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Brominated Flame Retardants in Irish Waste Polymers: Concentrations, Legislative Compliance, and Treatment Options

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Abstract:

A comprehensive survey was performed to construct an inventory of polybrominated diphenyl ethers (PBDEs) and hexabromocyclododecane (HBCDD) associated with waste polymers in Ireland. Based on our data, ~2,200 t/yr of waste generated in Ireland exceeds "Low POP Concentration Limits" (LPCLs) set by the European Commission, of 1,000 mg/kg of PBDEs (BDE-209 excluded) and HBCDD – collectively referred to as POP-BFRs. Waste articles containing concentrations exceeding the LPCL values require special treatment to remove POP-BFRs before they can be recycled. Waste articles exceeding LPCLs in our study consist primarily of expanded polystyrene used as building insulation (44 %), waste furniture foams and fabrics (41 %), with waste electrical and electronic equipment (WEEE) accounting for 13 % and end of life vehicle waste contributing 1.7 %. The recent listing of Deca-BDE under the Stockholm Convention means that a similar LPCL for its principal congener (BDE-209) is likely. Our data show that enforcement of an LPCL of 1,000 mg/kg for BDE-209 would result in a further 1,650 t/year of waste articles requiring special treatment. Our data show there to be 17,125 kg of POP-BFRs associated with waste polymers generated annually in Ireland. Enforcement of current LPCL values would prevent approximately 98 % of these POP-BFRs from entering recycled goods. Introduction and enforcement of a similar LPCL for BDE-209 would prevent 93 % of the 15,518 kg/yr of BDE-209 associated with Irish waste polymers from entering the recycling stream.

1.0 Introduction

Brominated flame retardants (BFRs) such as hexabromocyclododecane (HBCDD) and polybrominated diphenyl ethers (PBDEs) have found extensive use worldwide as flame retardants (FRs) in a wide variety of commercial, domestic and industrial applications. There are three main commercial PBDE formulations, namely Penta-, Octa- and DecaBDE. Applications of PBDEs include electrical and electronic equipment (EEE - such as TVs, PCs and small domestic appliances (SDAs)) and soft furnishings (such as sofas, mattresses, curtains, and pillows etc.). The primary use of HBCDD is as a FR in expanded and extruded polystyrene (EPS/XPS) used in building insulation foam (European Chemicals Agency, 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-, Octa-, DecaBDE and HBCDD respectively (Bromine Science and Environmental Forum (BSEF), 2003).

In Europe, approximately 95 % of PentaBDE was used in flexible polyurethane foam (PUF), mainly used for furniture and automotive applications (European Chemicals Bureau, 2000). Depending on the source, it is estimated that treated PUF contains ~3-18 % by weight of PentaBDE for upholstery, cushions, mattresses and carpet padding (European Commission, 2011, United Nations Environment Programme (UNEP), 2010). PentaBDE has had extensive use in cars, in particular in seating PUF. Approximately 5 % of European vehicles built from 1975 – 2004 were treated with PentaBDE (Morf et al., 2003). In 2012, 102,073 end-of-life vehicles (ELVs) were generated in Ireland, suggesting that approximately 16.3 t of PentaBDE entered the waste stream in Ireland 2012 from ELV alone (Expert Team to Support Waste Implementation (ESWI), 2011).

Historically, around 95 % of OctaBDE supplied in the EU was used in acrylonitrile butadiene styrene (ABS) (predominantly in housings of EEE, particularly for cathode ray tube (CRT) housing (e.g. PC monitors and TVs) and office equipment (e.g. copying machines and business printers). It was typically added to ABS at concentrations between 10-18 % by weight (European Commission, 2011). Minor uses of OctaBDE (< 5 %) were in high impact polystyrene (HIPS), polybutylene terephthalate (PBT), and polyamide polymers, with typical concentrations of 12-15 % by weight. Other possible uses were in nylon, low density polyethylene, polycarbonate, phenolformaldehyde resins, and unsaturated polyesters, as well as in adhesives and coatings (United Nations Environment Programme (UNEP), 2010).

DecaBDE 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, DecaBDE was added to products at about 10-25 % by weight with important fabric applications in: automotive upholstery, draperies for hotels and public buildings and institutional (e.g. office) upholstered furniture (Weil and Levchik, 2008).

The principal use of HBCDD (>95 %) is in the building industry, typically added at 2 % or 0.7 % by weight into EPS and XPS foam respectively in rigid insulation panels/boards. It has a relatively minor application (~2 %) as an FR in HIPS used for EEE (European Commission, 2011). 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, interior textiles, e.g. roller blinds and vehicle interior textiles. HBCDD can also be used in 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).

Over the last decade, the widespread use of PBDEs and HBCDDs 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 OctaBDE commercial formulations as "POP-BFRs" under the UNEP Stockholm Convention on Persistent Organic Pollutants (Health and Environment Alliance, 2013, Stockholm Convention, 2009). However, there is currently a derogation that permits HBCDD use within the EU in EPS and XPS for building insulation (European Commission, 2016). The same convention has recently agreed to add the DecaBDE formulation, although this is likely to contain a large list of exemptions, allowing for its continued use until suitable alternatives are found (Chemical Watch, 2017).

