PBDE concentrations in UK ambient air were statistically significant (paired samples *t*-test, $p < 0.01$). With respect to individual PBDE congeners, significant decreases were observed for BDE-99 ($p < 0.01$) and BDE-100 ($p < 0.01$) in indoor dust (independent samples *t*-test), for BDE-28 ($p < 0.01$), BDE-47 ($p < 0.01$), and BDE-99 ($p < 0.01$) in indoor air (independent samples *t*-test), and for BDE-28 ($p < 0.05$), BDE-47 ($p < 0.05$), BDE-154 ($p < 0.05$), and BDE-183 ($p < 0.01$) in outdoor air (paired samples *t*-test). Arithmetic mean concentrations of BDE-209 also decreased considerably in UK indoor dust (by 71%), indoor air (by 32%), and outdoor air (by 75%), but the differences were not significant ($p > 0.05$). These results likely reflect the much later global phase-out of deca-BDE in commercial products compared to penta- and octa-BDEs. Not surprisingly, concentrations of HBCDD also declined significantly in UK indoor dust (independent samples *t*-test, $p < 0.01$) and indoor air (independent samples *t*-test, $p < 0.01$) during 2015 and 2021, and in UK outdoor air (paired samples *t*-test, $p < 0.05$) during 2012 and 2021. It is notable that earlier studies conducted in the UK failed to observe any significant changes in HBCDD concentrations in indoor and outdoor samples (Drage et al., 2020; Tao et al., 2016a), suggesting that decreases in indoor contamination of HBCDD were slow and that

insufficient time had elapsed for significantly declined HBCDD concentrations to be observed when the studies were conducted (Drage et al., 2020). Therefore, this is the first report of significantly declining indoor and outdoor concentrations of HBCDD in the UK, suggesting active impacts on UK indoor and outdoor environments of restrictions on HBCDD use.

5.3.4.2 NBFRs

We observed a significant increase in NBFR concentrations in UK indoor dust ($p < 0.01$) and indoor air ($p < 0.01$) between 2015 and 2021 by using independent samples *t*-tests. Arithmetic mean concentrations of total NBFRs increased by 640% and 750%, respectively, in UK indoor dust and indoor air. The greatest increase was observed for DBDPE, the predominant NBFR. Arithmetic mean concentrations of DBDPE in UK house dust increased from 240 ng/g to 1,500 ng/g during 2015 and 2019 (Drage et al., 2020; Tao et al., 2016a), reaching 2,900 ng/g in 2021, i.e., an increase by 1,100% between 2015 and 2021 ($p < 0.01$). DBDPE concentrations also increased by 1,800% in UK indoor air ($p < 0.05$) during 2015 and 2021. This could be attributed to the extensive use of DBDPE as a replacement for deca-BDE in recent years (Ma et al., 2022). Arithmetic mean concentrations of BTBPE and BEH-TEBP, substitutes for penta- and octa-BDEs, also increased by 21% and 320% in indoor dust and by 69% and 300% in indoor air, respectively; these changes were significant for BEH-TEBP (independent samples *t*-test; indoor dust: $p < 0.01$; indoor air: $p < 0.05$). Significant increases were also found in PBBz concentrations in indoor air (independent samples *t*-test, $p < 0.05$), in PBT concentrations in indoor dust and indoor air (independent samples *t*-test, $p < 0.01$), and in HBBz concentrations in indoor dust (independent samples *t*-test, $p < 0.01$). While this might be due to their increasing consumption in the UK (data on UK consumption of PBT and HBBz is scarce), these bromobenzenes were more likely to be degradation products of deca-BDE or DBDPE (Ma et al., 2012; Venier et al., 2012). With respect to outdoor air, no reports other than the 2012 study (Drage et al., 2016) were identified of atmospheric concentrations of the target NBFRs in the UK. Most of the target NBFRs were not detected in UK ambient air in that study, with

BEH-TEBP and DBDPE the only exceptions detected in 33% and 50% of the UK outdoor air samples, respectively (Drage et al., 2016). Therefore, concentrations of the target NBFRs were not reported in this earlier study, making it hard to evaluate temporal changes in atmospheric NBFR concentrations in the UK. Notwithstanding this, the much higher detection frequencies of NBFRs in UK ambient air observed in the present study compared to those in the 2012 study suggest concentrations of NBFRs in UK outdoor air have risen over the last decade. Further investigations are encouraged to confirm this finding.

5.3.5 Estimates of human exposure to BFRs for UK residents

Daily intake of BFRs via dust ingestion and inhalation for UK adults (≥ 16 years old) and toddlers (≤ 3 years old) was estimated by using equations S1 and S2, with detailed explanations given in SI. Briefly, mean dust ingestion rates of 20 mg/day and 50 mg/day were assumed for UK adults and toddlers (Harrad et al., 2008; Jones-Otazo et al., 2005; Stuart et al., 2008), respectively, under the mean (median) exposure scenario where mean (median) concentrations of BFRs in house dust were applied; while high dust ingestion rates of 50 mg/day and 200 mg/day were assumed for UK adults and toddlers (Harrad et al., 2008; Jones-Otazo et al., 2005; Stuart et al., 2008), respectively, under the high exposure scenario alongside application of 95th percentile BFR concentrations in house dust. With respect to inhalation exposure to BFRs, mean, median, and 95th percentile concentrations of BFRs in indoor (outdoor) air were adopted to generate the mean, median, and high estimates of exposure to BFRs via indoor (outdoor) air inhalation. Air inhalation rates of 20 m^3/day and 3.8 m^3/day were assumed for UK adults and toddlers, respectively (Tao et al., 2016a).

5.3.5.1 Dust ingestion

Estimates of dust ingestion of BFRs for UK adults and toddlers are summarized in Tables S17 and S18. Mean (median) exposure to total BFRs via dust ingestion was estimated to be 2.8 ng/kg bw/day (1.3 ng/kg bw/day) and 61 ng/kg bw/day (30 ng/kg bw/day) for UK adults and toddlers, respectively, with the high exposure estimates of

30 ng/kg bw/day and 1,000 ng/kg bw/day. PBDEs (mainly BDE-209) dominated dust ingestion of BFRs, accounting for 68% on average of dust ingestion of total BFRs. This was followed by NBFRs (primarily DBDPE and BEH-TEBP) and HBCDD, which contributed an average of 27% and 5%, respectively, to dust ingestion of BFRs.

5.3.5.2 Inhalation

Human inhalation exposure to BFRs was estimated to be 0.25 ng/kg bw/day (0.11 ng/kg bw/day) and 0.41 ng/kg bw/day (0.19 ng/kg bw/day), respectively, for UK adults and toddlers under the mean (median) exposure scenario. The high exposure scenario estimates of BFRs were 0.60 ng/kg bw/day and 0.98 ng/kg bw/day for UK adults and toddlers, respectively. Inhalation of indoor air contributed the major proportion (93% mean) of inhalation exposure to BFRs, partly due to the higher concentrations of BFRs observed in indoor air compared to outdoor air, accentuated by the longer proportion of time spent indoors. Unlike dust ingestion of BFRs, NBFRs contributed most to inhalation exposure to BFRs (61% mean), followed by PBDEs (34% mean) and HBCDD (5% mean).

In this study, PAS were used for air sampling, and total BFR concentrations in TSP and gaseous phase of UK ambient air were used for human inhalation exposure estimates. We acknowledge the limitation of this approach that the relevance of different sizes of airborne particulates to human inhalation exposure to BFRs was not considered. Finer particulate matters (e.g., $PM_{2.5}$) are more relevant to health with respect to inhalation exposure to contaminants, and they generally have higher BFR concentrations due to their larger specific surface areas (Al-Omran and Harrad, 2016a; de la Torre et al., 2018; Ding et al., 2018). Therefore, follow-up studies are favoured to improve the assessment of human inhalation exposure to BFRs.

5.3.5.3 Comparisons with dietary intake

We have previously investigated human dietary intake of BFRs for UK residents (Ma et al., 2023), summarized in Tables S17 and S18. Under the mean exposure scenario,

human exposure to BFRs (sum of dust ingestion, inhalation, and dietary intake) was estimated to be 5.9 ng/kg bw/day and 69 ng/kg bw/day for adults and toddlers, with the high estimates of 48 ng/kg bw/day and 1,100 ng/kg bw/day, respectively. Fig. 5-3 compares the most abundant BFRs when the three exposure pathways were combined. Based on the mean estimates, dust ingestion contributed most to human exposure to BDE-209 (93% for adults and 99% for toddlers), DBDPE (76% for adults and 97% for toddlers), and HBCDD (67% for adults and 96% for toddlers) compared to inhalation exposure and dietary intake. By contrast, dietary intake accounted for 95% and 99% of adults' exposure to tri- to hepta-BDEs and BTBPE and accounted for 75% and 98% of toddlers' exposure to tri- to hepta-BDEs and BTBPE, respectively. This is likely due to the higher dust concentrations and lower bioavailability (Ma et al., 2023) of BDE-209, DBDPE, and HBCDD compared to tri- to hepta-BDEs and BTBPE.

5.3.5.4 Comparisons with earlier studies in the UK

Table 5-2 compares mean BFR exposure doses estimated for UK residents between 2015 and 2021. Total exposure (sum of dust ingestion, inhalation exposure, and dietary intake) to PBDEs and HBCDD estimated for UK toddlers declined from 100 ng/kg bw/day to 42 ng/kg bw/day and from 35 ng/kg bw/day to 3.2 ng/kg bw/day during 2015 and 2021, respectively. For adults the estimated exposure doses also decreased from 7.4 ng/kg bw/day to 2.3 ng/kg bw/day for PBDEs and from 2.3 ng/kg bw/day to 0.21 ng/kg bw/day for HBCDD, respectively. This highlights the positive impact of regulatory efforts aimed at controlling legacy BFRs in the UK. In the meantime, human exposure to NBFRs increased from 6.3 ng/kg bw/day to 24 ng/kg bw/day for UK toddlers, and from 2.0 ng/kg bw/day to 3.4 ng/kg bw/day for UK adults, respectively, possibly reflecting greater health burdens posed by use of NBFRs as substitutes in the UK.

5.3.5.5 Health risk assessment

The estimated daily intakes (EDIs) of most of the target BFRs both for UK adults and for toddlers were well below the corresponding reference doses (RfDs), reflected by EDI/RfD ratios that are much smaller than 1 for most BFRs (Table S19). This indicates

minimal health burdens posed by exposure to BFRs for UK populations. However, it is noticeable that the US EPA has assigned an oral slope factor for carcinogenic risk of 700 (ng/kg bw/day)$^{-1}$ for BDE-209 (USEPA, 2017). This was exceeded by the EDI of BDE-209 for UK toddlers (830 ng/kg bw/day) under the high exposure scenario. Importantly, we do not include all possible pathways of BFR exposure in this study (e.g., dermal uptake of BFRs was not investigated). The importance of dermal uptake of BFRs via contact with furniture fabrics, particularly in summer, has been highlighted previously (Abdallah and Harrad, 2018). For instance, dermal uptake of penta-BDEs via contact with furniture fabrics was estimated to exceed overall exposure to penta-BDEs via other pathways for American adults during summer, while for HBCDD the estimated dermal uptake of UK adults and toddlers exceeded the reported mean daily intakes via other pathways for these UK age groups (Abdallah and Harrad, 2018). This suggests total exposure to BFRs could be much higher than our estimates for UK adults and toddlers, raising deeper concerns over potential health risks posed by BFRs to toddlers, with BDE-209 of particular interest. Further studies are needed to evaluate this more fully.

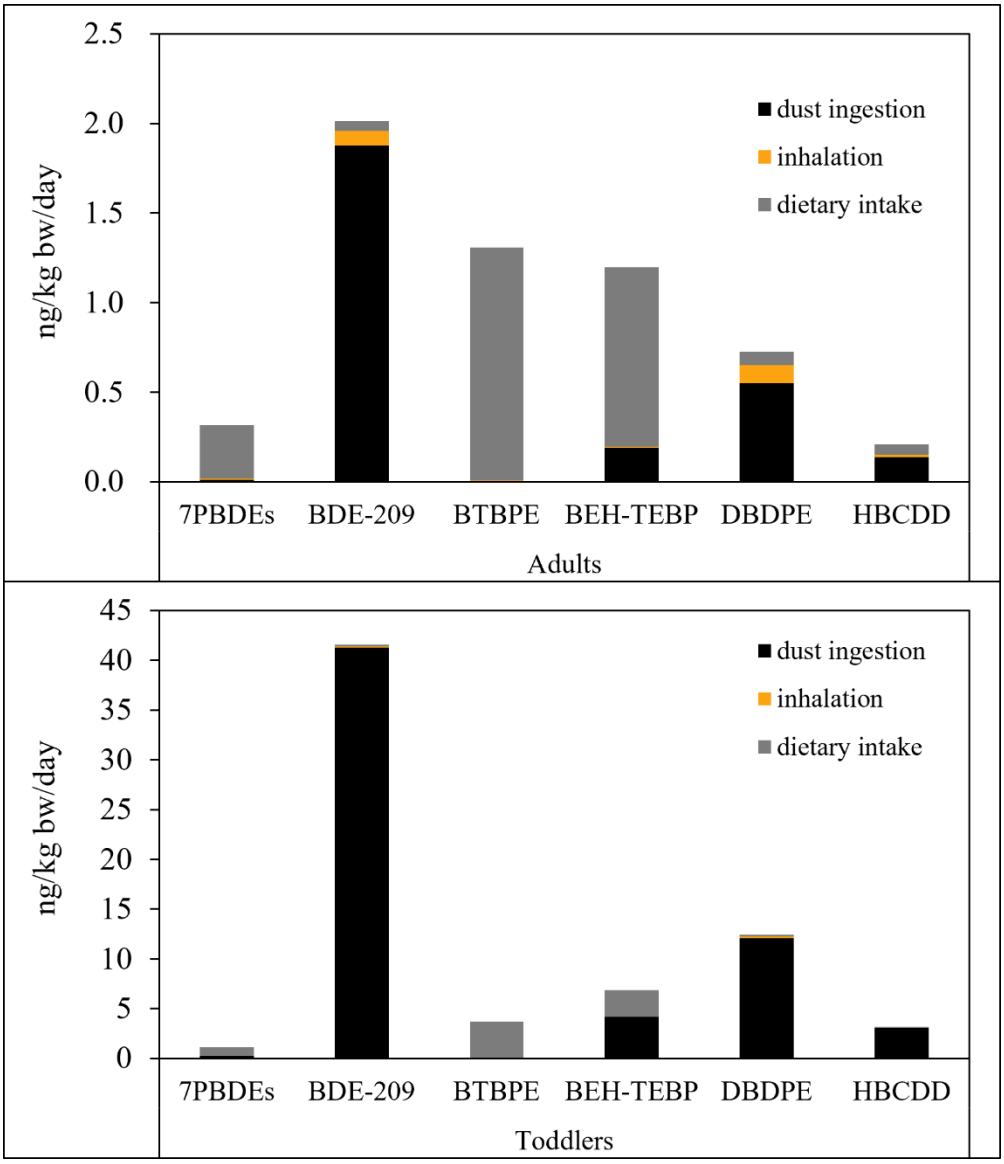


Fig. 5-3 Estimated mean daily intake of BFRs via dust ingestion (this study), inhalation (this study), and dietary intake (Ma et al., 2023) for UK adults and toddlers. 7PBDEs are sum of BDE-28, -47, -99, -100, -153, -154, and -183. Detailed data can be found in SI.

Table 5-2. Temporal changes in estimated mean exposure to BFRs for UK residents between 2015 and 2021 (ng/kg bw/day)

BFRs	Mean exposure estimates in 2015 [a]				Mean exposure estimates in 2021			
	Dust ingestion (Tao et al., 2016a)	Inhalation (Tao et al., 2016a)	Dietary intake (Tao et al., 2017)	Total exposure	Dust ingestion	Inhalation	Dietary intake (Ma et al., 2023)	Total exposure
Toddlers								
PBDEs	100	0.17	4.2	100	41	0.14	1.0	42
NBFRs	3.7	0.029	2.6	6.3	17	0.25	6.8	24
HBCDD	34	0.027	0.88	35	3.0	0.021	0.12	3.2
Total BFRs	140	0.22	7.7	150	61	0.41	7.9	69
Adults								
PBDEs	5.5	0.12	1.8	7.4	1.9	0.083	0.36	2.3
NBFRs	0.72	0.026	1.3	2.0	0.75	0.15	2.5	3.4
HBCDD	1.8	0.076	0.44	2.3	0.14	0.012	0.057	0.21
Total BFRs	8.0	0.22	3.5	12	2.8	0.25	2.9	5.9

[a] data converted from ng/day to ng/kg bw/day.

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Chapter Six

Are UK E-waste Recycling Facilities a Source of Environmental Contamination and Occupational Exposure to Brominated Flame Retardants?

This chapter has been published in *Science of the Total Environment*:

Ma, Y., Konecna, E., Cline-Cole, R., Harrad, S., Abdallah, M.A.E. (2023). Are UK E-waste recycling facilities a source of environmental contamination and occupational exposure to brominated flame retardants? *Science of the Total Environment*, 898: 165403.

Abstract

Investigations into the impacts of regulated electrical and electronic waste (e-waste) recycling activities on urban environments in Europe remain rather scarce. In this study, dust samples taken both inside and outside of five UK e-waste recycling facilities were analysed for concentrations of polybrominated diphenyl ethers (PBDEs), novel brominated flame retardants (NBFRs), and hexabromocyclododecane (HBCDD). Average concentrations of ∑BFRs in dust inside and outside UK e-waste recycling facilities were 12,000 ng/g and 180 ng/g, with median concentrations of 7,500 ng/g and 85 ng/g, respectively. BDE-209 and decabromodiphenyl ethane (DBDPE) were the most abundant BFRs in both indoor and kerb dust, making a combined contribution to ∑BFRs of ~90% on average. While four out of the five studied e-waste facilities showed a lack of significant impact on BFR contamination in surrounding environment, one of the studied e-waste recycling facilities was identified as a likely source of BFR contamination to UK urban environments, with industrial activities as another potential source of NBFRs. Occupational exposure of UK e-waste recycling workers to BFRs via dust ingestion was generally lower than that estimated for e-waste recyclers from other countries, but was comparable to BFR exposure via dust ingestion of UK office workers. Our estimates suggested that health burdens posed by dust ingestion of BFRs were minimal for UK e-waste recycling workers.

Keywords

e-waste recycling; BFRs; WEEE; occupational exposure; dust.

6.1 Introduction

Proper treatment of electrical and electronic waste (e-waste), also known as waste electrical and electronic equipment (WEEE), is a global concern due to sharply increasing volumes of e-waste and the presence of a range of hazardous chemicals such as brominated flame retardants (BFRs) (Forti et al., 2020). Global phase-out of legacy BFRs including polybrominated diphenyl ethers (PBDEs) and hexabromocyclododecane (HBCDD) has been implemented due to their persistence, bioaccumulation, and toxicity (Ma et al., 2022), e.g., these legacy BFRs bioaccumulate in humans and act as hormone disrupters (Ma et al., 2021). However, such legacy BFRs likely still present a contamination hazard due to their continuing presence in goods remaining in use, as well as in waste (Abbasi et al., 2019; Li and Wania, 2018). Restrictions on the use of legacy BFRs also resulted in increasing demand for novel BFRs (NBFRs) as replacements (Ma et al., 2022; Ma et al., 2021). This has generated a new challenge for public health, as some NBFRs showed similar or even stronger adverse effects on human health (Guo et al., 2019; Guo et al., 2018).

The impact of e-waste dismantling and recycling activities on BFR contamination to surrounding environments has been investigated in Asia and Africa, with China being the most studied area (Ma et al., 2022; Ma et al., 2021). Those studies revealed substantially increased concentrations of BFRs in soil or road dust in the vicinity of e-waste facilities, indicating e-waste activities, formal or informal, as an important source of BFR pollution in the studied regions (Ma et al., 2022; Ma et al., 2021). However, such investigations outside Asia and Africa are rather scarce, with only one study identified reporting considerably higher concentrations of PBDEs (median concentrations: 130–160 ng/g dw vs 21 ng/g dw) and NBFRs (median concentrations: 3.8–15 ng/g dw vs <0.02 ng/g dw) in urban soil surrounding two Australian e-waste recycling plants than in reference soil (McGrath et al., 2018). To the best of our knowledge, the impacts of regulated e-waste recycling activities on environmental contamination with BFRs have not hitherto been evaluated in Europe.

This is a potential oversight, as Europe has outperformed other regions in the world in e-waste recycling. The EU initially set a limit on the permissible concentration (1,000 mg/kg) of PBDEs and HBCDD in recyclable plastics in e-waste, known as the low persistent organic pollutant (POP) content limit (LPCL) (European Union, 2019), which has been further reduced from 1,000 mg/kg to 500 mg/kg in June 2022 (European Council, 2022). In 2019, around 42.5% of e-waste generated in Europe was documented to be recycled, with this figure 54.4% in the UK (Forti et al., 2020). This formally collected e-waste was expected to present environmental contamination and human health risks, even when environmentally-sound techniques and personal protective equipment are implemented (Ma et al., 2022; Nguyen et al., 2019). Given this background, the current study determines BFR concentrations in dust collected from both inside and outside of five UK e-waste recycling facilities. Our aims are to: 1) evaluate potential impacts of e-waste recycling activities on BFR contamination of the surrounding environment; and 2) estimate occupational exposure to BFRs via dust ingestion for UK e-waste recycling workers**,** and evaluate its potential health risks.

6.2 Materials and Methods

6.2.1 Sampling

Dust samples were collected from inside (n = 6; see Fig. 6-1) and outside (n = 30; see Fig. 6-2) of five e-waste recycling facilities located in the West Midlands of the UK between September and November 2022. Outdoor (kerb) dust was collected from the kerbs between roads and pavements in the immediate vicinity of the five investigated e-waste recycling facilities. Indoor dust was only collected from inside of Facility #1 due to limited access to other facilities. A vacuum cleaner equipped with pre-cleaned nylon mesh filters (25 μm pore size) was used for dust collection. Detailed information on dust collection protocol has previously been published (Al-Omran and Harrad, 2016b), and is given in Supplementary Materials (Appendix. E).

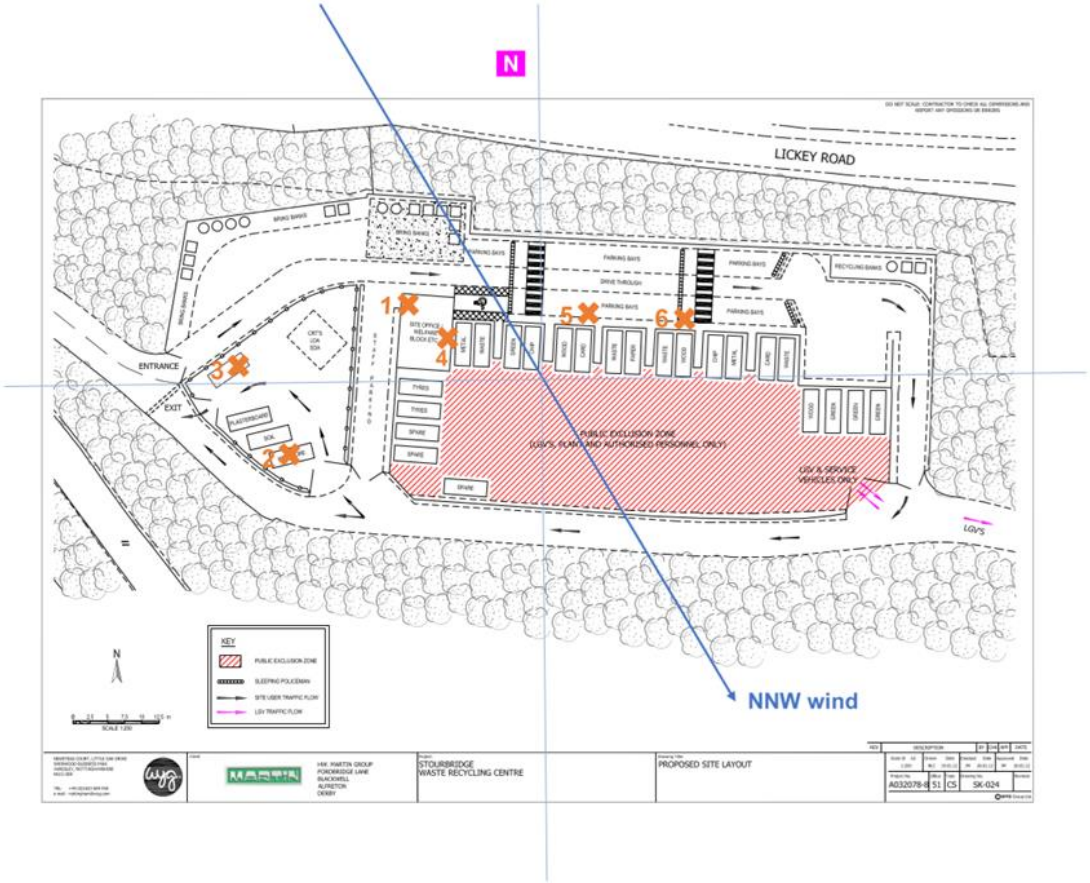


Fig. 6-1 Dust sampling sites inside a UK e-waste recycling facility (Facility #1).

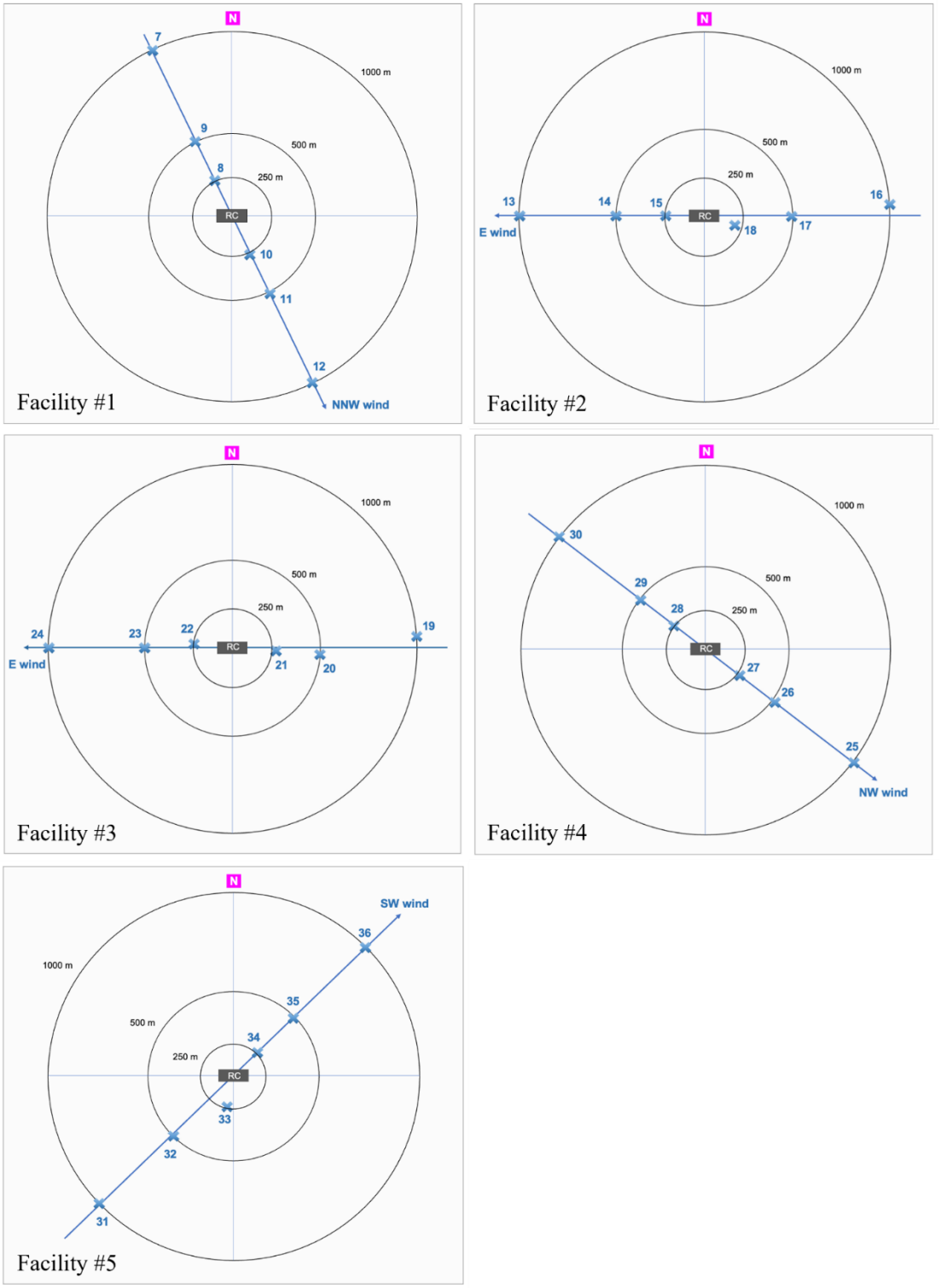


Fig. 6-2 Dust sampling sites outside five UK e-waste recycling facilities.

6.2.2 Analytical protocols

Chemicals and reagents used in this study are listed in SM, and protocols for extraction and clean-up of dust samples have been previously reported (Al-Omran and Harrad, 2016a). Briefly, dust samples were sieved with a stainless-steel test sieve of 500 μm pore size. Approximately 200 mg of dust was accurately weighed and spiked with 15 ng of internal (surrogate) standards (see SM for detailed information) prior to extraction with hexane and acetone (3:1, v/v). The crude extracts were split into two fractions via elution through a florisil column, before further purification with acid silica and aminopropyl functionalised silica, respectively. The two fractions were then combined and reconstituted into 100 μL of toluene containing 15 ng of $^{13}C_{12}$-BDE-100 and d_{18}-γ-HBCDD as recovery determination (syringe) standards prior to GC-MS and LC-MS/MS analysis (Ma et al., 2023). Detailed information on sample preparation and instrumental analysis is provided in SM. Specifically, dried kerb dust samples were heated at 500 ℃ for 4 h to allow organic matter content to be determined gravimetrically.

6.2.3 QA/QC

A five-point calibration was conducted for all the target BFRs (Table S1). Limits of detection (LODs) and limits of quantification (LOQs) for the target BFRs were calculated from a signal to noise ratio of 3 and 10, respectively (Table S2). One method blank was conducted along with each batch of 6 samples, generating 6 analyses of method blanks. No target BFRs were detected in the blanks, so the samples were not blank-corrected. Recoveries of the internal (surrogate) standards in blanks and samples are summarised in Table S3. Ten replicate analyses of NIST SRM 2585 (organic contaminants in house dust) were conducted prior to sample analyses, with results shown in Tables S3 and S4.

6.2.4 Health risk assessment

Daily intake of BFRs via dust ingestion was estimated by using equation (1) (Abdallah et al., 2008):

$$DI = \frac{CBFR \times IR \times FT}{BW} \quad (1)$$

where DI is the estimated daily intake of BFRs via dust ingestion (ng/kg bw/day), $CBFR$ is the concentrations of BFRs in dust (ng/g), IR is the daily ingestion rate of dust (mg/day), FT is the fraction of time e-waste recycling workers spend at work per working day, and BW is the average body weight of UK adults (85.1 kg for males and 71.8 kg for females, respectively (NHS Digital, 2021)). Specifically, the working time of 8 hours per day was assumed for occupational exposure to BFRs under both average and upper-bound exposure scenarios.

Non-carcinogenic risks from BFR exposure were evaluated by using equations (2) (Babalola and Adeyi, 2018):

$$HI = \sum \frac{EDI}{RfD} \quad (2)$$

where HI is hazard index, defined as sum of the ratios of estimated daily dust ingestion of BFRs to the corresponding reference dose (RfD). 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.

6.2.5 Statistical analysis

Statistical analysis was performed with Excel (Microsoft Office 365) and IBM SPSS Statistics 29.0 (Chicago, IL, USA). The data were logarithmically transformed and normality confirmed prior to application of one-way analysis of variance (ANOVA) or *t*-test as appropriate. Only data for those BFRs with a detection frequency (DF) exceeding 50% were included in statistical analyses, with values where BFR concentrations were below LOQ designated as 0.5×LOQ.

6.3 Results and Discussion

6.3.1 BFRs in dust inside UK e-waste facilities

Concentrations of BFRs in dust collected from inside Facility #1 are shown in Fig. 6-3 and Table S5. PBDEs, predominantly BDE-209, were the most abundant BFRs,

contributing an average of 51% to total BFRs. This was followed closely by NBFRs (principally decabromodiphenyl ethane (DBDPE)), which accounted for 44% of total BFRs on average; while HBCDDs (mainly γ-HBCDD) only contributed 5% of total BFRs. Average concentrations of PBDEs, NBFRs, and HBCDDs were 6,300 ng/g, 5,500 ng/g, and 600 ng/g in dust collected from Facility #1, with the corresponding median values being 5,600 ng/g, 1,100 ng/g, and 500 ng/g, respectively. These concentrations were generally higher than BFR concentrations reported in UK house dust in 2019 (see Table S6 for the concentrations) (Drage et al., 2020), but no significant differences were observed with an independent samples *t* test ($p > 0.05$). This is likely because Facility #1 has only been used for storage of e-waste, while dismantling and recycling of the e-waste were done elsewhere. While recognising the limited number of indoor dust samples analysed in this study, this study provides preliminary insights into BFR contamination inside UK e-waste facilities, and further investigations are encouraged to help better understand BFR contamination inside UK e-waste facilities.

The highest concentrations of BFRs were observed in dust collected from two containers used for storage of e-waste. Dust from container #1, which was used for storage of waste TVs and monitors, had higher concentrations of PBDEs (15,000 ng/g) and DBDPE (17,000 ng/g) than dust from container #2 (PBDEs: 6,200 ng/g; DBDPE: 9,400 ng/g), which was used to store waste fridges and freezers. Similar findings to our observations were also reported in a previous study, where considerably higher concentrations of PBDEs (DBDPE was not reported though) were found in plastics of waste displays than in plastics of waste large household appliances in Ireland (Drage et al., 2018). However, dust samples from containers #1 and #2 presented similar relative contributions of PBDEs (41% vs 36%) and DBDPE (48% vs 55%) to total BFRs. Interestingly, higher concentrations (3,600 ng/g vs 98 ng/g) and relative abundance (10% vs 0.58%) of Σ_8NBFRs (DBDPE excluded; predominantly BTBPE), but lower concentrations (530 ng/g vs 1,400 ng/g) and relative abundance (1.5% vs 8.3%) of HBCDD, were found in the dust from container #1 than in that from container #2. A possible explanation could be the much shorter lifespan of TVs and monitors (5-10

years) (US EPA Office of Resource Conservation and Recovery, 2011) than that of fridges and freezers (15 years) (Bawakyillenuo and Agbelie, 2016), which might allow more NBFRs, but not HBCDD, to enter the e-waste stream via waste TVs and monitors.

As shown in Table S6, indoor dust concentrations of PBDEs observed in this study were considerably lower than those reported inside four e-waste storage facilities in Thailand, while concentrations of DBDPE in indoor dust observed in this study were comparable to those observed in the Thai e-waste storage facilities (Muenhor et al., 2010). Further, our observed PBDE and bis(2-ethyl hexyl) tetrabromophthalate (BEH-TEBP) concentrations were one to two orders of magnitude lower than those found in floor dust (no e-waste recycling or dismantling activities were conducted in the areas where floor dust was collected) of a Canadian e-waste facility (Nguyen et al., 2019). When comparing with other facilities where e-waste was dismantled or recycled, indoor dust concentrations of PBDEs observed in this study were also considerably lower than those reported inside both regulated and unregulated e-waste recycling facilities in China (Xu et al., 2015; Zheng et al., 2015; Zhou et al., 2022), Vietnam (Wannomai et al., 2020), and Canada (Stubbings et al., 2019). Moreover, concentrations of 1,2-bis (2,4,6-tribromophenoxy) ethane (BTBPE), BEH-TEBP, and DBDPE in indoor dust inside Facility #1 were at the lower end of those observed in regulated e-waste recycling facilities in Canada (Stubbings et al., 2019) and in unregulated e-waste recycling facilities in China (Xu et al., 2015; Zheng et al., 2015) and Vietnam (Wannomai et al., 2020).

