



# Hexabromocyclododecane in polystyrene packaging: A downside of recycling?

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## HIGHLIGHTS

- HBCDD present in 90% of Irish and UK polystyrene packaging samples.
- Concentrations of  $\Sigma$ HBCDD range between  $<0.7 \mu\text{g kg}^{-1}$  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.

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## 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  $\alpha$  vs.  $\gamma$ -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  $\alpha$ -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  $\alpha$ -HBCDD compared to the  $\beta$ - and  $\gamma$ -isomers.

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## 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 and 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., 2009a,b; Yang et al., 2012), and fish (Harrad et al., 2009b; Tomy et al.,

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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  $^{13}\text{C}$ - $\alpha$ -,  $\beta$ - and  $\gamma$ -HBCDDs (50  $\mu\text{L}$  of 1 ng  $\mu\text{L}^{-1}$  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  $\text{N}_2$  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.  $\text{H}_2\text{SO}_4$  by vortexing for 1 min followed by centrifugation at 3000g for 5 min. 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  $\text{N}_2$  prior to reconstitution in 150  $\mu\text{L}$  of methanol containing 25 pg  $\mu\text{L}^{-1}$  of  $d_{18}$ - $\gamma$ -HBCDD used a recovery determination (syringe) standard for QA/QC purposes.

### 2.3. Instrumental analysis

Separation of  $\alpha$ -,  $\beta$ - and  $\gamma$ -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  $\text{C}_{18}$  reversed phase analytical column (150 mm  $\times$  2 mm i. d., 3  $\mu\text{m}$  particle size). A mobile phase program based upon (a) 1:1 methanol/water and (b) methanol at a flow rate of 150  $\mu\text{L min}^{-1}$  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  $\alpha$ -,  $\beta$ - and  $\gamma$ -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  $\rightarrow$  79.0,  $m/z$  652.4  $\rightarrow$  79.0 and  $m/z$  657.7  $\rightarrow$  79.0 for the native,  $^{13}\text{C}$ -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  $\pm$  standard deviation) of the  $^{13}\text{C}$ -labelled internal standards added to the polystyrene samples were:  $\alpha$ -HBCDD = 87  $\pm$  10%,  $\beta$ -HBCDD 84  $\pm$  7% and  $\gamma$ -HBCDD 90  $\pm$  12%. Detectable, but very low concentrations of  $\alpha$ - and  $\gamma$ -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  $\text{g}^{-1}$ , for  $\alpha$ - and  $\gamma$ -HBCDD, respectively. For  $\beta$ -HBCDD, the MQL was 0.1 ng  $\text{g}^{-1}$  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  $\Sigma\text{HBCDD}$  as well as those of individual  $\alpha$ -,  $\beta$ - and  $\gamma$ -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)),  $\Sigma\text{HBCDD}$  was detected at a concentration exceeding the EU's LPCL of 0.1% (1,000,000  $\mu\text{g kg}^{-1}$ ). 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

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