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POP-BFRs in consumer products: Evolution of the efficacy of XRF screening for legislative compliance over a 5-year interval and future trends

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

[a] *Physics Unit, School of Natural Sciences, National University of Ireland Galway, Galway City H91 CF50, Ireland*
[b] *School of Geography, Earth, and Environmental Sciences, University of Birmingham, Edgbaston, West Midlands B15 2TT, United Kingdom*
[c] *Queensland Alliance for Environmental Health Sciences (QAEHS), University of Queensland, 20 Cornwall Street, Woolloongabba, QLD 4103, Australia*
[d] *Institute of Science and Technology, São Paulo State University (UNESP), Av. Três de Março 511, Alto da Boa Vista, Soracaba, SP 18087-180, Brazil*

HIGHLIGHTS

- Reduced XRF screening efficacy due in part to decreased prevalence of POP-BFRs
- Higher likelihood of false exceedances in electrical and electronic goods
- Five-second XRF analysis time sufficient to screen for legislative compliance
- Elemental Sb not a qualifier for POP-BFRs, but may be suitable for ΣBFRs
- XRF as a rapid screening tool still necessary to ensure legislative compliance

GRAPHICAL ABSTRACT
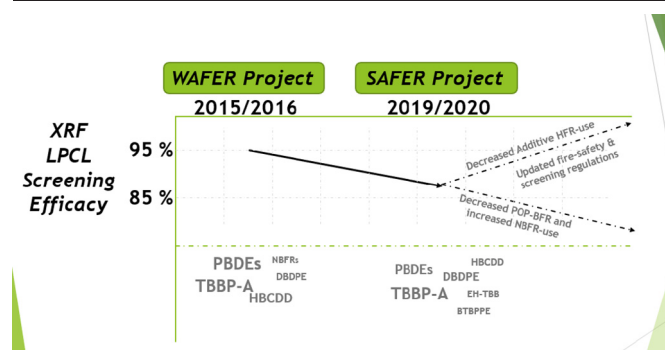
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ABSTRACT

In 2015–16, a study of approximately 500 waste plastic articles showed that portable X-ray fluorescence (XRF) was up to 95 % effective in screening for compliance with low persistent organic pollutant (POP) concentration limits (LPCLs) on brominated flame retardants (BFRs) in waste. The present study conducted in 2019–20 mirrors that conducted five years prior on a similar number and range of articles, testing the hypothesis that increased use of alternative BFRs as replacements for POP-BFRs will reduce the effectiveness of XRF as a tool for monitoring compliance with LPCLs. In comparing the results, the overall screening efficacy for LPCL compliance reduced from ~95 % to ~88 %, due in part to decreased prevalence of POP-BFRs and potentially increased presence of alternative flame retardants, particularly in goods with shorter lifecycles such as electronics. We additionally examined the impacts of a number of modifications to the XRF measurement protocol on its efficacy, including: using elemental Sb as a qualifier in detecting POP-BFRs in hard plastics; reduced XRF analysis time; and the elimination of background interference using a test stand. The rate at which hard plastics from electronic waste may be analysed by XRF can be substantially improved by reducing analysis time to 5 s, with minimal increase in false exceedances of the LPCL. Monitoring Sb does not appear an effective qualifier for the presence of POP-BFRs, as Sb seems to be used with a range of BFRs. Use of the test stand, while reducing interference, appeared to reduce accuracy when screening low density and thin samples. Despite a seeming increased use of alternative BFRs, screening of waste for compliance with LPCLs using rapid and low-cost screening methods such as portable XRF is still necessary as methods such as GC–MS cannot be scaled up to match the quantities of waste requiring screening.

1. Introduction

In the last half century, the vast increase in the quantities of plastics used in consumer articles has led to a commensurate rise in fire safety concerns due to the inherent flammability of polymer-based items (Junod, 1976). In the UK and Ireland for example, upholstered furniture is required to pass stringent ignition tests including the smouldering (i.e. cigarette), open flame (match), and "crib 5/7" (adjacent fire source) tests (BSI, 2006). One method for achieving this level of flame retardancy is through the use of chemicals such as halogenated flame retardants (HFRs) (van Esch, 1997). Over the last few decades, certain brominated flame retardants (BFRs) including polybrominated diphenyl ethers (PBDEs) and hexabromocyclododecane (HBCDD) have found widespread application: PBDEs and HBCDD in the textiles and foams of upholstered furniture and vehicle seating; HBCDD in insulation foams for buildings; and PBDEs and HBCDD in hard plastic casings of electronic equipment (Eljarrat and Barceló, 2011) (Drage et al., 2018). However, these chemicals display environmentally hazardous properties such as: environmental persistence; propensity for long-range environmental transport; ability to bioaccumulate and/or biomagnify; and toxicity to living organisms (Eljarrat and Barceló, 2011), which has resulted in PBDEs and HBCDD being listed as persistent organic pollutants (POPs) by the UNEP Stockholm Convention (UNEP, 2019).

Issues persist from these now-restricted chemicals due to their extensive historical use and because some of their applications (e.g. sofas) have turn-over times of a decade or more. As a consequence, items containing such BFRs will continue entering the waste stream for the foreseeable future, causing compliance issues for waste management operations and potential for further environmental contamination. One issue of concern is that uncontrolled recycling of products containing regulated BFRs at concentrations intended to meet fire safety regulations can lead to unintended contamination of new products partially or wholly made from recycled materials, for example: contamination of polystyrene packaging foams from reuse/recycling of polystyrene insulation foams (Abdallah et al., 2018; Knutsen and Arp, 2021); reuse of textiles contaminating down-cycled products such as carpet foams and mechanically recycled textiles (Bartl and Ipsmiller, 2021, Ipsmiller and Bartl, 2021, Sharkey et al., 2018); and recycling of hard plastic casings from e.g. electrical equipment into items such as kitchen utensils and children's products (Guzzonato et al., 2017; Kuang et al., 2018). In order to prevent such unintentional contamination, the EU has promulgated low POP concentration limits (LPCLs) for PBDEs and HBCDD. Waste containing concentrations of such BFRs that exceed the LPCL cannot be recycled and instead must be treated in such a way that its POP content is destroyed or irrevocably transformed. We recently completed a study of waste plastics collected in Ireland in 2015–16 that concluded that effective implementation of LPCLs would be highly effective in removing PBDEs and HBCDD from the waste stream (Harrad et al., 2019). However, it is apparent that without cost-effective methods for identifying waste articles exceeding LPCLs, there is a danger that a precautionary approach will be adopted whereby all plastics will be deemed non-recyclable, with concomitant adverse implications for the EU's move towards a Circular Economy.

