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Halogenated flame retardants in Irish waste polymers: Concentrations, legislative compliance, and preliminary assessment of temporal trends☆

Daniel Drage [a], Martin Sharkey [b], Layla Salih Al-Omran [a,c], William A. Stubbings [a], Harald Berresheim [b], Marie Coggins [b], André Henrique Rosa [a,d], Stuart Harrad [a,*]

[a] School of Geography, Earth and Environmental Sciences, University of Birmingham, Edgbaston, West Midlands, B15 2TT, United Kingdom
[b] School of Natural Sciences & Ryan Institute, National University of Ireland, Galway H91TK33, Ireland
[c] Department of Chemistry, College of Science, University of Basrah, Basrah, Iraq
[d] Institute of Science and Technology, São Paulo State University (UNESP), Av. Três de Março, 511, Alto da Boa Vista, 18087-180, Sorocaba- SP, Brazil

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ABSTRACT

Halogenated flame retardants (HFRs) were measured in 470 waste plastic articles from Ireland between 2019 and 2020. We identified articles containing concentrations of polybrominated diphenyl ethers (PBDEs), hexabromocyclododecane (HBCDD), and tetrabromobisphenol-A (TBBP-A) exceeding European Union limits. Enforcement of existing limits of 1000 mg/kg will render an estimated 3.1% (2800 t) of articles in the waste categories studied unrecyclable, increasing to: 4.0, 4.9, and 5.6% if limits were reduced to 500, 200, and 100 mg/kg respectively. Meanwhile, enforcing limits of 1,000, 500, 200, and 100 mg/kg will respectively remove 78, 82, 84, and 85% of PBDEs, HBCDD, and TBBP-A present in such waste. Other FRs targeted were detected infrequently and predominantly at very low concentrations. However, 2,4,6-tris(2,4,6-tribromophenoxy)-1,3,5-triazine (TTBP-TAZ) was detected in 3 display/IT product samples at 14,000 to 32,000 mg/kg, indicating elevated concentrations of FRs used as alternatives to PBDEs and HBCDD, will likely increase in future. Comparison with data for Ireland in 2015–16, revealed concentrations and exceedances of limits for PBDEs, HBCDD, and TBBP-A were similar or have declined. For end-of-life vehicle fabrics and foams, HBCDD and ΣPBDE concentrations declined significantly ($p < 0.05$) since 2015–16. Moreover, ΣPBDE concentrations in waste small domestic appliances are significantly lower in 2019–20, with a similarly significant decline for TBBP-A in waste IT and telecommunications articles. In contrast, HBCDD concentrations in waste extruded polystyrene increased significantly between 2015–16 and 2019–20. For other waste categories studied, no statistically significant temporal trends are evident ($p > 0.05$). Fewer samples exceeded PBDE and HBCDD limits in 2019–20 (7.8%) than 2015–16 (8.7%), while exceedances for TBBP-A fell from 2.4% in 2015–16 to 0.57% in 2019–20. While comparison between the 2015–16 and 2019-20 datasets provide a preliminary indication of changes, further monitoring is required if the impact of legislation designed to eliminate HFRs from the waste stream is to be fully evaluated.

1. Introduction

In its document "*Manifesto for a Resource Efficient Europe*" (EREP, 2012), the EU in keeping with other jurisdictions recognises that it has no choice but to transition to a resource-efficient and ultimately regenerative circular economy. An alternative to a traditional linear economy, a circular economy is one in which resources are kept in use for as long as possible. Maximum value is extracted from resources whilst in use, with products and materials recovered and regenerated at the end of each service life. Whilst a highly desirable objective, implementation of a circular economy is not entirely straightforward. One important consideration is that the presence of brominated flame retardants (BFRs) in plastic components of waste consumer products such as electronics, building insulation, as well as furniture fabrics and foam, presents a potential (yet surmountable) barrier to the ongoing use, re-use and recycling of such waste products. Indeed, evidence exists that

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* Corresponding author.
E-mail address: S.J.Harrad@bham.ac.uk (S. Harrad).

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Table 1
Categories and subcategories of waste products analysed for PBDEs, HBCDD, and TBBP-A in this study (2019–2020) and in 2015–2016.

Category	Sub-category	Number of Samples (2019–20)	Number of Samples (2015–16)
Construction and Demolition	EPS	12	40
	XPS	13	20
End of Life Vehicle (ELV) Foam and Fabrics		111	119
Soft Furnishings	Carpets	20	31
	Curtains	25	15
	Furniture Fabrics	16	22
	Furniture Foam Filling	16	20
	Mattress Foam Filling	27	17
	Mattress Fabric Covering	20	17
Waste Electrical and Electronic Equipment	Large Household Appliances	21	57
	Cooling Appliances	30	30
	Display	47	43
	Small Domestic Appliances	60	29
	IT and Telecommunications	52	78

uncontrolled recycling of waste polymers containing BFRs leads to the unintentional presence of such chemicals in articles which their presence is not required, such as food contact materials, children's toys, and polystyrene packaging (Abdallah et al., 2018; Kuang et al., 2018; Guzzonato et al., 2017; Turner, 2018; Leslie et al., 2016; Puype et al., 2015). In recognition of this, the EU has implemented Low POP Concentration Limit (LPCL) values for polybrominated diphenyl ethers (PBDEs) and hexabromocyclododecane (HBCDD) which forbid recycling of waste polymers containing such chemicals at concentrations exceeding 1000 mg/kg (European Union, 2019). Moreover, the EU classifies another widely used BFR tetrabromobispenol-A (TBBP-A) as both a H400 ("very toxic to aquatic life") and H410 ("very toxic to aquatic life with long lasting effects") substance. Consequently, waste which contains TBBP-A above 1000 mg/kg is classified as "HP 14 – Ecotoxic", treated as hazardous waste and cannot be recycled (European Union, 2008a, 2008b; European Chemicals Agency, 2022).

