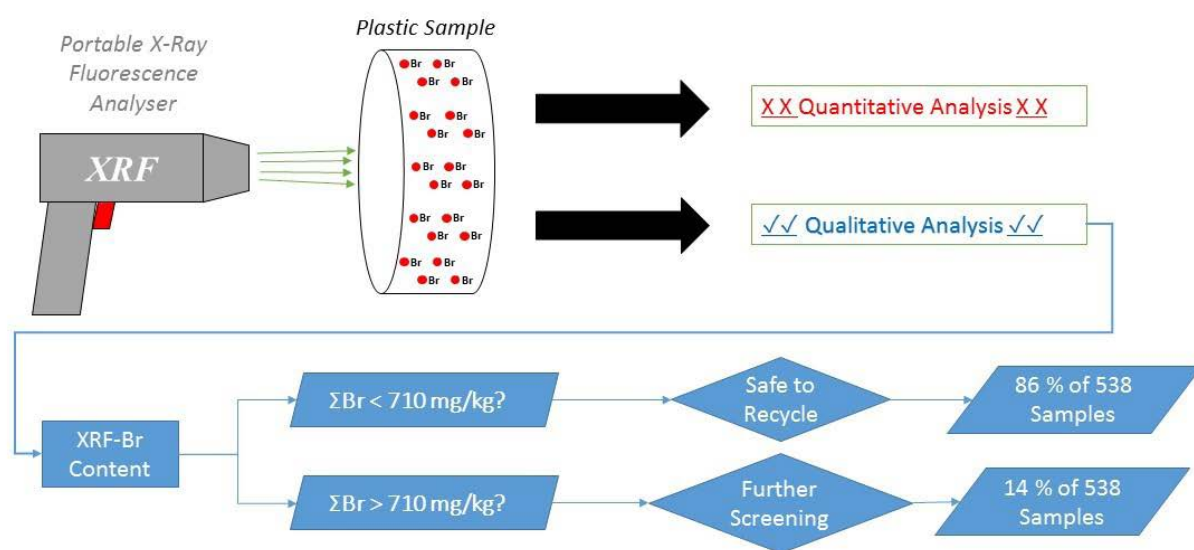


Evaluation of Hand-held XRF for Screening Waste Articles for Exceedances of Limit Values for Brominated Flame Retardants

Authors: Stuart Harrad, Daniel Drage, Mohamed Abdallah, Martin Sharkey and Harald Berresheim



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EPA RESEARCH PROGRAMME 2014–2020

Evaluation of Hand-held XRF for Screening Waste Articles for Exceedances of Limit Values for Brominated Flame Retardants

(2014-RE-MS-2)

EPA Research Report

End of project report available for download on <http://erc.epa.ie/safer/reports>

Prepared for the Environmental Protection Agency

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ACKNOWLEDGEMENTS

This report is published as part of 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. It is administered by the Environmental Protection Agency, which has the statutory function of co-ordinating and promoting environmental research.

The authors would like to acknowledge the members of the project steering committee, namely Darren Byrne (Department of Communications, Climate Action & Environment) and Maria Martin (EPA) for their constructive input throughout the project and also reviewer Martin Doyle (EPA) and Karen Roche (Project Manager on behalf of EPA Research). We also extend our thanks to all of the waste site owners and operatives who allowed us to procure samples.

Cover image: Portable XRF is a viable option for screening compliance with concentration limits on brominated flame retardants in waste polymers.

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The EPA Research Programme addresses the need for research in Ireland to inform policymakers and other stakeholders on a range of questions in relation to environmental protection. These reports are intended as contributions to the necessary debate on the protection of the environment.

EPA RESEARCH PROGRAMME 2014–2020

Published by the Environmental Protection Agency, Ireland

ISBN: 978-1-84095-820-1

March 2019

Price: Free

Online version

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Executive Summary

Recent research has demonstrated the presence of restricted persistent organic pollutant (POP) brominated flame retardants (BFRs) in items such as children's toys and food contact articles. As the presence of these contaminants in such items serves no useful purpose, they are thought to originate from the use of recycled plastics that were originally treated with BFRs. To address this issue, European Union (EU) Regulation 850/2004 specifies low POP concentration limit (LPCL) values such that articles containing such BFRs [selected polybrominated diphenyl ethers (PBDEs) and hexabromocyclododecane (HBCDD)] at concentrations exceeding the LPCL (1000 mg/kg) cannot be recycled and must be treated so that the BFR content of such articles is destroyed. Existing LPCLs for PBDEs cover PBDEs present in the penta- and octa-brominated diphenyl ether (BDE) formulations, with an LPCL for deca-BDE at a similar concentration scheduled for implementation from March 2019. Given the widespread use of PBDEs and HBCDD in applications such as electrical and electronic goods, polystyrene building insulation foam, seating foam and fabrics in homes, offices and cars, monitoring compliance with LPCLs represents a substantial undertaking, compounded by conventional methods for measuring PBDEs and HBCDD being destructive, time-consuming, expensive and incompatible with being conducted *in situ* at waste handling sites. Our principal objective was thus to evaluate the feasibility of using hand-held X-ray fluorescence (XRF) spectrometers to determine bromine in waste articles as a surrogate indicator of exceedance of LPCLs. Of particular concern is the incidence of false positives (where the concentration of bromine but not PBDEs or HBCDD exceeds the LPCL) and false negatives (where the concentration of PBDEs or HBCDD exceeds the LPCL but this is not indicated by the bromine concentration recorded by XRF). False positives may occur when a BFR other than a PBDE or a HBCDD (e.g. tetrabromobisphenol A) is present at a concentration above 1000 mg/kg.

We measured bromine in 769 waste articles and PBDEs and HBCDD in 538 of the same articles collected in Ireland between 2015 and 2016. These

articles comprised waste electronic and electrical equipment (WEEE), polystyrene building insulation and end-of-life vehicle foams and fabrics, as well as waste carpets, curtains, furniture foams and fabrics. Measurements revealed concentrations of PBDEs and HBCDD exceeding existing LPCLs in 29 of 538 articles (5.4%). Anticipating the introduction of an LPCL for deca-BDE (BDE-209), we found that the proportion of articles exceeding either existing LPCLs or the anticipated LPCL of 1000 mg/kg for BDE-209 was 8.7% (47/538). By comparison, false positives numbered 52 (9.7%) when existing LPCLs only were considered, reducing to 34 (6.3%) when the anticipated LPCL for BDE-209 was accounted for. No false negatives were detected. Based on our data, enforcement of existing LPCLs would prevent 97.9% of the estimated 17,721 kg/year of HBCDD, penta-BDEs and octa-BDEs generated currently in Ireland, as well as 13.0% of the 15,284 kg/year of BDE-209 generated, from being recycled. Enforcement of an LPCL of 1000 mg/kg for BDE-209 would prevent recycling of 98.1% of the 33,004 kg/year of PBDEs and HBCDD currently generated in Ireland. Although false positives will lead to some articles being incorrectly prevented from being recycled, the absence of false negatives in this study, combined with the cost- and time-effectiveness of hand-held XRF relative to conventional methods for measuring PBDEs and HBCDD, renders hand-held XRF potentially feasible for large-scale monitoring of LPCL compliance. Despite this, use of hand-held XRF to screen individual waste articles may still be considered overly time-consuming by waste treatment professionals. Consequently, automation of the screening process using a "fixed/bench-top" XRF instrument in conjunction with a conveyor belt carrying waste articles is considered a feasible approach for large-scale waste handling operations, albeit one requiring greater capital outlay. Short-term approaches to minimise the number of articles requiring checking for compliance with LPCLs merit consideration. These involve using data from this project that show very low BFR concentrations and no exceedances of current or anticipated LPCLs for some waste categories such as extruded polystyrene (XPS) building insulation foam.

On-site separation of XPS from expanded polystyrene (EPS) foam (for which 35% of samples were found to exceed the LPCL for HBCDD) to allow recycling or

reuse of XPS without checking for LPCL compliance would reduce the monitoring burden placed on the waste management industry.

1 Introduction

Brominated flame retardants (BFRs) such as hexabromocyclododecane (HBCDD) and polybrominated diphenyl ethers (PBDEs) have found extensive use worldwide as flame retardants in a wide variety of commercial, domestic and industrial applications. Applications of PBDEs include electrical and electronic equipment [EEE – such as televisions, personal computers (PCs) and small domestic appliances (SDAs)] and soft furnishings (such as sofas, mattresses, curtains and pillows). In EEE, PBDEs are added to both the polymer casing in the case of electronics [e.g. high-impact polystyrene (HIPS) or acrylonitrile butadiene styrene (ABS)] and internal circuit boards, whereas they are added both to the foam fillings and to the fabric covers of soft furnishings such as sofas and chairs in domestic, office or vehicular environments. With respect to HBCDD, the most important application [96% of all uses in the European Union (EU)] is its widespread use as a flame retardant in expanded and extruded polystyrene (EPS/XPS) used in building insulation foam in the construction industry (ECHA, 2009). As of 2001 (the last reliable figures publicly available), Europe accounted for 2%, 16%, 14% and 57% of the annual global demand for penta-brominated diphenyl ether (BDE), octa-BDE, deca-BDE and HBCDD respectively (BSEF, 2003).

The available data indicate that, to impart flame retardancy to articles, PBDEs (irrespective of the formulation) were added at concentrations between approximately 3% and 30% by weight (WHO, 1994). The exact concentration applied was determined by several considerations such as the degree of flame retardancy required, the efficacy of the flame retardant selected, whether or not it was applied in conjunction with a synergist (e.g. antimony oxide), the physical attributes of the end product (e.g. colour, density, stability) and its specific application (European Chemicals Bureau, 2000). However, in general, higher concentrations were used in EEE, with lower levels applied to soft furnishings.

In Europe, approximately 95% of penta-BDE was used in flexible polyurethane foam (PUF), mainly for furniture upholstery and automotive applications

(European Chemicals Bureau, 2000). The United Nations Environment Programme (UNEP) initially reported that treated PUF usually contained 10–18% by weight of penta-BDEs; however, this estimate was subsequently revised downwards to around 3–5% by weight for upholstery, cushions, mattresses and carpet padding (UNEP, 2006, 2010). A similar concentration range of between 6% and 18% by weight of penta-BDE in PUF was provided in the *Plastics Additives Handbook* (as cited in EC, 2011). The remaining minor uses of penta-BDE reported (totalling 5%) include textiles, printed circuit boards, insulation foam, cable sheaths, conveyor belts, lacquers and possibly drilling oils (UNEP, 2007). UNEP reported that the approximate distribution of global penta-BDE use was 60% in furniture and 36% in transport, with the remaining 4% deployed in other articles (UNEP, 2010).

Historically, around 95% of octa-BDE supplied in the EU was used in ABS, to which it was typically added at concentrations between 10% and 18% by weight (EC, 2011). The main uses for BFR-treated ABS were predominantly in plastic housing of EEE, particularly for cathode ray tube (CRT) housing (e.g. PC monitors and televisions), and office equipment (e.g. copying machines and business printers). The remaining approximately 5% of minor uses of octa-BDE reported were in HIPS, polybutylene terephthalate (PBT) and polyamide polymers, with typical concentrations of 12–15% by weight. Other possible uses were in low-density polyethylene, polycarbonate, phenol formaldehyde resins and unsaturated polyesters, as well as in adhesives and coatings (UNEP, 2010).

Widely used because of its relatively low cost, deca-BDE was employed in HIPS associated with EEE and as a back coating on a wide range of fabrics, including nylon, polypropylene, acrylics and many other blends such as polyester cotton (Weil and Levchik, 2008). Typically, deca-BDE was added at about 10–25% by weight in a 2:1 weight ratio with antimony oxide (Weil and Levchik, 2008). Important fabric applications were in automotive upholstery, draperies for hotels and public buildings and institutional (e.g. office) upholstered furniture (Weil and Levchik, 2008).

As highlighted above, the principal use of HBCDD (>90%) is in the building industry, with it typically being added at 2% or 0.7% by weight into EPS and XPS foam, respectively, in rigid insulation panels/boards (EC 2011; Marvin *et al.* 2011). A further approximately 2% is deployed in HIPS used for EEE (distribution boxes for electrical lines and electrical housings) (EC, 2011). However, HBCDD is also used as a textile coating agent in polymer dispersions applied to cotton or cotton/synthetic blends for upholstery fabrics, e.g. residential and commercial upholstered furniture and transportation seating, bed mattress ticking, draperies and wall coverings and interior textiles (e.g. roller blinds and vehicle interior textiles). HBCDD can also be used in thermosol treatment of polyester, polypropylene and nylon fabrics, where it is applied as an aqueous suspension or emulsion at a loading of 8–11% by weight (Weil and Levchik, 2008).

In addition to the above applications, PBDEs have found extensive use in motor vehicles, in particular in polyurethane seating foam and fabric covers. Although probably accompanied by substantial uncertainty, it was estimated that approximately 5% of European vehicles built between 1975 and 2004 were treated with penta-BDE, with each treated vehicle containing 160g of penta-BDE (Morf *et al.*, 2003, using data reported by the Danish EPA, 1999). On this basis, combined with information from the Environmental Protection Agency (EPA) of Ireland that 75,000 end-of-life vehicles (ELVs) were generated in 2015 in Ireland (EPA, 2017), the ELV waste stream in Ireland that year potentially contained 12 tonnes of penta-BDE. As highlighted above, there is likely to be substantial uncertainty in this and other related estimates, which are reliant on data provided by trade organisations such as the European Automobile Manufacturers' Association about the yearly consumption of penta-BDE in vehicular applications (EC, 2011). It is important to highlight in this context that obtaining data from product manufacturers on specific quantities of specific BFRs used in different applications is extremely difficult.

Over the last decade, the widespread use of PBDEs and HBCDD has been the subject of concern, owing to their documented presence in the environment, including human tissues, coupled with evidence of their toxicity. At a global level, this concern is exemplified by the listing of HBCDD and those PBDE congeners that constitute the penta- and octa-BDE

commercial formulations under the UNEP Stockholm Convention on Persistent Organic Pollutants (<http://chm.pops.int>). Moreover, in 2017 the deca-BDE formulation was listed under the same Convention. Within the EU, the manufacture and new use of penta- and octa-BDE has been banned since the mid-2000s, with the manufacture and new use of deca-BDE severely restricted since 2008. Since the 2013 listing of HBCDD under the Stockholm Convention, use of this BFR has also been restricted, although there is currently a time-limited (up to 5 years) derogation that permits its use within the EU in EPS and XPS for building insulation until 26 November 2019.