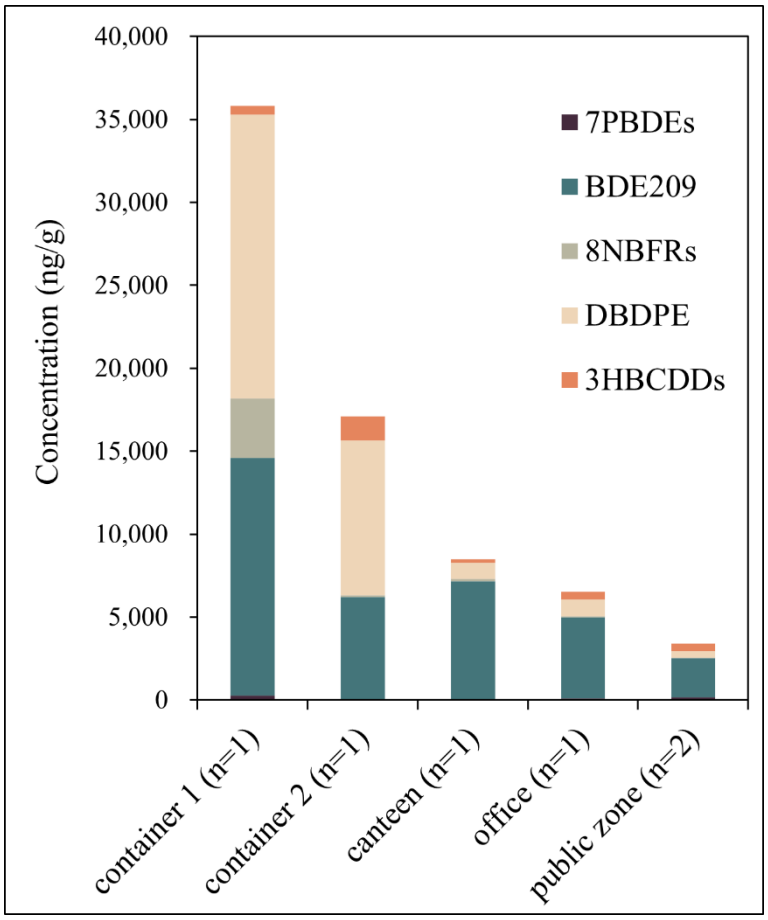


Fig. 6-3 Average concentrations of BFRs in dust inside UK e-waste recycling facilities; 7PBDEs are sum of BDE-28, -47, -99, -100, -153, -154, and -183; 8NBFRs are sum of PBBz, PBT, PBEB, DPTE, HBBz, EH-TBB, BTBPE, and BEH-TEBP; 3HBCDDs are sum of α-, β-, and γ-HBCDD; container 1 is used for storage of TVs & monitors; container 2 is used for storage of fridges & freezers.

6.3.2 BFRs in kerb dust outside UK e-waste recycling facilities

Average concentrations of PBDEs, NBFRs, and HBCDDs were 100 ng/g (2,900 ng/g OC, normalised to the organic carbon content of each dust sample), 66 ng/g (1,700 ng/g OC), and 11 ng/g (250 ng/g OC) in dust collected outside of UK e-waste facilities, with the corresponding median concentrations of 22 ng/g (430 ng/g OC), 47 ng/g (950 ng/g OC), and 6.3 ng/g (140 ng/g OC), respectively (Table S5). As this is the first study reporting BFRs in kerb dust in the UK, comparisons between our observations and BFR concentrations in non-e-waste impacted kerb dust in the UK are unlikely. However, urban soil samples collected from Birmingham, UK could be a reasonable substitute when OC normalised concentrations were used for comparison. Specifically, these concentrations were generally 2 to 3 orders of magnitude higher than OC normalised concentrations of BFRs in urban soils collected from sites with no direct input sources in Birmingham, UK (Table S6) (Drage et al., 2016). An independent samples *t*-test revealed significantly lower concentrations of BFRs in dust collected from kerbs outside Facility #1 than in dust collected inside the same facility (p = 0.001–0.029). Despite the significant differences in absolute concentrations of BFRs, similar profiles of BFRs were observed in dust sampled outside vs inside Facility #1 (Fig. S1). Overall, these results seem to suggest that e-waste recycling activities may be a substantial source of BFR contamination to the surrounding environment.

To verify this, BFRs in kerb dust samples were compared both upwind and downwind of each facility at distances from the sampling sites to the corresponding facility of 250 m, 500 m, and 1,000 m, respectively (Fig. 6-2). A paired samples *t* test revealed no significant difference between the upwind concentrations and the downwind concentrations of BFRs in dust near the UK e-waste recycling facilities (p = 0.134–0.976; see Table S7 for the concentrations). No significant correlations were observed with Spearman's rho ($p > 0.05$) between BFR concentrations in kerb dust and distances from Facilities #1, #2, #3, and #4, either suggesting a lack of significant impact of these e-waste facilities on BFR contamination of surrounding environment, or indicating the number of samples analysed in this study too small to allow any significant impacts to

be observed. However, negative correlations between BFR concentrations and distance from facility #5 were observed for all the target BFRs (Spearman's rho; r = -0.239 – -0.837). These negative correlations were statistically significant for BDE-47, -99, and -100 ($p < 0.05$). Such observations indicated significant impacts of e-waste recycling activities in Facility #5 on BFR contamination in kerb dust. Unlike Facility #1, which is only used for e-waste storage, Facility #5 receives a wide range of e-waste for recycling, including small devices, large domestic appliances, etc. It remains unclear how much e-waste is recycled in Facility #5 per day, but it is reasonable to presume that Facility #5 receives a much larger volume of e-waste compared to Facilities #1, #2, #3, and #4, as Facility #5 is located in a city with a much larger population (more than 1,000,000 vs less than 200,000). Overall, our observations could be strong evidence of e-waste recycling facilities as a potential source of BFR contamination to the urban environment in the UK.

Facility #5, located in an industrial city in the UK, also had significantly higher BFR concentrations in kerb dust than did other facilities (ANOVA, $p = 0.0028$). This might indicate industrial activities as another potential source of BFR contamination to the urban environment in the UK. To confirm this, BFR concentrations in kerb dust from different areas (categorized as: industrial, housing, supermarket, park, and agricultural) were compared (Fig. 6-4). Higher concentrations of BFRs (average: 450 ng/g vs 40–110 ng/g) were found in dust from industrial areas compared to non-industrial areas. An independent samples *t* test revealed a significant difference in concentrations of NBFRs ($p = 0.044$), but not PBDEs ($p = 0.253$) and HBCDDs ($p = 0.983$), between industrial areas and non-industrial areas. This could reflect the phase-out of PBDEs and HBCDDs and the continuous use of NBFRs in industrial activities, and likely indicated industrial activities as a potential source of NBFR contamination. Given the limited sample size of this study, further investigations are encouraged to confirm this.

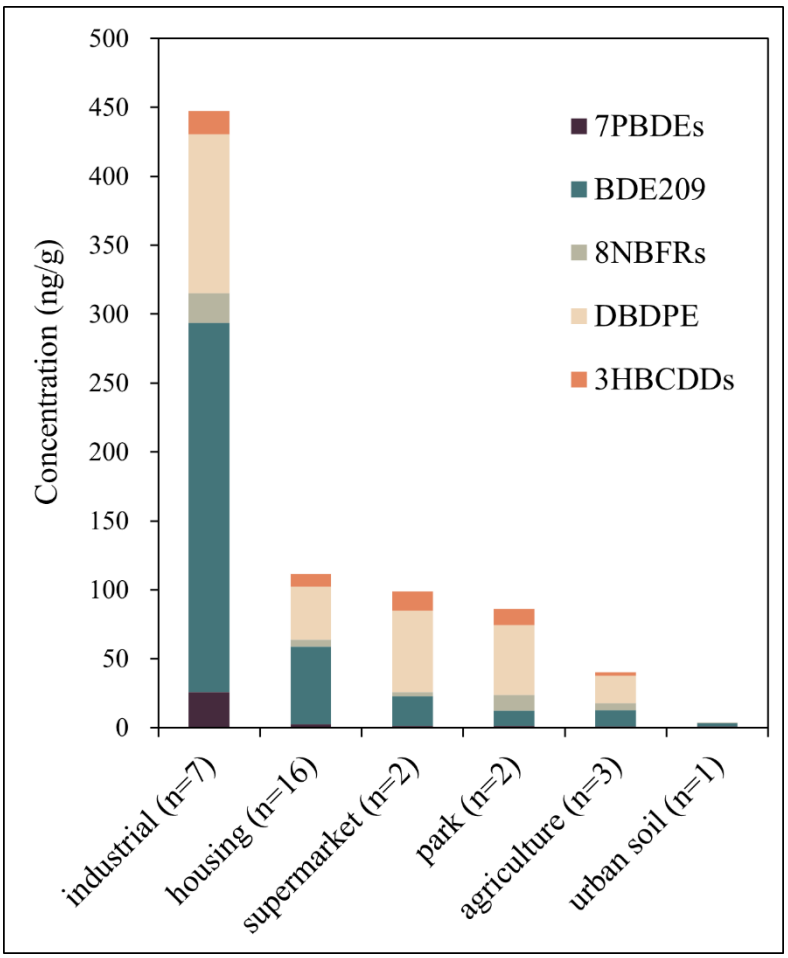


Fig. 6-4 Average concentrations of BFRs in kerb dust from different location categories in the vicinity of UK e-waste recycling facilities, and comparison with PBDE and DBDPE concentrations in an urban soil in the UK (Drage et al., 2016); 7PBDEs are sum of BDE-28, -47, -99, -100, -153, -154, and -183; 8NBFRs are sum of PBBz, PBT, PBEB, DPTE, HBBz, EH-TBB, BTBPE, and BEH-TEBP; 3HBCDDs are sum of α-, β-, and γ-HBCDD.

Concentrations of PBDEs and NBFRs in kerb dust observed here were generally lower than those observed in surface soil surrounding two regulated e-waste recycling facilities in Australia (McGrath et al., 2018), or in kerb dust and surface soil in the vicinity of informal e-waste facilities in China (Ling et al., 2022; Tang et al., 2016; Xu et al., 2015) and Vietnam (Matsukami et al., 2017). However, our observations of PBDE and NBFR concentrations in kerb dust were comparable to or slightly higher than the concentrations determined in urban road dust in China (Cao et al., 2017) and Vietnam (Anh et al., 2018).

6.3.3 Occupational exposure to BFRs via dust ingestion

Occupational exposure of UK e-waste recycling workers to BFRs via dust ingestion was estimated by using equation (1). Average BFR concentrations in indoor dust (or kerb dust) and the recommended central tendency of dust ingestion rate (20 mg/day for indoor dust and 10 mg/day for kerb dust) (US EPA, 2017) were assumed for the average exposure scenario; while the 95th percentile for BFR concentrations in indoor dust and the recommended upper percentile dust ingestion rate (60 mg/day for indoor dust and 50 mg/day for kerb dust) (US EPA, 2017) were assumed to derive the upper-bound estimates of BFR exposure.

Under the average exposure scenario, daily intake of BFRs via indoor dust ingestion was estimated to be 0.98 ng/kg bw/day for male workers and 1.2 ng/kg bw/day for female workers, with the upper-bound estimates of daily intake of BFRs of 7.5 ng/kg bw/day for males and 8.8 ng/kg bw/day for females, respectively. By comparison, daily intake of BFRs via kerb dust ingestion contributed less than 5% to dust ingestion of BFRs (sum of indoor dust ingestion and kerb dust ingestion) of UK e-waste workers (Table 6-1). BDE-209 and DBDPE predominated dust ingestion of BFRs for UK e-waste recycling workers, together contributing an average of 88% to daily intake of total BFRs.

Table 6-1. Occupational exposure of UK e-waste recycling workers to BFRs via dust ingestion (ng/kg bw/day)

Scenarios	Σ_7PBDEs [a]	BDE-209	Σ_8NBFRs [b]	DBDPE	Σ_3HBCDDs [c]
average estimates					
male (indoor dust ingestion)	0.010	0.49	0.052	0.38	0.047
male (kerb dust ingestion)	0.00091	0.011	0.0011	0.0067	0.0012
male (HI)	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001
female (indoor dust ingestion)	0.012	0.58	0.061	0.45	0.055
female (kerb dust ingestion)	0.0011	0.013	0.0013	0.0079	0.0015
female (HI)	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001
upper-bound estimates					
male (indoor dust ingestion)	0.080	2.9	0.66	3.6	0.30
male (kerb dust ingestion)	0.0075	0.16	0.010	0.074	0.020
male (HI)	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001
female (indoor dust ingestion)	0.094	3.5	0.78	4.2	0.36
female (kerb dust ingestion)	0.0089	0.19	0.012	0.088	0.024
female (HI)	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001

[a] sum of BDE-28, -47, -99, -100, -153, -154, and -183;

[b] sum of PBBz, PBT, PBEB, DPTE, HBBz, EH-TBB, BTBPE, and BEH-TEBP;

[c] sum of α-, β-, and γ-HBCDD.

As shown in Table S8, our estimates of dust ingestion of PBDEs for UK e-waste recycling workers were generally one order of magnitude lower than those for e-waste recyclers working in formal and informal e-waste recycling facilities in Canada (Nguyen et al., 2019), China (Xu et al., 2015; Zheng et al., 2015; Zhou et al., 2022), and Vietnam (Wannomai et al., 2020); but were comparable to dust ingestion of PBDEs estimated for UK office workers (Tao et al., 2016). In terms of dust ingestion of DBDPE, our estimates for UK e-waste recyclers were at the lower bound of dust ingestion of DBDPE estimated for informal e-waste recycling workers in China (Xu et al., 2015; Zheng et al., 2015), and were considerably lower than the estimates for informal e-waste recycling workers in Vietnam (Wannomai et al., 2020). Our estimates of dust ingestion of DBDPE for UK e-waste recyclers were also similar to the estimations generated for office workers in China (Sun et al., 2018) and the UK (Tao et al., 2016).

Table S9 shows the reference doses (RfDs) for BFRs of interest. Our estimates of BFR exposure doses were considerably lower than the RfDs (HI < 0.001, see Table 6-1), suggesting minimal health burdens posed by occupational exposure to BFRs to UK e-waste recycling workers. However, it is notable that dust ingestion of BFRs during working hours is likely to contribute only a small proportion to total BFR exposure for UK e-waste recyclers, especially given comparable or even higher concentrations of BFRs than those in this study have been reported in house dust in the UK (Drage et al., 2020; Tao et al., 2016). Also, we realise the limitations of this study, e.g., small sample size and lack of estimates of BFR exposure via inhalation and dermal uptake, could result in underestimation of occupational exposure to BFRs for UK e-waste recycling workers. Further investigations are encouraged to fill the gap.

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Chapter Seven

Conclusions

7.1 Overview of this study

Global restrictions on use of PBDEs and HBCDD have resulted in increased demand for NBFRs, which is expected to pose impacts on human exposure to these legacy and emerging BFRs. Dietary intake, dust ingestion, and inhalation are the main pathways of human exposure to BFRs. This study collected diet samples from two developed economies (i.e., the UK and the US) and one developing economy (i.e., Nigeria), and explored how legislations have impacted on BFR contaminations in foodstuffs and thus on human dietary exposure to BFRs in different economies. Following these investigations on human diet, this study further explored recent changes in BFR contaminations in UK indoor and outdoor environments, and identified impacts of BFR-related legislations on human inhalation exposure to and dust ingestion of BFRs. We also studied impacts of current e-waste recycling activities on urban contamination with BFRs in the UK, and estimated occupational exposure to BFRs via dust ingestion of UK e-waste workers. Overall, this study aims to provide a profound understanding of how global legislations impact on environmental contamination and human exposure to BFRs. The following is the main findings of this study.

7.2 BFRs in foodstuffs from Nigeria, the US, and the UK

(1) Concentrations of BFRs, including PBDEs, HBCDD, and NBFRs, were generally comparable in animal-derived food items collected from Nigeria (sampling time: 2021), the US (sampling time: 2022), and the UK (sampling time: 2020-2021). PBDEs and NBFRs were frequently observed in those foodstuffs, while HBCDD was barely detected.

(2) High concentrations of PBDEs were observed in foodstuffs of Nigerian origin in 2021, which is likely due to active domestic use of PBDEs in Nigeria. This study also reports the first record on NBFR concentrations in foodstuffs of Nigerian origin.

(3) PBDE concentrations in US foodstuffs seemed to be relatively constant with time, but the dominance of di- and tri-BDEs suggested more advanced aging of PBDEs in

US food during the past decade.

(4) Concentrations of NBFRs were reported in general foodstuffs in the US for the first time. Concentrations of NBFRs, but not PBDEs, in US food items were significantly impacted by price, raising the issue of environmental justice.

(5) Concentrations of PBDEs and HBCDD in UK foodstuffs declined significantly during 2015 and 2020-2021, while concentrations of NBFRs increased considerably. This reflects global restrictions in use of legacy BFRs and use of NBFRs as substitutes for legacy BFRs in the UK.

(6) Dietary intake of BFRs is unlikely to pose significant health burdens on residents of the three countries studied.

7.3 BFRs in UK indoor and outdoor environments

(1) BDE-209 and DBDPE contributed most to BFRs in indoor dust, indoor air, and outdoor air in Birmingham, UK. The maximum concentration of DBDPE (10,000 pg/m^3) in outdoor air is the highest reported anywhere to date.

(2) Significantly increased concentrations of NBFRs were observed in indoor dust and indoor air in Birmingham, UK between 2015 and 2021. In contrast, concentrations of PBDEs and HBCDD in UK indoor dust (2015-2021), indoor air (2015-2021), and outdoor air (2012-2021) declined considerably. This reflects restricted use of legacy BFRs and increasing use of NBFRs in the UK.

(3) Significant correlations between atmospheric concentrations of tri- to hepta-BDEs and HBCDD and temperature were observed, suggesting primary emissions from active use of these BFRs have diminished and are now outweighed by secondary emissions (e.g., evaporation of BFRs from soil).

(4) The lack of significant correlations between temperature and concentrations of BDE-209 and DBDPE in outdoor air indicates ongoing primary emissions from indoor sources remain important for these BFRs.

(5) Health burdens of BFR exposure are minimal for UK adults, but our estimates indicate dust ingestion of BDE-209 likely pose significant carcinogenic risk for UK toddlers.

7.4 BFRs in dust inside and outside UK e-waste recycling facilities

(1) BDE-209 and DBDPE were the most abundant BFRs in dust taken both inside and outside of UK e-waste recycling facilities.

(2) Of the five e-waste recycling facilities studied, the one which receives and processes the largest volume of e-waste was identified as a likely source of BFR contamination to UK urban environments.

(3) Industrial activities in the UK were also identified as a likely source of urban contamination with NBFRs, but not with legacy BFRs (i.e., PBDEs and HBCDD).

(4) Our estimates suggested occupational exposure of UK e-waste recycling workers to BFRs via dust ingestion was unlikely to pose significant health burdens on UK e-waste recycling workers.

7.5 Limitations and future directions

This study investigated temporal changes in BFR concentrations in animal-derived food items from three countries, i.e., Nigeria, the US, and the UK, as well as temporal changes in BFR contamination in UK indoor and outdoor environments. Their relevance to human exposure to BFRs was also explored. There are several limitations of this study that should be acknowledged:

(1) the different designs between this study and previous studies in Nigeria make our

observations less comparable to previous publications, and thus impacts of global restrictions on temporal changes in BFR concentrations in Nigerian foodstuffs remain unidentified;

(2) a very limited number of processed food samples of Nigerian origin rather than a whole diet were analysed for BFR contamination, which was likely to contribute to biased estimates of dietary intake of BFRs for Nigerians;

(3) total BFR concentrations in TSP and gaseous phase of UK ambient air were used for human inhalation exposure estimates, and the relevance of different sizes of airborne particulates to human inhalation exposure to BFRs was not considered;

(4) only a small number of dust samples were analysed to demonstrate impacts of regulated e-waste recycling activities on BFR contamination in UK urban environment, and therefore the findings need to be further validated.

Following this work, future studies are encouraged to:
(1) update NBFR concentrations in Nigerian and US foodstuffs, and understand how use of NBFRs contributes to temporal changes in NBFR concentrations in Nigerian and US diet;

(2) keep monitoring the presence of legacy BFRs in the environment, biota, and foodstuffs in Nigeria and other parts of Africa, and investigate impacts of global restrictions on BFR contamination in Africa;

(3) estimate human dietary exposure to legacy and emerging BFRs in Nigeria and other parts of Africa based on a wider range of food items;

(4) focus on the relevance of different sizes of airborne particulates to human inhalation exposure to BFRs;

(5) collect more data on BFR contamination in environmental media (e.g., dust, soil, air, etc.) inside and in the vicinity of formal e-waste recycling facilities in Europe, and learn how regulated e-waste recycling activities impact on urban environments;

(6) explore the significance of human dermal uptake of BFRs via direct contact with fabrics and furniture;

(7) focus on the cumulative health effect of complex mixtures containing a wide variety of BFRs.

Appendix A. Supplementary Materials for Chapter Two

Table S1. Sample information

Food item	n	Lipid content	note
meat	***5***	***21%***	
beef	4	23%	
bush meat	1	16%	African wild animal (oya)
freshwater fish	***7***	***22%***	
tilapia	4	21%	
catfish	3	24%	
saltwater fish	***8***	***13%***	
stockfish	1	10%	cod
shawa	1	18%	herring
sole fish	2	9%	
African knife fish	1	10%	
hake	1	17%	
lizard fish	2	14%	
other	***6***	***9%***	
prawn	1	12%	
periwinkle	1	10%	
African snail	4	8%	
sum	**26**	**16%**	

Table S2. Linearity of the 5-point calibrations

Target compounds	Linearity range (pg/μL)	R^2
BDE-28	10-200	0.9955
BDE-47	10-200	0.9917
BDE-99	10-200	0.9950
BDE-100	10-200	0.9970
BDE-153	10-200	0.9890
BDE-154	10-200	0.9927
BDE-183	10-200	0.9969
BDE-209	10-200	0.9999
PBBz	10-200	0.9935
PBT	10-200	0.9991
PBEB	10-200	0.9985
DPTE	10-200	0.9920
HBBz	10-200	0.9999
EH-TBB	10-200	0.9949
BTBPE	10-200	0.9917
BEH-TEBP	10-200	0.9943
DBDPE	10-200	0.9989
α-HBCDD	10-200	0.9995
β-HBCDD	10-200	0.9997
γ-HBCDD	10-200	0.9999

Table S3. Limit of quantification (LOQ) for each analyte (calculated from a signal to noise ratio of 10)

Target compounds	iLOQ (pg/injection) [a]	mLOQ (ng/g) [b]
BDE-28	0.54	0.11
BDE-47	0.21	0.042
BDE-99	0.46	0.093
BDE-100	0.53	0.11
BDE-153	0.25	0.051
BDE-154	0.22	0.043
BDE-183	0.64	0.13
BDE-209	5.0	1.0
PBBz	0.23	0.045
PBT	0.49	0.097
PBEB	0.36	0.071
DPTE	0.23	0.047
HBBz	0.35	0.069
EH-TBB	0.42	0.085
BTBPE	1.7	0.34
BEH-TEBP	2.2	0.44
DBDPE	10	2.0
α-HBCDD	4.8	0.096
β-HBCDD	9.7	0.19
γ-HBCDD	4.0	0.081

[a] instrument LOQ;

[b] method LOQ, 0.5 g sample (dry weight) was assumed.

Table S4. Recoveries of internal standards in blanks and food samples

Internal standards	Blanks (n=4)	Samples (n=26)
BDE-77	78%-82%	74%-91%
BDE-128	89%-95%	82%-105%
^{13}C-BDE-209	93%-117%	70%-133%
^{13}C-HBBz	82%-84%	70%-92%
^{13}C-EH-TBB	102%-106%	73%-100%
^{13}C-BTBPE	75%-107%	67%-133%
^{13}C-BEH-TEBP	61%-66%	49%-96%
^{13}C-α-HBCDD	90%-140%	31%-75%
^{13}C-β-HBCDD	89%-115%	74%-135%
^{13}C-γ-HBCDD	76%-84%	78%-97%

Table S5. Average dry-weight concentrations of BFRs in different Nigerian food items (ng/g)

BFRs	Meat		Freshwater fish		Saltwater fish						Other			All
	beef	bush meat	tilapia	catfish	stockfish	shawa	sole fish	knife fish	hake	lizard fish	prawn	periwinkle	snail	
BDE-28	<0.098	<0.087	<0.091	<0.098	<0.098	<0.092	<0.092	<0.095	<0.081	<0.094	<0.10	<0.096	<0.099	<0.095
BDE-47	0.036	0.034	0.081	0.13	0.038	0.12	<0.036	0.054	0.51	0.23	0.042	0.24	0.036	0.097
BDE-99	0.089	0.53	0.078	0.17	<0.084	<0.080	0.27	<0.082	0.076	<0.080	0.51	0.27	0.36	0.18
BDE-100	0.15	0.19	0.090	0.079	<0.096	<0.091	<0.092	0.094	0.41	0.14	0.92	0.10	0.093	0.14
BDE-153	<0.046	<0.041	<0.043	<0.046	<0.046	<0.043	<0.043	<0.045	0.055	<0.044	<0.049	<0.045	<0.047	0.024
BDE-154	<0.040	<0.035	0.082	0.027	<0.040	<0.039	<0.037	<0.039	0.22	0.15	<0.042	0.16	<0.040	0.053
BDE-183	<0.12	<0.10	<0.11	0.077	<0.12	<0.11	<0.11	<0.11	<0.097	0.083	<0.12	0.14	<0.12	0.064
Σ_7PBDEs	**0.42**	**0.88**	**0.45**	**0.55**	**0.28**	**0.34**	**0.47**	**0.34**	**1.4**	**0.72**	**1.6**	**0.99**	**0.64**	**0.61**
BDE-209	1.6	<0.81	<0.85	0.69	<0.91	<0.86	<0.86	<0.89	<0.76	<0.87	<0.97	<0.90	<0.93	0.64
Σ_8PBDEs	**2.0**	**1.3**	**0.87**	**1.2**	**0.73**	**0.77**	**0.90**	**0.78**	**1.7**	**1.2**	**2.1**	**1.4**	**1.1**	**1.3**
PBBz	<0.041	<0.037	<0.038	<0.041	<0.041	<0.039	<0.039	<0.040	<0.034	<0.040	<0.044	<0.040	<0.042	<0.040
PBT	<0.089	<0.079	<0.082	<0.089	<0.089	<0.084	<0.084	<0.087	<0.074	<0.042	<0.094	<0.087	<0.090	<0.086
PBEB	<0.065	<0.058	<0.060	<0.065	<0.065	<0.061	<0.061	<0.063	<0.054	<0.062	<0.069	<0.064	<0.066	<0.063
DPTE	0.040	0.21	0.054	<0.043	<0.043	<0.040	<0.040	<0.041	<0.035	0.083	<0.045	0.74	0.43	0.13
HBBz	0.041	<0.056	<0.059	<0.063	<0.063	<0.060	<0.059	<0.061	<0.052	0.047	<0.067	0.057	<0.064	0.034
EH-TBB	0.24	0.14	0.13	0.18	<0.076	0.20	0.15	0.18	<0.064	0.060	<0.082	0.11	0.083	0.13
BTBPE	<0.31	<0.28	0.19	0.38	<0.31	<0.29	<0.29	0.32	0.28	0.53	<0.33	<0.31	<0.32	0.22
BEH-TEBP	<0.40	1.5	<0.37	0.58	0.76	<0.38	<0.38	<0.39	1.1	0.45	<0.43	1.2	0.45	0.44
DBDPE	<1.8	<1.6	<1.7	<1.8	<1.8	<1.7	<1.7	<1.8	<1.5	2.7	<1.9	<1.8	<1.9	1.0
Σ_9NBFRs	**1.7**	**2.9**	**1.5**	**2.2**	**2.0**	**1.5**	**1.5**	**1.7**	**2.3**	**3.9**	**<3.1**	**3.2**	**2.2**	**2.1**
α-HBCDD	0.074	<0.086	1.3	<0.088	<0.086	<0.073	0.072	<0.086	<0.086	0.28	<0.085	<0.080	<0.086	0.27
β-HBCDD	<0.17	<0.17	<0.18	<0.18	<0.17	<0.15	<0.16	<0.17	<0.17	<0.17	<0.17	<0.16	<0.17	<0.17
γ-HBCDD	0.085	0.21	0.047	<0.074	<0.072	<0.061	0.062	<0.073	<0.072	0.055	<0.072	<0.067	0.11	0.067
Σ_3HBCDDs	**0.24**	**0.34**	**1.47**	**<0.34**	**<0.33**	**<0.28**	**0.22**	**<0.33**	**<0.33**	**0.42**	**<0.33**	**<0.31**	**0.24**	**0.42**

Table S6. Average lipid-weight concentrations of NBFRs in different Nigerian food items (ng/g lw)

BFRs	Meat		Freshwater fish		Saltwater fish						Other			All
	beef	bush meat	tilapia	catfish	stockfish	shawa	sole fish	knife fish	hake	lizard fish	prawn	periwinkle	snail	
BDE-28	<0.54	<0.53	<0.51	<0.54	<1.0	<0.50	<1.1	<0.98	<0.48	<0.80	<0.88	<0.97	<1.3	<0.78
BDE-47	0.16	0.21	0.42	0.45	0.40	0.64	<0.41	0.55	3.0	1.4	0.36	2.4	0.47	0.63
BDE-99	0.39	3.2	0.36	0.96	<0.88	<0.44	2.7	<0.85	0.44	<0.69	4.3	2.7	4.6	1.6
BDE-100	0.73	1.1	0.51	0.36	<1.1	<0.49	<1.1	0.97	2.4	0.90	7.8	1.1	1.3	1.1
BDE-153	<0.25	<0.25	<0.24	<0.25	<0.48	<0.23	<0.50	<0.46	0.32	<0.38	<0.41	<0.46	<0.64	0.19
BDE-154	<0.22	<0.22	0.43	0.13	<0.41	<0.20	<0.43	<0.40	1.3	0.96	<0.35	1.6	<0.55	0.37
BDE-183	<0.64	<0.63	<0.60	0.38	<1.2	<0.60	<1.3	<1.2	<0.56	0.62	<1.0	1.5	<1.6	0.51
Σ_7PBDEs	**2.1**	**5.4**	**2.4**	**2.7**	**2.9**	**1.9**	**5.0**	**3.4**	**7.9**	**4.8**	**14**	**10**	**8.4**	**4.8**
BDE-209	6.6	<5.0	<4.7	3.3	<9.5	<4.7	<9.8	<9.1	<4.4	<7.4	<8.2	<9.0	<13	4.4
Σ_8PBDEs	**8.7**	**7.9**	**4.7**	**6.0**	**7.7**	**4.2**	**9.9**	**8.0**	**10**	**8.5**	**18**	**15**	**15**	**9.2**
PBBz	<0.23	<0.22	<0.21	<0.23	<0.43	<0.22	<0.44	<0.41	<0.20	<0.34	<0.37	<0.41	<0.57	<0.33
PBT	<0.49	<0.48	<0.46	<0.49	<0.93	<0.46	<0.96	<0.89	<0.43	<0.73	<0.80	<0.88	<1.2	<0.71
PBEB	<0.36	<0.35	<0.34	<0.36	<0.68	<0.35	<0.70	<0.65	<0.32	<0.53	<0.58	<0.65	<0.90	<0.52
DPTE	0.23	1.3	0.34	<0.23	<0.44	<0.22	<0.46	<0.43	<0.21	0.93	<0.38	7.5	6.3	1.5
HBBz	0.27	<0.34	<0.33	<0.35	<0.66	<0.32	<0.68	<0.63	<0.31	0.46	<0.57	0.57	<0.87	0.29
EH-TBB	0.94	0.84	0.67	0.67	<0.81	1.1	1.4	1.8	<0.38	0.59	<0.69	1.1	1.2	0.88
BTBPE	<1.7	<1.7	1.0	3.1	<3.2	<1.6	<3.3	3.3	1.6	3.2	<2.8	<3.1	<4.3	1.8
BEH-TEBP	<2.2	9.0	<2.1	2.9	7.9	<2.1	<4.3	<4.0	6.3	4.7	<3.6	12	6.2	3.7
DBDPE	<10	<9.9	<9.4	<10	<19	<9.3	<20	<18	<8.9	29	<16	<18	<25	8.9
Σ_9NBFRs	**9.0**	**18**	**8.5**	**13**	**21**	**8.3**	**17**	**18**	**13**	**40**	**<26**	**33**	**30**	**18**
α-HBCDD	0.40	<0.53	6.8	<0.49	<0.91	<0.40	0.76	<0.89	<0.50	1.6	<0.72	<0.81	<1.1	1.5
β-HBCDD	<0.89	<1.1	<0.97	<0.99	<1.8	<0.80	<1.9	<1.8	<1.0	<1.5	<1.5	<1.6	<2.3	<1.4
γ-HBCDD	0.63	1.3	0.26	<0.41	<0.77	<0.33	0.65	<0.75	<0.42	0.42	<0.60	<0.68	1.5	0.60
Σ_3HBCDDs	**1.5**	**2.1**	**7.5**	**<1.9**	**<3.5**	**<1.5**	**2.3**	**<3.4**	**<1.9**	**2.8**	**<2.8**	**<3.1**	**3.3**	**2.8**

Table S7. Concentrations of PBDEs (pg/g ww in parentheses) in food items from different countries (ng/g lw)

Country	Sampling time	Sample type	BDE-209	ΣPBDEs	References
UK	2020-2021	meat	0.49 (24) [a]	1.3 (66) [a]	(Ma et al., 2023b)
		fish	3.5 (32) [a]	7.7 (210) [a]	
		eggs	0.36 (23) [a]	4.5 (310) [a]	
		cheese	0.15 (42) [a]	1.2 (310) [a]	
Latvia	2016-2019	meat	(12 [a] / 9.6 [b])	(34 [a] / 22 [b])	(Zacs et al., 2021)
		fish	(23 [a] / 7.5 [b])	(620 [a] / 390 [b])	
		eggs	(34 [a] / 24 [b])	(55 [a] / 36 [b])	
		cheese	(2.9 [a] / 2.9 [b])	(21 [a] / 8.5 [b])	
China	2013	meat	20 (3300) [a] / 13 (440) [b]	21 (3400) [a] / 14 (460) [b]	(Wang et al., 2019)
		fish/seafood	13 (1300) [a] / 5.5 (210) [b]	14 (1400) [a] / 6.3 (270) [b]	
		eggs	13 (1600) [a] / 11 (1600) [b]	13 (1700) [a] / 12 (1800) [b]	
		dairy products	5.5 (90) [a] / 3.0 (58) [b]	5.9 (96) [a] / 3.2 (66) [b]	
China [d]	2013	eggs		620-46000 [c]	(Zeng et al., 2016)
Netherlands	2009-2014	meat		0.060-0.58 [a] / 0.040-0.34 [b]	(Gebbink et al., 2019)
		eggs		0.22 [a] / 0.14 [b]	
		fish		(2.5-1300 [a])	
France	2014-2016	meat	(11 [b])	(170 [a])	(Venisseau et al., 2018)
		fish	(5.7 [b])	(540 [a])	
		egg	(22 [b])	(120 [a])	
Belgium	2015-2016	meat		(690 [a])	(Poma et al., 2018)
		fish		(370 [a])	
		eggs		(210 [a])	
		dairy products		(600 [a])	
Ireland	2015	fish	(<2.0-60 [c])	(20-1400 [c])	(Garcia Lopez et al., 2018)
		eggs	(<190-800 [c])	(30-960 [c])	
Spain		fish/shellfish	(<20 [c])	(400-1300 [c])	(Trabalon et al., 2017)
Japan	2011	fish		(2.0-880 [c])	(Kakimoto et al., 2012)
US	2022	sum	(16 [a])	(250 [a])	(Ma et al., 2023a)

[a] Mean concentrations

[b] Median concentrations

[c] Ranges

[d] E-waste recycling sites

Table S8. Concentrations of NBFRs (pg/g ww in parentheses) in food items from different countries (ng/g lw)

