Elevated concentrations of halogenated flame retardants in waste childcare articles from Ireland

Harrad, Stuart; Drage, Daniel; Sharkey, Martin; Stubbings, Will; Alghamdi, Misbah; Berresheim, Harald; Coggins, Marie; Rosa, André Henrique

DOI:
10.1016/j.envpol.2022.120732

Environmental Pollution 317 (2023) 120732

Contents lists available at ScienceDirect

Environmental Pollution

journal homepage: www.elsevier.com/locate/envpol

Elevated concentrations of halogenated flame retardants in waste childcare articles from Ireland

Stuart Harrad[a,*], Daniel Drage[a,b], Martin Sharkey[c], Will Stubbings[a], Misbah Alghamdi[a], Harald Berresheim[c], Marie Coggins[c], André Henrique Rosa[a,d]

[a] School of Geography, Earth and Environmental Sciences, University of Birmingham, Edgbaston, West Midlands, B15 2TT, United Kingdom
[b] Queensland Alliance for Environmental Health Sciences (QAEHS), The University of Queensland, 20 Cornwall Street, Woolloongabba, QLD, 4103, Australia
[c] School of Natural Sciences & Ryan Institute, National University of Ireland, Galway, H91TK33, Ireland
[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

ARTICLE INFO

Keywords:
Brominated flame retardants
Chlorinated organophosphate esters
Child car seats
Cot mattresses
Waste management

ABSTRACT

Concentrations of legacy and alternative halogenated flame retardants (HFRs) including chlorinated organophosphate esters (Cl-OPEs), were measured in waste childcare articles (n = 275 for Cl-OPEs, n = 187 for other HFRs) from the Republic of Ireland between 2019 and 2020. Articles studied comprised foams and fabrics from: child car seats, cot mattresses, changing mats, pushchairs, prams, and related items. Fifteen articles (7.7%) exceeded the European Union limit value of 1000 mg/kg for polybrominated diphenyl ethers (PBDEs) (all due to BDE-209), an additional 15 exceeded the limit for hexabromocyclododecane (HBCDD), with 7 articles exceeding the limit for both PBDEs and HBCDD. An even greater proportion of articles contained concentrations exceeding 1000 mg/kg for: tris(1-chloro-2-propyl) phosphate (TCIPP) (n = 73, 27%) and tris(1,3-dichloro-2-propyl) phosphate (TDCIPP) (n = 58, 21%), with concentrations greater than 1000 mg/kg also observed for: tris(2-chloroethyl) phosphate (TCEP) (n = 14, 5.1% articles), 2-ethylhexyl tetrabromobenzoate (EH-TBB) (n = 7, 3.7%), decabromodiphenyl ethane (DBDPE), and bis(2-ethylhexyl)tetrabromophthalate (BEH-TEBP) (both n = 5, 2.7%). Overall, 120 samples contained at least one HFR at a concentration exceeding 1000 mg/kg. In addition to the waste management implications of our findings, our data raise concerns about child exposure to HFRs during the use phase of these everyday items.

1. Introduction

In recent years, reports have emerged about the presence of a variety of halogenated flame retardants (HFRs) in childcare items such as cot mattresses and child car seats (Cooper et al., 2016; Stapleton et al., 2011; Wu et al., 2019). HFRs have found application as additives to polyurethane and polystyrene foams and fabric covers used in these and other items to help meet fire safety regulations in various jurisdictions. However, because of their environmental persistence, capacity for transboundary atmospheric transport, ability to bioaccumulate, and toxicity to humans and wildlife; the use of some HFRs, specifically hexabromocyclododecane (HBCDD), as well as the commercial penta-, octa-, and decabromodiphenyl ether products, is now banned under the UNEP Stockholm Convention on Persistent Organic Pollutants (POPs). In addition, although now suspended pending publication of the outcome of an evaluation of the carcinogenicity of TCIPP by the United States Toxicology Program (ECHA, 2019); in 2018 the European Chemicals Agency (ECHA) proposed a ban on the use of the following chlorinated organophosphate esters (Cl-OPEs) in childcare articles: tris (2-chloroethyl) phosphate (TCEP), tris(1-chloro-2-propyl) phosphate (TCIPP), and tris(1,3-dichloro-2-propyl) phosphate (TDCIPP) (ECHA, 2018). Moreover, one potential consequence of the ban on PBDEs and HBCDD without accompanying changes in fire safety regulations, may be increased use of alternative HFRs, such as: decabromodiphenyl ethane (DBDPE) (Wemken et al., 2019), as well as others such as: 2-ethylhexyl tetrabromobenzoate (EH-TBB), and bis(2-ethylhexyl) tetrabromophthalate (BEH-TEBP). In response to reports that recycling of waste articles containing PBDEs and HBCDD has led to their detection as unintentional trace contaminants in items not subject to fire safety regulations like food contact articles (Guzzonato et al., 2017; Puype et al., 2015), the EU has implemented Low POP Concentration Limit (LPCL) values which forbid recycling of waste polymers containing these