It is clear that there has been extensive (largely historical) global use of PBDEs and HBCDD in a wide range of applications. Moreover, in view of the turnover times of such articles (from a few years for some articles of EEE to 10–15 years for cars and 30–50 years for building insulation), it is further apparent that there is a growing quantity of materials containing restricted chemicals that have entered or will shortly be entering the waste stream, with consequent implications for their sustainable management. The potential scale of this issue is illustrated by estimates that, in 2014, 41.8 million tonnes of waste EEE (WEEE) was generated globally (Bakhiyi *et al.*, 2018). Within Ireland, 48,626 tonnes of WEEE were disposed of in 2015, with an estimated 3.14 million tonnes of construction and demolition (C&D) waste also generated in 2015 (EPA, 2017). Although data specific to Ireland are not available, figures are available (DEFRA, 2010) that estimate that, of UK arisings of C&D waste, approximately 2.8% is considered to comprise insulation material, of which EPS and XPS constitute around 5%, equating to an estimated 4639 tonnes/year of waste EPS and XPS generated in Ireland. Moreover, if we assume arisings of waste soft furnishings in Ireland to be identical per capita to the approximately 1,000,000 tonnes of waste furniture and textiles generated in the UK in 2010/11 (WRAP, 2012), approximately 75,000 tonnes of waste furniture and textiles will be generated per annum in Ireland. Against this backdrop, the scale at which these regulated environmental contaminants are expected to enter the waste stream over the next 5 years and beyond requires detailed research to generate the knowledge base required to allow regulatory bodies to formulate effective policies to address this important issue. To illustrate, the EU's Construction and Demolition

Waste Management Protocol, published in September 2016 (EC, 2016), explicitly identifies the presence of halogenated flame retardants as one of the criteria under which C&D waste may be classified as hazardous and lays out non-binding guidelines for how the construction industry should identify, separate and handle hazardous waste.

Regulation (EC) No. 850/2004 implements the commitments of the EU under the Stockholm Convention on Persistent Organic Pollutants and under the Protocol to the 1979 Convention on Long-Range Transboundary Air Pollution on Persistent Organic Pollutants (<https://www.unece.org/fileadmin/DAM/env/lrtap/full%20text/1998.POPs.e.pdf>). The persistent organic pollutant (POP) regulation aims to eliminate the release of POPs from their manufacture and use, including from waste, in order to protect human health and the environment from potential harm by prohibiting the manufacturing, placing on the market and use of POPs and by establishing provisions regarding environmentally sound treatment of waste consisting of, containing or contaminated by any of these substances. More specifically, regulation (EC) No. 850/2004 stipulates that wastes containing POPs must be treated in such a way as to ensure that the POP content is destroyed or irreversibly transformed, so that the remaining waste and releases do not exhibit characteristics of POPs, i.e. the POP content is below the limit value specified in Annex IV [low POP concentration limit (LPCL)]. The LPCLs define the threshold concentration above which wastes are classified as POP waste and subject to the management regime of the POP regulation. These limits define whether or not a waste, because of its POP content, will have to be treated in such a way to meet the above criterion. One of the purposes of the LPCLs is to minimise waste articles containing POPs from being recycled and thus address recent reports of the detection of POP-BFRs such as PBDEs in recycled items such as food contact articles and children's toys (e.g. Samsonik and Puype, 2013; Guzzonato *et al.*, 2017), that presumably contain POP-BFRs as unintentional contaminants.

As part of the European Commission's strategy for a non-toxic environment set out in the 7th EU Environmental Action Plan (EU, 2013), work has been conducted to investigate the various aspects of the production and use of chemicals in articles and material cycles. Such work outlines the challenges

in three main areas: regulation of the content of toxic substances in articles; communication on the content of toxic substances in articles and material cycles and the related potential risks; and information gaps as well as organisational problems arising from the avoidance of toxic substances (including POPs) in a circular economy.

According to the Commission, analysis of EU chemicals, products and waste policies reveals a lack of a consistent approach to limiting the content of toxic substances in articles and materials. In addition, legal requirements regarding communicating information on (toxic) substances along the supply chain and to consumers are limited in the substances that they cover, making little information available to authorities and stakeholders engaged in setting risk management priorities. Finally, the routines and infrastructure of the waste sector are inefficient in terms of decontaminating material streams from legacy chemicals contained in articles (EC, 2017a).

Monitoring compliance with LPCLs will require appreciable resources, however, first because of the considerable number of waste articles requiring such compliance checks and, second, because the methods required to measure POP-BFRs are expensive, requiring specialist equipment and highly skilled analytical chemists. These issues are exacerbated further by the fact that such methods are destructive (requiring removal of a portion of the sample under test), time-consuming (with analysis of each batch of samples taking at least 1 day) and cannot be conducted on site, thereby resulting in further delay while samples are transported from the waste site to the testing laboratory. There is therefore a clear and pressing need for a faster, less expensive, less complex, yet fit-for-purpose method for verifying compliance with LPCLs that may be conducted *in situ* at waste treatment centres.

Following its well-documented successful application for screening various elements (e.g. lead and cadmium) in a variety of samples (Allen *et al.*, 2008), the application of X-ray fluorescence (XRF) for quick, non-destructive and economic screening for bromine (Br) has expanded in the past few years to comply with the EU Restriction of Hazardous Substances Directive (2002/95/EC) and the on-going recast of the EU POPs regulation (EC 850/2004), as well as the WEEE Directive (2002/96/EC) and its recast (2012/19/EU),

which became effective in Ireland on 29 March 2014. A large study (1178 samples) conducted by Washington State Department of Ecology recommended hand-held XRF as a useful screening tool for Br in various consumer goods and children's products. Br was detected in 40.7% of the samples, with a mean level of 3800 mg/kg, with limits of detection of < 10 mg/kg and a relative standard deviation (RSD) of < 10% for triplicate measurements (Furl *et al.*, 2012). Another study conducted in Boston, USA, reported that XRF-measured Br was highly correlated with gas chromatography–mass spectrometry (GC/MS)-measured Br for furniture foam and plastic from electronics ($n=29$, $r=0.93$, $p<0.0001$) (Allen *et al.*, 2008). In a more recent study conducted in Australia, XRF successfully identified Br in 92% of 1714 sampled products later confirmed to contain BFRs via MS analysis (Gallen *et al.*, 2014). Despite these positive indications, a potential problem is that XRF measures only Br, imparting no information as to its chemical form, and is thus prone to source misclassification. Specifically, this means that portable XRF imparts no information on whether the Br present is organic or inorganic and, if the former, whether it is a regulated BFR such as penta-BDE, octa-BDE or HBCDD or a non-regulated but commonly used BFR such as tetrabromobisphenol A (TBBP-A), which was the most commonly used BFR in Europe (11,600 tonnes) in 2001 (BSEF, 2003). Given the likely cost implications of false identification of waste articles as exceeding an LPCL, information about the likely extent of such source misclassification is important.

1.1 Objectives

The principal objective of the WAFER project was to evaluate whether hand-held XRF is a viable screening tool for testing whether waste articles comply with existing LPCLs for HBCDD and those PBDEs associated with the penta- and octa-BDE commercial formulations, as well as an anticipated LPCL of 1000 mg/kg for BDE-209, the principal constituent of the deca-BDE formulation.

To achieve this, this project measured concentrations of PBDEs and HBCDD in 538 waste articles sampled in Ireland to verify whether these exceed LPCLs and compared these data with measurements of Br in the same articles using a hand-held XRF device. These data were examined for the accuracy with which XRF identified items exceeding LPCLs, including evidence of source misclassification.

Furthermore, having generated a substantial database on the presence of PBDEs and HBCDD in Irish waste articles, our secondary objective was to evaluate the impact of effective enforcement of LPCLs for POP-BFRs in Ireland. To do so, we:

- estimated the mass of PBDEs and HBCDD contained within relevant waste streams in Ireland, including the proportion of individual items within such waste streams that exceed LPCLs;
- estimated the mass of waste material and associated POP-BFRs that would be removed from circulation by effective enforcement of current LPCLs and that would thus require special treatment to destroy the POP-BFRs isolated; and
- evaluated the options available for such special treatment to destroy this reservoir of POP-BFRs.

2 Methodology

In this chapter we describe the sampling strategy and technical methods employed to obtain the data reported.

2.1 Sampling

The first phase involved collection of samples of individual articles of waste goods and materials from waste streams considered to potentially contain POP-BFRs. As the overall purpose of the WAFER project was to evaluate the potential of hand-held XRF as a tool for the rapid, inexpensive, *in situ* screening of waste articles containing POP-BFRs at concentrations exceeding LPCLs, our sampling strategy was not explicitly designed to provide a representative picture of any of the waste streams studied. This should be

borne in mind when drawing conclusions from our data.

Samples were collected between 5 October 2015 and 18 May 2016. Table 2.1 summarises the numbers of different sample types for which XRF measurements of Br were made, along with the number of samples subjected to analysis for concentrations of PBDEs, HBCDD and TBBP-A. Further details regarding the collection of samples from each waste stream are provided below.

2.1.1 Construction and demolition waste

The C&D waste samples collected were restricted to polystyrene insulation foams typically used as cavity wall insulation in homes and other buildings. Two

Table 2.1. Classes and subclasses of waste products analysed for Br and POP-BFR content

Waste stream	Sub-stream	Number of XRF measurements of Br made	Number of samples subjected to analysis for BFRs
C&D	XPS	22	20
	EPS	40	40
Automotive	ELV fabrics and foams	135 ^a	119 ^a
Soft furnishings	Carpets	32	31
	Curtains	15	15
	Furniture fabrics	22	22
	Furniture foam filling	20	20
	Mattresses	34 ^b	34 ^b
WEEE	Large household appliances	59	57
	Cooling appliances (fridges/freezers)	128 ^c	30 ^c
	Display items	122 ^d	43 ^d
	SDAs	62 ^e	29 ^e
	IT and telecommunications	78	78
Total	–	769	538

^aComprises a mixture of fabric seat covers, foam fillings, roof trims, floor mats and polystyrene padding.

^b17 mattresses were tested, with fabric coverings and foam fillings tested separately.

^c43 fridges/freezers were tested for Br, with XRF measurements taken at three points per appliance (except for one case for which only two measurements were taken, yielding 128 Br measurements); for logistical reasons, only 10 appliances (three samples from each) were tested for PBDEs, HBCDD and TBBP-A.

^d44 display items were tested for Br, with XRF measurements taken at one to three points per appliance (yielding 122 Br measurements); for logistical reasons, only 35 appliances (with usually one but occasionally two to three samples from each) were tested for PBDEs, HBCDD and TBBP-A.

^e26 SDAs were tested for Br, with XRF measurements taken at one to three points per appliance (yielding 62 Br measurements); for logistical reasons, only 14 appliances (with one to three samples from each) were tested for PBDEs, HBCDD and TBBP-A.

IT, information technology.

different types of polystyrene insulation foam were sampled, EPS and XPS, manufactured using the same base polymer but different processes.

Samples were collected from three main sources: (1) recently demolished buildings (samples taken directly from the source of waste); (2) a demolition company that stockpiles reusable waste insulation for future construction operations; and (3) a C&D waste collection site (specifically collecting waste from demolished buildings and waste furniture and furnishings). This provided a sample set that was at least to some extent representative of waste insulation at different stages of the end-of-life cycle in Ireland.

2.1.2 End-of-life vehicle waste

A mixture of soft furnishings was collected from ELVs, including seat PUF fillings, floor mats, ceiling padding and seat upholsteries. All samples were collected from the same facility, where cars are sent to scrap or parts are recycled. Where possible, car make, model and year of manufacture were collected for each sample.

2.1.3 Soft furnishing waste

Soft furnishings were divided into three sub-classes of waste:

1. *Carpets and curtains.* Carpet and curtain samples were collected from household waste sites in Ireland. Because of the nature of the samples, details about date/place of manufacture were not available.
2. *Furniture fabrics and foam fillings.* Samples from this sub-class were almost entirely taken from couches and armchairs containing expanded PUFs used as cushioning and fillers and fabric coverings. Samples were also taken from one footstool and a "patio umbrella". Overall, 21 separate furniture items were sampled from two recycling centres, resulting in 20 foam filling and 22 upholstery samples collected.
3. *Mattresses.* The "mattress" sub-class comprised discarded mattresses from consumers, with samples of fabric coverings and foam fillings collected separately.

2.1.4 Waste electrical and electronic equipment

Waste electrical and electronic equipment was divided into five sub-classes, which refer to the different categories of electronic and electrical items. These categories are as follows:

1. information technology (IT) and telecommunications devices: computer stacks, keyboards, printers, internet routers, television boxes, games consoles and CD players;
2. SDAs: blenders, kettles, toasters, portable heaters/coolers, portable vacuum cleaners, irons, deep fryers, steam cleaners and hairdryers;
3. large household appliances (LHAs): washing machines, vacuum cleaners, dryers, dishwashers and ovens;
4. audio-visual and recording devices (display items): televisions, computer monitors, DVD players, VCRs and combinations thereof;
5. refrigerators and freezers: refrigerators, freezers and combinations thereof.

2.2 Measurement of Concentrations of Br using Hand-held XRF

Prior to the sampling campaign, the XRF device (a Niton XL3t 700; Niton, UK) was calibrated by the manufacturer using proprietary standard reference materials. During the measurement campaign, a system check was carried out at the start and end of each day's measurements and at intervals of every 30 measurements.

Where applicable (e.g. furniture fabric coverings) an aliquot of the item under test was removed such that a minimum sample thickness was obtained. These minimum sample thicknesses depended on the waste category, thus:

- expanded PUF, as in furniture or vehicle seat foam: approximately 15–20 cm;
- EPS/XPS: approximately 10–15 cm;
- fabrics/textiles: approximately 3 cm;
- HIPS/ABS, as found in WEEE: approximately 2 cm.

The sample to be analysed was placed on a sampling table/surface in an accessible area with an adequate safety area (approximately 1 m radius from the sampling point). The surface of the article to be measured was marked/outlined using appropriate material (tape, marker pen, etc.) and cleared of dust and dirt using a clean tissue. XRF determination of Br was then carried out for no fewer than 30 seconds, keeping the device steady and centred over the target area throughout the measurement period. The analysis was repeated twice on separate areas of the same article, with each area several centimetres apart. Each measurement was recorded. The uncertainty with which Br could be measured in samples where Br fell in the range 500–2000 mg/kg (i.e. around the LPCL of 1000 mg/kg) was determined to be 5% for fabrics, 10% for PUF and 20% for EPS.

To obtain aliquots of each article tested by XFR for BFR measurement, a portion from the area from which XRF measurements were made was cut from the main sample body (approximately 1 cm²/approximately 1 cm³) using a cutting implement (cleaned before and after each use with an iso-propyl alcohol-soaked tissue), placed in a 40 mm × 60 mm polyethylene sampling bag, labelled appropriately and safely stored in a fridge at the National University of Ireland at Galway until transportation to the laboratory at the University of Birmingham.

2.3 Measurement of Concentrations of POP-BFRs

Full details of the methods deployed here are provided in Abdallah *et al.* (2017). As well as PBDEs and HBCDD, TBBP-A was also measured.

3 Results

This chapter presents the data obtained on concentrations of Br and BFRs in the waste articles tested in the WAFER project. In total, measurements of Br were taken for 769 articles, with BFRs measured for 538 of these.

3.1 Concentrations of Br in Waste Articles

Table 3.1 provides a statistical summary of the concentrations of Br detected in waste articles from the different sample categories.

3.2 Concentrations of BFRs in Waste Articles

Table 3.2 provides a statistical summary of the concentrations of target BFRs detected in waste articles from the different sample categories.

