

Hexabromocyclododecane in polystyrene packaging:

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

DOI:

[10.1016/j.chemosphere.2018.02.084](https://doi.org/10.1016/j.chemosphere.2018.02.084)

License:

Creative Commons: Attribution-NonCommercial-NoDerivs (CC BY-NC-ND)

Document Version

Peer reviewed version

Citation for published version (Harvard):

Abdallah, MA-E, Sharkey, M, Berresheim, H & Harrad, S 2018, 'Hexabromocyclododecane in polystyrene packaging: A downside of recycling?', *Chemosphere*, vol. 199, pp. 612-616.
<https://doi.org/10.1016/j.chemosphere.2018.02.084>

[Link to publication on Research at Birmingham portal](#)

General rights

Unless a licence is specified above, all rights (including copyright and moral rights) in this document are retained by the authors and/or the copyright holders. The express permission of the copyright holder must be obtained for any use of this material other than for purposes permitted by law.

- Users may freely distribute the URL that is used to identify this publication.
- Users may download and/or print one copy of the publication from the University of Birmingham research portal for the purpose of private study or non-commercial research.
- User may use extracts from the document in line with the concept of 'fair dealing' under the Copyright, Designs and Patents Act 1988 (?)
- Users may not further distribute the material nor use it for the purposes of commercial gain.

Where a licence is displayed above, please note the terms and conditions of the licence govern your use of this document.

When citing, please reference the published version.

Take down policy

While the University of Birmingham exercises care and attention in making items available there are rare occasions when an item has been uploaded in error or has been deemed to be commercially or otherwise sensitive.

If you believe that this is the case for this document, please contact UBIRA@lists.bham.ac.uk providing details and we will remove access to the work immediately and investigate.

Accepted Manuscript

Hexabromocyclododecane in polystyrene packaging: A downside of recycling?

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



PII: S0045-6535(18)30286-8

DOI: [10.1016/j.chemosphere.2018.02.084](https://doi.org/10.1016/j.chemosphere.2018.02.084)

Reference: CHEM 20842

To appear in: *ECSN*

Received Date: 30 November 2017

Revised Date: 12 February 2018

Accepted Date: 13 February 2018

Please cite this article as: Abdallah, M.A.-E., Sharkey, M., Berresheim, H., Harrad, S., Hexabromocyclododecane in polystyrene packaging: A downside of recycling?, *Chemosphere* (2018), doi: 10.1016/j.chemosphere.2018.02.084.

This is a PDF file of an unedited manuscript that has been accepted for publication. As a service to our customers we are providing this early version of the manuscript. The manuscript will undergo copyediting, typesetting, and review of the resulting proof before it is published in its final form. Please note that during the production process errors may be discovered which could affect the content, and all legal disclaimers that apply to the journal pertain.

1 **Hexabromocyclododecane in Polystyrene Packaging: A**
2 **Downside of Recycling?**

3 Mohamed Abou-Elwafa Abdallah^{1,3}, Martin Sharkey², Harald Berresheim², Stuart Harrad^{1*}

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

5 ² *School of Physics, National University of Ireland Galway*

6 ³ *Department of Analytical Chemistry, Faculty of Pharmacy, Assiut University, 71526 Assiut,*
7 *Egypt.*

8
9 *Author for correspondence

10 S.J.Harrad@bham.ac.uk

11 Tel. +44 (0)121 414 7298

12

13 **Keywords**

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

15

ACCEPTED MANUSCRIPT

16 **Abstract**

17 While there are no regulatory fire safety obligations for polystyrene (PS) when used as
18 packaging material, concerns exist that such packaging material may contain the flame
19 retardant hexabromocyclododecane (HBCDD) as a result of uncontrolled recycling activities.
20 To evaluate these concerns, we collected 50 samples of PS packaging materials from the UK
21 and 20 from Ireland. HBCDD was detected in 63 (90 %) of samples, with concentrations in 4
22 samples from Ireland exceeding the EU's low POP concentration limit (LPCL) of 0.1 %
23 above which articles may not be recycled. Moreover, 2 further samples contained HBCDD >
24 0.01 %. While our samples were obtained in the 12 month period prior to the March 2016
25 introduction of the EU's 0.01 % concentration limit above which articles may not be placed
26 on the market, our data suggest that continued monitoring is required to assess compliance
27 with this limit value. Ratios of α vs. γ -HBCDD in our EPS packaging samples (average =
28 0.63) exceeded significantly ($p=0.025$) those in EPS building insulation material samples
29 (average = 0.24) reported previously for Ireland. This shift towards α -HBCDD in packaging
30 EPS is consistent with the additional thermal processing experienced by recycled PS and
31 suggests the source of HBCDD in PS packaging is recycled PS insulation foam. This is of
32 concern owing to the higher bioavailability and lower metabolic clearance of α -HBCDD
33 compared to the β - and γ -isomers.

