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Abdallah, Mohamed Abou-Elwafa; Sharkey, Martin; Berresheim, Harald; Harrad, Stuart

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Mohamed Abou-Elwafa Abdallah, Martin Sharkey, Harald Berresheim, Stuart Harrad

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Hexabromocyclododecane in Polystyrene Packaging: A Downside of Recycling?

Mohamed Abou-Elwafa Abdallah[1,3], Martin Sharkey[2], Harald Berresheim[2], Stuart Harrad[1*]

[1] *School of Geography, Earth & Environmental Sciences, University of Birmingham, UK*

[2] *School of Physics, National University of Ireland Galway*

[3]*Department of Analytical Chemistry, Faculty of Pharmacy, Assiut University, 71526 Assiut, Egypt.*

*Author for correspondence

S.J.Harrad@bham.ac.uk

Tel. +44 (0)121 414 7298

Keywords

HBCDD; flame retardants; unintentional contaminants; recycled plastics; EPS; XPS

Abstract

While there are no regulatory fire safety obligations for polystyrene (PS) when used as packaging material, concerns exist that such packaging material may contain the flame retardant hexabromocyclododecane (HBCDD) as a result of uncontrolled recycling activities. To evaluate these concerns, we collected 50 samples of PS packaging materials from the UK and 20 from Ireland. HBCDD was detected in 63 (90 %) of samples, with concentrations in 4 samples from Ireland exceeding the EU's low POP concentration limit (LPCL) of 0.1 % above which articles may not be recycled. Moreover, 2 further samples contained HBCDD > 0.01 %. While our samples were obtained in the 12 month period prior to the March 2016 introduction of the EU's 0.01 % concentration limit above which articles may not be placed on the market, our data suggest that continued monitoring is required to assess compliance with this limit value. Ratios of α vs. γ-HBCDD in our EPS packaging samples (average = 0.63) exceeded significantly ($p=0.025$) those in EPS building insulation material samples (average = 0.24) reported previously for Ireland. This shift towards α-HBCDD in packaging EPS is consistent with the additional thermal processing experienced by recycled PS and suggests the source of HBCDD in PS packaging is recycled PS insulation foam. This is of concern owing to the higher bioavailability and lower metabolic clearance of α-HBCDD compared to the β- and γ-isomers.

1. Introduction

Polystyrene (PS) is widely used for thermal insulation of buildings as well as packaging for applications such as food, laboratory chemicals and electronic appliances, with a global market demand of 15 million tonnes in 2010 (Rani et al, 2014). To meet fire safety regulations, hexabromocyclododecane (HBCDD) has been used extensively throughout the world for a variety of purposes; one of the most important of which being its application at between 0.7–2.0 % w/w as an additive to impart flame retardancy to both expanded (EPS) and extruded (XPS) PS foam used to insulate buildings (European Commission, 2011; Marvin et al, 2011). As a result of this widespread use, HBCDD has been detected worldwide in a plethora of matrices, including indoor air and dust (Abdallah et al, 2008), outdoor air (Jo et al, 2017), soil (Meng et al 2011; Desborough et al, 2016), human tissues (Carignan et al, 2012; Rawn et al, 2014), lake sediments, (Harrad et al, 2009; Yang et al, 2012) and fish (Harrad et al, 2009b; Tomy et al, 2008). As a result of evidence of its persistent, bioaccumulative and toxic properties as well as its propensity for long-range transport, HBCDD has been listed as a persistent organic pollutant (POP) under the United Nations Environment Programme's Stockholm Convention on POPs (UNEP, 2014).

In recent years, there has been a drive in many jurisdictions, including the European Union towards the "circular economy" in which recycling and re-use of materials is maximised to, *inter alia*, minimise pressure on waste disposal infrastructure. However, concerns have been raised that new applications of recycled polymeric material that in its original application had been flame-retarded, has led to the undesirable presence of restricted brominated flame retardants (BFRs) in goods such as children's toys, food contact articles (Guzzonato et al, 2017; Kuang et al, 2018; Puype et al, 2015) and PS packaging (Rani et al, 2014). To prevent contamination with BFRs of such items, the EU has introduced a low POP concentration limit (LPCL) of 0.1 % w/w for restricted BFRs like HBCDD. Items containing restricted BFRs at concentrations exceeding the LPCL may not be recycled until their POP content has been removed to below LPCL limits. Moreover, items containing HBCDD as an unintentional contaminant (i.e. as a consequence of the use of HBCDD-containing recycled materials) at a concentration exceeding 0.01 % may after 22nd March 2016, no longer be placed on the market in the EU (European Commission, 2016).