Table 3.1. Statistical summary of concentrations of Br (mg/kg) in Irish waste samples

Waste category	Median concentration	Average concentration	Maximum concentration
C&D XPS+EPS (<i>n</i> =62)	29	1200	92,000
LHAs (<i>n</i> =59)	<DL	60	2100
Display (<i>n</i> =122)	31	15,000	150,000
Fridges/freezers (<i>n</i> =128)	<DL	8400	180,000
IT items (<i>n</i> =78)	18	2000	110,000
SDAs (<i>n</i> =62)	0.5	470	12,000
All ELV waste (<i>n</i> =135)	22	1000	35,000
All soft furnishings (<i>n</i> =123)	17	4000	87,000

DL, detection limit.

Table 3.2. Statistical summary of conc.s (mg/kg) of POP-BFRs and BDE-209 in Irish waste samples and percentage of samples exceeding LPCLs

Waste category	Σ Tri-octa-BDEs				Σ HBCDD				BDE-209					
	Median conc.	Average conc.	Maximum conc.	% > LPCL	Median conc.	Average conc.	Maximum conc.	% > LPCL	Median conc.	Average conc.	Maximum conc.	% > LPCL ^a	% > LPCL ^b	% > LPCL ^c
C&D XPS + EPS (n = 60)	< 0.0008	< 0.0008	< 0.0008	0	38	1300	10,000	23	< 0.0015	< 0.0015	< 0.0015	0	0	0
C&D XPS (n = 20)	< 0.0008	< 0.0008	< 0.0008	0	20	29	94	0	< 0.0015	< 0.0015	< 0.0015	0	0	0
C&D EPS (n = 40)	< 0.0008	< 0.0008	< 0.0008	0	83	2000	10,000	35	< 0.0015	< 0.0015	< 0.0015	0	0	0
LHAs (n = 57)	< 0.0008	0.15	3	0	< 0.0003	< 0.0003	< 0.0003	0	0.04	19	190	0	0	0
Display items (n = 43)	< 0.0008	38	1400	2.3	< 0.0003	14	330	0	< 0.0015	1900	60,000	4.7	4.7	4.7
Fridges/freezers (n = 30)	< 0.0008	0.02	0.16	0	< 0.0003	< 0.0003	< 0.0003	0	< 0.0015	0.5	4	0	0	0
IT items (n = 78)	< 0.0008	17	890	0	< 0.0003	20	1600	1.3	< 0.0015	260	7600	5.2	2.6	2.6
SDAs (n = 29)	< 0.0008	< 0.0008	1	0	< 0.0003	< 0.0003	< 0.0003	0	< 0.0015	170	1600	6.9	0	0
All ELV waste (n = 119)	< 0.0008	8	740	0	< 0.0003	45	3300	1.5	2	840	31,000	3.7	3.7	3.0
ELV fabrics (n = 50)	< 0.0008	2	20	0	< 0.0003	150	3300	4.0	4	1700	31,000	6.0	6.0	6.0
ELV PUF (n = 38)	0.05	20	740	0	< 0.0003	< 0.0003	2	0	0.73	10	120	0	0	0
ELV floor mats (n = 11)	0.01	0.2	2	0	< 0.0003	< 0.0003	< 0.0003	0	0.41	2100	24,000	9.1	9.1	9.1
ELV roof trim (n = 14)	0.02	0.44	6	0	< 0.0003	< 0.0003	< 0.0003	0	0.51	360	4000	7.1 ^d	7.1	0
ELV PS padding (n = 6)	0.03	0.06	0.2	0	< 0.0003	< 0.0003	< 0.0003	0	11	31	130	0	0	0
Carpets (n = 31)	< 0.0008	0.8	13	0	< 0.0003	1	26	0	< 0.0015	240	7000	3	3	3
Furniture PUF (n = 20)	0.17	0.8	7	0	0.27	1200	8000	25	15	660	7800	15	5	5
Furniture fabrics (n = 22)	0.26	21	160	0	1.1	9200	51,000	27	12	6800	73,000	27	27	18
Curtains (n = 15)	< 0.0008	0.2	1.7	0	< 0.0003	4	56	0	< 0.0015	4	52	0	0	0
Mattress PUF (n = 17)	0.08	0.14	0.9	0	< 0.0003	< 0.0003	< 0.0003	0	8	79	870	0	0	0
Mattress fabrics (n = 17)	0.02	0.11	0.6	0	0.06	2	12	0	7	10	49	0	0	0

^aAssuming that LPCL for BDE-209 is 1000 mg/kg.^bAssuming that LPCL for BDE-209 is 3000 mg/kg.^cAssuming that LPCL for BDE-209 is 5000 mg/kg.^dOne sample of ELV roof trim contained 978 mg/kg of BDE-209; treating this as an LPCL exceedance would raise the “% > LPCL” figure to 14%.

PS, polystyrene.

4 Discussion

This section interprets the data generated in the context of the objectives laid out in section 1.1.

4.1 How Effective is Hand-held XRF as a Screening Tool for Compliance with LPCLs for POP-BFRs?

As a first step, we compared the XRF-derived measurements of Br in each sample with the corresponding measurements of BFRs obtained via GC-MS and liquid chromatography-tandem mass spectrometry (LC-MS/MS). If XRF measurements of Br were a perfect indicator of the POP-BFR content of a sample, then correlation of the two metrics would display a positive linear relationship, with a correlation coefficient (R) of 1, a zero y -intercept and a slope of > 1 , which reflects the fact that Br constitutes only a fraction of the POP-BFR mass. To illustrate, Br constitutes approximately 75% of the total HBCDD mass and thus a Br measurement must be multiplied by 1.34 to convert it to the equivalent HBCDD concentration. This has important implications if hand-held XRF (or other metrics of Br) are to be used to check LPCL compliance for POP-BFRs. Specifically, the threshold value for Br must be lower than the LPCL for a given POP-BFR. For example, for HBCDD, the Br threshold should be $1000/1.34 = 746$ mg/kg, whereas, for penta-BDE, the Br threshold should be $1000/1.41 = 710$ mg/kg.

Inspection of our data for all 538 samples tested for both Br and BFRs combined revealed substantial deviation from the ideal described above. This is unsurprising, however, and does not necessarily invalidate the use of XRF as a tool for screening for LPCL compliance. The principal reason for this is source misclassification. Source misclassification is a situation in which the XRF measurement of Br is attributed only partially or not at all to the presence of a POP-BFR. For example, a sample may be indicated by XRF to contain a measurable concentration of Br that is not attributed to the presence of a POP-BFR, but to a BFR not covered by an LPCL, such as TBBP-A. The implications of source misclassification are most serious when the Br concentration incorrectly

indicates that the item under test exceeds the LPCL for a POP-BFR. We discuss this issue later in more detail but, for now, it provides an explanation for the lack of correlation between measurements of Br and measurements of POP-BFRs across the entire database of 538 samples. One inference of this is that better correlation should be obtained (1) when samples in a given waste category only rarely (if ever) contain a non-POP-BFR and (2) when BDE-209, which has very recently been listed as a POP under the Stockholm Convention and for which an LPCL is set to become effective from March 2019 (EC, 2017b), is assumed to be a POP-BFR for correlation purposes. An example of scenario (1) is C&D waste EPS and XPS, for which the only BFR detected was HBCDD. Figure 4.1 demonstrates the highly significant correlation ($R = 0.993$; $p < 0.001$) between Br and POP-BFR concentrations in C&D waste EPS and XPS samples, indicating that hand-held XRF is likely to be an effective tool for checking compliance with LPCLs for C&D EPS and XPS waste.

Examples of scenario (2) are provided by examination of the data for (i) waste soft furnishings and (ii) ELV waste. Figure 4.2 shows the correlation between Br and POP-BFR concentrations for waste soft furnishings (comprising both fabric coverings and PUF fillings). Although significant ($p < 0.001$), the correlation coefficient is relatively low ($R = 0.38$). Similar analysis of our data for ELV waste showed the correlation to be insignificant ($p > 0.1$). For ELV waste, in particular, this suggests that hand-held XRF is not an effective proxy measurement of POP-BFR concentrations.

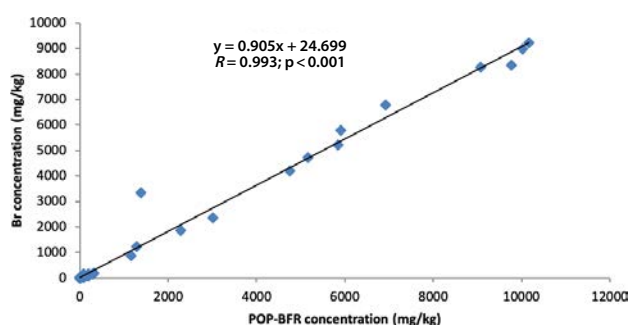


Figure 4.1. Plot of Br versus POP-BFR concentrations (mg/kg) for C&D waste (EPS/XPS).

That such imperfect correlations between Br and POP-BFR concentrations for these waste streams are attributable largely to source misclassification is well illustrated by Figure 4.3, which shows the highly significant ($p < 0.001$) positive linear correlation ($R = 0.919$) between Br and Σ BFR (i.e. the sum of all PBDEs, HBCDD and TBBP-A) concentrations for waste soft furnishings. A similar highly significant correlation ($R = 0.994$) was observed for ELV waste.

Importantly, Figure 4.4, which plots Br concentrations against the sum of POP-BFR and BDE-209 concentrations for waste soft furnishings, is near identical to the plot of Br concentrations against Σ BFR concentrations (see Figure 4.3); the corresponding two plots for ELV waste were completely identical. The inference of this is that for these two waste categories the source misclassification is either completely (ELV waste) or near completely (waste soft furnishings) attributable to the presence of BDE-209 in some articles. This is important given the recent listing of BDE-209 under the Stockholm Convention on POPs,

as it means that, on enforcement of an LPCL for BDE-209, hand-held XRF is indicated by our data to provide an effective proxy measurement of compliance with LPCLs for BFRs in ELV waste and waste soft furnishings, as well as C&D EPS and XPS. This may provide justification for adding any LPCL assigned to BDE-209 to the existing LPCL for the sum of tetra-, penta-, hexa- and hepta-BDEs.

The situation differs somewhat for the WEEE samples ($n = 237$) examined in this study. The WEEE samples examined consisted of LHAs, SDAs, IT equipment, fridges and freezers and display items (e.g. televisions and PC monitors). Although for some purposes we discuss data for different sub-categories of WEEE, such as LHAs and display items, separately, Figure 4.5 plots Br concentrations against POP-BFR concentrations for all 237 WEEE samples combined, revealing a relatively weak positive linear correlation ($R = 0.195$; $p = 0.003$), reflecting a number of samples for which elevated Br concentrations are not attributable to POP-BFRs

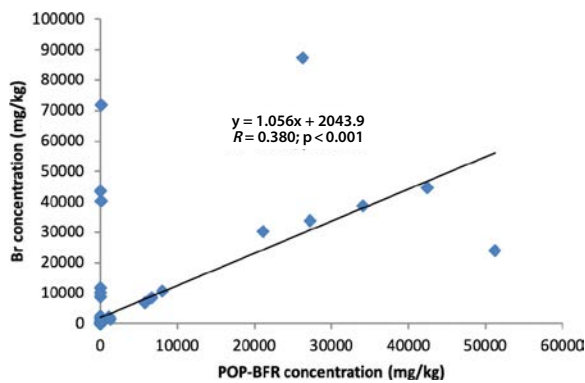


Figure 4.2. Plot of Br versus POP-BFR concentrations (mg/kg) for waste soft furnishings.

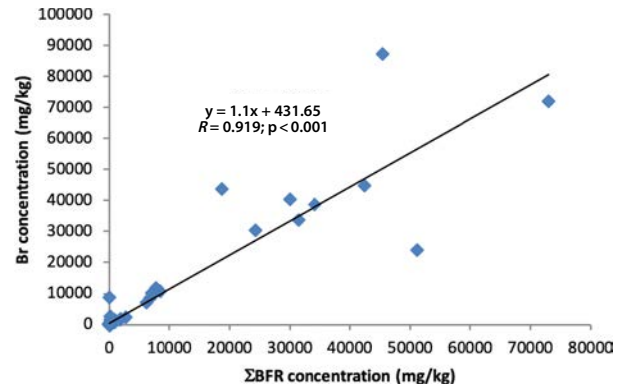


Figure 4.3. Plot of Br versus Σ BFR concentrations (mg/kg) for waste soft furnishings.

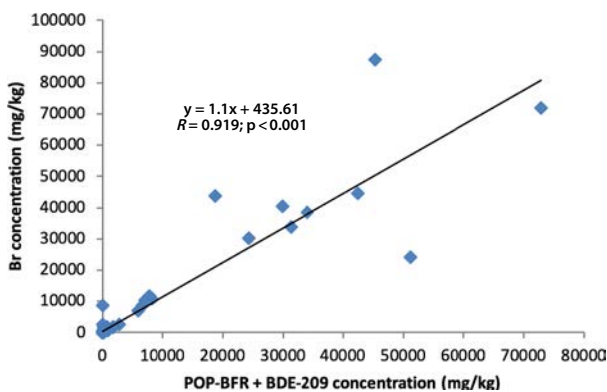


Figure 4.4. Plot of Br versus POP-BFR + BDE-209 concentrations (mg/kg) for waste soft furnishings.

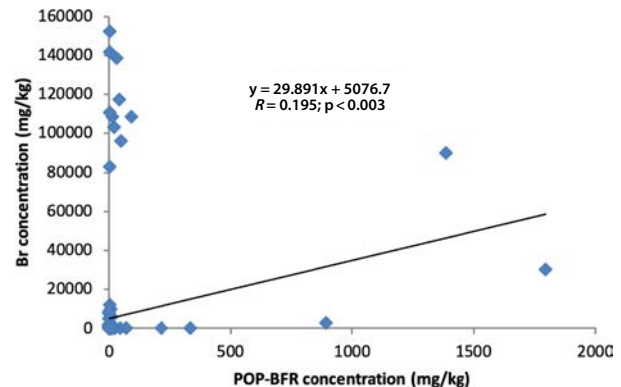


Figure 4.5. Plot of Br versus POP-BFR concentrations (mg/kg) in WEEE.

(top-left quadrant of figure). Although plotting Br concentration against the concentration of the sum of POP-BFRs and BDE-209 strengthens the correlation a little ($R=0.307$; $p<0.001$), close inspection reveals a number of samples for which a high Br concentration is not matched by an elevated POP-BFR + BDE-209 concentration (i.e. false positives). In contrast, a much stronger correlation is observed between Br and Σ BFR concentrations ($R=0.788$; $p<0.001$) (Figure 4.6), along with a marked reduction in the number of samples for which a high Br concentration is not matched by an elevated Σ BFR concentration, indicating that TBBP-A (which is not a POP-BFR) is the cause of source misclassification in many samples.