34

35 1. Introduction

36 Polystyrene (PS) is widely used for thermal insulation of buildings as well as packaging for
37 applications such as food, laboratory chemicals and electronic appliances, with a global
38 market demand of 15 million tonnes in 2010 (Rani et al, 2014). To meet fire safety
39 regulations, hexabromocyclododecane (HBCDD) has been used extensively throughout the
40 world for a variety of purposes; one of the most important of which being its application at
41 between 0.7–2.0 % w/w as an additive to impart flame retardancy to both expanded (EPS)
42 and extruded (XPS) PS foam used to insulate buildings (European Commission, 2011;
43 Marvin et al, 2011). As a result of this widespread use, HBCDD has been detected worldwide
44 in a plethora of matrices, including indoor air and dust (Abdallah et al, 2008), outdoor air (Jo
45 et al, 2017), soil (Meng et al 2011; Desborough et al, 2016), human tissues (Carignan et al,
46 2012; Rawn et al, 2014), lake sediments, (Harrad et al, 2009; Yang et al, 2012) and fish
47 (Harrad et al, 2009b; Tomy et al, 2008). As a result of evidence of its persistent,
48 bioaccumulative and toxic properties as well as its propensity for long-range transport,
49 HBCDD has been listed as a persistent organic pollutant (POP) under the United Nations
50 Environment Programme's Stockholm Convention on POPs (UNEP, 2014).

51
52 In recent years, there has been a drive in many jurisdictions, including the European Union
53 towards the “circular economy” in which recycling and re-use of materials is maximised to,
54 *inter alia*, minimise pressure on waste disposal infrastructure. However, concerns have been
55 raised that new applications of recycled polymeric material that in its original application had
56 been flame-retarded, has led to the undesirable presence of restricted brominated flame
57 retardants (BFRs) in goods such as children's toys, food contact articles (Guzzonato et al,
58 2017; Kuang et al, 2018; Puype et al, 2015) and PS packaging (Rani et al, 2014). To prevent
59 contamination with BFRs of such items, the EU has introduced a low POP concentration

60 limit (LPCL) of 0.1 % w/w for restricted BFRs like HBCDD. Items containing restricted
61 BFRs at concentrations exceeding the LPCL may not be recycled until their POP content has
62 been removed to below LPCL limits. Moreover, items containing HBCDD as an
63 unintentional contaminant (i.e. as a consequence of the use of HBCDD-containing recycled
64 materials) at a concentration exceeding 0.01 % may after 22nd March 2016, no longer be
65 placed on the market in the EU (European Commission, 2016).

66

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

74

75 **2. Methods**

76 *2.1. Sample collection*

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

81

82 *2.2. Sample extraction and purification*

83 Accurately weighed aliquots of the polystyrene products (~50 mg) were placed in clean,
84 solvent-rinsed 15 mL glass test tubes. The samples were spiked with 50 ng of ¹³C- α -, β - and

85 γ -HBCDDs (50 μL of 1 ng μL^{-1} solution in hexane) used as internal (surrogate) standard
86 prior to dissolving in 2 mL of dichloromethane by vortexing for 2 min. The solvent was
87 evaporated to incipient dryness under a gentle stream of N_2 and target analytes were
88 immediately reconstituted in 2 mL hexane by vortexing for 2 min. The hexane extract was
89 washed with 2 mL of conc. H_2SO_4 by vortexing for 1 min followed by centrifugation at 3000
90 g for 5 minutes. The organic layer was transferred to another clean tube and the acid layer
91 was washed twice with 2 mL of hexane. The combined hexane layer was evaporated to
92 dryness under N_2 prior to reconstitution in 150 μL of methanol containing 25 pg μL^{-1} of d_{18} -
93 γ -HBCDD used a recovery determination (syringe) standard for QA/QC purposes.