Recently, we published the findings of the WAFER project in which concentrations of PBDEs, HBCDD, and TBBP-A were measured in ~550 samples of waste polymeric materials collected from various sites in the Republic of Ireland between 2015 and 2016 (Drage et al., 2018; Harrad, 2018). Importantly, we found that 8.7% of articles analysed in the WAFER project exceeded the LPCL value of 1000 mg/kg for PBDEs and HBCDD. In the current study (the SAFER project), we tested the hypothesis that implementation of LPCLs for PBDEs and HBCDD would lead to: (a) lower concentrations of PBDEs and HBCDD in Irish waste polymers and a reduced proportion of samples exceeding the LPCL value; and (b) increased concentrations of halogenated FRs not covered by LPCLs such as decabromodiphenyl ethane (DBDPE) – referred to here as alternative (alt)-FRs. To test our hypothesis, between 2019 and 2020, the SAFER project determined concentrations of PBDEs, HBCDD, TBBP-A, and a range of alt-FRs in 470 samples of waste polymers of similar types to those collected in the WAFER project. In this paper, we compare data on HFR concentrations and exceedances of limit values from the two projects to test our hypotheses. While comparison of data collected at just two points in time is inherently fraught with uncertainty; such comparison provides useful information and an invaluable baseline against which future evaluations of concentrations of HFRs in waste plastic articles may be compared.

2. Materials & methods

2.1. Sample collection

Samples were collected from several waste handling facilities located in the Republic of Ireland between 2019 and 2020. The sampling campaign addressed those waste streams considered most likely to contain products treated with BFRs. In order to facilitate elucidation of temporal trends in concentrations of BFRs, the waste stream categories examined and numbers of samples collected from each category, were matched as closely as possible with the WAFER project conducted in 2015–16. A total of 470 samples were collected from 4 broad categories of waste: construction and demolition (C&D) extruded and expanded polystyrene foam (EPS/XPS) (n = 25; end of life vehicle (ELV) fabrics and foams (n = 111); soft furnishings (n = 124); and waste electrical and electronic equipment (WEEE) (n = 210). These categories were further divided as detailed in Table 1.

During the WAFER project, samples were collected between 2015 and 2016 from a broad range of sites across the country to assess any regional variances in BFR content in the wastes. No such variances were observed; thus, all samples in the SAFER project were collected from waste collection or waste transfer sites within the County Galway region. These sites included: three end of life vehicle scrapyards; two major recycling/waste transfer sites which process a wide range of household, commercial, and C&D wastes; and a selection of construction/demolition sites where some EPS/XPS samples were collected. Hard plastic samples were taken from various WEEE items representative of the major plastic component (i.e. largest surface area) of the item. These WEEE items include: IT & telecommunications equipment (IT); large household appliances (LHAs); small domestic appliances (SDAs); display items; and cooling equipment (i.e. fridges and freezers). Fabrics/upholstery and directly underlying polyurethane foams along with any other cushioning materials (wool, additional fabrics etc) were taken from ELV, furniture, and mattress samples.

Although concentrations of PBDEs, HBCDD, and TBBP-A are already available for samples from the WAFER project (Drage et al., 2018: Harrad, 2018), we also measured concentrations of (alternative) "alt-BFRs" in archived samples collected as part of the WAFER project for which sufficient material remained available for analysis. The numbers of WAFER project samples for which data are available for legacy BFRs (defined as PBDEs, HBCDD, and TBBP-A) are provided in Table 1. For alt-BFRs, concentrations were measured in the following archived samples from the WAFER project: carpets (n = 29), curtains (n = 11), ELV fabrics and foams (n = 25), and WEEE (n = 12).

2.2. Chemicals and standards

The following BFRs were targeted in this study: PBDEs 28, 47, 99, 100, 153, 154, 183, and 209; α-, β-, and γ-HBCDD, TBBP-A, DBDPE, tetrabromoethylcyclohexane (TBECH), 1,2-bis(2,4,6-tribromophenoxy) ethane (BTBPE), 2-ethylhexyl tetrabromobenzoate (EH-TBB), bis(2-ethylhexyl)tetrabromophthalate (BEH-TEBP), 2,4,6-tris(2,4,6-tribromophenoxy)-1,3,5-triazine (TTBP-TAZ), pentabromobenzene (PBB), hexabromobenzene (HBB), pentabromotoluene (PBT), 2,3-dibromopropyl-2,4,6-tribromophenyl ether (DBTE), as well as the chlorinated FRs *anti*- and *syn*-dechlorane plus (*anti*- and *syn*-DP).