It is clear that there has been extensive global use of PBDEs and HBCDD in a wide range of applications. There is thus a growing inventory of materials containing POP-BFRs that have or will shortly enter the waste stream with consequent implications for their sustainable management. The potential scale of this issue is illustrated by UNEP estimates that currently 20-50 million t of waste EEE (WEEE) is generated globally every year (Robinson, 2009). The EU POPs regulation (EC) No 850/2004 addresses this situation, stipulating that wastes containing POP-BFRs must be treated in such a way as to ensure the POP-BFR content is destroyed or irreversibly transformed so that the POP-BFR content is below the limit value specified in Annex IV "low POP concentration limit (LPCL)" (1,000 mg/kg for HBCDD and 1,000 mg/kg for the sum of all PBDEs representative of the Penta- and/or OctaBDE formulations). The LPCLs define the threshold concentration above which wastes are classified POP waste and subject to the management regime of the POP regulation (European Commission, 2016) – i.e. whether a waste item will have to be specially treated in order to remove its POP-BFR content prior to disposal/recycling. For compliance with this regulation, the concentrations of POP-BFRs within waste consumer products need to be known. Furthermore, with DecaBDE recently being listed as a POP under the Stockholm Convention, a similar LPCL will likely be enforced for its principal congener, BDE-209. With this in mind, it is important to gather evidence about the proportion of the volume of consumer products entering the waste stream that contains concentrations of restricted BFRs that exceed LPCLs (and theoretical LPCLs (tLPCLs) for DecaBDE). Therefore, the aims of the current study are to: (i) measure the concentrations of PBDEs and HBCDD in samples of waste EEE (WEEE), soft furnishings, construction and demolition waste EPS and XPS, as well as fabrics and PUF from ELVs in Ireland; (ii) use these concentration data to estimate 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; (iii) estimate the mass of waste material and associated POP-BFRs that would be removed from circulation by effective enforcement of current LPCLs and thus require special treatment to destroy the POP-BFRs thus isolated, and (iv) evaluate the options available for such special treatment to destroy this reservoir of POP-BFRs. To our knowledge, this is the first comprehensive survey of BFR concentrations in waste items.

2.0 Materials & Methods

2.1 Sample Collection

The sampling campaign addressed those waste streams considered most likely to contain products treated with POP-BFRs. A total of 538 samples were collected from 4 broad categories of waste stream: construction and demolition (C&D) EPS/XPS (n = 62); ELV fabrics and PUF (n = 135); soft furnishings (n = 123); and WEEE (n = 239). These categories were further divided as detailed in Table 1. It should be noted that whilst carpet samples were collected, we were unable to obtain samples of carpet underlay.

C&D EPS/XPS samples were collected from three main sources: (i) recently demolished buildings (samples taken directly from the source of waste); (ii) a demolition company which stockpiles re-usable waste insulation for future construction operations; and (iii) a construction and demolition waste collection site (specifically collecting waste from demolished buildings). All ELV waste samples were collected from a single vehicle scrap site. All WEEE and soft furnishing samples were collected from various household waste centres located in Ireland.

Sub-samples of waste items in each of our 4 waste categories were obtained using tin snips, hammer and scissors. Sub-samples selected for chemical analysis comprised: plastic housing from large WEEE items (e.g. fridges and TVs), with preference given to areas encasing electronic components or near power cords; in the case of fabric and polystyrene items, sub-samples were taken from the centre of each article, with PUF sub-samples taken from the surface in contact with the fabric covering. To help select relevant sub-samples, all items were scanned at several points for bromine content using a hand-held XRF analyser (Niton GOLDDXL3t 900) with preference given to areas of high bromine content.

2.1 Chemicals and standards

All solvents used for extraction and analytical procedures for GC/MS and LC-MS/MS were of HPLC grade quality (Fisher Scientific, Loughborough, UK). Silica (70-130 mesh), with concentrated sulfuric acid was purchased from Sigma-Aldrich (St Louis, MA, USA).

Native α-, β- and γ-HBCDD standards, $^{13}C_{12}$ α-, β- and γ-HBCDD, d_{18}- γ-HBCDD, individual standards of native BDEs -28, -47, -99, -100, -153, -154, -183, -196, -197, -209, -77 and -128, $^{13}C_{12}$-BDE 209, and native PCB-129 were obtained from Wellington Laboratories (Guelph, ON, Canada).

Certified reference materials for polyethylene (ERM-EC590) and polypropylene (ERM-EC591) were purchased from IRMM (Brussels, Belgium).

2.3 Sample Extraction & Clean-up

Full extraction and clean-up parameters have been reported previously (Abdallah et al., 2017). Briefly, aliquots of samples (10-100 mg) were accurately weighed into a 15 mL glass tube and spiked with internal standards (30 ng of BDE-77, BDE-128, $^{13}C_{12}$-α-HBCDD, $^{13}C_{12}$-β-HBCDD, $^{13}C_{12}$-γ-HBCDD and 60 ng of $^{13}C_{12}$-BDE-209). Samples were extracted using a combination of vortexing and ultrasonication with dichloromethane (DCM), followed by precipitation of polymer matrix by addition of hexane. Sample extracts were then purified by washing with concentrated sulfuric acid. Cleaned extracts were concentrated and solvent exchanged into 100 µL isooctane (containing 0.2 ng/µL PCB-129 as a recovery standard) and transferred into inserted autosampler vials ready for instrumental analysis. After analysis of PBDEs via GC/MS, samples were solvent exchanged into 100 µL methanol (containing 0.2 ng/µL d_{18}- γ-HBCDD as a recovery standard) for HBCDD analysis.

2.4 Instrumental Analysis

Quantitative analysis of PBDEs (BDEs -17, -28, 47, -99, -100, -153, -154, -183, -196, -197, and -209) was performed on a Thermo Fisher Trace 1310 gas chromatograph coupled to a Thermo Fisher ISQ mass spectrometer (MS). The MS was operated in electron ionisation mode using selective ion monitoring (SIM). Full details of ions monitored are provided in Abdallah et al. (2017). One µL of the purified extract was injected for analysis using a programmable temperature vaporiser (PTV) onto a Restek Rxi-5Sil MS column (15 m x 0.25 mm x 0.25 µm film thickness). Helium was used as the carrier gas at a flow rate of 1.5 mL/min.

HBCDDs were measured using a Shimadzu LC-20AB Prominence binary pump liquid chromatograph, equipped with a SIL-20A autosampler, a DGU-20A3 vacuum degasser coupled to an AB Sciex API 2000 triple quadrupole MS. Separation of α-, β- and γ- HBCDD was achieved using a Varian Pursuit XRS3 C_{18} analytical column (150 x 2 mm I.D. 3 µm particle size). Full LC-MS/MS details have been reported previously (Abdallah et al., 2008).