94 2.3. Instrumental analysis

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

104 Mass spectrometric analysis was performed using a Sciex API 2000 triple quadrupole mass
105 spectrometer operated in electrospray negative ionisation mode. MS/MS detection operated
106 in the MRM mode was used for quantitative determination based on m/z 640.6 \rightarrow 79.0, m/z
107 652.4 \rightarrow 79.0 and m/z 657.7 \rightarrow 79.0 for the native, ^{13}C -labelled and d_{18} -labelled HBCDD

108 diastereomers, respectively. Specific instrumental calibration parameters are given in Table
109 SI-2.

110 2.4. *Quality Assurance/ Quality Control (QA/QC)*

111
112 Recoveries (average \pm standard deviation) of the ^{13}C -labelled internal standards added to the
113 polystyrene samples were: α -HBCDD = 87 ± 10 %, β -HBCDD 84 ± 7 % and γ -HBCDD $90 \pm$
114 12 %. Detectable, but very low concentrations of α - and γ -HBCDD (i.e. $<5\%$ of those
115 detected in samples) were obtained in two field blanks (n=6). Field blanks consisted of
116 sodium sulfate (0.2 g) treated as a sample. Concentrations in each batch of 10 samples were
117 thus corrected for the contamination detected in the associated field blank. Method
118 quantitation limits (MQLs) for individual HBCDD diastereomers were governed by the field
119 blanks (calculated as average + 3 SD of the blanks) and were 0.1 and 0.6 ng g^{-1} , for α - and γ -
120 HBCDD, respectively. For β -HBCDD, the MQL was 0.1 ng g^{-1} based on a S/N ratio of 10:1.

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

129

130 **3. Results and Discussion**

131 *3.1. Similarities and Differences in Samples from the UK and Ireland*

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

146 3.2. Do HBCDD concentrations differ between EPS and XPS?

147 A comparable study in Korea reported HBCDD concentrations in EPS to exceed those in
148 XPS, although some of the EPS samples in the Korean study were building insulation and
149 thus likely to be have been intentionally treated with HBCDD to impart flame retardancy
150 (Rani et al, 2014). We thus examined our data to see if significant differences existed
151 between concentrations in EPS and XPS. To do so, we used a t-test to compare log-
152 normalised concentrations of Σ HBCDD in EPS and XPS samples from: (a) the UK, (b)
153 Ireland, and (c) the UK and Ireland combined. While no significant difference ($p>0.05$) was
154 observed between concentrations of HBCDD in EPS and XPS samples in Ireland;
155 concentrations were significantly higher in EPS (average = 26,000 $\mu\text{g kg}^{-1}$) than XPS
156 (average 1,200 $\mu\text{g kg}^{-1}$) in the UK samples ($p<0.001$), and when both countries were

157 combined. Overall, our data suggest that while high concentrations of HBCDD are more
158 frequently detected in EPS, XPS can also contain elevated concentrations. Although reports
159 indicate that HBCDD is typically applied at higher concentrations in EPS (2 %) than XPS
160 (0.7 %) insulation foams (European Commission, 2011), the presence of elevated
161 concentrations of HBCDD in some of our XPS samples are not surprising. This is because
162 HBCDD levels detected in the studied samples are mainly due to uncontrolled recycling
163 activities, which is more likely to produce randomly distributed concentrations among the
164 different products studied, regardless of the PS type.

165

166 3.3. What annual mass of HBCDD is associated with EPS and XPS packaging?