HPLC grade hexane and dichloromethane (DCM) and Optima grade methanol (Fisher Scientific, Loughborough, UK) were used for extraction and analytical procedures.

Native α-, β- and γ-HBCDD standards, $^{13}C_{12}$ α-, β- and γ-HBCDD, individual standards of native BDEs −28, −47, −99, −100, −153, −154, −183, −196, −197, −209, −77 and −128, $^{13}C_{12}$-BDE 209, native TBBPA, $^{13}C_{12}$-TBBPA, native TBECH, BTBPE, EH-TBB, BEH-TEBP, PBB, HBB, PBT, d_{17}-$^{13}C_6$-EH-TBB, d_{17}-$^{13}C_6$-BEH-TEBP $^{13}C_6$-BTBPE, and native PCB-129 were obtained from Wellington Laboratories (Guelph, ON, Canada). Native TTBP-TAZ was purchased from Chem Service Inc

Table 2
Summary of concentrations (mg/kg) of PBDEs, HBCDD, and TBBP-A and percentage of samples exceeding 1000 mg/kg limit value in samples from waste streams in Ireland collected in 2019–2020 (this study) and 2015–2016 (WAFER study).

Waste Category	Sub-Category	Statistical parameter	∑HBCDD 2015-16	∑HBCDD 2019-20	ΣPBDEs 2015-16	ΣPBDEs 2019-20	TBBP-A 2015-16	TBBP-A 2019-20	ΣPBDEs + HBCDD 2015-16	ΣPBDEs + HBCDD 2019-20
Construction & Demolition	**EPS**	**average**	2100	390	<LOQ	<LOQ	<LOQ	<LOQ		
		median	100	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ		
		Range	<LOQ-10000	<LOQ-1600	<LOQ	<LOQ	<LOQ	<LOQ		
		%>limit value	35	23	0	0	0	0	35	23
	XPS	**average**	27	660	<LOQ	<LOQ	<LOQ	<LOQ		
		median	19	0.82	<LOQ	<LOQ	<LOQ	<LOQ		
		Range	<LOQ-94	<LOQ-6000	<LOQ	<LOQ	<LOQ	<LOQ		
		%>limit value	0	15	0	0	0	0	0	15
End of Life Vehicles	**Foams and Upholstery**	**average**	45	13	960	300	<LOQ	0.60		
		median	<LOQ	0.31	3.0	7.0	<LOQ	<LOQ		
		Range	<LOQ-3300	<LOQ-550	<LOQ-31000	0.80–8400	<LOQ	<LOQ-58		
		%>limit value	1.7	0	4.2	5.4	0	0	5.9	5.4
Soft Furnishings	**Carpets**	**average**	1.1	<LOQ	240	2.9	<LOQ	<LOQ		
		median	<LOQ	<LOQ	1.0	<LOQ	<LOQ	<LOQ		
		range	<LOQ-26	<LOQ	<LOQ-7000	<LOQ-12	<LOQ	<LOQ-0.05		
		%>limit value	0	0	3.2	0	0	0	3.2	0
	Curtains	**average**	3.8	1.7	3.8	3.8	<LOQ	0.23		
		median	<LOQ	0.62	<LOQ	<LOQ	<LOQ	0.20		
		range	<LOQ-56	<LOQ-8.7	<LOQ-53	<LOQ-53	<LOQ	<LOQ-0.82		
		%>limit value	0	0	0	0	0	0	0	0
	Furniture Fabrics	**average**	9200	640	6800	600	<LOQ	<LOQ		
		median	1.1	2.0	12	13	<LOQ	<LOQ		
		range	<LOQ-51000	0.47–4100	<LOQ-73000	0.85–2100	<LOQ	<LOQ		
		%>limit value	27	19	27	31	0	0	35	19
	Furniture Foam Filling	**average**	1100	20	660	470	25	<LOQ		
		median	0.31	0.02	16	7.3	<LOQ	<LOQ		
		range	<LOQ-8000	<LOQ-250	<LOQ-7800	0.70–1900	<LOQ-250	<LOQ		
		%>limit value	25	0	15	19	0	0	0	0
	Mattress Foam Filling	**average**	<LOQ	7.7	89	6.5	<LOQ	<LOQ		
		median	<LOQ	0.30	8.4	1.6	<LOQ	<LOQ		
		range	<LOQ	<LOQ-190	<LOQ-870	<LOQ-92	<LOQ	<LOQ		
		%>limit value	0	0	0	0	0	0	0	0
	Mattress Fabric Covering	**average**	2.2	1.4	10	11	0.02	<LOQ		
		median	0.06	0.58	6.7	2.1	<LOQ	<LOQ		
		range	<LOQ-12	<LOQ-6.2	0.17–49	<LOQ-100	<LOQ-0.11	<LOQ		
		%>limit value	0	0	0	0	0	0	0	0
WEEE	**Large Household Appliances**	**average**	<LOQ	0.21	19	<LOQ	36	1.4		
		median	<LOQ	<LOQ	0.039	<LOQ	<LOQ	0.41		
		range	<LOQ	<LOQ-2.1	<LOQ-190	<LOQ	<LOQ-2000	<LOQ-16		
		%>limit value	0	0	0	0	1.8	0	0	0
	Cooling Appliances	**average**	<LOQ	0.65	0.48	1.5	<LOQ	4.1		
		median	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	0.35		
		range	<LOQ	<LOQ-16	<LOQ-3.6	<LOQ-16	<LOQ	<LOQ-59		
		%>limit value	0	0	0	0	0	0	0	0
	Display	**average**	14	5.8	1900	730	3000	1700		
		median	0.014	0.07	<LOQ	0.80	4.8	037		
		Range	<LOQ	<LOQ-140	<LOQ-62000	<LOQ-32000	<LOQ-274000	<LOQ-38000		
			0	0	4.7	4.3	19	6.4	4.7	4.3