Country	Sampling time	Sample type	DPTE	HBBz	EH-TBB	BTBPE	BEH-TEBP	DBDPE	References
UK	2020-2021	meat	0.29 (25) [a]	<LOD [c]	0.63 (43) [a]	4.3 (190) [a]	8.5 (510) [a]	0.38 (18) [a]	(Ma et al., 2023b)
		fish	2.0 (33) [a]	<LOD [c]	3.3 (17) [a]	22 (200) [a]	20 (390) [a]	1.2 (45) [a]	
		eggs	0.63 (39) [a]	<LOD [c]	<LOD [c]	36 (2,300) [a]	2.0 (130) [a]	<LOD [a]	
		cheese	<LOD [c]	<LOD [c]	<LOD [c]	0.39 (97) [a]	0.52 (140) [a]	<LOD [a]	
Latvia	2016-2019	meat		(1.4-9.8 [c])					(Zacs et al., 2021)
		fish		(2.8-18 [c])					
		eggs		(0.93-5.7 [c])					
		cheese		(1.9-12 [c])					
France	2014-2016	meat		(<LOD-150 [c])	(<LOD-12 [c])	(<LOD-15 [c])			(Venisseau et al., 2018)
		fish		(<LOD-38 [c])	(<LOD-10 [c])	(<LOD-10 [c])			
		egg		(<LOD-16 [c])	(<LOD-1.3 [c])	(<LOD-12 [c])			
Belgium	2015-2016	meat					(6.0 [a])		(Poma et al., 2018)
		fish					(<LOD [c])		
		eggs					(<LOD [c])		
		dairy products					(<LOD [c])		
Spain		fish/shellfish		(<20-200 [c])				(<10 [c])	(Trabalon et al., 2017)
China	2011	meat	<LOD-0.081 [c]	<LOD-0.16 [c]		<LOD-0.067 [c]		<LOD-23 [c]	(Shi et al., 2016)
		fish	0.030-1.6 [c]	<LOD-2.2 [c]		<LOD-1.9 [c]		<LOD-70 [c]	
		eggs	<LOD-0.057 [c]	<LOD-0.076 [c]		<LOD-4.1 [c]		<LOD-20 [c]	
China [d]	2011	fish		6.5 [a]	62 [a]	6.8 [a]	15 [a]	<0.45 [a]	(Labunska et al., 2015)
		meat		0.41-0.56 [a]	24-38 [a]	1.5-5.4 [a]	7.2-12 [a]	<0.45 [a]	
		eggs		<0.15 [a]	3.1-5.4 [a]	<0.35-3.8 [a]	0.88-1.6 [a]	<0.45 [a]	
China	2011	fish		<0.15 [a]	4.0 [a]	2.1 [a]	1.9 [a]	<0.45 [a]	(Labunska et al., 2015)
		meat		<0.15 [a]	2.1-2.7 [a]	<0.35-2.7 [a]	<0.25-1.8 [a]	<0.45 [a]	
		eggs		<0.15 [a]	1.2-1.7 [a]	<0.35 [a]	<0.25 [a]	<0.45 [a]	
China	2018	meat		0.13 [a]		<LOD [a]			(Jian et al., 2020)
		poultry		0.017 [a]		<LOD [a]			
		aquatic food		0.049 [a]		<LOD [a]			
		eggs		0.016 [a]		<LOD [a]			
		dairy products		0.0070 [a]		<LOD [a]			
Tanzania	2012	eggs				<LOD-9.8 [c]			(Polder et al., 2016)
US	2022	sum		(2.2 [a])	(6.9 [a])	(1.1 [a])	(4.2 [a])	(18 [a])	(Ma et al., 2023a)

[a] Mean concentrations

[b] Median concentrations

[c] Ranges

[d] E-waste recycling sites

Table S9. Concentrations of HBCDD (pg/g ww in parentheses) in food items from different countries (ng/g lw)

Country	Sampling time	Sample type	HBCDD	References
UK	2020-2021	meat	0.16 (8.9) [a]	(Ma et al., 2023b)
		fish	0.83 (67) [a]	
		eggs	0.19 (16) [a]	
		cheese	0.050 (12) [a]	
Latvia	2016-2019	meat	(270 [a] / 160 [b])	(Zacs et al., 2021)
		fish	(730 [a] / 480 [b])	
		eggs	(24 [a] / 16 [b])	
		cheese	(330 [a] / 160 [b])	
China	2013	meat	2.8 (570) [a] / 2.4 (180) [b]	(Wang et al., 2019)
		fish/seafood	7.0 (410) [a] / 5.6 (290) [b]	
		eggs	4.5 (600) [a] / 4.0 (500) [b]	
		dairy products	1.4 (140) [a] / 1.1 (44) [b]	
China [d]	2013	eggs	56-7600 [c]	(Zeng et al., 2016)
China [d]	2011	fish	310 [a]	(Labunska et al., 2015)
		meat	<0.060-79 [a]	
		eggs	2.2-47 [a]	
China	2011	fish	5.9 [a]	(Labunska et al., 2015)
		meat	0.090-3.1 [a]	
		eggs	0.50-1.70 [a]	
France	2014-2016	meat	(130 [a])	(Venisseau et al., 2018)
		fish	(140 [a])	
Belgium	2015-2016	meat	(43 [a])	(Poma et al., 2018)
		fish	(130 [a])	
		eggs	(970 [a])	
		dairy products	(0.10 [a])	
Ireland	2015	fish	(70-410 [c])	(Garcia Lopez et al., 2018)
		eggs	(10-20 [c])	
Tanzania	2012	eggs	<LOD-63 [c]	(Polder et al., 2016)
Japan	2011	fish	(<LOD-22000 [c])	(Kakimoto et al., 2012)
Sweden	1999	meat	<1.0-6.5 [a]	(Remberger et al., 2004)
		fish	48 [a]	
		egg	9.4 [a]	
US	2022	sum	(17 [a])	(Ma et al., 2023a)

[a] Mean concentrations

[b] Median concentrations

[c] Ranges

[d] E-waste recycling sites

Table S10. Food consumption rates (g/day) of Nigerian adults and toddlers (Bradley et al., 2020; Ingenbleek et al., 2017)

Food items	Adults		Toddlers [a]	
	Mean	95th percentile	Mean	95th percentile
Beef	7.8	48.1	3.5	21.6
Bush meat	0.4	61.2	0.2	27.5
Saltwater fish	10.6	57.8	4.8	26.0
Freshwater fish [b]	25.8	140.7	11.6	63.3
Others [c]	0.9	15	0.4	6.8

[a] food consumption rates of Nigerian toddlers (1-4 years old) were suggested to be 0.45 × food consumption rates of Nigerian adults (Ingenbleek et al., 2017);

[b] fish consumption rate in Nigeria was reported to be 13.3 kg/capita/year (Bradley et al., 2020), which was equivalent to 36.4 g/capita/day, therefore, consumption of freshwater fish was assumed to be consumption of fish subtracted by consumption of saltwater fish.

[c] consumption rates of crustaceans/mollusks were applied (Ingenbleek et al., 2017).

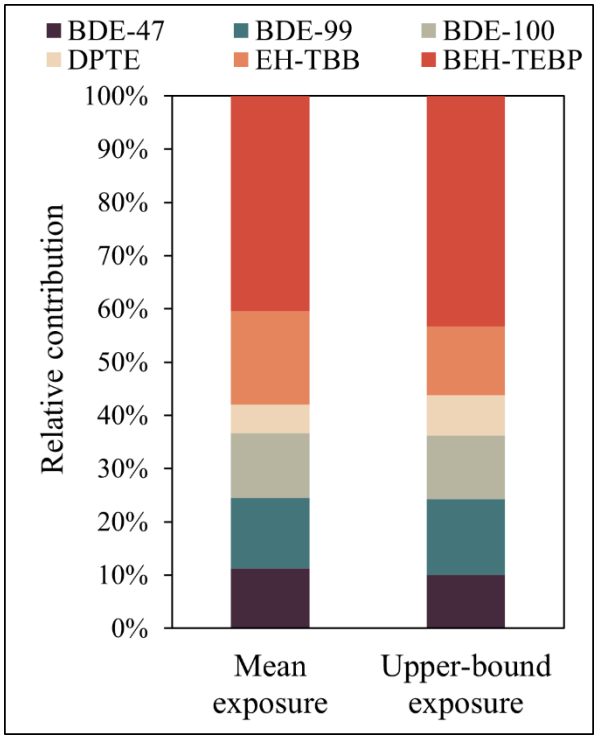


Fig. S1 Contribution of individual BFRs (DF > 30%) to dietary exposure to total BFRs of Nigerian people

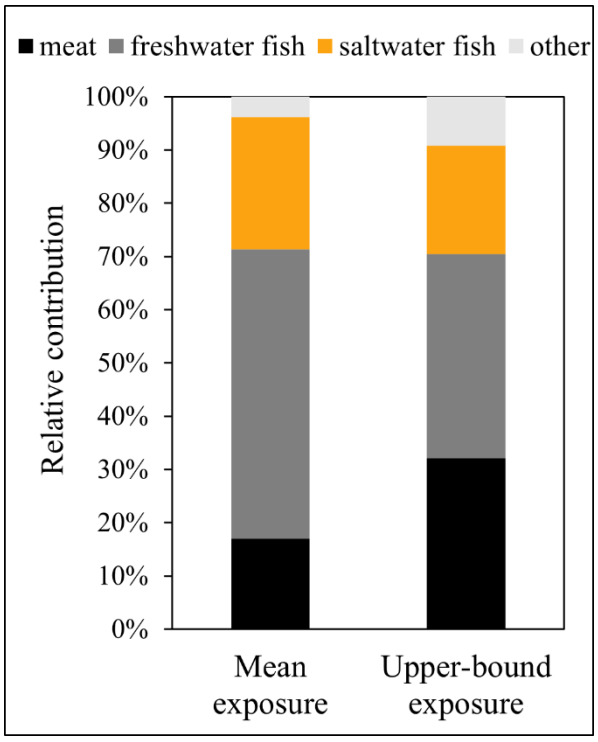


Fig. S2 Contribution of different food items to dietary exposure to total BFRs of Nigerian people

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Appendix B. Supplementary Materials for Chapter Three

Chemicals and reagents

All the solvents used in this study were purchased from OmniSolv® (Burlington, MA, USA), and were of HPLC analytical grade. Sulfuric acid (95-98%, ACS grade) was purchased from VWR Int. LLC. (Radnor, PA, USA). Potassium Chloride (ACS grade) was purchased from Fisher Scientific (Ottawa, ON, Canada). Alumina was purchased from Fisher Scientific (Ottawa, ON, Canada), and was baked at 300℃ for 8h and then activated with 6% deionized water prior to use. All the native and labelled standards were purchased from Wellington Laboratories (Guelph, ON, Canada), except for BDE-77 (obtained from AccuStandard Inc. (New Haven, CT, USA)) as well as native HBCDDs (obtained from Sigma-Aldrich Company Ltd. (Dorset, UK)).

Sample extraction and clean-up

The concentrations of 21 PBDEs (di-BDE (BDE-15), tri-BDE (BDE-17, -28), tetra-BDE (BDE-49, -47, -66), penta-BDE (BDE-100, -99, -85), hexa-BDE (BDE-154, -153, -139, -140), hepta-BDE (BDE-183), octa-BDE (BDE-201, -197, -203), nona-BDE (BDE-208, -207, -206), and deca-BDE (BDE-209)), 8 NBFRs (2,3,5,6-tetrabromo-p-xylene (pTBX), pentabromobenzene (PBBz), pentabromoethylbenzene (PBEB), 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), and decabromodiphenyl ethane (DBDPE)), HBCDD, and DP (*syn*-DP and *anti*-DP) were measured in food samples.

Approximately 0.5 g of freeze-dried food samples were precisely weighted and spiked with 3 ng of BDE-77, 5 ng of BDE-166, and 4 ng of 13C-BDE-209 as surrogate standards before extraction. Hexane/Acetone (1:1, v/v) was used to extract the samples on an accelerated solvent extractor (Dionex ASE 350). The ASE cells (34 mL) were filled from bottom to top with: pre-cleaned hydromatrix, 6 g of alumina, samples, and pre-cleaned hydromatrix. The extraction programme was set as: *Temperature: 100℃; Heating time: 5 min; Static time: 4 min; Cycles: 3; Pressure: 1500 psi. Purge time: 90 s; Flush volume: 60%.* The extracts were collected in pre-cleaned ASE collection

bottles, and then were concentrated to 5 mL under a gentle nitrogen stream before being transferred into pre-weighted 15 mL glass tubes. Approximately 10% of the concentrated extracts were transferred into pre-weighted aluminum disks. The aluminum disks were then stored at room temperature overnight before being weighted again. This allowed lipid content of the samples to be determined gravimetrically. The remaining ~90% of the extracts were vortexed with 4 mL KCl solution (1% in water). Then the samples were centrifuged at 3000 RPM for 5 min, and the upper layer was transferred into another 15 mL glass tube, with the bottom layer extracted with 4 mL hexane twice and the extracts combined. Following this, the extracts were concentrated to 5 mL before shaking with 5 mL sulfuric acid (95%) to remove lipids and proteins. The samples were then centrifuged at 3500 RPM for 20 min, and the solvent phase (upper layer) was collected. The acid phase (bottom layer) was extracted with 5 mL hexane twice and then centrifuged, and the solvents were collected and combined. The purified extracts were concentrated to < 1 mL under a gentle stream of nitrogen, and then were reconstituted into 1 mL hexane containing 5 ng of BDE-118 and 10 ng of BDE-181 as internal standards before GC-MS analysis.

Instrumental analysis

Analyses of BFRs and DPs were performed on an Agilent 7890A gas chromatograph coupled with an Agilent 5975C mass spectrometer (GC/MS) operated in electron capture negative ionization (ENCI) mode. Chromatographic resolution is achieved with a Restek Rtx-1614 (15 m length, 0.25 mm ID, 0.1 μm film thickness) fused silica capillary column (Restek Corporation, Bellefonte, CA) with helium (99.999%; Liquid Carbonic, Chicago, USA) as the carrier gas and methane (99.97%; Praxair, Indianapolis, USA) as the reagent gas. Injections were analysed by GC/MS under selected ion monitoring (SIM) mode, and the quantitation parameters were summarized in Table S2.

QA/QC

Table S3 shows linearity of target analytes and surrogate standards obtained from the 11-point calibration. Limit of detection (LOD) for each analyte was calculated based on a signal/noise ratio of 3, and the data is presented in Table S4. Recoveries of surrogate (internal) standards in all the blanks, matrix spikes, and samples are given in Table S5. Most target analytes were not detected in the blanks, and thus the corresponding samples were not blank-corrected. Only BDE-15, -47, -99, -

153, -139, -140, -183, -209, EH-TBB, BEH-TEBP, and anti-DP were detected in at least 1 blank at very low concentrations (slightly higher than the LODs), so the corresponding samples were blank-corrected by subtracting their mass in blanks from the mass detected in samples. Recoveries of the target analytes in matrix spikes are shown in Table S6.

Estimation of daily dietary intake of HFRs

Daily dietary intake of HFRs for the US population were estimated with equation 1. Daily consumption of various food items was calculated from US per capita loss-adjusted food availability,[1] after conversion from lb/year to g/day (Tables S14-S15). Data on body weight (kg) for the US population is summarized in Tables S16-S17.[2] Median concentrations of HFRs in different food items were used to estimate a median human dietary exposure to HFRs. Fig. S3 shows estimated daily dietary intake of HFRs for US children (< 20 years old) and adults (≥ 20 years old), with detailed data provided in Table S18. Daily dietary intake of HFRs was also estimated for US adults (≥ 20 years old) of different races namely Hispanic (including Mexican-Americans), non-Hispanic white, non-Hispanic black, and non-Hispanic Asian. We recognize that grouping all children in the same category is a limitation that was forced by the availability of data on daily food consumption in the US.

Table S1. Detailed information on US food items analyzed in the present study

Food items	Number of composite samples analyzed	Number of individual samples included	Water content %	Lipid content %
Meat	**18**	**34**	**-**	**-**
beef (organic vs non-organic)	4	9	70	6.3
pork (organic vs non-organic)	4	9	64	12
chicken (organic vs non-organic)	6	11	74	3.5
turkey (organic vs non-organic)	4	5	73	4.3
Fish	**13**	**17**	**-**	**-**
Salmon	3	5	69	8.4
Cod	3	4	82	0.52
Catfish	2	3	82	4.5
Tilapia	3	3	80	0.85
Tuna	2	2	73	0.43
cheese (organic vs non-organic)	**6**	**6**	**36**	**27**
egg (organic vs non-organic)	**5**	**15**	**76**	**5.5**

Table S2. HFR analyte list and quantitation parameters

Compound	Elute Order	Type	Internal Standard	Quant	Confirmation		
				Ion	Ion I	Ion II	Ion III
BDE-15	1	Target	BDE-118	81	79		
pTBX	2	Target	BDE-118	81	79		
PBBz	3	Target	BDE-118	81	79	471.7	
BDE-17	4	Target	BDE-118	81	79	160.8	
BDE-28	5	Target	BDE-118	81	79		
PBEB	6	Target	BDE-118	81	79		
HBBz	7	Target	BDE-118	81	79	471.7	
BDE-49	8	Target	BDE-118	81	79	160.8	
BDE-47	9	Target	BDE-118	81	79	160.8	
BDE-66	10	Target	BDE-118	81	79	160.8	
BDE-77	11	Surrogate	BDE-118	81	79		
BDE-100	12	Target	BDE-118	81	79		
BDE-99	13	Target	BDE-118	81	79		
EH-TBB	14	Target	BDE-118	357	359	79	81
BDE-118	15	Internal		81	79		
BDE-85	16	Target	BDE-118	81	79		
BDE-154	17	Target	BDE-118	81	79		
BDE-153	18	Target	BDE-118	81	79		
BDE-139	19	Target	BDE-118	81	79		
BDE-140	20	Target	BDE-118	81	79		
HBCDD	21	Target	BDE-118	159.8	81	79	
BDE-166	22	Surrogate	BDE-118	81	79		
BDE-183	23	Target	BDE-118	81	79		
BTBPE	24	Target	BDE-181	81	79		
BDE-181	25	Internal		81	79		
BEH-TEBP	26	Target	BDE-181	463.7	461.7	81	79
syn-DP	27	Target	BDE-181	653.8	651.8		
BDE-201	28	Target	BDE-181	408.7	406.7		
anti-DP	29	Target	BDE-181	653.8	651.8		
BDE-197	30	Target	BDE-181	408.7	406.7		
BDE-203	31	Target	BDE-181	81	79		
BDE-208	32	Target	BDE-181	486.8	488.8	81	79
BDE-207	33	Target	BDE-181	486.8	488.8	81	79
BDE-206	34	Target	BDE-181	81	79	486.8	488.8
BDE-209	35	Target	BDE-181	486.8	488.8		
^{13}C-BDE-209	36	Surrogate	BDE-181	494.6	496.6		
DBDPE	37	Target	BDE-181	81	79		

Table S3. Linearity of target analytes and surrogate standards (SS) obtained from the 11-point calibration

FRs	Linearity Range (ng/mL)	R^2
BDE-15	0.0050 - 40	0.9913
BDE-17	0.0050 - 38	0.9958
BDE-28	0.0050 - 40	0.9966
BDE-49	0.010 - 80	0.9975
BDE-47	0.010 - 80	0.9964
BDE-66	0.010 - 80	0.9979
BDE-77 (SS)	0.011 - 86	0.9986
BDE-100	0.010 - 80	0.9967
BDE-99	0.010 - 80	0.9976
BDE-85	0.010 - 80	0.9937
BDE-154	0.021 - 160	0.9934
BDE-153	0.010 - 80	0.9938
BDE-139	0.010 - 80	0.9949
BDE-140	0.010 - 80	0.9961
BDE-166 (SS)	0.012 - 90	0.9945
BDE-183	0.021 - 160	0.9948
BDE-201	0.021 - 160	0.9949
BDE-197	0.021 - 160	0.9951
BDE-203	0.021 - 160	0.9942
BDE-208	0.051 - 400	0.9912
BDE-207	0.051 - 400	0.9915
BDE-206	0.051 - 400	0.9876
BDE-209	0.051 - 400	0.9943
^{13}C-BDE-209	0.0030 - 8.0	0.9977
pTBX	0.0050 - 40	0.9919
PBBz	0.0050 - 40	0.9927
PBEB	0.0050 - 40	0.9944
HBBz	0.0050 - 40	0.9944
EH-TBB	0.010 - 80	0.9300
BTBPE	0.010 - 80	0.9951
BEH-TEBP	0.010 - 80	0.9995
DBDPE	0.10 - 800	0.9971
HBCDD	0.021 - 160	0.9978
syn-DP	0.010 - 80	0.9912
anti-DP	0.010 - 80	0.9899

Table S4. Limit of detection (LOD) for each analyte (calculated from a S/N ratio of 3)

BFRs	LOD (S/N=3)		
	ng/ml	pg/injection	ng/g dw [a]
BDE-15	0.015	0.15	0.03
BDE-17	0.005	0.05	0.01
BDE-28	0.005	0.05	0.01
BDE-49	0.01	0.1	0.02
BDE-47	0.01	0.1	0.02
BDE-66	0.01	0.1	0.02
BDE-100	0.01	0.1	0.02
BDE-99	0.0085	0.085	0.017
BDE-85	0.01	0.1	0.02
BDE-154	0.0078	0.078	0.0156
BDE-153	0.0075	0.075	0.015
BDE-139	0.0091	0.091	0.0182
BDE-140	0.0091	0.091	0.0182
BDE-183	0.013	0.13	0.026
BDE-201	0.0035	0.035	0.007
BDE-197	0.021	0.21	0.042
BDE-203	0.021	0.21	0.042
BDE-208	0.051	0.51	0.102
BDE-207	0.051	0.51	0.102
BDE-206	0.051	0.51	0.102
BDE-209	0.01	0.1	0.02
pTBX	0.0025	0.025	0.005
PBBz	0.0025	0.025	0.005
PBEB	0.005	0.05	0.01
HBBz	0.005	0.05	0.01
EH-TBB	0.015	0.15	0.03
BTBPE	0.01	0.1	0.02
BEH-TEBP	0.005	0.05	0.01
DBDPE	0.14	1.4	0.28
HBCDD	0.04	0.4	0.08
syn-DP	0.0025	0.025	0.005
anti-DP	0.003	0.03	0.006

[a] 0.5 g sample (dw) was assumed to calculate the method LODs.

Table S5. Recoveries of surrogate (internal) standards in blanks, matrix spikes, and food samples

Surrogate standards	Blanks (n=9)	Matrix spikes (n=9)	Samples (n=42)
BDE-77	84%-107%	77%-96%	65%-113%
BDE-166	79%-97%	70%-102%	45%-87%
^{13}C-BDE-209	66%-81%	65%-88%	39%-73%

Table S6. Recoveries of target analytes and surrogate (internal) standards in matrix spikes (MS; n=9) [a]

FRs	Theoretical concentration	Recovery (%)		
	ng/mL	Min	Max	Mean±SD
BDE-15	4.0	58	118	73±18
BDE-17	4.0	66	140	85±22
BDE-28	4.0	63	83	73±5.6
BDE-49	4.0	71	90	78±6.2
BDE-47	4.0	72	94	80±7.3
BDE-66	4.0	76	97	87±7.8
BDE-77 (SS)	7.0	77	96	85±5.7
BDE-100	4.0	66	83	76±5.4
BDE-99	4.0	73	89	81±5.2
BDE-85	4.0	73	90	81±5.3
BDE-154	8.0	59	74	68±4.6
BDE-153	8.0	66	78	74±4.0
BDE-166 (SS)	5.0	70	102	87±11
BDE-183	8.0	67	82	76±5.0
BDE-197	8.0	62	79	71±5.4
BDE-207	20	62	82	74±6.4
BDE-206	20	69	87	80±5.7
$^{13}C_{12}$-209 (SS)	4.0	65	88	79±7.7
BDE-209	20	64	84	76±6.6
pTBX	2.5	65	89	74±6.9
PBBz	2.5	68	92	76±7.0
EH-TBB	5.0	70	133	92±17
BEH-TEBP	5.0	72	94	84±7.4
HBCDD	10	82	126	100±14
syn-DP	5.0	75	98	87±7.4
anti-DP	5.0	76	98	88±7.3

[a] Matrix spikes were analyzed here as part of the QA/QC procedure because standard reference materials for BFR analyses in food items are currently not available for purchase.

Table S7. HFR concentrations in US food items (pg/g ww)

HFRs	Detection frequency	Max	Min	Average
BDE-15	83%	620	n.d.	98
BDE-17	71%	500	n.d.	39
BDE-28	79%	130	n.d.	20
BDE-49	52%	40	n.d.	8.8
BDE-47	33%	58	n.d.	6.4
BDE-66	12%	13	n.d.	0.94
BDE-100	76%	26	n.d.	6.7
BDE-99	45%	80	n.d.	7.6
BDE-85	21%	10	n.d.	1.3
BDE-154	88%	51	n.d.	13
BDE-153	60%	20	n.d.	4.2
BDE-139	33%	40	n.d.	6.2
BDE-140	48%	83	n.d.	11
BDE-183	36%	15	n.d.	2.0
BDE-201	10%	7.7	n.d.	0.51
BDE-197	10%	21	n.d.	1.1
BDE-203	21%	8.7	n.d.	0.46
BDE-208	0%	0	n.d.	n.d.
BDE-207	10%	54	n.d.	4.2
BDE-206	10%	34	n.d.	1.8
BDE-209	60%	200	n.d.	16
Σ_{21}PBDEs		**1,100**	**49**	**250**
pTBX	40%	83	n.d.	6.1
PBBz	79%	25	n.d.	3.5
PBEB	19%	110	n.d.	3.7
HBBz	21%	30	n.d.	2.2
EH-TBB	36%	57	n.d.	6.9
BTBPE	14%	12	n.d.	1.1
BEH-TEBP	33%	72	n.d.	4.2
DBDPE	17%	200	n.d.	18
Σ_{8}NBFRs		**270**	**0.10**	**46**
HBCDD	**17%**	**260**	**n.d.**	**17**
syn-DP	38%	12	n.d.	0.84
anti-DP	33%	23	n.d.	1.8
Σ_{2}DPs		**28**	**n.d.**	**2.7**
Σ_{32}HFRs		**1,400**	**54**	**310**

Table S8. Concentrations of PBDEs (pg/g ww in parentheses) in food items from different countries (ng/g lw)

Country	Sampling time	Sample type	BDE-209	ΣPBDEs	References
UK	2020-2021	meat	0.49 (24) [a]	1.3 (66) [a]	[3]
		fish	3.5 (32) [a]	7.7 (210) [a]	
		eggs	0.36 (23) [a]	4.5 (310) [a]	
		cheese	0.15 (42) [a]	1.2 (310) [a]	
UK	2015	meat	0.28-0.63 (21-32) [a]	2.4-21 (520-1000) [a]	[4]
		fish	0.34-1.7 (32-150) [a]	14-40 (400-2800) [a]	
		eggs	0.53 (56) [a]	2.4 (250) [a]	
		cheese	0.21 (37) [a]	5.3 (940) [a]	
UK	2013	meat		(40-590 [c])	[5]
		fish		(170-8900 [c])	
		egg		(60-450 [c])	
		dairy products		(20-260 [c])	
Latvia	2016-2019	meat	(12 [a] / 9.6 [b])	(34 [a] / 22 [b])	[6]
		fish	(23 [a] / 7.5 [b])	(620 [a] / 390 [b])	
		eggs	(34 [a] / 24 [b])	(55 [a] / 36 [b])	
		cheese	(2.9 [a] / 2.9 [b])	(21 [a] / 8.5 [b])	
China	2013	meat	20 (3300) [a] / 13 (440) [b]	21 (3400) [a] / 14 (460) [b]	[7]
		fish/seafood	13 (1300) [a] / 5.5 (210) [b]	14 (1400) [a] / 6.3 (270) [b]	
		eggs	13 (1600) [a] / 11 (1600) [b]	13 (1700) [a] / 12 (1800) [b]	
		dairy products	5.5 (90) [a] / 3.0 (58) [b]	5.9 (96) [a] / 3.2 (66) [b]	
China [d]	2013	eggs		620-46000 [c]	[8]
Netherlands	2009-2014	meat		0.060-0.58 [a] / 0.040-0.34 [b]	[9]
		eggs		0.22 [a] / 0.14 [b]	
		fish		(2.5-1300 [a])	
France	2014-2016	meat	(11 [b])	(170 [a])	[10]
		fish	(5.7 [b])	(540 [a])	
		egg	(22 [b])	(120 [a])	
France	2007-2009	meat	(52 [a])	(540 [a])	[11]
		fish	(43 [a])	(79 [a])	
		eggs	(49 [a])	(68 [a])	
		cheese	(40 [a])	(65 [a])	
Belgium	2015-2016	meat		(690 [a])	[12]
		fish		(370 [a])	
		eggs		(210 [a])	
		dairy products		(600 [a])	
Belgium	2006-2007	egg	2.0-7.1 [a]	3.5-7.8 [a]	[13]
Ireland	2015	fish	(<2.0-60 [c])	(20-1400 [c])	[14]
		eggs	(<190-800 [c])	(30-960 [c])	
Spain		fish/shellfish	(<20 [c])	(400-1300 [c])	[15]
Tanzania	2012	eggs		1.1-350 [c]	[16]
Japan	2011	fish		(2.0-880 [c])	[17]
US	2001-2002	fish		(56-3300 [a])	[18]
US	2009	meat		(14-210 [c])	[19]
		fish		(25-1500 [c])	
		eggs		(89 [c])	
		dairy products		(11-6200 [c])	
US	2013	formula [e]	(42 [a] / 26 [b])	(130 [a] / 42 [b])	[20]
		cereal [e]	(47 [a] / 14 [b])	(38 [a] / 13 [b])	
		puree [e]	(42 [a] / 41 [b])	(190 [a] / 100 [b])	

[a] Mean concentrations, [b] Median concentrations, [c] Ranges, [d] E-waste recycling sites, [e] Baby food

Table S9. Concentrations of NBFRs (pg/g ww in parentheses) in food items from different countries (ng/g lw)

Country	Sampling time	Sample type	pTBX	PBBz	PBT	PBEB	HBBz	EH-TBB	BTBPE	BEH-TEBP	DBDPE	References
UK	2020-2021	meat		0.026 (1.2) [a]	<LOD [c]	<LOD [c]	<LOD [c]	0.63 (43) [a]	4.3 (190) [a]	8.5 (510) [a]	0.38 (18) [a]	[3]
		fish		<LOD [c]	<LOD [c]	<LOD [c]	<LOD [c]	3.3 (17) [a]	22 (200) [a]	20 (390) [a]	1.2 (45) [a]	
		eggs		<LOD [c]	<LOD [c]	<LOD [c]	<LOD [c]	<LOD [c]	36 (2,300) [a]	2.0 (130) [a]	<LOD [a]	
		cheese		<LOD [c]	<LOD [c]	<LOD [c]	<LOD [c]	<LOD [c]	0.39 (97) [a]	0.52 (140) [a]	<LOD [a]	
UK	2015	meat		<LOD [c]	<LOD [c]	<LOD [c]	<LOD [c]	0.19-1.4 [a]	<0.040-2.4 [a]	0.20-0.57 [a]	<1.1-4.6 [a]	[4]
		fish		<LOD [c]	<LOD [c]	<LOD [c]	<LOD [c]	0.22-0.43 [a]	<0.040-0.78 [a]	<0.10-1.1 [a]	<0.63-21 [a]	
		eggs		<LOD [c]	<LOD [c]	<LOD [c]	<LOD [c]	0.10 [a]	0.18 [a]	1.8 [a]	<1.2 [a]	
		cheese		<LOD [c]	<LOD [c]	<LOD [c]	<LOD [c]	0.11 [a]	0.20 [a]	0.22 [a]	<0.74 [a]	
Latvia	2016-2019	meat				(0.34-5.7 [c])	(1.4-9.8 [c])					[6]
		fish				(<0.96-3.1 [c])	(2.8-18 [c])					
		eggs				(<0.43-1.8 [c])	(0.93-5.7 [c])					
		cheese				(<0.30-2.9 [c])	(1.9-12 [c])					
France	2014-2016	meat		(<LOD-18 [c])	(<LOD-7.0 [c])	(<LOD-0.071 [c])	(<LOD-150 [c])	(<LOD-12 [c])	(<LOD-15 [c])			[10]
		fish		(<LOD-6.4 [c])	(<LOD-20 [c])	(<LOD-0.17 [c])	(<LOD-38 [c])	(<LOD-10 [c])	(<LOD-10 [c])			
		egg		(<LOD-4.0 [c])	(<LOD-12 [c])	(<LOD-0.13 [c])	(<LOD-16 [c])	(<LOD-1.3 [c])	(<LOD-12 [c])			
Belgium	2015-2016	meat								(6.0 [a])		[12]
		fish								(<LOD [c])		
		eggs								(<LOD [c])		
		dairy products								(<LOD [c])		
Spain		fish/shellfish				(<20 [c])	(<20-200 [c])				(<10 [c])	[15]
China [d]	2010	eggs						(<LOD-100 [c])		(<LOD-1800 [c])		[21]
China	2010	eggs						(<LOD [c])		(<LOD-540 [c])		[21]
China [d]	2013	eggs					2.0-6.8 [c]		0.40-78 [c]		4.5-190 [c]	[8]
China	2011	meat			0.026-0.16 [c]		<LOD-0.16 [c]		<LOD-0.067 [c]		<LOD-23 [c]	[22]
		fish			0.030-0.37 [c]		<LOD-2.2 [c]		<LOD-1.9 [c]		<LOD-70 [c]	

		eggs			0.0080-0.10 [c]		<LOD-0.076 [c]		<LOD-4.1 [c]		<LOD-20 [c]	
China [d]	2011	fish				<0.17 [a]	6.5 [a]	62 [a]	6.8 [a]	15 [a]	<0.45 [a]	23
		meat				<0.17-0.87 [a]	0.41-0.56 [a]	24-38 [a]	1.5-5.4 [a]	7.2-12 [a]	<0.45 [a]	
		eggs				<0.17 [a]	<0.15 [a]	3.1-5.4 [a]	<0.35-3.8 [a]	0.88-1.6 [a]	<0.45 [a]	
China	2011	fish				<0.17 [a]	<0.15 [a]	4.0 [a]	2.1 [a]	1.9 [a]	<0.45 [a]	23
		meat				<0.17-1.2 [a]	<0.15 [a]	2.1-2.7 [a]	<0.35-2.7 [a]	<0.25-1.8 [a]	<0.45 [a]	
		eggs				<0.17 [a]	<0.15 [a]	1.2-1.7 [a]	<0.35 [a]	<0.25 [a]	<0.45 [a]	
China	2018	meat	0.038 [a]	<LOD [a]	0.010 [a]		0.13 [a]		<LOD [a]			24
		poultry	0.032 [a]	<LOD [a]	<LOD [a]		0.017 [a]		<LOD [a]			
		aquatic food	<LOD [a]	0.091 [a]	0.021 [a]		0.049 [a]		<LOD [a]			
		eggs	<LOD [a]	<LOD [a]	<LOD [a]		0.016 [a]		<LOD [a]			
		dairy products	0.022 [a]	<LOD [a]	<LOD [a]		0.0070 [a]		<LOD [a]			
Tanzania	2012	eggs							<LOD-9.8 [c]			16
US	2013	formula [e]		(1.3 [a])			(6.2 [a] / 6.2 [b])				(19 [a] / 21 [b])	20
		cereal [e]		<LOD			(2.4 [a] / 1.4 [b])				(18 [a] / 11 [b])	
		puree [e]		<LOD			(5.6 [a] / 1.0 [b])				<LOD	

[a] Mean concentrations

[b] Median concentrations

[c] Ranges

[d] E-waste recycling sites

[e] baby food

Table S10. Concentrations of HBCDDs (pg/g ww in parentheses) in food items from different countries (ng/g lw)

Country	Sampling time	Sample type	ΣHBCDDs	References
UK	2020-2021	meat	0.16 (8.9) [a]	[3]
		fish	0.83 (67) [a]	
		eggs	0.19 (16) [a]	
		cheese	0.050 (12) [a]	
UK	2015	meat	0.32-4.6 (26-200) [a]	[4]
		fish	3.6-16 (180-830) [a]	
		eggs	1.3 (300) [a]	
		cheese	<0.24 (<43) [a]	
UK	2013	meat	(40 [a])	[5]
		fish	(1400 [a])	
		egg	(<20 [a])	
		dairy products	(40 [a])	
Latvia	2016-2019	meat	(270 [a] / 160 [b])	[6]
		fish	(730 [a] / 480 [b])	
		eggs	(24 [a] / 16 [b])	
		cheese	(330 [a] / 160 [b])	
China	2013	meat	2.8 (570) [a] / 2.4 (180) [b]	[7]
		fish/seafood	7.0 (410) [a] / 5.6 (290) [b]	
		eggs	4.5 (600) [a] / 4.0 (500) [b]	
		dairy products	1.4 (140) [a] / 1.1 (44) [b]	
China [d]	2013	eggs	56-7600 [c]	[8]
China [d]	2011	fish	310 [a]	[23]
		meat	<0.060-79 [a]	
		eggs	2.2-47 [a]	
China	2011	fish	5.9 [a]	[23]
		meat	0.090-3.1 [a]	
		eggs	0.50-1.70 [a]	
France	2014-2016	meat	(130 [a])	[10]
		fish	(140 [a])	
France	2007-2009	meat	(130 [a])	[11]
		fish	(140 [a])	

		eggs	(26 [a])	
		cheese	(20 [a])	
Belgium	2015-2016	meat	(43 [a])	[12]
		fish	(130 [a])	
		eggs	(970 [a])	
		dairy products	(0.10 [a])	
Belgium	2006-2007	egg	6.5-8.5 [a]	[13]
Ireland	2015	fish	(70-410 [c])	[14]
		eggs	(10-20 [c])	
Tanzania	2012	eggs	<LOD-63 [c]	[16]
Japan	2011	fish	(<LOD-22000 [c])	[17]
Sweden	1999	meat	<1.0-6.5 [a]	[25]
		fish	48 [a]	
		egg	9.4 [a]	
US	2009	meat	(23-190 [c])	[19]
		fish	(<29-590 [c])	
		eggs	(<11 [c])	
		dairy products	(<64 [c])	

[a] Mean concentrations

[b] Median concentrations

[c] Ranges

[d] E-waste recycling sites

Table S11. Concentrations of DPs (pg/g ww in parentheses) in food items from different countries (ng/g lw)

Country	Sampling time	Sample type	*syn*-DP	*anti*-DP	ΣDPs	f_{anti}	References
Lebanon	2017	meat	(10-12 [a])	(7.4-8.1 [a])	(17-20 [a])	0.26-0.76	[26]
		fish	(2.0-4.2 [a])	(3.0-3.9 [a])	(5.0-8.0 [a])	0.26-0.76	
		egg	(1.7-3.1 [a])	(5.2-5.8 [a])	(6.9-8.9 [a])	0.26-0.76	
		dairy products	(1.0-2.0 [a])	(0.70-1.1 [a])	(1.7-3.1 [a])	0.26-0.76	
Latvia	2016-2019	meat	(0.77-4.7 [c])	(1.5-11 [c])	(2.3-16 [c])	0.63-0.81	[6]
		fish	(2.7-7.7 [c])	(4.8-14 [c])	(7.5-21 [c])	0.56-0.77	
		eggs	(2.3-20 [c])	(8.1-54 [c])	(10-75 [c])	0.66-0.78	
		cheese	(0.50-3.9 [c])	(2.1-14 [c])	(2.6-18 [c])	0.67-0.80	
China [d]	2013	eggs			30-2200 [c]	0.74-0.76	[8]
Belgium	2015-2016	meat			(10 [a])	0.80	[12]
		fish			(<LOD [a])		
		eggs			(160 [a])	0.80	
		dairy products			(9.0 [a])	0.80	
Japan	2011	fish	(<LOD-6.1 [c])	(<LOD-8.1 [c])	(<LOD-14 [c])	0.56-0.72	[17]
Japan	2012	meat & eggs	(1.0)	(0.90)	(1.9)	0.47	[27]
		fish	(0.60)	(0.90)	(1.5)	0.60	
		dairy products	<LOD	<LOD	<LOD		

[a] Mean concentrations

[b] Median concentrations

[c] Ranges

[d] E-waste recycling sites

Table S12. Median concentrations (pg/g ww) of PBDEs and NBFRs in food items by price range and ANOVA test results

Price	Number of individual samples included	Number of composite samples analyzed	Σ_{13}PBDEs	Σ_{4}NBFRs
low	18	11	170	26
medium	27	17	180	4.5
high	27	14	170	9.8
F value (ANOVA)	-	-	0.187	3.202
Sig. (ANOVA)	-	-	0.830	0.052

Table S13. Median concentrations (pg/g ww) of PBDEs and NBFRs in organic and non-organic US food items and Paired-Samples t test results

Food category	Number of individual samples included	Number of composite samples analyzed	Σ_{13}PBDEs	Σ_4NBFRs
organic				
beef	1	1	170	1.5
pork	5	2	190	1.2
chicken	8	4	120	21
turkey	3	2	280	17
cheese	3	3	450	26
egg	6	2	130	18
sum	26	14	190	18
non-organic				
beef	8	3	94	4.4
pork	4	2	170	40
chicken	3	2	190	17
turkey	2	2	190	38
cheese	3	3	530	3.3
egg	9	3	180	4.5
sum	29	15	180	5.9
p value	-	-	0.941	0.735

Table S14. Average daily consumption of food items (g/day) [a] for US children (< 20 years old) and adults (≥ 20 years old)[1]

Age	Gender	Beef	Pork	Chicken	Turkey	Salmon [b]	Cod [b]	Catfish [b]	Tilapia [b]	Tuna [b]	Cheese	Egg
< 20 years	Male	54	32	55	8.0	0.96	0.96	0.96	0.96	0.96	26	19
	Female	35	21	49	7.1	0.81	0.81	0.81	0.81	0.81	23	15
	All	45	27	52	7.6	0.89	0.89	0.89	0.89	0.89	25	17
≥ 20 years	Male	82	58	72	13	3.7	3.7	3.7	3.7	3.7	32	32
	Female	44	31	54	11	2.3	2.3	2.3	2.3	2.3	24	21
	All	63	44	63	12	3.0	3.0	3.0	3.0	3.0	28	26

[a] US per capita loss-adjusted food availability; unit is converted from lb/year to g/day.