These issues have driven evaluation of various rapid and low-cost methods for screening of waste for compliance with legislative limits such as LPCLs, as conventional quantification methods (such as GC–MS and LC-MS) are too expensive and time-consuming to be viable on the scales required (Harrad et al., 2019). Among the more promising of these rapid screening methods is portable X-ray fluorescence (XRF) which can quantify the elemental content (including bromine) of polymer-based materials in a very user-friendly (essentially point-and-shoot), relatively cheap (typical analyser costing ca. €30,000 but with minimal consumable costs after capital outlay), and rapid way (analysis time typically between 30 and 60 s). Some studies investigating XRF found it effective in screening various waste materials for their PBDE and HBCDD content (Gallen et al., 2014; Jeannerat et al., 2016; Kajiwara et al., 2011; Sharkey et al., 2018).

However, these studies have also shown that screening for legislative compliance using portable XRF is as yet an imperfect method. For instance,

the exact quantification of elemental Br in plastic materials is subject to error, due in part to the attenuation of primary and secondary X-rays in the low density matrices (e.g. hard plastics, textiles) and the additional air in expanded materials (e.g. insulation and cushioning foams). Another major issue is the inability of XRF screening to determine the exact chemical form of the Br detected. As LPCLs only cover certain BFRs, the presence of another non-regulated BFR results in a so-called "false exceedance", thereby incorrectly designating the material as hazardous with regards to POP content. In this context, an important consequence of restrictions on BFRs like PBDEs and HBCDD is an increased prevalence of alternatives which in turn would lead to an increase in false-exceedances as the phase-out of restricted BFRs continues (Blum et al., 2019; Drage et al., 2022). Given that such false exceedances of LPCLs were often due to high concentrations of other BFRs such as tetrabromobisphenol-A (TBBP-A) and decabromodiphenyl ethane (DBDPE) that are also of environmental concern, Harrad et al. (2019) argued that the rate of false exceedances detected in our 2015–16 study (ca 5 % of all LPCL exceedances identified by XRF) may be deemed acceptable. However, this may not remain the case should the false exceedance rate increase substantially as a consequence of a shift from PBDEs and HBCDD towards novel brominated flame retardants (NBFRs) and other HFRs.

The study reported here follows on from prior work conducted by the project team in 2015–16 (Harrad et al., 2019; Sharkey et al., 2018), with several refinements based on subsequent developments. The XRF screening methodology used was updated to control for factors noted previously such as background interference. Further modifications of the screening methodology were also investigated, including: the potential use of elemental Sb (typically Sb_2O_3, a synergist commonly used with PBDEs (Guzzonato et al., 2017)) as a qualifier specifically intended to distinguish between Br derived from PBDEs and that from other BFRs; and a reduction in screening time towards a potentially more rapid throughput of waste materials without an increase in false-exceedances. A much broader suite of BFRs were also investigated in the collected samples (Table 1, Drage et al. (2022)), thereby facilitating evaluation of the extent to which false exceedances of LPCLs are attributable to the presence of BFRs other than PBDEs and HBCDD. Overall therefore, this study evaluates the extent to which portable XRF remains an effective method of evaluating compliance with LPCLs on POP BFRs, against the rapidly-evolving regulatory and chemical landscape regarding BFR and HFR use in consumer goods.

2. Materials and methods

2.1. Materials

Chemical standards for native BDEs -28, -47, -77, -99, -100, -128, -153, -154, -183, and -209, DBDPE, α- and β-TBECH, BTBPE, EH-TBB, BEH-TEBP,

Table 1

Brominated flame retardants (BFRs) quantified through mass-spectrometric analysis (see Section 2) including relevant hazard labels as recognised by the European Chemicals Agency.

Acronym	Chemical compound/family	Restrictions/hazard labels
PBDEs	Polybrominated diphenyl ether	Persistent organic pollutant
HBCDD	Hexabromocyclododecane	Persistent organic pollutant
TBBP-A	Tetrabromobisphenol-A	H400, H410
DBDPE	Decabromodiphenyl ethane	H413 (under PBT assessment)
TBECH	Tetrabromocyclohexane	H302, H411
BTBPE	1,2-Bis(2,4,6-tribromophenoxy) ethane	H315, H318, H335
TTBP-TAZ	2,4,6-Tris (tribromophenoxy)-1,3,5-triazine	(Under PBT assessment)
EH-TBB	2-Ethylhexyl-2,3,4,5-tetrabromobenzoate	None
BEH-TEBP	Bis(2-ethylhexyl) tetrabromophthalate	H319, vPvB (under PBT assessment)
HBB	Hexabromobenzene	H302, H312, H315, H319, H332, H335, H413
PBT	Pentabromotoluene	H315. H319, H335, H400, H410

HBB, PBT native α-HBCDD, β-HBCDD, γ-HBCDD, $^{13}C_{12}$-BDE-209, $^{13}C_{12}$-α-HBCDD, $^{13}C_{12}$- β-HBCDD, $^{13}C_{12}$-γ-HBCDD, $^{13}C_{12}$-TBBP-A, $^{13}C_6$-BTBPE, d_{17}-$^{13}C_6$-EH-TBB, d_{17}-$^{13}C_6$-BEH-TEBP and $^{13}C_6$-HBB were purchased from Wellington Laboratories (Guelph, ON, Canada). All solvents (HPLC grade hexane, dichloromethane (DCM), and Optima LC/MS grade methanol (MeOH)) were purchased from Fisher Scientific (Loughborough, UK).

2.2. Samples and sample collection

Samples of plastics, textiles, and foams from various article types shown previously to have been treated to varying degrees with BFRs (Drage et al., 2018) were collected in 2019 and 2020 from a range of consumer articles: hard plastic casings from waste electrical and electronic equipment (WEEE); textiles, polyurethane foams, and other foam fillings from end of life vehicles (ELVs), furniture, and mattresses; and expanded/extruded polystyrene (EPS/XPS) foams from construction and demolition foams and other applications (e.g. packaging foams) (Table 2). The majority of samples were collected from waste and recycling sites across Ireland. Small aliquots were cut from each item (several cm^2 for plastics/textiles and several cm^3 for foams and other cushioning materials) and sealed separately in labelled polyethylene containers. In total, 468 samples were collected, screened for elemental Br and Sb via XRF analysis, and laboratory mass-spectrometric analysis for a range of brominated flame retardants (data reported elsewhere – (Drage et al., 2022)).

2.3. Analysis

2.3.1. XRF analysis and calibration details

The instrument used for analysis was a Niton XL3t GOLDD + X-ray fluorescence (XRF) analyser used in its "desktop" mode, i.e. mounted into a dedicated test-stand, specially designed to avoid escape of harmful primary or secondary X-rays during analysis of low density materials. Quantification of Br and Sb in samples was conducted using the "plastics" operational mode using the Kα1 and Kα2 lines for Br (11.9242 keV and 11.8776 keV) and Sb (2.6111 keV and 2.6359 keV).