(continued on next page)

Table 2 (*continued*)

Waste Category	Sub-Category	Statistical parameter	∑HBCDD 2015-16	∑HBCDD 2019-20	ΣPBDEs 2015-16	ΣPBDEs 2019-20	TBBP-A 2015-16	TBBP-A 2019-20	ΣPBDEs + HBCDD 2015-16	ΣPBDEs + HBCDD 2019-20
		%>limit value								
	Small Domestic Appliances	**average**	<LOQ	1.8	170	5.5	350	1.8		
		median	<LOQ	<LOQ	0.019	<LOQ	<LOQ	<LOQ		
		Range	<LOQ	<LOQ-42	<LOQ-1600	<LOQ-140	<LOQ-8600	<LOQ-42		
		%>limit value	0	0	6.9	0	3.4	0	6.9	0
	It and Telecommunications	**average**	20	1.1	260	48	1700	74		
		median	<LOQ	<LOQ	0.21	<LOQ	<LOQ	1.2		
		Range	<LOQ-1600	<LOQ-56	<LOQ-7600	<LOQ-2200	<LOQ-110000	<LOQ-900		
		%>limit value	1.3	0	6.4	1.9	5.1	0	7.7	1.9

*when calculating averages, concentrations below limit of quantification were assumed to be equal to zero.

(West Chester, PA, US). Native *anti*- and *syn*- DP standards and $^{13}C_{10}$-*syn*-DP were purchased from Cambridge Isotope Laboratories (Tewksbury, MA, US).

2.3. Sample extraction & clean-up

Full extraction parameters have been reported previously (Abdallah et al., 2017; Drage et al., 2018). Briefly, aliquots of samples (10–100 mg) were accurately weighed into a 15 mL glass tube Samples were extracted using a combination of vortexing and ultrasonication with 5 mL DCM. Aliquots (50 μL) of extracts were collected and transferred to a separate glass tube containing internal standards (50 ng each of BDEs −77 and −128, $^{13}C_{12}$-α-, β- and γ-HBCDD, $^{13}C_6$-BTBPE, d_{17}-$^{13}C_6$-EH-TBB, $^{13}C_{10}$-*syn*-DP, and 100 ng each of $^{13}C_{12}$-BDE-209 and d_{17}-$^{13}C_6$-BEH--TEBP). Extracts were concentrated to near-dryness followed by precipitation of polymer matrix by addition of hexane and concentration to 200 μL. Diluted extracts were vortexed for 20 seconds and transferred into inserted autosampler vials ready for GC/MS analysis. After analysis of PBDEs via GC/MS, samples were solvent exchanged into 200 μL methanol for LC-TOF/MS analysis.

2.4. Instrumental analysis

Quantitative analysis of PBDEs (BDEs −17, −28, 47, −99, −100, −153, −154, −183, and −209) and alt-BFRs was performed on a Thermo Fisher Trace 1310 gas chromatograph coupled to a Thermo Fisher ISQ mass spectrometer (MS). The MS was operated in electron ionisation mode using selective ion monitoring (SIM). Full details of ions monitored are provided in Abdallah et al. (2017) and Tongue et al. (2021). One μL of the purified extract was injected for analysis using a programmable temperature vaporiser (PTV) onto a Restek Rxi-Rtx-1614 MS column (15 m × 0.25 mm x 0.1 μm film thickness). Helium was used as the carrier gas at a flow rate of 1.0 mL/min.

HBCDDs and TBBPA were measured using a Sciex Exion UPLC coupled to a Sciex 5600+ Triple TOF MS. Chromatographic separation was achieved with an AccucoreTM RP-MS column (100 × 2.1 cm, 2.6 μm, Thermo Scientific, Bremen, Germany). Full details on chromatographic separation and full MS parameters are reported in Drage et al. (2020).

2.5. Quality control

A reagent blank consisting of 100 mg of anhydrous sodium sulfate was analysed with every 11 samples. "Negative Control" samples were created using plastics and textiles that contain no BFRs and were also analysed throughout the study. Three such control samples were assessed for each matrix. None of the target compounds were found above the limits of detection in the blanks. Therefore results were not corrected for blank residues and method limits of detection (LOD) and quantification (LOQ) were estimated based on a signal to noise ratio (S/N) of 3:1 and 10:1 respectively. LOQs for target compounds ranged from 0.1 to 0.5 mg/kg for PBDEs; 0.01 mg/kg for α-, β- and γ- HBCDD and TBBPA; 0.2 mg/kg for TBECH, PBT, DPTE, HBB, BTBPE, EH-TBB, BEH-TEBP, and *anti*-DP; 0.6 mg/kg for *syn*-DP; 1.0 mg/kg for DBDPE; and 6.0 mg/kg for TTBP-TAZ.