2.5 Quality Control

A reagent blank consisting of 100 mg of anhydrous sodium sulfate was analysed with every 11 samples. "Negative Control" samples were created using plastics and textiles that contain no BFRs and were also analysed throughout the study. Three such control samples were assessed for each matrix. None of the target compounds were found above the limits of detection in the blanks. Therefore results were not corrected for blank residues and method limits of detection (LOD) and quantification (LOQ) were estimated based on a signal to noise ratio (S/N) of 3:1 and 10:1 respectively. LOQs for target compounds ranged from 0.8 - 1.5 ng/g for PBDEs and were 0.3 ng/g for α-, β- and γ- HBCDD.

Method accuracy and precision was assessed via repeated analysis of certified reference materials (CRMs) ERM-EC591 (polypropylene), ERM-EC590 (polyethylene) in addition to textiles (polyester fabrics), extruded polystyrene and expanded polystyrene that have been previously measured by this laboratory and another. All values were found to be close to certified or indicative levels, with a relative standard deviation of <15 %. Full details of method precision and accuracy can be found in Abdallah et al. (2017)

2.6 Statistical Analysis

All statistics were performed using Microsoft Excel 2013 and IBM SPSS Statistics for Windows Version 22. A significance level of 95 % ($p \leq 0.05$) was applied.

3.0 Results & Discussion

3.1 Concentrations of BFRs in Irish Waste Samples

HBCDDs and PBDEs indicative of the Penta- and Octa- formulations ($\sum_9$PBDE = BDEs -28, -47, -99, -100, -153, -154, -183, -196 and -197) and BDE-209 were detected in 33 %, 56 % and 65 % respectively of all samples. The mean concentrations measured were 580 mg/kg (range: <0.0003 – 51,000 mg/kg), 8.1 mg/kg (range: <0.0003 – 1,400 mg/kg) and 730 mg/kg (range <0.0008 – 73,000 mg/kg) for HBCDDs, $\sum_9$PBDEs and BDE-209 respectively (Table 2).

C&D EPS/XPS Waste

HBCDD was detected in 100 % of EPS samples at concentrations ranging between 0.08 and 10,000 mg/kg and in 100 % of XPS samples at concentrations between <0.34 and 94 mg/kg. Median concentrations were 100 mg/kg and 19 mg/kg for EPS and XPS respectively. No PBDEs (including BDE-209) were detected in any of the C&D samples.

Out of 60 C&D EPS/XPS samples 14 (all EPS) contained HBCDDs above the LPCL of 1,000 mg/kg. Notwithstanding this, median concentrations of HBCDD in our C&D EPS/XPS waste samples were substantially lower than suggested previously (HBCDD was reported to be added to new EPS and XPS insulation panels at concentrations of 20,000 and 7,000 mg/kg respectively (European Commission, 2011, Marvin et al., 2011) raising the possibility that much of the HBCDD originally present in the EPS/XPS samples we analysed, will have been emitted into the surrounding environment during the lifespan of the product. Surprisingly, no EPS/XPS samples contained HBCDD at concentrations close to their reported treatment levels. It was expected that "newly treated" EPS/XPS would be present to some extent in the waste stream, from off-cuts and waste materials from recent construction work. However this is likely to form a represent a very small proportion of the total volume of waste EPS/XPS and therefore would require a larger sampling campaign to detect this. It is also plausible that EPS and XPS were treated at lower HBCDD concentrations, than previously reported. In EPS and XPS samples where HBCDD was not detected, it is most likely that they were installed prior to the use of HBCDD to treat EPS/XPS insulation. An alternative scenario is that they had been treated with PolyFR – a replacement for HBCDD, however this is unlikely as PolyFR did not begin replacing HBCDD in the EU until 2013, with a planned phase-out by 2015 (Plastics Today, 2014) meaning that it is unlikely that this will form a noticeable proportion of currently-generated end of life EPS/XPS.

ELV Waste

HBCDD, $\sum PBDE_{28:197}$ and BDE-209 were all detected in ELV samples analysed. HBCDD was detected in 36 out of 119 ELV samples. The median concentration was <0.0003 mg/kg (range: <0.0003 – 3,300 mg/kg) with only two exceedances of the LPCL. $\sum PBDE_{28:197}$ was detected in 98 out of 119 samples with a median concentration of 0.09 mg/kg (range: <0.0008 – 740 mg/kg). There were no exceedances of the LPCL for PBDEs.

BDE-209 (the principal congener in the DecaBDE formulation) was detected in 105 samples with a median concentration of 1.6 mg/kg (range: <0.0008-31,000 mg/kg). From this point onwards a tLPCL of 1,000 mg/kg is assumed for DecaBDE. DecaBDE exceeded the tLPCL in only five ELV samples, whilst it was just below the tLPCL in one sample (980 mg/kg). All exceedances of the tLPCL for DecaBDE were in upholstery (roof trim, seat covers, and floor mats) rather than PUF. This is consistent with DecaBDE's use as back-coating on a variety of fabrics (Weil and Levchik, 2008). Interestingly, of the five samples that exceeded the tLPCL, four were from vehicles manufactured by companies based in Asia (Japan (Mazda, n=2) and Hyundai (South Korea, n=2) with an mean concentration of 27,000 mg/kg (22,000-31,000 mg/kg). The remaining sample contained 4,000 mg/kg and was from a manufacturer based in Germany (BMW). Unfortunately data on vehicle model and age was not always available and therefore it was not always possible to determine when and where vehicles were manufactured. The vehicle with the highest BDE-209 concentration (Hyundai I-20, 31,000 mg/kg) was registered in 2012 demonstrating that products containing DecaBDE were still entering the European market, several years after the introduction of restrictions on its use in 2008. Interestingly, a PUF sample was also taken from a seat in this car and found to contain 2.8 mg/kg of BDE-209 and trace levels of other POP-BFRs. This may imply transfer of BDE-209 from the fabric covering to the foam within.