The instrument underwent calibration by Niton UK using proprietary standards containing varying concentrations of relevant inorganic compounds in a polymer matrix. This calibration uses ranges of analytes of various concentrations in a sample of "infinite thickness", i.e. a sample where virtually all of the primary X-rays are attenuated, scattered, and/or absorbed by the material and its component elements. For materials of finite thickness, this introduces a source of error as the instrument assumes a sample of infinite thickness unless a specific calibration factor is used to compensate for the disparity. The revised screening method outlined here made use of a dedicated test-stand in order to eliminate the issue of background interference, i.e. target elements being detected in underlying materials and/or materials of various density interfering with the instrument's estimations (for example, the instrument typically uses Compton scattering in order to determine the density of analyte materials, which is adversely affected by the presence of air within the samples – as is the case for PUF,

EPS, and XPS foams – or primary X-rays passing through thin and low density samples – as is the case for fabrics and EEE plastic casings).

Our previous work on XRF screening established a conservative screening threshold of ca. 710 mg kg^{-1} Br attributable to 1000 mg kg^{-1} penta-BDE congeners, the lowest brominated congener by molecular weight of the BFRs covered by the LPCLs (UNEP, 2019). However, measurements in this study, reveal BDE-209 to be the dominant POP in each sample group (with the exception of EPS and XPS foams, in which HBCDD dominates). In light of this, in this study, we employ a revised screening threshold of 833 mg kg^{-1} Br (attributable to BDE-209) for EEE, upholstery, and foam samples, while a threshold of 743 mg kg^{-1}, (attributable to HBCDD) is used for EPS/XPS foam.

2.3.2. XRF analysis measurement time

All samples were analysed for 60 s, in triplicate, using the above parameters with the resulting average concentrations and standard deviations used for comparison against mass-spectrometric analysis results (Drage et al., 2022). Samples of WEEE hard plastics containing concentrations of BFRs exceeding 100 mg kg^{-1} were additionally screened using the XRF for shorter time intervals (10 and 5 s), in triplicate. XRF data obtained for the same samples using different analysis times were then compared to assess the feasibility of using decreased analysis times while maintaining acceptable accuracy.

2.3.3. GC/MS and LC-MS/MS analysis

Elemental quantification via XRF analyses were accompanied by mass-spectrometric quantification of PBDEs, HBCDD, and a range of emerging/novel BFRs (NBFRs) – see Table 1, the results of which are reported elsewhere (Drage et al., 2022).

2.3.4. GC/MS and LC-MS/MS sample preparation

Extraction and analysis methods are described in detail by Drage et al. (2022). Briefly, aliquots of 100 mg plastic were accurately weighed into an extraction tube and 5 mL hexane:DCM:MeOH added. Samples were vortexed for 2 min and transferred to an ultrasonic bath for 20 min. The vortex and ultrasonication steps were repeated twice (three times in total) to ensure maximum extraction efficiency. 50 μL of the extract was transferred to a clean glass tube containing 10 μL of internal standard solution (containing 1 ng/μL of BDE-77, BDE-128, $^{13}C_{12}$-α-HBCDD, $^{13}C_{12}$-β-HBCDD, $^{13}C_{12}$-γ-HBCDD, $^{13}C_{12}$-TBBP-A, $^{13}C_6$-BTBPE, d_{17}-$^{13}C_6$-EH-TBB, and $^{13}C_6$-HBB; and 2 ng/μL of $^{13}C_{12}$-BDE-209 and d_{17}-$^{13}C_6$-BEH-TEBP). Extracts were concentrated to incipient dryness, and reconstituted in 200 μL hexane and transferred to autosampler vials ready for analysis of PBDEs and NBFRs via GC/MS. After GC/MS analysis, extracts were solvent exchanged into 200 μL MeOH and analysed for HBCDDs and TBBP-A via LC-TOF/MS.

3. Results

3.1. Screening of waste articles for low-POP concentration limits (LPCLs)

As reported elsewhere (Drage et al., 2022), BDE-209 is the dominant POP-BFR present in these samples, exceeding LPCLs in 16 of the 468 samples examined. A further 14 LPCL exceedances were attributable to HBCDD (11 in EPS/XPS foam samples) and a single sample exceeded the LPCL due to the presence of penta/octaBDEs (Table 3). Using portable XRF and a screening threshold of 833 mg kg^{-1} (743 mg kg^{-1} for EPS/XPS – Section 2.3.1), 16 of these 25 samples were successfully identified as exceeding LPCLs (Table 4). In addition, 47 samples (10 %) were identified as ones for which the XRF measurement was a "false-exceedance", i.e. where the XRF measurement suggests the LPCL to be exceeded but the POP-BFR concentration is <1000 mg kg^{-1}. In 10 cases, the false-exceedance can be at least partially attributed to the presence of BFRs not covered by LPCLs such as TBBP-A (5), TTBP-TAZ (3), and DBDPE (2). However, in the majority of cases (37/47), the false exceedance was not attributable to any of the BFRs we targeted, though high concentrations

Table 2
Overview of samples collected and variety of material types within each sample group.

Sample group	Plastic	Upholstery/textile	Foam filling	EPS/XPS	Total
WEEE	210	–	–	–	210
Furniture	–	16	16	–	32
Mattress	–	20	25	–	45
Curtain	–	25	–	–	25
Carpet	–	20	–	–	20
ELV	–	42	69	–	111
EPS	–	–	–	12	12
XPS	–	–	–	13	13
Total	**210**	**123**	**110**	**25**	**468**

Table 3

Summary of all samples collected and analysed for POP-BFR content as well as screened for legislative compliance via XRF analysis.

Sample group	# of samples	# above LPCL (# successfully screened)	# false-exceedances	# false-negatives
IT & telecoms	52	1 (1)	8	0
Display	47	2 (2)	11	0
Small domestic appliances	60	0	4	0
Large household appliances	21	0	1	0
Refrigeration & cooling	30	0	4	0
Furniture foams	16	3 (1)	5	2
Furniture upholstery	16	8 (6)	2	2
Mattress foams	25	0	2	0
Mattress upholstery	20	0	2	0
Curtain	25	0	0	0
Carpet	20	0	0	0
End of life vehicle foam	69	6 (1)	2	5
End of life vehicle upholstery	42	0	3	0
Expanded polystyrene	12	3 (3)	2	0
Extruded polystyrene	13	2 (2)	1	0
Total	**468**	**25 (16)**	**47**	**9**

of elemental Br detected via XRF indicates the potential presence of another brominated compound not listed in Table 1. Alternatively, the relative accuracy of the XRF is also questionable as illustrated by regression plots of XRF-determined Br against MS-determined equivalent Br (for targeted BFRs) (Supplementary Information – SI 1.1–1.4). Significant slopes (m_{EEE} = 4.3, m_{Up} = 4.5, m_{foam} = 0.26, m_{PS} = 2.3) were observed for these plots of XRF and MS-derived measurements of Br. There are two potential (non-exclusive) reasons for this: (i) the aforementioned presence of a non-targeted brominated compound in many samples; or (ii) XRF measurement errors caused by the finite thickness and/or low density of the sample under investigation. The latter is particularly noteworthy as, in this study, XRF analyses were conducted in a purpose-built test-stand, where thin and low density samples could not be manipulated to improve accuracy (e.g. by folding fabrics or compressing PUFs) as in our previous survey (Sharkey et al., 2018).