Method accuracy and precision for PBDEs was assessed via repeated analysis of certified reference materials (CRMs) ERM-EC591 (polypropylene), ERM-EC590 (polyethylene) in addition to textiles (polyester fabrics), extruded polystyrene and expanded polystyrene that have been previously measured by this laboratory and another. All values were found to be close to certified or indicative levels, with a relative standard deviation of <15%. Full details of method precision and accuracy can be found in Abdallah et al. (2017). Matrix spikes of native target analytes were also performed with every other batch of samples analysed. For a batch to be accepted, the measured concentration for each compound was required to be within 80–120% of the spiked concentration.

2.6. Statistical analysis

All statistics were performed using Microsoft Excel for Mac v16.59. A significance level of 95% ($p \leq 0.05$) was applied. Concentration data were $\log_{10}$ transformed before t-tests were performed.

3. Results & discussion

3.1. Concentrations of PBDEs and HBCDD and exceedances of the LPCL in Irish Waste Plastic Samples collected in 2019–20 compared to 2015-16

Table 2 summarises the concentrations of ∑PBDEs (i.e. BDEs −28, −47, −99, −100, −153, −154, −183, and −209) and ΣHBCDDs (α-, β-, and γ-HBCDD) detected in samples from various waste categories collected in 2019–2020. Table 2 also provides the percentage of samples that exceeded the current LPCL for PBDEs and HBCDD of 1000 mg/kg. The equivalent data reported previously for samples from the same waste categories obtained in 2015–216 are provided for comparison.

3.1.1. C&D EPS/XPS waste

As in the 2015-16 study, no PBDEs were detected in any of the C&D samples collected in 2019–20. In contrast, out of 25 C&D EPS/XPS samples, 5 (20%) contained HBCDDs above the LPCL of 1000 mg/kg. This is slightly lower than the 23% LPCL exceedance for HBCDD observed in 2015–16. Interestingly, whilst in 2015–16 samples, all LPCL exceedances for HBCDD were observed in EPS samples (35%), in 2019–20 samples, there were 3 exceedances in EPS (25%) and 2 in XPS

Table 3
Estimated Annual Masses[a] of Different Categories of Waste Generated in Ireland in 2019 and Mass[a] of PBDEs, HBCDD, and TBBP-A Associated with such Waste.

Category	t waste/yr	PBDEs (kg/yr)	HBCDD (kg/yr)	POP-BFR (kg/yr)[g]	TBBP-A (kg/yr)	ΣBFRs (kg/yr)[g]
C&D	5500	5.1	2900	2900	0.20	2900
ELV	3800	2300	110	2400	0.50	2400
Carpets	7600	22	91	110	0.08	110
Curtains	740	2.9	1.3	4.2	0.17	4.4
Furniture foam	2600	1200	51	1300	0.01	1300
Furniture fabrics	880	530	560	1100	0.004	1100
Mattress foam	6100	40	47	87	0.61	88
Mattress fabrics	2500	27	3.5	30	0.04	30
LHA[b]	37,000	0.09	0.02	7.7	0.15	7.9
Cooling[c]	10,000	1.5	0.65	2.2	4.1	6.3
Display[d]	5000	660	5.2	660	1500	2200
SDA[e]	8100	0.33	0.001	0.34	0.11	0.44
IT & Telecommunication articles[f]	1900	16	0.37	17	25	42
Total[g]	92,000	4800	3800	8600	1600	10,000

[a] Rounded to two significant figures.
[b] Assuming 0.29% w/w of LHA is Br-containing plastic (WRc, 2012).
[c] Assuming 10% w/w of Waste Cooling Appliances is Br-containing plastic (WRc, 2012).
[d] Assuming 18% w/w of Display waste is Br-containing plastic (WRc, 2012).
[e] Assuming 0.75% w/w of SDA is Br-containing plastic (WRc, 2012).
[f] Assuming 18% IT equipment is Br-containing plastic (WRc, 2012).
[g] Totals may differ due to rounding.

(15%). As a result, concentrations of HBCDD in XPS are significantly higher ($p < 0.05$) in 2019–20 than in 2015–16. No such significant difference was observed for EPS, nor for EPS and XPS combined. This may suggest that the apparent increase in HBCDD concentrations in C&D XPS is an artefact of the small sample numbers analysed, while also highlighting the likely long lag time between introduction of restrictions on HBCDD use and its removal from the waste stream. For example, the service life of EPS and XPS building insulation materials has been estimated at 35–50 years for EPS and to equal the building lifetime for XPS (Kono et al., 2016).

3.1.2. ELV waste fabrics and foams

Out of the 111 ELV fabric and foam samples collected in 2019–20, concentrations of ΣPBDEs exceeded the LPCL in 6 samples (5.4%) while no LPCL exceedances were detected for HBCDD. The incidence of LPCL exceedances in the current project is broadly similar to that in 2015–16, where of the 119 ELV samples studied, 5 (4.2%) and 2 (1.7%) exceeded the LPCL for PBDEs and HBCDD respectively. This similarity in LPCL exceedance was reflected in the absence of any significant temporal change in concentrations of both PBDEs and HBCDD.