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

https://doi.org/10.1016/j.envpol.2022.120732
Received 1 September 2022; Received in revised form 21 November 2022; Accepted 22 November 2022
Available online 22 November 2022

BFRs at concentrations above 1000 mg/kg (European Commission, 2016). Thus, in the event of restrictions on the use of Cl-OPEs, it is not inconceivable that similar limit values will be introduced to limit recycling of these HFRs. Moreover, in Ireland, childcare articles such as car seats, cot mattresses, pushchairs, and prams etc are required to meet the requirements of the Industrial Research and Standards (Fire Safety) (Domestic Furniture) Order of 1995. While the use of chemical additives to meet these requirements is not specified, the use of HFRs is one way in which compliance may be achieved with this Order that requires articles covered by the Order to withstand ignition by a small open flame – specifically a match test.

Against this backdrop, the overall aim of this study was to characterise the presence of HFRs in foams and fabrics from waste childcare items in Ireland. Specific objectives were to evaluate the extent to which: (a) the LPCL values for PBDEs and HBCDD are exceeded in waste childcare articles and (b) concentrations of other HFRs exceed 1000 mg/kg. To achieve our aim and objectives, between 2019 and 2020, we determined as part of the SAFER project: concentrations of PBDEs, HBCDD, Cl-OPEs, and a range of other HFRs in samples of waste foams and fabrics taken from a variety of waste childcare products in Ireland. To our knowledge, this study is one of the most extensive conducted to date and provides the first report on concentrations of HFRs in foams and fabrics from childcare items in Europe.

2. Materials & methods

2.1. Sample collection

Samples of a variety of childcare articles were collected from several waste handling facilities located in the Republic of Ireland between 2019 and 2020. A total of 275 samples were collected from five broad categories of waste childcare articles: car seats; pushchairs; prams; cot mattresses; and changing mats. These categories were further divided as detailed in Table 1 based on the materials collected which included overlaying fabrics (polyurethane and polyvinylchloride) and filling foams (polyurethane foams, wool, expanded polystyrene (EPS), and extruded polystyrene (XPS)).

For most samples, samples of overlaying fabric were collected along with underlying cushioning foams directly beneath the fabric samples; multiple foam samples were taken if various filling materials were present. For pushchairs, little cushioning materials were present, thus samples of fabrics and (if available) foam cushioning were collected using the same methods. In the case of car seats, additional layers of EPS foams were present between a rigid plastic frame as an additional safety feature; samples of these foams were also collected for analysis.

Table 1
Categories and subcategories of waste childcare articles analysed for Cl-OPEs and BFRs in this study.

Category	number analysed for Cl-OPEs	number analysed for BFRs
Child car seat foam	63	40
Child car seat fabrics	88	48
Pushchair foam	11	3
Pushchair fabric	35	31
Pram foam	6	4
Pram fabrics	18	18
Cot mattress foam	13	13
Cot mattress fabric	8	7
Change mat foam	8	8
Change mat fabrics	15	15
Miscellaneous childcare article foam		0
Miscellaneous childcare article fabrics	7	0

2.2. Chemicals and standards

Details of the HFRs targeted in this study as well as details of where reagents and HFR standards were obtained from are provided as supplementary data.

2.3. Sample extraction and clean-up

Full extraction parameters have been reported previously (Abdallah et al., 2017; Drage et al., 2018), with a brief outline provided in supplementary data. Following extraction, diluted extracts were vortexed for 20 s and transferred into vials prior to analysis via gas chromatography-mass spectrometry (GC/MS). Following determination of PBDEs and Cl-OPEs via GC/MS, concentrated extracts were exchanged into 200 μL methanol for measurement of HBCDDs and TBBPA via liquid chromatography-time of flight mass spectrometry (LC-TOF/MS).

2.4. Instrumental analysis

For all samples in which BFR concentrations were determined, analysis of Cl-OPEs, PBDEs (BDEs −17, −28, 47, −99, −100, −153, −154, −183, and −209) and alt-BFRs was performed in a single injection onto 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). The ions (m/z) monitored for quantification/qualification of Cl-OPEs were 249/251 (TCEP), 261/263 (d_{12}-TCEP), 277/279 (TCIPP), 381/379 (TDCIPP), 396/394 (d_{15}-TDCIPP). Full details of BFR ions monitored are provided elsewhere (Abdallah et al., 2017; 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.

In an additional 88 samples, concentrations of Cl-OPEs only were measured. Following sample extraction as outlined above, 1 μL of the final sample extract was injected in splitless mode at 290 °C onto an Agilent 5975 mass selective detector fitted with a DB-5 column (30 m × 0.25 mm id x 0.25 μm film thickness) operated in EI SIM mode. Ions monitored were as given above. The GC temperature programme was: 65 °C for 0.75 min, then 20 °C/min to 250 °C, hold for 1 min, increased at 5 °C/min to 260 °C, then 30 °C/min to 305 °C and hold for 1 min.