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

182

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

189

190 *3.4. HBCDD Diastereomer patterns – implications for HBCDD origins and environmental*
191 *impacts of HBCDD in polystyrene packaging waste*

192 Figure 1, Tables 1 and SI-1 also provide information on the relative percentage abundance of
193 the three diastereomers. It is noticeable that the relative abundance of the α -HBCDD
194 diastereomer in all our samples (EPS and XPS combined - expressed as the α : γ ratio in Table s
195 1 and SI-1) is - at an average of 0.83 - higher than reported for commercial HBCDD, in
196 which the γ -diastereomer predominates (α : γ ratio <0.14) (Peled et al, 1995). We therefore
197 hypothesised that the additional thermal processing experienced during the production of EPS
198 and XPS when recycled PS is used will result in a greater shift towards α -HBCDD
199 (manifested by lower α : γ ratios) than observed in first-use materials like building insulation.
200 To test this hypothesis, we compared using a t-test, the α : γ ratios in our UK and Ireland EPS
201 samples with those detected in 14 samples of waste EPS building insulation material sourced
202 from Irish waste sites in 2016 in which the concentration of Σ HBCDD exceeded 1,000 mg
203 kg⁻¹ (average = 5,500 mg kg⁻¹), on which basis we assumed the HBCDD present had been
204 added intentionally to impart flame retardancy. This comparison revealed that α : γ ratios in
205 our EPS packaging samples (average = 0.84) exceeded significantly (p=0.011) those in the
206 EPS building insulation material samples (average = 0.24). This substantial shift in the

207 diastereomer profile has potential implications for the long-term fate of HBCDD, given the
208 aqueous solubility of α -HBCDD ($49 \mu\text{g L}^{-1}$) exceeds that of γ -HBCDD ($2.4 \mu\text{g L}^{-1}$) at 20°C
209 (Hunziker et al, 2004), and observations of enhanced leaching potential of α -HBCDD c.f. γ -
210 HBCDD from landfilled waste (Stubbings and Harrad, 2016). This assumes additional
211 importance given that the bioconcentration (BCF) and biomagnification factors (BMF) of α -
212 HBCDD in various aquatic species exceed substantially those of the β - and γ -diastereomers
213 (Harrad et al, 2009; Zhang et al, 2014). Moreover, a recent study revealed higher toxicity of
214 α -HBCDD compared to its β - and γ -isomers in the marine copepod (*Tigriopus japonicas*)
215 (Hong et al, 2017). The toxic mechanism was mainly attributed to generation of reactive
216 oxygen species (ROS) causing higher malformation rates during embryonic development
217 (Hong et al, 2017). Therefore, the higher contribution of α -HBCDD to Σ HBCDD measured in
218 recycled PS products potentially poses a higher risk to the aquatic environment via a
219 combination of higher solubility, bioaccumulation and toxic potential to marine biota.

220

221 3.5. Implications for Human Exposure to HBCDD

222 Human exposure arising from the presence of HBCDD in PS packaging may occur via both
223 direct and indirect pathways. The former may occur via dermal contact (Abdallah et al,
224 2015a), while indirect pathways include: (a) transfer of HBCDD to foodstuffs via direct
225 contact with food packaging or disposable plates (Kuang et al, 2018), and (b) emissions of
226 HBCDD from packaging to indoor air and dust (Rauert et al, 2016). Moreover, there is
227 substantial potential for emissions of HBCDD from landfilled PS packaging via volatilisation
228 and/or leaching to groundwater (Stubbings and Harrad, 2016), with further potential for
229 environmental contamination arising via emissions from discarded PS packaging that has
230 entered both the marine and terrestrial environment.

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

242

243 **Conclusions**

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

255

256 **Acknowledgements**

257 Funding for this study was provided by the Environmental Protection Agency of Ireland
258 Project Reference 2014-RE-MS-2. We are grateful to Darren Byrne at the Department of
259 Communications, Climate Action, and Environment, Ireland, for insightful discussions.

260

261 **References**

262 Abdallah, M.A.E., Harrad, S., Covaci, A. 2008. Hexabromocyclododecanes and
263 Tetrabromobisphenol-A in Indoor Air and Dust in Birmingham, UK: Implications for
264 Human Exposure. *Environ. Sci. Technol.* 42, 6855–6861.

265 Abdallah, M.A.E., Tilston, E., Harrad, S., Collins, C., 2012. In vitro assessment of the
266 bioaccessibility of brominated flame retardants in indoor dust using a colon extended
267 model of the human gastrointestinal tract. *J Environ Monitor* 14, 3276-3283.

268 Abdallah, M.A.E., Pawar, G., Harrad, S. 2015a. Evaluation of 3D-human skin equivalents for
269 assessment of human dermal absorption of some brominated flame retardants. *Environ.*
270 *Int.* 84, 64-70.