Soft Furnishings

HBCDD was detected in 32 out of 122 soft furnishing samples. The median concentration was <0.0003 mg/kg (range: <0.0003-51,000 mg/kg). It exceeded the HBCDD LPCL in 11 samples (6 upholstery and 5 furniture foam samples. In all other samples where HBCDDs were found above the detection limits, but below the LPCL (range: 1 – 400 mg/kg, median: 4 mg/kg) it is likely to be due to migration out of other treated products during contact and/or the result of using recycled products during the manufacturing process that have previously been treated with HBCDD. This argument is supported by the fact that 83 % of furniture upholstery samples exceeding the LPCL contain substantially higher levels than the PUF sample from the same item. No mattresses (foam or upholstery), carpets or curtains contained HBCDDs above LPCLs.

$\sum_9$PBDEs was detected in 93 out of 122 soft furnishing samples with a median concentration of 0.058 mg/kg (range: <0.0003 – 160 mg/kg). No soft furnishing samples exceeded current LPCLs for PBDEs. BDE-209 was detected in 75 samples with a median concentration of 5.4 mg/kg (range: <0.0008 – 73,000 mg/kg). In total, there were 10 tLPCL exceedances, specifically in: 6/22 furniture fabrics, 3/20 furniture foam, and 1/31 carpet samples. As with ELV samples, the four with the highest BDE-209 concentrations were fabric covers, however, three foam samples and one carpet sample exceeded the tLPCL for BDE-209. Of these three foam samples, two exceeded the tLPCL in the corresponding upholstered fabric sample collected from the same item of furniture. As there is no known treatment of PUF with DecaBDE, this suggests migration of BDE-209 from back-coated fabric to underlying foam via direct contact. No curtains, mattress foams, or mattress upholstery samples exceeded tLPCLs for BDE-209.

WEEE

HBCDD was detected in 25 out of 237 WEEE samples. The median concentration was <0.0003 mg/kg (range: <0.0003 – 1,600 mg/kg). It only exceeded the HBCDD LPCL in one sample (a computer CD player). Moreover, two samples from the same display item (a CRT TV/DVD combination) contained 210 and 330 mg/kg of HBCDD. HBCDD has previously been detected in dust collected from inside a CRT TV at a highly elevated concentration, demonstrating its application in HIPS (Harrad et al., 2009). This suggests that whilst a small proportion of HBCDD has been used to treat electronics items, it has not been widely used for this purpose. However, contamination may occur through the use of recycled plastics. This is consistent with the literature that only a minor proportion (<1 %) of the globally produced HBCDD was used in the treatment of HIPS for electronic items (European Commission, 2011). It is possible, however, that since usage data was last reported for HBCDD that its use in EEE could have increased. This is due to the development of a more thermally stable HBCDD commercial formulation meaning it could meet flame retardancy standards (e.g. UL94-HB in Europe) for TVs and other audio visual equipment (Weil and Levchik, 2008).

$\sum_9$PBDEs was detected in 110 out of 237 samples. The median concentration was <0.0003 mg/kg (range: <0.0003 – 1400 mg/kg). The LPCL was exceeded for PBDEs in only one sample (the front panel of a CRT television). BDE-183 was responsible for the majority (75

%) of $\sum_9$PBDEs content in this sample, with smaller quantities also coming from BDEs -197 (9.1 %), -196 (7.7 %), -153 (7.0%) and -154 (1.5 %). These congeners are representative of Octa-BDE commercial formulations – especially given the absence of BDEs -47, -99 and -100, which were not detected. However, it is likely the LPCL exceedance for this sample is due to treatment with the DecaBDE formulation which was found in the same sample at 60,000 mg/kg. This could be due to one or more of the following: (i) OctaBDE impurities in one of the commercial mixtures (Bromkal 82-0DE), which has been reported to contain OctaBDE impurities at 5-10 % (La Guardia et al., 2006); (ii) debromination of BDE-209 at the high temperatures experienced during the process of incorporating it into the molten polymer and (iii) debromination at high temperatures during use of the treated product.

BDE-209 was detected in 151 out of 237 WEEE samples with a median concentration of 0.43 mg/kg (range: <0.005-60,000 mg/kg). It exceeded the tLPCL in 8 samples (4 IT, 2 display, and 2 SDAs (1 electric heater and 1 power drill). It was also close to the tLPCL (>500 – 1,000 mg/kg) in 2 further samples (1 IT and 1 SDA (a kettle)). All LHAs and fridges contained <170 mg/kg BDE-209. The majority of samples exceeding tLPCLs for BDE-209 were IT samples (5.2 % > tLPCL), display units (4.7% > tLPCL) and SDAs (6.9% > tLPCL).

3.2 Preliminary estimation of mass of products exceeding LPCLs and mass of POP-BFRs annually entering the waste streams studied in Ireland

Using publicly available data (Table 3) the mass of waste materials in Ireland that are currently exceeding LPCLs and tLPCLs (and would therefore require treatment in order to comply with EU regulation) were estimated for each category (Figure 1). In addition, we combined the data in Table 3 with our concentration data to generate preliminary estimates of the mass of POP-BFRs annually entering the waste streams studied in Ireland. The uncertainties inherent in these estimates are acknowledged, and their preliminary nature underlined; nevertheless we believe them to be informative.

C&D Waste

In 2011, approximately 3 million t of C&D waste was produced in Ireland (Environmental Protection Agency (EPA), 2014). There is no specific data for C&D waste in Ireland, however the UK estimates that around 2.8 % of its C&D waste is likely to be EPS and XPS (DEFRA, 2010) which would lead to approximately 4,200 t/yr of waste EPS/XPS generated in Ireland in 2011. Assuming the mean HBCDD concentration from all EPS/XPS in this study (1,313 mg/kg), approximately 5,500 kg of HBCDD is entering the Irish waste stream via C&D waste. With 23 % of waste EPS/XPS exceeding the LPCL for HBCDDs, this equates to 966 t of waste EPS/XPS that could not be recycled or landfilled (Figure 1). With the current EU exemptions in place for HBCDD to still be used in EPS/XPS insulation until a suitable alternative can be found, this is likely to be a long term issue. It is therefore imperative that viable treatment options are established.