3.1.3. Soft furnishings

As indicated in Table 1, the soft furnishing samples collected consisted of a mix of carpets, curtains, as well as fabric coverings and polyurethane foam fillings for mattresses, sofas, and chairs. Consistent with what we reported in samples collected in 2015–16, concentrations of PBDEs and HBCDD in samples of carpets, curtains, and mattresses collected in 2019–20 were low, with no LPCL exceedances in such samples. In contrast, in 2019–20, 8/16 (50%) samples of furniture fabrics exceeded the LPCL (5 and 3 for PBDEs and HBCDD respectively). This proportion of exceedances is consistent with that observed for samples collected in 2015–16, for which 9 samples of furniture fabrics (41%) exceeded the LPCL (6 for PBDEs only, 6 for HBCDD only, and 3 for both PBDEs and HBCDD in the same sample). With respect to furniture foam filling samples, both concentrations and the incidence of LPCL exceedances were lower than for furniture fabrics. Specifically, in 2015–16, 7 furniture foam samples (35%) exceeded the LPCL (2 for PBDEs only, 4 for HBCDD only, and 1 for both PBDEs and HBCDD in the same sample). For the 2019-20 samples, there were fewer LPCL exceedances than in 2015–16; i.e. none for HBCDD and 3 (19%) for PBDEs. Despite this, there was no significant difference between concentrations of either PBDEs or HBCDD between 2015–16 and 2019–20.

3.1.4. WEEE

As observed for such waste items collected in 2015–16, concentrations of both PBDEs and HBCDD in LHA and cooling appliances collected in 2019–20 were low, with none exceeding the LPCL. Similarly, low concentrations and zero LPCL exceedances were also seen in SDA collected in 2019–20. However, this contrasts with what was observed for SDA in 2015–16, for which there were 2 LPCL exceedances (6.9%) for PBDEs only, and was reflected in concentrations of ΣPBDEs declining significantly ($p < 0.05$) between 2015–16 and 2019–20. For display items, the incidence of LPCL exceedances showed little change: 2 exceedances (4.3%) for PBDEs only in 2019–20, compared to 2 (4.7%) also for PBDEs only in 2015–16. Finally, for IT and telecommunications items, while there was no significant difference between the two studies with respect to concentrations of PBDEs and HBCDD; LPCL exceedances were proportionally lower in 2019–20 than in 2015–16. Explicitly, while in 2015–16, 5/78 (6.4%) and 1/78 (1.3%) of IT samples exceeded the LPCL for PBDEs and HBCDD respectively; in 2019–20, the LPCL was exceeded for PBDEs only in a single sample (1.9%) out of 52 samples.

3.2 Concentrations of TBBP-A in Irish Waste Plastic Samples in 2019–20 compared to 2015-16.

Table 2 also provides a summary of concentrations of TBBP-A in Irish waste plastic samples collected in both 2019–20 and reported previously in 2015–16 (Harrad, 2018). Also included in Table 2 are the percentage of samples containing TBBP-A at >1000 mg/kg and thus deemed unrecyclable in the EU. In summary and consistent with observations for samples collected in 2015–16, concentrations of TBBP-A in C&D, ELV, soft furnishings, and cooling appliances collected in 2019–20 were well-below the limit value of 1000 mg/kg. We also detected only very low concentrations (<1000 mg/kg) of TBPP-A in LHA collected in 2019–20. Although in 2015–16, there was one LHA sample that exceeded 1000 mg/kg TBBP-A, concentrations in LHA did not differ significantly ($p > 0.05$) between the two studies. In contrast, there were proportionally fewer samples of both display, SDA, and IT samples in 2019–20 that contained >1000 mg/kg TBBP-A than in 2015–16. Specifically, while in 2015–16, 19%, 3.4%, and 5.1% of display, SDA, and IT samples contained >1000 mg/kg TBBP-A; the corresponding figures in 2019–20 were: 6.4%, 0%, and 0%. While the decline in the proportion of IT samples containing >1000 mg/kg TBBP-A between the two studies was not reflected by a significant difference in concentrations; concentrations of TBBP-A in both SDA and display samples declined significantly ($p < 0.05$) between 2015–16 and 2019–20.

3.3 Concentrations of alt-FRs in Irish Waste Plastic Samples in

Table 4
Estimated Annual Mass (t/year[a]) of material in each waste category studied that exceeds limit value of 1000 mg/kg and annual mass of PBDEs, HBCDD, and TBBP-A (kg/year[a]) associated with such material.

Category	t > 1000 mg/kg/yr	PBDEs associated with material >1000 mg/kg (kg/yr)	HBCDD associated with material >1000 mg/kg (kg/yr)	POP-BFRs associated with material >1000 mg/kg (kg/yr)	TBBP-A associated with material >1000 mg/kg (kg/yr)	ΣBFRs associated with material >1000 mg/kg (kg/yr)
C&D	1100	0.78	2700	2700	0.01	2700
ELV	210	1100	4.2	1100	0.01	1100
Carpets	0	0	0	0	0	0
Curtains	0	0	0	0	0	0
Furniture foam	490	910	5.5	920	0.002	920
Furniture fabrics	440	520	560	1100	0.002	1100
Mattress foam	0	0	0	0	0	0
Mattress fabrics	0	0	0	0	0	0
LHA[a]	0	0	0	0	0	0
Cooling[b]	0	0	0	0	0	0
Display[c]	530	650	0.49	650	1500	2200
SDA[d]	0	0	0	0	0	0
IT & Telecommunication articles[e]	36	14	0	14	0.10	14
Total[g]	2800	3200	3300	6400	1500	7900
% captured by Limit implementation		65	86	74	97	78
%>1000 mg/kg	3.1					