Despite the introduction of LPCLs, it is likely that a substantial quantity of FR-treated waste has already been recycled. We thus hypothesise that while PS used in packaging materials is not required to meet flame retardancy regulations, recycling of flame-retarded PS building insulation foam may lead to the presence of HBCDD in packaging materials in the EU, in similar fashion to Korea, where HBCDD was detected in ~30 PS packaging samples (Rani et al, 2014). To test this hypothesis, we measured concentrations of HBCDD in 50 samples of PS packaging materials from the UK and 20 from Ireland.

2. Methods

2.1. Sample collection

Convenience samples of both XPS and EPS packaging were obtained by the authors in Birmingham, UK and in Galway, Ireland between October 2015 and April 2016. Table S1 gives information about each sample collected. In summary, we analysed 37 EPS and 13 XPS samples from the UK, and 6 EPS and 14 XPS samples from Ireland.

2.2. Sample extraction and purification

Accurately weighed aliquots of the polystyrene products (~50 mg) were placed in clean, solvent-rinsed 15 mL glass test tubes. The samples were spiked with 50 ng of ^{13}C-α-, β- and γ- HBCDDs (50 µL of 1 ng µL^{-1} solution in hexane) used as internal (surrogate) standard prior to dissolving in 2 mL of dichloromethane by vortexing for 2 min. The solvent was evaporated to incipient dryness under a gentle stream of N_2 and target analytes were immediately reconstituted in 2 mL hexane by vortexing for 2 min. The hexane extract was washed with 2 mL of conc. H_2SO_4 by vortexing for 1 min followed by centrifugation at 3000 g for 5 minutes. The organic layer was transferred to another clean tube and the acid layer was washed twice with 2 mL of hexane. The combined hexane layer was evaporated to dryness under N_2 prior to reconstitution in 150 µL of methanol containing 25 pg µL^{-1} of d_{18}-γ-HBCDD used a recovery determination (syringe) standard for QA/QC purposes.

2.3. Instrumental analysis

Separation of α–, β- and γ-HBCDD was achieved using a dual pump Shimadzu LC-20AB Prominence liquid chromatograph equipped with SIL-20A autosampler, a DGU-20A3 vacuum degasser and an Agilent Pursuit XRS3 C_{18} reversed phase analytical column (150 mm × 2 mm i.d., 3 µm particle size). A mobile phase program based upon (a) 1:1 methanol/water and (b) methanol at a flow rate of 150 µL min^{-1} was applied for elution of the target compounds; starting at 50 % (b) then increased linearly to 100 % (b) over 4 min, held for 7 min followed by a linear decrease to 60 % (b) over 4 min, held for 1 min and finishing with 100 % (a) for 10 min. HBCDD diastereomers were baseline separated with retention times of 10.6, 11.2 and 11.7 min for α-, β- and γ-HBCDD, respectively.

Mass spectrometric analysis was performed using a Sciex API 2000 triple quadrupole mass spectrometer operated in electrospray negative ionisation mode. MS/MS detection operated in the MRM mode was used for quantitative determination based on *m/z* 640.6→79.0, *m/z* 652.4→79.0 and *m/z* 657.7→79.0 for the native, ^{13}C-labelled and d_{18}-labelled HBCDD diastereomers, respectively. Specific instrumental calibration parameters are given in Table SI-2.

