Regulated Brominated Flame Retardants in Irish Waste Plastics: Obstacles to the Circular Economy?

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Introduction

Large quantities of brominated flame retardants (BFRs) have been used in a wide range of consumer goods to meet fire safety regulations. Subsequently, some BFRs have been found to exhibit traits congruent with those of persistent organic pollutants (POPs), i.e. long environmental life times, propensity for bioaccumulation in the fatty tissue of living organisms, and toxicity to both humans and wildlife (UNEP, 2009).

Consequently, such BFRs have been listed under the Stockholm Convention on persistent organic pollutants (POPs). These “POP-BFRs” are, specifically, two of the three commercial mixtures of polybrominated diphenyl ethers (PBDEs) – commercial penta-BDE and commercial octa-BDE (UNEP, 2009) – and hexabromocyclododecane (HBCDD) (UNEP, 2013). Moreover, the third main commercial PBDE mixture, deca-BDE, is under active consideration for listing under the convention (UNEP, 2015). In an effort to “close the loop” and prevent polymers containing POP-BFRs from being recycled thus leading to the presence of unintentional trace contaminants (UTCs) in new goods and materials, the European Union has set low-POP concentration limits (LPCLs) of 1000 ppm (0.1% by weight) for POP-BFRs in waste polymers (EC, 2004, EC, 2010, EC, 2016). Items containing concentrations that exceed these LPCLs cannot be recycled. The presence of POP-BFRs in the waste stream therefore presents a challenge to the EU’s desire to promote a circular economy.

Historically, large quantities of BFRs were used in a wide range of consumer plastics. These include: high impact polystyrene (HIPS) and acrylonitrile butadiene styrene (ABS) casings of electrical and electronic equipment (EEE); textiles, upholstery and furniture foams in soft furnishings; expanded and extruded polystyrene (EPS/XPS) used as building insulation foams and packaging materials; and foam padding and upholstery from vehicle seats (Marvin et al., 2011, UNEP, 2010, Weil and Levchik, 2009). While restrictions on POP-BFRs means they are no longer used intentionally in new items, substantial quantities of older goods containing POP-BFRs dating from before the introduction of use-restrictions are now entering the waste stream. In this study, 557 samples of waste plastic items were obtained in 2015 and 2016 from a number of recycling and waste transfer stations in Ireland. Concentrations of PBDEs (including Deca-BDE), tetrabromobisphenol-A (TBBP-A), and HBCDD were measured in these samples to provide, inter alia, an overview of their current presence and distribution in the Irish waste stream and identify the frequency with which LPCLs are exceeded.

Materials and Methods

Sample Collection

Table 1 shows the number of samples taken from each waste category studied. These comprised: plastic casings from waste electrical and electronic equipment (WEEE); polyurethane foams, upholstery, and textiles from end-of-life vehicles (ELVs) and household/office soft furnishings; and extruded and expanded polystyrene (XPS/EPS) used either as building insulation foam from construction and demolition (C&D) waste or as packaging materials. 557 samples were collected from two recycling sites, three waste transfer stations, one vehicle scrapyard and a construction company. The specific sampling protocol involved removal of a small piece of the item (~1 cm^2) under test; in the case of WEEE items, multiple samples were taken from different areas of a single WEEE item in order to determine the uniformity of BFR content throughout the body of the item.

WEEE Casings	Soft Furnishings	Packaging and Insulation
Display (41)	Furniture (42)	XPS Insulation (20)
IT & Telecoms (IT&T) (78)	Mattresses (34)	EPS Insulation (40)
Small Domestic Appliances (SDAs) (29)	Curtains (15)	XPS Packaging (14)
Large Household Appliances (LHAs) (57)	Carpets (31)	EPS Packaging (7)
Refrigerators (30)	Vehicle Interior (118)	

Table 1 – Overview of the types of samples gathered (WEEE and Soft Furnishings) and the encompassed sample-groups, along with quantities of samples gathered in each case (number of samples per sample group shown in brackets).

BFR Analysis

Aliquots of samples (20-100 mg) were weighed into clean 15 mL glass test-tubes. They were spiked with internal standards (30 ng of BDEs -77 and -128, $^{13}C_{12}$-labelled α-, β-, and γ-HBCDD, $^{13}C_{12}$-TBBPA, and 60 ng of $^{13}C_{12}$-BDE-209). Approximately 3 mL of DCM was added and the samples vortexed for 2 min. followed by 30 minutes sonication. The extraction process was repeated three times with the combined extracts collected in a separate glass tube. Crude extracts were concentrated under a gentle stream of N_2 to near dryness and reconstituted in 2 mL n-hexane. Approximately 2 mL >95% conc. H_2SO_4 was added and extracts vortexed for 30 s prior to centrifugation for 5 min. at 3000 RPM. The supernatant organic layer was collected in a separate tube and concentrated to near-dryness and reconstituted in 200 µL iso-octane. Samples were analysed for PBDEs using GC-MS before reconstituting in methanol for analysis of TBBPA and HBCDD via LC-MS/MS.

