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Review article

A meta-analysis of recent data on UK environmental levels of POP-BFRs in an international context: Temporal trends and an environmental budget

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ABSTRACT

This study collates and synthesises UK data on environmental levels of POP-BFRs published between 1999 and March 2015. Target POP-BFRs are: the polybrominated diphenyl ether (PBDE) formulations Penta-BDE, Octa-BDE, and Deca-BDE (the latter as a candidate Stockholm Convention POP), as well as hexabromocyclododecane (HBCDD). Environmental compartments covered include: sediments (freshwater and marine), atmospheric deposition (both measured directly and inferred from sediment core data), soil, herbage, outdoor air, indoor air, indoor dust, freshwater (rivers and lakes), human tissues (blood serum and milk), wildlife, and the human diet. Temporal trends in contamination were examined for evidence of environmental responses to regulatory and voluntary actions banning/restricting the manufacture and use of POP-BFRs. Good evidence exists that – with some exceptions – concentrations of Penta-BDE congeners like BDEs-47 and 99 have responded well to the use restrictions introduced in the mid-2000s. However, it appears that human body burdens of these contaminants do not appear to have responded in a similar way, as levels in UK human milk in 2010–2012, are not discernibly different to those reported in 2002–03. The evidence for HBCDD and BDEs-183 and 209 is less abundant, but signs exist that absolute concentrations of BDE-183 are falling in the UK environment. With respect to BDE-209, evidence from analysis of lake sediment core and UK diet samples, suggests that levels have yet to respond discernibly to the more recent curbs on manufacture and use of Deca-BDE. The limited evidence for HBCDD is strongly consistent with a declining trend in environmental contamination with this chemical. Broadly, examination of the UK database in an international context, suggests UK levels are generally within the range of those found in other industrialised countries. Interestingly, while UK concentrations of BDE-209 in abiotic matrices such as indoor dust, are at the high end of those reported globally; concentrations in UK human milk are amongst the lowest reported to date. This suggests that the bioavailability of BDE-209 from indoor dust is likely very low. An environmental budget was estimated for the UK burden of POP-BFRs. As with previous comparable exercises for polychlorinated biphenyls (PCBs) and chlorinated dioxins, the majority (>90%) of the UK burden of POP-BFRs resides in soil. Moreover, the POP-BFR burden identifiable as present in the UK environment is much lower than data on production and use of POP-BFRs in Europe. This may be explained by POP-BFRs: (a) undergoing environmental transport away from the UK; (b) undergoing environmental degradation; (c) remaining in use; and (d) entering the waste stream. While the UK database appears relatively strong for some environmental compartments and POP-BFRs – e.g. BDEs-47 and -99 are well-characterised in the human diet, indoor air/dust, and human milk – substantial gaps exist for BDE-209 and HBCDD in air (indoor and outdoor), herbage, and soil.

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Contents

1. Introduction

Since the turn of the current century, a substantial body of evidence has been generated concerning environmental contamination with and human exposure to brominated flame retardants (BFRs), such as polybrominated diphenyl ethers (PBDEs) and hexabromocyclododecane (HBCDD). These chemicals have been used extensively worldwide to impart flame retardancy to consumer materials like electrical electronic equipment, textiles, furniture and building insulation foams [51]. Evidence about environmental and human contamination with these chemicals has been generated in response to concerns about the adverse environmental and human health impacts of these chemicals. Currently, those PBDEs present in the Penta-BDE and Octa-BDE commercial formulations, as well as HBCDD have been listed under the United Nations Environment Programme's Stockholm Convention on Persistent Organic Pollutants (POPs). Moreover, the Deca-BDE commercial product is currently being considered for listing as a POP under the same convention [120]. For the purposes of this study, we henceforth refer to these chemicals as POP-BFRs.

Measurements of POP-BFRs have been made in many countries, with a substantial quantity of such monitoring conducted in the UK. However, until now there has been no systematic attempt to collate and critically review the evidence for the UK environment. Consequently, this study collates and reviews available data for the UK environment relating to concentrations of recognised and candidate POP-BFRs. The objectives of this study are to:

(a) Place UK environmental levels in an international context.
(b) Evaluate the efficacy of recent legislative and voluntary actions in bringing about a reduction in UK environmental levels. This will be achieved by examining temporal trends in such levels.
(c) Construct an environmental budget for the UK. This allows comparison of the mass of POP-BFRs present in the contemporary environment with estimates of manufacture and use, as well as informing our understanding of the long-term environmental fate of these (and related) chemicals by facilitating estimation of their relative partitioning between different environmental compartments.

The following chemicals were included in this study:

- Those PBDE congeners present in the Penta-, Octa-, and Deca-BDE formulations.
- All diastereomers of HBCDD. With very few exceptions, reported data are for the α−, β−, and γ- diastereomers, although very occasionally data for the δ-HBCDD *meso* form are reported (e.g. Ref. [48].

As well as data on temporal trends, data on POP-BFR concentrations in the following environmental compartments are included:

- Sediments (freshwater and marine)
- Atmospheric deposition (both measured directly and inferred from sediment core data)
- Soil
- Herbage
- Outdoor Air
- Indoor Air
- Indoor Dust
- Freshwater (rivers and lakes)

- Human tissues (blood serum and milk)
- Wildlife
- Human diet

2. Methodology

Papers were sourced via searching databases such as Science Direct and those for specific journals such as *Environmental Science and Technology* using key search terms. In addition, papers identified in this way were checked for citations to other relevant studies, and later papers citing them.

To facilitate comparison across studies (where a range of different PBDE congeners are reported), data are reported in this study for BDEs-47 and -99 (as the principal constituents of the Penta-BDE formulation), BDE-183 (as the principal congener in Octa-BDE), and BDE-209 (as the main component of Deca-BDE) [70]. HBCDD concentrations are reported here as the sum of all diastereomers.

To be included in this study, data had to be reported in studies reported in the peer-reviewed literature between 1st January 1999 and 1st March 2015. Where in the judgement of the author, relevant data were reported in non-peer-reviewed outlets (e.g. conference proceedings), or were in review, these were also included. Studies that replicated data reported elsewhere (e.g. a conference paper later superseded by a peer-reviewed paper) were not considered.

3. Results

3.1. Concentrations of POP-BFRs in the UK environment

Concentrations of POP-BFRs in each of the targeted environmental compartments of UK origin are reported in this section. Illustrative pertinent data from other countries are included for comparison. The relevant papers are cited in each Table.

3.2. Sediments

Concentrations are summarised in Table 1. Overall, 9 relevant UK studies were identified. Of these, six report data for BDEs-47 and -99, one for BDE-183, two for BDE-209, and three for HBCDD. Substantial spatial variation in concentrations exists. For PBDEs, BDE-209 appears the predominant congener, followed by BDE-99, then BDE-47. There are insufficient data for BDE-183 to judge its relative abundance, though in the one study in which it was reported (in which BDEs −47 and −99 were not measured), the range of concentrations for BDE-183 were lower than for BDE-209, but similar to HBCDD.

3.3. Deposition

Data are summarised in Table 2. Overall, 2 relevant UK studies were identified. Of these, both report data for BDEs-47, 99, 183, and 209, while that of [133] also includes data for HBCDD. The study of [12] reports data (ng/m^2/month) for 47 samples of bulk atmospheric deposition at Lochnagar, Scotland. The second study reports depositional inputs accumulated between ~1950 and 2011–12 (ng/cm^2) measured using dated sediment cores from 7 English lakes.

3.4. Soil

Data are provided as Table 3. A total of 7 pertinent UK studies were identified. Of these, 4 report congener-specific data for BDEs-47 and 99, with 3 of these also reporting BDE-183 separately. Two additional studies report unspeciated data for a range of PBDEs including BDEs-47, 99, and 183. Only one study reports concentrations for BDE-209, with a further single study reporting concentrations of HBCDD in UK soil – in both cases, neither study is yet reported in the peer-reviewed literature. As with sediment concentrations, substantial spatial variation exists, with concentrations spanning 2–3 orders of magnitude. For BDEs-47, and -99, both the range and the average concentrations reported display consistency between different studies. For BDE-183, both the average and the range of concentrations reported in the 3 relevant studies are generally consistent.

3.5. Vegetation

Just 2 studies report concentrations of POP-BFRs in herbage, with neither reporting data for BDE-209 or HBCDD. The available data are listed in Table 4. While a very limited comparison, the concentrations appear consistent between the two studies.

3.6. Outdoor air

The available data relating to concentrations of POP-BFRs in UK outdoor air comprises 12 studies with data listed in Table 5. Eleven studies report data for BDEs-47 and 99, four for BDE-183, and two each for BDE-209 and HBCDD. Data for BDEs-47 and 99 are consistent between the various studies, with reported concentrations in the low to low tens of pg/m^3. Likewise, albeit based on a smaller database, concentrations of BDE-183 vary consistently between non-detectable (sub-pg/m^3) to tens of pg/m^3 in a few samples. The very few data relating to BDE-209, suggests it is the predominant congener in UK outdoor air, ranging from not detectable to 1500 pg/m^3. The limited data on HBCDD essentially consists of two small sampling campaigns both conducted at the same monitoring station on the University of Birmingham campus 2 years apart. The data are thus unsurprisingly similar in magnitude and reveal average HBCDD concentrations to be a little lower than those of BDE-209, but ~10 times higher than those of BDEs-47, 99, and 183. There is also a report of HBCDD in a single sample of air taken from just inside the perimeter of an e-waste handling facility in the UK. The concentration in this sample was ~1000 times higher than the average detected in Birmingham. This sample suggests further study of the potential for HBCDD emissions from e-waste handling facilities is warranted.