2.4. Quality Assurance/ Quality Control (QA/QC)

Recoveries (average ± standard deviation) of the ^{13}C-labelled internal standards added to the polystyrene samples were: α-HBCDD = 87 ± 10 %, β-HBCDD 84 ± 7 % and γ-HBCDD 90 ± 12 %. Detectable, but very low concentrations of α- and γ-HBCDD (i.e. <5% of those detected in samples) were obtained in two field blanks (n=6). Field blanks consisted of sodium sulfate (0.2 g) treated as a sample. Concentrations in each batch of 10 samples were thus corrected for the contamination detected in the associated field blank. Method quantitation limits (MQLs) for individual HBCDD diastereomers were governed by the field blanks (calculated as average + 3 SD of the blanks) and were 0.1 and 0.6 ng g^{-1}, for α- and γ-HBCDD, respectively. For β-HBCDD, the MQL was 0.1 ng g^{-1} based on a S/N ratio of 10:1.

The accuracy and precision of the analytical method for HBCDD was assessed via replicate analysis (n=3) of NIST SRM 2585 (organics in indoor dust), as well as in-house reference materials (RMs) of EPS and XPS samples (n=5). These materials have previously been analysed for HBCDDs by our research group and another laboratory (NIES, Japan), the results of which are used here as indicative values. The obtained results compared favourably to the certified and indicative values (Table SI-3) indicating good accuracy of our method. Furthermore, replicate analysis of 5 samples was performed with RSD <5 % indicating good precision.

3. Results and Discussion

3.1. Similarities and Differences in Samples from the UK and Ireland

Table 1 summarises the concentrations of ΣHBCDD as well as those of individual α-, β-, and γ-HBCDD diastereomers in our samples, with Table SI-1 providing concentrations in each individual sample. Of particular note, is that in 4 samples from Ireland (3 packaging "peanuts" (1 XPS and 2 EPS) and 1 packaging for laboratory glassware (XPS)), ΣHBCDD was detected at a concentration exceeding the EU's LPCL of 0.1 % (1,000,000 µg kg^{-1}). Moreover, a further 2 samples (1 each from the UK – packaging for laboratory equipment (EPS) - and Ireland – packaging "peanuts" (XPS)), contained HBCDD at a concentration between 0.01 % and 0.1 %. Overall therefore, 6 of our samples would not be allowed onto the EU market currently. We scrutinised our data for differences in concentrations of HBCDD in samples from Ireland with those from the UK. To do so, we used t-tests to compare log-normalised concentrations between: (a) UK EPS and Irish EPS; (b) UK XPS and Irish XPS; and (c) all UK and all Irish samples. Notwithstanding the 4 Irish samples that exceeded the LPCL, no significant differences were observed between samples acquired in both countries.

3.2. Do HBCDD concentrations differ between EPS and XPS?

A comparable study in Korea reported HBCDD concentrations in EPS to exceed those in XPS, although some of the EPS samples in the Korean study were building insulation and thus likely to be have been intentionally treated with HBCDD to impart flame retardancy (Rani et al, 2014). We thus examined our data to see if significant differences existed between concentrations in EPS and XPS. To do so, we used a t-test to compare log-normalised concentrations of ΣHBCDD in EPS and XPS samples from: (a) the UK, (b) Ireland, and (c) the UK and Ireland combined. While no significant difference ($p>0.05$) was observed between concentrations of HBCDD in EPS and XPS samples in Ireland; concentrations were significantly higher in EPS (average = 26,000 µg kg^{-1}) than XPS (average 1,200 µg kg^{-1}) in the UK samples ($p<0.001$), and when both countries were combined. Overall, our data suggest that while high concentrations of HBCDD are more frequently detected in EPS, XPS can also contain elevated concentrations. Although reports indicate that HBCDD is typically applied at higher concentrations in EPS (2 %) than XPS (0.7 %) insulation foams (European Commission, 2011), the presence of elevated concentrations of HBCDD in some of our XPS samples are not surprising. This is because HBCDD levels detected in the studied samples are mainly due to uncontrolled recycling activities, which is more likely to produce randomly distributed concentrations among the different products studied, regardless of the PS type.