Results and Discussion

Sample Group	Number of Samples	# Samples w/ BFRs > 100 ppm	Total BFR Range (ppm)	Avg. BFR per sample (ppm)	Avg. POP-BFR per sample (ppm)
C&D EPS	40	19	0 – 10,200	1,960	1,960
C&D XPS	20	0	0 - 94	29.3	29.3
Packing EPS	7	2	0 – 5,900	1,000	1,000
Packing XPS	14	3	0 – 369	117	117
Furniture Foam	20	10	0 – 8,470	1,830	1,150
Furniture Upholstery	22	11	0 – 73,000	17,600	10,100
Mattress Foam	17	2	0 – 869	79.5	0.14
Mattress Upholstery	17	0	0 – 59	12.6	2.32
Curtain	15	0	0 – 58	7.74	0.20
Carpet	31	2	0 – 7,040	231	1.78
ELV Foam	38	3	0 – 736	33.3	20.5
ELV Upholstery	50	9	0 – 30,700	1,790	108

ELV (Other)	30	4	0 – 23,500	960	> 0.01
IT&T	78	22	0 – 112,000	1,950	37.2
SDAs	29	7	0 – 10,100	518	0.11
Display	41	21	0 – 233,000	32,300	46.5
LHAs	57	1	0 – 2,010	52.9	0.15
Refrigerators	30	0	0 – 4	0.48	0.02

Table 2 – Summary of BFR and POP-BFR concentrations in the various sample-groups/waste types as determined by GC-MS for concentrations of PBDEs and TBBP-A and LC-MS/MS for HBCDD; note that "POP-BFRs" indicate presence of tri/octa-BDEs and HBCDD, while "BFRs" refers to the aforementioned as well as deca-BDE and TBBP-A.

HBCDD in Expanded and Extruded Polystyrene

Polystyrene insulation and packaging foams are unique among these wastes in that literature and current data suggests that where such materials are flame-retarded, the solely FR used is HBCDD. Concentrations of HBCDD in EPS and XPS ranged from 0 – 10,000 ppm and 0 – 200 ppm respectively. 35% of C&D EPS samples contained HBCDD above LPCLs while none of the C&D XPS exceeded even 200 ppm. The polystyrene packaging material samples (7 EPS and 14 XPS) showed 8 samples containing HBCDD in excess of 1 ppm, of which 4 exceeded LPCLs: 2 EPS at 1,120 and 5,900 ppm; 2 XPS at 1,010 and 1,060 ppm. Packaging foams of these material types require no such flame retardancy treatment and thus the HBCDD content of some samples, particularly at such elevated concentrations, merits further investigation.

BFRs and POP-BFRs in WEEE

BFR concentrations varied considerably within different WEEE categories. The IT&T and Display groups showed the largest variations in BFR content, with concentrations ranging from 0 – 112,000 ppm (11.2% w/w) and 0 – 275,000 ppm (27.5% w/w) respectively. SDAs and LHAs showed a similarly wide range of BFR concentrations: roughly 0 – 10,000 ppm (1.0% w/w) and 0 – 2,000 ppm (0.2% w/w) respectively. The specific BFR compositions of these samples are also noteworthy, with Deca-BDE and TBBP-A being the most commonly found in all four WEEE sample groups; in particular, TBBP-A was found in several samples at concentrations exceeding 10% w/w. HBCDD and $\sum PBDE_{Penta+Octa}$ were detected in roughly 40% of WEEE samples; however, in the majority of these cases, the concentrations were several hundred times below LPCLs, with LPCLs exceeded in only two instances: one IT&T sample (HBCDD = 1,600 ppm) and one Display sample ($\sum PBDE_{Penta+Octa}$ = 1,400 ppm – although this may be due to debromination of deca-BDE which was measured at 60,000 ppm in the same sample). However, were Deca-BDE to be listed under the Stockholm Convention leading to an LPCL for BDE-209 similar to that for other PBDEs and HBCDD (i.e. 1,000 ppm), 8 more samples (approx. 4.3% of total from WEEE sample groups) would then exceed LPCLs, potentially creating a more substantial obstacle to WEEE recycling in Ireland.

BFRs and POP-BFRs in Waste Soft Furnishings

Textiles and foams from household furniture and ELV seats showed similar high variations within sample groups: furniture upholstery showing ranges of 0 – 73,000 ppm (7.3% w/w); ELV upholstery, 0 – 31,000 ppm (3.1% w/w); carpets, 0 – 7,000 ppm (0.7% w/w); and furniture foams, 0 – 8,000 ppm (0.8% w/w). TBBP-A was rarely detected in the soft furnishings samples (occurring in only 2 samples from furniture foams) with deca-BDE and HBCDD making up almost the entirety of BFR content in the sample-groups. 13 of the samples from the soft furnishings exceeded LPCLs due to HBCDD content, with $\sum PBDE_{Penta+Octa}$ only detected at concentrations between 100 and 1,000 ppm in 1.2% of soft furnishings samples. 12 more samples of waste soft furnishings would exceed an LPCL of 1,000 ppm in the event that deca-BDE were listed as a POP, rendering 10% of soft furnishing samples non-recyclable under EU legislation.

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