Table 4

XRF-determined Br concentrations in 25 samples with concentrations of POP-BFRs above LPCLs.

Sample	Successfully screened?	XRF-determined Br (mg kg^{-1})	ΣPOP-BFRs (mg kg^{-1})
IT & telecom 26	Yes	2760	2201
Display 24	Yes	86,300	32,002
Display 31	Yes	3400	1252
Furniture foam 1	No (false-negative)	0	1842
Furniture foam 5	No (false-negative)	0	1801
Furniture foam 13	Yes	23,900	1933
Furniture upholstery 4	Yes	36,600	3192
Furniture upholstery 5	No (false-negative)	51	1903
Furniture upholstery 6	Yes	79,200	4151
Furniture upholstery 10	No (false-negative)	461	2101
Furniture upholstery 11	Yes	50,000	2101
Furniture upholstery 12	Yes	128,000	1300
Furniture upholstery 13	Yes	71,00	2127
Furniture upholstery 15	Yes	59,000	2877
End of life vehicle foam 2	No (false-negative)	695	2002
End of life vehicle foam 7	Yes	1470	3402
End of life vehicle foam 1 (b)	No (false-negative)	0	8315
End of life vehicle foam 6 (b)	No (false-negative)	28	6205
End of life vehicle foam 13 (b)	No (false-negative)	0	5001
End of life vehicle foam 39 (b)	No (false-negative)	0	5810
Expanded polystyrene 1	Yes	4260	1370
Expanded polystyrene 4	Yes	5630	1620
Expanded polystyrene 5	Yes	3930	1070
Extruded polystyrene 1	Yes	6090	5964
Extruded polystyrene 12	Yes	7660	2218

The 2015–2016 study showed an overall screening efficacy for legislative compliance of approximately 94.8 %, with the remainder of the total being false-exceedances, attributed to – in decreasing order of relevance: (i) presence of BFRs not covered by the LPCL values (largely TBBP-A); (ii) interference from underlying materials containing target elements; or (iii) instrumental error. By contrast, the current study shows successful screening for LPCL compliance at 88.1 %. Of the remaining 11.9 %, 10.0 % are false-exceedances, of which up to 8.9 % are at least partially due to the presence of BFRs not covered by LPCLs and up to 7.0 % being at least partially attributable to XRF instrument error (the overlap highlighting that, without complete knowledge of the Br-based compounds in the samples, non-POP BFR presence cannot be guaranteed as the only source of error). The remaining 1.9 % of samples incorrectly screened were identified as "false-negatives", where PBDE and/or HBCDD concentrations exceeded LPCLs but this was not indicated by the results of XRF screening. Using this method it can be understood that, unlike in the 2015–16 study, background interference from underlying materials was not a source of error for LPCL screening. However, it is also evident that the presence of NBFRs is a continuing barrier to LPCL screening, and that instrumental error remains an issue despite the refined methods employed here.

3.2. False-exceedances and false-negatives with regard to LPCL compliance

Comparing the results in the current work to those obtained in the previous 2015–16 study (Sharkey et al., 2018), it is evident that the instances of false-exceedances have increased overall (Fig. 1). In 2019–20, almost 60 % (28/47) of false-exceedances occurred in the WEEE samples compared to 76 % (19/25) in the 2015–16 survey; in both cases, WEEE comprised roughly 45 % of total samples collected. During both studies, the majority of LPCL exceedances were from non-WEEE sample groups (Drage et al., 2022). The relatively quick turnover of EEE items in comparison to the other sample groups could provide an explanation as to why POP-BFRs are less prevalent and lead to a greater proportion of false exceedances, as legislative restrictions prohibit the use of POP-BFRs in newly manufactured items. Meanwhile, other consumer items such as furniture, household insulation, and vehicles have longer turn over times, thus stock which was historically treated with POPs are likely to remain in circulation for longer and enter the waste stream over a more gradual period (Harrad et al., 2019; Wagner and Schlummer, 2020) as evidenced by the similar proportions of wastes containing POP-BFRs in 2015–16 compared to the current study (Fig. 2). Thus, new items placed on the market which have a relatively short life-cycle seem more likely to be mis-classified as exceeding LPCLs using XRF screening methods.

An important difference between this study and our earlier work is the observance of false-negatives in 9 samples (1.9 %) here. Seven of these occurred in furniture and ELV foam samples, with the other two observed in furniture upholstery fabric samples. Several of these false-negatives are likely due to inhomogeneous mixing of BFRs in mixed/recycled materials (i.e. foams made from an amalgamation of various materials such as in bonded carpet cushions), while others may also be due to inaccurate XRF quantification of Br, exacerbated by the relatively low density nature of the samples concerned. For thin and low density samples such as foams and fabrics, accuracy in measurements can be improved by folding/stacking thin materials (i.e. fabrics), or compressing low density as has been reported previously (Sharkey et al., 2018). A potential drawback therefore of using the test stand is the inability to compress expanded foam samples or stack thin samples without interference: using the XRF in portable mode and pressing stacked materials into a surface will hold otherwise irregularly-shaped fabrics in place. Finally, the two upholstery fabric samples identified as false-negatives were composed of a linoleum-like material, which were unique among the other upholstery samples collected and analysed (in terms of simultaneous material-type and excess BFR presence).