Full details of chromatographic separation and full MS parameters used for the determination of concentrations of HBCDDs and TBBPA are reported elsewhere (Drage et al., 2020), with a summary provided in supplementary data.

2.5. Quality control and quality assurance procedures

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 BFRs were found above the limits of detection in the blanks. BFR data were thus 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. Low levels of Cl-OPEs were detected in blank samples. Where the blank concentration was 5–25% of the sample concentration, the sample concentration was corrected by subtracting the blank concentration. If the blank concentration was >25% of the sample concentration, then the sample was reported as < LOQ. LOQs for Cl-OPEs were reported as the average blank concentration (0.02 mg/kg for TCEP and TCIPP; and 0.25 mg/kg for TDCIPP). LOQs for target BFRs 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/g for TBECH, PBT, DPTE, HBB, BTBPE, EH-

TBB, BEH-TEBP, and *anti*-DP; 0.6 mg/g 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 (RSD) of <15%. Full details of method precision and accuracy for BFRs have been reported previously (Abdallah et al., 2017). For Cl-OPEs, in the absence of an appropriate reference material, matrix spikes (of pre-extracted polyurethane foam (PUF) treated with known concentrations of Cl-OPE standards) were performed at 50 mg/kg (n = 5) and 1000 mg/kg (n = 5). All measured values were found to be within 80–120% of the spiked concentrations with a relative standard deviation of <15% (Table S1). 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. Determination of concentrations of elemental Cl using portable XRF

As discussed later, for those samples displaying elevated concentrations of TDCIPP and TCIPP (i.e. >100,000 mg/kg), we also measured elemental Cl, as a check on the accuracy of our GC-MS measurements of these Cl-OPEs at such high concentrations. This was achieved using a Niton XLt3-900 GOLDD portable x-ray fluorescence (XRF) analyser used in its "desktop mode" mounted on a dedicated test-stand to minimise backscatter and background interference. Small samples (min. 2 cm^2) were analysed for 60 s with quantification of elemental Cl achieved using the K α1 and K α2 emission lines. The instrument was used in the plastics operational mode to optimise quantification in fixed thickness low density samples. Calibration was conducted by the instrument manufacturers as described previously (Sharkey et al., 2018).

3. Results & discussion

Table 2 provides a summary of concentrations of those target HFRs detected at >1000 mg/kg in at least one sample. The same table also gives the percent of samples that contain a given HFR at >1000 mg/kg. A full list of concentrations of all HFRs targeted in each sample are provided as supplementary information (Table S2). Fig. 1 shows the percent of childcare articles in this study that contained >1000 mg/kg for various HFRs. Fig. 2 depicts the percent of articles containing >1000 mg/kg for various HFRs according to the article category. It is important to note that we were unable to obtain information about the date or jurisdiction of manufacture of the articles analysed in this study. We are therefore unable to evaluate the impact of where and when the article was manufactured – and thus concomitant temporal and geographical variation in fire safety regulations - on the HFR concentrations detected.

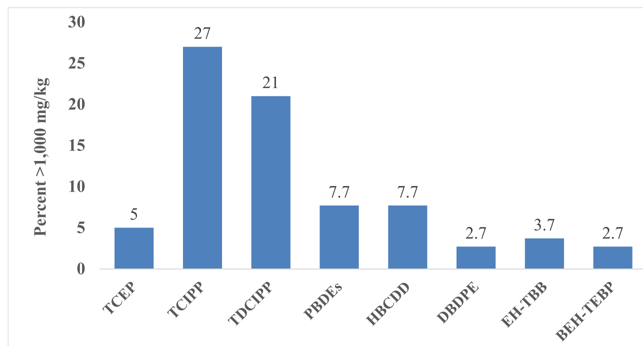

Fig. 1. Percent of hildcare articles >1000 mg/kg for various HFRs.

Table 2
Summary of concentrations (mg/kg) of selected HFRs in waste childcare article foam and fabric samples from Ireland.