3.7. Indoor air

Table 6 gives the available UK data related to POP-BFR concentrations in indoor air. There are 3 studies that report BDEs-47 and -99, of which one reports concentrations of BDEs-183 and -209 also. The latter study also provides data for HBCDD, with the database for HBCDD further augmented by a further study. All of these studies relate to the West Midlands, but cover offices, homes, cars, and public microenvironments. In general, the data for indoor air reveal concentrations of POP-BFRs to exceed those in outdoor air by an order of magnitude. As with outdoor air, the relative abundance of individual POP-BFRs in UK indoor air are: BDE-209 > HBCDD > BDE-47 ~ BDE-99>BDE-183.

3.8. Indoor dust

UK data relating to concentrations of POP-BFRs in indoor dust are given in Table 7. There are four studies of note that report concentrations of BDEs-47, 99, 183, and 209 in UK homes, cars, offices, and primary school/nursery classrooms. While most of the samples were taken in the West Midlands, a few samples originated from Hampshire and Newcastle-upon-Tyne in south and

Table 1
Summary of Concentrations of POP-BFRs in UK River and Lake Sediments, with selected international data for comparison.

BDE-47	BDE-99	BDE-183	BDE-209	HBCDD	Reference	Comments
1.35	1.20	–	10.20	–	[7]	R. Tees, median, μg/kg
4.77	7.62	–	109.23	–	[7]	R. Tees, average, μg/kg
<0.2–32.2	<0.2–38	–	<0.2–1400	–	[7]	R. Tees, range, μg/kg
3.6	4.7	–	–	–	[8]	Median, Rivers Tweed, Nith, Avonmouth, Tees, Skerne, Calder, Ouse, Ribble etc. μg/kg
40.42	74.51	–	–	–	[8]	Average, Rivers Tweed, Nith, Avonmouth, Tees, Skerne, Calder, Ouse, Ribble etc. μg/kg
<0.3–368	<0.6–898	–	–	–	[8]	Range, River Tweed, Nith, Avonmouth, Tees, Skerne, Calder, Ouse, Ribble etc. μg/kg
–	–	BDL-32.15	0.304–1333	BDL-47.2	[13]	Range, μg/kg, various UK locations (n = 42), sum of BDEs, 17,28,47,66,85,99,100,138,153,154,183
–	–	–	–	2.21	[48]	Average, μg/kg dw, various English lakes, (n = 9), 2008
–	–	–	–	0.88–4.8	[48]	Range, μg/kg dw, various English lakes, (n = 9), 2008
–	–	–	–	1093	[88]	Average, μg/kg dw, various UK rivers, n = 9, 2000
–	–	–	–	<2.4–9750	[88]	Range, μg/kg dw, various UK rivers, n = 9, 2000
<0.4	0.43	–	–	–	[99]	Median, 10 UK lakes, μg/kg dw
<0.4–1.2	<0.4–2.4	–	–	–	[99]	Range, 10 UK lakes, μg/kg dw
BDL-0.25		–	–	–	[102]	Range, Marine sediments from 3 Scottish aquaculture areas, μg/kg dw, n = 43, sum BDEs 28,47,66,99,100,85,154,153,190
0.23		–	–	–	[102]	Median, Marine sediments from 3 Scottish aquaculture areas, μg/kg dw, n = 43, sum BDEs 28,47,66,99,100,85,154,153,190
BDL-0.16			–	–	[128]	Range of averages, Various Scottish sea areas, n = 248, samples collected 1999–2009, μg/kg dw, sum BDEs 28, 47, 66, 85, 99, 100, 153, 154 and 183
BDL-8.05			–	–	[128]	Range of averages, River Clyde, n = 69, samples collected 1999–2009, μg/kg dw, sum BDEs 28, 47, 66, 85, 99, 100, 153, 154 and 183
0.16–6.44			1.63–116	0.42–7.9	[131]	Range, 7 English lakes, top layer, sampled 2011, μg/kg dw
1.89			27	2.5	[131]	Average, 7 English lakes, top layer, sampled 2011, μg/kg dw
Non-UK						
–	–	2.2–219		BDL-15.1	[94]	Range, Italian river sediments sampled 2011–2012 (n = 13 from 2 rivers) μg/kg dw, sum hepta-Deca-BDE
–	–	65		7.75	[94]	Average, Italian river sediments sampled 2011–2012 (n = 13 from 2 rivers) μg/kg dw, sum hepta-Deca-BDE
–	–	7.1–28		2.6–5.1	[94]	Range, Lake Maggiore, surficial sediments (n = 6) μg/kg dw, sum hepta-Deca-BDE
–	–	14.3		3.95	[94]	Average, Lake Maggiore, surficial sediments (n = 6) μg/kg dw, sum hepta-Deca-BDE
–	–	–	0.87–106	0.04–3.1	[134]	Range, Great Lakes, 2007, μg/kg dw
–	–	–	–	7.5–2057	[85]	Range, Rivers Yodo (populated area) & Kuzuryu (source-impacted), Japan, 2008, μg/kg dw
<0.03–0.70	<0.03–0.90	–	<0.10	<0.12–5.3	[67]	Range, Cork Harbour, Ireland, 2002, μg/kg dw
1.02–3.97			21.5–95.6	–	[112]	Range, Lakes Huron and Michigan, 2002, μg/kg dw, sum of PBDEs exc. BDE-209
–	–	–	–	1.35–634	[138]	Range, n = 51, river and harbour sediments, China, 2010, μg/kg dw
–	–	–	–	31.00	[138]	Average, n = 51, river and harbour sediments, China, 2010, μg/kg dw

northeast England respectively. No obvious regional differences were apparent. Of these studies, two also reported data for HBCDD in dust from classrooms, as well as car boots and cabins. These data for HBCDD are augmented by two additional studies that report concentrations in dust from UK homes, car cabins, offices, and public microenvironments. The relative abundance of the individual POP-BFRs is broadly similar to that observed for indoor air, but with a shift towards greater relative abundance of BDE-209 and HBCDD, such that the order of relative abundance is: BDE-209 > HBCDD > BDE-99 ~ BDE-47 > BDE-183. Very striking is the exceptionally wide range of concentrations for BDE-209 in particular for which concentrations range from below detection

Table 2
Summary of UK Depositional Fluxes of POP-BFRs, with selected international data for comparison.

BDE-47	BDE-99	BDE-183	BDE-209	HBCDD	Reference	Comments
15.9	15	5.38	119	–	[12]	Average, Lochnagar, Scotland (n = 47), ng/m^2/month
0.07–77.7	BDL-95.7	BDL-19.3	BDL-318	–	[12]	Range, Lochnagar, Scotland (n = 47), ng/m^2/month
3.21		1.53	60.1	9.38	[133]	Average inventory (ng/cm^2) derived from input fluxes measured in sediment cores dating back to ~1950 sampled in 2011–12 from 7 English lakes
Non-UK						
2.27–89.7	BDL-29.7	BDL-16.8	BDL-704	–	[12]	Range, 3 mountain lakes in Austria, Spain, Slovakia (n = 141), ng/m^2/month

Table 3
Summary of Concentrations of POP-BFRs in UK Soil, with selected international data for comparison.

BDE-47	BDE-99	BDE-183	BDE-209	HBCDD	Reference	Comments
210–3230			–	–	[71]	Range, n = 10, ng/kg dw, River Trent, sum BDEs 28, 47, 99, 100, 153, 154, and 183
844			–	–	[71]	Average, n = 10, ng/kg dw, River Trent, sum BDEs 28, 47, 99, 100, 153, 154, and 183
25–940	3.4–1850	–	–	–	[44]	Range, West Midlands, England, 10 sites, 12 monthly samples at each, ng/kg dw
167	339	–	–	–	[44]	Average of site averages, West Midlands, England, 10 sites, 12 monthly samples at each, ng/kg dw
–	–	–	–	0.07–424	[49]	Range, n = 24 UK locations, μgk/g dw
–	–	–	–	0.77	[49]	Average, n = 24 UK locations, μg/kg dw
7–1400	78–3200	10–7000	–	–	[55]	Range, 1998, 42 UK rural/remote locations, ng/kg dw, 0–5 cm depth
275	590	48	–	–	[55]	Average of medians for woodland and grassland, 1998, 42 UK rural/remote locations, ng/kg dw, 0–5 cm depth
5–4900	20–7600	25–4300	–	–	[98]	Range, Scotland, ng/kg dw, n = 183, sampled 2007–09, sum BDEs 28,47,99,100,153,154,183
209	315	257	–	–	[98]	Average of averages for 3 years/areas, Scotland, ng/kg dw, n = 183, sampled 2007–09
20–1820		–	–	–	[109]	Range, 2008, 30 UK rural/remote locations, ng/kg dw, 0–5 cm depth
450		–	–	–	[109]	Average, 2008, 30 UK rural/remote locations, ng/kg dw, 0–5 cm depth
210	213	75	1898	–	[27]	Average, 8 sites West Midlands, England, 2011, ng/kg dw
33–440	57–420	<4.5–280	140–4100	–	[27]	Range, 8 sites West Midlands, England, 2011, ng/kg dw
Non-UK						
–	–	–	–	1.7–5.6	[135]	Range, n = 3, Guangzhou, China, μg/kg dw
–	–	–	–	0.023 ± 0.019	[86]	Average ± standard deviation, Chongming Island, China, n = 22), μg/kg dw
–	–	–	–	0.18	[22]	Median, Belgium, n = 20 μg/kg dw
2.9–1450		–	–	–	[109]	Range, 2008, 40 Norway rural/remote locations, ng/kg dw, 0–5 cm depth
210		–	–	–	[109]	Average, 2008, 40 Norway rural/remote locations, ng/kg dw, 0–5 cm depth
21–280	25–65	BDL	BDL-1000	–	[119]	Range, n = 9, surface soil layer, Bratislava, ng/kg dw
91	35	all samples < BDL	only 2 samples > BDL	–	[119]	Average, n = 9, surface soil layer, Bratislava, ng/kg dw
10–6300	10–5800	–	<40–41,000	–	[136]	Range, n = 26, soil, US, ng/kg dw
659	595	–	5358	–	[136]	Average, n = 26, soil, US, ng/kg dw