3.3. Elemental Sb as a qualifier for POP-BFRs in WEEE plastics

Antimony trioxide (Sb_2O_3) is known to be used with additive BFRs as a synergist during the manufacturing/treatment process. It has been
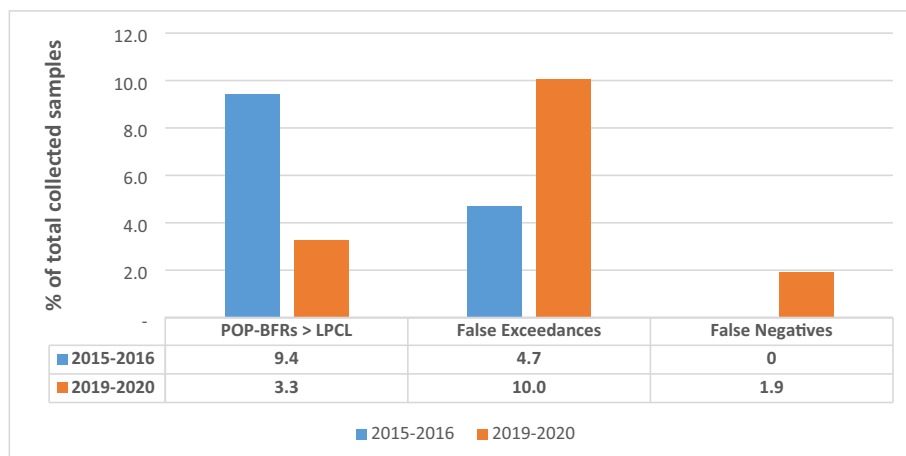
Fig. 1. Difference in proportion of samples exceeding LPCLs and instances of "false-exceedances" & false-negatives on the part of the XRF instrument between the survey conducted by the project team in 2015–16 and the current study.

suggested that this practice is largely confined to PBDEs and thus the use of XRF measurements of elemental Sb has been proposed as a means of differentiating between genuine and false LPCL exceedances (Guzzonato et al., 2017). The results of this previous study suggested that detection of Br alongside Sb at ratios between ~4:1 and 2:1 would confirm that concentrations of Br measured by XRF that exceeded the LPCL in hard plastic samples were attributable to the presence of PBDEs, while this would not be observed if the Br detected was due to other BFRs. Of the 31 hard plastic samples for which XRF analysis indicated an exceedance of the LPCL, three were genuine exceedances due to PBDEs with measured Br:Sb ratios of 5.1, 5.5, and 6.8 respectively; outside the hypothesised range. Eleven of these 31 samples fell within the 4:1–2:1 range, the Br content within 4 of which were attributable to TBBP-A and the remainder either to another Br-based compound or instrument error. The remaining 17 samples showed Br:Sb rations which were outside the prescribed range (largely between 4.4:1 and 14.0:1 or non-detects in terms of Sb) for which the XRF did indicate an exceedance of the LPCL though which wasn't due to the presence of PBDEs (or HBCDD).

Due to the juxtaposition of observations between our results and those of Guzzonato et al. (2017), a more in-depth investigation was conducted into the general relationship between Sb and the measured range of BFRs in WEEE hard plastics. Limits of detection (LoDs) for quantification of elemental Sb in WEEE hard plastics, upholstery, and PUFs are estimated at 86, 36, and 69 mg kg^{-1} respectively (Sharkey, 2019). Using these LoDs, a selection of data with measurable concentrations of Sb were correlated against the summed concentrations of POP-BFRs, novel BFRs (NBFRs), and all BFRs (Table 5). For WEEE samples, statistically significant correlations ($p < 0.01$) were observed between Sb and NBFRs. Though BDE-209 was detected in several samples at relatively high concentrations, NBFRs such as TBBP-A and TTBP-TAZ were detected much more frequently and at higher concentrations than POP-BFRs (POP-BFR Mean = 1100 mg kg^{-1}, Median = 2 mg kg^{-1}, detection frequency (df) = 65 %; NBFR Mean = 3800 mg kg^{-1}, Median = 58 mg kg^{-1}, df = 82 %). A significant correlation is also observed for the sum of all BFRs in WEEE samples, virtually identical to that observed for NBFRs, while no such correlation is seen for POP-BFRs. Previous work (Sharkey, 2019) has also shown that ratios of elemental Br with elemental Sb from samples which contain PBDEs go beyond the 2:1–4:1 range. Results of this study show the 2:1–4:1ratio between PBDEs and elemental Sb does indeed occur for some samples, though these ratios are also seen for non-POP-BFRs and the majority are shown to be outside this range. This strongly suggests that Sb$_2$O$_3$ is more generally used alongside a broad range of additive BFRs, both novel and legacy, and that the concentrations at which the synergist is applied similarly varies significantly.
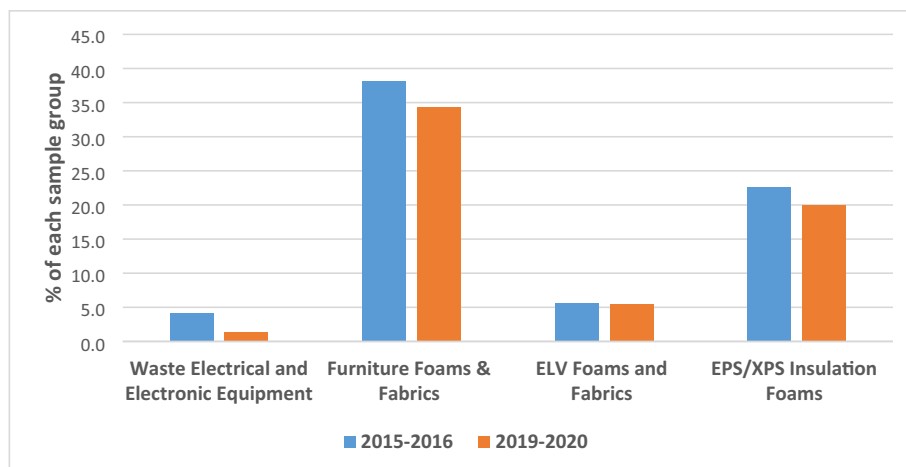

Fig. 2. Difference in proportion of each sample group exceeding LPCLs in 2015–16 compared to 2019–20. (Adapted from Drage et al. (2022).)

Table 5
Results of regression analysis for elemental Sb quantified via XRF analysis and concentrations of relevant BFRs via MS-analyses (Supplementary Information – SI 2.1–2.3).

Material type/sample group	Sb LoD (mg kg^{-1})	# > LoD	POP-BFRs		NBFRs		ΣBFRs	
			Slope	R^2	Slope	R^2	Slope	R^2
WEEE hard plastic (34)	86.0	34	0.039	0.009	0.306	0.191*	0.560	0.193*
Upholstery (74)	35.7	74	0.179	0.423*	−0.0002	0.004	2.36	0.423*
Cushioning foam (30)	69.1	22	0.966	0.046	−0.001	0.002	0.9223	0.046

* R^2 values demonstrated to be statistically significant (p < 0.01).