271 Abdallah, M.A.E., Zhang, J.K., Pawar, G., Viant, M.R., Chipman, J.K., D'Silva, K.,
272 Bromirski, M., Harrad, S., 2015b. High-resolution mass spectrometry provides novel
273 insights into products of human metabolism of organophosphate and brominated flame
274 retardants. *Anal Bioanal Chem* 407, 1871-1883.

275 AEA, 2010. Costs and Benefits of the Addition of Hexabromocyclododecane (HBCD) to the
276 Stockholm Convention and the 1998 POPs Protocols, Ref: AEA/ED56226/Issue Number
277 5

278 <http://randd.defra.gov.uk/Document.aspx?Document=ED56226CostBenefitHBCDReport>
279 [CND0101Oct2010v16FINAL.PDF](http://randd.defra.gov.uk/Document.aspx?Document=ED56226CostBenefitHBCDReport) accessed 2/11/17

- 280 Carignan, C., Abdallah, M.A., Wu, N., Heiger-Bernays, W., McClean, M., Harrad, S.,
281 Webster, T. 2012. Predictors of Tetrabromobisphenol-A (TBBP-A) and
282 Hexabromocyclododecanes (HBCD) in Milk from Boston Mothers. *Environ. Sci.*
283 *Technol.* 46, 12146-12153.
- 284 Desborough, J., Evans, T., Mueller, J., Harrad, S. 2016. Polychlorinated biphenyls (PCBs),
285 hexabromocyclododecanes (HBCDDs) and degradation products in topsoil from
286 Australia and the United Kingdom. *Emerging Contaminants*, 2, 37-41.
- 287 Drage, D. S., Sharkey, M., Abdallah, M.A., Berresheim, H., Harrad, S. 2018. Brominated
288 Flame Retardants in Irish Waste Polymers: Concentrations, Legislative Compliance, and
289 Treatment Options. *Sci. Tot. Environ.* 625, 1535–1543.
- 290 Erratico, C., Zheng, X.B., van den Eede, N., Tomy, G., Covaci, A., 2016. Stereoselective
291 Metabolism of alpha-, beta-, and gamma-Hexabromocyclododecanes (HBCDs) by
292 Human Liver Microsomes and CYP3A4. *Environ Sci Technol* 50, 8263-8273.
- 293 European Commission. 2011. Final Report: Study on waste related issues of newly listed
294 POPs and candidate POPs. [http://ec.europa.eu/environment/waste/studies/pdf/](http://ec.europa.eu/environment/waste/studies/pdf/POP_Waste_2011.pdf)
295 [POP_Waste_2011.pdf](http://ec.europa.eu/environment/waste/studies/pdf/POP_Waste_2011.pdf) [Accessed 4 August 2017]
- 296 European Commission. 2016. Regulation (EC) No 850/2004 of the European Parliament and
297 of the Council of 29 April 2004 on persistent organic pollutants and amending Directive
298 79/117/EEC. [http://eur-lex.europa.eu/legal-content/EN/TXT/?uri=CELEX:02004R0850-](http://eur-lex.europa.eu/legal-content/EN/TXT/?uri=CELEX:02004R0850-20160930)
299 [20160930](http://eur-lex.europa.eu/legal-content/EN/TXT/?uri=CELEX:02004R0850-20160930)
- 300 Guzzonato, A., Puype, F., Harrad, S. 2017. Evidence of bad recycling practices: BFRs in
301 children's toys and food-contact articles. *Environ. Sci. Proc. Imp.* 19, 956-963.
- 302 Harrad, S., Abdallah, M. A., Covaci, A. 2009a. Causes of variability in concentrations and
303 diastereomer patterns of Hexabromocyclododecanes in indoor dust. *Environ. Int.* 35,
304 573–579.