End of Life Vehicles & Soft Furnishings

In 2012, Ireland produced 102,373 t of end of life vehicles, with an mean vehicle weight of 1,069 kg (Environmental Protection Agency, 2013). Automotive shredder residue data from the UK was used to estimate that 2.4 % of ELV waste is PUF and textiles (based on 27,222 t of 1,123,873 t ELV generated in the UK (WRc, 2012a). This equates to approximately 2,651 t of PUF and upholstery associated with ELV waste generated in Ireland in 2012. Using the mean concentrations from this study of $\sum_9$PBDEs = 7.5 mg/kg, DecaBDE = 950 mg/kg HBCDD = 45 mg/kg), approximately 20 kg $\sum_9$PBDEs, 2,500 kg of DecaBDE and 119 kg of HBCDD are entering the waste stream through end of life vehicles. Until an LPCL for BDE-209 is introduced, only 1.5 % (39 t) of this waste, courtesy of its HBCDD content, requires special treatment to remove POPs. However, were an LPCL of 1,000 mg/kg to be introduced for Deca-BDE, this will rise to 5.2 % (137 t) of ELV waste requiring hazardous waste treatment.

Soft furnishings followed a similar trend to ELV waste with a mixture of POP-BFRs and BDE-209 detected. However, it should be noted that there were no LPCL exceedances in curtains (maximum concentrations: HBCDD = 56 mg/kg, $\sum_9$PBDEs = 2 mg/kg, BDE-209 = 52 mg/kg), mattress foams (maximum concentrations: HBCDD = not detected, $\sum_9$PBDEs = 1 mg/kg, BDE-209 = 870 mg/kg), and mattress upholstery (maximum concentrations: HBCDD = 12 mg/kg, $\sum_9$PBDEs = 1 mg/kg, BDE-209 = 49 mg/kg). Therefore, it is likely that no treatment is necessary for these waste materials.

There were no exceedances of current LPCLs for carpet samples (maximum HBCDD = 26 mg/kg, $\sum_9$PBDEs = 13 mg/kg). However, 3.2 % (1/31) of carpet samples exceeded the tLPCL for DecaBDE. Based on our data, under current legislation, it is not necessary to treat carpets prior to disposal or recycling, however if an LPCL for DecaBDE of 1,000 mg/kg is introduced, then approximately 250 t/yr of waste carpet would require treatment.

Currently, there are no published data regarding the volume of furniture entering the waste stream in Ireland. However, assuming an identical *per capita* rate of generation of such waste to that in the UK in 2010/11 (i.e. 237,516 t/yr of sofas, armchairs and chairs combined (WRAP, 2012)); ~17,900 t/yr of waste furniture are generated in Ireland. Therefore it is estimated that 2,685 t/yr of PUF and 895 t/yr upholstery fabrics are produced in Ireland (assuming that sofa is 15 % foam, and 5 % fabrics by weight).Whilst there were no exceedances of LPCLs for $\sum_9$PBDEs, both furniture foam and upholstery samples had multiple LPCL exceedances for HBCDD. 25 % (5/20) of our furniture foam samples contained HBCDDs at a concentration range of 1,000 – 8,000 mg/kg. Meanwhile, a further

25 % (6/24) of our furniture upholstery samples exceeded HBCDD LPCLs at a concentration range of 21,000 – 51,000 mg/kg – up to 51 times the LPCL. This equates to 671 t/yr of furniture foam and 242 t/yr of furniture upholstery in Ireland requiring removal of BFRs. In the event of an LPCL being enforced for BDE-209, the percentage of LPCL exceedances would increase to 35 % (940 t/yr) and 38 % (366 t/yr) of furniture foam and upholstery, respectively.

WEEE

In 2012, an estimated 40,818 t of WEEE was produced in Ireland (Environmental Protection Agency (EPA), 2014). However a full breakdown of this was not available; instead a breakdown from the 2011 National Waste Report for Ireland (Environmental Protection Agency, 2013) was used. There are clear differences in the BFR content of different WEEE sub-categories. There were no LPCL exceedances for samples of either large household appliances (LHA), or cooling appliances (fridges/freezers), with only low levels of POP-BFRs measured (<10 mg/kg). Furthermore, only low levels (<200 mg/kg) of BDE-209 were measured in LHA and cooling appliances. Therefore, treatment of LHA and cooling appliances to remove BFRs appears unlikely to be necessary.

A similar pattern was seen for small domestic appliances (SDA) and IT samples, with no exceedances for $\sum_9$PBDEs. However, as mentioned above, one IT sample also exceeded the LPCL for HBCDDs. Therefore, under current legislation it is estimated that approximately 127 t/yr of SDA and IT waste would require treatment for POP-BFR removal. When including samples that exceeded the tLPCL for DecaBDE, this figure would rise to 929 t/yr.

As 2 % (1/45) display samples exceeded current LPCLs, this means that 153 t/yr display item waste requires treatment to remove its POP-BFR content. When including tLPCLs for DecaBDE, an estimated 306 t/yr of display waste requires POP-BFR removal.

Based on the above information it is estimated that 2,198 t/yr of waste in Ireland exceeds current LPCLs and therefore requires treatment to remove POP-BFRs prior to disposal or recycling. In the event of an LPCL of 1,000 mg/kg DecaBDE being enforced, this figure would rise to 3,894 t/yr.

3.3 Potential waste treatment options

All waste items that contain PBDEs and/or HBCDDs above the LPCLs require treatment to remove BFRs before they can be legally recycled or disposed of. An investigation into treatment options by the German UBA (Federal Environment Office) examined waste incineration as a potential pathway to meeting LPCL requirements (Umwelt Bundesamt, 2015). The study found that when EPS/XPS is co-incinerated (up to 2 % of total content) with other waste (using best available techniques (BAT) – 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-p-dioxins/furans (PCDD/Fs), polybrominated dibenzo-p-dioxins/furans (PBDD/Fs), mixed halogenated dioxins/furans (PXDD/Fs) and polychlorinated biphenyls (PCBs)), whilst the process also removes ozone-depleting substances (Umwelt Bundesamt, 2015). Treating waste plastics/textiles in this way will not only destroy the HBCDD content at a far greater efficiency than is required by EU law, but it would also be used as a “renewable” fuel source. However, this “solution” requires substantial capacity for incineration as BFR-containing waste plastics can only make up to 2 % of each incineration to avoid risk of corrosion due to formation of HBr (Umwelt Bundesamt, 2015). A further issue is that increased levels of bromine in the incinerator feedstock arising from other waste containing elevated BFR concentrations could potentially cause increased corrosion through the production of hydrobromic acid (HBr) (Tange and Drohmann, 2003). However, it has been determined by previous experiments reported by the European Brominated Flame Retardant Industry Panel