Waste Category	Statistical parameter	TCEP	TCIPP	TDCIPP	ΣPBDEs	DBDPE	EH-TBB	BEH-TEBP	∑HBCDD
Child car seats	Median	6.7	120	15	4.8	<LOD	<LOD	<LOD	1.3
	Average	1400	3600	25,000	1900	6.2	2800	1100	500
	Maximum	66,000	51,000	390,000	23,000	220	100,000	39,000	7400
	%>1000 mg/kg	9.3	25	33	7.3	0	4.7	3.3	7.3
Pushchairs	Median	1.4	40	<LOD	6.9	0.0	<LOD	<LOD	1.3
	Average	9.0	510	2300	630	80	0.15	<LOD	5.1
	Maximum	270	11,000	80,000	11,200	1200	5.2	<LOD	74
	%>1000 mg/kg	0	6.1	4.1	4.1	2.0	0	0	0
Prams	Median	0.49	580	72	11	<LOD	<LOD	<LOD	2.5
	Average	15	5600	13,000	870	1200	0.82	<LOD	7700
	Maximum	270	52,000	170,000	11,203	9600	18	<LOD	140,000
	%>1000 mg/kg	0	33	21	8.3	17	0	0	17
Cot mattresses	Median	1.1	310	<LOD	0.59	0.06	<LOD	<LOD	0.33
	Average	2.0	16,000	0.3	37	0.12	0.05	<LOD	0.35
	Maximum	11.0	170,000	2.9	590	0.46	0.54	<LOD	1.3
	%>1000 mg/kg	0	38	0	0	0	0	0	0
Change mats	Median	1.8	1100	<LOD	5.2	<LOD	<LOD	<LOD	1.0
	Average	7.0	13,000	3900	4.6	<LOD	0.96	<LOD	1.0
	Maximum	48	84,000	60,000	11	0	12	<LOD	1.5
	%>1000 mg/kg	0	52	8.7	0	0	0	0	0
Miscellaneous childcare articles	Median	0.51	640	4.6	–	–	–	–	–
	Average	0.55	5000	110	–	–	–	–	–
	Maximum	0.86	44,000	570	–	–	–	–	–
	%>1000 mg/kg	0	50	0	–	–	–	–	–
Childcare articles overall	Median	2.4	140	3.2	6.4	<LOD	<LOD	<LOD	1.2
	Average	800	5700	16,000	1100	160	1400	540	1200
	Maximum	66,000	170,000	390,000	23,000	9600	100,000	39,000	140,000
	%>1000 mg/kg	5.0	27	21	7.7	2.7	3.7	2.7	7.7

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

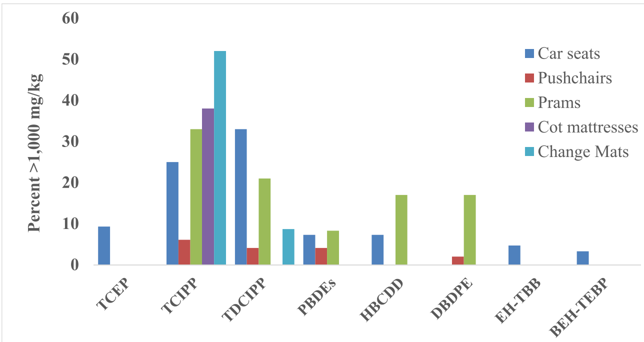

Fig. 2. Percent of childcare articles >1000 mg/kg for various HFRs according to waste category.

3.1. Concentrations of PBDEs and HBCDD and exceedances of the LPCL in Irish waste childcare article samples collected in 2019–20

Table 2 provides a summary of 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 reports the percent of samples that exceeded the current LPCL for PBDEs and HBCDD of 1000 mg/kg. Out of the 187 samples overall, 8.0% (n = 15) exceed the LPCL for ΣPBDEs, with all exceedances due to BDE-209 which was by far the dominant PBDE congener detected. The same proportion of samples overall exceeded the LPCL for ΣHBCDD. For BDE-209, all samples containing >1000 mg/kg were fabric coverings. By contrast, while 9 samples containing HBCDD at >1000 mg/kg were fabrics, 5 were expanded polystyrene (EPS) components, with one (which contained the maximum ΣHBCDD concentration in this study) underlay material from a pram. There were no exceedances for either PBDEs or HBCDD for change mats and cot mattresses, with zero exceedances for HBCDD also observed for pushchairs. Instead, exceedances were observed for car seats and prams (both PBDEs and HBCDD), as well as pushchairs for PBDEs. Maximum concentrations detected were 23,000 mg/kg (i.e. 2.3%) and 140,000 mg/kg (i.e. 14%) for ΣPBDEs and ΣHBCDD respectively, indicating intentional use of these BFRs in such articles. Data from a previous study on 101 samples of foam taken from similar childcare articles acquired in the USA in 2010, reported concentrations of those congeners associated with the Penta-BDE formulation to be on average 32,000 mg/kg, with a range of 17,000-52,000 mg/kg (Stapleton et al., 2011). In contrast, a more recent study of 10 foam samples from childcare articles (changing pads, sleep positioners, and bath products) collected in the USA in 2015, did not detect either PBDEs or HBCDD above the detection limit of 1 mg/kg (Gloekler et al., 2021). Likewise, in 18 child car seats purchased in the USA in 2018, only BDEs 28, 47, and 49 were detected, with the maximum concentration being 5.9 mg/kg of BDE-49 (Wu et al., 2019). While based on comparison with relatively few data from North America; our data suggest more recent BFR use in childcare articles in Ireland than in the USA. In line with concentrations of PBDEs in indoor dust from Ireland collected in 2016–17 (Wemken et al., 2019), the PBDE profile in childcare products in Ireland is predominantly BDE-209, with lower brominated congeners associated with the Penta-BDE formulation rarely detected.