[b] Consumption of salmon (cod/catfish/tilapia/tuna) is assumed to be total consumption of fish divided by 5.

Table S15. Average daily consumption of food items (g/day) [a] for US adults (≥ 20 years old) of different races[1]

Race	Beef	Pork	Chicken	Turkey	Salmon [b]	Cod [b]	Catfish [b]	Tilapia [b]	Tuna [b]	Cheese	Egg
Hispanic [c]	60	34	62	6.5	2.3	2.3	2.3	2.3	2.3	22	26
Non-Hispanic white	60	40	57	11	2.2	2.2	2.2	2.2	2.2	30	23
Non-Hispanic black	54	39	78	15	2.7	2.7	2.7	2.7	2.7	22	24
Non-Hispanic Asian	39	43	57	7.6	4.3	4.3	4.3	4.3	4.3	17	23

[a] US per capita loss-adjusted food availability; unit is converted from lb/year to g/day.

[b] Consumption of salmon (cod/catfish/tilapia/tuna) is assumed to be total consumption of fish divided by 5.

[c] Includes Mexican-American persons.

Table S16. Average body weight (kg) of US children (< 20 years old) and adults (≥ 20 years old)[2]

Age	Male	Female	All
< 20 years	37.8	35.9	36.9
≥ 20 years	90.6	77.5	83.9

Table S17. Average body weight (kg) of US adults (≥ 20 years old) by race[2]

Race	Male	Female	All
Hispanic [a]	87.9	76.2	81.6
Non-Hispanic white	92.2	77.5	84.9
Non-Hispanic black	90.8	85.5	88.0
Non-Hispanic Asian	76.2	61.2	68.5

[a] Includes Mexican-American persons.

Table S18. Estimated median dietary intake of HFRs (ng/kg bw/day) [a] for US children and adults

HFRs	Children (< 20 years old)			Adults (20 + years old)		
	Boys	**Girls**	**All**	**Men**	**Women**	**All**
BDE-15	0.37	0.30	0.34	0.23	0.17	0.21
BDE-17	0.12	0.10	0.11	0.068	0.055	0.062
BDE-28	0.042	0.036	0.039	0.030	0.023	0.027
BDE-49	0.031	0.026	0.029	0.019	0.015	0.017
BDE-47	0.0036	0.0033	0.0035	0.0038	0.0030	0.0035
BDE-100	0.030	0.025	0.028	0.019	0.014	0.017
BDE-99	0.016	0.013	0.015	0.011	0.0086	0.0097
BDE-154	0.064	0.054	0.060	0.039	0.030	0.035
BDE-153	0.021	0.018	0.020	0.013	0.010	0.012
BDE-139	0.041	0.034	0.038	0.024	0.018	0.021
BDE-140	0.021	0.015	0.018	0.015	0.010	0.013
BDE-183	0.0068	0.0055	0.0063	0.0047	0.0034	0.0041
BDE-209	0.036	0.031	0.033	0.023	0.018	0.020
Σ_{13}PBDEs	**0.80**	**0.67**	**0.74**	**0.50**	**0.38**	**0.45**
pTBX	0.0082	0.0075	0.0079	0.0063	0.0051	0.0058
PBBZ	0.012	0.0095	0.011	0.0075	0.0056	0.0066
EHTBB	0.0064	0.0044	0.0055	0.0050	0.0032	0.0041
BEHTBP	0.0017	0.0015	0.0016	0.0012	0.0011	0.0012
Σ_4NBFRs	**0.028**	**0.023**	**0.026**	**0.020**	**0.015**	**0.018**
syn-DP	0.0012	0.0012	0.0012	0.00088	0.00073	0.00081
anti-DP	0.00034	0.00031	0.00033	0.00046	0.00035	0.00041
Σ_2DPs	**0.0016**	**0.0015**	**0.0015**	**0.0013**	**0.0011**	**0.0012**
Σ_{19}HFRs	**0.83**	**0.69**	**0.77**	**0.52**	**0.40**	**0.47**

[a] Median concentrations of HFRs in US food items were applied. Only HFRs with a DF exceeding 30% were included.

Table S19. Estimated median dietary intake of HFRs (ng/kg bw/day) [a] for US adults by race

HFRs	Hispanic	Non-Hispanic white	Non-Hispanic black	Non-Hispanic Asian
BDE-15	0.17	0.20	0.18	0.20
BDE-17	0.053	0.062	0.050	0.054
BDE-28	0.023	0.023	0.025	0.032
BDE-49	0.015	0.016	0.016	0.018
BDE-47	0.0026	0.0028	0.0032	0.0049
BDE-100	0.015	0.015	0.016	0.017
BDE-99	0.0090	0.0086	0.0089	0.0099
BDE-154	0.031	0.033	0.031	0.034
BDE-153	0.010	0.011	0.012	0.012
BDE-139	0.021	0.020	0.022	0.021
BDE-140	0.011	0.011	0.011	0.013
BDE-183	0.0035	0.0036	0.0040	0.0048
BDE-209	0.018	0.019	0.020	0.021
Σ_{13}PBDEs	**0.39**	**0.42**	**0.39**	**0.44**
pTBX	0.0053	0.0047	0.0060	0.0079
PBBZ	0.0061	0.0061	0.0060	0.0066
EHTBB	0.0033	0.0037	0.0035	0.0052
BEHTBP	0.00087	0.0010	0.0012	0.0012
Σ_4NBFRs	**0.016**	**0.015**	**0.017**	**0.021**
syn-DP	0.00076	0.00068	0.00087	0.0011
anti-DP	0.00031	0.00031	0.00038	0.00067
Σ_2DPs	**0.0011**	**0.00099**	**0.0012**	**0.0017**
Σ_{19}HFRs	**0.40**	**0.44**	**0.41**	**0.46**

[a] Median concentrations of HFRs in US food items were applied. Only HFRs with a DF exceeding 30% were included.

Table S20. Reference dose (RfD) values (ng/kg bw/day) for HFRs

BFRs	RfD	References
BTBPE	243,000	[28]
EH-TBB	20,000	[28]
BEH-TEBP	20,000	[28]
DBDPE	333,333	[28]
BDE-209	7,000 [a]	[29]
Octa-BDE	3,000	[29]
Penta-BDE	2,000	[29]
BDE-47	100	[29]
BDE-99	100	[29]
BDE-153	200	[29]
∑HBCDDs	200,000	[30]
∑DPs	5,000,000	[31]

[a] For decaBDE-209, EPA has assigned an oral slope factor for carcinogenic risk of 700 $(ng/kg\ bw/day)^{-1}$ (EPA IRIS 2008).

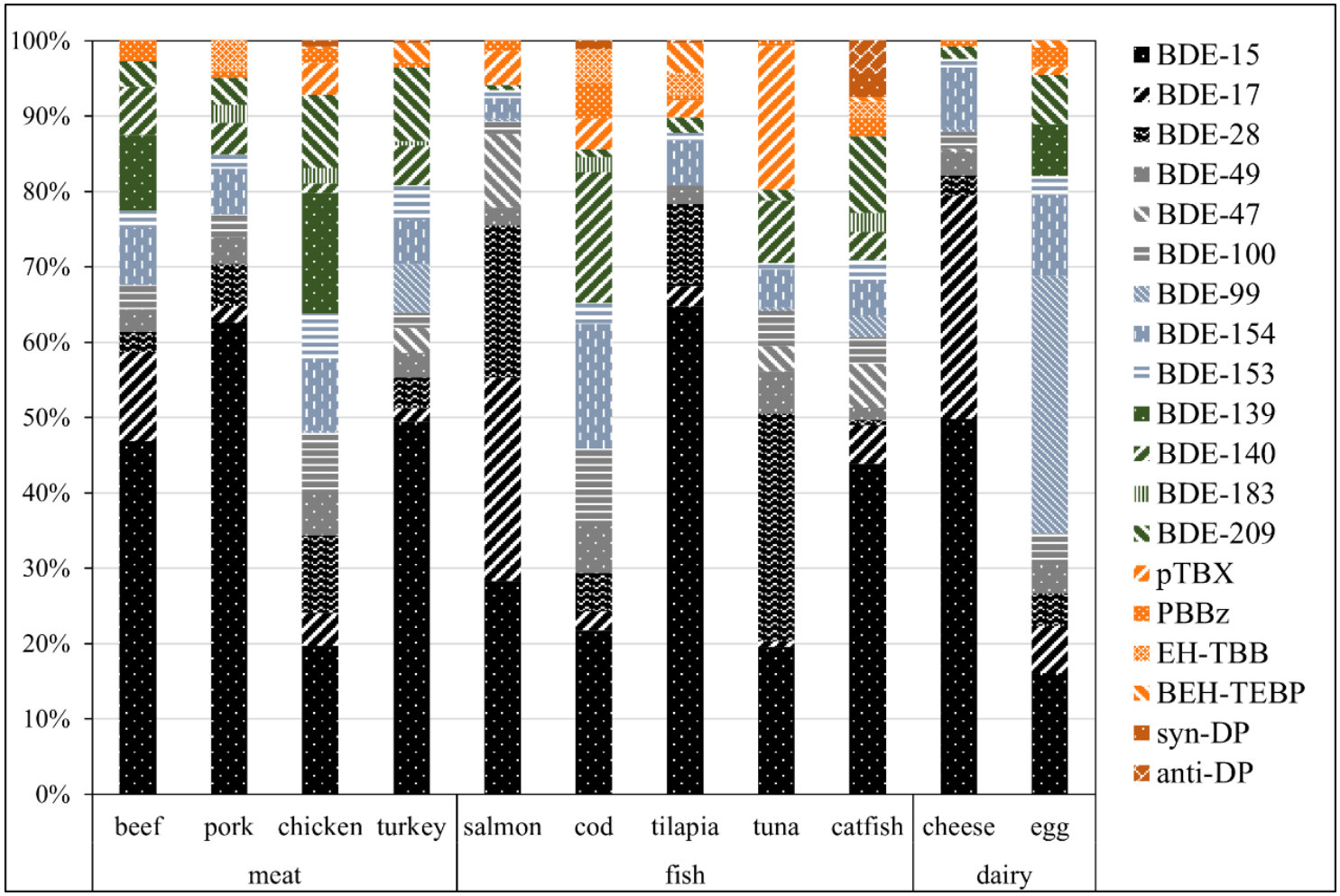


Fig. S1 Relative contribution of HFRs in different US food items. Median concentrations were used. Only HFRs with a DF exceeding 30% were included.

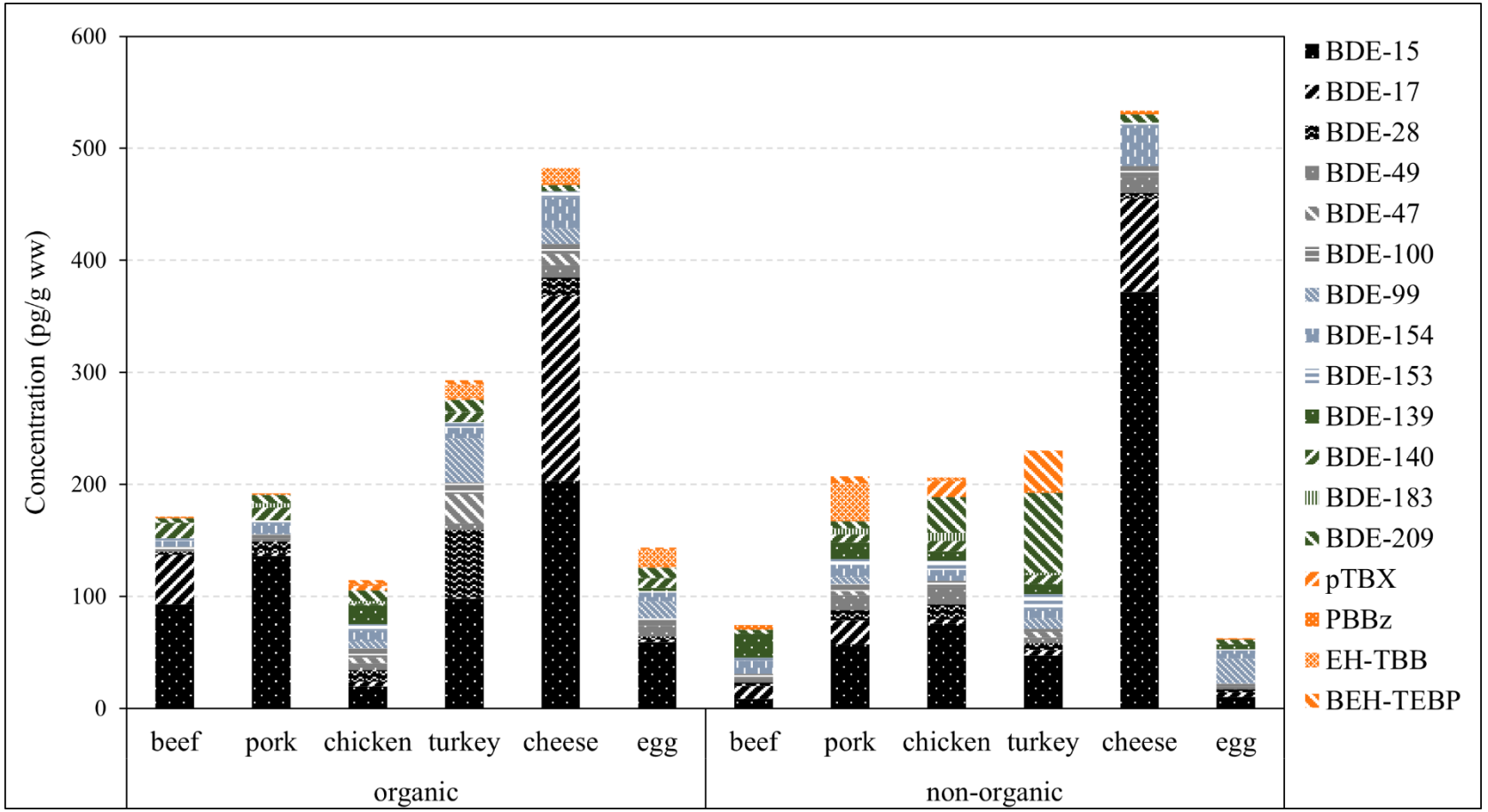


Fig. S2 Median concentrations of PBDEs and NBFRs in organic and non-organic US food items. Only PBDEs and NBFRs with a DF exceeding 30% are included.

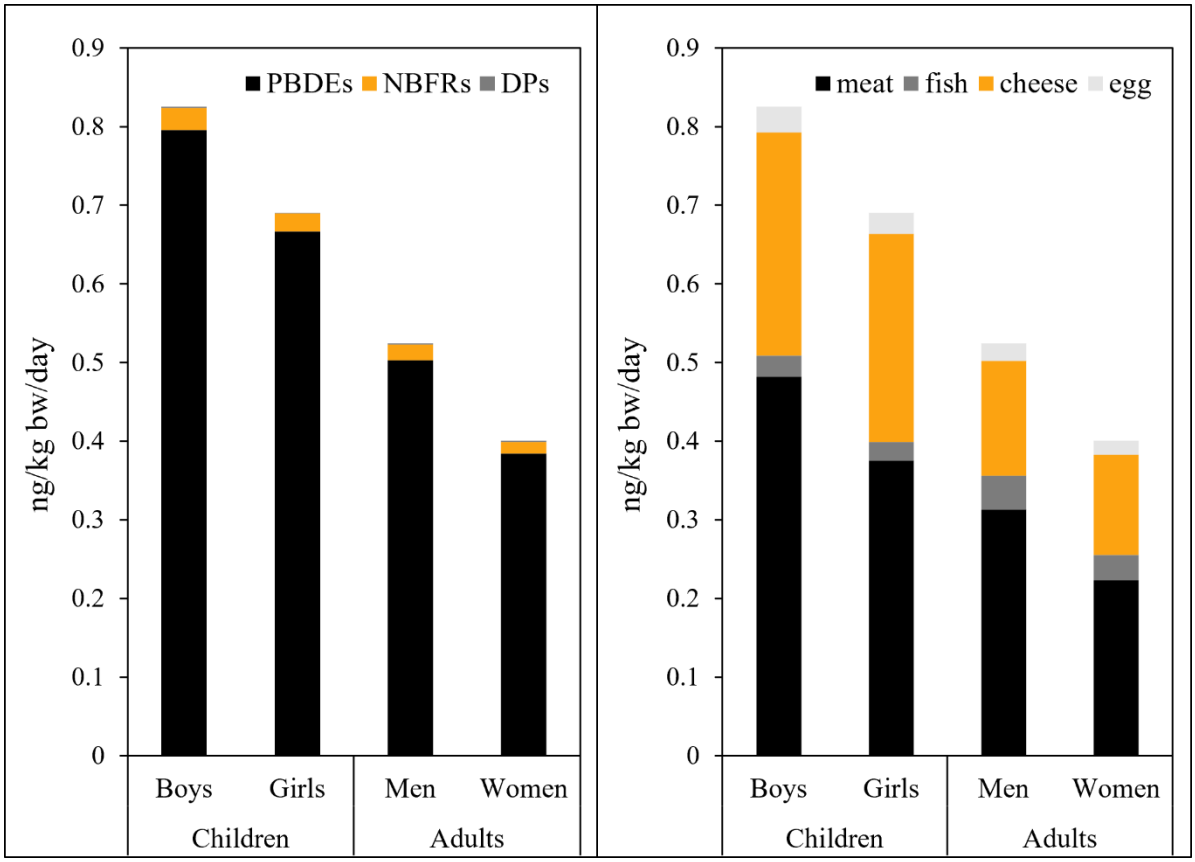


Fig. S3 Estimated median dietary intake of HFRs for US children (< 20 years old) and adults (≥ 20 years old): contribution of different FR classes (left) and food categories (right). See Table S18 for detailed data.

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Appendix C. Supplementary Materials for Chapter Four

1. Materials and Methods

1.1 Chemicals and reagents

All the solvents used in this study were purchased from Fisher Scientific (Loughborough, UK), and were of HPLC analytical grade. Sulfuric acid (>95%) was purchased from Fisher Scientific (Loughborough, UK), and was of analytical reagent grade. All the native and labelled standards were purchased from Wellington Laboratories (Guelph, ON, Canada), except for BDE-77 and BDE-128 (obtained from AccuStandard Inc. (New Haven, CT, USA)) as well as native HBCDDs (obtained from Sigma-Aldrich Company Ltd. (Dorset, UK)). Florisil® (60-100 mesh) was purchased from Acros Organics (New Jersey, USA), and was baked at 450℃ for 1h prior to use. Alumina was purchased from Fisher Scientific (Loughborough, UK), and was baked at 450℃ for 4h prior to use.

1.2 Sample extraction and clean-up

Fig. S1 explains sample extraction and clean-up protocols adopted in this study. Approximately 0.5 g of freeze-dried food samples were precisely weighted and spiked with 60 ng of 13C-BDE-209 and 15 ng of BDE-77, BDE-128, 13C-HBBz, 13C-EH-TBB, 13C-BTBPE, 13C-BEH-TEBP, 13C-α-HBCDD, 13C-β-HBCDD, and 13C-γ-HBCDD as internal standards before extraction. Hexane/Acetone (3:1, v/v) was used to extract the samples on 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 extraction programme was set as below:

Temperature: 100℃; Heating time: 5 min; Static time: 4 min; Cycles: 3; Pressure: 1500 psi. Purge time: 90 s; Flush volume: 60%.

The extracts were collected in pre-cleaned ASE collection bottles. Approximately 10% of the extracts were transferred into pre-weighted glass tubes. The glass tubes were then stored at 50℃ overnight before being weighted again. This allowed lipid content to be determined gravimetrically. The remaining ~90% of the extracts were concentrated to 5 mL before shaking with 5 mL sulfuric

acid (95%) to remove lipids and proteins. The samples were then centrifuged at 3900 RPM for 20 min, and the solvent phase (upper layer) was collected. The acid phase (bottom layer) was extracted with 2 mL hexane twice and then centrifuged, and the solvents were collected and combined. The purified extracts were concentrated to incipient dryness under a gentle stream of nitrogen, and then were reconstituted into 50 μL toluene containing 200 pg/μL 13C-BDE-100 and d18-γ-HBCDD as recovery determination standards before GC-MS and LC-MS/MS analysis.

1.3 Instrumental analysis

1.3.1 PBDEs and NBFRs

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 with a programmable-temperature vaporizer (PTV) injector. The ion source was operated in EI SIM mode at 280℃, and the MS transfer line temperature was 300℃. A capillary fused silica column (RESTEK, USA, 15 m x 0.25 mm inner diameter, 0.25 μm film thickness) was equipped and the GC oven temperature was set as below:

(1) initial temperature 80℃, held for 2 min;

(2) oven temperature ramped to 170℃ at a rate of 20℃/min and held for 5.5 min;

(3) oven temperature then ramped to 320℃ at a rate of 25℃/min and held for 10 min.

1.3.2 HBCDD

Analysis of HBCDDs 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). The MS was operated in electrospray negative ionization - multiple reaction monitoring (ESI^--MRM) mode, and was applied for quantitative determination of the target compounds based on m/z 640.6/79 for native HBCDDs, m/z 652.4/79 for 13C-HBCDDs, and m/z 657.7/79 for d18-γ-HBCDD, respectively. 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. The LC program was set as below:

(1) mobile phase B commenced with 25% composition, and then ramped to 50% over 1 min;

(2) mobile phase B increased linearly to 100% over 5 min and held for 10 min;

(3) mobile phase B returned to 25% and held for 1 min to equilibrate for the next sample.

1.4 QA/QC

Table S1 summarised concentrations of the native compounds (target analytes), internal standards, and recovery determination standards in a full 5-point calibration. The relative response factors (defined as the instrument response for a unit amount of target pollutant relative to the instrument response obtained for the same amount of the internal standard) for each analyte in the 5-point calibration were given in Table S2. Limit of detection (LOD) and limit of quantification (LOQ) for each analyte were calculated based on the signal/noise ratio of 3 and 10, respectively, and the data was presented in Table S3. Recoveries of internal standards in all the blanks and samples were given in Table S4. Five replicates of an egg sample were conducted to evaluate the consistency of the method, and the data was shown in Table S5.

2 Tables

Table S1. Concentrations of the target compounds (TC), internal standards (IS), and recovery determination standards (RDS) in 5-point calibrations

Concentrations (pg/μL)	Calibration A	Calibration B	Calibration C	Calibration D	Calibration E
TC	10	20	50	100	200
IS	200	200	200	200	200
RDS	200	200	200	200	200

Table S2. The relative response factors (RRFs) for each analyte in the 5-point calibrations

Target compounds	Calibration A	Calibration B	Calibration C	Calibration D	Calibration E	RSD (%)	R^2
BDE-28	0.60	0.59	0.60	0.58	0.54	4.3	0.9955
BDE-47	0.58	0.54	0.56	0.58	0.58	3.1	0.9917
BDE-99	1.2	1.2	1.2	1.1	1.2	3.0	0.9950
BDE-100	0.99	1.0	1.0	0.98	0.98	1.3	0.9970
BDE-153	0.85	1.0	0.84	0.96	1.0	9.2	0.9890
BDE-154	0.88	0.91	0.78	0.90	0.94	6.9	0.9927
BDE-183	0.59	0.60	0.54	0.56	0.58	4.2	0.9969
BDE-209	1.1	1.1	1.0	1.1	1.0	4.1	0.9999
PBBz	27	31	32	30	27	7.9	0.9935
PBT	18	18	17	16	17	5.5	0.9991
PBEB	14	15	14	13	13	4.0	0.9985
DPTE	46	44	41	42	47	5.8	0.9920
HBBz	19	18	17	19	16	6.9	0.9999
EH-TBB	1.1	1.1	1.0	1.0	1.1	6.5	0.9949
BTBPE	1.4	1.3	1.5	1.5	1.4	6.9	0.9917
BEH-TEBP	0.99	1.1	0.98	0.96	0.98	6.4	0.9943
DBDPE	3.0	3.1	2.6	2.6	2.7	8.4	0.9989
α-HBCDD	1.3	1.1	1.3	1.2	1.2	8.7	0.9995
β-HBCDD	1.2	1.1	1.2	1.1	1.1	6.4	0.9997
γ-HBCDD	0.90	0.84	0.83	0.74	0.72	8.8	0.9999

Table S3. Limit of detection (LOD) and limit of quantification (LOQ) for each analyte

Target compounds	LODs (S:N=3:1)		LOQs (S:N=10:1)
	pg/injection [a]	pg/g dw [b]	pg/g dw [b]
BDE-28	0.055	11	37
BDE-47	0.017	3.4	11
BDE-99	0.014	2.8	9.3
BDE-100	0.017	3.4	11
BDE-153	0.011	2.2	7.3
BDE-154	0.014	2.8	9.3
BDE-183	0.063	13	42
BDE-209	0.074	15	49
PBBz	0.030	6.0	20
PBT	0.049	9.8	33
PBEB	0.020	4.0	13
DPTE	0.18	36	120
HBBz	0.022	4.4	15
EH-TBB	0.15	30	100
BTBPE	0.83	170	550
BEH-TEBP	0.86	170	570
DBDPE	0.45	90	300
α-HBCDD	0.93	17	62
β-HBCDD	1.6	32	110
γ-HBCDD	0.49	9.8	33

[a] 1 μL of calibration A was injected into GC-MS for the calculation of instrument LODs of PBDEs and NBFRs; 10 μL of calibration A was injected into HPLC-MS/MS for the calculation of instrument LODs of HBCDDs.

[b] 0.5 g sample (dw) was assumed to calculate the method LODs and LOQs.

Table S4. Recoveries of internal standards in blanks, food samples, and replicate analyses

Internal standards	Blanks (n=10)	Samples (n=36)	Replicates (n=5)
BDE-77	78%-103%	48%-128%	92%-104%
BDE-128	82%-128%	62%-137%	77%-102%
13C-BDE-209	61%-120%	47%-123%	92%-123%
13C-HBBz	60%-88%	62%-119%	99%-119%
13C-EH-TBB	63%-94%	45%-88%	47%-54%
13C-BTBPE	100%-120%	70%-128%	119%-128%
13C-BEH-TEBP	69%-117%	39%-127%	84%-111%
13C-α-HBCDD	36%-86%	31%-86%	37%-58%
13C-β-HBCDD	40%-103%	44%-108%	64%-73%
13C-γ-HBCDD	86%-129%	90%-140%	96%-114%

Table S5. BFR concentrations in 5 replicate analyses of chicken eggs (pg/g dw)

FRs	Replicate 1	Replicate 2	Replicate 3	Replicate 4	Replicate 5	Mean	RSD
BDE-28	ND [a]	ND	ND	ND	ND	ND	-
BDE-47	120	140	130	150	150	140	9.3%
BDE-99	600	700	540	640	730	640	12%
BDE-100	87	92	77	90	89	87	6.8%
BDE-153	ND	ND	ND	ND	ND	ND	-
BDE-154	ND	ND	ND	ND	ND	ND	-
BDE-183	ND	ND	ND	ND	ND	ND	-
BDE-209	520	470	520	510	520	510	4.2%
PBBz	ND	ND	ND	ND	ND	ND	-
PBT	ND	ND	ND	ND	ND	ND	-
PBEB	ND	ND	ND	ND	ND	ND	-
DPTE	ND	ND	ND	ND	ND	ND	-
HBBz	ND	ND	ND	ND	ND	ND	-
EH-TBB	ND	ND	ND	ND	ND	ND	-
BTBPE	27000	25000	26000	22000	24000	25000	7.6%
BEH-TEBP	ND	ND	ND	ND	ND	ND	-
DBDPE	ND	ND	ND	ND	ND	ND	-
α-HBCDD	ND	ND	ND	ND	ND	ND	-
β-HBCDD	ND	ND	ND	ND	ND	ND	-
γ-HBCDD	ND	ND	ND	ND	ND	ND	-

[a] ND = not detected

Table S6. Mean concentrations of total BFRs (sum of PBDEs, NBFRs, and HBCDDs; pg/g ww in parentheses) in UK foodstuffs (ng/g lw)

Food items	Number of composite samples	Number of individual samples included	Water content (%)	Lipid content (%)	Total BFR concentrations
Beef	3	9	69	4.3	7.8 (360)
Lamb	2	6	64	20	2.6 (510)
Chicken	3	9	65	12	12 (480)
Pork	3	9	73	3.9	16 (2100)
Turkey	1	3	65	0.65	75 (490)
ΣMeat	**12**	**36**	**-**	**-**	**16 (860)**
Salmon	3	9	58	20	6.0 (1200)
Prawn	3	9	78	0.49	160 (770)
Cod	2	6	77	2.1	44 (690)
Tuna	2	6	74	1.0	65 (410)
Basa	1	3	78	3.0	20 (600)
Trout	1	3	68	12	7.5 (900)
Tilapia	1	3	80	0.50	29 (150)
Mackerel	1	3	50	29	13 (3700)
ΣFish/Prawns	**14**	**42**	**-**	**-**	**57 (960)**
Cheese	5	15	40	25	2.3 (580)
Chicken eggs	5	15	77	6.8	44 (2800)

Table S7. Mean concentrations of NBFRs (pg/g ww in parentheses) in UK foodstuffs (ng/g lw)

Food items	PBBz	PBT	PBEB	DPTE	HBBz	EH-TBB	BTBPE	BEH-TEBP	DBDPE	Σ_9NBFRs
Beef	0.098 (4.6)	<0.071 (<3.0)	<0.029 (<1.2)	<0.26 (<11)	<0.032 (<1.3)	2.1 (97)	2.7 (120)	<1.2 (<52)	<0.65 (<27)	5.7 (260)
Lamb	<0.011 (<2.2)	<0.018 (<3.5)	<0.0074 (<1.4)	<0.065 (<13)	<0.0081 (<1.6)	0.53 (110)	1.3 (240)	0.33 (65)	<0.17 (<32)	2.2 (430)
Chicken	<0.046 (<1.6)	<0.074 (<2.6)	<0.030 (<1.1)	<0.27 (<9.4)	<0.033 (<1.2)	<0.22 (<7.9)	6.9 (270)	3.3 (120)	0.43 (13)	11 (400)
Pork	<0.019 (<2.1)	<0.031 (<3.4)	<0.013 (<1.4)	0.93 (94)	<0.014 (<1.5)	<0.094 (<10)	1.6 (190)	12 (1700)	0.58 (45)	15 (2000)
Turkey	<0.33 (<2.1)	<0.53 (<3.4)	<0.21 (<1.4)	<1.9 (<12)	<0.24 (<1.5)	<1.6 (<10)	15 (98)	55 (360)	<4.8 (<31)	71 (460)
ΣMeat	**0.026 (1.2)**	**<0.091 (<3.1)**	**<0.037 (<1.3)**	**0.29 (25)**	**<0.041 (<1.4)**	**0.63 (43)**	**4.3 (190)**	**8.5 (510)**	**0.38 (18)**	**14 (790)**
Salmon	<0.013 (<2.6)	<0.021 (<4.1)	<0.0085 (<1.7)	<0.075 (<15)	<0.0094 (<1.8)	<0.063 (<12)	1.3 (230)	1.5 (310)	0.64 (150)	3.5 (690)
Prawn	<0.39 (<1.4)	<0.63 (<2.2)	<0.26 (<0.89)	2.8 (22)	<0.28 (<0.98)	<1.9 (<6.6)	83 (420)	51 (210)	<5.7 (<20)	140 (660)
Cod	<0.092 (<1.4)	<0.15 (<2.2)	<0.060 (<0.90)	6.8 (110)	<0.066 (<0.99)	5.1 (46)	15 (220)	13 (210)	<1.3 (<20)	40 (600)
Tuna	<0.27 (<1.6)	<0.43 (<2.5)	<0.17 (<1.0)	<1.5 (<9.1)	<0.19 (<1.1)	18 (65)	5.2 (47)	34 (240)	2.5 (11)	60 (370)
Basa	<0.045 (<1.3)	<0.072 (<2.2)	<0.029 (<0.88)	5.1 (150)	<0.032 (<0.97)	<0.22 (<6.5)	2.1 (62)	6.6 (200)	3.3 (99)	17 (510)
Trout	<0.016 (<2.0)	<0.026 (<3.1)	<0.011 (<1.3)	<0.094 (<11)	<0.011 (<1.4)	<0.079 (<9.5)	0.75 (90)	0.76 (91)	<0.24 (<29)	1.6 (190)
Tilapia	<0.24 (<1.2)	<0.39 (<2.0)	<0.16 (<0.80)	<1.4 (<7.0)	<0.18 (<0.88)	<1.2 (<5.9)	11 (56)	11 (57)	2.6 (13)	26 (130)
Mackerel	<0.011 (<3.1)	<0.017 (<4.9)	<0.0069 (<2.0)	<0.061 (<18)	<0.0076 (<2.2)	<0.051 (<15)	<0.30 (<84)	9.3 (2700)	<0.15 (<45)	9.4 (2700)
ΣFish/Prawns	**<0.16 (<1.8)**	**<0.26 (<2.9)**	**<0.10 (<1.2)**	**2.0 (33)**	**<0.12 (<1.30)**	**3.3 (17)**	**22 (200)**	**20 (390)**	**1.2 (45)**	**48 (680)**
Cheese	<0.015 (<3.7)	<0.024 (<5.9)	<0.0099 (<2.4)	<0.087 (<21)	<0.011 (<2.7)	<0.073 (<18)	0.39 (97)	0.52 (140)	<0.31 (<51)	1.0 (260)
Chicken eggs	<0.021 (<1.4)	<0.034 (<2.3)	<0.014 (<0.94)	0.63 (39)	<0.015 (<1.0)	<0.10 (<6.9)	36 (2300)	2.0 (130)	<0.31 (<21)	39 (2500)