In the context of the potential use of XRF as a tool for testing compliance with POP-BFR LPCLs, the incidence of “false positives” and “false negatives” is crucial. A “false positive” is defined here as a specific source misclassification scenario, that is, a situation in which the XRF measurement of Br indicates that the LPCL for a POP-BFR has been exceeded but the POP-BFR concentration is below the LPCL. By comparison, a “false negative” occurs when the POP-BFR concentration is above the LPCL but this is not indicated by the XRF measurement of Br. For the purposes of this discussion, we have assumed a conservative Br LPCL based on the Br detected being attributable to penta-BDE. Thus, any sample exceeding 710 mg of Br/kg is assumed here to exceed the POP-BFR LPCL of 1000 mg of POP-BFR/kg.

Of the 538 items tested, there were 52 false positives and no false negatives when only the current LPCLs for POP-BFRs (i.e. excluding BDE-209) were considered. Of these false positives, 18 were the result of BDE-209

concentrations of >1000 mg/kg, with the remaining 34 instances resulting from concentrations of >1000 mg/kg of TBBP-A alone ($n=13$), as yet unidentified Br-containing compounds ($n=18$) and three separate instances of moderate concentrations of BDE-209, HBCDD or penta-octa-BDEs approaching but not exceeding 1000 mg/kg. By inference, introduction of an LPCL of 1000 mg/kg for BDE-209 would reduce the number of false positives to 34. Translating these incidences into percentages, our data show that use of hand-held XRF to monitor compliance with current LPCLs for PBDEs and HBCDD would mean that 9.7% of articles from the waste categories studied would be incorrectly identified as unrecyclable. This compares with 29 articles (5.4%) identified as genuinely exceeding current LPCLs and 47 articles (8.7%) exceeding LPCLs when BDE-209 is included. In the event of an LPCL of 1000 mg/kg being introduced for BDE-209, then the percentage of false positives would fall to 6.3%. The implications of such false positives are essentially that a small additional percentage of articles will not be available for recycling and that there will be an additional unnecessary economic cost incurred when such articles are subjected to special treatment. Balanced against these issues, it may be argued that, as the cause of the false positives is likely to be either known or unidentified BFRs, which may become subject to future legislative restriction, false positives can potentially be viewed as an acceptable limitation of the use of XRF as a screening tool for LPCL compliance. By comparison, false negatives would exert a more detrimental impact as they would allow regulated POP-BFRs to remain in circulation. However, as shown by the absence of false negatives in our 538 samples, our data suggest that use of hand-held XRF will only very rarely – if ever – fail to identify articles that exceed LPCLs.

The strength of correlation between Br and either POP-BFRs or POP-BFRs + BDE-209 indicates that hand-held XRF could be a viable tool for testing compliance with LPCLs for C&D EPS/XPS, as well as ELV waste and waste soft furnishings. Our data on false positives confirm this view, while further underlining the potential issues with the use of hand-held XRF to test for LPCL compliance in WEEE, because of the more frequent presence of TBBP-A and other as yet unidentified compounds in such items.

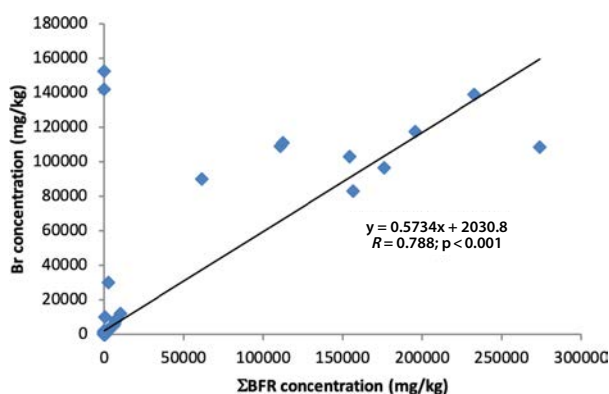


Figure 4.6. Plot of Br versus Σ BFR concentrations (mg/kg) in WEEE.

Specifically, of the 34 false-positives observed that are not due to BDE-209 concentrations of > 1000 mg/kg, 26 were found for WEEE items (one LHA, 12 display items, six SDAs and seven IT items), with the remainder found for three ELV fabrics, one carpet, one furniture fabric, two furniture foams and one mattress foam. One alternative possible cause of false positives in WEEE is that the XRF Br measurement may reflect in some cases not only the polymer casing ostensibly under test but also the BFR content of the underlying electronics. Further work to determine the cause of false positives is recommended.

4.2 What is the Extent of the Presence of POP-BFRs in the Irish Waste Stream?

To estimate the mass of POP-BFRs generated annually in Ireland for the waste categories examined in this study, as a first step we derived estimates of the total mass of waste generated in Ireland that could plausibly contain POP-BFRs above the LPCL and that could therefore not be recycled and would instead require special treatment to remove or destroy the POP-BFR content. These estimates are provided in Table 4.1 for the different waste categories for which POP-BFR data have been obtained in the WAFER project. Table 4.1 also provides explanations of how the estimates were derived. It should be noted, however, that these waste stream figures are those collected through “official channels” and there is scope for quantities of such waste to be collected outside such official channels, e.g. WEEE sent directly to a scrap dealer, illegal treatment of ELVs.

4.2.1 Which waste categories contain items exceeding current LPCLs?

A statistical summary of the concentrations of POP-BFRs and BDE-209 detected in the samples analysed in this project was provided in Table 3.2. Table 3.2 also gives the percentage of samples analysed from different waste categories that contained concentrations of POP-BFRs that exceeded LPCLs. Overall, only 29 items (5.4%) contained POP-BFR concentrations that exceeded existing LPCLs.

Table 3.2 shows inter alia how many of the 538 individual waste items analysed in this study exceeded current LPCLs. Specifically:

- For Σ tri-octa-BDEs (essentially those representing penta- and octa-BDE formulations), there was only one exceedance for a single display item (a CRT television housing). Notably, though, this item also exceeded to a far greater extent the notional LPCL for BDE-209 (1400 mg/kg of Σ tri-octa-BDE c.f. 60,000 mg/kg of BDE-209). Although there were two other individual items (a PC keyboard and foam upholstery from a vehicle) that contained concentrations of Σ tri-octa-BDEs that approached the LPCL (890 and 740 mg/kg, respectively), the evidence overall is that very few items currently entering the waste stream in Ireland exceed existing LPCLs for PBDEs.
- In contrast, LPCL exceedances for HBCDD were quite frequent, being observed for 35% ($n=14/40$) of the C&D EPS samples measured, 25% and 27% of the furniture PUF ($n=5/20$) and fabric ($n=6/22$) samples, respectively, 1.3% ($n=1/78$) of the IT items and 4% ($n=2/50$) of the ELV fabric samples.

Although exceedances were observed for some waste categories, there were other waste categories for which no exceedances of existing LPCLs were observed. These were:

- C&D XPS;
- LHAs;
- SDAs;
- ELV PUF, floor mats, roof trim and padding;
- carpets;
- curtains;
- mattresses (both PUF and fabrics).

In addition, no exceedances were observed for the plastic samples removed for BFR analysis from fridges and freezers. However, a substantial caveat to this is that some XRF measurements revealed Br concentrations of > 1000 mg/kg in 12 fridges/freezers when measurements were taken on the black plastic housing of the electric motors. For logistical reasons, samples of these plastics were not removed for BFR analysis. Although the contribution of such black plastic housing to the overall mass of plastic contained within each fridge/freezer will be low, it is recommended that such analyses should be conducted in future to elucidate whether the Br can be attributed to POP-BFRs. In the meantime, it would be prudent to separate such electrical housing from

Table 4.1. Estimated annual mass (tonnes/year) of waste generated in Ireland for the waste categories examined in this study

Waste category	Estimated annual mass generated in Ireland	Source
C&D EPS/XPS	4639	In 2015, approximately 3,313,858 tonnes of C&D waste were produced in Ireland (EPA, 2017). There are no specific data for the proportion of C&D waste in Ireland that is insulation material; however, in the UK it has been estimated that 2.8% of C&D waste is insulation material, 5% of which is EPS and XPS (DEFRA, 2010). Assuming an identical proportion for Ireland generates an estimate of 4639 tonnes/year of waste EPS/XPS generated in Ireland
LHAs	16,098	Estimate for 2015 when the EPA (2017) reported that 48,616 tonnes of WEEE were collected for treatment and assuming that the mass proportion of total WEEE represented by LHAs was the same as in 2011 (i.e. 33.1%; 13,604 tonnes of LHAs out of a total WEEE mass of 41,092 tonnes) (EPA, 2013)
Display items	7870	Estimate for 2015 when the EPA (2017) reported that 48,616 tonnes of WEEE were collected for treatment and assuming that the mass proportion of total WEEE represented by display items was the same as in 2011 (i.e. 16.2%; 6651 tonnes of display items out of a total WEEE mass of 41,092 tonnes) (EPA, 2013)
Fridges/freezers	7066	Estimate for 2015 when the EPA (2017) reported that 48,616 tonnes of WEEE were collected for treatment and assuming that the mass proportion of total WEEE represented by fridges/freezers was the same as in 2011 (i.e. 14.5%; 5971 tonnes of fridges/freezers out of a total WEEE mass of 41,092 tonnes) (EPA, 2013)
SDAs and other IT waste	16,806	Estimate for 2015 when the EPA (2017) reported that 48,616 tonnes of WEEE were collected for treatment and assuming that the mass proportion of total WEEE represented by SDAs was the same as in 2011 (i.e. 34.5%; 14,202 tonnes of SDAs and other IT items out of a total WEEE mass of 41,092 tonnes) (EPA, 2013). As separate estimates for arisings of SDAs and items included in the "IT items" category are unavailable, we derived an estimate for combined arisings of these categories by assuming that it is equivalent to the figure cited for "other WEEE" (e.g. stereos, phones, toys, vacuum cleaners, toasters, computers) (EPA, 2013)
ELV foam and fabrics	1924	Assuming 75,000 ELVs generated in 2012 (EPA, 2017) and an average vehicle weight of 1069 kg (EPA, 2013). We then assumed that ELV foam and fabrics were identical to light auto shredder residue, which WRc (2012a) reported represented 27,222 tonnes of the 1,123,873 tonnes of ELV generated annually in the UK, i.e. 2.4%
Carpets	7834	Assuming Irish mass pro-rata ^a to UK 2010–11 arisings of 103,972 tonnes (WRAP, 2012)
Furniture foam	2685	Assuming Irish mass pro-rata ^a to UK 2010–11 waste arisings for sofas, armchairs and chairs combined of 237,516 tonnes (WRAP, 2012) and authors' own estimate that of this 15% is foam
Furniture fabrics	895	Assuming Irish mass pro-rata ^a to UK 2010–11 waste arisings for sofas, armchairs and chairs combined of 237,516 tonnes (WRAP, 2012) and authors' own estimate that of this 5% is fabrics
Curtains	754	Assuming Irish mass pro rata ^a to UK 2010–11 arisings of 20,000 tonnes for "all other bulky textiles" (WRAP, 2012) and authors' own estimate that 50% of this is curtains
Mattress foam	6272	Assuming Irish mass pro rata ^a to UK 2010–11 arisings of 166,474 tonnes (WRAP, 2012) and authors' own estimate that 50% of this is foam
Mattress fabrics	2509	Assuming Irish mass pro rata ^a to UK 2010–11 arisings of 103,972 tonnes (WRAP, 2012) and authors' own estimate that 20% of this is fabrics

^aPro rata calculations based on 2011 census data for the UK population of 63,182,000 and 2016 Irish census data for the population of Ireland of 4,761,185.

the rest of the fridge/freezer and treat it as potentially exceeding LPCLs.

It is also important to highlight that the average concentrations of currently designated POP-BFRs in the samples analysed here (see Table 3.2) exceed existing LPCLs only in C&D EPS, furniture PUF and furniture fabrics and only for HBCDD alone. This suggests that, if monitoring for LPCL compliance is conducted on shredded waste composites [as generated during, for example, fragmentising of waste vehicles to yield auto shredder residue (ASR)], then the occasional LPCL exceedance for individual items from waste categories such as display items, IT items and ELV fabric samples will not be detected, with the result that LPCL exceedances will be restricted to C&D EPS, furniture PUF and fabric items. Further analysis is recommended to evaluate whether individual items in these last three waste categories should be monitored for LPCL compliance in order to identify those items that do not require special treatment or whether instead it would be more

cost-effective to assume that all such waste items require special treatment, thereby avoiding the need to monitor for LPCL compliance and its associated cost.

Another implication of the observation that no LPCL exceedances would occur based on average concentrations in waste categories such as display items, IT items and ELV fabric samples is that the small number of LPCL-exceeding individual items in such categories would not be diverted from the recycling stream if monitoring was conducted on waste composite samples. However, given the relatively low mass of POP-BFRs associated with such waste categories (Table 4.2), it may be considered more cost-effective to monitor compliance using shredded/fragmentised waste composites for these categories. However, removal/separation at source of individual waste items containing POPs should be viewed as the preferred option. Similar considerations apply when BDE-209 concentrations and exceedances are taken into account (see section 4.2.2).

Table 4.2. Estimated annual mass (kg/year) of POP-BDEs, HBCDD and BDE-209 associated with Irish waste categories

Waste category	POP-BDEs	HBCDD	ΣPOP-BFRs	BDE-209	ΣPOP-BFRs + BDE-209
C&D XPS + EPS	0	6092	6092	0	6092
LHAs ^a	0.0069	0	0.0069	0.86	0.87
Display items ^b	53.4	19.7	73.1	2680	2753
Fridges/freezers ^c	0.012	0	0.012	0.325	0.34
SDAs and other IT equipment ^d	33.3	40.2	73.5	628	702
ELV foam and fabrics	14.5	119	134	1827	1961
Carpets	6.0	8.3	14.3	1797	1811
Furniture foam	2.1	3079	3081	1776	4857
Furniture fabrics	18.5	8224	8243	6048	14,291
Curtains	0.15	2.9	3.1	2.8	5.9
Mattress foam	0.88	0	0.88	498	499
Mattress fabrics	0.27	5.5	5.8	25.6	31.4
Total	129	17,590	17,721	15,284	33,004

^aAssuming that 0.29% w/w of LHAs is Br-containing plastic (WRc, 2012b).

^bAssuming that 18% w/w of display waste is Br-containing plastic (WRc, 2012b).

^cAssuming that 10% w/w of waste fridges and freezers is Br-containing plastic (WRc, 2012b).

^dAssuming that 16.1% w/w of SDAs and other IT equipment is Br-containing plastic (WRc, 2012b). This is based on estimates that 0.75% and 18% w/w of SDAs and IT equipment, respectively, is Br-containing plastic and data for the UK which show that the mass of waste IT equipment is 8.21 times higher than the mass of waste SDAs (WRc, 2012b).

4.2.2 Which waste categories contain items exceeding LPCLs when these are extended to cover BDE-209?

Table 3.2 provides the percentage of samples analysed in each of the different waste categories studied that contained BDE-209 at concentrations exceeding plausible LPCLs of 1000 mg/kg (as currently envisaged; EC, 2017b), 3000 mg/kg and 5000 mg/kg. Overall, 47 items (8.7%) contained concentrations of Σ POP-BFRs or BDE-209 that exceeded 1000 mg/kg.