3.2. Concentrations of chlorinated organophosphate esters in Irish waste childcare article samples

Concentrations of TCEP, TCIPP, and TDCIPP detected in this study, along with the percent of samples containing one or more of these Cl-OPEs at >1000 mg/kg, are summarised in Table 2. In summary, out of the 274 samples analysed for these Cl-OPEs, concentrations exceeded 1000 mg/kg in 27% (n = 73), 21% (n = 58), and 5.0% (n = 14) of samples for TCIPP, TDCIPP, and TCEP respectively. Samples for which concentrations exceeded 1000 mg/kg for TCIPP were observed in each of the different sample categories studied; reflected by average TCIPP concentrations of: 3600 mg/kg, 510 mg/kg, 5600 mg/kg, 16,000 mg/kg, 13,000 mg/kg, and 5000 mg/kg in car seats, pushchairs, prams, cot mattresses, change mats, and miscellaneous childcare articles respectively. In car seats, pushchairs, prams, and change mats, at least one sample of each such waste category contained TDCIPP at >1000 mg/kg, with average concentrations in these categories being: 25,000 mg/kg, 2300 mg/kg, 13,000 mg/kg, and 3900 mg/kg respectively. By comparison, samples displaying TCEP concentrations >1000 mg/kg were only observed in car seats. These findings point to widespread intentional use of Cl-OPEs in childcare articles.

A particularly notable feature of our data is that for a small number of samples, we recorded some very high concentrations of TDCIPP and to a lesser extent TCIPP – up to 390,000 mg/kg (39%) of TDCIPP in one instance. In total, there were 12 samples for which concentrations of TDCIPP or TCIPP exceeded 100,000 mg/kg (10%). For each of these samples which comprised 9 car seats, 2 prams, and 1 cot mattress, we converted our concentrations of TDCIPP and TCIPP (as the major Cl-OPEs detected) into an equivalent Cl concentration by multiplying the TDCIPP concentration by the fraction of TDCIPP that is Cl – i.e. 213/430.89 = 0.494 and adding this to the equivalent Cl concentration for TCIPP derived in similar fashion. We then compared these Cl equivalent TDCIPP + TCIPP concentrations with the concentration of elemental Cl measured in the same samples using portable XRF. These data are presented in Table 3. Overall, there is broad agreement between the two measurements of Cl. Specifically, for only two of the samples examined in this way, did our Cl equivalent TDCIPP + TCIPP concentrations exceed the concentration of elemental Cl measured in the same sample. For those two samples, the discrepancy is relatively minor and is likely attributable to uncertainties of measurement associated with both techniques, as well as inhomogeneous distribution of Cl-OPEs within the products in question, as the sub-samples used for GC-MS and XRF analysis were not identical. Overall however, the data provided in Table 3 provides additional assurance that the very high TDCIPP and TCIPP concentrations detected in some samples are genuine.

Interestingly, while most samples containing at least Cl-OPE at >1000 mg/kg were polyurethane foam (PUF) fillings; we also detected high TCIPP and TDCIPP concentrations in 9 polyvinyl chloride (PVC) coverings of change mats. In 5 instances, concentrations exceeded 29,000 mg/kg, with TDCIPP present at 60,000 mg/kg in one case. Moreover, concentrations of TCIPP, TDCIPP, and TCEP exceeded 1000 mg/kg in 25, 25, and 5 fabric covering samples respectively. In every such instance, the concentration of the Cl-OPE in question was >1000 mg/kg in a PUF sample from the same childcare item. This suggests that Cl-OPEs added intentionally to foam filling material, transfer to overlying fabric coverings.

We compared our data for Ireland with those reported for foam samples obtained from childcare articles in previous studies from the USA. The largest such study reported concentrations of Cl-OPEs in 101 such samples collected in 2010 (Stapleton et al., 2011). The products tested comprised: car seats (n = 21), changing table pads (n = 16), infant sleep positioners (n = 15), portable crib mattresses (n = 13), and nursing pillows (n = 11), plus a few miscellaneous others. Average concentrations (range in parentheses) of TCEP, TCIPP, and TDCIPP were: 5900 (1100-5900), 5500 (1100-14,000), and 39,000 (2400–120,000) mg/kg respectively. A later study measured Cl-OPEs in child car seats (n = 98), child mattresses (n = 36), and other childcare products (n = 49) collected in 2014–16 in the USA (Cooper et al., 2016). The authors reported on whether an article contained an FR using a definition of a concentration >10,000 mg/kg. Based on this definition, 50%, 14%, and 29% of car seats, child mattresses, and other childcare articles respectively contained TDCIPP, with corresponding figures for TCIPP being: 27%, 8.3%, and 22%. Meanwhile, detection frequencies of TCEP, TCIPP, and TDCIPP in 36 samples of fabric and foam collected from 18 child car

Table 3
Comparison of concentrations of TDCIPP and TCIPP with those of elemental chlorine in samples containing >100,000 mg/kg TDCIPP or TCIPP.