- 305 Harrad, S., Abdallah, M.A., Rose, N. L., Turner, S.D., Davidson, T.A. 2009b. Current-Use
306 Brominated Flame Retardants in Water, Sediment, and Fish from English Lakes.
307 Environ. Sci. Technol. 43, 9077–9083.
- 308 Hong, H.Z., LV, D.M., Liu, W.X., Huang, L.M., Chen, L.Y., Shen, R., Shi, D.L. 2017.
309 Toxicity and bioaccumulation of three hexabromocyclododecane diastereoisomers in the
310 marine copepod *Tigriopus japonicus*. Aquat. Toxicol. 188, 1-9.
- 311 Hunziker, R.W., Gonsior, S., MacGregor, J.A., Desjardins, D., Ariano, J., Friederich, U.
312 2004. Fate and effect of hexabromocyclododecane in the environment. Organohalogen
313 Compd. 66, 2300–2305.
- 314 Jo, H., Son, M-H., Seo, S-H., Chang, Y-S. 2017. Matrix-specific distribution and
315 diastereomeric profiles of hexabromocyclododecane (HBCD) in a multimedia
316 environment: Air, soil, sludge, sediment, and fish. Environ. Poll. 226, 515-522.
- 317 Kuang, J., Abdallah, M., Harrad, S. 2018. Brominated flame retardants in black plastic
318 kitchen utensils: Concentrations and human exposure implications. Sci. Tot. Environ.
319 610–611, 1138-1146.
- 320 Marvin, C. H., Tomy, G. T., Armitage, J. M., Arnot, J. A., McCarty, L., Covaci, A., Palace,
321 V. H. 2011. Hexabromocyclododecane: Current Understanding of Chemistry,
322 Environmental Fate and Toxicology and Implications for Global Management. Environ.
323 Sci. Technol. 45, 8613-8623.
- 324 Meng, X.Z., Duan, Y.P., Yang, C., Pan, Z.Y., Wen, Z.H., Chen, L. 2011. Occurrence,
325 sources, and inventory of hexabromocyclododecanes (HBCDDs) in soils from
326 Chongming Island, the Yangtze River Delta (YRD), Chemosphere 82, 725-731.
- 327 Peled, M., Scharia, R., Sondack, D. 1995. Thermal Rearrangement of
328 Hexabromocyclododecane (HBCD). In Advances in Organobromine Chemistry II;

- 329 Desmurs, J. -R., Gérard, B., Goldstein, M.J., Eds.; Elsevier: Amsterdam, The
330 Netherlands, pp 92–99.
- 331 Puype, F., Samson, J., Knoop, J., Egelkraut-Holtus, M., Ortlieb, M. 2015. Evidence of
332 waste electrical and electronic equipment (WEEE) relevant substances in polymeric
333 food-contact articles sold on the European market. *Food. Addit. Contam. Part A.* 32,
334 410-426.
- 335 Rani, M., Shim, W.J., Han, G.M., Jang, M., Song, Y.K., Song, S.H. 2014.
336 Hexabromocyclododecane in polystyrene based consumer products: An evidence of
337 unregulated use. *Chemosphere*, 110, 111-119.
- 338 Rauert, C., Kuribara, I., Kataoka, Wada, T., Kajiwara, N., Suzuki, G., Takigami, G., Harrad,
339 S. 2016. Direct contact between dust and HBCD-treated fabrics is an important pathway
340 of source-to dust transfer. *Sci. Tot. Environ.* 545–546, 77–83.
- 341 Rawn, D.F., Gaertner, D.W., Weber, D., Curran, I.H., Cooke, G.M., Goodyer, C.G., 2014.
342 Hexabromocyclododecane concentrations in Canadian human fetal liver and placental
343 tissues. *Sci. Total Environ.* 468-9, 622-9.
- 344 Stubbings, W.A., Kajiwara, N., Takigami, H., Harrad, S. 2016. Leaching behaviour of
345 hexabromocyclododecane from treated curtains. *Chemosphere* 144, 2091-2096.
- 346 Tao, F., Abdallah, M.A., Ashworth, D.C., Douglas, P., Toledano, M.B., Harrad, S., 2017.
347 Emerging and legacy flame retardants in UK human milk and food suggest slow
348 response to restrictions on use of PBDEs and HBCDD. *Environ Int* 105, 95-104.
- 349 Tomy, G. T., Pleskach, K., Oswald, T., Halldorson, T., Helm, P. A., MacInnis, G., Marvin, C.
350 H. 2008. Enantioselective Bioaccumulation of Hexabromocyclododecane and Congener-
351 Specific Accumulation of Brominated Diphenyl Ethers in an Eastern Canadian Arctic
352 Marine Food Web. *Environ Sci Technol* 42, 3634–3639
- 353 UNEP. 2014. Stockholm convention on POPs, <http://chm.pops.int/>

354 Yang, R., Wei, H., Guo, J., Li, A., 2012. Emerging Brominated Flame Retardants in the
355 Sediment of the Great Lakes. *Environ. Sci. Technol.* 46, 3119-3126.