3.3. What annual mass of HBCDD is associated with EPS and XPS packaging?

The British Plastics Federation (BPF) estimated that 20,600 t of EPS and XPS were sold in the UK in 2008, and further estimated that 40 % of the PS sold in the UK was treated intentionally with HBCDD (AEA, 2010). Here we assume that this 40 % was used for building insulation foam, and furthermore, that of the total mass of EPS and XPS sold in the UK, 50 % (10,300 t) was used for packaging foam, with the rest used in minor applications such as for rigid PS material in TVs (Harrad et al, 2009a). We also assume that the quantity of PS packaging foam used in Ireland is *per capita* identical to that in the UK (based on 2011 Census data for the UK of 63,182,000 and 2016 Irish Census data for Ireland of 4,761,185), resulting in 776 t of PS packaging foam generated each year in Ireland. If we then multiply the 5th and the 95th percentile concentrations of HBCDD we found in PS packaging from the UK (19,000 $\mu g\ kg^{-1}$) and Ireland (480,000 $\mu g\ kg^{-1}$) by these masses of PS packaging, we conclude that between 0.009 and 820 kg and 0.006-1,100 kg HBCDD are associated with the PS packaging produced each year in the UK and Ireland, respectively. Using the median values as a central estimate, these figures translate to 47 kg and 0.4 kg HBCDD for the UK and Ireland respectively.

The considerable uncertainties associated with these estimates are evident – not least the small sample size for Ireland – but we believe they give a reasonable preliminary estimate of the magnitude of HBCDD circulating in this product stream, despite there being no need for its presence. To place these estimates in context, they are unsurprisingly substantially lower than our recently-published estimates of the annual mass of HBCDD associated with waste building insulation foam in Ireland of 5,500 kg year^{-1} (Drage et al, 2018).

3.4. HBCDD Diastereomer patterns – implications for HBCDD origins and environmental impacts of HBCDD in polystyrene packaging waste

Figure 1, Tables 1 and SI-1 also provide information on the relative percentage abundance of the three diastereomers. It is noticeable that the relative abundance of the α-HBCDD diasteromer in all our samples (EPS and XPS combined - expressed as the α:γ ratio in Table s 1 and SI-1) is - at an average of 0.83 - higher than reported for commercial HBCDD, in which the γ-diastereomer predominates (α:γ ratio <0.14) (Peled et al, 1995). We therefore hypothesised that the additional thermal processing experienced during the production of EPS and XPS when recycled PS is used will result in a greater shift towards α-HBCDD (manifested by lower α:γ ratios) than observed in first-use materials like building insulation. To test this hypothesis, we compared using a t-test, the α:γ ratios in our UK and Ireland EPS samples with those detected in 14 samples of waste EPS building insulation material sourced from Irish waste sites in 2016 in which the concentration of ΣHBCDD exceeded 1,000 mg kg^{-1} (average = 5,500 mg kg^{-1}), on which basis we assumed the HBCDD present had been added intentionally to impart flame retardancy. This comparison revealed that α:γ ratios in our EPS packaging samples (average = 0.84) exceeded significantly (p=0.011) those in the EPS building insulation material samples (average = 0.24). This substantial shift in the diastereomer profile has potential implications for the long-term fate of HBCDD, given the aqueous solubility of α-HBCDD (49 µg L^{-1}) exceeds that of γ-HBCDD (2.4 µg L^{-1}) at 20 ˚C (Hunziker et al, 2004), and observations of enhanced leaching potential of α-HBCDD c.f. γ-HBCDD from landfilled waste (Stubbings and Harrad, 2016). This assumes additional importance given that the bioconcentration (BCF) and biomagnification factors (BMF) of α-HBCDD in various aquatic species exceed substantially those of the β- and γ-diastereomers (Harrad et al, 2009; Zhang et al, 2014). Moreover, a recent study revealed higher toxicity of α-HBCDD compared to its β- and γ-isomers in the marine copepod (*Tigriopus japonicas*) (Hong et al, 2017). The toxic mechanism was mainly attributed to generation of reactive oxygen species (ROS) causing higher malformation rates during embryonic development (Hong et al, 2017). Therefore, the higher contribution of α-HBCDD to ΣHBCDD measured in recycled PS products potentially poses a higher risk to the aquatic environment via a combination of higher solubility, bioaccumulation and toxic potential to marine biota.