Sample type	TDCIPP	TDCIPP as Cl[a]	TCIPP	TCIPP as Cl[a]	ΣTDCIPP + TCIPP	ΣTDCIPP + TCIPP as Cl[a]	XRF-Cl[b]
Car seat 2.3b	160,000	79,000	570	190	160,000	79,000	140,000
Car seat 5.1b	270,000	130,000	410	130	270,000	130,000	250,000
Car seat 5.2b	390,000	190,000	520	170	390,000	190,000	320,000
Car seat 7.1b	240,000	120,000	51,000	17,000	290,000	140,000	360,000
Car seat 7.2b	160,000	79,000	39,000	13,000	200,000	92,000	260,000
Car seat 7.3	210,000	100,000	45,000	15,000	260,000	120,000	330,000
Car seat 19.1b	280,000	140,000	2700	880	280,000	140,000	110,000
Car seat 20.1b	290,000	140,000	1300	420	290,000	140,000	250,000
Car seat 20.2b	370,000	180,000	960	310	370,000	180,000	290,000
Cot Mattress	<LOD	–	170,000	55,000	170,000	55,000	88,000
Pram 3.3	130,000	65,000	52,000	17,000	184,000	82,000	73,000
Pram 4.3b	170,000	83,000	38,000	12,000	210,000	95,000	160,000

[a] Concentration of Cl-OPE expressed as equivalent concentration of elemental Cl.
[b] Concentration of elemental Cl measured using portable XRF (average of 3 measurements).

seats purchased in 2018 in the USA were 25%, 8%, and 19%; with maximum concentrations of TCEP, TCIPP, and TDCIPP being: 0.16, 0.68, and 0.94 mg/kg (Wu et al., 2019). The most recent study measured TCIPP and TDCIPP in 10 foam samples from childcare articles on the US market (Gloekler et al., 2021). TCIPP was detected in all samples tested (range 149–38,400 mg/kg) and TDCIPP in a single sample at 75 mg/kg.

Overall, our data on Cl-OPE concentrations in childcare foam and fabric samples collected in Ireland in 2019–20 are broadly consistent with those reported in the USA, although TDCIPP appears essentially absent from USA articles purchased after 2011 likely because of its addition to Proposition 65 in California in 2011 (Cooper et al., 2016). Such restrictions are not in place in Ireland and may explain why TDCIPP is the major HFR detected in this study.

3.3. Concentrations of other halogenated FRs in Irish waste childcare article samples

Of the other HFRs targeted in this study, only three (DBDPE, EH-TBB, and BEH-TEBP) were detected at >1000 mg/kg in at least one sample. Concentrations of these HFRs exceeded 1000 mg/kg in 5 (2.7%), 7 (3.7%), and 5 (2.7%) of articles tested with maximum concentrations of 9,600, 100,000, and 39,000 mg/kg for DBDPE, EH-TBB, and BEH-TEBP respectively. With respect to the latter two HFRs, we calculated the fraction of EH-TBB ($f_{\text{EH-TBB}}$) in the 7 articles in which the concentration of the former >1000 mg/kg. In line with a previous report (Ma et al., 2012), $f_{\text{EH-TBB}}$ is calculated as:

$$f_{\text{EH}-\text{TBB}} = [\text{EH}-\text{TBB}] / ([\text{EH}-\text{TBB}] + [\text{BEH}-\text{TEBP}]) \tag{1}$$

Values of $f_{\text{EH-TBB}}$ ranged between 0.70 and 0.80, with a median of 0.73 and an arithmetic mean of 0.74. These data are in very close agreement with the value of 0.77 reported elsewhere for the flame retardant commercial formulation known as Firemaster-550 (FM-550) (Ma et al., 2015). We therefore suspect strongly that the articles in question had been treated with either FM-550 or Firemaster-BZ54 (FM-BZ54), which also contains EH-TBB and BEH-TEBP at a similar ratio to FM-550 (Ma et al., 2012).

The detection of DBDPE in a small number of childcare articles at up to 9600 mg/kg is unsurprising given we recently reported elevated concentrations of DBDPE in indoor air and dust from Ireland (Wemken et al., 2019). Moreover, the maximum concentration we detected is nearly 40 times the maximum concentration of 248 mg/kg reported in a study of 18 child car seats purchased in the US (Wu et al., 2019). We did not measure either EH-TBB or BEH-TEBP in our study of indoor air and dust, however both have been detected frequently in indoor air and dust from the UK (Tao et al., 2016) but at concentrations that are an order of magnitude below those of HBCDD and BDE-209 and not suggestive of widespread use in Ireland. While we do not have information about the provenance of the articles containing elevated EH-TBB and BEH-TEBP, we believe it plausible that they were imported directly from the USA where FM-550 and FM-BZ54 were used widely (Ma et al., 2012). However, we note that neither EH-TBB and BEH-TEBP were detected in a study of 18 child car seats purchased in the USA (Wu et al., 2019).