limits to 2,600,000 ng/g (0.26%). Concentrations of HBCDD also vary widely over 3 orders of magnitude, up to 140,000 ng/g.

3.9. Freshwater

Three studies have reported concentrations of POP-BFRs in UK freshwater. These are summarised in Table 8. The first reports concentrations at 13 points on the River Aire in northern England. Concentrations of BDEs-47, 99, and 183 were below detection limits in all samples. However, this study provides the only published data to the author's knowledge on concentrations of BDE-209 in UK freshwater. The other two studies both report concentrations of HBCDD as well as of the sum of tri-through hexa-BDE congeners (of which the major constituents were BDEs-47 and 99) detected in 9 English lakes. Based on this limited dataset, the relative abundance of POP-BFRs in UK freshwater is BDE-209>>HBCDD > BDEs-47, 99, and 183.

3.10. Human tissues

The available data on concentrations of POP-BFRs in samples of breast milk and blood from the UK population are summarised in Table 9. Of these, five report concentrations in milk only, one reports concentrations in blood serum only, while one reports data for both milk and blood. While there may be some differences in the relative partitioning of POP-BFRs between breast milk and blood serum, these are likely minor, and by expressing concentrations from all of these studies in μg/kg lipid weight, a reasonable comparison of concentrations across all studies may be achieved. Five studies report concentrations of BDEs- 47 and 99,

Table 4
Summary of concentrations of POP-BFRs in UK vegetation.

BDE-47	BDE-99	BDE-183	BDE-209	HBCDD	Reference	Comments
90–410			–	–	[71]	Range, n = 10, ng/kg dw, sum BDEs 28, 47, 99, 100, 153, 154, and 183
168			–	–	[71]	Average, n = 10, ng/kg dw, sum BDEs 28, 47, 99, 100, 153, 154, and 183
73.9	78.4	<12.2	–	–	[56]	Herbage, n = 1, archived from 2004, Rothamsted, England, ng/kg dw

Table 5
Summary of Concentrations of POP-BFRs in UK Outdoor Air, with selected international data for comparison.

BDE-47	BDE-99	BDE-183	BDE-209	HBCDD	Reference	Comments
–	–	–	–	34–40	[5]	Range, Birmingham, n = 5, pg/m^3
–	–	–	–	37	[5]	Average, Birmingham, n = 5, pg/m^3
0.12–34.3	0.11–9.18	BDL-2.2	–	–	[15]	Range, Hazelrigg, High Muffles, London, Manchester, n = 64, 1999–2010, pg/m^3
4.62	2.10	0.35	–	–	[15]	Average, Hazelrigg, High Muffles, London, Manchester, n = 64, 1999–2010, pg/m^3
0.33	0.56	–	–	–	[40]	Average, 2 sites in N. England, 2005, pg/m^3
0.93–36	0.24–19.9	–	–	–	[44]	Range, West Midlands, 10 sites, 12 monthly samples at each, pg/m^3, 2004–05
6.0	1.9	–	–	–	[44]	Average of site averages, West Midlands, 10 sites, 12 monthly samples at each, pg/m^3, 2004–05
<0.95–13.5	<1.47–20.7	–	–	–	[58]	Range, various UK locations, 2002, n = 9, pg/m^3
4.24	6.35	–	–	–	[58]	Average, various UK locations, 2002, n = 9, pg/m^3
0.3–1.0	0.3–0.8	–	–	–	[59]	Range, TWA, 2000–02, 5 UK locations (n = 5), pg/m^3
0.66	0.54	–	–	–	[59]	Average of TWAs, 2000–02, 5 UK locations (n = 5), pg/m^3
0.72–15	0.53–15	–	–	–	[82]	Range, Hazelrigg and Chilton, n = 36 at each, 2001, pg/m^3
3.9	3.1	–	–	–	[82]	Average, Hazelrigg and Chilton, n = 36 at each, 2001, pg/m^3
1.3–4.4	0.8–2.0	0.32–1.3	–	–	[20]	Range, n = 8, 1 location, April–June 2006, pg/m^3
3.1	1.4	0.58	–	–	[20]	Average, n = 8, 1 location, April–June 2006, pg/m^3
BDL-1.3	BDL-1.8	BDL-92	BDL-100	–	[130]	Range, Hazelrigg, n = 28, 2004, particle phase only, pg/m^3
0.14	0.31	BDL* (median)	20	–	[130]	Average, Hazelrigg, n = 28, 2004, particle phase only, pg/m^3
–	–	–	–	34–130	[49]	Range, Birmingham, n = 12, 2009, pg/m^3
–	–	–	–	47	[49]	Median, Birmingham, n = 12, 2009, pg/pg/m^3
–	–	–	–	22,000	[49]	Single sample on perimeter of UK e-waste handling facility, 2009, pg/m^3
3.4–18	1.6–7.5	–	–	–	[45]	Range, Birmingham, n = 6, 2002–03, pg/m^3
9.4	5	–	–	–	[45]	Average, Birmingham, n = 6, 2002–03, pg/m^3
<0.3–31	<0.5–43	<1.4–57	<2.2–1500	–	[27]	Range, West Midlands, 8 sites, 6 monthly samples at each, pg/m^3, 2011–12
4.6	3.8	3.4	148	–	[27]	Average, West Midlands, 8 sites, 6 monthly samples at each, pg/m^3, 2011–12
Non-UK						
4.8–66				–	[123]	Range, 2005–2006, n = 60, 5 Great Lakes locations, pg/m^3
3.2–19.8	4.5–15.5	–	1.7–34.3	–	[84]	Range of averages, n~1000, 2005–2011, 5 Great Lakes sites, pg/m^3
2.7–41	1.2–13	0.18–0.57	0.2–65	–	[61]	Range, US sites, n = 10, 2002–03, pg/m^3
–	–	–	up to 960	0.2–9.6 (1.8)	[60]	Range (average of site averages), 5 US sites, n = 60 at each site, pg/m^3
–	–	–	–	76 & 610	[97]	Stockholm, 2000–01, n = 2, pg/m^3
0.2–5.6	0.2–4.3	–	1.1–75	–	[116]	Range, n = 19, Baltic Sea Island, 2001, pg/m^3
1.8	1.2	–	6.1	–	[116]	Median, n = 19, Baltic Sea Island, 2001, pg/m^3
0.53	0.27	–	0.14	0.066	[92]	Geometric Mean, Stockholm, 2012, n = 12, pg/m3

with four of these also reporting BDE-209 and BDE-183. Just two studies report concentrations of HBCDD – both in human milk. Concentrations of individual congeners vary across a range of typically an order of magnitude and up to two orders of magnitude for some congeners in some study populations. The relative abundance of POP-BFRs is: HBCDD > BDE-47>BDE-99>BDE-209>BDE-183.

3.11. Wildlife

By comparison with that available for other environmental compartments/matrices; the database relating to POP-BFRs in wildlife (both aquatic and terrestrial) is quite substantial, with concentrations of one or more POP-BFRs reported in 22 studies. More studies were identified, but in some instances it appeared that data reported were replicated elsewhere. Expert judgement was exercised to select the most relevant studies, which are summarised in Table 10. Data span a wide range of species including different fish (both freshwater and marine), cetaceans, shellfish, otters, seals, and birds, sampled over a period spanning the late 1990s to 2013. Seventeen studies report one or more of BDE-47 and 99, 9 report BDE-183, 6 report BDE-209, and 5 report data for HBCDD. While there have been no studies that have measured all of our target POP-BFRs in the same samples, inspection of the database as a whole, suggests the relative abundance of POP-BFRs in UK wildlife is broadly: HBCDD ~ BDE-47 > BDE-99 > BDE-183 ~ BDE-209. However, given no studies have reported concentrations of all our target POP-BFRs in the same samples, coupled with the fact that comparisons are made across different species, tissue type (e.g. liver c.f. blubber c.f. eggs), and different sampling dates, this estimate of relative abundance carries substantial uncertainty. For example, while HBCDD levels in freshwater fish appear similar to those of Penta-BDE congeners, HBCDD concentrations are substantially lower than those of the sum of PBDEs (excluding BDE-209) in deep water fish.