More specifically, exceedances were observed for:

- each of the three notional LPCLs for 4.7% ($n=2/43$) of display items;
- 5.2% ($n=4/78$) of IT items at an LPCL of 1000 mg/kg or 2.6% ($n=2/78$) if either of the higher LPCLs was assumed;
- 6.9% ($n=2/29$) of SDAs at an LPCL of 1000 mg/kg, with no exceedances at either of the higher LPCLs;
- 6% ($n=3/50$) of ELV fabrics (regardless of which LPCL was assumed);
- 9.1% ($n=1/11$) of ELV floor mats (regardless of which LPCL was assumed);
- 7.1% ($n=1/14$) of ELV roof trim samples if an LPCL of either 1000 or 3000 mg/kg was assumed (as the concentration in this item was 4000 mg/kg, there was no exceedance if an LPCL of 5000 mg/kg was assumed);
- 3.2% ($n=1/31$) of carpets (regardless of which LPCL was assumed);
- 15% ($n=3/20$) of furniture PUF at an LPCL of 1000 mg/kg or 5% ($n=1/20$) if either of the higher LPCLs was assumed; and
- 27% ($n=6/22$) of furniture fabrics at an LPCL of either 1000 or 3000 mg/kg or 18% ($n=4/22$) if an LPCL of 5000 mg/kg was assumed.

Notwithstanding the above, there were some waste stream categories for which no exceedances of either existing or anticipated LPCLs (for BDE-209) were observed. These were:

- C&D XPS;
- LHAs;
- fridges and freezers (with the aforementioned caveat that XRF measurements of Br of > 1000 mg/kg were found in 12 black plastic electric motor housings);
- ELV PUF;
- curtains;
- mattresses (both PUF and fabrics).

It is also important to highlight that the average concentrations of currently designated POP-BFRs and BDE-209 in the samples analysed here exceed existing and anticipated future LPCLs only in C&D EPS, display items, ELV fabrics, ELV floor mats, furniture PUF and furniture fabrics. This suggests that, if monitoring for LPCL compliance is conducted on pooled waste composites, then the occasional LPCL exceedance for individual items from waste categories such as IT items, SDAs, carpets and ELV roof trim would not be detected, with exceedances then restricted to C&D EPS, as well as display items, ELV fabrics and floor mats, furniture PUF and fabric items.

Further analysis is recommended to evaluate whether individual items of these waste categories (i.e. in C&D EPS, display items, ELV fabrics, ELV floor mats, furniture PUF and furniture fabrics) should be monitored for LPCL compliance in order to identify those items that do not require special treatment, or whether instead it would be more cost-effective to assume that all such waste items require special treatment, thereby avoiding the need to monitor for LPCL compliance. It is also highlighted that the average BDE-209 concentration in all 119 ELV items tested was, at 840 mg/kg, not far below the LPCL of 1000 mg/kg for BDE-209. This suggests that ASR in Ireland may exceed such an LPCL for BDE-209 when introduced.

4.2.3 What are the human exposure implications of reuse of discarded soft furnishings?

Table 3.2 shows that furniture foam (PUF) and furniture fabrics demonstrate the highest proportion of items that exceed either existing LPCLs for PBDEs and HBCDD or anticipated future values for BDE-209. Our data show that exceedances occur for HBCDD and BDE-209 only, with no exceedances observed for penta- and octa-BDE congeners. Given that such furniture items are far more likely to be reused (e.g. via charity shops) than any of the other waste categories studied in this project, it is prudent to consider the possible human exposure implications of such reuse. As it has been demonstrated that BFRs may be transferred from fabrics to dust via a combination of (1) volatilisation followed by deposition to dust, (2) abrasion of fabric fibres and (3) transfer via direct fabric–dust contact (Rauert *et al.*, 2016), there is clear potential for human exposure when such items are reused. It is also plausible that enhanced emissions to

dust may occur via more facile abrasion of fabric fibres from older, more worn fabrics. Given these exposure implications, it would appear prudent to recommend that reuse of items exceeding LPCLs be ceased.

4.2.4 *What mass of different waste items would exceed existing and notional future LPCLs and require special treatment?*

Based on the mass estimates provided in Table 4.1, which represent a worst-case scenario in terms of the mass of material requiring special treatment, we calculated the estimated mass of material that our data (Table 3.2) indicate contains concentrations of POP-BFRs that exceed current LPCLs for penta- and octa-BDE, as well as HBCDD, and that therefore would require special treatment. These estimates are provided in Table 4.3. The total mass requiring special treatment amounts to 2369 tonnes/year, 3.1% of the estimated 75,352 tonnes/year generated. These estimates would increase substantially if it were decided that it would be more cost-effective to divert all items within some waste streams (i.e. those for which a substantial proportion of items exceed LPCLs) for special treatment. For example, diverting all display items would result in an additional 7870 tonnes/year of waste requiring special treatment.

In the event of an LPCL for BDE-209 being introduced, then these annual masses would increase to

4030 tonnes/year (5.3%), 3268 tonnes/year (4.3%) or 3252 tonnes/year (4.3%), depending on whether the LPCL assumed is 1000, 3000 or 5000 mg/kg, respectively. This suggests that using a higher LPCL for BDE-209 does not have a substantial impact on the mass of material requiring special treatment. Specifically, using an LPCL of 5000 mg/kg as opposed to 1000 mg/kg reduces the mass of material requiring special treatment by 778 tonnes/year, just 1% of the total mass of material generated annually. This has significant implications for the debate about what concentration should be set as the LPCL for BDE-209.

4.2.5 *What mass of POP-BFRs and BDE-209 would be diverted from the waste stream by enforcement of existing and notional future LPCLs?*

Table 4.2 gives the annual mass flows of POP-BFRs and BDE-209 associated with different waste categories in Ireland. In total, an estimated 129, 17,590 and 15,284 kg/year of PBDEs (excluding BDE-209), HBCDD and BDE-209, respectively, are generated currently in Ireland.

Combining the data in Tables 3.2 and 4.1, Table 4.4 provides estimates of the annual mass flow of POP-BFRs and BDE-209 that would be diverted from the waste stream for special treatment if existing LPCLs were enforced. Table 4.5 extends this to provide similar estimates assuming enforcement of various

Table 4.3. Estimated annual mass (tonnes/year) of the waste categories generated in Ireland that would require “special treatment” under various scenarios

Waste category	Current LPCL legislation	Assuming an LPCL of 1000 mg/kg for BDE-209	Assuming an LPCL of 3000 mg/kg for BDE-209	Assuming an LPCL of 5000 mg/kg for BDE-209
C&D EPS/XPS	1082	1082	1082	1082
LHAs	0	0	0	0
Display items	183	366	366	366
Fridges/freezers	0	0	0	0
SDA and other IT equipment	157	942	314	314
ELV foam and fabrics	32	81	81	65
Carpets	0	253	253	253
Furniture foam	671	940	806	806
Furniture fabrics	244	366	366	366
Curtains	0	0	0	0
Mattress foam	0	0	0	0
Mattress fabrics	0	0	0	0
Total	2369	4030	3268	3252

Table 4.4. Estimated annual mass (kg/year) of POP-BDEs, HBCDD and BDE-209 associated with Irish waste categories that would be diverted from the waste stream by enforcement of existing LPCLs

Waste category	POP-BDEs	HBCDD	ΣPOP-BFRs	BDE-209	ΣPOP-BFRs + BDE-209
C&D EPS/XPS	0	5884	5884	0	5884
LHAs ^a	0	0	0	0	0
Display items ^b	45.4	0	45.4	1969	2014
Fridges/freezers ^c	0	0	0	0	0
SDAs and other IT equipment ^d	5.1	40	45.1	11	56.1
ELV foam and fabrics	0	104	104	0	104
Carpets	0	0	0	0	0
Furniture foam	0	3058	3058	0	3058
Furniture fabrics	0	8219	8219	0	8219
Curtains	0	0	0	0	0
Mattress foam	0	0	0	0	0
Mattress fabrics	0	0	0	0	0
Total	50.5	17,305	17,356	1980	19,340

^aAssuming that 0.29% w/w of LHAs is Br-containing plastic (WRc, 2012b).

^bAssuming that 18% w/w of display waste is Br-containing plastic (WRc, 2012b).

^cAssuming that 10% w/w of waste fridges and freezers is Br-containing plastic (WRc, 2012b).

^dAssuming that 16.1% w/w of SDAs and other IT equipment is Br-containing plastic (WRc, 2012b). This is based on estimates that 0.75% and 18% w/w of SDAs and IT equipment, respectively, is Br-containing plastic and data for the UK which show that the mass of waste IT equipment is 8.21 times higher than the mass of waste SDAs (WRc, 2012b).

Table 4.5. Estimated annual mass (kg/year) of POP-BDEs, HBCDD and BDE-209 associated with Irish waste categories that would be diverted from the waste stream by enforcement of existing LPCLs and assuming various LPCLs for BDE-209

Waste category	POP-BDEs	HBCDD	ΣPOP-BFRs	BDE-209	ΣPOP-BFRs + BDE-209
C&D EPS/XPS	0	5884	5884	0	5884
LHAs ^a	0	0	0	0	0
Display items ^b	46.6	0	46.6	2634	2681
Fridges/freezers ^c	0	0	0	0	0
SDAs and other IT equipment ^d	24.7 (4.7 ^{e,f})	40	64.7 (44.7 ^{e,f})	481 (355 ^{e,f})	525 (400 ^{e,f})
ELV foam and fabrics	0	103	103	1785 (1717 ^f)	1888 (1,820 ^f)
Carpets	3	0	3	1715	1718
Furniture foam	0.8	3055	3056	1534 (1204 ^{e,f})	4580 (4262 ^{e,f})
Furniture fabrics	17.5	8220	8238	6006	14,244
Curtains	0	0	0	0	0
Mattress foam	0	0	0	0	0
Mattress fabrics	0	0	0	0	0
Total	92.6 (72.6 ^{e,f})	17,302	17,395 (17,375 ^{e,f})	14,155 (13,699 ^e) (13,631 ^f)	31,520 (31,077 ^e) (31,099 ^f)

^aAssuming that 0.29% w/w of LHAs is Br-containing plastic (WRc, 2012b).

^bAssuming that 18% w/w of display waste is Br-containing plastic (WRc, 2012b).

^cAssuming that 10% w/w of waste fridges and freezers is Br-containing plastic (WRc, 2012b).

^dAssuming that 16.1% w/w of SDAs and other IT equipment is Br-containing plastic (WRc, 2012b). This is based on estimates that 0.75% and 18% w/w of SDAs and IT equipment, respectively, is Br-containing plastic and data for the UK which show that the mass of waste IT equipment is 8.21 times higher than the mass of waste SDAs (WRc, 2012b).

^eMass diverted if a LPCL for BDE-209 of 3000 mg/kg is assumed; if no figure is given in parentheses, then the mass diverted under this LPCL scenario is identical to that assuming a BDE-209 LPCL of 1000 mg/kg

^fMass diverted if a LPCL for BDE-209 of 5000 mg/kg is assumed; if no figure is given in parentheses, then the mass diverted under this LPCL scenario is identical to that assuming a BDE-209 LPCL of 1000 mg/kg

notional future LPCLs for BDE-209. It is of note that higher LPCLs for BDE-209 reduce the mass of this contaminant diverted from the waste stream by only a small extent. Table 4.6 then expresses the effectiveness of enforcement of the current LPCLs in terms of the percentages of the annual POP-BFR and BDE-209 annual mass flows that would be diverted from the waste stream. Specifically, Table 4.6 shows that 97.9% of the estimated 17,721 kg of POP-BFRs generated annually in Ireland is projected to be diverted from the Irish waste stream by enforcement of existing LPCLs. Moreover, even though existing LPCLs do not address BDE-209, Table 4.6 highlights that, of the 33,004 kg of POP-BFRs + BDE-209 generated every year in Ireland, 58.6% would be diverted. Viewed another way, enforcement of *existing* LPCLs would divert 13.0% of the 15,284 kg of BDE-209 generated annually in Ireland.

The impact of enforcing an anticipated LPCL for BDE-209 on the percentage of annual POP-BFRs and BDE-209 mass flows diverted from the waste stream is provided in Table 4.7, which reveals that 98.1% of POP-BFRs is projected to be diverted from the Irish waste stream by enforcement of existing and future

LPCLs. This figure decreases to between 94.0% and 95.5% diversion of POP-BFRs *and* BDE-209 depending on which BDE-209 LPCL is assumed. It is important to note here that the zero percentage diversion figures for waste categories such as curtains, mattress foam and fabrics arise from the fact no such items were found to exceed LPCLs in the WAFER study. Reassuringly, inspection of Table 4.2 reveals that such waste categories have only minimal quantities of POP-BFRs associated with them, with the caveat that approximately 500 kg/year of BDE-209 is associated with mattress foam.

Combined, these figures suggest that existing LPCLs would be highly effective at reducing the mass of POP-BFRs remaining in the product loop and, indeed, would even result in a modest decrease in the amount of BDE-209 remaining in circulation. Moreover, introduction of LPCLs for BDE-209 in addition to those existing for POP-BFRs would be similarly effective at reducing the proportion of BDE-209 continuing to circulate.

Having identified waste items exceeding LPCLs, the next step is to remove the BFRs present in such items. This is addressed in the following section.

Table 4.6. Percentage of the estimated annual mass of POP-BDEs, HBCDD and BDE-209 associated with Irish waste categories that would be diverted from the waste stream by enforcement of existing LPCLs^a

Waste category	POP-BDEs	HBCDD	ΣPOP-BFRs	BDE-209	ΣPOP-BFRs + BDE-209
C&D XPS+EPS	0	96.6	96.6	0	96.6
LHAs ^b	0	0	0	0	0
Display items ^c	85.0	0	62.1	73.5	73.2
Fridges/freezers ^d	0	0	0	0	0
SDAs and other IT equipment ^e	15.3	99.5	61.4	1.8	8.0
ELV foam and fabrics	0	87.4	77.6	0	5.3
Carpets	0	0	0	0	0
Furniture foam	0	99.3	99.3	0	63.0
Furniture fabrics	0	99.94	99.7	0	57.6
Curtains	0	0	0	0	0
Mattress foam	0	0	0	0	0
Mattress fabrics	0	0	0	0	0
Total	39.1	98.4	97.9	13.0	58.6

^aCalculated as $100 \times [\text{annual mass diverted (Table 4.4)}/\text{annual mass generated (Table 4.2)}]$.

^bAssuming that 0.29% w/w of LHAs is Br-containing plastic (WRc, 2012b).

^cAssuming that 18% w/w of display waste is Br-containing plastic (WRc, 2012b).

^dAssuming that 10% w/w of waste fridges and freezers is Br-containing plastic (WRc, 2012b).

^eAssuming that 16.1% w/w of SDAs and other IT equipment is Br-containing plastic (WRc, 2012b). This is based on estimates that 0.75% and 18% w/w of SDAs and IT equipment, respectively, is Br-containing plastic and data for the UK which show that the mass of waste IT equipment is 8.21 times higher than the mass of waste SDAs (WRc, 2012b).