3.4. Human exposure implications of HFR concentrations detected

While not the primary focus of this study, given that all articles examined were no longer in use; there is clear potential for exposure to our target FRs of young children using similar items. Indeed, it is likely that HFR concentrations in the articles analysed in this study and thus associated exposure of users will be lower than when first purchased. Several authors have highlighted such exposure to occur via a variety of pathways, specifically: inhalation of volatilised FRs (Stapleton et al., 2011), and dermal uptake via direct contact with treated items (Stapleton et al., 2011; Gloekler et al., 2021). Moreover, young children are likely to mouth materials with which they are in close contact, with such contact highlighted as a substantial potential exposure pathway to PBDEs for children mouthing plastic toys (Ionas et al., 2016). Other studies have demonstrated significant correlation between concentrations in infants of BDCIPP (bis(1,3-dichloro-2-propyl) phosphate) (a urinary metabolite of TDCIPP) and reported numbers of foam containing childcare articles owned by parents. Moreover, participants with more than 16 infant products had BDCIPP levels 6.8 times those of infants with fewer than 13 products (Hoffman et al., 2015). A later study found that estimated TDCIPP exposure of US infants was a potential health risk. Exposures were estimated based on BDCIPP concentrations in urine and ranged from 0.01 to 15.03 μg/kg bw/day compared to the US Consumer Product Safety Commission's acceptable daily intake of 5 μg TDCIPP/kg bw/day for non-cancer health risks. Depending on modeling assumptions, the authors found that 2−9% of infants had TDCIPP intake estimates above this threshold (Hoffman et al., 2017).

Given the difficulties in deriving reliable estimates of exposure, for instance, while data exist on dermal uptake of Cl-OPEs, Penta-BDE, and HBCDD from furniture fabrics (Abdallah and Harrad, 2018; Abdallah and Harrad, 2022), the exact extent to which such uptake is mitigated by the barriers presented by sheets covering cot mattresses and infant clothing, is unknown; we have not attempted to quantify exposure here. Notwithstanding this, we note that a dermal exposure estimate of 1.57 μg TCIPP/kg bw/day was derived from infant contact with an uncovered foam bath product containing 21,600 mg/kg TCIPP (Gloekler et al., 2021). Six articles in our study contained TCIPP at concentrations above this (Table 3), with a further 11 articles exceeding this concentration level for TDCIPP. Studies of the exposure levels arising from use of childcare articles containing halogenated FRs and related chemicals and the risk these present are recommended.

4. Conclusions

A comprehensive survey of a variety of HFRs in waste childcare items sampled in 2019–20 in Ireland identified that a high proportion of such items contain one or more HFRs at concentrations exceeding 1000 mg/kg. Notably, 44% of articles analysed in this study contained at least 1 HFR at a concentration >1000 mg/kg, with 12% of articles exceeding the legislative limit for PBDEs or HBCDD, meaning that the article concerned cannot be recycled, therefore presenting a substantial issue for the management of such chemicals in the waste stream. Moreover, while the samples tested in this study were diverted from the waste stream, the presence in these items previously used by infants and young children of a wide range of chemicals that are either banned or under consideration for similar restriction is of concern. In particular, the potential for exposure of infants using such articles appears substantial and represents an urgent research priority.

Credit author statement

Stuart Harrad: Supervision; Writing – Original manuscript preparation; Funding acquisition, **Daniel Drage**: Investigation; Writing – review & editing, **Martin Sharkey**: Investigation; Writing – review & editing, **Will Stubbings**: Investigation; Writing – review & editing, **Misbah Alghamdi**: Investigation; Writing – review & editing, **Harald Berresheim**: Supervision; Writing – review & editing; Funding acquisition, **Marie Coggins**: Supervision; Writing – review & editing, **André Henrique Rosa**: Investigation; Writing – review & editing

Funding

This project (SAFER, reference 2018-RE-LS-3) is funded under the EPA Research Programme 2014-2020. The EPA Research Programme is a Government of Ireland initiative funded by the Department of Communications, Climate Action, and Environment. A.H. Rosa thanks the São Paulo Research Foundation (FAPESP, grants 2019/06800–5; 2022/00985–6) for fellowship and financial support. M. Alghamdi acknowledges her PhD scholarship award from the Department of Laboratory Medicine, Faculty of Applied Medical Sciences, Umm al-Qura University, Mecca, Saudi Arabia. Scholarship decision reference 4001065578.

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.2022.120732.