3.12. Human dietary exposure

The data on human foodstuffs consumed by the UK population are summarised in Table 11. Eleven studies were identified that reported relevant data in mainly peer-reviewed outlets. The data summarised, span studies reporting typical adult intakes based on analysis of foods included in the total diet study projects from various years between 1992 and 2012, to those reporting concentrations in individual foodstuff categories like fish, shellfish, milk, and duck eggs. All studies report concentrations of BDEs-47 and -99, with six reporting data for BDE-183 and 209. Only one study – of concentrations in shellfish – appears in the peer-reviewed literature relating to the presence of HBCDD in the UK diet. However, this is augmented significantly by the FSA's

Table 6
Summary of Concentrations of POP-BFRs in UK Indoor Air, with selected international data for comparison.

BDE-47	BDE-99	BDE-183	BDE-209	HBCDD	Reference	Comments
58–7140	9.0–6510	–	–	–	[45]	Range, workplace, n = 10, pg/m^3
1670	852	–	–	–	[45]	Average, workplace, n = 10, pg/m^3
45–1330	8.7–209	–	–	–	[45]	Range, homes, n = 7, pg/m^3
424	70	–	–	–	[45]	Average, homes, n = 7, pg/m^3
7–671	8–588	<0.4–171	200–4000	70–745	[2]	Range, Car cabins, n = 20, pg/m^3
136	128	32	1700	367	[2]	Average, Car cabins, n = 20, pg/m^3
16–419	9–394	<0.4–97	90–3700	161–871	[2]	Range, Car boots, n = 19, pg/m^3
126	112	28	1200	427	[2]	Average, Car boots, n = 19, pg/m^3
–	–	–	–	67–1300	[5]	Range, homes, n = 33, pg/m^3
–	–	–	–	250	[5]	Average, homes, n = 33, pg/m^3
–	–	–	–	70–460	[5]	Range, offices, n = 25, pg/m^3
–	–	–	–	180	[5]	Average, offices, n = 25, pg/m^3
–	–	–	–	17–32	[5]	Range, public microenvironments, n = 4, pg/m^3
–	–	–	–	26	[5]	Average, public microenvironments, n = 4, pg/m^3
1.9–107	BDL-80	–	–	–	[43]	Range, homes, n = 31, pg/m^3
18.4	12.5	–	–	–	[43]	Average, homes, n = 31, pg/m^3
4.0–570	3.9–630	–	–	–	[43]	Range, offices, n = 33, pg/m^3
77	59	–	–	–	[43]	Average, offices, n = 33, pg/m^3
2.9–4700	BDL-2300	–	–	–	[43]	Range, Car cabins, n = 25, Birmingham, pg/m^3
380	170	–	–	–	[43]	Average, Car cabins, n = 25, Birmingham, pg/m^3
10.3–57	10.3–43	–	–	–	[43]	Range, public microenvironments, n = 3, pg/m^3
26	21	–	–	–	[43]	Average, public microenvironments, n = 3, pg/m^3
Non-UK						
2500	760	–	–	–	[14]	Average, 12 US homes, pg/m^3
160	42	–	–	–	[129]	Average, Ottawa, n = 74, homes, 2002–03, pg/m^3
9.1	4.4	0.2	–	–	[39]	Average, Kuwait, homes, n = 46, 2004, pg/m^3
24	19	–	48	3.1	[92]	Geometric Mean, Stockholm, 2012, n = 13 (mix of homes, offices, stores, schools), pg/m^3

Table 7
Summary of Concentrations of POP-BFRs in UK Indoor Dust, with selected international data for comparison.

BDE-47	BDE-99	BDE-183	BDE-209	HBCDD	Reference	Comments
–	–	–	–	140–140,000	[5]	Range, homes, n = 45, ng/g
–	–	–	–	8300	[5]	Average, homes, n = 45, ng/g
–	–	–	–	90–6600	[5]	Range, offices, n = 28, ng/g
–	–	–	–	1600	[5]	Average, offices, n2 = 5, ng/g
–	–	–	–	190–69,000	[5]	Range, public microenvironments, n = 4, ng/g
–	–	–	–	19,000	[5]	Average, public microenvironments, n = 4, ng/g
–	–	–	–	2300–3200	[5]	Range, cars, n = 20, ng/g
–	–	–	–	220	[5]	Average, cars, n = 20, ng/g
–	–	–	–	330–141,000	[1]	Range, homes, n = 20, ng/g
–	–	–	–	10,402	[1]	Average, homes, n = 20, ng/g
–	–	–	–	280–4000	[1]	Range, offices, n = 21, ng/g
–	–	–	–	1756	[1]	Average, offices, n = 21, ng/g
–	–	–	–	194–55,800	[1]	Range, cars, n = 12, ng/g
–	–	–	–	18,483	[1]	Average, cars, n = 12, ng/g
28–3600	45–4200	<1–59	28,000–620,000	1580–23,700	[52]	Range, car cabins, n = 14, ng/g
501	619	11	264,758	9073	[52]	Average, car cabins, n = 14, ng/g
5.0–71	14–100	<1–11	180–11,000	200–3100	[52]	Range, car boots, n = 14, ng/g
28	47	2.4	3744	1459	[52]	Average, car boots, n = 14, ng/g
1.2–58	2.8–180	BDL-550	BDL-2,200,000	–	[47]	Range, homes, n = 30, ng/g
15	36	71	260,000	–	[47]	Average, homes, n = 30, ng/g
2.6–380	4.2–490	BDL-24	620–280,000	–	[47]	Range, offices, n = 18, ng/g
67	120	11	30,000	–	[47]	Average, offices, n = 18, ng/g
19–7500	23–8000	BDL-67	12,000–2,600,000	–	[47]	Range, cars, n = 20, ng/g
720	990	19	410,000	–	[47]	Average, cars, n = 20, ng/g
1.6–120	1.1–270	<2–48	49–88,000	72–89,000	[50]	Range, classrooms, n = 43, ng/g
32	54	5.1	8500	8900	[50]	Average, classrooms, n = 43, ng/g
7–180	10–300	<3–18	910–54,000	–	[111]	Range, homes, n = 10, ng/g
22	28	5	10,000	–	[111]	Median, homes, n = 10, ng/g
Non-UK						
6400	4600	840	11,000	–	[14]	Average, 12 US homes, ng/g
5000	9300	–	15,000,000	–	[14]	Average, 12 US cars, ng/g
16	32	–	90	190	[92]	Geometric Mean, Homes, Stockholm, 2012, n = 27, ng/g
–	–	–	–	810	[6]	Average, n = 13, US homes, ng/g
–	–	–	–	670	[6]	Average, n = 8, Toronto homes, ng/g
–	–	–	–	4800	[41]	Average, n = 23, Belgian offices & homes, ng/g
810	1400	28	1600	–	[47]	Average, n = 20, Texas homes, ng/g
300	510	13	670	–	[47]	Average, n = 10, Canada homes, ng/g
36	87	–	–	–	[47]	Average, n = 20, New Zealand homes, ng/g
2.6			13.8	160	[103,104]	Average, n = 16, Belgian homes, ng/g, Sum BDEs 28, 47, 99, 100, 153, 154, 183

Table 8
Summary of Concentrations of POP-BFRs in UK River and Lake Water, with selected international data for comparison.

BDE-47	BDE-99	BDE-183	BDE-209	HBCDD	Reference	Comments
BDL	BDL	BDL	17–295	–	[23]	Range, R. Aire, (n = 13) ng/L
–	–	–	–	0.16	[48]	Average, 9 English Locations, n = 3 at each, ng/L
–	–	–	–	0.08–0.27	[48]	Average, 9 English Locations, n = 3 at each
0.009–0.171		–	–	–	[132]	Range for 9 English Freshwater lakes, n = 13 at each lake 2008–2012, ng/L, sum BDE-17, -28, –49, –47, –66, –100, –99, –85, –154, and –153.
0.06		–	–	–	[132]	Average of Site averages,9 English Freshwater lakes, n = 13 at each lake 2008–2012, ng/L, sum BDE-17, -28, –49, –47, –66, –100, –99, –85, –154, and –153.
Non-UK						
0.021			–	–	[114]	Average, Lake Michigan, 2004, sum BDEs, 47,99,100,153,154,183, ng/L
<0.003		–	–	–	[106]	Urban estuary, NE US, ng/L
0.017	0.0125	–	–	0.011	[74]	Average, L. Winnipeg, dissolved phase only, n = 3, 2004, ng/L
0.054	–	–	–	–	[93]	Average, San Francisco Bay, 2002–06, ng/L
0.036		–	–	–	[16]	Average, L. Thun, Switzerland, n = 5, ng/L
0.046–0.205	0.046–0.181	0.01–0.032	2.1–3.8	–	[68]	R.Précedelle, Paris, 2008, ng/L, n = 5

estimate of UK dietary exposure based on analysis of 2004 TDS samples, plus more recently, a report by FERA for the FSA based on analysis of 20 food group categories from the 2012 TDS study [35]. In this latter study, HBCDD was detected in 10 such food groups. A further FERA report on HBCDD concentrations in samples of 101 individual food items purchased in 2007 also exists [34]. This study reveals that while HBCDD is below detection limits in many foods of non-animal origin, it is present at relatively low levels in meat, offal, and eggs, and is present at comparatively high levels in 31 out of the 37 fish samples analysed.