Table 4.7. Percentage of the estimated annual mass of POP-BDEs, HBCDD and BDE-209 associated with Irish waste categories that would be diverted from the waste stream by enforcement of existing LPCLs and assuming various LPCLs for BDE-209^a

Waste category	POP-BDEs	HBCDD	ΣPOP-BFRs	BDE-209	ΣPOP-BFRs + BDE-209
C&D XPS+EPS	0	96.6	96.6	0	96.6
LHAs ^b	0	0	0	0	0
Display items ^c	87.3	0	63.7	98.3	97.4
Fridges/freezers ^d	0	0	0	0	0
SDAs and other IT equipment ^e	74.2 (14.1 ^{f,g})	99.5	88.0 (60.8 ^{f,g})	76.6 (56.5 ^{f,g})	74.8 (57.0 ^{f,g})
ELV foam and fabrics	0	86.6	76.9	97.7 (94.0 ^g)	96.3 (92.8 ^g)
Carpets	50	0	21.0	95.4	94.9
Furniture foam	38.1	99.2	99.2	86.4 (67.8 ^g)	94.3 (87.7 ^g)
Furniture fabrics	94.6	99.95	99.94	99.3	99.7
Curtains	0	0	0	0	0
Mattress foam	0	0	0	0	0
Mattress fabrics	0	0	0	0	0
Total	71.8 (56.3 ^{f,g})	98.4	98.1 (98.0 ^{f,g})	92.6 (89.6, ^f 89.2 ^g)	95.5 (94.2, ^f 94.0 ^g)

^aCalculated as $100 \times [\text{annual mass diverted (Table 4.5)/annual mass generated (Table 4.2)}]$.

^bAssuming that 0.29% w/w of LHAs is Br-containing plastic (WRc, 2012b).

^cAssuming that 18% w/w of display waste is Br-containing plastic (WRc, 2012b).

^dAssuming that 10% w/w of waste fridges and freezers is Br-containing plastic (WRc, 2012b).

^eAssuming that 16.1% w/w of SDAs and other IT equipment is Br-containing plastic (WRc, 2012b). This is based on estimates that 0.75% and 18% w/w of SDAs and IT equipment, respectively, is Br-containing plastic and data for the UK which show that the mass of waste IT equipment is 8.21 times higher than the mass of waste SDAs (WRc, 2012b).

^fPercentage diverted if an LPCL for BDE-209 of 3000 mg/kg is assumed; if no figure is given in parentheses, then the percentage diverted under this LPCL scenario is identical to that assuming a BDE-209 LPCL of 1000 mg/kg.

^gPercentage diverted if an LPCL for BDE-209 of 5000 mg/kg is assumed; if no figure is given in parentheses, then the percentage diverted under this LPCL scenario is identical to that assuming a BDE-209 LPCL of 1000 mg/kg.

4.2.6 What treatment options are available to destroy BFRs present in materials that exceed LPCLs?

There are a number of potential ways in which items identified as exceeding LPCLs may be treated to remove or destroy their POP-BFR content. Given Ireland's objective of eliminating landfills as an option for waste disposal (EPA, 2016), a clear strategy is required for the disposal of materials containing POP-BFRs. The current approach for all waste treatment is geared towards the circular economy, in which waste is viewed as a resource and the focus is on waste reuse and recycling and use of waste as a fuel. However, with EU regulation 850/2004 setting LPCLs for all Member States, waste containing POPs must be treated appropriately before it can be recycled and/or disposed of. As noted, this is set to be further complicated by the addition of BDE-209 to the list of POPs under the Stockholm Convention, increasing the number of products that will exceed LPCLs.

Before discussing treatment options that could possibly be implemented in Ireland, it is instructive to consider approaches under consideration in other EU Member States. The most recent National Implementation Plan (NIP) submitted by Germany (UNEP, 2017a) states that "brominated and thus PBDE-containing plastics are usually treated in thermal recovery and removal/disposal methods". Moreover, it is implied that in Germany false positives are tolerated as the same document also states that "The separating out of brominated plastic parts does not differentiate between different fire retardants; plastic parts with permitted brominated fire retardants are therefore also separated out and recovered thermally". It is not clear how "non-brominated" plastics are identified, but the document does state that non-brominated plastics are considered to be "generally ABS and PS [polystyrene]". This implies that BFR-containing plastics are separated out on the basis of the polymer itself rather than by empirical measurement of BFR concentration. On

this specific issue, the NIP of the Czech Republic (UNEP, 2017b) reports that WEEE processors in that country “separate plastics (such as on the dry basis by lasers detecting Br, or on the wet basis by weight, as bromide is relatively heavy)”. Finally, the NIP for Sweden (UNEP, 2017c) implies that, as in Germany, incineration is the favoured treatment option, stating that “E-waste plastics containing brominated flame retardants are most commonly incinerated in Sweden in high temperature incineration of hazardous waste”.

Against this backdrop of approaches used elsewhere in the EU, the following sections address possible treatment options for those waste products that exceed LPCLs in Ireland, drawing on currently available guidance published by the United Nations (2017).

Construction and demolition waste

An investigation into treatment options by the German Umwelt Bundesamt (Federal Environment Agency; Umwelt Bundesamt, 2015) examined waste incineration as a potential pathway to meet LPCL requirements. The study found that, when EPS/XPS is co-incinerated (up to 2% of total content) with other waste (using best available techniques, i.e. total energy recovery), HBCDDs are destroyed with 99.99% efficiency. Furthermore, the process does not increase the risk of releasing other POPs [such as PBDEs, polychlorinated dibenzo dioxins and furans (PCDD/Fs), polybrominated dibenzo dioxins and furans (PBDD/Fs), polyhalogenated dibenzo dioxins and furans (PXDD/Fs) and polychlorinated biphenyls (PCBs)] and also removes ozone-depleting substances. Treating EPS/XPS in this way would not only destroy the HBCDD content with a far greater efficiency than required by EU law but would also use it as a fuel source, which would assist in meeting Ireland’s energy requirements. Therefore, it is suggested that the best treatment option for EPS/XPS that is “at risk” of exceeding LPCLs is total energy recovery waste incineration. A concern in this scenario is that the current infrastructure in Ireland may not be able to handle the current volumes of HBCDD-containing waste EPS/XPS (as it can constitute up to 2% only of each incineration batch). However, use of XRF to identify waste that does not require treatment should considerably reduce this issue, as a substantial amount of EPS/XPS does not contain HBCDD (or any other POP-BFR) in concentrations close to LPCLs

and can therefore be recycled without any treatment. A further potential problem is that increased levels of Br in the incinerator could potentially cause increased corrosion through the production of hydrobromic acid (HBr) (Tange and Drohmann, 2003). However, it has been determined by previous experiments that corrosion by HBr formation is only a risk when BFRs are in excess of 3% of the total weight present in the incinerator (Tange and Drohmann, 2005). In the EPS/XPS samples measured in this study, the highest concentration of HBCDD measured in an individual sample was 10,000 ppm (1% of total weight); therefore, the risk of corrosion by HBr formation is considered extremely low, especially considering that it is recommended that EPS/XPS constitutes up to 2% only of each incineration batch.

Although incineration currently appears to be the best available treatment for HBCDD-containing C&D waste, it is likely to be expensive, with operators charging up to €1000/tonne (CreaCycle, 2016). Over the last decade, industries and governments have attempted to modify the CreaSolv process (a mechanical separation followed by a solvent-based process that removes BFRs from WEEE-based plastics) to include removing HBCDD from EPS/XPS (WRAP, 2006; CreaCycle, 2016). It has already been demonstrated that >99.7% of HBCDD is removed from contaminated polystyrene, allowing for the product to be recycled into new EPS containing <100 mg/kg of HBCDD (CreaCycle, 2016). Current plans are in motion to develop and build a demonstration plant by 2018 with the capacity to treat and recycle up to 3000 tonnes of HBCDD-containing EPS/XPS per annum (CreaCycle, 2016), which comfortably exceeds the approximately 1000 tonnes/year of C&D EPS/XPS generated in Ireland that this project has identified as exceeding LPCLs. Although this would be the most attractive option in terms of cost, and maximum recycling of EPS/XPS, this is not currently a commercially available option. Therefore, it is recommended that EPS/XPS containing HBCDD above the LPCL is incinerated using total energy recovery until CreaSolv or equivalent technology becomes an available option. All other items should be recycled as normal.

End-of-life vehicle waste and soft furnishings

As with C&D waste, ELV and soft furnishings that exceed POP-BFR LPCLs cannot be recycled.

Furthermore, Irish Government policy is the “virtual elimination of landfilling” (EPA, 2016). Unlike for C&D waste and WEEE, CreaSolv has not yet been adapted to remove BFRs from PUF and textiles (UNEP 2010; United Nations, 2017). Therefore, without being able to send products to landfill or recycle them, incineration is the only viable option to remove POPs from ELV and furniture waste. However, with the POP-BFR concentrations being higher in these types of samples than in EPS/XPS, along with the additional issue of the high concentrations of BDE-209, further considerations need to be taken into account.

As mentioned above for C&D EPS/XPS, when BFRs are present at concentrations of >3% of the total incineration weight, the risk of corrosion from HBr is increased. Soft furnishing samples from this study have been found to contain up to 5% HBCDD, whereas ELV samples contained up to 3% BDE-209. Therefore, ELV and furniture waste will require dilution with other waste that is less contaminated with POP-BFRs to ensure that there is no corrosion as a result of HBr formation. This is likely to raise the cost of disposing of these types of waste. Furthermore, BDE-209 and PBDEs are considered precursors to more toxic compounds such as PBDD/Fs, which have been seen to form in thermal processes (Wang and Chang-Chien, 2007). However, in controlled combustion systems, such as total energy recovery waste incineration, the risk of this is considered low, with precursor compounds such as PBDEs destroyed with high efficiency (Weber and Kuch, 2003).

Therefore, it is recommended that ELV and furniture waste items (foams and textiles) that exceed LPCLs are treated by total energy recovery incineration until a more cost-effective alternative solution is commercially available. All other items should be recycled as normal.

Waste electrical and electronic equipment

As with waste EPS/XPS, work has been conducted to develop a technique for the removal of BFRs from

styrene plastics in WEEE. It has been demonstrated that it is a viable option for the CreaSolv process to be used commercially as a technique for the removal of BFRs from these waste goods (WRAP, 2006).

This technique, when commercially available, would provide a potential solution to the mass of WEEE generated each year that exceeds LPCLs, as it would allow much of the waste to be recycled, thereby allowing some of the treatment costs to be offset. However, current infrastructure would not be able to cope with the current or projected quantities of LPCL-exceeding WEEE produced in Ireland each year and therefore CreaSolv is not currently a viable option to treat all BFR-contaminated WEEE in Ireland.

An alternative to the CreaSolv process is total energy recovery waste incineration. However, in this study, BFRs were measured in some display items at close to 30% by weight. Although in most cases the BFR detected was TBBP-A, this does not negate the risk of corrosion from HBr formation during the incineration process (as stated above, increased corrosion occurs at Br concentrations exceeding 3% by weight). This means that, when treating WEEE by incineration, it must be heavily diluted with other waste products to ensure that HBr corrosion does not occur. This will increase the overall cost of this treatment option whilst placing greater strain on current infrastructure, as waste will have to be incinerated in small “batches”. Furthermore, although this means that WEEE can be used as an energy source, it also means that no items treated by this method can be recycled. Further issues associated with incineration include conversion of BDE-209 and PBDEs to the more toxic PBDD/Fs; however, total energy recovery waste incineration is a controlled combustion situation, which uses best available techniques, ensuring that the risk of this is considered low, with precursor compounds such as PBDEs destroyed with high efficiency (Weber and Kuch, 2003).

Therefore, it is recommended that, if current infrastructure permits, BFRs should be removed from items of WEEE that exceed LPCLs using the CreaSolv process. All other items should be recycled as normal.

5 Recommendations

5.1 Practical Implementation of Hand-held XRF as a Tool for Screening Compliance with LPCLs

The preceding material in this report highlights that there is potential for XRF to be a useful tool for the comparatively rapid, cost-effective, on-site testing of waste articles for compliance with LPCLs, particularly given the anticipated enforcement of an LPCL for BDE-209. This chapter discusses issues related to how this might work in practice.

5.2 Costs of Hand-held XRF Screening

The instrument used in the WAFER study cost €38,000. Outside the 12-month warranty period, annual calibration and a degree of breakdown maintenance cover may be purchased for approximately €1000–1500/annum. Apart from this, on-going maintenance costs are relatively low and our experience is that hand-held XRF is a reliable and robust technology. Over the course of an 8-hour working day, it would be feasible for a single hand-held XRF instrument to measure Br in triplicate in 100 waste articles. Over a 3-year period, assuming a 220-day working year, this equates to 66,000 articles. If one assumes that the XRF operative costs totalled €100,000 over the 3 years, then the cost per article would be €2.15. By comparison, conventional gas chromatography/liquid chromatography–mass spectrometry (GC/LC-MS) analysis of POP-BFRs would cost a minimum of €100/article, amounting to €6.6M.

Despite the lower cost of hand-held XRF, its use to screen individual waste articles is still likely to be considered overly time-consuming. Although beyond our remit, automation of the screening process using a “fixed/bench-top” XRF instrument in conjunction with a conveyor belt carrying waste articles is considered a feasible approach, albeit one requiring greater capital outlay, for large-scale waste handling operations. It is also possible to envisage development and application of a dedicated ion mobility spectrometer in

advanced waste handling facilities that would permit rapid, on-site differentiation between regulated and non-regulated BFRs in samples identified by XRF as exceeding LPCLs. Such an approach would essentially eliminate false positives. Although such technology does not currently exist, viable analogous instruments exist, namely the ion mobility spectrometers used to screen for explosives at airports. The volumes of waste requiring testing provide a plausible driver for the development of such an instrument.

5.3 How User-friendly is Hand-held XRF? How Could it Feasibly be Implemented as a Tool for Verifying LPCL Compliance by Waste Site Operatives?

As part of this project, the project team designed a simple instruction leaflet (supported by a more detailed user manual) aimed at providing simple guidance to individuals tasked with using XRF on-site to check Br concentrations against LPCLs. We consider that, with some practical hands-on instruction and support from instrument vendors and EPA personnel, hand-held XRF is a sufficiently user-friendly technology to permit its wide-scale use for this purpose. An important part of the guidance supplied to on-site operatives would be the provision by the EPA of a website that would be maintained and regularly updated to provide current LPCLs (thereby future-proofing against subsequent revisions of the LPCLs). Importantly, the LPCLs on this website would be given as Br (rather than POP-BFR) concentrations for ease of comparison with the Br readings supplied by the XRF, thereby minimising any calculation burden on the operators. This leads to an important point for consideration: what POP-BFR is assumed to be the source of the Br reading provided by the XRF? As discussed in section 4.1, Br constitutes approximately 75% of the total HBCDD mass and thus a Br measurement must be multiplied by 1.34 to convert it to the equivalent HBCDD concentration. The LPCL as an equivalent Br concentration is $1000/1.34 = 746$ mg/kg. In similar fashion, if Br is assumed to be produced from penta-BDE, the equivalent Br concentration is

$1000/1.41 = 710 \text{ mg/kg}$; for BDE-209, the Br equivalent concentration is $1000/1.2 = 833 \text{ mg/kg}$.