f Assuming 18% IT equipment is Br-containing plastic (WRc, 2012).
[a] Rounded to 2 significant figures.
[b] Assuming 0.29% w/w of LHA is Br-containing plastic (WRc, 2012).
[c] Assuming 10% w/w of Waste Cooling Appliances is Br-containing plastic (WRc, 2012).
[d] Assuming 18% w/w of Display waste is Br-containing plastic (WRc, 2012).
[e] Assuming 0.75% w/w of SDA is Br-containing plastic (WRc, 2012).
[g] Totals may differ due to rounding.

2019–20 and 2015-16.

Our target alt-FRs were rarely detected in samples collected in this study in 2019–20. Indeed, *anti*-DP and DBDPE were the only alt-FRs targeted that were detected in at least one waste category at a detection frequency >20%, at maximum concentrations of 96 and 1100 mg/kg respectively. Table SD-1 summarises concentrations of these two alt-FRs in samples collected in 2019–20. As in the 2019-20 samples, the presence of our target alt-FRs in samples (mainly soft furnishings and ELV fabrics and foams, as well as a small number of WEEE samples) collected in 2015–16 was negligible. As in 2019–20, only *anti*-DP and DBDPE were detected in >20% of samples from at least one waste category, at maximum concentrations of 33 and 8.8 mg/kg respectively. However, despite these generally very low concentrations of most of our target alt-FRs in most samples; it is important to note that in the 2019-20 study, TTBP-TAZ was detected at concentrations of 22,000 mg/kg in one IT sample (an internet router) and at 14,000 and 32,000 mg/kg in two display samples (both TVs). Moreover, another display sample (a TV) contained 1100 mg/kg DBDPE. While to our knowledge, no data yet exist of concentrations of TTBP-TAZ in Irish indoor air and dust; those of DBDPE in indoor air and dust collected in Ireland in 2016–2018 were the highest reported globally to date (Wemken et al., 2019). This suggests that while concentrations of alt-FRs in the Irish waste stream remain well below those of PBDEs, HBCDD, and TBBP-A; the high concentrations observed in a very small number of items now entering the waste stream, indicate that alt-FRs such as TTBP-TAZ and DBDPE may become more prevalent in plastic items reaching the waste stream over the next decade.

3.4 Preliminary estimation of mass of products exceeding limit values and mass of PBDEs, HBCDD, and TBBP-A annually entering the waste streams studied in Ireland.

Estimates of the mass of our target waste materials generated in Ireland in 2019 were derived as described in Table SD-2. Combining these data with our concentration data, generated preliminary estimates of the mass of PBDEs, HBCDD, and TBBP-A annually entering the waste streams studied in Ireland (Table 3). The uncertainties inherent in these estimates are acknowledged, and their preliminary nature underlined. Specifically, estimates of the mass of waste materials generated annually involve a substantial degree of uncertainty – for example, direct estimates of waste furniture foam for Ireland are not available, and we have therefore extrapolated from estimated UK arisings of waste furniture and applied our own judgement to estimate how much of this is foam (see Table SD-2). Coupled with this, while this study and the earlier WAFER study are to our knowledge one of the largest of their kind to date anywhere; the extent to which the samples analysed are representative of all such articles in Ireland is unknown. Notwithstanding these caveats, we believe our estimates provide an informative overview of HFR contamination in the Irish waste stream.

Of note is that of the ~10,200 kg PBDEs, HBCDD, and TBBP-A estimated to be entering the Irish waste stream in 2019; 28.6% were associated with C&D insulation foam, with ELV foams/fabrics, display items, furniture foams, and furniture fabrics contributing a further 23.8, 21.6, 12.5, and 10.6%. In contrast only 2.9% were found in waste carpets, curtains, mattresses, cooling appliances, large and small household appliances, and IT/telecommunications articles combined. Such information may help focus monitoring resources on those waste categories most contaminated with PBDEs, HBCDD, and TBBP-A.

Implications of enforcement of limit values on mass of BFRs removed from the waste stream and mass of waste rendered unrecyclable

In October 2021, the European Parliament published a proposal for the upcoming revision of the POPs Regulation (EU, 2019/1021) to include revised LPCLs for PBDEs and HBCDD (among other chemicals). Specifically, they cite revised LPCLs for both HBCDD and PBDEs of 500 mg/kg, reduced to 200 mg/kg five years after entry into force of the POPs Regulation (European Union, 2022). A follow-up report from the European Parliament in February 2022 further proposes more stringent LPCLs for these POPs of 200 mg/kg, reduced to 100 mg/kg after 5 years (Hojsik, 2022). While the revised LPCLs have not been finalised, whichever revisions are made are set to be added to the POPs Regulation following the Stockholm Convention CoP (Convention of the Parties) meeting in June 2022 and to be implemented 6 months after publication (ca. 1st quarter 2023). Against this shifting legislative backdrop, we calculated what proportion of PBDEs, HBCDD, and TBBP-A which would

Table 5
Summary of estimated annual mass (t/year[a]) of material exceeding various limit values and associated ΣBFR removal percentages.