A similar if contrasting trend is observable in upholstery samples, where statistically significant correlations (p < 0.01) are seen between XRF-determined Sb and concentrations of POP-BFRs in upholstery. However, in the upholstery samples analysed, only trace amounts of NBFRs were detected – <10 mg kg^{-1} in most cases, with three containing up to 200 mg kg^{-1} TBBP-A. This signifies the broader use of Sb as a synergist with a range of BFRs beyond POPs in materials other than hard plastics also. No significant correlations were observed in ELV or furniture foam samples due to the relatively low concentrations of Sb measured in the samples. This shows that although POP-BFRs were detected at concentrations in-excess of LPCLs, supplementary quantification of elemental Sb would not serve as a qualifier for POP-BFR identification in XRF screening.

3.4. Impacts of reduced measurement time on XRF efficacy

All reported data in Sections 3.1–3.3 are based on triplicate measurements each conducted for 60 s using the XRF in its "desktop" mode (i.e. in the dedicated XRF test-stand); however, it remained unclear as to whether this length of measurement time was required for the purposes of screening. Following this, WEEE plastic samples which contained Br above 100 mg kg^{-1} (45 out of the total 210 WEEE samples) were subjected to further tests using the same methodology as previously described, but using reduced measurement times (10 s and 5 s respectively) and intercompared. The results of these measurements are shown in Fig. 3, which shows the relative standard deviation (RSD – Minimum, Quartiles, and Maximum) for Br concentrations determined for each measurement time for this subset of WEEE samples. One-way repeated measures ANOVA conducted on these measurements showed no statistically significant differences in average concentrations between measurement times (p = 0.89) though significant differences in RSDs (p < 0.01).

Assuming all the Br in a given sample is due to BDE-209 gives an equivalent XRF-based LPCL of 833 mg kg^{-1}. This gives a LPCL screening threshold for each measurement time of 833 mg kg^{-1} plus the maximum RSD for each interval (35, 38, and 70 mg kg^{-1} for 60, 10, and 5 s respectively). Using a 60 s measurement interval, 28 samples of the 210 WEEE samples screened were false-exceedances. Decreasing the measurement time to 10 s did not cause any additional false exceedances, while further reduction to 5 s results in just one additional false-exceedance. Using these 210 data points, approximately 86.7 % of WEEE is successfully screened for LPCL compliance using a 60 s screening time, while it is slightly reduced to 86.2 % for 5 s measurements.

The most up to date data states that roughly 52,600 tonnes of WEEE (not including lamps) were collected and prepared for reuse or recycling in 2019 (EPA, 2021) which equates to roughly 22.3 million WEEE units (WEEE_Ireland, 2020).[1] Previous work on the use of a single XRF instrument as a screening tool using 60 s measurements in triplicate (with a 30–35 s downtime per measurement) showed an estimated processing rate of up to 66,000 items over a period of three years, assuming 100

screened units over an 8 h working day and a 220 day working year (Harrad et al., 2019). There is additionally no necessity for triplicate measurements for screening based on these results as the RSD for individual measurements, even for 5 s measurement time, would not affect the success rate; therefore, a single measurement per item would suffice. Assuming a single 60 s screening on the surface plastic per item, of this screened volume some 57,200 units (or ca. 134.4 tonnes) would be successfully screened as safe to recycle or requiring diversion for special treatment due to POP content in a single year. A 5 s measurement interval, along with the associated 30 s downtime between measurements, would improve the screening rate by up to one-third: up to 200,000 items per annum processible with a single instrument. With a slightly higher 13.8 % of screened materials mislabelled as hazardous in terms of POP-BFR content, this would equate to up to 172,400 units (ca. 431 tonnes) successfully screened as safe to recycle or hazardous.

4. Discussion

In terms of screening for legislative compliance, the LPCL screening methods discussed herein are shown to have reduced efficacy compared to the preceding study conducted 4–5 years earlier: from ca. 95 % efficacy to ca. 88 % efficacy using the same criteria, due variously to the decreasing prevalence of POP-BFRs in shorter lifetime items and a commensurate increasing shift to alternative flame retardants, as well as instrumental errors on the part of the XRF. A key test herein was also an attempt to improve the LPCL screening efficacy by: (i) using Sb as a POP-BFR qualifier and (ii) using the test-stand as a method to achieve more accurate and cleaner measurements. In the former case, the detection of elemental Sb alongside both POP- and novel-BFRs indicates that using this as a qualifier for LPCL compliance would not be effective. However, it may prove useful as a qualifier for the presence of BFRs rather than other brominated compounds. In the case of the use of the test-stand, this measurement method did indeed virtually nullify the issue of background interference observed in the 2015–16 study (Sharkey, 2019). However, the inability to manipulate (fold, compress, stack, etc.) thin and low density samples is a possible factor in increasing instrumental uncertainty as well as the detection of false-negatives in the current study where none were observed previously. Contrastingly, the proposed reduction in XRF analysis time to 5 s appears a viable way to triple the rate at which XRF screening of WEEE can occur, albeit with an accompanying ~0.5 % increase in false-exceedances. This reduction in XRF analysis time could be further lowered by focusing screening on those WEEE items with higher instances of LPCL exceedances, notably display units, small domestic appliances, and large household appliances.

In the case of the WEEE plastics specifically, the majority of false-exceedances are due to the presence of non-restricted BFRs, whereas instrumental error appears a more prevalent factor in terms of soft furnishings, mattresses, and vehicular fabrics and foams (though alt-BFRs are shown to be present above 1000 mg kg^{-1} in one instance there also (Drage et al., 2022)). While disregarding the specific species of Br-based compound in the material will result in simpler and seemingly more effective screening, these limits are being imposed on chemicals which are neither regulated as POPs nor limited as such in end of life materials, i.e. on BFRs other than PBDEs and HBCDD. Therefore, there is currently no regulatory requirement for the employment of broader screening criteria for WEEE

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[1] Assuming 2.35 kg per WEEE unit. Based on most recent WEEE Ireland collection statistics which outlines 38,724 tonnes collected in the designated period, equating to ca. 16.2 million units of refrigeration equipment, LHAs, SDAs, IT & Telecoms equipment, and display units.
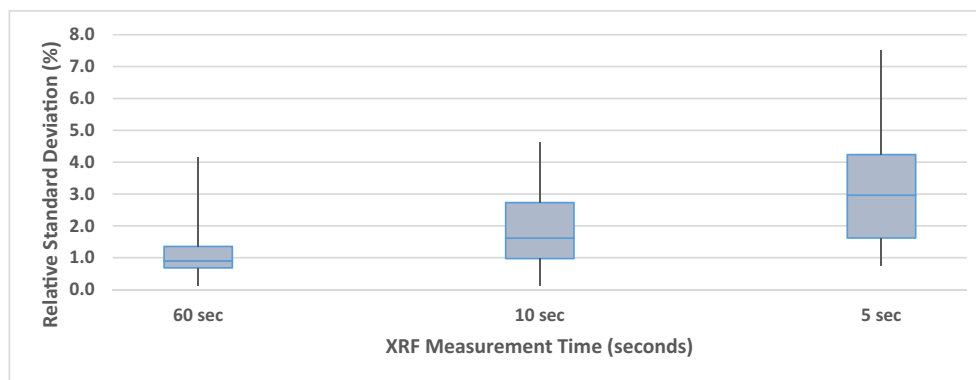
Fig. 3. Box plot showing relative standard deviations (RSD - %) for each of 60, 10, and 5 s measurement times on 45 WEEE samples showing Br > 100 mg kg^{-1} from initial screening (60s measurements in triplicate). Median, 1st and 3rd quartiles, and maximum/minimum RSDs are shown.

plastics. Similarly, as restricted BFRs are gradually replaced by NBFRs, both methods will be removing greater quantities of legally recyclable materials from circulation without future changes in regulations.