We suggest two approaches to this:

1. A conservative but simple approach whereby it is assumed that the Br is always produced from penta-BDE so that the BFR LPCL is divided by the correction factor for this formulation (which is the largest and will thus give the lowest Br-equivalent LPCL). However, as our data show, penta-BDE is rarely detected and, in C&D EPS, the Br detected is always produced from HBCDD.
2. An alternative approach in which different correction factors are applied to different waste types; therefore, the HBCDD factor is applied to C&D EPS and the penta-BDE factor is applied to other wastes.

Whichever approach is taken will need to be updated at such time as enforcement of an LPCL for deca-BDE commences, given that deca-BDE exceedances of the likely LPCL for this formulation are far more prevalent than those for HBCDD or penta- or octa-BDE.

Another consideration is how to take into account the reproducibility in XRF measurements of Br that are just below or just above the LPCLs. The conservative approach would be to reduce the Br-equivalent LPCL by the percentage uncertainty of measurement. As mentioned in section 2.2, the uncertainty associated with hand-held XRF measurements of Br in the concentration range of 500–2000 mg/kg varies between 5% and 20%, depending on the matrix analysed. We propose therefore that the highest uncertainty (20%) is assumed and that the Br-equivalent LPCL is reduced accordingly, e.g. from 710 mg/kg to 568 mg/kg. Such a conservative approach will inevitably lead to some false positives, with some items being incorrectly identified as exceeding the LPCL. However, as discussed in section 4.1, some degree of false positives could be viewed as an acceptable limitation of the use of XRF for this purpose.

5.4 Future Perspectives

Under the recast of the WEEE Directive, it is likely that national targets for collection of WEEE in Ireland will substantially increase over the coming years. One implication of this is that there will be a greater

number of POP-BFR-containing WEEE articles that will require checking for compliance with LPCLs. As highlighted in section 5.1, in terms of cost, hand-held XRF provides a more attractive solution to this potential increased monitoring burden than conventional GC/LC-MS testing. Moreover, as discussed in section 4.2.6, some minimisation of the likely increased monitoring burden may be achieved by excluding from measurement those WEEE categories (LHAs and fridges/freezers, except for motor housing) for which no LPCL exceedances were observed in our study. Set against this, it is important to consider that, if an LPCL for BDE-209 of 1000 mg/kg were to be enforced, of the 34 false positives identified in this project out of 538 items tested, 26 came from WEEE items (out of 237 WEEE items tested). These false positives for WEEE (defined as cases in which a Br concentration greater than the LPCL is *not* due to a BFR for which an LPCL exists) are predominantly caused by concentrations of TBBP-A of >1000 mg/kg. This enhanced frequency of false positives for WEEE means that this waste category is the least suited to the use of hand-held XRF screening. Notwithstanding this, the fact that such false positives would occur in approximately 10% of WEEE items could be viewed as an acceptable compromise given that use of XRF screening would still result in effective identification of all items genuinely exceeding LPCLs, while also diverting some items that, although not containing POP-BFRs, contain other BFRs such as TBBP-A.

Considering more generally the potential relevance of XRF screening to all waste stream categories considered here, over time, exceedances as a result of PBDEs and HBCDD will decline as the number of waste articles containing such contaminants falls. Unless the restrictions on PBDEs and HBCDDs are matched by concomitant relaxations in fire safety regulations, there is the potential for increased use of other currently non-regulated BFRs such as decabromodiphenyl ethane (DBDPE). Unless such BFRs are regulated in future, such a trend would lead to an increased incidence of false positives. It is therefore recommended that periodic studies to identify trends in the precise BFRs present in the waste stream are conducted.

Other recommendations emerging from the work conducted in this project are as follows:

- Further work is recommended to determine the causes of observed “false positives”. Although a good proportion were attributable to TBBP-A, others could not be attributed to any of the contaminants targeted in this project, and research to identify which chemicals (presumably other non-regulated BFRs) are present is advised.
- Analysis is required to elucidate the cause of the high Br concentrations detected in black plastic motor housing of some cooling appliances in this study, specifically whether or not these elevated Br concentrations can be attributed to POP-BFRs. If so, this would suggest that such motor housings should be tested for LPCL compliance separately from the rest of the fridge/freezer.
- Finally, average concentrations of currently designated POP-BFRs and BDE-209 in the samples analysed in this project exceeded existing and/or notional LPCLs for some waste categories, despite such categories containing some individual items that do not exceed LPCLs. Further analysis is thus recommended to evaluate whether individual items in such waste categories (i.e. C&D EPS, display items, ELV fabrics and ELV floor mats, as well as furniture PUF and fabric items) should be monitored for LPCL compliance in order to identify those items that do not require special treatment or whether instead it would be more cost-effective to assume that all such waste items require special treatment, thereby avoiding the need to monitor for LPCL compliance and its associated cost.

References

- Abdallah, M.A., Drage, D.S., Sharkey, M., Berresheim, H. and Harrad, S., 2017. A rapid method for the determination of brominated flame retardant concentrations in plastics and textiles entering the waste stream. *Journal of Separation Science* 40: 3873–3881.
- Allen, J.G., McClean, M.D., Stapleton, H.M. and Webster, T.F., 2008. Linking PBDEs in house dust to consumer products using X-ray fluorescence. *Environmental Science and Technology* 42: 4222–4228.
- Bakhiya, B., Gravel, S., Ceballos, D., Flynn, M.A. and Zayed, J., 2018. Has the question of e-waste opened a Pandora's box? An overview of unpredictable issues and challenges. *Environment International* 110: 173–192.
- BSEF (Bromine Science Environmental Forum), 2003. *Major Brominated Flame Retardants Volume Estimates. Total Market Demand by Region in 2001*. Available online: <http://www.bsef.com> (accessed January 2004).
- CreaCycle, 2016. PolyStyrene-Loop. Available online: <http://www.creacycle.de/en/projects/recycling-of-expanded-poly-styrene-eps/polystyrene-loop-2016.html> (accessed 24 January 2017).
- Danish EPA (Danish Environmental Protection Agency), 1999. *Brominated Flame Retardants – Substance Flow Analysis and Assessment of Alternatives*. Danish EPA, Copenhagen. Available online: www2.mst.dk/Udgiv/publications/1999/87-7909-416-3/199987-7909-416-3.pdf (accessed 4 August 2017).
- DEFRA (Department for Environment, Food and Rural Affairs), 2010. *Costs and Benefits of the Addition of Hexabromocyclododecane (HBCD) to the Stockholm Convention and the 1998 POPs Protocols*. Available online: <http://randd.defra.gov.uk/Document.aspx?Document=ED56226CostBenefitHBCDReportCND0101Oct2010v16FINAL.PDF> (accessed 27 May 2017).
- EC (European Commission), 2011. *Final Report: Study on Waste Related Issues of Newly Listed POPs and Candidate POPs*. Available online: http://ec.europa.eu/environment/waste/studies/pdf/POP_Waste_2011.pdf (accessed 4 August 2017).
- EC (European Commission), 2016. *EU Construction and Demolition Waste Management Protocol and Guidelines*. Available online: https://ec.europa.eu/growth/content/eu-construction-and-demolition-waste-protocol-0_en (accessed 20 April 2018).
- EC (European Commission), 2017a. *Study for the Strategy for a Non-toxic Environment of the 7th Environment Action Programme, Final Report*. Available online: http://ec.europa.eu/environment/chemicals/non-toxic/index_en.htm (accessed 5 July 2018).
- EC (European Commission), 2017b. Commission Regulation (EU) 2017/227 of 9 February 2017 amending Annex XVII to Regulation (EC) No 1907/2006 of the European Parliament and of the Council concerning the Registration, Evaluation, Authorisation and Restriction of Chemicals (REACH) as regards bis(pentabromophenyl)ether. Available online: <http://eur-lex.europa.eu/legal-content/EN/TXT/PDF/?uri=CELEX:32017R0227&from=EN> (accessed 31 July 2017).
- ECHA (European Chemicals Agency), 2009. *Background Document for Hexabromocyclododecane and All Major Diastereoisomers Identified (HBCDD)*. Available online: https://echa.europa.eu/documents/10162/13640/hbccd_en.pdf/9b8562be-30e9-4017-981b-1976fc1b8b56 (accessed 4 August 2017).
- EPA (Environmental Protection Agency), 2013. *National Waste Report for 2011*. EPA, Johnstown Castle, Ireland.
- EPA (Environmental Protection Agency), 2016. *Waste*. Available online: <http://www.epa.ie/irelandsenvironment/waste/> (accessed 21 December 2016).
- EPA (Environmental Protection Agency), 2017. *National Waste Statistics – Reports and Bulletins*. Available online: <http://www.epa.ie/pubs/reports/waste/stats/> (accessed 12 April 2018).
- EU (European Union), 2013. Decision No. 1386/2013/ EU of the European Parliament and of the Council of 20 November 2013 on a General Union Environment Action Programme to 2020 'Living well, within the limits of our planet'. OJ L 354, 28.12.2013, p. 171–200.
- European Chemicals Bureau, Institute for Health and Consumer Protection, 2000. *European Union Risk Assessment Report, Diphenyl Ether, Pentabromo Derivative (Pentabromodiphenylether)*. Available online: <http://echa.europa.eu/documents/10162/781ee1e9-6c90-467e-998b-8910ca2793e5> (accessed 4 August 2017).

- Furl, C., Mathieu, C. and Roberts, T., 2012. *Evaluation of XRF as a Screening Tool for Metals and PBDEs in Children's Products and Consumer Goods*. Available online: <https://fortress.wa.gov/ecy/publications/publications/1203009.pdf> (accessed 23 January 2019).
- Gallen, C., Banks, A., Brandsma, S., Baduel, C., Thai, P., Eaglesham, G., Heffernan, A., Leonards, P., Bainton, P. and 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. *Science of the Total Environment* 491–492: 255–265.
- Guzzonato, A., Puype, F. and Harrad, S., 2017. Evidence of bad recycling practices: BFRs in children's toys and food-contact articles. *Environmental Science: Processes and Impacts* 19: 956–963.
- Marvin, C.H., Tomy, G.T., Armitage, J.M., Arnot, J.A., McCarty, L., Covaci, A. and Palace, V.H., 2011. Hexabromocyclododecane: current understanding of chemistry, environmental fate and toxicology and implications for global management. *Environmental Science and Technology* 45: 8613–8623.
- Morf, L., Smutny, R., Taverna, R. and Daxbeck, H., 2003. *Selected Polybrominated Flame Retardants PBDEs and TBBPA. Substance Flow Analysis*. Environmental Series No. 338. Environmental Hazardous Substances. Available online: <https://www.bafu.admin.ch/bafu/en/home/topics/chemicals/publications-studies/publications/selected-polybrominated-flame.html> (accessed 4 August 2017).
- Rauert, C., Kuribara, I., Kataoka, T., Wada, T., Kajiwara, N., Suzuki, G., Takigami, H. and Harrad, S., 2016. Direct contact between dust and HBCD-treated fabrics is an important pathway of source-to dust transfer. *Science of the Total Environment* 545–546: 77–83.
- Samsonsek, J. and Puype, F., 2013. Occurrence of brominated flame retardants in black thermo cups and selected kitchen utensils purchased on the European market. *Food Additives and Contaminants, Part A* 30: 1976–1986.
- Tange, L. and Drohmann, D., 2003. *Waste Management Concept for WEEE Plastics Containing Brominated Flame Retardants, Including Bromine Recycling and Energy Recovery*. Belgian Plastics and Rubber Institute, Brussels. Available online: https://www.researchgate.net/publication/242198374_WASTE_MANAGEMENT_CONCEPT_FOR_WEEE_PLASTICS_CONTAINING_BROMINATED_FLAME_RETARDANTS_INCLUDING_BROMINE_RECYCLING_AND_ENERGY_RECOVERY (accessed 4 August 2017).
- Tange, L. and Drohmann, D., 2005. Waste electrical and electronic equipment plastics with brominated flame retardants – from legislation to separate treatment – thermal processes. *Polymer Degradation and Stability* 88: 35–40.
- Umwelt Bundesamt, 2015. *Identification of Potentially POP-containing Wastes and Recyclates – Derivation of Limit Values*. Available online: <https://www.umweltbundesamt.de/publikationen/identification-of-potentially-pop-containing-wastes> (accessed 21 November 2016).
- UNEP (United Nations Environment Programme), 2006. *Pentabromodiphenyl Ether, Risk Profile. Report of the Persistent Organic Pollutants Review Committee on the Work of its Second Meeting (UNEP/POPS/POPRC.2/17/Add.1)*. Available online: <http://chm.pops.int/TheConvention/POPsReviewCommittee/Meetings/POPRC2/POPRC2ReportandDecisions/tabid/349/Default.aspx> (accessed 4 August 2017).
- UNEP (United Nations Environment Programme), 2007. *Commercial Pentabromodiphenyl Ether, Risk Management Evaluation*. Report of the Persistent Organic Pollutants Review Committee on the work of its third meeting (UNEP/POPS/POPRC.3/20/Add.1). Available online: <http://www.pops.int/TheConvention/POPsReviewCommittee/Meetings/POPRC3/POPRC3ReportandDecisions/tabid/348/Default.aspx> (accessed 4 August 2017).
- UNEP (United Nations Environment Programme), 2010. *Technical Review of the Implications of Recycling Commercial Penta and Octabromodiphenyl Ethers*. Stockholm Convention document for 6th POP Reviewing Committee meeting (UNEP/POPS/POPRC.6/2). Available online: <http://www.pops.int/TheConvention/POPsReviewCommittee/Meetings/POPRC6/POPRC6Documents/tabid/783/Default.aspx> (accessed 4 August 2017).
- UNEP (United Nations Environment Programme), 2017a. *National Implementation Plan of the Federal Republic of Germany*. Available online: <http://chm.pops.int/Implementation/NationalImplementationPlans/NIPTransmission/tabid/253/Default.aspx> (accessed 18 May 2018).
- UNEP (United Nations Environment Programme), 2017b. *Updated National Implementation Plan for Implementation of Stockholm Convention on Persistent Organic Pollutants in the Czech Republic for the Period 2018–2023*. Available online: <http://chm.pops.int/Implementation/NationalImplementationPlans/NIPTransmission/tabid/253/Default.aspx> (accessed 18 May 2018).