Table S8. Mean concentrations of PBDEs (pg/g ww in parentheses) in UK foodstuffs (ng/g lw)

Food items	BDE-28	BDE-47	BDE-99	BDE-100	BDE-153	BDE-154	BDE-183	BDE-209	Σ_8PBDEs
Beef	<0.080 (<3.4)	0.12 (5.5)	<0.021 (<0.87)	0.28 (12)	0.25 (12)	0.063 (2.9)	0.48 (20)	0.76 (36)	2.0 (88)
Lamb	<0.020 (<4.0)	0.023 (4.2)	<0.0052 (<1.0)	<0.0063 (<1.2)	0.094 (19)	<0.0051 (<0.98)	0.18 (36)	<0.027 (<5.3)	0.32 (62)
Chicken	<0.083 (<2.9)	<0.030 (<1.0)	0.32 (18)	<0.026 (<0.90)	0.15 (3.9)	<0.021 (<0.73)	0.23 (7.5)	0.83 (38)	1.5 (69)
Pork	<0.035 (<3.8)	0.13 (14)	<0.0089 (<0.99)	0.21 (17)	<0.0069 (<0.77)	<0.0086 (<0.96)	0.064 (7.5)	0.24 (19)	0.65 (58)
Turkey	<0.59 (<3.8)	<0.22 (<1.4)	<0.15 (<0.99)	<0.18 (<1.2)	<0.12 (<0.77)	<0.15 (<0.96)	2.4 (15)	<0.80 (<5.2)	3.0 (19)
ΣMeat	**<0.10 (<3.5)**	**0.079 (5.8)**	**0.086 (4.8)**	**0.13 (7.5)**	**0.12 (7.1)**	**0.020 (0.86)**	**0.42 (16)**	**0.49 (24)**	**1.3 (66)**
Salmon	<0.023 (<4.6)	1.4 (270)	<0.0060 (<1.2)	<0.0072 (<1.4)	0.050 (8.1)	0.29 (56)	0.12 (21)	0.21 (46)	2.1 (400)
Prawn	<0.70 (<2.5)	1.2 (9.8)	3.4 (29)	<0.22 (<0.76)	<0.14 (<0.49)	4.3 (20)	0.90 (2.2)	14 (44)	24 (110)
Cod	<0.16 (<2.5)	1.5 (19)	<0.042 (<0.64)	1.5 (47)	<0.033 (<0.50)	<0.041 (<0.62)	0.62 (17)	0.70 (6.9)	4.3 (90)
Tuna	<0.48 (<2.9)	<0.19 (<1.0)	<0.12 (<0.73)	<0.15 (<0.88)	2.3 (8.4)	<0.12 (<0.71)	0.89 (12)	1.4 (21)	4.8 (42)
Basa	<0.081 (<2.4)	<0.028 (<0.87)	<0.021 (<0.62)	1.3 (40)	<0.016 (<0.48)	<0.020 (<0.60)	<0.096 (<2.9)	1.3 (40)	2.7 (83)
Trout	<0.029 (<3.5)	1.9 (230)	<0.0075 (<0.90)	<0.0090 (<1.1)	<0.0059 (<0.70)	0.33 (39)	0.13 (15)	<0.040 (<4.7)	2.4 (290)
Tilapia	<0.44 (<2.2)	<0.16 (<0.79)	<0.11 (<0.56)	<0.14 (<0.68)	<0.088 (<0.44)	<0.11 (<0.55)	2.7 (13)	<0.59 (<3.0)	3.2 (16)
Mackerel	<0.019 (<5.5)	1.7 (500)	0.15 (45)	<0.0058 (<1.7)	<0.0038 (<1.1)	0.32 (93)	0.11 (32)	0.30 (88)	2.6 (760)
ΣFish/Prawns	**<0.29 (<3.2)**	**1.1 (120)**	**0.76 (10)**	**0.34 (9.9)**	**0.35 (3.0)**	**1.0 (26)**	**0.64 (13)**	**3.5 (32)**	**7.7 (210)**
Cheese	<0.027 (<6.6)	0.11 (25)	0.76 (190)	0.10 (24)	0.016 (5.0)	<0.0068 (<1.6)	0.086 (23)	0.15 (42)	1.2 (310)
Chicken eggs	<0.039 (<2.6)	0.21 (15)	3.2 (220)	0.50 (34)	0.031 (1.9)	<0.0096 (<0.64)	0.17 (11)	0.36 (23)	4.5 (310)

Table S9. Mean concentrations of HBCDDs (pg/g ww in parentheses) in UK foodstuffs (ng/g lw)

Food items	α-HBCDD	β-HBCDD	γ-HBCDD	Σ_3HBCDDs
Beef	<0.12 (<5.1)	0.082 (3.6)	0.041 (1.8)	0.15 (6.4)
Lamb	<0.031 (<6.0)	0.044 (8.6)	0.065 (13)	0.12 (23)
Chicken	<0.12 (<4.4)	<0.24 (<8.4)	<0.074 (<2.6)	<0.29 (<10)
Pork	<0.052 (<5.8)	<0.099 (<11)	0.042 (4.9)	0.074 (8.5)
Turkey	<0.89 (<5.8)	<1.7 (<11)	<0.53 (<3.4)	<2.4 (<14)
ΣMeat	**<0.15 (<5.3)**	**0.078 (3.6)**	**0.051 (4.2)**	**0.16 (8.9)**
Salmon	0.40 (71)	0.026 (5.5)	0.042 (8.4)	0.46 (85)
Prawn	<1.1 (<3.7)	0.83 (3.3)	<0.63 (<2.2)	1.2 (4.7)
Cod	<0.25 (<3.7)	<0.47 (<7.1)	<0.15 (<2.2)	<0.57 (<9.5)
Tuna	<0.73 (<4.3)	<1.4 (<8.2)	<0.43 (<2.5)	<2.0 (<12)
Basa	<0.12 (<3.6)	0.18 (5.3)	<0.072 (<2.2)	0.22 (6.6)
Trout	3.1 (370)	0.42 (50)	<0.026 (<3.1)	3.5 (420)
Tilapia	<0.66 (<3.3)	<1.3 (<6.3)	<0.39 (<2.0)	<1.9 (<9.7)
Mackerel	0.75 (220)	<0.054 (<16)	0.017 (5.0)	0.79 (230)
ΣFish/Prawns	**0.44 (58)**	**0.30 (6.7)**	**0.087 (2.7)**	**0.83 (67)**
Cheese	0.017 (4.1)	<0.078 (<4.2)	0.015 (3.5)	0.050 (12)
Chicken eggs	0.14 (11)	0.038 (2.5)	0.015 (2.4)	0.19 (16)

Table S10. Concentrations of NBFRs (pg/g ww in parentheses) in foodstuffs from different countries (ng/g lw)

Country	Sampling time	Sample type	PBBz	PBT	PBEB	DPTE	HBBz	EH-TBB	BTBPE	BEH-TEBP	DBDPE	References
UK	2015	meat	<LOD [c]	<LOD [c]	<LOD [c]		<LOD [c]	0.19-1.4 [a]	<0.040-2.4 [a]	0.20-0.57 [a]	<1.1-4.6 [a]	(Tao et al., 2017)
		fish	<LOD [c]	<LOD [c]	<LOD [c]		<LOD [c]	0.22-0.43 [a]	<0.040-0.78 [a]	<0.10-1.1 [a]	<0.63-21 [a]	
		eggs	<LOD [c]	<LOD [c]	<LOD [c]		<LOD [c]	0.10 [a]	0.18 [a]	1.8 [a]	<1.2 [a]	
		cheese	<LOD [c]	<LOD [c]	<LOD [c]		<LOD [c]	0.11 [a]	0.20 [a]	0.22 [a]	<0.74 [a]	
Latvia	2016-2019	meat			(0.34-5.7 [c])		(1.4-9.8 [c])					(Zacs et al., 2021)
		fish			(<0.96-3.1 [c])		(2.8-18 [c])					
		eggs			(<0.43-1.8 [c])		(0.93-5.7 [c])					
		cheese			(<0.30-2.9 [c])		(1.9-12 [c])					
France	2014-2016	meat	(<LOD-18 [c])	(<LOD-7.0 [c])	(<LOD-0.071 [c])		(<LOD-150 [c])	(<LOD-12 [c])	(<LOD-15 [c])			(Venisseau et al., 2018)
		fish	(<LOD-6.4 [c])	(<LOD-20 [c])	(<LOD-0.17 [c])		(<LOD-38 [c])	(<LOD-10 [c])	(<LOD-10 [c])			
		egg	(<LOD-4.0 [c])	(<LOD-12 [c])	(<LOD-0.13 [c])		(<LOD-16 [c])	(<LOD-1.3 [c])	(<LOD-12 [c])			
Belgium	2015-2016	meat								(6.0 [a])		(Poma et al., 2018)
		fish								(<LOD [c])		
		eggs								(<LOD [c])		
		dairy products								(<LOD [c])		
Spain		fish/shellfish			(<20 [c])		(<20-200 [c])				(<10 [c])	(Trabalon et al., 2017)
China [d]	2010	eggs						(<LOD-100 [c])		(<LOD-1800 [c])		(Zheng et al., 2016)
China	2010	eggs						(<LOD [c])		(<LOD-540 [c])		(Zheng et al., 2016)
China [d]	2013	eggs					2.0-6.8 [c]		0.40-78 [c]		4.5-190 [c]	(Zeng et al., 2016)
China	2011	meat		0.026-0.16 [c]		<LOD-0.081 [c]	<LOD-0.16 [c]		<LOD-0.067 [c]		<LOD-23 [c]	(Shi et al., 2016)
		fish		0.030-0.37 [c]		0.030-1.6 [c]	<LOD-2.2 [c]		<LOD-1.9 [c]		<LOD-70 [c]	
		eggs		0.0080-0.10 [c]		<LOD-0.057 [c]	<LOD-0.076 [c]		<LOD-4.1 [c]		<LOD-20 [c]	
China [d]	2011	fish			<0.17 [a]		6.5 [a]	62 [a]	6.8 [a]	15 [a]	<0.45 [a]	(Labunska et al., 2015)
		meat			<0.17-0.87 [a]		0.41-0.56 [a]	24-38 [a]	1.5-5.4 [a]	7.2-12 [a]	<0.45 [a]	
		eggs			<0.17 [a]		<0.15 [a]	3.1-5.4 [a]	<0.35-3.8 [a]	0.88-1.6 [a]	<0.45 [a]	
China	2011	fish			<0.17 [a]		<0.15 [a]	4.0 [a]	2.1 [a]	1.9 [a]	<0.45 [a]	(Labunska et al., 2015)
		meat			<0.17-1.2 [a]		<0.15 [a]	2.1-2.7 [a]	<0.35-2.7 [a]	<0.25-1.8 [a]	<0.45 [a]	
		eggs			<0.17 [a]		<0.15 [a]	1.2-1.7 [a]	<0.35 [a]	<0.25 [a]	<0.45 [a]	
Tanzania	2012	eggs							<LOD-9.8 [c]			(Polder et al., 2016)

[a] Mean concentrations

[b] Median concentrations

[c] Ranges

[d] E-waste recycling sites

Table S11. Concentrations of PBDEs (pg/g ww in parentheses) in foodstuffs from different countries (ng/g lw)

Country	Sampling time	Sample type	BDE-209	ΣPBDEs	References
UK	2015	meat	0.28-0.63 (21-32) [a]	2.4-21 (520-1000) [a]	(Tao et al., 2017)
		fish	0.34-1.7 (32-150) [a]	14-40 (400-2800) [a]	
		eggs	0.53 (56) [a]	2.4 (250) [a]	
		cheese	0.21 (37) [a]	5.3 (940) [a]	
UK	2013	meat		(40-590 [c])	(Fernandes et al., 2016)
		fish		(170-8900 [c])	
		egg		(60-450 [c])	
		dairy products		(20-260 [c])	
Latvia	2016-2019	meat	(12 [a] / 9.6 [b])	(34 [a] / 22 [b])	(Zacs et al., 2021)
		fish	(23 [a] / 7.5 [b])	(620 [a] / 390 [b])	
		eggs	(34 [a] / 24 [b])	(55 [a] / 36 [b])	
		cheese	(2.9 [a] / 2.9 [b])	(21 [a] / 8.5 [b])	
China	2013	meat	20 (3300) [a] / 13 (440) [b]	21 (3400) [a] / 14 (460) [b]	(Wang et al., 2019)
		fish/seafood	13 (1300) [a] / 5.5 (210) [b]	14 (1400) [a] / 6.3 (270) [b]	
		eggs	13 (1600) [a] / 11 (1600) [b]	13 (1700) [a] / 12 (1800) [b]	
		dairy products	5.5 (90) [a] / 3.0 (58) [b]	5.9 (96) [a] / 3.2 (66) [b]	
China [d]	2013	eggs		620-46000 [c]	(Zeng et al., 2016)
Netherlands	2009-2014	meat		0.060-0.58 [a] / 0.040-0.34 [b]	(Gebbink et al., 2019)
		eggs		0.22 [a] / 0.14 [b]	
		fish		(2.5-1300 [a])	
France	2014-2016	meat	(11 [b])	(170 [a])	(Venisseau et al., 2018)
		fish	(5.7 [b])	(540 [a])	
		egg	(22 [b])	(120 [a])	
France	2007-2009	meat	(52 [a])	(540 [a])	(Riviere et al., 2014)
		fish	(43 [a])	(79 [a])	
		eggs	(49 [a])	(68 [a])	
		cheese	(40 [a])	(65 [a])	
Belgium	2015-2016	meat		(690 [a])	(Poma et al., 2018)
		fish		(370 [a])	
		eggs		(210 [a])	
		dairy products		(600 [a])	
Belgium	2006-2007	egg	2.0-7.1 [a]	3.5-7.8 [a]	(Covaci et al., 2009)
Ireland	2015	fish	(<2.0-60 [c])	(20-1400 [c])	(Garcia Lopez et al., 2018)
		eggs	(<190-800 [c])	(30-960 [c])	
Spain		fish/shellfish	(<20 [c])	(400-1300 [c])	(Trabalon et al., 2017)
Tanzania	2012	eggs		1.1-350 [c]	(Polder et al., 2016)
Japan	2011	fish		(2.0-880 [c])	(Kakimoto et al., 2012)
US	2001-2002	fish		(56-3300 [a])	(Hites et al., 2004)
US	2009	meat		(14-210 [c])	(Schecter et al., 2010)
		fish		(25-1500 [c])	
		eggs		(89 [c])	
		dairy products		(11-6200 [c])	

[a] Mean concentrations [b] Median concentrations [c] Ranges [d] E-waste recycling sites

Table S12. Concentrations of HBCDDs (pg/g ww in parentheses) in foodstuffs from different countries (ng/g lw)

Country	Sampling time	Sample type	ΣHBCDDs	References
UK	2015	meat	0.32-4.6 (26-200) [a]	(Tao et al., 2017)
		fish	3.6-16 (180-830) [a]	
		eggs	1.3 (300) [a]	
		cheese	<0.24 (<43) [a]	
UK	2013	meat	(40 [a])	(Fernandes et al., 2016)
		fish	(1400 [a])	
		egg	(<20 [a])	
		dairy products	(40 [a])	
Latvia	2016-2019	meat	(270 [a] / 160 [b])	(Zacs et al., 2021)
		fish	(730 [a] / 480 [b])	
		eggs	(24 [a] / 16 [b])	
		cheese	(330 [a] / 160 [b])	
China	2013	meat	2.8 (570) [a] / 2.4 (180) [b]	(Wang et al., 2019)
		fish/seafood	7.0 (410) [a] / 5.6 (290) [b]	
		eggs	4.5 (600) [a] / 4.0 (500) [b]	
		dairy products	1.4 (140) [a] / 1.1 (44) [b]	
China [d]	2013	eggs	56-7600 [c]	(Zeng et al., 2016)
China [d]	2011	fish	310 [a]	(Labunska et al., 2015)
		meat	<0.060-79 [a]	
		eggs	2.2-47 [a]	
China	2011	fish	5.9 [a]	(Labunska et al., 2015)
		meat	0.090-3.1 [a]	
		eggs	0.50-1.70 [a]	
France	2014-2016	meat	(130 [a])	(Venisseau et al., 2018)
		fish	(140 [a])	
France	2007-2009	meat	(130 [a])	(Riviere et al., 2014)
		fish	(140 [a])	
		eggs	(26 [a])	
		cheese	(20 [a])	
Belgium	2015-2016	meat	(43 [a])	(Poma et al., 2018)
		fish	(130 [a])	
		eggs	(970 [a])	
		dairy products	(0.10 [a])	
Belgium	2006-2007	egg	6.5-8.5 [a]	(Covaci et al., 2009)
Ireland	2015	fish	(70-410 [c])	(Garcia Lopez et al., 2018)
		eggs	(10-20 [c])	
Tanzania	2012	eggs	<LOD-63 [c]	(Polder et al., 2016)
Japan	2011	fish	(<LOD-22000 [c])	(Kakimoto et al., 2012)
Sweden	1999	meat	<1.0-6.5 [a]	(Remberger et al., 2004)
		fish	48 [a]	
		egg	9.4 [a]	
US	2009	meat	(23-190 [c])	(Schecter et al., 2010)
		fish	(<29-590 [c])	
		eggs	(<11 [c])	
		dairy products	(<64 [c])	

[a] Mean concentrations, [b] Median concentrations, [c] Ranges, [d] E-waste recycling sites

Table S13. Body weight (kg) of UK citizens in 2019 (data obtained from NHS Digital (2019))

Age	Male	Female	All
0-1 years	9.7	9.2	9.5
2-4 years	16.5	15.9	16.2
5-7 years	23.2	22.4	22.8
8-10 years	33.8	34.3	34.1
11-12 years	46.9	47.1	47
13-15 years	61	58.3	59.7
16-24 years	77.5	65.8	71.9
25-34 years	85.7	72.6	79
35-44 years	86.8	74.5	80.6
45-54 years	88.8	75.7	82.2
55-64 years	88	73.9	80.7
65-74 years	87.4	71.7	79.4
75+ years	80	67.3	73

Table S14. Daily consumption of foodstuffs (g/day) for UK citizens (males and females) from different age groups (data obtained from University of Cambridge et al. (2022))

Age	Daily consumption	Beef	Lamb	Pork	Chicken [a]	Turkey [a]	Salmon [b]	Prawn [c]	Cod [c]	Tuna [c]	Basa [c]	Trout [b]	Tilapia [c]	Mackerel [b]	Cheese	Chicken egg
0-1	mean	18.2	1.5	2.8	11.3	11.3	1.5	2.2	2.2	2.2	2.2	1.5	2.2	1.5	6.7	13.4
	SD	54.4	15.3	22.5	20.7	20.7	7.0	5.6	5.6	5.6	5.6	7.0	5.6	7.0	14.9	32.6
2-4	mean	20.1	2.4	2.1	15.6	15.6	0.7	2.5	2.5	2.5	2.5	0.7	2.5	0.7	10.5	10.5
	SD	61.6	16.4	14.6	29.6	29.6	5.0	6.6	6.6	6.6	6.6	5.0	6.6	5.0	22.6	30.4
5-7	mean	21.7	3.3	3.9	18.1	18.1	1.0	2.9	2.9	2.9	2.9	1.0	2.9	1.0	11.0	10.1
	SD	64.7	25.1	23.4	31.8	31.8	7.5	7.2	7.2	7.2	7.2	7.5	7.2	7.5	23.5	32.9
8-10	mean	26.4	4.7	6.0	24.7	24.7	1.4	3.0	3.0	3.0	3.0	1.4	3.0	1.4	11.1	11.7
	SD	79.6	37.6	32.7	41.0	41.0	8.5	8.9	8.9	8.9	8.9	8.5	8.9	8.5	22.8	36.4
11-12	mean	30.6	5.3	5.1	29.2	29.2	1.4	3.4	3.4	3.4	3.4	1.4	3.4	1.4	14.6	14.6
	SD	89.0	36.3	26.3	47.5	47.5	9.0	9.8	9.8	9.8	9.8	9.0	9.8	9.0	38.1	40.5
13-15	mean	32.8	7.4	7.3	33.3	33.3	1.5	3.2	3.2	3.2	3.2	1.5	3.2	1.5	11.9	12.5
	SD	100.1	41.3	36.2	60.3	60.3	11.8	10.4	10.4	10.4	10.4	11.8	10.4	11.8	30.7	40.5
16-24	mean	36.9	5.7	11.2	42.7	42.7	1.7	3.2	3.2	3.2	3.2	1.7	3.2	1.7	12.2	18.9
	SD	120.0	46.3	57.7	72.7	72.7	11.5	11.9	11.9	11.9	11.9	11.5	11.9	11.5	30.4	50.4
25-34	mean	39.3	6.0	14.7	38.1	38.1	4.0	4.5	4.5	4.5	4.5	4.0	4.5	4.0	17.4	33.0
	SD	115.9	45.8	78.0	71.0	71.0	19.0	14.5	14.5	14.5	14.5	19.0	14.5	19.0	46.5	76.3
35-44	mean	42.0	10.7	8.5	40.0	40.0	3.6	4.0	4.0	4.0	4.0	3.6	4.0	3.6	17.9	30.3
	SD	132.9	68.9	51.6	71.6	71.6	16.6	13.6	13.6	13.6	13.6	16.6	13.6	16.6	48.6	67.1
45-54	mean	49.8	6.6	10.0	37.4	37.4	4.0	5.1	5.1	5.1	5.1	4.0	5.1	4.0	14.5	27.5
	SD	138.8	48.1	53.7	74.0	74.0	16.3	17.4	17.4	17.4	17.4	16.3	17.4	16.3	40.2	63.3
55-64	mean	43.3	8.8	9.0	28.4	28.4	4.4	5.6	5.6	5.6	5.6	4.4	5.6	4.4	15.4	29.9
	SD	121.4	51.8	58.7	63.1	63.1	17.1	15.8	15.8	15.8	15.8	17.1	15.8	17.1	33.2	68.6
65-74	mean	40.5	7.0	8.2	24.1	24.1	5.3	5.6	5.6	5.6	5.6	5.3	5.6	5.3	15.2	28.7
	SD	114.1	45.1	43.0	54.8	54.8	16.4	15.6	15.6	15.6	15.6	16.4	15.6	16.4	32.5	56.8
75+	mean	39.6	17.4	5.8	24.5	24.5	5.0	4.4	4.4	4.4	4.4	5.0	4.4	5.0	13.6	23.8
	SD	113.0	83.2	29.1	61.1	61.1	15.7	12.8	12.8	12.8	12.8	15.7	12.8	15.7	30.7	54.2

[a] Consumptions of chicken (turkey) are estimated to be total consumptions of chicken and turkey divided by 2

[b] Consumptions of salmon (trout/mackerel) are estimated to be total consumptions of oily fish divided by 3

[c] Consumptions of prawns (cod/tuna/basa/tilapia) are estimated to be total consumptions of white fish divided by 5

Table S15. Daily consumption of foodstuffs (g/day) for UK citizens (males) from different age groups (data obtained from University of Cambridge et al. (2022))

Age	Daily consumption	Beef	Lamb	Pork	Chicken [a]	Turkey [a]	Salmon [b]	Prawn [c]	Cod [c]	Tuna [c]	Basa [c]	Trout [b]	Tilapia [c]	Mackerel [b]	Cheese	Chicken egg
0-1	mean	19.6	2.6	4.1	12.6	12.6	1.7	2.9	2.9	2.9	2.9	1.7	2.9	1.7	5.6	13.4
	SD	52.8	20.9	29.4	23.6	23.6	7.9	6.3	6.3	6.3	6.3	7.9	6.3	7.9	11.6	31.8
2-4	mean	19.4	2.3	2.4	16.0	16.0	0.6	2.7	2.7	2.7	2.7	0.6	2.7	0.6	11.1	9.4
	SD	60.4	15.7	17.2	28.9	28.9	3.8	6.9	6.9	6.9	6.9	3.8	6.9	3.8	24.0	29.5
5-7	mean	19.9	3.0	3.7	18.8	18.8	1.2	2.6	2.6	2.6	2.6	1.2	2.6	1.2	11.0	11.4
	SD	61.1	21.8	23.2	34.5	34.5	8.3	6.4	6.4	6.4	6.4	8.3	6.4	8.3	24.7	37.0
8-10	mean	28.6	3.2	6.0	25.0	25.0	1.4	2.8	2.8	2.8	2.8	1.4	2.8	1.4	11.6	11.4
	SD	86.6	29.4	31.2	43.4	43.4	8.9	7.8	7.8	7.8	7.8	8.9	7.8	8.9	23.8	38.1
11-12	mean	32.0	6.0	6.5	28.9	28.9	1.9	3.5	3.5	3.5	3.5	1.9	3.5	1.9	14.5	14.0
	SD	91.1	35.0	30.3	49.0	49.0	10.9	10.8	10.8	10.8	10.8	10.9	10.8	10.9	42.7	39.4
13-15	mean	35.5	8.6	9.1	36.0	36.0	2.2	2.8	2.8	2.8	2.8	2.2	2.8	2.2	13.5	13.8
	SD	108.2	46.9	40.5	67.8	67.8	15.7	9.6	9.6	9.6	9.6	15.7	9.6	15.7	35.4	45.3
16-24	mean	38.1	8.1	11.6	51.4	51.4	1.1	3.7	3.7	3.7	3.7	1.1	3.7	1.1	12.6	23.1
	SD	128.4	56.2	54.8	83.9	83.9	7.9	12.1	12.1	12.1	12.1	7.9	12.1	7.9	30.1	57.7
25-34	mean	37.3	5.5	19.7	45.9	45.9	4.6	5.0	5.0	5.0	5.0	4.6	5.0	4.6	18.1	38.0
	SD	111.3	45.5	83.6	80.5	80.5	21.6	15.8	15.8	15.8	15.8	21.6	15.8	21.6	44.2	81.3
35-44	mean	51.7	17.0	8.1	44.7	44.7	3.9	3.9	3.9	3.9	3.9	3.9	3.9	3.9	18.5	32.0
	SD	158.6	90.4	50.9	78.1	78.1	20.0	12.5	12.5	12.5	12.5	20.0	12.5	20.0	59.1	71.0
45-54	mean	53.2	6.9	13.3	35.4	35.4	3.5	5.5	5.5	5.5	5.5	3.5	5.5	3.5	16.7	27.4
	SD	143.7	47.2	63.0	67.8	67.8	14.3	20.7	20.7	20.7	20.7	14.3	20.7	14.3	45.8	61.2
55-64	mean	44.0	10.8	9.2	32.4	32.4	4.2	6.3	6.3	6.3	6.3	4.2	6.3	4.2	14.5	29.2
	SD	123.3	59.9	73.4	66.8	66.8	19.6	17.5	17.5	17.5	17.5	19.6	17.5	19.6	32.8	68.9
65-74	mean	43.1	9.5	10.9	30.8	30.8	6.1	4.4	4.4	4.4	4.4	6.1	4.4	6.1	13.9	29.6
	SD	115.4	50.3	53.1	64.5	64.5	17.8	13.0	13.0	13.0	13.0	17.8	13.0	17.8	29.3	60.8
75+	mean	41.0	20.2	4.6	24.4	24.4	4.7	4.6	4.6	4.6	4.6	4.7	4.6	4.7	15.9	28.1
	SD	112.3	95.0	24.4	56.9	56.9	15.6	13.6	13.6	13.6	13.6	15.6	13.6	15.6	35.5	60.0

[a] Consumptions of chicken (turkey) are estimated to be total consumptions of chicken and turkey divided by 2

[b] Consumptions of salmon (trout/mackerel) are estimated to be total consumptions of oily fish divided by 3

[c] Consumptions of prawns (cod/tuna/basa/tilapia) are estimated to be total consumptions of white fish divided by 5

Table S16. Daily consumption of foodstuffs (g/day) for UK citizens (females) from different age groups (data obtained from University of Cambridge et al. (2022))

Age	Daily consumption	Beef	Lamb	Pork	Chicken [a]	Turkey [a]	Salmon [b]	Prawn [c]	Cod [c]	Tuna [c]	Basa [c]	Trout [b]	Tilapia [c]	Mackerel [b]	Cheese	Chicken egg
0-1	mean	16.7	0.2	1.4	9.9	9.9	1.3	1.4	1.4	1.4	1.4	1.3	1.4	1.3	7.8	13.3
	SD	56.4	2.1	10.0	16.9	16.9	6.0	4.6	4.6	4.6	4.6	6.0	4.6	6.0	17.9	33.7
2-4	mean	20.9	2.5	1.6	15.1	15.1	0.8	2.2	2.2	2.2	2.2	0.8	2.2	0.8	9.8	11.8
	SD	62.9	17.1	11.0	30.3	30.3	6.0	6.2	6.2	6.2	6.2	6.0	6.2	6.0	20.9	31.2
5-7	mean	23.7	3.7	4.1	17.3	17.3	0.8	3.1	3.1	3.1	3.1	0.8	3.1	0.8	10.9	8.7
	SD	68.2	28.2	23.5	28.6	28.6	6.5	8.0	8.0	8.0	8.0	6.5	8.0	6.5	22.2	28.1
8-10	mean	23.7	6.3	5.9	24.3	24.3	1.4	3.3	3.3	3.3	3.3	1.4	3.3	1.4	10.4	12.2
	SD	70.8	45.3	34.4	38.0	38.0	8.0	10.1	10.1	10.1	10.1	8.0	10.1	8.0	21.6	34.5
11-12	mean	29.0	4.5	3.4	29.6	29.6	0.9	3.2	3.2	3.2	3.2	0.9	3.2	0.9	14.6	15.4
	SD	86.6	38.0	20.5	45.7	45.7	5.8	8.3	8.3	8.3	8.3	5.8	8.3	5.8	31.6	41.7
13-15	mean	30.3	6.4	5.7	30.8	30.8	0.8	3.5	3.5	3.5	3.5	0.8	3.5	0.8	10.5	11.4
	SD	92.2	35.5	31.7	52.6	52.6	6.5	11.0	11.0	11.0	11.0	6.5	11.0	6.5	25.7	35.6
16-24	mean	35.9	3.8	10.8	36.1	36.1	2.2	2.8	2.8	2.8	2.8	2.2	2.8	2.2	11.9	15.6
	SD	113.2	36.9	60.0	62.1	62.1	13.6	11.7	11.7	11.7	11.7	13.6	11.7	13.6	30.7	43.8
25-34	mean	40.6	6.3	11.6	33.2	33.2	3.7	4.1	4.1	4.1	4.1	3.7	4.1	3.7	16.9	29.8
	SD	118.8	46.0	74.2	63.9	63.9	17.1	13.7	13.7	13.7	13.7	17.1	13.7	17.1	47.8	73.0
35-44	mean	35.7	6.5	8.8	36.8	36.8	3.4	4.1	4.1	4.1	4.1	3.4	4.1	3.4	17.4	29.1
	SD	112.3	49.5	52.1	66.8	66.8	13.9	14.3	14.3	14.3	14.3	13.9	14.3	13.9	40.3	64.3
45-54	mean	47.2	6.3	7.4	39.0	39.0	4.5	4.8	4.8	4.8	4.8	4.5	4.8	4.5	12.8	27.6
	SD	135.0	48.9	45.0	78.5	78.5	17.6	14.3	14.3	14.3	14.3	17.6	14.3	17.6	35.1	65.0
55-64	mean	42.7	7.4	8.8	25.2	25.2	4.5	5.0	5.0	5.0	5.0	4.5	5.0	4.5	16.1	30.4
	SD	120.0	44.6	44.4	60.1	60.1	14.9	14.4	14.4	14.4	14.4	14.9	14.4	14.9	33.5	68.5
65-74	mean	38.4	4.9	6.0	18.7	18.7	4.7	6.5	6.5	6.5	6.5	4.7	6.5	4.7	16.3	27.9
	SD	113.1	40.4	32.5	44.8	44.8	15.1	17.3	17.3	17.3	17.3	15.1	17.3	15.1	34.9	53.3
75+	mean	38.7	15.6	6.6	24.5	24.5	5.2	4.3	4.3	4.3	4.3	5.2	4.3	5.2	12.0	20.9
	SD	113.7	74.2	31.9	63.8	63.8	15.7	12.2	12.2	12.2	12.2	15.7	12.2	15.7	27.0	49.7

[a] Consumptions of chicken (turkey) are estimated to be total consumptions of chicken and turkey divided by 2

[b] Consumptions of salmon (trout/mackerel) are estimated to be total consumptions of oily fish divided by 3

[c] Consumptions of prawns (cod/tuna/basa/tilapia) are estimated to be total consumptions of white fish divided by 5

Table S17. Estimations of daily dietary exposure to BFRs for UK citizens: comparison between 2015 (Tao et al., 2017) and 2020/2021 (ng/kg bw/day)

BFRs		Toddlers [a]		Adults [b]	
		2015	2020/2021	2015	2020/2021
NBFRs [c]	Average	2.6	5.1-8.4	1.3	2.3-2.8
	High-end [d]	16	32-51	6.7	13-17
PBDEs	Average	4.2	0.73-1.3	1.8	0.29-0.39
	High-end	23	5.1-8.8	8.1	2.2-2.8
HBCDDs	Average	0.88	0.071-0.18	0.44	0.035-0.071
	High-end	5.4	0.77-1.6	2.1	0.39-0.54

[a] Toddlers: 0-3 years old

[b] Adults: 18 + years old

[c] Estimated dietary exposure to individual NBFRs was not available in (Tao et al., 2017), thus data on dietary exposure to total NBFRs was used here

[d] Assuming daily food consumption of average + 2SD for each food item

Table S18. Estimated daily intake (DI, ng/kg bw/day) of BFRs for infants (0-1 year old) and comparison with reference doses (RfD, ng/kg bw/day) (Ma et al., 2021)

BFRs	DI for infants		RfD	DI/RfD ratios for infants	
	Average intake	High-end intake		Average intake	High-end intake
BTBPE	4.4	27	243,000	<0.001	<0.001
EH-TBB	0.19	1.2	20,000	<0.001	<0.001
BEH-TEBP	3.3	20	20,000	<0.001	0.0010
DBDPE	0.24	1.5	333,333	<0.001	<0.001
BDE-209	0.20	1.4	7,000	<0.001	<0.001
Octa-BDE	-	-	3,000	-	-
Penta-BDE	0.51	3.5	2,000	<0.001	0.0018
BDE-47	0.35	2.4	100	0.0035	0.024
BDE-99	0.41	2.9	100	0.0041	0.029
BDE-153	0.030	0.21	200	<0.001	0.0011
∑HBCDDs	0.18	1.6	200,000	<0.001	<0.001