356 Zhang, Y., Sun, H., Ruan, Y., 2014. Enantiomer-specific accumulation, depuration,
357 metabolization and isomerization of hexabromocyclododecane (HBCD) diastereomers in
358 mirror carp from water. *J. Hazard. Mater.* 264, 8–15.

359

360

ACCEPTED MANUSCRIPT

361 **Table 1: Statistical Summary of Concentrations ($\mu\text{g kg}^{-1}$) of HBCDD, % Contributions**
 362 **to Σ HBCDD of Individual Diastereomers, and α : γ -HBCDD Ratios in Polystyrene**
 363 **Packaging Samples from the UK and Ireland**

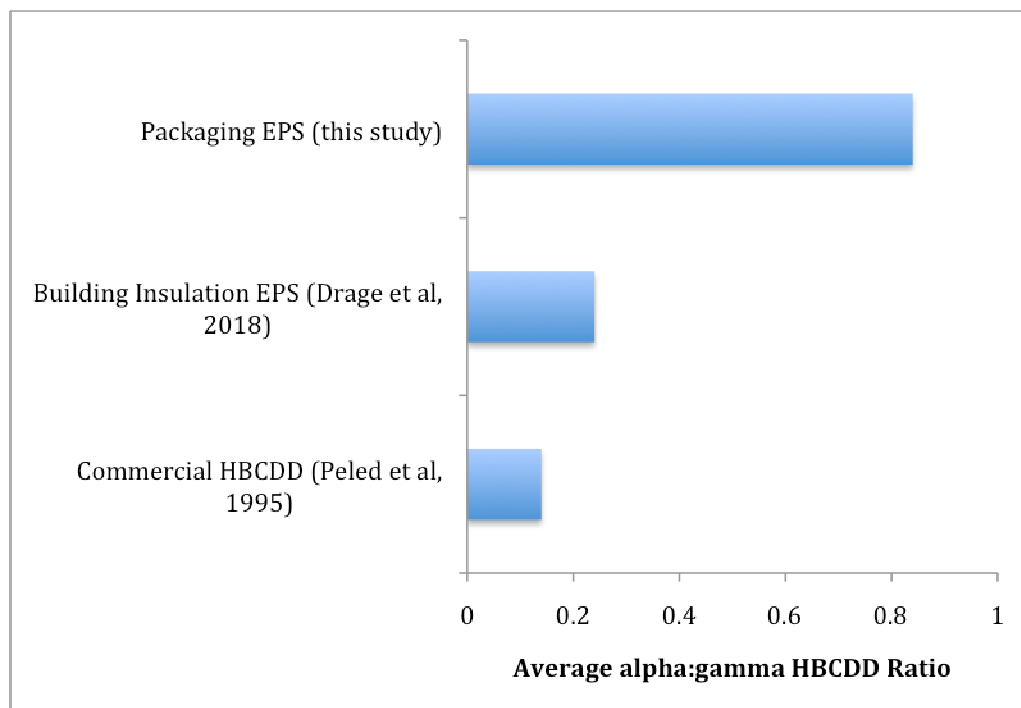
Parameter	α -HBCDD	% α -HBCDD	β -HBCDD	% β -HBCDD	γ -HBCDD	% γ -HBCDD	Σ HBCDD	α : γ Ratio
UK EPS								
Minimum	<0.1	7	<0.1	4	<0.7	27	<0.7	0.07
Median	3,200	26	2,100	14	7,800	58	13,000	0.44
Average	5,300	29	3,000	14	17,000	58	26,000	0.59
Maximum	34,000	56	22,000	20	79,000	90	130,000	2.07
UK XPS								
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

364

365

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

368



369

Highlights

- HBCDD present in 90 % of Irish and UK polystyrene packaging samples
- Concentrations of Σ 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