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Hexabromocyclododecane in Polystyrene Packaging: A Downside of Recycling?

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13   **Keywords**

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

15

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

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

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 ^{13}C-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 × 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 µL 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→79.0, *m/z*

107 652.4→79.0 and *m/z* 657.7→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 ± 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 ±

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 ΣHBCDD 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)), ΣHBCDD

136 was detected at a concentration exceeding the EU's LPCL of 0.1 % (1,000,000 µg 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.

145

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 ΣHBCDD 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 µg kg^{-1}) than XPS

156 (average 1,200 µg 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 µg kg^{-1}) and Ireland (480,000 µg 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 diasteromer 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 ΣHBCDD 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 µg L^{-1}) exceeds that of γ-HBCDD (2.4 µg 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 ΣHBCDD 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 ΣHBCDD 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

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361 **Table 1: Statistical Summary of Concentrations (µg kg^{-1}) of HBCDD, % Contributions**

362 **to ΣHBCDD 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	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

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366 **Figure 1: Ratios of $\alpha:\gamma$-HBCDD in Commercial HBCDD, Building Insulation EPS, and**
367 **EPS packaging**

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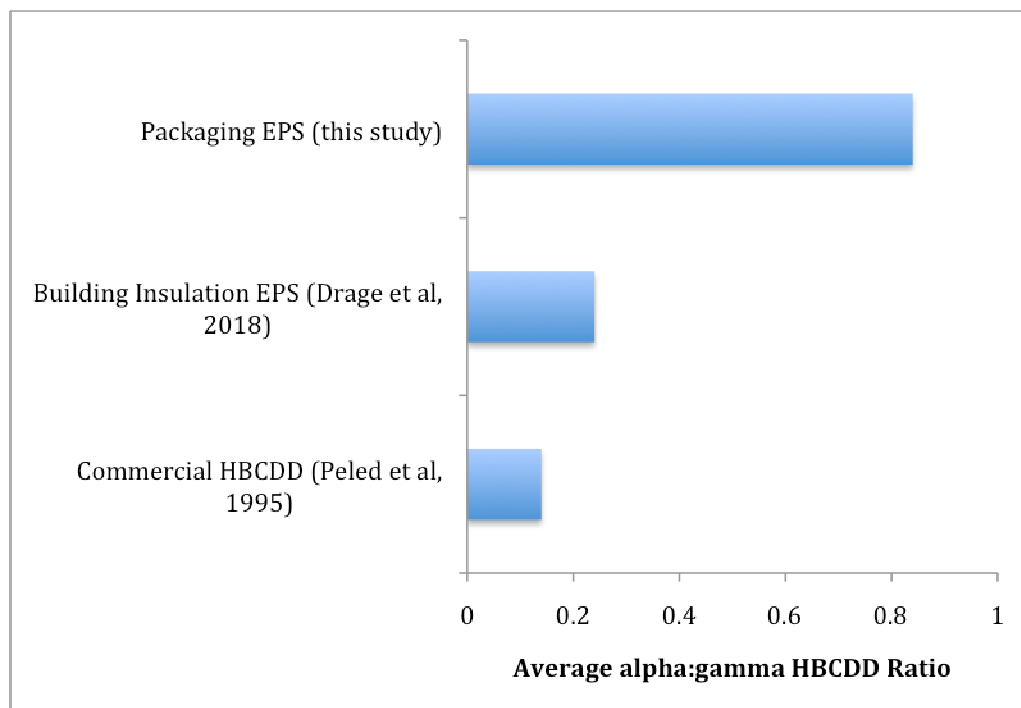
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Highlights

- 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