- UNEP (United Nations Environment Programme), 2017c. *National Implementation Plan Sweden, Update 2017*. Available online: <http://chm.pops.int/Implementation/NationalImplementationPlans/NIPTransmission/tabid/253/Default.aspx> (accessed 18 May 2018).
- United Nations, 2017. *Guidance on Best Available Techniques and Best Environmental Practices for the Recycling and Disposal of Articles Containing Polybrominated Diphenyl Ethers (PBDEs) Listed under the Stockholm Convention on Persistent Organic Pollutants. Updated January 2017*. Available online: <http://chm.pops.int/Implementation/NationalImplementationPlans/Guidance/GuidanceonBATBEPforPBDEs/tabid/3172/Default.aspx> (accessed 31 January 2019).
- Wang, L. and Chang-Chien, G., 2007. Characterizing the emissions of polybrominated dibenzo-p-dioxins and dibenzofurans from municipal and industrial waste incinerators. *Environmental Science & Technology* 41: 1159–1165.
- Weber, R. and Kuch, B., 2003. Relevance of BFRs and thermal conditions on the formation pathways of brominated and brominated–chlorinated dibenzodioxins and dibenzofurans. *Environment International* 29: 699–710.
- Weil, E.D. and Levchik, S.V., 2008. Flame retardants in commercial use or development for textiles. *Journal of Fire Sciences* 26: 243–281.
- WHO (World Health Organization), 1994. *Environmental Health Criteria 162: Brominated Diphenyl Ethers*. WHO, Geneva. Available online: <http://www.inchem.org/documents/ehc/ehc/ehc162.htm> (accessed 31 January 2019).
- WRAP, 2006. *Develop a Process to Separate Brominated Flame Retardants from WEEE Polymers*. Available online: <http://www.wrap.org.uk/sites/files/wrap/BrominatedWithAppendices.3712.pdf> (accessed 4 August 2017).
- WRAP, 2012. *Composition of Kerbside and HWRC Bulky Waste*. Project MDP006–002. Available online: <http://www.wrap.org.uk/content/study-re-use-potential-household-bulky-waste> (accessed 4 August 2017).
- WRc, 2012a. *Analysis of Poly-Brominated Diphenyl Ethers (PBDEs) in UK Waste Streams: PBDEs in End of Life Vehicles (ELV)*. Addendum to WRc Report UC8720.05. WRc reference UC9303.04.
- WRc, 2012b. *Analysis of Poly-Brominated Diphenyl Ethers (PBDEs) in Selected UK Waste Streams: PBDEs in Waste Electrical and Electronic Equipment (WEEE) and End of Life Vehicles (ELV)*. WRc Ref: UC8720.05. Available online: http://randd.defra.gov.uk/Document.aspx?Document=11410_WR1126FinalReport.pdf (accessed 31 January 2019).

Abbreviations

ABS	Acrylonitrile butadiene styrene
ASR	Auto shredder residue
BDE	Brominated diphenyl ether
BFR	Brominated flame retardant
C&D	Construction and demolition
CRT	Cathode ray tube
EEE	Electrical and electronic equipment
ELV	End-of-life vehicle
EPA	Environmental Protection Agency
EPS	Expanded polystyrene
EU	European Union
GC/LC–MS	Gas chromatography/liquid chromatography–mass spectrometry
GC/MS	Gas chromatography–mass spectrometry
HBCDD	Hexabromocyclododecane
HBr	Hydrobromic acid
HIPS	High-impact polystyrene
IT	Information technology
LHA	Large household appliance
LPCL	Low POP concentration limit
NIP	National Implementation Plan
PBDD/Fs	Polybrominated dibenzo dioxins and furans
PBDE	Polybrominated diphenyl ether
PC	Personal computer
POP	Persistent organic pollutant
PUF	Polyurethane foam
SDA	Small domestic appliance
TBBP-A	Tetrabromobisphenol A
UNEP	United Nations Environment Programme
WEEE	Waste electronic and electrical equipment
XPS	Extruded polystyrene
XRF	X-ray fluorescence

AN GHNÍOMHAIREACHT UM CHAOMHNÚ COMHSHAOIL
Tá an Gníomhaireacht um Chaomhnú Comhshaoil (GCC) freagrach as an gcomhshaoil a chaomhnú agus a fheabhsú mar shócmhainn luachmhar do mhuintir na hÉireann. Táimid tiomanta do dhaoine agus don chomhshaoil a chosaint ó éifeachtaí díobhálacha na radaíochta agus an truaillithe.

Is féidir obair na Gníomhaireachta a roinnt ina trí phríomhréimse:

Rialú: Déanaimid córais éifeachtacha rialaithe agus comhlionta comhshaoil a chur i bhfeidhm chun torthaí maithe comhshaoil a sholáthar agus chun díriú orthu siúd nach gcloíonn leis na córais sin.

Eolas: Soláthraimid sonraí, faisnéis agus measúnú comhshaoil atá ar ardchaighdeán, spriocdhírthe agus tráthúil chun bonn eolais a chur faoin gcinnteoireacht ar gach leibhéal.

Tacaíocht: Bimid ag saothrú i gcomhar le grúpaí eile chun tacú le comhshaoil atá glan, táirgiúil agus cosanta go maith, agus le hiompar a chuirfidh le comhshaoil inbhuanaithe.

Ár bhFreagrachtaí

Ceadúnú

Déanaimid na gníomhaíochtaí seo a leanas a rialú ionas nach ndéanann siad dochar do shláinte an phobail ná don chomhshaoil:

- saoráidí dramhaíola (*m.sh. láithreáin líonta talún, loisceoirí, stáisiúin aistrithe dramhaíola*);
- gníomhaíochtaí tionsclaíocha ar scála mór (*m.sh. déantúsaíocht cógaisíochta, déantúsaíocht stroighne, stáisiúin chumhachta*);
- an diantalmhaíocht (*m.sh. muca, éanlaith*);
- úsáid shrianta agus scaoileadh rialaithe Orgánach Géinmhodhnaithe (*OGM*);
- foinsí radaíochta ianúcháin (*m.sh. trealamh x-gha agus radaiteiripe, foinsí tionsclaíocha*);
- áiseanna móra stórála peitril;
- scardadh dramhuisce;
- gníomhaíochtaí dumpála ar farraige.

Forfheidhmiú Náisiúnta i leith Cúrsaí Comhshaoil

- Clár náisiúnta iniúchtaí agus cigireachtaí a dhéanamh gach bliain ar shaoráidí a bhfuil ceadúnas ón nGníomhaireacht acu.
- Maoirseacht a dhéanamh ar fhreagrachtaí cosanta comhshaoil na n-údarás áitiúil.
- Caighdeán an uisce óil, arna sholáthar ag soláthraithe uisce phoiblí, a mhaoirsiú.
- Obair le húdaráis áitiúla agus le gníomhaireachtaí eile chun dul i ngleic le coireanna comhshaoil trí chomhordú a dhéanamh ar líonra forfheidhmiúcháin náisiúnta, trí dhíriú ar chiontóirí, agus trí mhaoirsiú a dhéanamh ar leasúchán.
- Cur i bhfeidhm rialachán ar nós na Rialachán um Dhramhthrealamh Leictreach agus Leictreonach (DTLL), um Shrian ar Shubstaintí Guaiseacha agus na Rialachán um rialú ar shubstaintí a ídionn an ciseal ózóin.
- An dlí a chur orthu siúd a bhriseann dlí an chomhshaoil agus a dhéanann dochar don chomhshaoil.

Bainistíocht Uisce

- Monatóireacht agus tuairisciú a dhéanamh ar cháilíocht aibhneacha, lochanna, uisce idirchriosacha agus cósta na hÉireann, agus screamhuisc; leibhéil uisce agus sruthanna aibhneacha a thomhas.
- Comhordú náisiúnta agus maoirsiú a dhéanamh ar an gCreat-Treoir Uisce.
- Monatóireacht agus tuairisciú a dhéanamh ar Cháilíocht an Uisce Snámha.

Monatóireacht, Anailís agus Tuairisciú ar an gComhshaoil

- Monatóireacht a dhéanamh ar cháilíocht an aeir agus Treoir an AE maidir le hAer Glan don Eoraip (CAFÉ) a chur chun feidhme.
- Tuairisciú neamhspleách le cabhrú le cinnteoireacht an rialtais náisiúnta agus na n-údarás áitiúil (*m.sh. tuairisciú tréimhsiúil ar staid Chomhshaoil na hÉireann agus Tuarascálacha ar Tháscairí*).

Rialú Astaíochtaí na nGás Ceaptha Teasa in Éirinn

- Fardail agus réamh-mheastacháin na hÉireann maidir le gáis cheaptha teasa a ullmhú.
- An Treoir maidir le Trádáil Astaíochtaí a chur chun feidhme i gcomhair breis agus 100 de na táirgeoirí dé-ocsaíde carbóin is mó in Éirinn.

Taighde agus Forbairt Comhshaoil

- Taighde comhshaoil a chistiú chun brúnna a shainathint, bonn eolais a chur faoi bheartais, agus réitigh a sholáthar i réimsí na haeráide, an uisce agus na hinbhuanaitheachta.

Measúnacht Straitéiseach Timpeallachta

- Measúnacht a dhéanamh ar thionchar pleananna agus clár beartaithe ar an gcomhshaoil in Éirinn (*m.sh. mórfhleananna forbartha*).

Cosaint Raideolaíoch

- Monatóireacht a dhéanamh ar leibhéil radaíochta, measúnacht a dhéanamh ar nochtadh mhuintir na hÉireann don radaíocht ianúcháin.
- Cabhrú le pleananna náisiúnta a fhorbairt le haghaidh éigeandálaí ag eascairt as taismí núicléacha.
- Monatóireacht a dhéanamh ar fhorbairtí thar lear a bhaineann le saoráidí núicléacha agus leis an tsábháilteacht raideolaíochta.
- Sainseirbhísí cosanta ar an radaíocht a sholáthar, nó maoirsiú a dhéanamh ar sholáthar na seirbhísí sin.

Treoir, Faisnéis Inrochtana agus Oideachas

- Comhairle agus treoir a chur ar fáil d’earnáil na tionsclaíochta agus don phobal maidir le hábhair a bhaineann le caomhnú an chomhshaoil agus leis an gcosaint raideolaíoch.
- Faisnéis thráthúil ar an gcomhshaoil ar a bhfuil fáil éasca a chur ar fáil chun rannpháirtíocht an phobail a spreagadh sa chinnteoireacht i ndáil leis an gcomhshaoil (*m.sh. Timpeall an Tí, léarscáileanna radóin*).
- Comhairle a chur ar fáil don Rialtas maidir le hábhair a bhaineann leis an tsábháilteacht raideolaíoch agus le cúrsaí práinnfhreagartha.
- Plean Náisiúnta Bainistíochta Dramhaíola Guaisí a fhorbairt chun dramhaíl ghuaiseach a chos agus a bhainistiú.

Múscailt Feasachta agus Athrú Iompraíochta

- Feasacht chomhshaoil níos fearr a ghiniúint agus dul i bhfeidhm ar athrú iompraíochta dearfach trí thacú le gnóthais, le pobail agus le teaghlaigh a bheith níos éifeachtúla ar acmhainní.
- Tástáil le haghaidh radóin a chur chun cinn i dtithe agus in ionaid oibre, agus gníomhartha leasúcháin a spreagadh nuair is gá.

Bainistíocht agus struchtúr na Gníomhaireachta um Chaomhnú Comhshaoil

Tá an ghníomhaíocht á bainistiú ag Bord lánaimseartha, ar a bhfuil Ard-Stiúrthóir agus cúigear Stiúrthóirí. Déantar an obair ar fud cúig cinn d’Oifigí:

- An Oifig um Inmharthanacht Comhshaoil
- An Oifig Forfheidhmithe i leith cúrsaí Comhshaoil
- An Oifig um Fianaise is Measúnú
- Oifig um Chosaint Radaíochta agus Monatóireachta Comhshaoil
- An Oifig Cumarsáide agus Seirbhísí Corparáideacha

Tá Coiste Comhairleach ag an nGníomhaireacht le cabhrú léi. Tá dáréag comhaltaí air agus tagann siad le chéile go rialta le plé a dhéanamh ar ábhair inní agus le comhairle a chur ar an mBord.

Evaluation of Hand-held XRF for Screening Waste Articles for Exceedances of Limit Values for Brominated Flame Retardants



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Identification and Treatment Options for Waste Streams of Certain Bromine Containing Flame Retardants (WAFER)

Identifying Pressures

Recent research has demonstrated the presence of restricted persistent organic pollutant brominated flame retardants (POP-BFRs) in items such as children's toys and food contact articles. As the presence of these contaminants in such items serves no useful purpose, they are thought to originate from the use of recycled plastics originally treated with POP-BFRs. To address this issue, European Union (EU) Regulation 850/2004 inter alia specifies low POP concentration limits (LPCLs) such that articles exceeding the LPCL (1000 mg/kg) cannot be recycled and must be treated so that their POP-BFR content is destroyed. Given the very substantial use of POP-BFRs in applications such as electrical and electronic goods, polystyrene building insulation foam, and seating foam and fabrics in homes, offices and cars, monitoring compliance with LPCLs represents a substantial undertaking, compounded by conventional laboratory methods for measuring POP-BFRs being destructive, time-consuming, expensive, and incompatible with being conducted in situ at waste handling sites. This research thus evaluated the feasibility of using hand-held X-ray fluorescence (XRF) spectrometers to measure bromine in waste articles as a surrogate indicator of compliance with LPCLs.

Informing Policy

Data from this project demonstrate that removal of articles exceeding LPCLs would remove 98% of the 33 tonnes/year of POP-BFRs currently generated in Ireland within the plastic recycling stream. To evaluate hand-held XRF as a low-cost, user-friendly tool for monitoring compliance with LPCLs, XRF was used to measure total bromine in 538 samples from various waste categories. These data were compared with POP-BFR concentrations for the same samples. Although XRF correctly identified all articles exceeding LPCLs, it incorrectly indicated that 6.3% of articles exceeded the LPCLs. This was because of the presence of BFRs, for which LPCLs do not currently exist as they are not restricted. Such "false exceedances" result in a small proportion of articles being incorrectly diverted from recycling, with unnecessary economic costs when such articles are subjected to special treatment to destroy their POP-BFR content, most probably by incineration. Balanced against this, as false exceedances are caused by BFRs that, although not presently restricted, may be so in the future, and whose presence in the recycling stream cannot be considered desirable, they are deemed an acceptable limitation of the use of XRF.

Developing Solutions

Although the cost- and time-effectiveness of hand-held XRF relative to conventional methods for measuring POP-BFRs renders the former potentially feasible for large-scale monitoring of LPCL compliance, use of hand-held XRF to screen individual waste articles may still be considered overly time-consuming by waste treatment professionals. Consequently, automation of the screening process using a "fixed/bench-top" XRF instrument in conjunction with a conveyor belt carrying waste articles is considered a feasible approach for large-scale waste handling operations, albeit one requiring greater capital outlay. In the shorter term, approaches to minimise the number of articles requiring checking for compliance with LPCLs merit consideration. These involve using data from this project that show very low BFR concentrations and no exceedances of current or anticipated LPCLs for some waste categories such as extruded polystyrene (XPS) building insulation foam. On-site separation of XPS from expanded polystyrene (EPS) foam (for which 35% of samples were found to exceed the LPCL) to allow recycling or reuse of XPS without checking for LPCL compliance would reduce the monitoring burden placed on the waste management industry.