In the case of non-WEEE materials, the comparatively higher ratio of POP-BFRs to NBFRs show that screening using LPCL compliance criteria is still reasonably effective (89.1 % in 2021 compared to 95.6 % in 2016). For the PUF and upholstery related sub-groups (ELVs, Furniture, and Mattresses) the proportion of false-positives increased by only 1.7 % between 2015–16 and 2019–20, largely due to the presence of a Br-based compounds not included in this study (based on Br levels found during XRF screening). False-exceedances were also seen in this study in 12 % of EPS and XPS samples where none were observed previously. For EPS samples, this is suspected to be due to the increased use of polymeric flame retardants (Poly-FRs) as a replacement for HBCDD (Minet et al., 2021). This is also likely in XPS materials, though results of Drage et al. (2022) show that certain organophosphate flame retardants are prevalent in these materials, potentially being utilised as a replacement for HBCDD.

However, the LPCL compliance screening method may be impacted in the future by the lowering of LPCLs for PBDEs and HBCDD to 500, 200, or 100 mg kg^{-1}, as has been postulated by a recent draft report published from the European parliament (Hojsik, 2022). Table 6 gives an overview of the impact of decreasing proposed LPCL values on screening efficacy using portable XRF. The proportion of waste which exceeds proposed LPCLs does indeed increase (approximately linearly) with decreasing limit values (Drage et al., 2022), this is accompanied by a comparably dramatic increase in the proportion of false-exceedances (Fig. 3). These exceedances are due in large part to the presence of NBFRs present at concentrations under 1000 mg kg^{-1}, though likely is also due to the inherent inaccuracy of the instrument, particularly for the lower density and thinner materials, which is shown to be exacerbated by lower analyte concentrations (Sharkey, 2019; Zawisza, 2012).

Despite the instances of false-negatives and false-exceedances which XRF-based screening shows (based on current legislation), adoption of such a screening method will allow for the "opening up" of recycling systems where more conservative approaches are adopted in terms of disposal of hazardous materials. Hennebert and Filella (2018) discuss the crucial need for low-cost screening methods to enforce EU regulations regarding (i) segregation of hazardous and non-hazardous waste plastics, (ii) maximising quantities of "clean" plastics to be recycled, and (iii) closing the "… *unwanted global loop of substances via the international trade of plastic scrap*" (Turner and Filella, 2017). Similarly, the encroaching need for significant textile recycling efforts introduces the similar barrier of hazardous substances such as POPs which would render waste materials unrecyclable under current EU regulations (Sharkey and Coggins, 2022). While the underlying issues facing textile recycling are extensive in terms of waste volume, available technologies, and insufficient oversight, adoption of an XRF-based or other rapid low cost screening method would prevent a conservative approach being adopted for potentially hazardous textile waste as is observed in other areas (Charbonnet et al., 2020); in that, a non-zero fraction of clean textile waste can be segregated for reuse and recycling as opposed to all waste being disposed of in order to ensure regulatory compliance.

5. Conclusion

Rapid screening of waste articles for hazardous chemicals such as POPs remains something which must be more widely adopted into our waste management system. Though the ability of portable XRF to successfully monitor compliance of waste plastics with LPCL values for POP-BFRs has declined between 2015–16 and 2019–20 due to various factors (notably the gradual shift away from POP-BFRs since restrictions have been adopted), large volumes of historically-treated materials remain in use. XRF and other such rapid screening methods still have a potential role to play. This study shows portable XRF to be capable of successfully screening roughly 90 % of waste materials for compliance with LPCL values and thus successfully removing large quantities of hazardous materials from circulation. Given the vast quantities of waste articles requiring screening for compliance with LPCLs, a particularly noteworthy finding of this study is that faster XRF analysis times can significantly increase the rate at which articles are screened, without seriously comprising screening accuracy. Continued efficacy of such rapid screening methods will however be intrinsically linked with evolutions in regulations regarding the use and/or requirement for additive flame retardants in consumer articles.

CRediT authorship contribution statement

Martin Sharkey: Conceptualization, Data curation, Formal analysis, Investigation, Methodology, Resources, Validation, Visualization, Writing – original draft, Writing – review & editing. **Daniel Drage:** Conceptualization, Investigation, Methodology, Resources, Validation, Writing – review & editing. **Stuart Harrad:** Conceptualization, Funding acquisition, Investigation, Methodology, Project administration, Resources, Supervision, Writing – review & editing. **William Stubbings:** Investigation, Methodology,

Table 6
Overview of screening efficacy of XRF using LPCL screening criteria at different proposed limit values as have been proposed by the European Commission (Hojsik, 2022).

LPCL screening criteria	# samples	Samples > LPCL	Successfully screened > LPCL using XRF	False exceedances	False negatives
1000 mg kg^{-1} (current LPCL)	468	5.3 %	3.4 %	10.0 %	1.9 %
500 mg kg^{-1}		6.4 %	4.5 %	12.8 %	1.9 %
200 mg kg^{-1}		7.5 %	5.1 %	16.9 %	2.4 %
100 mg kg^{-1}		9.4 %	6.6 %	21.4 %	2.6 %

Resources, Validation, Writing – review & editing. **André Henrique Rosa:** Investigation, Writing – review & editing. **Marie Coggins:** Project administration, Resources, Supervision, Writing – review & editing. **Harald Berresheim:** Conceptualization, Funding acquisition, Investigation, Methodology, Project administration, Resources, Supervision, Writing – review & editing.

Data availability

The authors do not have permission to share data.

Declaration of competing interest

The authors declare that there are no known competing financial interests of personal relationships that could have inappropriately biased these works.

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Appendix A. Supplementary data

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References

Abdallah, M.A.-E., Sharkey, M., Berresheim, H., Harrad, S., 2018. Hexabromocyclododecane in polystyrene packaging: a downside of recycling? Chemosphere 199, 612–616.