3.5. *Implications for Human Exposure to HBCDD*

Human exposure arising from the presence of HBCDD in PS packaging may occur via both direct and indirect pathways. The former may occur via dermal contact (Abdallah et al, 2015a), while indirect pathways include: (a) transfer of HBCDD to foodstuffs via direct contact with food packaging or disposable plates (Kuang et al, 2018), and (b) emissions of HBCDD from packaging to indoor air and dust (Rauert et al, 2016). Moreover, there is substantial potential for emissions of HBCDD from landfilled PS packaging via volatilisation and/or leaching to groundwater (Stubbings and Harrad, 2016), with further potential for environmental contamination arising via emissions from discarded PS packaging that has entered both the marine and terrestrial environment.

The observed higher contribution of α-HBCDD to ΣHBCDD in recycled PS raises concern over its human exposure implications. This is due to the reported higher dermal bioavailability (Abdallah et al., 2015a) and oral bioaccessibility of α-HBCDD compared to the β- and γ- diastereomers (Abdallah et al., 2012). In addition, *in vitro* metabolic studies in human liver microsomes (Erratico et al., 2016) and hepatic cell lines (Abdallah et al., 2015b) revealed the metabolic rate of α-HBCDD was less than γ-HBCDD, leading to a higher bioaccumulation potential for this diastereomer, confirmed by higher concentrations of α-HBCDD detected in human milk samples (Tao et al., 2017). Collectively, our data indicate that both the concentrations and isomer profiles of HBCDD detected in recycled PS packaging material may have significant implications for human exposure to this flame retardant.

Conclusions

The data presented here augment significantly the global database showing that recycling of waste PS containing HBCDD has resulted in a widespread and in some cases substantial inadvertent presence of this restricted chemical in materials in which there is no legislative requirement for that presence. A concern is that even effective enforcement of current LPCL values would fail to remove most of the HBCDD associated with the packaging analysed in our study as the concentrations present do not exceed the LPCL. As a consequence, elimination of HBCDD from such packaging may take some time. Moreover, concentrations in 6 samples would currently prevent them being placed on the EU market. While recycling PS packaging material has many positive benefits, our study shows that it may bear significant risks for the environment and human exposure if prescribed concentration limits are not enforced at national and global levels.

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Table 1: Statistical Summary of Concentrations (µg kg^{-1}) of HBCDD, % Contributions to ΣHBCDD of Individual Diastereomers, and α:γ-HBCDD Ratios in Polystyrene Packaging Samples from the UK and Ireland

Parameter	α-HBCDD	% α-HBCDD	β-HBCDD	% β-HBCDD	γ-HBCDD	% γ-HBCDD	ΣHBCDD	α:γ Ratio
UK EPS								
Minimum	<0.1	7	<0.1	4	<0.7	27	<0.7	0.07
Median	3,200	26	2,100	14	7,800	58	13,000	0.44
Average	5,300	29	3,000	14	17,000	58	26,000	0.59
Maximum	34,000	56	22,000	20	79,000	90	130,000	2.07
UK XPS								
Minimum	<0.1	18	<0.1	4	<0.7	35	<0.7	0.0009
Median	26	33	11	15	57	58	95	0.51
Average	420	32	99	14	690	58	1,200	0.62
Maximum	5,100	45	1,100	21	8,100	100	14,000	1.26
All UK								
Minimum	<0.1	7	<0.1	4	<0.7	27	<0.7	0.0009
Median	1,700	27	590	14	2,100	58	4,600	0.45
Average	4,000	30	2,200	14	13,000	58	19,000	0.59
Maximum	34,000	56	22,000	21	79,000	100	135,000	2.07
Ireland EPS								
Minimum	15	25	5	5	17	8	36	0.40
Median	1,200	42	510	13	1,800	47	3,400	0.87
Average	580,000	47	65,000	12	520,000	41	1,200,000	2.40
Maximum	2,600,000	81	270,000	16	3,000,000	64	5,900,000	9.57
Ireland XPS								
Minimum	<0.1	12	<0.1	6	<0.7	30	<0.7	0.20
Median	100	45	30	13	96	44	230	0.69
Average	94,000	40	20,000	14	64,000	46	180,000	0.97
Maximum	570,000	53	120,000	28	380,000	61	1,100,000	2.62
All Ireland								
Minimum	<0.1	12	<0.1	5	<0.7	8	<0.7	0.20
Median	180	40	49	13	220	47	500	0.86
Average	230,000	40	32,000	14	220,000	46	480,000	1.42
Maximum	2,600,000	81	270,000	29	3,000,000	69	5,900,000	9.57
All EPS (UK & Ireland)								
Minimum	<0.1	7	<0.1	4	<0.7	8	<0.7	0.07
Median	3,000	27	1,900	14	7,000	56	11,000	0.46
Average	88,000	32	12,000	13	89,000	55	190,000	0.84
Maximum	2,600,000	81	270,000	20	3,000,000	90	5,900,000	9.57
All XPS (UK & Ireland)								
Minimum	<0.1	12	<0.1	4	<0.7	20	<0.7	0.0009
Median	30	35	14	13	68	54	120	0.64
Average	38,000	35	9,000	14	45,000	53	92,000	0.81
Maximum	570,000	54	120,000	29	690,000	100	1,100,000	2.62
All UK & Ireland								
Minimum	<0.1	7	<0.1	4	<0.7	8	<0.7	0.0009
Median	1,100	30	420	14	1,200	56	2,400	0.50
Average	69,000	33	11,000	14	72,000	54	150,000	0.83
Maximum	2,600,000	81	270,000	29	3,000,000	100	5,900,000	9.57