3.13. Temporal trends

This review identified 13 studies that addressed temporal trends in contamination of the UK environment with POP-BFRs as their main or one of their principal objectives. These are summarised in Table 12. Matrices examined are: sediment cores (n = 2), bird eggs

Table 9
Summary of Concentrations of POP-BFRs in UK Human Tissues, with selected international data for comparison.

BDE-47	BDE-99	BDE-183	BDE-209	HBCDD	Reference	Comments
0.29–10.28	<0.12–3.75	<0.1–9.7	–	–	[29]	Range, Human milk, UK, 15 pooled samples, taken in 2002–03, μg/kg lw
3.13	1.08	<0.1	–	–	[29]	Average, Human milk, UK, 15 pooled samples, taken in 2002–03, μg/kg lw
–	–	–	–	1.0–22	[3]	Range, Human milk, Birmingham, 34 individual samples, taken in 2010, μg/kg lw
–	–	–	–	5.95	[3]	Average, Human milk, Birmingham, 34 individual samples, taken in 2010, μg/kg lw
0.17–14.65	<0.06–3.43	–	<0.06–0.92	–	[4]	Range, Human milk, Birmingham, 35 individual samples, taken in 2010, μg/kg lw
3.3	0.71	–	0.31	–	[4]	Average, Human milk, Birmingham, 35 individual samples, taken in 2010, μg/kg lw
0.32–13.1	0.12–3.74	0.02–0.23	<0.2–1.04	–	[19]	Human milk, Range, n = 6, Newcastle, 2011–12, μg/kg lw
1.92	0.88	0.05	0.52	–	[19]	Human milk, Median, n = 6, Newcastle, 2011–12, μg/kg lw
<0.36–4.87	<0.26–5.61	<0.03–0.33	<1.24–19.8	–	[19]	Blood serum, Range, n = 20, Newcastle, 2011–12, μg/kg lw
0.63	0.79	0.05	<LOD	–	[19]	Blood serum, Median, n = 20, Newcastle, 2011–12, μg/kg lw
0.64–7.42	0.03–5.12	–	<0.045–0.47	1.46–20.7	[53]	Range, Human milk, Birmingham, 12 individual monthly samples from 10 mothers, taken in 2010–11, μg/kg lw
2.97	1.58	–	0.14	6.54	[53]	Average, Human milk, Birmingham, 12 individual monthly samples from 10 mothers, taken in 2010–11, μg/kg lw
0.1–37	BDL-13	–	–	–	[64]	Range, Human milk, Lancaster & London, 54 individual samples, taken in 2001–03, μg/kg lw
2.7	0.8	–	–	–	[64]	Median, Human milk, Lancaster & London, 54 individual samples, taken in 2001–03, μg/kg lw
<0.3–180	<0.16–150	<0.14–1.8	<15–240	–	[117]	Range, Blood serum, 13 UK locations, 153 donors, taken in 2003, μg/kg lw
0.82	<0.16	0.3	<15	–	[117]	Median, Blood serum, 13 UK locations, 153 donors, taken in 2003, μg/kg lw
Non-UK						
0.95–21			–	<0.3–20	[118]	Range, Norway, n = 151 (85 for HBCDD),1993–2001, ng/g lw
3.7–580		–	–	0.4–19	[105]	Range, Canada, 2005, n = 34 (8 for HBCDD), ng/g lw
0.64–2.34	0.11–0.6	–	0.37–7.2	1.7–5.9	[96]	Range, Ireland, n = 11 pooled samples from 109 primaparas, ng/g lw
1.4–11.6			0.39–6.8	BDL-5	[11]	Range, France, n = 23, ng/g lw
–	–	–	–	3–188	[32]	Range, Spain, n = 33, 2006–07, ng/g lw

(n = 2), outdoor air (n = 3), food (n = 2), archived herbage (n = 1), harbour porpoise blubber (n = 2), and soil (n = 1). Of these, 11 report data for PBDEs, of which only 5 include BDE-209; while only 2 studies report on HBCDD. In addition, we have also considered evidence for such temporal trends from other studies where for example similar matrices have been analysed at different times. In interpreting temporal trend data, it is important to note that the comparatively rapid mixing time of the atmosphere, renders it particularly responsive to changes in contaminant inputs. Given this, one would expect concentrations of POP-BFRs to decline most rapidly in air in response to voluntary and legislative curbs on their use; followed by matrices from environmental compartments with the next fastest mixing times and that receive substantial contaminant atmospheric inputs such as herbage.

3.14. HBCDD

Temporal trends in HBCDD in the UK were examined by Ref. [79]. This study examined trends in concentrations of HBCDD in blubber of stranded harbour porpoise originating from UK

Table 10
Summary of Concentrations of POP-BFRs in UK Wildlife, with selected international data for comparison.

BDE-47	BDE-99	BDE-183	BDE-209	HBCDD	Reference	Comments
–	–	–	–	113.13	[48]	Average, various freshwater fish, n = 31, ng/g lw
–	–	–	–	14–290	[48]	Range, various freshwater fish, n = 31, ng/g lw
1.5–31	–	–	–	–	[63]	Range μg/kg ww, n = 38, various freshwater fish
309.33			–	–	[63]	Average μg/kg lw, n = 38, various freshwater fish, sum of BDEs 28,47,99,100,153,154
7.32	0.60	<0.64	<3.0	–	[66]	Average of medians from 14 sites, eels, various locations Scotland, μg/kg ww
<0.58–96	<0.52–5.4	–	<3–10	–	[66]	Range, n = 14, eels, various locations Scotland, μg/kg ww
–	–	–	–	769	[88]	Sea star, Tees Estuary, 2001, μg/kg LW
–	–	–	–	384, 1018	[88]	Harbour porpoise blubber (n = 2), Tyne/Tees, Humber (1998), μg/kg LW
–	–	–	–	1086, 1319	[88]	Cormorant liver (n = 2), S.England (2000), Wales (1999), μg/kg LW
16.74	0.1	<0.01	0.02	–	[100]	Median various fish species, various UK locations, Phase 1, n = 17, μg/kg ww
0.07–103.7	<0.01–6.13	<0.01–0.03	0.01–0.15	–	[100]	Range various fish species, various UK locations, Phase 1, n = 17, μg/kg ww
2.35	0.03	<0.01	0.06	–	[100]	Median various fish species, various UK locations, Phase 2, n = 29, μg/kg ww
0.04–27.32	<0.01–2.97	<0.01–0.09	<0.01–0.22	–	[100]	Range various fish species, various UK locations, Phase 2, n = 29, μg/kg ww
11.7			–	<0.3	[101]	Average, Black dogfish, Scotland, μg/kg lw, sum 17 BDEs exc 209
34.5			–	<0.3	[101]	Average, Black scabbard, Scotland, μg/kg lw, sum 17 BDEs exc 209
50.5			–	<0.3	[101]	Average, Roundnose Grenadier, Scotland, μg/kg lw, sum 17 BDEs exc 209
1.69–69.3	0.51–14.57	–	–	–	[10]	Range, cormorant liver (n = 20), various locations in England, μg/kg WW
13.46	3.58	–	–	–	[10]	Average, cormorant liver (n = 20), various locations in England, μg/kg WW
368 (23.7)	945 (56.7)	63.8 (3.66)	–	–	[26]	Geometric mean, Sparrowhawk livers, 1998–2009, England and Wales, n = 59, μg/kg lw (ww in parentheses)
22.1–14,400	44.4–28,700	1.36–2100	–	–	[26]	Range, Sparrowhawk livers, 1998–2009, England and Wales, n = 59, μg/kg lw
3.3–1200	1.5–100	–	–	–	[65]	Seal pup blubber, range, μg/kg lw, n = 110, Farne Islands, 1998–99
210	16	–	–	–	[65]	Seal pup blubber, geometric mean, μg/kg lw, n = 110, Farne Islands, 1998–99
1.1–76	<0.2–15	–	–	–	[75]	Range, Cormorant livers, n = 47, μg/kg ww, various locations, England & Wales
9.83	2.99	–	–	–	[75]	Average, Cormorant livers, n = 47, μg/kg ww, various locations, England & Wales
<5–6110	<5–1287	–	–	–	[75]	Range, Harbour porpoise blubber, n = 60, μg/kg ww, various locations, England & Wales
1158.41	316.70	–	–	–	[75]	Average, Harbour porpoise blubber, n = 60, μg/kg ww, various locations, England & Wales
<5–9500	<5–3700	<5–<50	–	–	[78]	Range, blubber, various marine mammals, various UK locations, n = 34, μg/kg ww
1269.91	330.71	BDL	–	–	[78]	Average, blubber, various marine mammals, various UK locations, n = 34, μg/kg ww
17.8–488	3.78–68.1	0.63–2.0	BDL	–	[81]	Range, harbour porpoise blubber, n = 21, μg/kg ww, UK, 2008
104.47	19.50	0.98	BDL	–	[81]	Average, harbour porpoise blubber, n = 21, μg/kg ww, UK, 2008
–	–	–	<1.5–412	–	[83]	Range, eggs, liver & muscle, various UK predatory bird species, n = 103. μg/kg lw
–	–	–	<1.8–108	8.9–1150	[83]	Range, peregrine falcon eggs, UK, n = 12, μg/kg lw
–	–	–	–	439	[83]	Average, peregrine falcon eggs, UK, n = 12, μg/kg lw
–	–	–	13–275	8.4–2360	[83]	Range, sparrowhawk muscle, UK, n = 8, μg/kg lw