References

Abdallah, M.A.-E., Drage, D.S., Sharkey, M., Berresheim, H., Harrad, S., 2017. A rapid method for the determination of brominated flame retardant concentrations in plastics and textiles entering the waste stream. J. Separ. Sci. 40, 3749–3922.
Abdallah, M.A.-E., Harrad, S., 2018. Dermal contact with furniture fabrics is a significant pathway of human exposure to brominated flame retardants. Environ. Int. 118, 26–33.
Abdallah, M.A.-E., Harrad, S., 2022. Dermal uptake of chlorinated organophosphate flame retardants via contact with furniture fabrics, implications for human exposure. Environ. Res. 209, 112847.
Cooper, E.M., Kroeger, G., Davis, K., Clark, C.R., Ferguson, P.L., Stapleton, H.M., 2016. Results from screening polyurethane foam based consumer products for flame retardant chemicals: assessing impacts on the change in the furniture flammability standards. Environ. Sci. Technol. 50, 10653–10660.
Drage, D.S., Sharkey, M., Abdallah, M.A.-E., Berresheim, H., Harrad, S., 2018. Brominated flame retardants in Irish waste polymers: concentrations, legislative compliance, and treatment options. Sci. Total Environ. 625, 1535–1543.
Drage, D.S., Waiyarat, S., Harrad, S., Abdallah, M.A.E., Boontanon, S.K., 2020. Temporal trends in concentrations of legacy and novel brominated flame retardants in house dust from Birmingham in the United Kingdom. Emerg. Contam. 6, 323–329.
Draft Screening Report – an Assessment of whether the Use of TCEP, TCPP, and TDCP in Articles Should Be Restricted, 2018. ECHA. Available at: https://echa.europa.eu/documents/10162/df7715f2-e413-8396-119b-63f929bcde0c. accessed 11th July 2022.
ECHA, 2019. Registry of Restriction Intentions until Outcome accessed 11th July 2022. https://echa.europa.eu/registry-of-restriction-intentions/-/dislist/details/0b0236e1829a30b8.
European Commission, 2016. Commission regulation (EU) 2016/460 of 30 March 2016 amending Annexes IV and V to regulation No 850/2004 of the European Parliament and of the Council on persistent organic pollutants. Off. J. Eur. Commun.
Gloekler, L.E., Barlow, C.A., Tvermoes, B., La Guardia, M.J., Sahmel, J., 2021. A pilot study to characterize hand-to-mouth transfer efficiency of organophosphate flame retardants identified in infant products. Hum. Ecol. Risk Assess. 27, 2288–2310.
Guzzonato, A., Puype, F., Harrad, S., 2017. Evidence of bad recycling practices: BFRs in children's toys and food-contact articles. Environ. Sci.: Process. Impacts 19, 956–963.
Hoffman, K., Butt, C.M., Chen, A., Limkakeng, A.T., Stapleton, H.M., 2015. High exposure to organophosphate flame retardants in infants: associations with baby products. Environ. Sci. Technol. 49, 14554–14559.
Hoffman, K., Gearhart-Serna, L., Lorber, M., Webster, T.F., Stapleton, H.M., 2017. Estimated tris(1,3-dichloro-2-propyl) phosphate exposure levels for U.S. Infants suggest potential health risks. Environ. Sci. Technol. Lett. 4, 334–338.
Ionas, A.C., Ulevicus, J., Gómez, A.B., Brandsma, S.H., Leonards, P.E.G., van de Bor, M., Covaci, A., 2016. Children's exposure to polybrominated diphenyl ethers (PBDEs) through mouthing toys. Environ. Int. 87, 101–107.
Ma, Y., Venier, M., Hites, R.A., 2012. 2-Ethylhexyl tetrabromobenzoate and bis(2-ethylhexyl) tetrabromophthalate flame retardants in the great lakes atmosphere. Environ. Sci. Technol. 46, 204–208.
Puype, F., Samsonek, J., Knoop, J., Egelkraut-Holtus, M., Ortlieb, M., 2015. Evidence of waste electrical and electronic equipment (WEEE) relevant substances in polymeric food-contact articles sold on the European market. Fd. Add. Contam. A 32, 410–426.
Sharkey, M., Abdallah, M.A.-E., Drage, D.S., Harrad, S., Berresheim, H., 2018. Portable X-ray fluorescence for the detection of POP-BFRs in waste plastics. Sci. Total Environ. 639, 49–57.
Stapleton, H.M., Klosterhaus, S., Keller, A., Ferguson, P.L., van Bergen, S., Cooper, E., Webster, T.F., Blum, A., 2011. Identification of flame retardants in polyurethane foam collected from baby products. Environ. Sci. Technol. 45, 5323–5331.
Tao, T., Abdallah, M., Harrad, S., 2016. Emerging and legacy flame retardants in UK indoor air and dust: evidence for replacement of PBDEs by emerging flame retardants? Environ. Sci. Technol. 50, 13052–13061.
Tongue, A.D.W., Fernie, K., Harrad, S., Drage, D.S., McGill, R.A.R., Reynolds, J., 2021. Interspecies comparisons of brominated flame retardants in relation to foraging ecology and behaviour of gulls frequenting a UK landfill. Sci. Total Environ. 764, 142890.
Wemken, N., Drage, D.S., Abdallah, M.A.-E., Harrad, S., Coggins, M.A., 2019. Concentrations of brominated flame retardants in indoor air and dust from Ireland reveal elevated exposure to decabromodiphenyl ethane. Environ. Sci. Technol. 53, 9826–9836.
Wu, Y., Miller, G.Z., Gearhart, J., Romanak, K., Lopez-Avila, V., Venier, M., 2019. Children's car seats contain legacy and novel flame retardants. Environ. Sci. Technol. Lett. 6, 14–20.