366 **Figure 1: Ratios of α:γ-HBCDD in Commercial HBCDD, Building Insulation EPS, and**
367 **EPS packaging**

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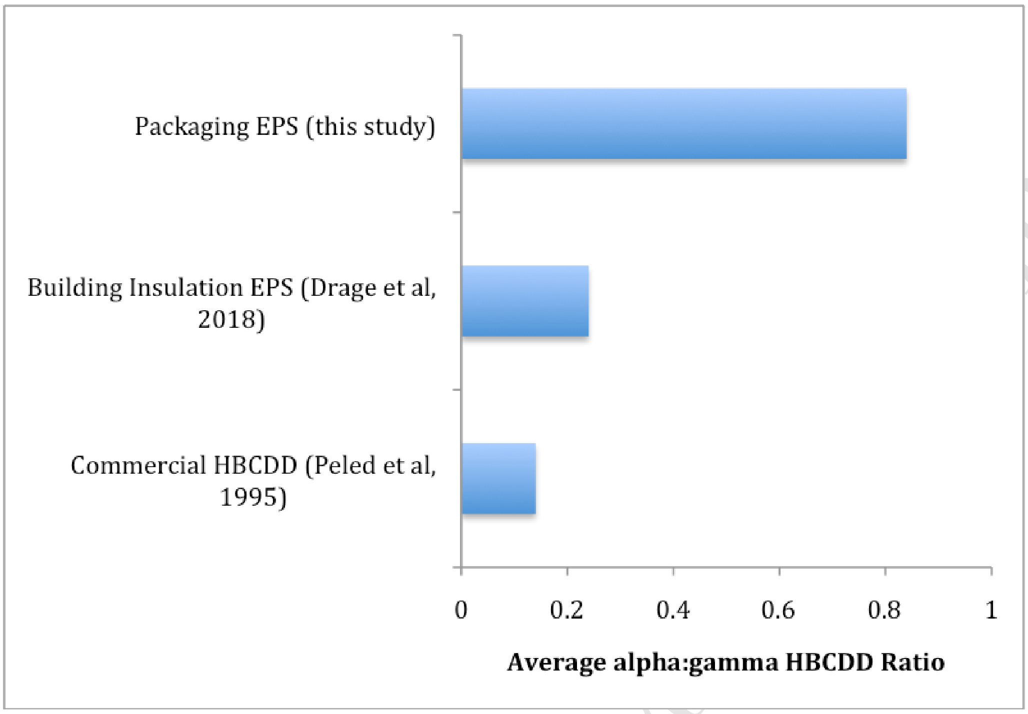

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Highlights

- HBCDD present in 90 % of Irish and UK polystyrene packaging samples
- Concentrations of ΣHBCDD range between <0.7 µg kg^{-1} to 0.59 %
- HBCDD concentrations in 6 samples would prevent them being placed on EU market
- Source of HBCDD in polystyrene packaging is recycled insulation foam