(EBFRIP) 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 was 10,000 pm (1 % of total weight), therefore the risk of corrosion by HBr formation is considered extremely low. In contrast, the POP-BFR concentrations in soft furnishings and ELV waste were considerably higher than in EPS/XPS (up to 5 % HBCDD content). There is also the additional issue of the high concentrations of BDE-209 in multiple waste streams (up to 3 % in ELV, 7 % soft furnishings and 6 % in WEEE). Moreover, tetrabromobisphenol A (TBBPA), (a BFR widely used in EEE without any current restrictions) was also measured in WEEE in concentrations up to 12 % by weight (not reported here). Therefore ELV, furniture waste and WEEE would require considerable dilution with other (BFR-free) waste to ensure that there is no corrosion as a result of HBr formation. This is likely to raise the cost of disposing of these waste streams. Furthermore, BDE-209 and PBDEs are considered potential precursors to more toxic compounds such as polybrominated dibenzo-p-dioxins/furans (PBDD/Fs), which have been seen to form in thermal processes (Wang and Chang-Chien, 2007) although 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).

Whilst incineration currently appears the best available treatment option for waste exceeding LPCLs, it is likely to be expensive with operators charging up to €1,000 per tonne (Creacycle, 2016). Over the last decade industries and governments have attempted to improve and modify a technique that removes BFRs from WEEE based plastics. It has been demonstrated that it can effectively remove BFRs from WEEE-based styrene plastics, as well as EPS/XPS with >99.7 % efficiency (Schlummer et al. 2006, Schlummer et al. 2017). This technique is thus a potentially viable treatment option for the huge volumes of WEEE and

EPS/XPS generated each year as it would allow much of the waste to be recycled – thereby allowing some of the treatment costs to be recovered/subsidised. A demonstration plant with a capacity of 3,000 t/year is currently on track to be opened in 2018 Terneuzen (The Netherlands). This will go some way to coping with waste EPS/XPS across Europe (Creacycle 2016). However, it is to our knowledge not currently a commercially viable option, and at the current time it appears that total energy recovery incineration is currently the best available treatment option for all waste exceeding LPCL values, with the caveat that such waste articles will require dilution with other "BFR-free" waste to minimise formation of corrosive HBr during the treatment process.

3.4 Effectiveness of LPCL enforcement

Using the concentrations measured from this study, and estimates of the annual masses of impacted waste streams generated in Ireland of impacted waste streams (Table 3), the mass of POP-BFRs and BDE-209 entering the Irish waste stream each year were estimated (Table 4). In total, an estimated 32,524 kg/year of waste ∑POP-BFRs+BDE-209 are generated in Ireland (121, 17,005, and 15,519 kg/year for $\sum_9$PBDEs, HBCDD, and BDE-209 respectively). By enforcing existing LPCLs, it is estimated that 98 % of ∑POP-BFRs would be diverted from the Irish waste stream – 43 % of $\sum_9$PBDEs, 99 % of HBCDD (Figure 2). This demonstrates that enforcement of current LPCLs would result in the interception of a significant proportion of POP-BFRs and BDE-209 re-entering the environment through disposal and/or recycling. Furthermore, under current LPCLs, approximately 22 % of all BDE-209 would also be intercepted through diversion of the exact same waste products. Taking into account the recent listing of DecaBDE as a POP under the Stockholm Convention, it is likely that an LPCL for its principal congener (BDE-209) will be imposed. If a similar LPCL of 1,000 mg/kg is applied for BDE-209 then ~99 % of waste POP-BFRs would be intercepted along with ~93 % of all waste BDE-209 (96 % of ∑POP-BFRs+BDE-209). Even if a higher LPCL of 5,000 mg/kg is imposed for BDE-209, ~91 % of BDE-209 associated with waste articles (~95 % of waste ∑POP-BFRs+BDE-209) would be prevented from re-entering the environment, demonstrating the effectiveness of LPCLs.

Conclusions

- A comprehensive survey of POP-BFRs and BDE-209 entering the waste stream in Ireland identified that there is a large volume of waste (~2,200 t/yr) that requires treatment to meet current legislation (Annex IV of EU POPs regulation (EC) No 850/2004)
- Enforcement of current LPCL legislation would result in removal of 98 % of POP-BFRs from re-entering environment
- Waste EPS from the C&D industry is likely to produce the highest volume of waste requiring treatment in Ireland (966 t/yr), with waste furniture closely behind (913 t/yr) under existing LPCLs
- The likely implementation of a similar LPCL for BDE-209 will cause a 75 % increase in waste requiring treatment in Ireland, with waste furniture the biggest contributor under this scenario (1,306 t/yr)
- Only 280 t/year of WEEE exceeds existing LPCLs in Ireland – however, introduction of an LPCL of 1,000 mg/kg for BDE-209 would increase this to 1,235 t/year
- Current treatment options to destroy or remove POP-BFRs from waste articles exceeding LPCLs are limited, with total energy recovery waste incineration as the most realistically viable option. However, due to its high Br content, LPCL-exceeding waste treated by this process requires dilution with “low-BFR” articles to avoid corrosion of the incinerator by HBr.