3 Figures

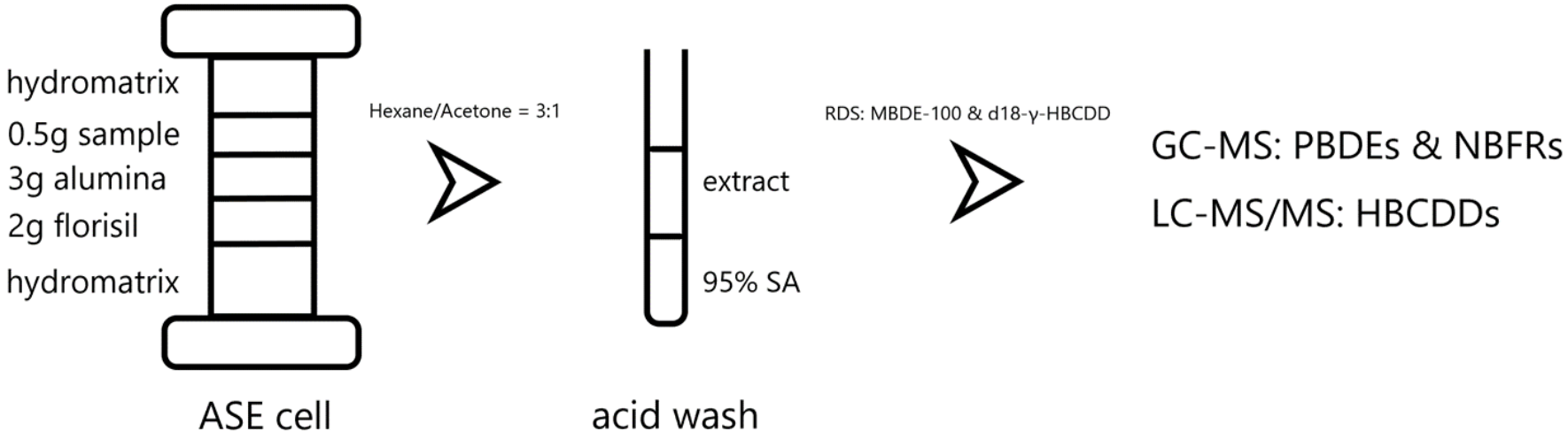


Fig. S1 Sample extraction and clean-up protocols (SA = sulfuric acid)

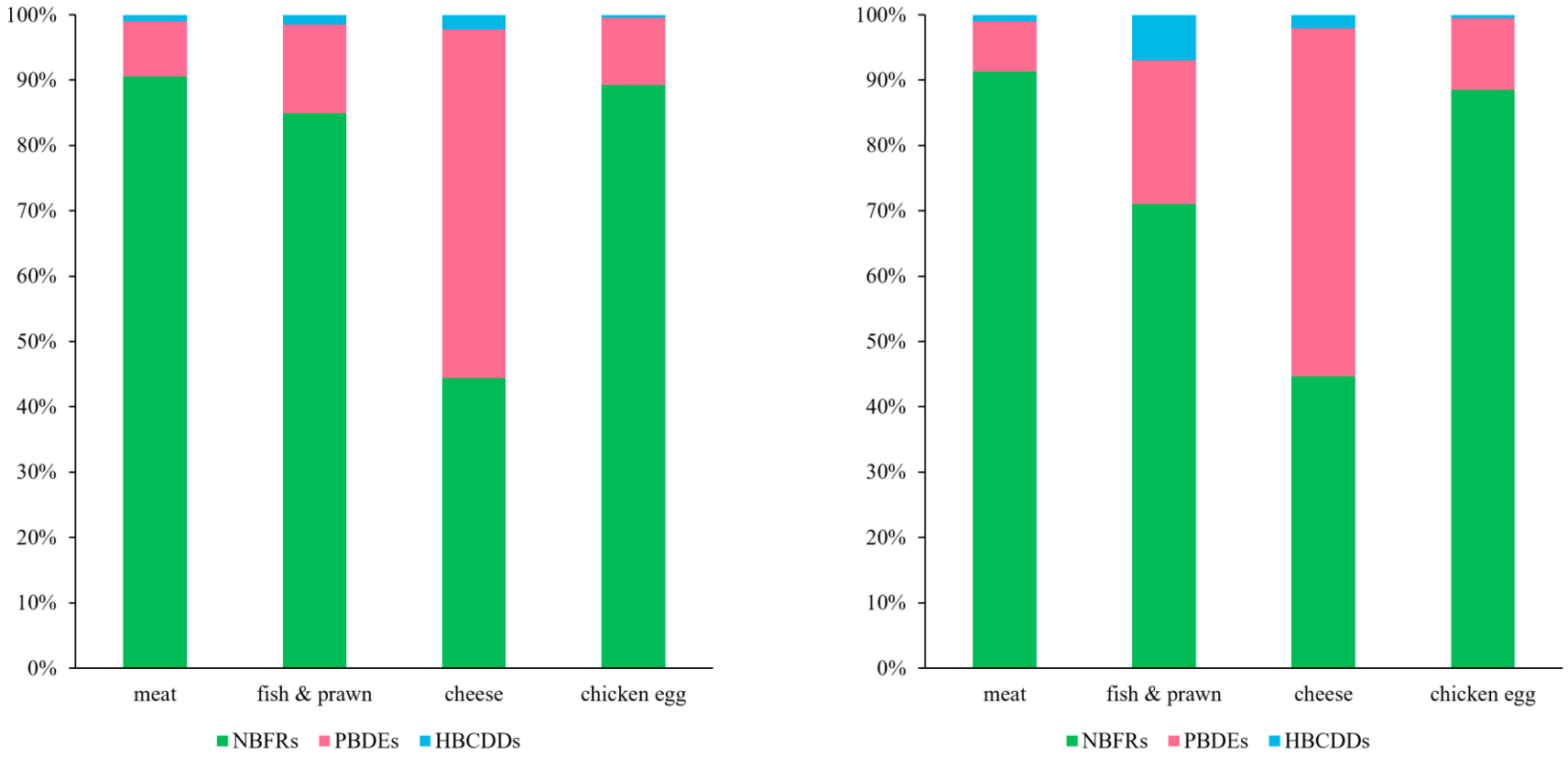


Fig. S2 Relative contribution of NBFRs, PBDEs, and HBCDDs to total BFRs in different UK food items (left: calculated from lipid-weight concentrations; right: calculated from wet-weight concentrations)

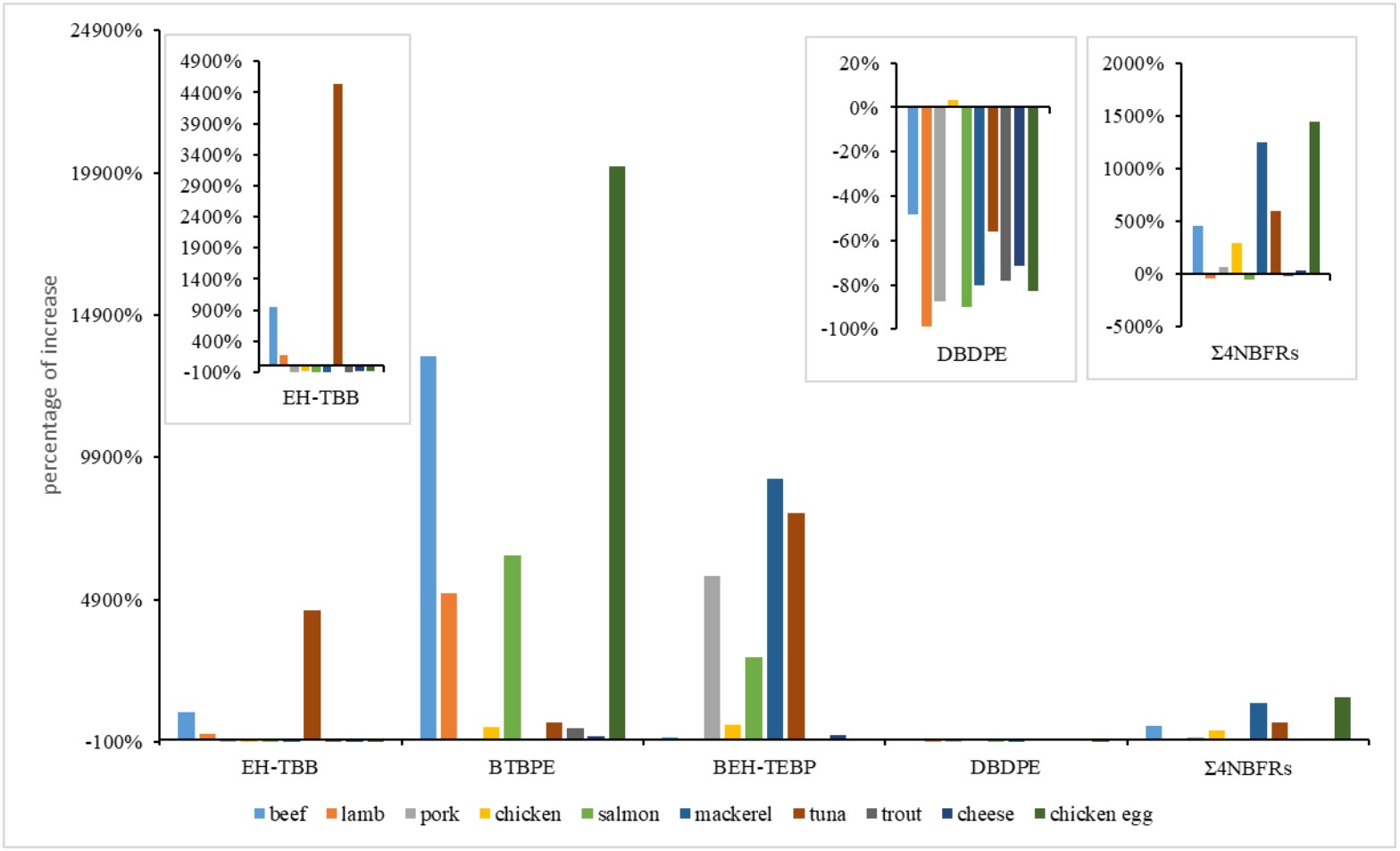


Fig. S3a Increase in NBFR concentrations in UK foodstuffs between 2015 and 2020/2021 (data based on lipid-weight concentrations)

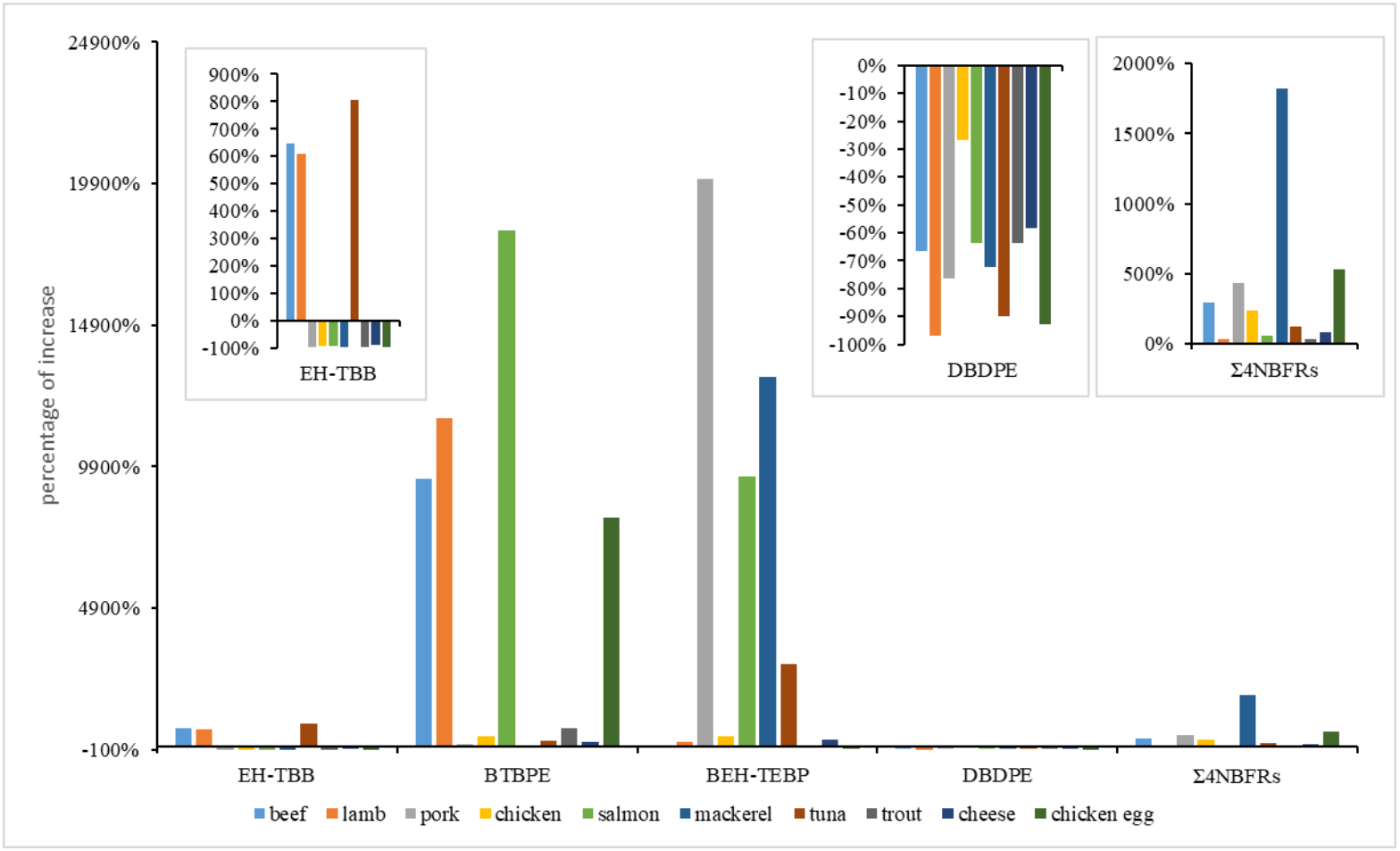


Fig. S3b Increase in NBFR concentrations in UK foodstuffs between 2015 and 2020/2021 (data based on wet-weight concentrations)

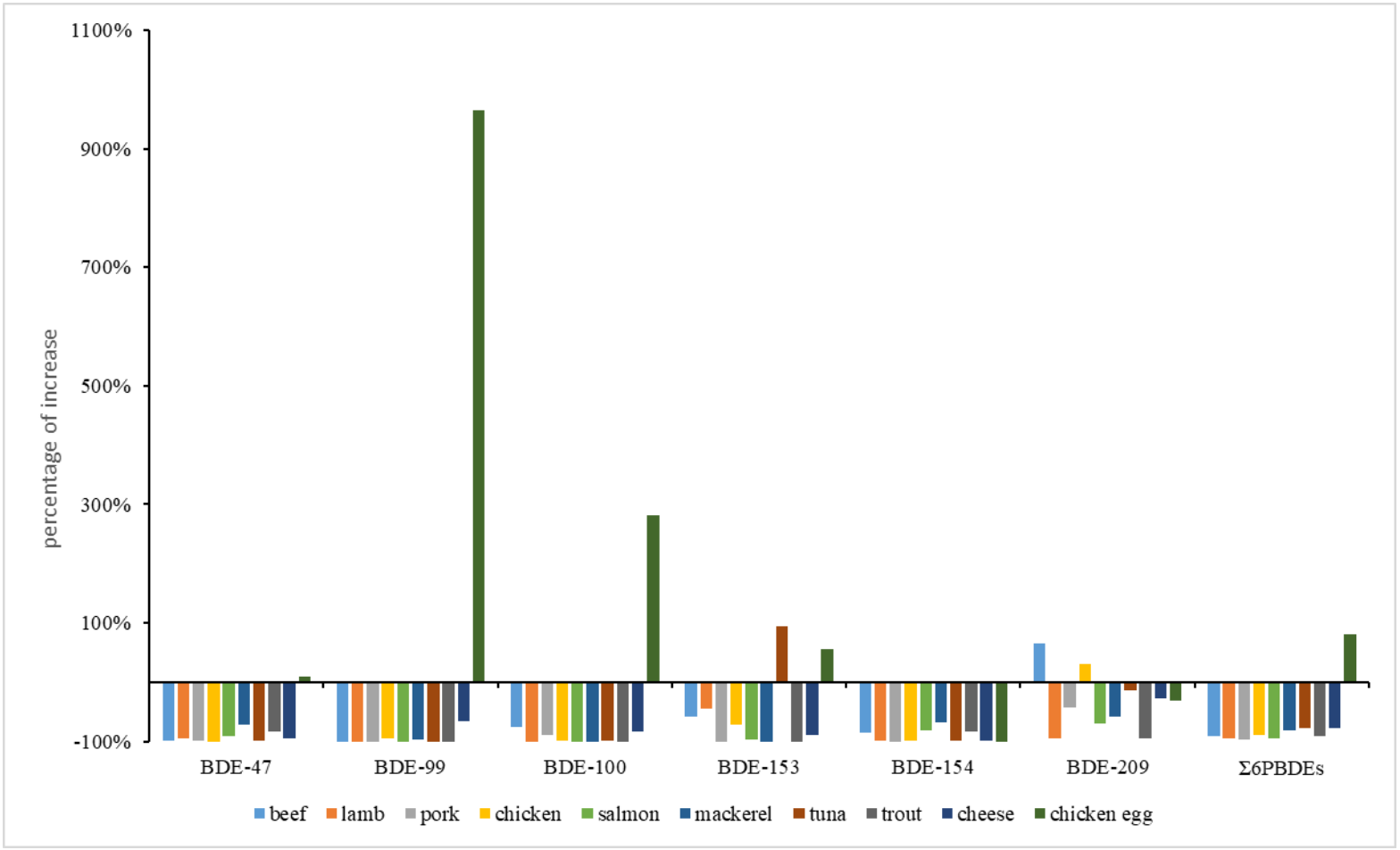


Fig. S4a Increase in PBDE concentrations in UK foodstuffs between 2015 and 2020/2021 (data based on lipid-weight concentrations)

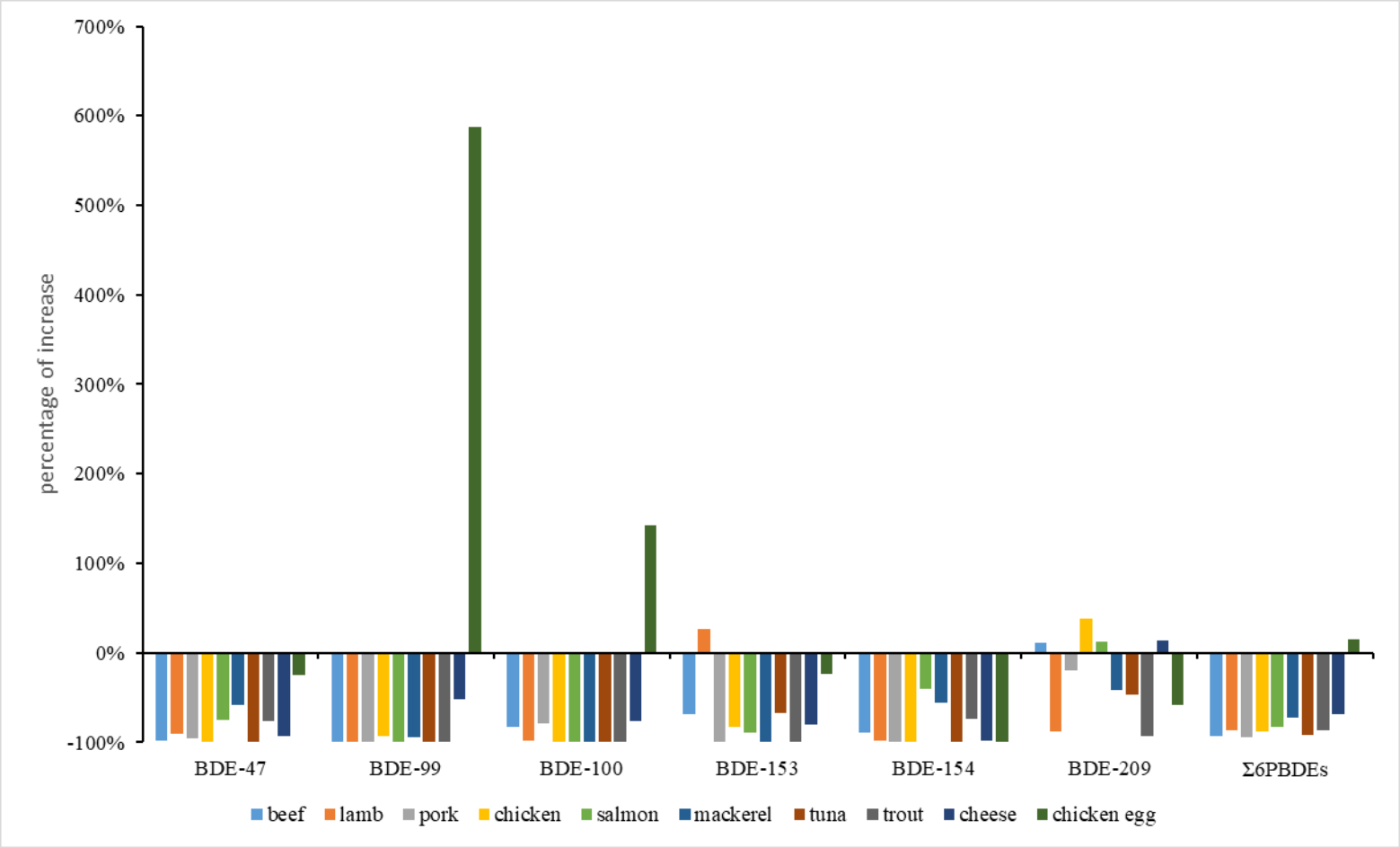


Fig. S4b Increase in PBDE concentrations in UK foodstuffs between 2015 and 2020/2021 (data based on wet-weight concentrations)

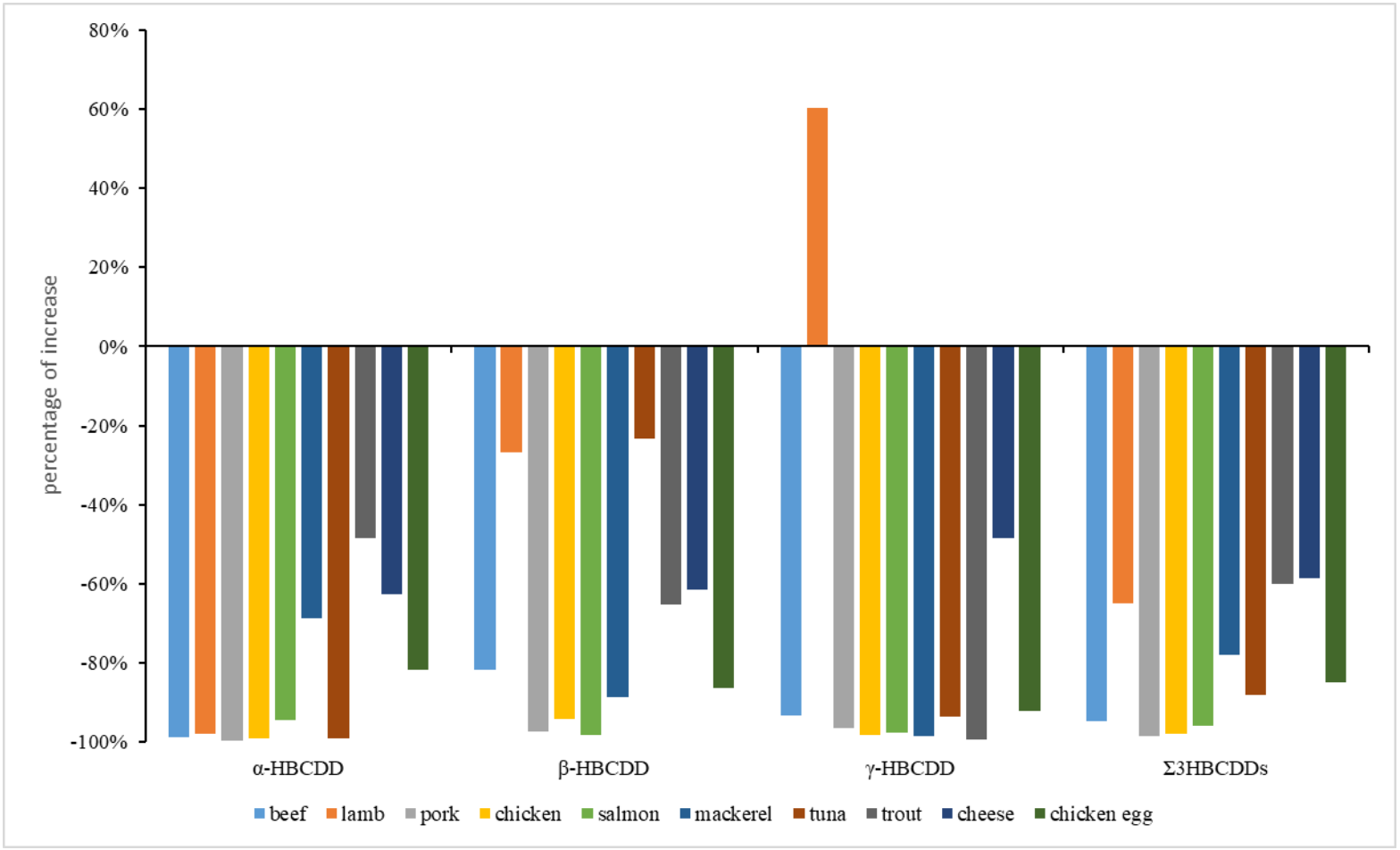


Fig. S5a Increase in HBCDD concentrations in UK foodstuffs between 2015 and 2020/2021 (data based on lipid-weight concentrations)

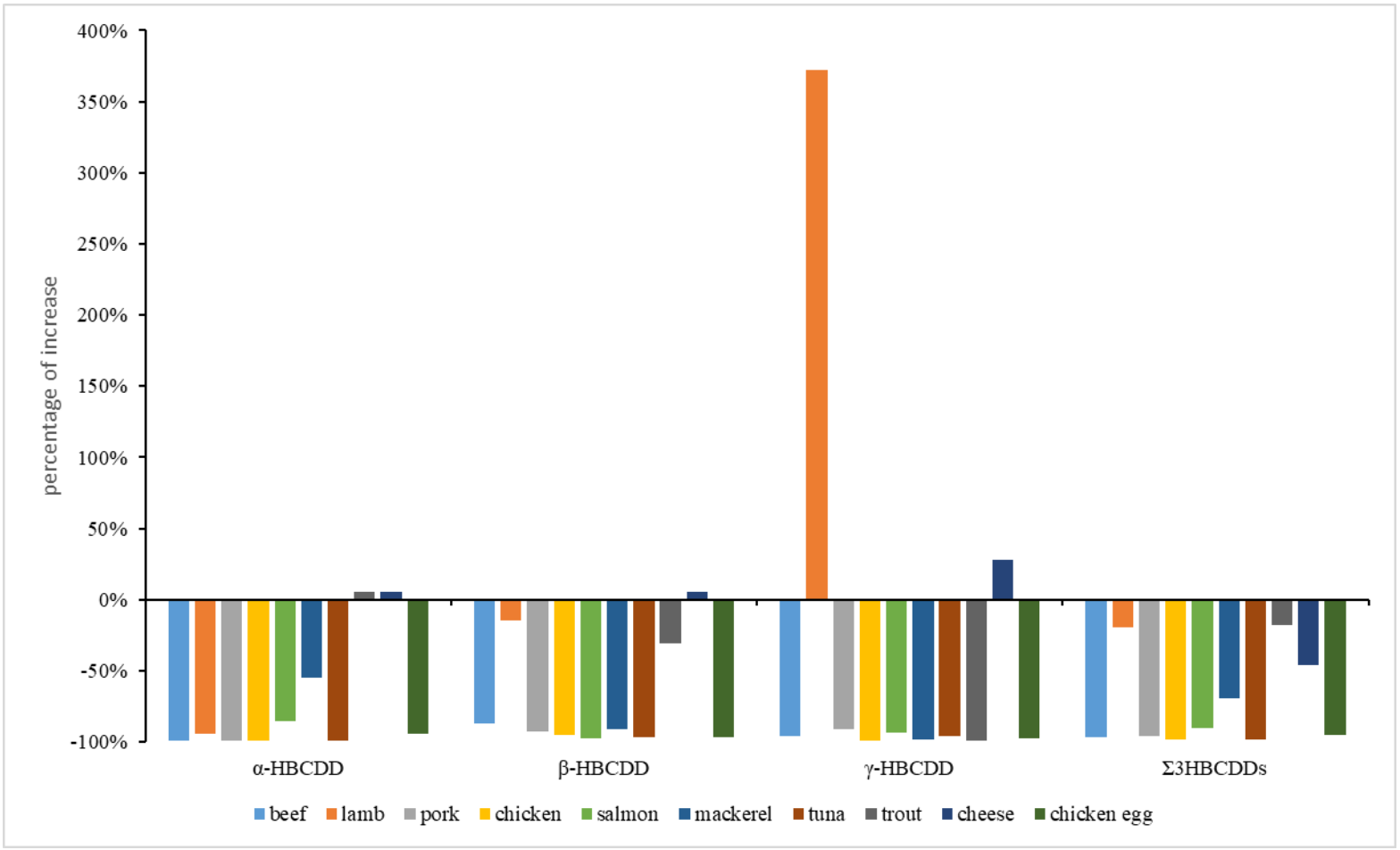


Fig. S5b Increase in HBCDD concentrations in UK foodstuffs between 2015 and 2020/2021 (data based on wet-weight concentrations)

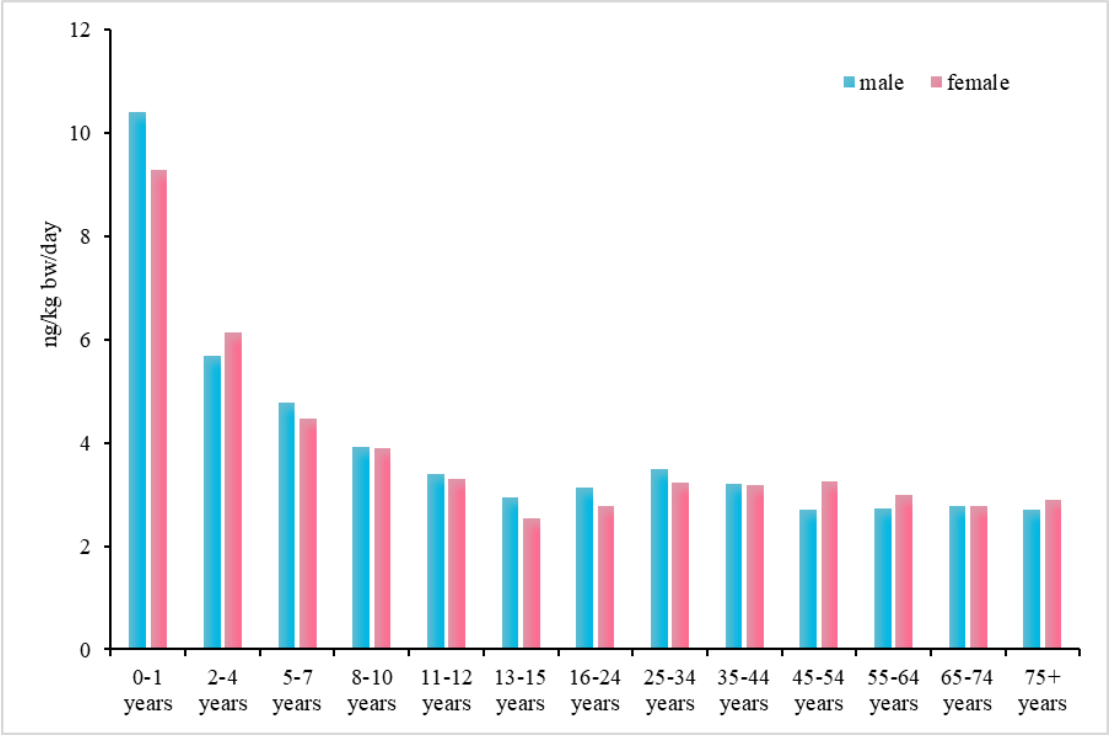


Fig. S6a Average estimations for dietary intakes of BFRs for UK citizens: gender differences

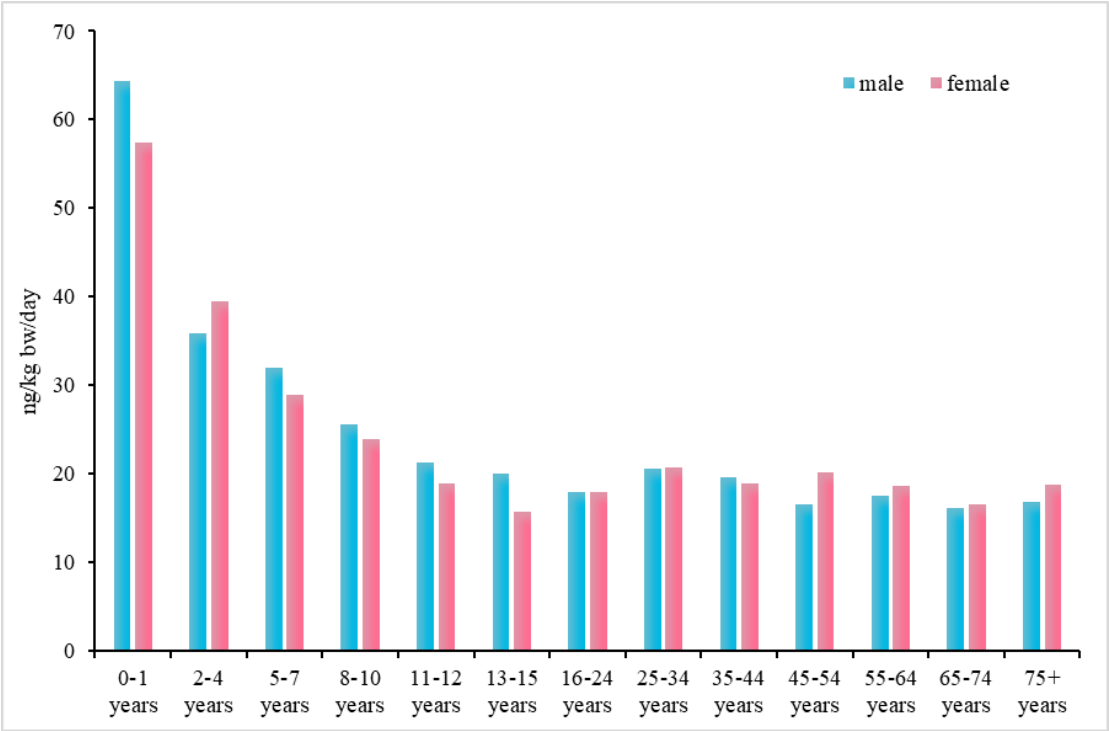


Fig. S6b High-end estimations for dietary intakes of BFRs for UK citizens: gender differences (high-end food intakes of mean + 2SD were assumed)

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Appendix D. Supplementary Materials for Chapter Five

Sampling

A total of 30 floor dust samples were collected from living rooms (n = 6; 4 non-carpeted and 2 carpeted), kitchens (n = 6; all non-carpeted), and bedrooms (n = 18; 1 non-carpeted and 17 carpeted) of 8 UK homes in Birmingham during July 2021 and December 2021. Dust samples were collected with a portable vacuum cleaner installed with pre-cleaned nylon mesh filters of 25 μm pore size. On each sampling site, a square of 1 m^2 (i.e., 1 m × 1 m) was measured on carpeted floor, or a square of 4 m^2 (i.e., 2 m × 2 m) was measured on smooth floor. Then each square was vacuumed evenly and thoroughly for 2 min in case of carpeted floor or 4 min in case of smooth floor. This allows dust to be collected inside the nylon filters. Then the nylon filters with dust were sealed properly and wrapped with aluminium foil before being placed in plastic bags, and all the dust samples were stored at -18 ℃ at the University of Birmingham prior to extraction.

Paired indoor air samples (n = 30) to indoor dust samples were collected in this study. Passive air samplers (PAS, see Fig. S1) were deployed for 28 days in living rooms (n = 6), kitchens (n = 6), and bedrooms (n = 18) of 8 UK homes in Birmingham during July 2021 and December 2021. One unit of PAS was deployed at each site for indoor air sampling. Each PAS was equipped with a polyurethane foam disk (140 mm diameter, 12 mm thickness, 360.6 cm^2 surface area, 0.07 g/cm^3 density, PACS, Leicester, UK) and a glass fiber filter (GFF, 12.5 cm diameter, 1 μm pore size, Whatman, UK). PUF disks were pre-cleaned with hexane and dichloromethane (1:1, v/v) on an accelerated solvent extractor (Dionex ASE 350), and GFFs were baked under 450 ℃ for 5 h prior to use. Stainless-steel shelters of PAS were cleaned carefully with deionized water and were wrapped with aluminium foil before and after deployment. Harvested PUFs and GFFs were properly sealed with aluminium foil in plastic bags and stored at 4 ℃ at the University of Birmingham prior to analysis.