Limit 1000 mg/kg		Limit 500 mg/kg		Limit 200 mg/kg		Limit 100 mg/kg	
Annual mass waste > Limit (t/yr)	%Removal ΣBFR	Annual mass waste > Limit (t/yr)	%Removal ΣBFR	Annual mass waste > Limit (t/yr)	%Removal ΣBFR	Annual mass waste > Limit (t/yr)	%Removal ΣBFR
2800	78	3600	82	4500	84	5200	85

[a] To two significant figures.

need to be removed from the waste stream were these revised limit values in place in 2019.

Table 4 shows that enforcement of the current limit values for PBDEs, HBCDD, and TBBP-A of 1000 mg/kg, will result in 3.1% of the estimated ~91,000 t per year of the waste materials studied generated in Ireland in 2019 exceeding these limit values (~2800 t). Balanced against this, this material exceeding limit values contains ~7900 t of PBDEs, HBCDD, and TBBP-A or 78% of the total mass of these BFRs associated with the waste materials studied. As noted above, proposals exist to lower the current limit values for PBDEs and HBCDD progressively to 500, 200, and 100 mg/kg. We therefore examined the potential impact of such changes to the limit values (which also assume similar changes in the limit value for TBBP-A to 500, 200, and 100 mg/kg) on the mass of unrecyclable waste generated, compared to changes in the extent to which the limit values remove BFRs from the waste stream. Full results of this evaluation are provided in Tables SD-3, 4, and 5, with a summary provided in Table 5. While lowering the limit value progressively to 500, 200, and 100 mg/kg removes respectively 82, 84, and 85% of ΣBFRs (PBDEs, HBCDD, and TBBP-A) from the waste stream compared to the 78% removed under the existing 1000 mg/kg limit; the mass of waste rendered unrecyclable increases by an estimated 4.0, 4.9, and 5.6% compared to the 3.1% unrecyclable under the current limits. Notwithstanding the clear environmental benefits in minimising the mass of regulated BFRs able to enter the recycling stream; policymakers should take into consideration the associated implications for the circular economy of promulgating stricter limit values in reducing recycling of plastic waste materials. For example, while stricter limits on BFR concentrations in waste eligible for recycling will remove more BFRs; such limits will also increase the mass of plastic waste that cannot be recycled as a result of its POPs content.

4. Conclusions

A comprehensive survey of PBDEs, HBCDD, and TBBP-A entering the waste stream in Ireland in 2019–20 identified that there is a large volume of waste (~2800 t/yr) that exceeds legislative limits on concentrations of such substances and cannot therefore be recycled.

Concentrations of and exceedances of the LPCL for PBDEs, HBCDD, and TBBP-A have remained broadly similar or declined since a previous similar study conducted in 2015–2016. Proportionally fewer samples exceeded the LPCL for PBDEs and HBCDD in 2019–20 (7.8%) than in 2015–16 (8.7%), while those exceeding the limit for TBBP-A declined more markedly from 2.4% in 2015–16 to 0.57% in 2019–20.

Enforcement of the current 1000 mg/kg limit for PBDEs, HBCDD, and TBBP-A would result in removal of 78% of the sum of these BFRs from the Irish recycling stream. Evaluation of the impact of introducing lower limit values reveals this value would increase to 82, 84, and 85% depending on whether the limit was 500, 200, or 100 mg/kg. Conversely, while enforcement of the current limit results in 3.1% of the mass of our target waste categories being unrecyclable; this increases to 4.0, 4.9, and 5.6% when the limit value is 500, 200, and 100 mg/kg respectively. Further research into the implications of such changes to limit values is recommended.

Approximately 97% of the estimated 10,200 kg of PBDEs, HBCDD, and TBBP-A present in the waste categories examined in Ireland in 2019–20 were associated with C&D insulation foam, ELV foams/fabrics, display items, furniture foams, and furniture fabrics. Where monitoring resources are limited, focusing on these waste categories is recommended.

Other halogenated FRs were rarely detected in this study and no significant increase in concentrations of such alt-FRs was detected between 2015–16 and 2019–20 - likely reflecting the long turnover times - i.e. periods of time between manufacture and disposal - of articles falling into the waste categories studied. Despite this, TTBP-TAZ was detected in 3 WEEE samples at between 14,000 and 32,000 mg/kg. Future studies are likely to reveal increasing contamination of the waste stream with such alternative FRs used as replacements for PBDEs, HBCDD, and TBBP-A since their restriction, as items currently in use gradually enter the waste stream.

Author statement

Daniel Drage: Investigation, Writing – review & editing Martin Sharkey: Investigation, Writing – review & editing Layla Salih Al-Omran: Investigation William Stubbings: Investigation Harald Berresheim: Conceptualization, Writing – review & editing, Funding acquisition Marie Coggins: Writing – review & editing André Henrique Rosa: Investigation Stuart Harrad: Conceptualization, Methodology, Formal analysis, Writing – original draft, Writing – review & editing, Funding acquisition.

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Declaration of competing interest

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

Data availability

Data will be made available on request.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.envpol.2022.119796.

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