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Figures and Tables

Table 1 Classes and subclasses of waste products analysed for POP-BFRs

Class	Sub-class	Number of Samples
Construction and Demolition	EPS	40
	XPS	20
End of Life Vehicles (ELV)	Foam	38
	Fabrics	81
Soft Furnishings	Carpets	31
	Curtains	15
	Furniture Fabrics	22
	Furniture Foam Filling	20
	Mattresses	34
Waste Electrical and Electronic Equipment	Large Household Appliances	57
	Cooling Appliances	30
	Display	43
	Small Domestic Appliances	29
	It and Telecommunications	78

Table 2 Mean, median, minimum and maximum concentrations (mg/kg) of POP-BFRs and BDE-209 in samples from waste streams in Ireland

Waste Stream	*Sub-Category*	*Statistical parameter*	*∑HBCDD*	*$\sum_9$PBDEs*	*BDE-209*
Construction & Demolition	***EPS***	***mean***	*2100*	*<0.0003*	*<0.0008*
		median	*100*	*<0.0003*	*<0.0008*
		min	*<0.0003*	*<0.0003*	*<0.0008*
		max	*10000*	*<0.0003*	*<0.0008*
	XPS	***mean***	*27*	*<0.0003*	*<0.0008*
		median	*19*	*<0.0003*	*<0.0008*
		min	*<0.0003*	*<0.0003*	*<0.0008*
		max	*94*	*<0.0003*	*<0.0008*
End of Life Vehicles	***ELV Foams***	***mean***	*<0.0003*	*20*	*10*
		median	*<0.0003*	*0.05*	*0.73*
		min	*<0.0003*	*<0.0003*	*<0.0008*
		max	*2*	*740*	*120*
	ELV Upholstery	***mean***	*67*	*1.4*	*1400*
		median	*<0.0003*	*0.095*	*3.6*
		min	*<0.0003*	*<0.0003*	*<0.0008*
		max	*3300*	*20*	*31000*
Soft Furnishings	***Carpets***	***mean***	*1*	*0.77*	*240*
		median	*<0.0003*	*<0.0003*	*0.008*
		min	*<0.0003*	*<0.0003*	*<0.0008*
		max	*26*	*13*	*7000*
	Curtains	***mean***	*3.8*	*0.2*	*3.7*
		median	*<0.0003*	*<0.0003*	*<0.0008*
		min	*<0.0003*	*<0.0003*	*<0.0008*
		max	*56*	*1.7*	*52*
	Furniture Fabrics	***mean***	*9200*	*21*	*6800*
		median	*1.1*	*0.26*	*12*
		min	*0.005*	*0.00014*	*<0.0008*
		max	*51000*	*160*	*73000*
	Furniture Foam Filling	***mean***	*1100*	*0.79*	*660*
		median	*0.27*	*0.17*	*15*
		min	*<0.0003*	*<0.0003*	*<0.0008*
		max	*8000*	*7.2*	*7800*
	Mattresses	***mean***	*1.1*	*0.1*	*45*
		median	*<0.0003*	*0.056*	*6.8*
		min	*<0.0003*	*0.0035*	*<0.0008*
		max	*12*	*0.87*	*870*
WEEE	***Large Household Appliances***	***mean***	*<0.0003*	*0.15*	*19*
		median	*<0.0003*	*<0.0003*	*0.036*
		min	*<0.0003*	*<0.0003*	*<0.0008*

		max	*<0.0003*	*2.6*	*190*
	Cooling Appliances	***mean***	*<0.0003*	*0.017*	*0.46*
		median	*<0.000001*	*<0.0003*	*<0.0008*
		min	*<0.000001*	*<0.0003*	*<0.0008*
		max	*<0.0003*	*0.16*	*3.6*
	Display	***mean***	*14*	*38*	*1900*
		median	*0.014*	*<0.0003*	*<0.0008*
		min	*<0.0003*	*<0.0003*	*<0.0008*
		max	*330*	*1400*	*60000*
	Small Domestic Appliances	***mean***	*<0.0003*	*0.106*	*170*
		median	*<0.0003*	*0.016*	*0.019*
		min	*<0.0003*	*<0.0003*	*<0.0008*
		max	*<0.0003*	*0.84*	*1600*
	It and Telecommunications	***mean***	*20*	*17*	*260*
		median	*<0.0003*	*0.089*	*0.21*
		min	*<0.0003*	*<0.0003*	*<0.0008*
		max	*1600*	*890*	*7600*

**when calculating means sampled below limit of quantification were assumed to be equal to zero*

***Table 3: Estimated* annual masses (t/year) generated in Ireland for each waste category examined in this study**

Waste Category	**Estimated Annual Mass Generated in Ireland (t/year)**	**Source**
C&D EPS/XPS	4,200	In 2011 ~ 3 million t of C&D waste was produced in Ireland (EPA, 2014). There are no specific data for C&D waste in Ireland, however the UK estimates that around 2.8 % of its C&D waste is insulation material, 5 % of which is EPS and XPS (Defra, 2010) which would lead to ~ 4,200 t/yr of waste EPS/XPS generated in Ireland.
LHA	13,604	EPA (2013)
Display	6,651	EPA (2013)
Fridges/Freezers	5,971	EPA (2013)
SDA and other IT	14,202	As separate estimates for arisings of SDA and items included in the “IT items” category are unavailable, we derived an estimate for combined arisings of these categories by assuming it to be equivalent to the figure cited for “Other WEEE” (e.g. stereos, phones, toys, vacuum cleaners, toasters, computers etc.) (EPA, 2013)
ELV foam & fabrics	2,651	Assuming 102,373 ELVs generated in 2012 (EPA, 2014), and an average vehicle weight of 1,069 kg (EPA, 2013). We then assumed that ELV foam and fabrics were identical to light ASR which WRc (2012a) reported represented 27,222 t of the 1,123,873 t ELV generated annually in the UK – i.e. 2.4 %
Carpets	7,834	Assuming Irish mass pro-rata[a] to UK 2010-11 arisings of 103,972 t (WRAP, 2012)
Furniture foam	2,685	Assuming Irish mass pro-rata[a] to UK 2010-11 waste arisings for sofas, armchairs and chairs combined of 237,516 t (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 t (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 t for “all other bulky textiles” (WRAP, 2012) and authors’ own estimate that 50 % of this is curtains
Mattress foam	6,272	Assuming Irish mass pro-rata[a] to UK 2010-11 arisings of 166,474 t (WRAP, 2012) and authors’ own estimate that 50 % of this is foam
Mattress fabrics	2,509	Assuming Irish mass pro-rata[a] to UK 2010-11 arisings of 103,972 t (WRAP, 2012) and authors’ own estimate that 20 % of this is fabrics