PAS (including PUFs and GFFs) used for outdoor air sampling were the same to those used for indoor air sampling and experienced the same pre-cleaning protocol before and after deployment.

Outdoor air samples were collected in backyards of 4 UK homes in Birmingham during July 2021 and December 2021 (n = 4), and at the Elms Road Observatory Site (EROS, University of Birmingham, Edgbaston, UK) during September 2021 and August 2022 (n = 12). Four units of PAS were deployed at each site for 28 days, and then were combined into one analysis. Samples at the EROS were taken monthly to enable seasonal changes of BFR concentrations to be observed. Harvested PUFs and GFFs were properly sealed with aluminium foil in plastic bags and stored at 4 ℃ at the University of Birmingham prior to analysis.

Analytical protocols

All the solvents used in this study were purchased from Fisher Scientific (Loughborough, UK), and were of HPLC analytical grade. Sulfuric acid (>95%) was purchased from Fisher Scientific (Loughborough, UK), and was of analytical reagent grade. All the native and labelled standards were purchased from Wellington Laboratories (Guelph, ON, Canada), except for BDE-77 and BDE-128 (obtained from AccuStandard Inc. (New Haven, CT, USA)) as well as native HBCDDs (obtained from Sigma-Aldrich Company Ltd. (Dorset, UK)). Florisil® (60-100 mesh) was purchased from Acros Organics (New Jersey, USA), and was baked at 450℃ for 1h prior to use.

Dust samples were sieved with a pre-cleaned stainless-steel test sieve of 500 μm pore size. Approximately 200 mg of dust was precisely 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. Each sample was extracted with 2 mL of hexane and acetone mixture (3:1, v/v) for 3 times, and the extracts were combined into a pre-cleaned 15mL test tube. The extracts were further concentrated and reconstituted into 0.5 mL of hexane before being split into two fractions with a florisil column (2 g). The florisil columns were conditioned with 15 mL of hexane before the sample extracts were added. Fraction 1 was eluted with 12 mL of hexane, and fraction 2 was eluted with 15 mL of ethyl acetate, respectively. The two fractions were then concentrated to nearly dryness and reconstituted into 0.5 mL of hexane separately. After this, fraction 1 was cleaned with 2 g of acid silica (preconditioned with 15 mL of hexane and eluted with 15 mL of hexane and dichloromethane mixture (1:1, v/v)), and fraction 2 was cleaned with 0.5 g of aminopropyl functionised silica (preconditioned with 6 mL of hexane,

and eluted with 12 mL of hexane and dichloromethane mixture (1:1, v/v)), respectively. The two fractions were then combined 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 prior to GC-MS and LC-MS/MS analysis.

Indoor and outdoor air samples (PUFs and GFFs) were put into ASE cells (34 mL in case of indoor air samples, or 100 mL in case of outdoor air samples), and were 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. Hexane and acetone (3:1, v/v) were used to extract the samples on an accelerated solvent extractor (Dionex ASE 350). The extraction programme was set as below:

Temperature: 100℃; Heating time: 5 min; Static time: 4 min; Cycles: 3; Pressure: 1500 psi. Purge time: 90 s; Flush volume: 60%.

The crude extracts were collected in pre-cleaned ASE collection bottles and were reconstituted into 2 mL of hexane prior to purification with 4-6 mL sulfuric acid (95%). The samples were then centrifuged at 3900 RPM for 20 min, and the solvent phase (upper layer) was collected. The acid phase (bottom layer) was extracted with 2 mL hexane twice and then centrifuged, and the solvents were collected and combined. The purified extracts were concentrated to incipient dryness under a gentle stream of nitrogen and were finally reconstituted into 100 μL of toluene containing 15 ng of ^{13}C-BDE-100 and d_{18}-γ-HBCDD as recovery determination (syringe) standards prior to 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 with a programmable-temperature vaporizer (PTV) injector. The ion source was operated in EI SIM mode at 280℃, and the MS transfer line temperature was 300℃. A capillary fused silica column (RESTEK, USA, 15 m × 0.25 mm inner diameter, 0.25 μm film thickness) was equipped and the GC oven temperature was set as below:

(1) initial temperature 80℃, held for 2 min;

(2) oven temperature ramped to 170℃ at a rate of 20℃/min and held for 5.5 min;

(3) oven temperature then ramped to 320℃ at a rate of 25℃/min and held for 10 min.

Analysis of HBCDD 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). The MS was operated in electrospray negative ionization - multiple reaction monitoring (ESI--MRM) mode and was applied for quantitative determination of the target compounds based on m/z 640.6/79 for native HBCDDs, m/z 652.4/79 for ^{13}C-HBCDDs, and m/z 657.7/79 for d_{18}-γ-HBCDD, respectively. 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. The HPLC program was set as below:

(1) mobile phase B commenced with 25% composition, and ramped to 50% over 1 min;

(2) mobile phase B increased linearly to 100% over 5 min and held for 10 min;

(3) mobile phase B returned to 25% and held for 1 min to equilibrate for the next sample.

Passive air sampling rates

Indoor air sampling rates for PBDEs and HBCDDs were obtained from a previous study,[1] as the same PAS units to this earlier study were used in our study; while the sampling rates for NBFRs were assumed equivalent to literature reported sampling rates for PBDEs of similar K_{OA} and K_{OW} values.[1, 2] Indoor air sampling rates for all the target BFRs are summarized in Table S6.

Outdoor air sampling rates for PBDEs were estimated to be 2.26 m^3/day for deca-BDE and 3.92 m^3/day for tri- to hepta- BDEs in an earlier study.[2] We adopted the same sampling rates for PBDEs in our work because the same PAS units to that earlier study were used in our study. Further, following the same rules, the sampling rates for NBFRs were assumed equivalent to literature reported sampling rates for PBDEs of similar K_{OA} and K_{OW} values.[1, 2] (Table S6).

Estimated human exposure to BFRs via inhalation and dust ingestion.

Typical activity patterns were assumed for UK population, i.e., 10% of time spent outdoors and 90%

of time spent indoors for both adults (≥ 16 years old) and toddlers (≤ 3 years old).[3] For adults a working time of 8 h per day was assumed during weekdays, while the rest of the time spent indoors was assumed to be at home. For toddlers all the time spent indoors was assumed to be at home. Therefore, 10% of time spent outdoors, 66% of time spent at home, and 24% of time spent in office (which was not included in this study) were assumed for UK adults in terms of inhalation exposure to BFRs; and 10% of time spent outdoors and 90% of time spent at home were assumed for UK toddlers in terms of inhalation exposure to BFRs. With respects to indoor dust ingestion of BFRs, dust ingestion was assumed to occur pro-rata to typical indoor activity patterns, i.e., 74% home and 26% office for adults, and 100% home for toddlers. An absorption rate of 100% was assumed for UK adults and toddlers when estimating human exposure to BFRs via inhalation and dust ingestion.[1]

Inhalation exposure to BFRs of UK citizens was estimated with the equation below:

$$EDI = \Sigma \frac{CBFR \times AIR \times FT}{BW} \quad (S1)$$

where EDI is the estimated daily intake of BFRs via inhalation (ng/kg bw/day); $CBFR$ is the concentrations of BFRs in indoor or outdoor air (pg/m^3); AIR is the air inhalation rate of UK adults (20 m^3/day) and toddlers (3.8 m^3/day);[1] FT is the fraction of time spent in indoor and outdoor environments; and BW is the average body weight of UK adults (78 kg) and toddlers (12 kg).[4]

Estimates of dust ingestion of BFRs for UK people were achieved by using equation (2):

$$EDI = \Sigma \frac{CBFR \times DIR \times FT}{BW} \quad (S2)$$

where EDI is the estimated daily intake of BFRs via dust ingestion (ng/kg bw/day); $CBFR$ is the concentrations of BFRs in house dust (ng/g); DIR is the dust ingestion rate of UK adults (average: 20 mg/day; high: 50 mg/day) and toddlers (average: 50 mg/day; high: 200 mg/day);[5-7] FT is the fraction of time spent in indoor and outdoor environments; and BW is the average body weight of UK adults (78 kg) and toddlers (12 kg).[4]

Table S1. Relative response factors (RRFs) for each analyte in the 5-point calibration

BFRs	Calibration A	Calibration B	Calibration C	Calibration D	Calibration E	RSD (%)	R^2
BDE-28	0.60	0.59	0.60	0.58	0.54	4.3	0.9955
BDE-47	0.58	0.54	0.56	0.58	0.58	3.1	0.9917
BDE-99	1.2	1.2	1.2	1.1	1.2	3.0	0.9950
BDE-100	0.99	1.0	1.0	0.98	0.98	1.3	0.9970
BDE-153	0.85	1.0	0.84	0.96	1.0	9.2	0.9890
BDE-154	0.88	0.91	0.78	0.90	0.94	6.9	0.9927
BDE-183	0.59	0.60	0.54	0.56	0.58	4.2	0.9969
BDE-209	1.1	1.1	1.0	1.1	1.0	4.1	0.9999
PBBz	27	31	32	30	27	7.9	0.9935
PBT	18	18	17	16	17	5.5	0.9991
PBEB	14	15	14	13	13	4.0	0.9985
DPTE	46	44	41	42	47	5.8	0.9920
HBBz	19	18	17	19	16	6.9	0.9999
EH-TBB	1.1	1.1	1.0	1.0	1.1	6.5	0.9949
BTBPE	1.4	1.3	1.5	1.5	1.4	6.9	0.9917
BEH-TEBP	0.99	1.1	0.98	0.96	0.98	6.4	0.9943
DBDPE	3.0	3.1	2.6	2.6	2.7	8.4	0.9989
α-HBCDD	1.3	1.1	1.3	1.2	1.2	8.7	0.9995
β-HBCDD	1.2	1.1	1.2	1.1	1.1	6.4	0.9997
γ-HBCDD	0.90	0.84	0.83	0.74	0.72	8.8	0.9999

Table S2. Limits of quantification (LOQs) for each analyte for indoor and outdoor air analysis

BFRs	Instrumental LOQs (pg/μL)	Method LOQs for indoor air (pg/m^3)	Method LOQs for outdoor air (pg/m^3)
BDE-28	0.31	0.32	0.036
BDE-47	0.11	0.13	0.012
BDE-99	0.23	0.41	0.026
BDE-100	0.26	0.46	0.030
BDE-153	0.34	0.90	0.039
BDE-154	0.22	0.56	0.025
BDE-183	0.13	0.41	0.014
BDE-209	1.0	3.2	0.20
PBBz	0.11	0.11	0.013
PBT	0.14	0.14	0.016
PBEB	0.12	0.15	0.014
DPTE	0.17	0.17	0.019
HBBz	0.18	0.22	0.020
EH-TBB	0.37	0.96	0.042
BTBPE	1.0	3.3	0.11
BEH-TEBP	1.0	3.2	0.20
DBDPE	1.3	3.9	0.26
α-HBCDD	1.0	2.2	0.11
β-HBCDD	0.95	2.2	0.11
γ-HBCDD	0.67	1.6	0.076

Table S3. Limits of quantification (LOQs) for each analyte for indoor dust analysis

BFRs	Instrumental LOQs (pg/μL)	Method LOQs for indoor dust (ng/g)
BDE-28	0.11	0.22
BDE-47	0.074	0.15
BDE-99	0.097	0.19
BDE-100	0.088	0.18
BDE-153	0.071	0.14
BDE-154	0.055	0.11
BDE-183	0.13	0.26
BDE-209	0.83	1.7
PBBz	0.055	0.11
PBT	0.11	0.22
PBEB	0.075	0.15
DPTE	0.073	0.15
HBBz	0.075	0.15
EH-TBB	0.096	0.19
BTBPE	0.37	0.74
BEH-TEBP	0.55	1.1
DBDPE	0.92	1.8
α-HBCDD	0.18	0.54
β-HBCDD	0.17	0.51
γ-HBCDD	0.12	0.36

Table S4. Recoveries of internal standards (I.S.) in method blanks (n = 5), field blanks (n = 8), dust samples (n = 30), indoor air samples (n = 30), outdoor air samples (n = 16), and NIST SRM 2585 dust (n = 10)

I.S.	Method blanks	Field blanks	Dust samples	Indoor air samples	Outdoor air samples	SRMs
BDE-77	72-75%	63-78%	67-94%	50-84%	55-80%	67-86%
BDE-128	45-53%	46-64%	40-101%	35-74%	43-67%	62-81%
^{13}C-BDE-209	98-113%	30-55%	52-137%	30-48%	32-53%	34-118%
^{13}C-HBBz	63-69%	57-69%	69-113%	35-85%	35-76%	-
^{13}C-EH-TBB	48-55%	79-95%	49-79%	70-99%	66-104%	-
^{13}C-BTBPE	40-47%	39-57%	42-88%	34-60%	39-55%	-
^{13}C-BEH-TEBP	49-55%	37-61%	42-64%	35-60%	39-72%	-
^{13}C-α-HBCDD	64-86%	54-99%	32-68%	32-98%	34-93%	-
^{13}C-β-HBCDD	67-81%	64-115%	36-103%	50-107%	34-73%	-
^{13}C-γ-HBCDD	80-84%	87-111%	66-111%	53-113%	72-93	-

Table S5. Ten replicate analyses of NIST SRM 2585 house dust (ng/g)

PBDEs	Measurements	Certified values	Recovery
BDE-28	29.2 ± 1.3	46.9 ± 4.4	62%
BDE-47	573 ± 28	497 ± 46	115%
BDE-99	746 ± 54	892 ± 53	84%
BDE-100	131 ± 8.0	145 ± 11	90%
BDE-153	120 ± 11	119 ± 1.0	101%
BDE-154	80.7 ± 7.3	83.5 ± 2.0	97%
BDE-183	48.8 ± 4.4	43.0 ± 3.5	113%
BDE-209	2840 ± 280	2510 ± 190	113%

Table S6. Passive air sampling rates for each analyte

BFRs	Indoor air sampling rates (m^3/day)[1]	Outdoor air sampling rates (m^3/day)[2]
BDE-28	1.74	3.92
BDE-47	1.472	3.92
BDE-99	0.992	3.92
BDE-100	1.014	3.92
BDE-153	0.685	3.92
BDE-154	0.691	3.92
BDE-183	0.550	3.92
BDE-209	0.567	2.26
PBBz	1.74	3.92
PBT	1.74	3.92
PBEB	1.472	3.92
DPTE	1.74	3.92
HBBz	1.472	3.92
EH-TBB	0.688	3.92
BTBPE	0.550	3.92
BEH-TEBP	0.567	2.26
DBDPE	0.567	2.26
α-HBCDD	0.807	3.92
β-HBCDD	0.775	3.92
γ-HBCDD	0.761	3.92

Table S7. BFR concentrations (ng/g) in UK house dust collected in 2021 (n=30)

BFRs	DF	Max	Min	Median	Arithmetic mean
BDE-28	20%	3.1	<0.039	<0.089	0.20
BDE-47	100%	27	1.4	3.5	5.8
BDE-99	97%	53	<0.068	3.2	6.3
BDE-100	50%	11	<0.017	0.50	1.1
BDE-153	93%	340	<0.062	1.8	17
BDE-154	93%	190	<0.039	0.66	9.0
BDE-183	100%	540	1.1	4.0	28
Σ_7PBDEs		**1,100**	**4.4**	**13**	**65**
BDE-209	100%	80,000	38	2,300	9,900
Σ_8PBDEs		**80,000**	**48**	**2,300**	**9,900**
PBBz	100%	17	0.20	1.9	3.3
PBT	100%	150	1.6	5.9	24
PBEB	47%	1.2	<0.040	<0.12	0.18
DPTE	70%	19	<0.014	1.1	3.0
HBBz	100%	7.7	0.37	1.9	2.7
EH-TBB	90%	200	<0.068	4.5	20
BTBPE	83%	89	<0.071	15	17
BEH-TEBP	100%	12,000	38	190	1,000
Σ_8NBFRs		**12,000**	**61**	**250**	**1,100**
DBDPE	100%	10,000	130	930	2,900
Σ_9NBFRs		**12,000**	**190**	**2,200**	**4,000**
α-HBCDD	100%	2,100	16	57	250
β-HBCDD	100%	680	5.1	18	73
γ-HBCDD	100%	5,300	2.8	16	400
Σ_3HBCDDs		**8,100**	**39**	**98**	**730**

Table S8. BFR concentrations (pg/m^3) in indoor air collected from UK houses in 2021 (n=30)

BFRs	DF	Max	Min	Median	Arithmetic mean
BDE-28	50%	1.4	<0.32	0.33	0.51
BDE-47	60%	130	<0.13	1.0	5.6
BDE-99	60%	200	<0.41	0.98	8.8
BDE-100	53%	64	<0.46	0.46	4.2
BDE-153	3%	42	<0.90	<0.90	2.3
BDE-154	10%	23	<0.56	<0.56	1.5
BDE-183	33%	90	<0.41	<0.41	3.5
Σ_7PBDEs		550	3.0	7.4	26
BDE-209	80%	2,000	<3.1	220	460
Σ_8PBDEs		2,200	6.3	230	480
PBBz	100%	330	0.99	6.5	49
PBT	100%	1,600	1.7	51	150
PBEB	93%	22	<0.15	0.72	2.0
DPTE	20%	500	<0.17	<0.17	19
HBBz	100%	30	0.65	3.5	6.0
EH-TBB	70%	77	<0.96	3.8	10
BTBPE	33%	120	<3.2	<3.2	19
BEH-TEBP	10%	490	<3.1	<3.1	40
Σ_8NBFRs		2,000	13	74	290
DBDPE	70%	10,000	<3.9	46	490
Σ_9NBFRs		12,000	31	140	780
α-HBCDD	90%	180	<2.2	7.4	37
β-HBCDD	70%	99	<2.2	2.2	16
γ-HBCDD	47%	100	<1.6	<1.6	19
Σ_3HBCDDs		370	3.1	11	72

Table S9. BFR concentrations (pg/m^3) in outdoor air collected from rear gardens of UK homes in 2021 (n=4), and comparisons with BFRs in ambient air collected from Birmingham between 2012-2013 (n=6)[2]

BFRs	Home 1	Home 2	Home 3	Home 4	Birmingham[2]
BDE-28	<0.036	<0.036	0.063	0.10	0.50-26
BDE-47	0.52	<0.012	0.29	0.93	1.3-27
BDE-99	0.43	<0.026	<0.026	0.34	<0.49-27
BDE-100	0.71	0.26	1.1	4.0	<0.45-14
BDE-153	0.15	<0.039	0.11	0.22	<1.1-70
BDE-154	0.11	<0.025	<0.025	0.13	<0.89-42
BDE-183	0.085	<0.014	0.057	0.088	<1.5-57
Σ_7PBDEs	**2.0**	**0.42**	**1.7**	**5.8**	**4.5-310**
BDE-209	<0.20	9.0	28	18	<2.2-360
Σ_8PBDEs	**2.2**	**9.4**	**29**	**24**	**50-380**
PBBz	0.83	0.22	0.26	0.28	
PBT	2.0	0.74	0.42	0.47	
PBEB	0.36	0.26	0.11	0.24	
DPTE	<0.019	1.1	<0.019	<0.019	
HBBz	0.23	0.13	0.11	0.17	
EHTBB	2.5	0.17	<0.042	1.2	
BTBPE	24	0.26	0.62	<0.11	
BEHTEBP	<0.20	<0.20	<0.20	<0.20	
Σ_8NBFRs	**30**	**3.1**	**1.8**	**2.7**	
DBDPE	230	19	150	15	
Σ_9NBFRs	**260**	**22**	**150**	**18**	
α-HBCDD	0.80	0.84	0.20	13	5.5-210
β-HBCDD	0.27	0.22	0.013	4.0	2.0-77
γ-HBCDD	0.24	0.11	<0.076	6.1	6.8-130
Σ_3HBCDDs	**1.3**	**1.2**	**0.29**	**23**	**14-410**

Table S10. BFR concentrations (pg/m^3) in outdoor air collected from EROS site between 2021-2012 (n=12), and comparisons with data obtained at EROS between 2012-2013 (n=6)[2]

BFRs	Sep. 2021	Oct. 2021	Nov. 2021	Dec. 2021	Jan. 2022	Feb. 2022	Mar. 2022	Apr. 2022	May. 2022	Jun. 2022	Jul. 2022	Aug. 2022	Jun 2012 – Jan 2013[2]
BDE-28	0.08	<0.036	0.13	0.10	0.07	0.07	0.14	0.12	0.08	0.09	0.09	0.14	<0.23-26
BDE-47	0.79	0.94	0.64	0.43	0.76	0.68	0.79	0.90	0.74	0.99	0.88	1.38	0.40-31
BDE-99	0.31	0.27	0.25	0.49	0.58	0.21	0.72	0.44	0.39	0.46	0.82	1.04	<0.49-43
BDE-100	1.75	1.25	1.85	1.53	0.96	0.87	2.17	1.47	1.59	1.42	2.52	2.20	<0.45-30
BDE-153	0.16	0.25	0.23	0.15	0.22	0.18	0.50	0.75	0.23	0.29	0.53	0.46	<1.1-62
BDE-154	0.08	0.11	0.19	0.12	0.14	0.11	0.28	0.19	<0.025	0.12	0.12	0.21	<0.89-57
BDE-183	0.16	0.16	0.19	0.26	0.31	0.12	0.47	0.64	0.04	0.13	0.10	0.15	<1.5
Σ_7PBDEs	**3.34**	**3.01**	**3.47**	**3.08**	**3.04**	**2.24**	**5.08**	**4.50**	**3.09**	**3.51**	**5.06**	**5.57**	**1.9-300**
BDE-209	16.61	32.39	8.97	14.62	41.62	5.10	48.06	299.39	16.39	10.24	35.33	51.62	<2.2-270
Σ_8PBDEs	**19.94**	**35.40**	**12.44**	**17.70**	**44.66**	**7.34**	**53.13**	**303.89**	**19.48**	**13.75**	**40.39**	**57.18**	**31-300**
PBBz	0.80	0.91	0.63	0.43	0.39	0.36	0.66	0.49	0.64	0.98	1.06	0.80	
PBT	0.97	0.98	0.73	0.65	0.52	0.49	0.69	0.86	0.91	2.21	2.70	1.39	
PBEB	0.72	0.65	0.82	0.36	0.34	0.82	0.43	0.41	0.45	0.62	0.87	0.81	
DPTE	1.04	1.27	0.75	0.98	0.66	0.70	0.78	1.35	0.79	0.80	1.35	1.09	
HBBz	0.59	0.85	0.34	0.32	0.24	0.37	0.21	0.62	0.44	0.41	0.35	0.31	
EHTBB	0.20	<0.042	0.10	<0.056	<0.042	0.23	0.08	0.18	0.20	0.19	<0.042	<0.041	
BTBPE	<0.11	<0.11	<0.11	<0.15	1.46	14.07	2.15	17.95	15.13	2.36	33.30	41.25	
BEHTEBP	<0.19	8.85	<0.20	<0.26	<0.20	<0.20	8.29	5.33	9.65	11.31	12.81	18.37	
Σ_8NBFRs	**4.62**	**13.68**	**3.70**	**3.21**	**3.86**	**17.23**	**13.29**	**27.19**	**28.23**	**18.87**	**52.48**	**64.06**	
DBDPE	9.64	12.66	30.48	<0.33	35.22	45.60	367.22	10333.02	71.48	163.88	126.57	200.73	
Σ_9NBFRs	**14.25**	**26.34**	**34.18**	**3.54**	**39.08**	**62.82**	**380.51**	**10360.21**	**99.71**	**182.75**	**179.05**	**264.79**	
α-HBCDD	0.65	0.29	0.34	<0.15	0.24	0.19	1.31	5.68	2.07	1.64	21.13	0.85	6.8-110
β-HBCDD	0.23	0.27	0.20	0.10	0.09	0.12	0.34	2.24	0.42	0.43	5.78	0.77	2.3-59
γ-HBCDD	0.27	0.25	0.14	0.27	0.09	0.18	0.26	4.43	0.17	4.98	5.39	1.44	3.1-59
Σ_3HBCDDs	**1.15**	**0.82**	**0.68**	**0.52**	**0.42**	**0.49**	**1.90**	**12.35**	**2.66**	**7.05**	**32.30**	**3.06**	**5.2-230**

Table S11. Literature data on arithmetic mean concentrations of BFRs (medians in parentheses) in house dust (ng/g)

Country	Year	BDE-209	PBDEs [a]	PBBz	PBT	PBEB	DPTE	HBBz	EH-TBB	BTBPE	BEH-TEBP	DBDPE	HBCDD
Ireland[8]	2016	58,000	58,000									39,000	2,900
		(13,000)										(4,200)	(490)
Spain[9]	2020	510	550			<LOD		<LOD	16		630	230	11,000
Spain[10]	2016	(150)	(180)			(0.030)		(0.22)		(1.6)		(86)	
Belgium[10]	2016	(180)	(210)			(0.020)		(0.26)		(0.87)		(140)	
Italy[10]	2016	(230)	(280)			(0.060)		(0.36)		(1.7)		(120)	
Iraq[11]	2013	960	1,000			0.28			7.1	17	110	150	
US[12]	2013	2,800	4,000	2.6		1.4		13	920	22	2,500	370	
Canada[12]	2013	1,200	2,600	3.3		1.2		6.4	2,400	27	2,700	95	
Czech Republic[12]	2013	220	240	0.44		<LOD		2.1	17	5.8	60	20	
South Africa[13]	2018	1,400	1,500						3,200		1,600		
Nepal[14]	2015	6.7	7.7			0.060		0.24	0.28	0.42	29	490	
Korea[15]	2015	1,300	1,700							42		260	
China[16]	2020	1,900	2,400										340
China[17]	2013	2,200	2,200						86	13	2,500	650	
Australia[18]	2019	1,400	2,000	<LOD	0.75	0.010			120	6.5	66	14,000	

[a] including BDE-209.

Table S12. Literature data on arithmetic mean concentrations of BFRs (medians in parentheses) in indoor air (household) and outdoor air (pg/m^3)

Country	Year	BDE-209	PBDEs [a]	PBBz	PBT	PBEB	DPTE	HBBz	EH-TBB	BTBPE	BEH-TEBP	DBDPE	HBCDD
Indoor air													
Ireland[8]	2016	880 (410)	930									390 (48)	110 (20)
Spain[9]	2020	54	180			<LOD		<LOD	590		180	180	<LOD
US[12]	2013	840	1,100	3.8		9.0		9.6	23	0.18	16	42	
Canada[12]	2013	83	220	8.8		4.0		9.9	32	1.3	6.8	13	
Czech Republic[12]	2013	11	16	4.9		0.66		7.2	6.6	0.49	3.0	<LOD	
China[19]	2013	(70)	(70)									(75)	
China[20]	2017	(210)							(3.0)	(5.9)		(750)	
Japan[21]	2006	19	36										110
Outdoor air													
Spain[22]	2013		11			32		<LOD		<LOD		<LOD	
China[23]	2008	57	69	0.46	6.1	0.34	0.30	4.8		1.1		11	150
China[19]	2013	(400)	(450)									(130)	
China[20]	2017	(120)							(10)	(1.9)		(38)	
Japan[21]	2006	14	22										14
South Africa[24]	2017	120	770						380	350	370		60

[a] including BDE-209.

Table S13. Correlation coefficients (Spearman's rho) of BFR concentrations between indoor and outdoor environments

BFRs	lg K_{OA}[1]	Indoor air vs indoor dust [a]	Indoor air vs outdoor air [a]
BDE-28	9.50	n.a.	n.a.
BDE-47	10.53	0.175	n.a.
BDE-99	11.31	0.317	n.a.
BDE-100	11.13	0.190	n.a.
BDE-153	11.82	n.a.	n.a.
BDE-154	11.92	n.a.	n.a.
BDE-183	11.96	n.a.	n.a.
BDE-209	15.27	0.185	0.400
PBBz	9.10	0.764**	0.400
PBT	9.66	0.856**	1.000**
PBEB	9.97	n.a.	1.000**
DPTE	8.01	n.a.	n.a.
HBBz	10.26	0.776**	0.800
EH-TBB	12.34	0.075	0.000
BTBPE	15.67	n.a.	n.a.
BEH-TEBP	16.86	n.a.	n.a.
DBDPE	19.22	0.153	0.200
α-HBCDD	14.43	0.014	-0.400
β-HBCDD	14.64	0.271	-0.800
γ-HBCDD	14.17	n.a.	-0.800

[a] only BFRs with a DF exceeding 50% were included.

* $p < 0.05$.

** $p < 0.01$.

Table S14. Arithmetic mean atmospheric concentrations of BFRs observed at EROS in different seasons (pg/m^3)

BFRs	Autumn 2021	Winter 2021	Spring 2022 [a]	Summer 2022
Σ_7PBDEs	3.3	2.8	4.2 (4.1)	4.7
BDE-209	19	20	120 (32)	32
PBBz	0.78	0.39	0.60 (0.65)	0.94
PBT	0.90	0.55	0.82 (0.80)	2.1
PBEB	0.73	0.51	0.43 (0.44)	0.77
DPTE	1.0	0.78	0.98 (0.79)	1.1
HBBz	0.60	0.31	0.42 (0.33)	0.36
EH-TBB	0.12	0.11	0.15 (0.14)	0.091
BTBPE	<0.11	5.2	12 (8.6)	26
BEH-TEBP	3.1	<0.20	7.8 (9.0)	14
DBDPE	18	27	3,600 (220)	160
Σ_9NBFRs	25	35	3,600 (240)	210
Σ_3HBCDDs	0.89	0.48	5.6 (2.3)	14

[a] arithmetic mean concentrations in parentheses when the April 2022 sample is excluded.

Table S15. Weather conditions (℃) in Birmingham, UK during September 2021 and August 2022

Month	Average monthly high temperature (℃)	Average monthly low temperature (℃)	Average monthly temperature (℃)	Rainy days	Air humidity (%)	Wind Speed (mph)
Sep. 2021	17.5	9.4	13.5	3	81	6.7
Oct, 2021	13.6	6.9	10.3	5	84	8.1
Nov. 2021	9.8	4.2	7.0	2	87	7.6
Dec. 2021	7.2	2.2	4.7	8	91	8.7
Jan. 2022	6.9	1.7	4.3	2	88	7.4
Feb. 2022	7.5	1.1	4.3	9	81	11.2
Mar. 2022	9.4	2.2	5.8	4	80	8.7
Apr. 2022	12.8	4.2	8.5	4	74	8.3
May. 2022	15.8	7.2	11.5	8	74	7.6
Jun. 2022	18.6	10.0	14.3	3	69	7.6
Jul. 2022	20.8	12.2	16.5	7	67	7.6
Aug. 2022	20.4	11.7	16.1	5	69	6.9

Table S16. Temporal changes in arithmetic mean concentrations of BFRs in UK indoor and outdoor environments

BFRs	Indoor dust (ng/g)		Indoor air (pg/m^3)		Outdoor air (pg/m^3) [a]	
	2015[1]	2021	2015[1]	2021	2012[2]	2021
BDE-28	1.9	0.20	22	0.51	5.4	0.093
BDE-47	14	5.8	120	5.6	7.6	0.83
BDE-99	31	6.3	130	8.8	7.6	0.54
BDE-100	4.2	1.1	44	4.2	5.4	1.7
BDE-153	4.8	17	24	2.3	11	0.28
BDE-154	2.0	9.0	14	1.5	13	0.14
BDE-183	7.4	28	2.8	3.5	0.75	0.19
BDE-209	34,000	9,900	660	460	110	29
Σ_8PBDEs	**34,000**	**9,900**	**1,000**	**480**	**150**	**33**
PBBz	3.3	3.3	6.6	49		0.72
PBT	7.1	24	17	150		1.1
PBEB	2.3	0.18	1.6	2.0		0.65
DPTE	6.6	3.0	3.5	19		1.0
HBBz	1.8	2.7	11	6.0		0.43
EH-TBB	21	20	4.8	10		0.075
BTBPE	14	17	11	19		11
BEH-TEBP	240	1,000	10	40		5.8
DBDPE	240	2,900	26	490		59
Σ_9NBFRs	**540**	**4,000**	**92**	**780**		**80**
α-HBCDD	2,300	250	43	37	42	3.4
β-HBCDD	1,100	73	17	16	22	1.1
γ-HBCDD	4,900	400	270	19	22	1.1
Σ_3HBCDDs	**8,300**	**730**	**330**	**72**	**86**	**5.6**

[a] data obtained in certain months (June 2012 to January 2013 vs June 2021 to January 2022) at EROS are compared.

Table S17. Estimated daily intake of BFRs via inhalation, dust ingestion, and dietary intake for UK adults (ng/kg bw/day)

BFRs	Indoor dust ingestion			Inhalation of indoor air			Inhalation of outdoor air			Dietary intake[25]		Total exposure	
	Mean	Median	High	Mean	Median	High	Mean	Median	High	Mean	High	Mean	High
Σ_7PBDEs [a]	0.012	0.0025	0.079	0.0045	0.0013	0.0038	0.000088	0.000082	0.00014	0.30	2.1	0.32	2.2
BDE-209	1.9	0.44	24	0.077	0.037	0.31	0.0010	0.00044	0.0029	0.057	0.39	2.0	24
Σ_8PBDEs	**1.9**	**0.44**	**24**	**0.082**	**0.040**	**0.34**	**0.0011**	**0.00056**	**0.0030**	**0.36**	**2.5**	**2.3**	**26**
PBBz	0.00063	0.00035	0.0061	0.0083	0.0011	0.042	0.000016	0.000016	0.000026	0	0	0.0089	0.048
PBT	0.0046	0.0011	0.055	0.025	0.0086	0.10	0.000027	0.000021	0.000060	0	0	0.029	0.15
PBEB	0.000034	0.000023	0.00034	0.00034	0.00012	0.0017	0.000013	0.000011	0.000021	0	0	0.00039	0.0020
DPTE	0.00057	0.00021	0.0056	0.0032	0.000029	0.0036	0.000020	0.000020	0.000035	0.075	0.45	0.079	0.46
HBBz	0.00052	0.00035	0.0031	0.0010	0.00059	0.0036	0.0000092	0.0000086	0.000017	0	0	0.0015	0.0067
EH-TBB	0.0038	0.00085	0.057	0.0017	0.00065	0.0084	0.0000085	0.0000036	0.000040	0.059	0.35	0.064	0.42
BTBPE	0.0032	0.0028	0.017	0.0031	0.00054	0.017	0.00025	0.000046	0.00090	1.3	8.1	1.3	8.1
BEH-TEBP	0.19	0.036	3.1	0.0067	0.00052	0.055	0.00012	0.0000059	0.00036	1.0	6.0	1.2	9.2
DBDPE	0.55	0.18	4.2	0.083	0.0077	0.18	0.019	0.0015	0.073	0.073	0.44	0.72	4.8
Σ_9NBFRs	**0.75**	**0.43**	**5.2**	**0.13**	**0.024**	**0.30**	**0.019**	**0.0021**	**0.074**	**2.5**	**15**	**3.4**	**21**
HBCDD	**0.14**	**0.019**	**2.1**	**0.012**	**0.0018**	**0.058**	**0.00014**	**0.000032**	**0.00065**	**0.057**	**0.48**	**0.21**	**2.6**
Σ_{20}BFRs	**2.8**	**1.3**	**30**	**0.23**	**0.11**	**0.52**	**0.021**	**0.0026**	**0.077**	**2.9**	**18**	**5.9**	**48**

[a] sum of BDE-28, -47, -99, -100, -153, -154, and -183.