(continued on next page)

Table 10 (*continued*)

BDE-47	BDE-99	BDE-183	BDE-209	HBCDD	Reference	Comments
–	–	–	101	984	[83]	Average, sparrowhawk muscle, UK, n = 8, μg/kg lw
57–14,052			–	–	[89]	Range, European Dipper Eggs, England and Wales, n = 69, μg/kg lw, sum BDEs 30,32,17,28,35,37,51,49,71,47,66,77,100, 119,99,118,85,126,154,153,138,183,128
772			–	–	[89]	Geometric mean, European Dipper Eggs, England and Wales, n = 69, μg/kg lw, sum BDEs 30,32,17,28,35,37, 51,49,71,47,66,77,100,119,99,118,85,126,154,153,138, 183,128
<10–35,000	<1.5–2600	–	<8.5–6800	–	[95]	Range, otter livers, n = 129, England & Wales, μg/kg lw, 1995–2006
2200	51	–	170	–	[95]	Average, otter livers, n = 129, England & Wales, μg/kg lw, 1995–2006
1100	16	–	62	–	[95]	Median, otter livers, n = 129, England & Wales, μg/kg lw, 1995–2006
2.17–465	BDL-37.5	BDL-29.8	BDL-35.5	–	[124]	Range, otter livers, n = 64 (47 only for BDE-99), 2010–11, μg/kg ww
32.4	1.31	–	–	–	[124]	Geometric mean, otter livers, n = 64 (47 only for BDE-99), 2010–11, μg/kg ww, only 3 and 2 detectable values for BDE-183 & 209 respectively
BDL-3.71			–	–	[126]	Range, mussels, Scotland, μg/kg ww, n = 56, BDEs 28, 47, 66, 85, 99, 100, 153, 154, 183,
13–5780	12–1480	–	–	–	[76,77]	Range, various cetacean species, England & Wales, n = 10, μg/kg ww
949	280	–	–	–	[76,77]	Average, various cetacean species, England & Wales, n = 10, μg/kg ww
67–1780	BDL-329	–	–	–	[76,77]	Range, various marine mammal species, England & Wales, n = 11, μg/kg ww, 1991–95
508	79	–	–	–	[76,77]	Average, various marine mammal species, England & Wales, n = 11, μg/kg ww, 1991–95
3.5	3.9	–	–	–	[8]	Mussels, the Wash, n = 1, μg'kg ww
1.9	1.8	–	–	–	[8]	Periwinkles, River Tweed, n = 1, μg/kg ww
–	–	–	–	<1.2–6758	[9]	Range, brown trout, 6 locations, Rivers Skerne & Tees, μg/kg ww
–	–	–	–	253	[9]	Average, brown trout, 6 locations, Rivers Skerne & Tees, μg/ kg ww
36.4–10275		–	–	–	[9]	Range, eels, 4 locations, Rivers Skerne & Tees, μg/kg ww, sum BDEs 28,47,99,100,153,154
647		–	–	–	[9]	Average, eels, 4 locations, Rivers Skerne & Tees, μg/kg ww, sum BDEs 28,47,99,100,153,154
–	–	–	–	71–5500	[79]	Range of averages, 1994–2006, harbour porpoises, UK, (n = 223), μg/kg lw
Non-UK						
–	–	–	–	25–210	[38]	Range, whitefish, Swiss Lakes, 2002, μg/kg lw
48–189	24–127	BDL	2.2–24	49–324	[21]	Range, L. Geneva, lake trout, n = 9, 2004, μg/kg lw
0.82–436		–	–	–	[113]	Range, river otter liver, New Jersey, n = 31, 2005, μg/kg lw
	30–4500		–	–	[62]	Range, bottlenose dolphin, Florida, 1993–2004, μg/kg lw
	300–51,000		–	–	[73]	Range, Indo-Pacific dolphin, Hong Kong, 1997–2008, μg/kg lw
–	–	–	<4–412	–	[83]	Range, peregrine falcon eggs, Sweden, n = 20, μg/kg lw
–	–	–	<7–<36	–	[83]	Range, cormorant liver, The Netherlands, n = 4, μg/kg lw
–	–	–	–	79–143	[137]	Range, Harbour porpoise, n = 3, NW Spain, 2001–03, μg/kg lw

waters. There was a sharp increase between 2000 and 2001, followed by a rapid decrease between 2003 and 2004. The authors attributed this to the closure in 2003 of an HBCDD production facility in northeast England coupled with reduced HBCDD sales in the UK leading up to that point. A second study is that of [133]; who examined trends in input fluxes between ~1950 and 2011–12 in radiometrically dated sediment cores from 7 English lakes. This study's findings are broadly consistent with those of [79]. Specifically, at most locations, HBCDD input fluxes increased rapidly following their first emergence in the 1960s. While at the most urban site (Edgbaston Pool, Birmingham), HBCDD fluxes increased throughout the monitored core and showed no sign of decreasing or levelling off; fluxes at most sites peaked earlier at various points between the late-1980s and early-2000s, followed by a clear decline. Taken together, these two studies suggest that the UK environment has responded to actions designed to limit contamination with HBCDD.

3.15. Penta-BDE (BDEs-47 and 99)

European background airborne PBDE concentrations (BDEs –28, –47, –49, –99, –100, –153, –154, and –183) were reported to have declined with a half-life of 2.2 ± 0.4 years between 2000 and 2008 [109]. Likewise, concentrations in air of a similar range of PBDEs were reported to be declining during the 2000s at three out of four UK monitoring locations with average half-lives between 2.0 and 3.5 years [15]. The same study however, observed no decline in atmospheric PBDE concentrations at one of the two UK rural sites monitored [15].

Table 11
Summary of Concentrations of POP-BFRs in UK Diet, with selected international data for comparison.

BDE-47	BDE-99	BDE-183	BDE-209	HBCDD	Reference	Comments
0.039–2.74			0.006–0.089	0.030–12.1	[33]	Range, Scottish mussels (n = 10), oysters (n = 5), scallops (n = 10), μg/kg ww, sum BDEs 17, 28, 47, 49, 66, 71, 77, 85, 99, 100, 119, 126, 138, 153, 154, and 183
0.227			0.023	0.285	[33]	Median, Scottish mussels (n = 10), oysters (n = 5), scallops (n = 10), μg/kg ww, sum BDEs 17, 28, 47, 49, 66, 71, 77, 85, 99, 100, 119, 126, 138, 153, 154, and 183
130.4			–	–	[29]	Adult intake, TDS 1992, ng/day
163.1			–	–	[29]	Adult intake, TDS 1997, ng/day
106.3			–	–	[29]	Adult intake, TDS 2000, ng/day
78.4			–	–	[29]	Adult intake, TDS 2001, ng/day
76.2			265.6	–	[30]	Adult intake, TDS 2003, ng/day
46.4	42.6	–	–	–	[45]	Duplicate diet, median lower bound, UK adult intake ng/day
90.5		–	–	–	[45]	Duplicate diet, median lower bound, UK adult intake ng/day, sum BDEs 47, 99, 100, 153, 154
0.04–0.38	0.02–0.32	–	<0.01–0.03	–	[34]	Range, UK native oysters (n = 5), μg/kg ww
0.1	0.05	–	0.01	–	[34]	Median, UK native oysters (n = 5), μg/kg ww
0.06–1.34	0.03–0.55	–	0.01–0.53	–	[34]	Range, UK mussels (n = 17), μg/kg ww
0.14	0.07	–	0.04	–	[34]	Median, UK mussels (n = 17), μg/kg ww
0.03–0.39	0.02–0.32	–	0.01–0.04	–	[34]	Range, UK scallop gonads (n = 10), μg/kg ww
0.07	0.05	–	0.02	–	[34]	Median, UK scallop gonads (n = 10), μg/kg ww
0.01–0.07	0.01–0.06	–	0.02–0.22	–	[34]	Range, UK cockles (n = 4), μg/kg ww
0.03	0.03	–	0.07	–	[34]	Median, UK cockles (n = 4), μg/kg ww
BDL	BDL	BDL	BDL	–	[69]	Devon duck eggs, n = 10
280			–	–	[71]	Median, Cows milk, n = 10, ng/kg lw, sum BDEs 28, 47, 99, 100, 153, 154, and 183
140–320			–	–	[72]	Range, cows milk, n = 18, samples taken every 6 weeks from 2 farms, ng/kg lw, sum BDEs 17, 28, 47, 49, 66, 71, 77, 85, 99, 100, 119, 126, 138, 153, 154, and 183)
14	9.8	2.1	179.2	–	[90]	Average adult intake, TDS 2012, ng/day, assuming 70 kg bw
	2.44–10.92		<0.1	–	[57]	Range of averages, Scottish Farmed Salmon, μg/kg ww, sum all PBDEs, N.B. BDE-209 BDL
6.95			<0.1	–	[57]	Average of averages, Scottish Farmed Salmon, μg/kg ww, sum all PBDEs, N.B BDE-209 BDL
				413	[37]	Upper bound exposure (ng/day) of UK adults in 2004
Non-UK						
50.3				16	[107]	US adult dietary intake estimate, based on 310 composite samples from 31 food types 2008–09, ng/d (assuming 70 kg bw)
23–48				–	[122]	Belgium, adult daily intake, based on food basket analysis, ng/d,
5.9–22			50–238	1.0–20	[103,104]	Belgium, duplicate diet intake ng/d, n = 19 individuals, 2008

Meanwhile, the sediment core study of [133] reported that while fluxes of Penta-BDE appear to have peaked in the late 1990s/early 2000s at three out of seven English lakes examined; in cores from our other locations, fluxes were still increasing. While the apparent peak at some locations may be interpreted as an encouraging sign of a positive response to the introduction of EU control measures in 2004 on new production and usage of Penta-BDE; the continuing increase in fluxes at other locations suggests the full beneficial impact of these control measures has yet to be felt. By comparison, variable temporal trends were observed in concentrations of BDE-209 and Σ16penta-nona-BDEs in six sediment cores collected in 2002/3 from the highly industrialized inner Clyde Estuary in Scotland, UK [121].