Bartl, A., Ipsmiller, W., 2021. Textile waste: where is the journey heading? 18th International Symposium on Waste Management and Sustainable Landfilling, Sardinia, Italy. Eurowaste Srl.

Blum, A., Behl, M., Birnbaum, L., Diamond, M., Phillips, A., Singla, V., Sipes, N., Stapleton, H., Venier, M., 2019. Organophosphate Ester flame retardants: are they a regrettable substitution for polybrominated diphenyl ethers? Environ. Sci. Technol. Lett. 6.

BSI, 2006. BS5852:2006 - Method of Test for Assessment of Ignitability of Upholstered Seating by Smouldering and Flaming Ignition Sources. British Standards Institute, pp. 1–46.

Charbonnet, J.A., Weber, R., Blum, A., 2020. Flammability standards for furniture, building insulation and electronics: benefit and risk. Emerg. Contam. 6, 432–441. https://doi.org/10.1016/j.emcon.2020.05.002. (In this issue).

Drage, D., Sharkey, M., Abdallah, M.A., 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., Sharkey, M., Al-Omran, L.S., Stubbings, W.A., Berresheim, H., Coggins, M., Rosa, A.H., Harrad, S., 2022. Halogenated flame retardants in irish waste polymers: concentrations, legislative compliance, and preliminary assessment of temporal trends. Environ. Pollut. 309, 119796. https://doi.org/10.1016/j.envpol.2022.119796.

Eljarrat, E., Barceló, D., 2011. Handbook of Environmental Chemistry - Brominated Flame Retardants, Handbook of Environmental Chemistry. Springer Verlag, Verlag Berlin Heidelberg.

EPA, 2021. WEEE statistics for Ireland. Available: https://www.epa.ie/our-services/monitoring–assessment/waste/national-waste-statistics/weee/. (Accessed 28 June 2022).

Gallen, C., Banks, A., Brandsma, S., Baduel, C., Thai, P., Eaglesham, G., Heffernan, A., Leonards, P., Bainton, P., Mueller, J.F., 2014. Towards development of a rapid and effective non-destructive testing strategy to identify brominated flame retardants in the plastics of consumer products. Sci. Total Environ. 491–492, 255–265.

Guzzonato, A., Puype, F., Harrad, S.J., 2017. Evidence of bad recycling practices: BFRs in children's toys and food-contact articles. Environ Sci Process Impacts 19 (7), 956–963.

Harrad, S., Drage, D.S., Abdallah, M.A.-E., Sharkey, M., Berresheim, H., 2019. Research 272: Evaluation of Hand-held XRF for Screening Waste Articles for Exceedances of Limit Values for Brominated Flame Retardants. Environmental Protection Agency of Ireland, Dublin, Ireland (online).

Hennebert, P., Filella, M., 2018. WEEE plastic sorting for bromine essential to enforce EU regulation. Waste Manag. 71, 390–399.

Hojsik, M., 2022. Draft Report on the Proposal for a Regulation of the European Parliament and of the Council Amending Annexes IV and V to Regulation (EU) 2019/1021 of the European Parliament and of the Council on Persistent Organic Pollutants. Online (European Parliament Proceedings): European Parliament, Committee on the Environment, Public Health, and Good Policy.

Ipsmiller, W., Bartl, A., 2021. Textile waste: an inventory of available and emerging recycling technologies. 18th International Symposium on Waste Management and Sustainable Landfilling, Italy. Eurowaste Srl.

Jeannerat, D., Pupier, M., Schweizer, S., Mitrev, Y.N., Favreau, P., Kohler, M., 2016. Discrimination of hexabromocyclododecane from new polymeric brominated flame retardant in polystyrene foam by nuclear magnetic resonance. Chemosphere 144, 1391–1397.

Junod, T.L., 1976. Gaseous Emissions and Toxic Hazards Associated With Plastics in Fire Situations - A Literature Review. National Aeronautics and Space Administration, Washington D.C.

Kajiwara, N., Noma, Y., Takigami, H., 2011. Brominated and organophosphate flame retardants in selected consumer products on the japanese market in 2008. J. Hazard. Mater. 192 (3), 1250–1259.

Knutsen, H., Arp, H.P.H., 2021. Preventing brominated flame retardants from occurring in recycled expanded polystyrene: comparing Norwegian visual sorting with advanced screening methods. J. Hazard. Mater. Lett. 2, 100016.

Kuang, J., Abdallah, M.A.-E., Harrad, S., 2018. Brominated flame retardants in black plastic kitchen utensils: concentrations and human exposure implications. Sci. Total Environ. 610–611, 1138–1146.

Minet, L., Blum, A., Fernández, S.R., Rodgers, K.M., Singla, V., Soehl, A., Diamond, M.L., 2021. High production, low information: we need to know more about polymeric flame retardants. Environ. Sci. Technol. 55 (6), 3467–3469.

Sharkey, M., Abdallah, M.A.-E., Drage, D., Harrad, S., Berresheim, H., 2018. Portable X-ray fluorescence for the detection of POP-BFRs in waste plastics. Sci. Total Environ. 639C, 49–57.

Sharkey, M., Coggins, M., 2022. The Invisible Barrier to Textile Recycling. Frontiers in Sustainability, Sustainability Assessment of Chemicals in Consumer Products.

Sharkey, M.J., 2019. Sources, concentrations, and screening of hazardous brominated flame retardants from waste streams in Ireland. ARAN - Access to Research at NUI Galway. National University of Ireland Galway, p. 126.

Turner, A., Filella, M., 2017. Bromine in plastic consumer products – evidence for the widespread recycling of electronic waste. Sci. Total Environ. 601–602 (Supplement C), 374–379.

UNEP, 2019. All POPs listed in the Stockholm Conventiion. Available: http://chm.pops.int/TheConvention/ThePOPs/AllPOPs/tabid/2509/Default.aspx. (Accessed 16 March 2021).

van Esch, G.J., 1997. Flame retardants: a general introduction. Available: http://www.inchem.org/documents/ehc/ehc/ehc192.htm#SectionNumber:2.2. (Accessed 22 February 2016).

Wagner, S., Schlummer, M., 2020. Legacy additives in a circular economy of plastics: current dilemma, policy analysis, and emerging countermeasures. Resour. Conserv. Recycl. 158, 104800.

WEEE_Ireland, 2020. WEEE Ireland annual environmental report 2020. Available: https://www.weeeireland.ie/2021/06/16/weee-ireland-annual-report-results-2020/. (Accessed 28 June 2022).

Zawisza, R.S.B., 2012. Quantification in X-Ray fluorescence spectrometry. In: Sharma, S.K. (Ed.), X-Ray Spectroscopy. InTech, pp. 137–162.