Table S18. Estimated daily intake of BFRs via inhalation, dust ingestion, and dietary intake for UK toddlers (ng/kg bw/day)

BFRs	Indoor dust ingestion			Inhalation of indoor air			Inhalation of outdoor air			Dietary intake[25]		Total exposure	
	Mean	Median	High	Mean	Median	High	Mean	Median	High	Mean	High	Mean	High
Σ_7PBDEs [a]	0.27	0.056	2.8	0.0075	0.0021	0.0064	0.00011	0.00010	0.00018	0.83	5.9	1.1	8.7
BDE-209	41	9.6	830	0.13	0.062	0.53	0.0013	0.00055	0.0036	0.16	1.1	41	830
Σ_8PBDEs	**41**	**9.6**	**830**	**0.14**	**0.067**	**0.57**	**0.0014**	**0.00069**	**0.0038**	**1.0**	**7.0**	**42**	**840**
PBBz	0.014	0.0077	0.21	0.014	0.0019	0.070	0.000019	0.000020	0.000032	0	0	0.028	0.28
PBT	0.10	0.025	1.9	0.041	0.015	0.17	0.000033	0.000025	0.000074	0	0	0.14	2.1
PBEB	0.00075	0.00050	0.012	0.00058	0.00021	0.0028	0.000016	0.000014	0.000026	0	0	0.0014	0.015
DPTE	0.013	0.0046	0.20	0.0055	0.000048	0.0060	0.000025	0.000025	0.000043	0.20	1.2	0.22	1.4
HBBz	0.011	0.0077	0.11	0.0017	0.0010	0.0060	0.000011	0.000011	0.000022	0	0	0.013	0.11
EH-TBB	0.083	0.019	2.0	0.0028	0.0011	0.014	0.000011	0.0000044	0.000049	0.16	0.96	0.25	3.0
BTBPE	0.071	0.063	0.59	0.0053	0.00091	0.029	0.00030	0.000057	0.0011	3.6	22	3.7	23
BEH-TEBP	4.2	0.79	110	0.011	0.00088	0.093	0.00015	0.0000073	0.00045	2.7	16	6.9	130
DBDPE	12	3.9	150	0.14	0.013	0.30	0.023	0.0019	0.091	0.19	1.2	12	150
Σ_9NBFRs	**17**	**9.4**	**180**	**0.22**	**0.040**	**0.51**	**0.024**	**0.0026**	**0.091**	**6.8**	**42**	**24**	**220**
HBCDD	**3.0**	**0.41**	**74**	**0.021**	**0.0031**	**0.098**	**0.00018**	**0.000039**	**0.00081**	**0.12**	**1.2**	**3.2**	**75**
Σ_{20}BFRs	**61**	**30**	**1,000**	**0.38**	**0.19**	**0.88**	**0.025**	**0.0033**	**0.095**	**7.9**	**50**	**69**	**1,100**

[a] sum of BDE-28, -47, -99, -100, -153, -154, and -183.

Table S19. Reference doses (RfD, ng/kg bw/day) for BFRs of interest,[26] and comparisons with the estimated daily intake (EDI) of BFRs for UK adults and toddlers

BFRs	RfD	EDI/RfD ratios for toddlers		EDI/RfD ratios for adults	
		Mean	High	Mean	High
BTBPE	243,000	< 0.001	< 0.001	< 0.001	< 0.001
EH-TBB	20,000	< 0.001	< 0.001	< 0.001	< 0.001
BEH-TEBP	20,000	< 0.001	0.0065	< 0.001	< 0.001
DBDPE	333,333	< 0.001	< 0.001	< 0.001	< 0.001
BDE-209	7,000	0.0059	0.12	< 0.001	0.0035
	(700) [a]	0.059	1.2	0.0029	0.035
Penta-BDE	2,000	< 0.001	< 0.001	< 0.001	0.0016
BDE-47	100	0.0010	0.0070	0.0030	0.023
BDE-99	100	0.0012	0.0083	0.0036	0.026
BDE-153	200	< 0.001	< 0.001	< 0.001	0.0047
∑HBCDDs	200,000	< 0.001	< 0.001	< 0.001	< 0.001

[a] For BDE-209, EPA has assigned an oral slope factor for carcinogenic risk of 700 $(ng/kg\ bw/day)^{-1}$.

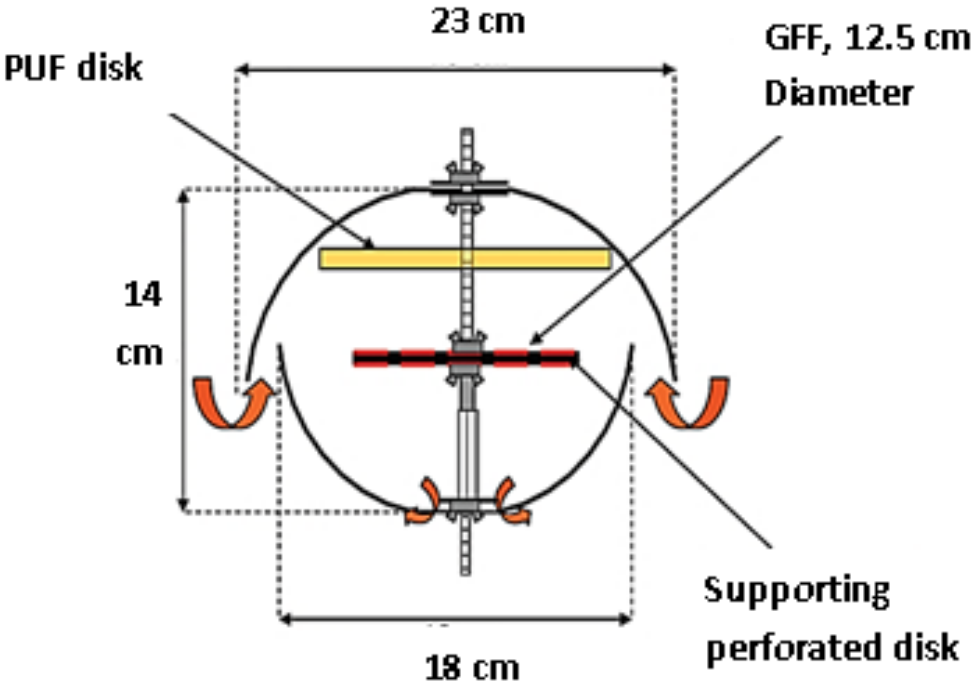


Fig. S1 Passive sampler configuration used for indoor and outdoor air sampling. Figure reprinted from Abdallah and Harrad (2010)[27]

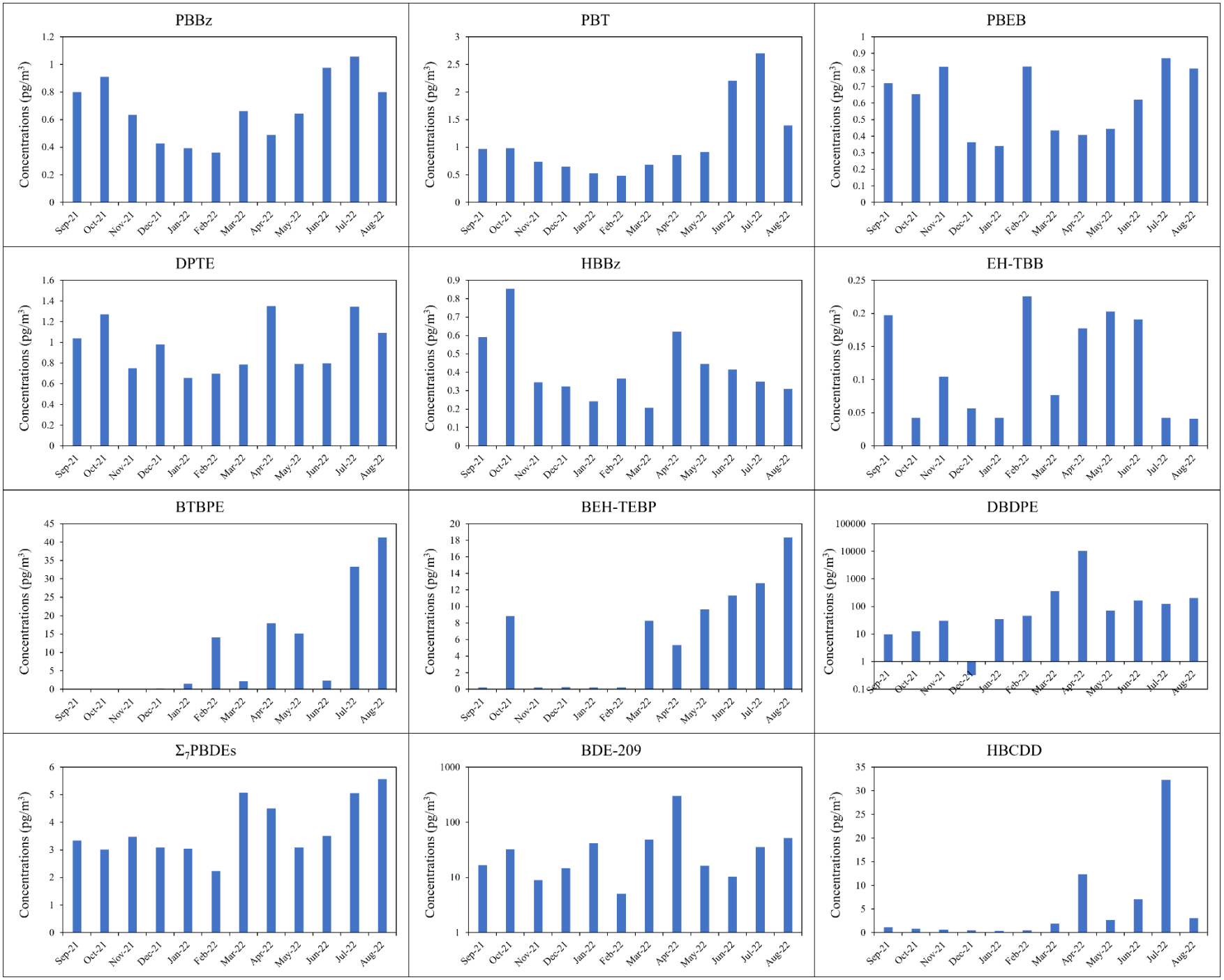


Fig. S2 Seasonal variations in atmospheric BFR concentrations observed at EROS during September 2021 and August 2022. Logarithmic axis was used for BDE-209 and DBDPE.

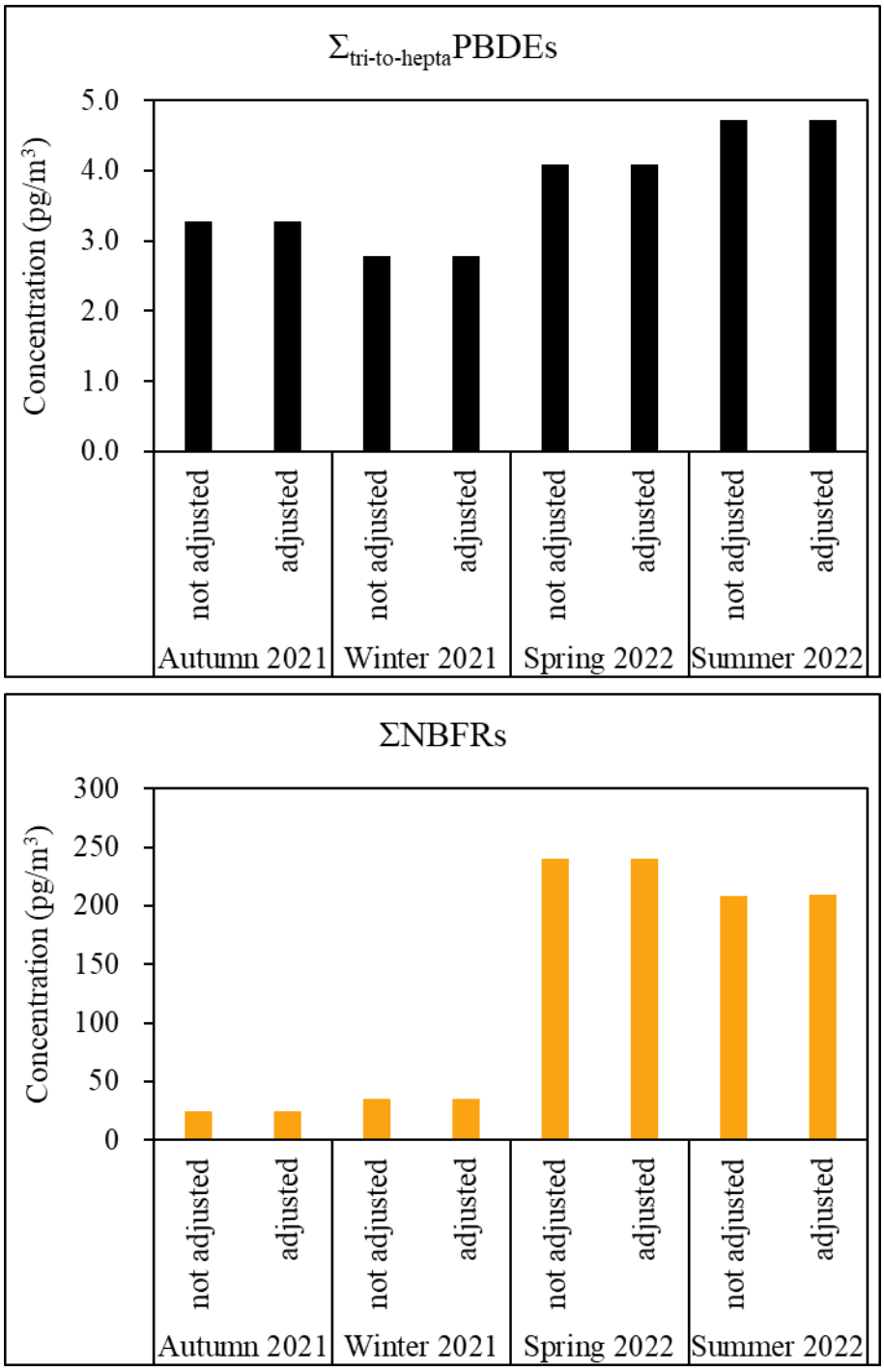


Fig. S3 Seasonal variations in atmospheric concentrations of BFRs: comparisons of BFR concentrations before vs after temperature-driven adjustments in air sampling rates of PAS.

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Appendix E. Supplementary Materials for Chapter Six

Sampling

Six dust samples were collected from inside of an e-waste recycling facility (Facility #1) located in the West Midlands, UK. Dust samples were collected from an office (site 1), two e-waste storage containers (sites 2 and 3), a canteen (site 4), and a public zone in front of e-waste storage containers (sites 5 and 6), respectively. Another thirty dust samples were collected from outside of five e-waste recycling facilities located in the West Midlands, UK during September and November 2022. Specifically, three dust samples were collected from the upwind side of each facility, with another three samples collected from the downwind side.

A vacuum cleaner equipped with pre-cleaned nylon mesh filters (25 μm pore size) was used for dust collection. A square of 4 m^2 (i.e., 2 m × 2 m) was measured on each sampling site, and the square was vacuumed evenly and thoroughly for 4 min. This allows dust to be collected inside the nylon filters. Then the nylon filters with dust were sealed properly and wrapped with aluminium foil before being placed in plastic bags, and all the dust samples were stored at 4 ℃ in the University of Birmingham prior to extraction.

Analytical protocols

All the solvents used in this study were purchased from Fisher Scientific (Loughborough, UK), and were of HPLC analytical grade. Sulfuric acid (>95%) was purchased from Fisher Scientific (Loughborough, UK), and was of analytical reagent grade. All the native and labelled standards were purchased from Wellington Laboratories (Guelph, ON, Canada), except for BDE-77 and BDE-128 (obtained from AccuStandard Inc. (New Haven, CT, USA)) as well as native HBCDDs (obtained from Sigma-Aldrich Company Ltd. (Dorset, UK)). Florisil® (60-100 mesh) was purchased from Acros Organics (New Jersey, USA), and was baked at 450℃ for 1h prior to use.

Dust samples were sieved with a pre-cleaned stainless-steel test sieve of 500 μm pore size. Approximately 200 mg of dust was precisely 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 standards. Each sample was extracted with 2 mL of hexane and acetone mixture (3:1, v/v) for 3 times, and the extracts were combined into a pre-cleaned 15mL test tube. The extracts were further concentrated and reconstituted into 0.5 mL of hexane before being fractionised into two fractions with a florisil column (2 g). The florisil columns were conditioned with 15 mL of hexane before the sample extracts were added. Fraction 1 was eluted with 12 mL of hexane, and fraction 2 was eluted with 15 mL of ethyl acetate, respectively. The two fractions were then concentrated to nearly dryness and reconstituted into 0.5 mL of hexane separately. After this, fraction 1 was cleaned with 2 g of acid silica (preconditioned with 15 mL of hexane, and eluted with 15 mL of hexane and dichloromethane mixture (1:1, v/v)), and fraction 2 was cleaned with 0.5 g of aminopropyl functionised silica (preconditioned with 6 mL of hexane, and eluted with 12 mL of hexane and dichloromethane mixture (1:1, v/v)), respectively. The two fractions were then combined and reconstituted into 100 μL of toluene containing 15 ng of ^{13}C-BDE-100 and d_{18}-γ-HBCDD as recovery determination standards prior to GC-MS and LC-MS/MS analysis.

GC-MS analysis of PBDEs and NBFRs has been reported previously (Ma et al., 2023). 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 with a programmable-temperature vaporizer (PTV) injector. The ion source was operated in EI SIM mode at 280 ℃, and the MS transfer line temperature was 300 ℃. A capillary fused silica column (RESTEK, USA, 15 m x 0.25 mm inner diameter, 0.10 μm film thickness) was equipped and the GC oven temperature was set as below:

(1) initial temperature 80℃, held for 2 min;

(2) oven temperature ramped to 170℃ at a rate of 20℃/min and held for 5.5 min;

(3) oven temperature then ramped to 320℃ at a rate of 25℃/min and held for 10 min.

Instrumental analysis of HBCDDs has been described in our previous work (Ma et al., 2023). Analysis of HBCDDs 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). The MS was operated in electrospray negative ionization - multiple reaction monitoring (ESI^--MRM) mode, and was applied for quantitative determination of the target compounds based on m/z 640.6/79 for native HBCDDs, m/z 652.4/79 for 13C-HBCDDs, and m/z 657.7/79 for d18-γ-HBCDD, respectively. 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. The LC program was set as below:

(1) mobile phase B commenced with 25% composition, and then ramped to 50% over 1 min;

(2) mobile phase B increased linearly to 100% over 5 min and held for 10 min;

(3) mobile phase B returned to 25% and held for 1 min to equilibrate for the next sample.

Table S1. Relative response factors (RRFs) for each analyte in the 5-point calibration

BFRs	Calibration A	Calibration B	Calibration C	Calibration D	Calibration E	RSD (%)	R^2
BDE-28	0.60	0.59	0.60	0.58	0.54	4.3	0.9955
BDE-47	0.58	0.54	0.56	0.58	0.58	3.1	0.9917
BDE-99	1.2	1.2	1.2	1.1	1.2	3.0	0.9950
BDE-100	0.99	1.0	1.0	0.98	0.98	1.3	0.9970
BDE-153	0.85	1.0	0.84	0.96	1.0	9.2	0.9890
BDE-154	0.88	0.91	0.78	0.90	0.94	6.9	0.9927
BDE-183	0.59	0.60	0.54	0.56	0.58	4.2	0.9969
BDE-209	1.1	1.1	1.0	1.1	1.0	4.1	0.9999
PBBz	27	31	32	30	27	7.9	0.9935
PBT	18	18	17	16	17	5.5	0.9991
PBEB	14	15	14	13	13	4.0	0.9985
DPTE	46	44	41	42	47	5.8	0.9920
HBBz	19	18	17	19	16	6.9	0.9999
EH-TBB	1.1	1.1	1.0	1.0	1.1	6.5	0.9949
BTBPE	1.4	1.3	1.5	1.5	1.4	6.9	0.9917
BEH-TEBP	0.99	1.1	0.98	0.96	0.98	6.4	0.9943
DBDPE	3.0	3.1	2.6	2.6	2.7	8.4	0.9989
α-HBCDD	1.3	1.1	1.3	1.2	1.2	8.7	0.9995
β-HBCDD	1.2	1.1	1.2	1.1	1.1	6.4	0.9997
γ-HBCDD	0.90	0.84	0.83	0.74	0.72	8.8	0.9999

Table S2. Limits of detection (LODs) and limits of quantification (LOQs) for each analyte

BFRs	LODs (S:N = 3:1)		LOQs (S:N = 10:1)	
	pg/injection [a]	pg/g sample [b]	pg/injection [a]	pg/g sample [b]
BDE-28	0.54	0.27	1.8	0.89
BDE-47	0.21	0.10	0.69	0.35
BDE-99	0.46	0.23	1.5	0.77
BDE-100	0.53	0.27	1.8	0.89
BDE-153	0.25	0.13	0.84	0.42
BDE-154	0.22	0.11	0.72	0.36
BDE-183	0.64	0.32	2.1	1.1
BDE-209	5.0	2.5	17	8.3
PBBz	0.23	0.11	0.75	0.38
PBT	0.49	0.24	1.6	0.81
PBEB	0.36	0.18	1.2	0.60
DPTE	0.23	0.12	0.78	0.39
HBBz	0.35	0.17	1.2	0.58
EH-TBB	0.42	0.21	1.4	0.71
BTBPE	1.7	0.85	5.7	2.8
BEH-TEBP	2.2	1.1	7.4	3.7
DBDPE	4.7	2.3	16	7.8
α-HBCDD	9.1	0.45	30	1.5
β-HBCDD	17	0.86	57	2.9
γ-HBCDD	5.0	0.25	17	0.83

[a] 1 μL of calibration C was injected into GC-MS for the calculation of instrument LODs (LOQs) of PBDEs and NBFRs; 10 μL of calibration B was injected into HPLC-MS/MS for the calculation of instrument LODs (LOQs) of HBCDDs.

[b] 0.2 g sample was assumed to calculate the method LODs (LOQs).

Table S3. Recoveries of internal standards (I.S.) in method blanks (n = 6), dust samples (n = 36), and NIST SRM 2585 dust (n = 10)

I.S.	Blanks	Samples	SRMs
BDE-77	94-100%	74-96%	67-86%
BDE-128	40-54%	62-103%	62-81%
13C-BDE-209	71-126%	73-126%	34-118%
13C-HBBz	87-103%	71-97%	-
13C-EH-TBB	56-68%	79-130%	-
13C-BTBPE	69-108%	81-141%	-
13C-BEH-TEBP	66-112%	31-81%	-
13C-α-HBCDD	110-137%	53-141%	-
13C-β-HBCDD	90-128%	68-150%	-
13C-γ-HBCDD	91-103%	55-111%	-

Table S4. Ten replicate analyses of NIST SRM 2585 house dust (ng/g)

PBDEs	Measurements	Certified values	Recovery
BDE-28	29.2 ± 1.3	46.9 ± 4.4	62%
BDE-47	573 ± 28	497 ± 46	115%
BDE-99	746 ± 54	892 ± 53	84%
BDE-100	131 ± 8.0	145 ± 11	90%
BDE-153	120 ± 11	119 ± 1.0	101%
BDE-154	80.7 ± 7.3	83.5 ± 2.0	97%
BDE-183	48.8 ± 4.4	43.0 ± 3.5	113%
BDE-209	2840 ± 280	2510 ± 190	113%

Table S5. Concentrations of BFRs in dust from inside and outside of UK e-waste recycling facilities (inside: n = 6; outside: n = 30)

BFRs	Inside (ng/g)					Outside (ng/g)					Outside (ng/g OC) [a]			
	DF	Min	Median	Max	Average	DF	Min	Median	Max	Average	Min	Median	Max	Average
BDE28	83%	<0.23	0.56	1.4	0.69	3%	<0.14	<0.20	0.77	0.12	<2.4	<4.5	25	3.1
BDE47	100%	4.2	24	97	39	90%	<0.077	0.39	42	2.0	<1.8	8.1	1,400	61
BDE99	100%	7.4	41	82	43	80%	<0.16	0.72	75	3.6	<2.1	13	2,500	110
BDE100	100%	2.4	4.7	19	7.1	57%	<0.17	0.25	14	0.79	<2.5	6.4	460	23
BDE153	100%	2.0	3.5	37	8.8	57%	<0.080	0.10	6.1	0.39	<1.3	2.0	200	11
BDE154	100%	1.2	2.5	6.9	3.1	33%	<0.069	<0.085	4.2	0.24	<0.98	<2.4	140	7.1
BDE183	100%	1.1	4.6	160	29	83%	<0.22	0.30	5.1	0.62	<2.9	6.3	170	17
BDE209	100%	1,900	5,500	14,000	6,200	100%	4.3	21	1,300	96	150	380	42	2,700
ΣPBDEs	**-**	**2,100**	**5,600**	**15,000**	**6,300**	**-**	**5.4**	**22**	**1,400**	**100**	**170**	**430**	**47,000**	**2,900**
PBBz	100%	0.26	0.42	3.2	0.94	17%	<0.060	<0.086	0.35	0.066	<1.0	<2.1	11	1.7
PBT	100%	0.46	1.3	27	6.8	10%	<0.13	<0.18	1.3	0.14	<2.2	<4.4	43	3.9
PBEB	67%	<0.14	0.30	2.1	0.55	17%	<0.095	<0.14	40	1.5	<1.6	<3.2	1,300	49
DPTE	50%	<0.087	0.44	6.2	1.8	0%	<0.062	<0.088	<0.11	0.043	<1.1	<2.0	2.0	1.1
HBBz	100%	0.27	0.57	19	4.0	33%	<0.092	<0.13	1.3	0.17	<1.6	<3.8	43	4.5
EH-TBB	100%	0.77	3.9	8.1	4.1	30%	<0.11	<0.16	3.9	0.39	<2.0	<4.7	130	10
BTBPE	100%	2.0	29	3,500	600	63%	<0.54	1.2	62	3.4	<8.5	20	2,100	100
BEH-TEBP	100%	19	29	100	39	60%	<0.59	2.3	11	3.4	<10	54	320	82
DBDPE	100%	200	990	17,000	4,900	87%	<1.7	40	390	57	<45	810	13,000	1,400
ΣNBFRs	**-**	**220**	**1,100**	**21,000**	**5,500**	**-**	**2.5**	**47**	**510**	**66**	**57**	**950**	**17,000**	**1,700**
α-HBCDD	100%	15	61	290	91	97%	<0.34	3.8	20	5.6	<16	92	670	120
β-HBCDD	100%	17	32	200	60	63%	<0.46	0.86	6.3	1.2	<12	20	210	28
γ-HBCDD	100%	75	360	920	450	97%	<0.19	1.4	36	3.8	<8.6	35	1,200	100
ΣHBCDDs	**-**	**120**	**500**	**1,400**	**600**	**-**	**<1.2**	**6.3**	**50**	**11**	**<54**	**140**	**1,600**	**250**
ΣBFRs	**-**	**3,300**	**7,500**	**36,000**	**12,000**	**-**	**16**	**85**	**2,000**	**180**	**370**	**1,700**	**65,000**	**4,800**

[a] organic carbon (OC) normalised concentrations.

Table S6. Literature data on average concentrations (medians in parentheses) of BFRs in dust inside and outside (soil) e-waste facilities, and comparisons with road dust, house dust, and soil in urban areas (ng/g)

Sample Type	Facility Type [a]	Sampling Year	BDE-209	ΣPBDEs [b]	BTBPE	BEH-TEBP	DBDPE	HBCDD
indoor dust (Thailand) (Muenhor et al., 2010)	formal	2008	33,000 (20,000)	43,000 (28,000)			1,300 (890)	
indoor dust (China) (Li et al., 2023)	formal	2020	n.a. [c]	n.a. [c]	16-42	130-160	n.a. [c]	380-790
indoor dust (China) (Zhou et al., 2022)	formal	2020	(12,000)	(12,000)	n.a. [c]	n.a. [c]	n.a. [c]	(20)
indoor dust (Canada) (Nguyen et al., 2019)	formal	2017	97,000 (89,000)	99,000	n.a. [c]	2,000 (1,900)	n.a. [c]	n.a. [c]
indoor dust (Canada) (Stubbings et al., 2019)	formal	2017	(110,000)	(120,000)	(3,500)	(2,000)	(41,000)	n.a. [c]
outdoor dust (China) (Li et al., 2023)	formal	2020	n.a. [c]	n.a. [c]	4.6	130	n.a. [c]	370
surface soil (Australia) (McGrath et al., 2018)	formal	2017	460-6,000	470-6,000	3.2-3.9	n.a. [c]	55-2,100	n.a. [c]
indoor dust (China) (Zheng et al., 2015)	informal	2013	(640-55,000)	(690-63,000)	(28-3,900)	(49-7,100)	(1,200-45,000)	n.a. [c]
indoor dust (China) (Xu et al., 2015)	informal	2013	20,000	27,000	n.a. [c]	n.a. [c]	4,800	n.a. [c]
indoor dust (Vietnam) (Wannomai et al., 2020)	informal	2015	27,000-57,000	31,000-65,000	700-1,300	260-470	8,800-11,000	n.a. [c]

road dust (China) (Xu et al., 2015)	informal	2013	4,100	7,100	n.a. [c]	n.a. [c]	670	n.a. [c]
road dust (China) (Tang et al., 2016)	informal	2011	1,400	1,500	n.a. [c]	n.a. [c]	n.a. [c]	n.a. [c]
surface soil (China) (Ling et al., 2022)	informal	2018	820	1,900	14	n.a. [c]	190	n.a. [c]
surface soil (Vietnam) (Matsukami et al., 2017)	informal	2014	(370)	(490)	(1.6)	n.a. [c]	(63)	n.a. [c]
road dust (China) (Cao et al., 2017)	urban area [d]	2014	58-210	65-220	n.a. [c]	3.3-71	n.a. [c]	n.a. [c]
road dust (Vietnam) (Anh et al., 2018)	urban area [d]	2016	(20)	(24)	0.020	n.a. [c]	14	n.a. [c]
house dust (UK) (Drage et al., 2020)	urban area [d]	2019	4,800 (1,600)	4,800 (1,700)	11 (0.84)	n.a. [c]	1,500 (660)	46,000 (280)
house dust (UK) (Tao et al., 2016)	urban area [d]	2013-2015	34,000 (4,500)	34,000 (4,600)	14 (5.6)	240 (65)	240 (41)	8,300 (610)
office dust (UK) (Tao et al., 2016)	urban area [d]	2013-2015	9,100 (2,700)	9,400 (3,000)	100,000 (160)	1,000 (160)	1,600 (440)	2,000 (1,700)
surface soil (UK) (Drage et al., 2016)	urban area [d]	2013	11 (7.2) [e]	15 (10) [e]	n.a. [c]	n.a. [c]	0.38 (0.35) [e]	n.a. [c]

[a] formal (regulated) e-waste recycling facility vs informal (unregulated) e-waste recycling facility.

[b] including BDE-209.

[c] data not available.

[d] urban areas with no known impact of e-waste recycling activities.

[e] data were normalised with organic carbon content (ng/g OC).

Table S7. Average concentrations of BFRs in road dust in the vicinity of UK e-waste recycling facilities (only BFRs with a DF exceeding 50% are included)

BFRs	Facility 1		Facility 2		Facility 3		Facility 4		Facility 5	
	upwind	downwind	upwind	downwind	upwind	downwind	upwind	downwind	upwind	downwind
n	3	3	3	3	3	3	3	3	3	3
BDE47	0.47	0.40	0.22	0.36	0.22	0.71	0.30	0.32	15	2.0
BDE99	0.71	0.79	0.46	0.55	0.68	1.1	0.43	0.36	27	4.2
BDE100	0.095	0.34	0.096	0.36	0.19	0.54	0.10	0.46	4.8	0.92
BDE153	0.29	0.11	0.062	0.13	0.17	0.13	0.071	0.098	2.2	0.64
BDE183	0.16	0.27	0.29	0.30	0.27	0.48	0.20	0.61	2.3	1.3
BDE209	51	19	16	18	8.2	83	38	18	530	180
BTBPE	0.89	1.1	0.81	1.8	1.2	1.6	0.33	0.60	22	3.6
BEH-TEBP	2.6	6.2	1.8	2.3	1.8	2.6	3.7	1.7	5.7	5.9
DBDPE	59	26	39	69	24	32	25	24	210	64
α-HBCDD	10	7.5	1.2	5.4	0.81	6.5	1.9	5.7	8.7	7.8
β-HBCDD	2.2	0.77	0.75	1.3	0.33	1.7	0.50	1.2	2.7	0.88
γ-HBCDD	3.8	1.8	0.75	2.0	0.36	1.7	1.7	1.3	10	14

Table S8. Average/median estimates (upper-bound estimates in parentheses) of occupational exposure to BFRs via dust ingestion: comparisons between e-waste recycling and other occupations (ng/kg bw/day)

Occupation	Country	Year	BDE-209	ΣPBDEs [a]	DBDPE	HBCDD
formal e-waste recycling workers (this study)	UK	2022	0.49-0.58 (2.9-3.5)	0.50-0.59 (3.0-3.6)	0.38-0.45 (3.6-4.2)	0.047-0.055 (0.30-0.36)
formal e-waste recycling workers (Zhou et al., 2022)	China	2020	4.3 (24)	4.4 (25)	n.a. [b]	0.0099 (0.18)
formal e-waste recycling workers (Nguyen et al., 2019)	Canada	2017	28-33 (53-61)	29-33 (54-63)	n.a. [b]	n.a. [b]
informal e-waste recycling workers (Zheng et al., 2015)	China	2013	n.a. [b]	1.1-24 (2.8-60)	0.73-20 (1.83-51)	n.a. [b]
informal e-waste recycling workers (Xu et al., 2015)	China	2013	18 (44)	23 (60)	2.7 (9.4)	n.a. [b]
informal e-waste recycling workers (Anh et al., 2017)	Vietnam	2015	n.a. [b]	1.3 (3.3)	n.a. [b]	n.a. [b]
informal e-waste recycling workers (Wannomai et al., 2020)	Vietnam	2015	56	65	21	n.a. [b]
office workers (Sun et al., 2018)	China	2014	n.a. [b]	n.a. [b]	0.40	0.026
office workers (Tao et al., 2016)	UK	2015	1.2 (2.9)	1.3 (3.4)	0.061 (0.15)	0.42 (1.1)
college students (Sun et al., 2018)	China	2014	n.a. [b]	n.a. [b]	0.31	0.11
college students (Li et al., 2018)	China	2016	12	13	n.a. [b]	n.a. [b]

[a] including BDE-209.

[b] data not available.

Table S9. Reference dose (RfD) values (ng/kg bw/day) for BFRs

BFRs	RfD	References
BTBPE	243,000	(Ali et al., 2012)
EH-TBB	20,000	(Ali et al., 2012)
BEH-TEBP	20,000	(Ali et al., 2012)
DBDPE	333,333	(Ali et al., 2012)
BDE-209	7,000 [a]	(US EPA, 2017)
Octa-BDE	3,000	(US EPA, 2017)
Penta-BDE	2,000	(US EPA, 2017)
BDE-47	100	(US EPA, 2017)
BDE-99	100	(US EPA, 2017)
BDE-153	200	(US EPA, 2017)
HBCDD	200,000	(Pakalin et al., 2007)

[a] For decaBDE-209, EPA has assigned an oral slope factor for carcinogenic risk of 700 $(ng/kg\ bw/day)^{-1}$ (EPA IRIS 2008).

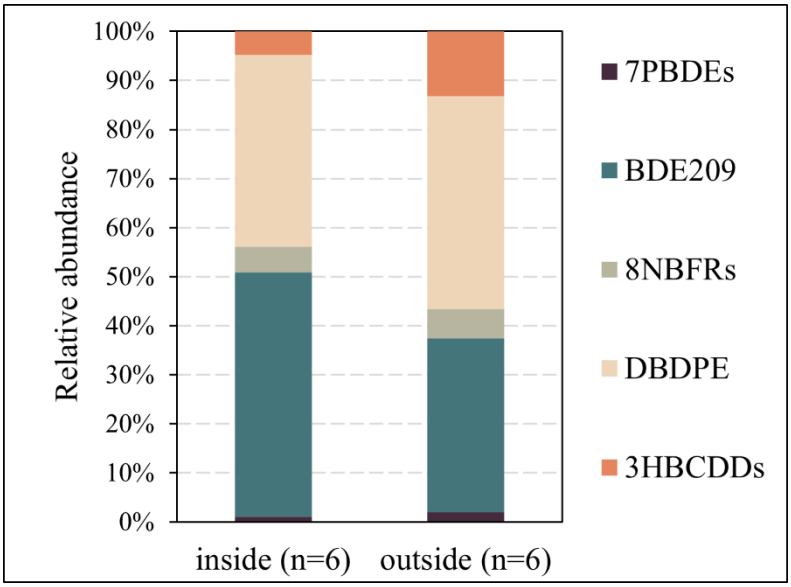


Fig. S1 Relative abundance of BFRs in dust inside and outside Facility #1. Average concentrations of BFRs in dust were used. 7PBDEs are sum of BDE-28, -47, -99, -100, -153, -154, and -183; 8NBFRs are sum of PBBz, PBT, PBEB, DPTE, HBBz, EH-TBB, BTBPE, and BEH-TEBP; 3HBCDDs are sum of α-, β-, and γ-HBCDD.

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