Zhang et al. [139] compared concentrations of Penta-BDE congeners in Scottish soils collected in three different surveys in 1990, 1999, and 2007–09. They found that there was a substantial and

Table 12
Summary of Studies Addressing Temporal Trends in UK environmental concentrations of POP-BFRs.

Reference	Comment
[121]	Clyde Estuary, n = 6, samples collected 2002–03, PBDEs in sediment cores
[24]	Sparrowhawk eggs, 1985–2007, BDE-209 not measured
[25]	Gannet eggs, 1977–2007, BDE-209 not measured
[15]	Outdoor air, 4 TOMPS sites, Hazelrigg, High Muffles, Manchester, London, 2000–2010, BDE-209 not measured
[36]	10 food categories collected in 2003,07,12 analysed, only sum PBDE data given but includes BDE-209
[90]	19 food groups from 2003 to 2012 TDS samples, 47,99 and 209 reported
[56]	Archived herbage Rothamsted (n = 49), BDE-209 not measured, BDE-47, 99, & 183 trends examined separately, 1903,1930,1940,1950,1960, 1961–2004
[79]	HBCDs in harbour porpoise blubber, 1994–2006
[80]	PBDEs in harbour porpoise blubber, 1992–2008
[108]	UK soils sampled at same locations in 1998 and 2008
[109]	UK air, 2000–08
[115]	UK air from TOMPs sites, adds data for 2011 and 2012 to that of [15]
[133]	Sediment core data for 7 English lakes, ~1950–2011–12 at 5 year intervals, Penta-, Octa, BDE-209 and HBCDs measured
[139]	Scottish soil data, measuring sum of BDEs 28, 47, 99, 100, 153, 154 &183 in soils taken in 1990, 1997, and 2007–09

significant increase in contamination between 1990 and 1999, and that while there was a further increase between 1999 and 2007–09, the increase over the latter period was not significant. Of particular note with respect to the Penta-BDE congeners, while the relative proportion of BDEs-47 and -99 increased from 66% to 86% of ΣPBDE between 1990 and 1999 indicating increasing Penta-BDE use; it decreased substantially to 44% ΣPBDE by 2007–09.

In the marine environment, Law et al. [80] reported trends in Penta-BDE congeners based on analysis of blubber samples from 415 stranded harbour porpoise sampled between 1992 and 2008. The authors' analysis of these data suggests that, overall, median ΣBDE concentrations peaked around 1998 and subsequently reduced by between 53.8% and 73.5% to 2008. The authors' best point estimate was that the reduction was 67.6%. This decline was highly statistically significant ($p < 0.001$) and was not confounded by a range of other factors that were also considered (area, season, nutritional status, bycaught/stranded, and age class).

Crosse et al. [25] reported long term trends in Penta-BDE concentrations in gannet eggs from two UK colonies in the Western Atlantic and the North Sea. Concentrations in eggs from both colonies increased mainly from the late 1980s, peaked in 1994, and then rapidly declined so that concentrations in 2002 were similar to or lower than those in the 1970s and 1980s.

By way of comparison for the terrestrial environment, Crosse et al. [24] examined temporal trends in concentrations of Penta-BDE congeners in archive sparrowhawk eggs collected between 1985 and 2007. They found concentrations to increase significantly up until the early 1990s, after which point concentrations remained similar until 2007. The authors hypothesised that this may indicate some formation of Penta-BDE congeners as a result of debromination of BDE-209.

With respect to human dietary exposure, Mortimer et al. [90] reported on concentrations of BDEs 47 and 99 in 19 food group samples analysed as part of the TDS in 2003 and 2012. Data revealed that in general, levels appear to have fallen since 2003, which may be a reflection of the reduction in use of the commercial Penta-BDE mixture since use restrictions were introduced in the mid-2000s. Use of these data to derive population-based dietary exposure estimates revealed UK exposure based on 2012 TDS samples to be ~50% lower than those in 2003. Further detail to this story was provided by Ref. [36]; who reported concentrations of the sum of PBDEs (including BDE-209) in 10 food group categories collected as part of the 2003, 2007, and 2012 TDSs. The clear and substantial decline in ΣPBDE concentrations (which were dominated by Penta-BDE congeners) between 2003 and 2012 was confirmed. This clear declining temporal trend in UK dietary exposure to BDEs 47, 99, and 183 is further supported by the data of [29,30,90].

Finally, Schuster et al. [108] analysed UK soils for concentrations of Penta-BDE congeners from the same locations in both 1998 and 2008. Comparison of the 2008 and 1998 data sets showed concentrations to be significantly lower in 2008.

3.16. Octa-BDE (BDE-183)

Based on analysis of input fluxes determined in English lake sediment cores, Yang et al. [133] concluded that temporal trends in BDE-183 input fluxes varied between the 7 sites examined. Its first emergence at all sites studied was always (with one exception) later than that of BDE-209 and either at the same time or later than Penta-BDE. While fluxes of BDE-183 appeared to have peaked at most of the studied lakes in the late-1990s/early-2000s; at other sites, fluxes peaked in surficial sediment. In general, these trends suggest the 2004 EU restrictions on manufacture and use of the Octa-BDE product has not yet been fully successful in reducing environmental contamination. Perhaps not inconsistent with this view, the Scottish soil study of [139] found that BDE-183 contributed significantly more (30.9%) of ΣPBDE in 2007–09 compared to 1999 (5.8%). It is not possible to say with certainty whether this increasing relative abundance of BDE-183 c.f. BDEs-47 and -99 is due to relative emission trends or/and the relative persistence of these congeners in soils. In the study of gannet eggs by Ref. [25]; concentrations of BDE-183 followed a similar trend to that of Penta-BDE congeners in the same samples. Specifically, a rise from the first samples in the 1980s to a peak in the early-mid-1990s, and a marked decline thereafter. Interestingly, Crosse et al. [25] reported a similar recent increase in gannet eggs of the relative abundance of heavier congeners like BDE-183 compared to the Penta-BDE congeners.

3.17. Deca-BDE (BDE-209)

In contrast to BDE-183, Yang et al. [133] found that input fluxes of BDE-209 generally increased smoothly following its initial emergence at most sites around 1960, and showed no obvious decline in more recent layers except at Marton Mere, the most contaminated lake studied. The continuing increase in input fluxes of BDE-209 at all but one location, implies strongly that recent (2008) EU restrictions on manufacture and use of Deca-BDE have yet to translate into reduced contamination of the UK environment. Not inconsistent with this, the dietary exposure study of [90] reported that while concentrations of BDE 209 were lower in 2012 than 2003 in 6 food groups, concentrations in 9 including some of the fish and non-animal product food groups, had risen. Likewise, the follow-up study of [36]; reported that there was poor correlation between the temporal trends in dietary contamination with Penta-BDE congeners (which had declined significantly between 2003 and 2012), and those of BDE-209. The authors suggested this may reflect the later introduction of use restrictions on Deca-BDE. A final piece of evidence may be gleaned from comparison of the TDS exposure estimates for 2003 and 2012 [30,90], which show a slight fall from 265.5 ng/day to 179.2 ng/day between 2003 and 2012.

3.18. Summary of recent UK temporal trends for POP-BFRs

Overall, there is good evidence that – with some exceptions – concentrations of Penta-BDE congeners have responded well to the use restrictions introduced in the mid-2000s. However, it appears that human body burdens do not appear to have responded in a similar way, as levels in UK human milk in 2010–2012 [4,19], are not dissimilar to those reported in 2002–03 [29,64].

The evidence for HBCDD and BDEs-183 and 209 is less abundant and conclusions concomitantly less certain, but there are signs that absolute concentrations of BDE-183 are falling in the UK environment. However – likely due to its greater environmental persistence – its abundance relative to Penta-BDE congeners is increasing. With respect to BDE-209, the evidence from both lake sediment core and UK diet samples, suggests that levels have yet to respond discernibly to the more recent curbs on manufacture and use of Deca-BDE. The limited evidence for HBCDD is strongly consistent with a declining trend in environmental contamination with this chemical.