[a]pro-rata calculations based on 2011 Census data for UK population of 63,182,000 and 2016 Irish Census data for the population of Ireland of 4,761,185

Table 4: Estimated annual mass (kg/year) of POP-BDEs, HBCDD, and BDE-209 associated with Irish waste categories

Annual Mass (kg/year)					
Waste Category	**POP-BDEs**	**HBCDD**	**ΣPOP-BFRs**	**BDE-209**	**ΣPOP-BFRs + BDE-209**
C&D	0	5,515	5,515	0	5,515
LHAs[a]	0.058	0	0.058	0.71	0.730
Display[b]	45.2	16.6	61.8	2,265	2,327
Fridges/Freezers[c]	0.01	0	0.01	0.28	0.29
SDAs & other IT equipment[d]	28.1	34	62.1	531	593
ELV foam & fabrics	20	119	139	2,517	2,656
Carpets	6.0	8.3	14	1,854	1,868
Furniture Foam	2.1	3,079	3,081	1,776	4,857
Furniture Fabrics	18.5	8,224	8,243	6,048	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	121	17,004	17,125	15,518	32,643

[a]Assuming 0.29 % w/w of LHA is Br-containing plastic (WRc, 2012b)

[b]Assuming 18 % w/w of Display waste is Br-containing plastic (WRc, 2012b)

[c]Assuming 10 % w/w of Waste Fridges and Freezers is Br-containing plastic (WRc, 2012b)

[d]Assuming 16.1 % w/w of SDAs and other IT equipment is Br-containing plastic (WRc, 2012b). This based on estimates cited in WRc (2012b) that 0.75 % and 18 % of SDA and IT equipment respectively are Br-containing plastic and WRc (2012b) data for the UK that show mass of waste IT equipment is 8.21 times that of SDA

Figure 1 – Estimated mass (t/yr) of waste requiring POP-BFR treatment prior to disposal/recycling with and without the tLPCL for DecaBDE

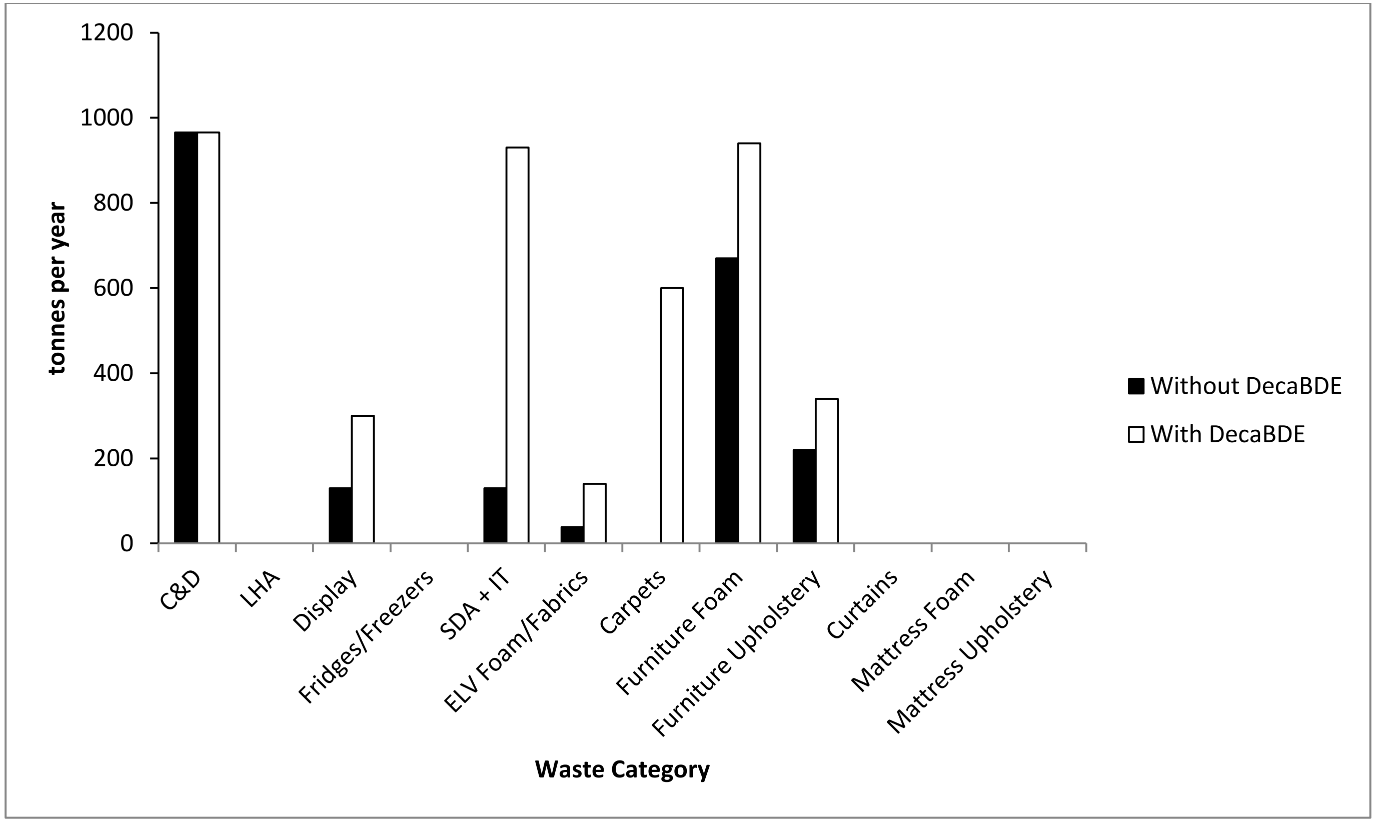

Figure 2 Proportion (%) of total mass of POP-BFRs and DecaBDE diverted from Irish waste stream as a result of enforcement of existing LPCLs (for HBCDD, Penta- and Octa-BDE) and tLPCL for DecaBDE