3.19. Data gaps relating to the presence of POP-BFRs in the UK environment

In total, around 90 studies were identified meeting the search criteria that address one or more aspects of contamination of the UK environment with POP-BFRs. More exist in the “grey” literature, with additional papers available that replicate data reported here. Areas in which there appear particular gaps in information for the UK are:

- Concentrations of BDE-209 and HBCDD in soil – only 1 study for each compound exists, with neither of these as yet published in the peer-reviewed literature.
- Levels of BDE-209 and HBCDD in herbage – no data exist for these in the UK; Moreover, only 2 studies (totalling 11 samples) exist that report data for BDEs 47, 99, and 183 in UK herbage;
- Only 2 studies report concentrations of BDE-209 in outdoor air, with only 1 of these (that is not yet reported in the peer-reviewed literature) conducted since 2004. Likewise, only 2 studies exist that report concentrations in outdoor air of HBCDD;
- No data exist related to concentrations of either BDE-183 or BDE-209 in indoor air for UK homes and offices;
- With respect to contamination of river and lake water, only a single study of 13 samples from a single English river exists that reports concentrations of BDE-183 and 209. While concentrations of HBCDD and BDEs 47 and 99 are reasonably well-characterised in English lake water, no data for BDE-183 and 209 exist for water from UK lakes;
- Only 2 studies – one of which was conducted in 2001–2003 – exist that report concentrations of PBDEs in human blood serum. No such data exist for HBCDD;
- Only 1 recent study exists (and not in the peer-reviewed literature) reporting BDE-209 in sediments. There is 1 earlier study for the Tees dating to the turn of the century.
- Only 1 study exists that provides data – for a single Scottish mountain lake – on the atmospheric depositional fluxes for BDEs 47, 99, 183, and 209, but not for HBCDD. Another study reports input fluxes (combining inputs both from atmospheric deposition and soil run-off etc) to 7 English lakes for all POP-BFRs.

Areas in which the UK appears comparatively well-characterised with respect to contamination with POP-BFRs are:

- Concentrations of all target POP-BFRs in indoor dust;
- Concentrations of BDEs-47 and 99 in human milk;
- Concentrations of BDEs-47, 99, and 183 in wildlife;
- Concentrations of all POP-BFRs in the human diet – with the caveat that there is a need for a dietary exposure assessment to be conducted based on the available data for HBCDD in 2012 TDS samples.

3.20. Comparison of UK contamination with POP-BFRs in an international context

In each of Tables 1–11 inclusive summarising UK concentrations of POP-BFRs in each environmental compartment considered, comparative data from selected representative studies from elsewhere in the world are included for comparison.

Broadly, these reveal UK levels to be generally in line with those found in other industrialised countries. Key points of note are highlighted below:

- UK concentrations of BDEs-47 and 99 (and by extension other congeners prevalent in the Penta-BDE formulation) are lower than those reported for North America, but are broadly consistent with those for other industrialised countries both within the EU and beyond;
- Concentrations of BDE-183 in the UK are in line with those reported in most other regions globally;
- For BDE-209, UK concentrations in abiotic matrices such as indoor dust, are at the high end of those reported globally. However, concentrations in UK human milk are amongst the lowest reported to date. This suggests that the bioavailability of BDE-209 is likely very low;
- Concentrations in the UK of HBCDD fall within the mid-range of those detected globally. While UK dietary exposure appears ~ ten times higher than the US and Belgium; this is based on analysis of samples from the 2004 TDS in which HBCDD concentrations in a substantial proportion of food groups were below detection limits, and may therefore be an overestimate of exposure. This is supported by the available data on human milk for HBCDD. This shows UK levels to be consistent with that reported for both other European countries and North America.
- The highly diverse number of species covered within the biota environmental compartment (Table 11), means placing UK data in an international context is difficult. However, the study of [31] examined concentrations of PBDEs in European starling eggs from 13 countries in 2009–10. Concentrations in the UK were significantly higher than in the other European countries studied, and were the highest except for the US and Canada. Concentrations in the UK were ~half those in the US eggs, and ~20 times lower than those from Canada. With respect to HBCDD,

Table 13
Estimated UK Burdens (t) of POP-BFRs (this study, using assumptions of [42].

BDE-47	**Burden (t)**	**Concentration**	**Concentration units**	**Source**
Sediments	0.051	0.60	μg/kg dw	[131],[a]
Soil	2.1	0.17	μg/kg dw	[44]
Vegetation	0.005	0.07	μg/kg dw	[56]
Outdoor Air	0.001	4.60	pg/m^3	[27]
Freshwater	0.001	27	ng/m^3	[132],[c]
Biota[d]	0.035	3.30	μg/kg lw	[4]
Total	2.2			
BDE-99	**Burden (t)**	**Concentration**	**Concentration units**	**Source**
Sediments	0.076	0.90	μg/kg dw	[131],[a]
Soil	4.2	0.34	μg/kg dw	[44]
Vegetation	0.005	0.08	μg/kg dw	[56]
Outdoor Air	0.001	3.80	pg/m^3	[27]
Freshwater	0.001	27	ng/m^3	[132],[c]
Biota[d]	0.008	0.71	μg/kg lw	[4]
Total	4.3			
BDE-183	**Burden (t)**	**Concentration**	**Concentration units**	**Source**
Sediments	0.017	0.20	μg/kg dw	[131],[a]
Soil	0.93	0.08	μg/kg dw	[27]
Vegetation	0.004	0.06	μg/kg dw	[56],[b]
Outdoor Air	0.001	3.40	pg/m^3	[27]
Freshwater	–	–		na
Biota[d]	0.001	0.05	μg/kg lw	[19]
Total	1.0			
BDE-209	**Burden (t)**	**Concentration**	**Concentration units**	**Source**
Sediments	2.282	27	μg/kg dw	[131]
Soil	23.6	1.90	μg/kg dw	[27]
Vegetation	–	–	μg/kg dw	na
Outdoor Air	0.037	148	pg/m^3	[27]
Freshwater	–	–		na
Biota[d]	0.003	0.31	μg/kg lw	[4]
Total	25.9			
HBCDD	**Burden (t)**	**Concentration**	**Concentration units**	**Source**
Sediments	0.187	2.21	μg/kg dw	[48]
Soil	9.5	0.77	μg/kg dw	[49]
Vegetation	–	–	μg/kg dw	na
Outdoor Air	0.012	47	pg/m^3	[49]
Freshwater	0.004	160	ng/m^3	[48]
Biota[d]	0.064	6	μg/kg lw	[3]
Total	9.8			

[a] Sediment concentrations for BDE-47, 99 and 183 based on Σtri-hexa-BDEs = 1.89 μg/kg & "typical" 47:99:183 ratio in other studies.
[b] Herbage concentration for BDE-183 assumed to be 0.5 detection limit reported.
[c] Freshwater concentrations for BDEs-47 & 99 estimated by assuming each contribute 45% of the Σtri-hexa-BDE concentration reported in Ref. [132].
[d] Biota burden estimated to be 10 × that calculated for humans.

concentrations in UK lake fish appear consistent with those reported in two separate studies in Swiss lakes.

3.21. Estimated UK environmental budget for POP-BFRs

We calculated estimates of the burden of POP-BFRs (BDEs-47, 99, 183, 209, and HBCDD) in the following environmental compartments.

- Sediments
- Soil
- Vegetation
- Outdoor Air
- Freshwater
- Biota

To do so, we used the same assumptions and calculation methodology as [42]; with the concentration values chosen as representative of each compartment given in Table 13. These individual compartment values were summed to provide a total estimated burden for the UK, with results shown in Table 13. Comparison of estimated burdens for different POP-BFRs, reveals their relative abundance in the UK environment to be as follows: Deca-BDE > HBCDD > Penta-BDE > Octa-BDE. Moreover, as with similar environmental budgets for other POPs such as PCBs [42], Table 13 suggests that the majority (>90%) of the UK environmental burden of POP-BFRs resides in soil.

The other salient point that emerges on consideration of these estimates of the UK burden, is that the mass identifiable as present in the UK environment is considerably lower than expected given data on production and use of POP-BFRs in Europe. Specifically, European market demand for Deca-BDE, Octa-BDE, Penta-BDE, and HBCDD in Europe in 2001 (the last date for which such figures are available) were: 7600, 610, 150, and 9500 t respectively [18]. Harrad et al. [42] made a similar finding for PCBs in the early 1990s, with the calculated UK burden amounting to ~1% of estimated UK use. This suggests a number of possibilities, each of which can plausibly account to at least some degree for the POP-BFR use figures exceeding substantially the current environmental burden for the UK. These are:

- POP-BFRs have undergone environmental transport from the UK;
- POP-BFRs have undergone environmental degradation;
- POP-BFRs remain in use. In view of the high levels of POP-BFRs added to soft furnishings, EEE and building insulation to impart flame retardancy, and the numbers of such goods in circulation, this may represent a substantial mass of POP-BFRs. As time continues to elapse since the cessation of new use of POP-BFRs, this factor will assume progressively less importance as treated goods reach end-of-life;
- POP-BFRs have entered the waste stream. Their subsequent fate in the waste stream could involve accumulation in landfill, incineration, or other treatment. It is unlikely that the data reviewed in this study will have captured the magnitude of the mass of POP-BFRs in the waste stream, but the highly elevated concentrations of HBCDD detected around a UK e-waste handling facility [49–51] – Table 5) are a possible indication that this mass may be substantial.

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