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Leaching behaviour of hexabromocyclododecane from treated curtains

Stubbings, William; Kajiwara, Natsuko; Takigami, Hidetaka; Harrad, Stuart

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Chemosphere

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Title: LEACHING BEHAVIOUR OF HEXABROMOCYCLODODECANE FROM TREATED CURTAINS

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Brominated flame retardants;
Leaching

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Corresponding Author's Institution: University of Birmingham

First Author: William Andrew Stubbings

Order of Authors: William Andrew Stubbings

Response to Reviewers: Ms. Ref. No.: CHEM37214

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Response to reviewers

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26 **Abstract**

27 A series of laboratory experiments were conducted, whereby two HBCDD treated polyester
28 curtain samples were contacted with deionised Milli-Q water as leaching fluid and HBCDD
29 determined in the resulting leachate. As well as single batch (no replenishment of leaching
30 fluid), serial batch (draining of leachate and replenishment with fresh leaching fluid at
31 various time intervals) experiments were conducted. In single batch experiments at 20°C,
32 Σ HBCDD concentrations increased only slightly with increasing contact time (6 h, 24 h, and
33 48 h). This is supported by serial batch tests at 20 °C in which leaching fluid was replaced
34 after 6 h, 24 h, 48 h, 72 h, 96 h, and 168 h. Data from these experiments show that while
35 concentrations of HBCDD in leachate after 24 h cumulative contact time exceed those at 6
36 h; concentrations in samples collected at subsequent contact times remained steady at
37 ~50% of those in the 24 h sample. Consistent with this, leaching is shown to be second
38 order, whereby a period of initially intense dissolution of more labile HBCDD is followed by a
39 slower stage corresponding to external diffusion of the soluble residue within the textile. In
40 experiments conducted at 20°C, α -HBCDD is preferentially leached compared to β - and γ -
41 HBCDD. However, at higher temperatures, the relatively more hydrophobic diastereomers
42 are proportionally more readily leached, i.e. raising the temperature from 20°C to 80°C
43 increased concentrations of γ -HBCDD in the leachate by a factor of 28–33 while
44 corresponding α -HBCDD concentrations only increased by a factor of 4.3-4.8.

45

46 **Keywords**

47 Hexabromocyclododecane;

48 Waste soft furnishings;

49 Landfill;

50 Brominated flame retardants;

51 Leaching

52

53 1. Introduction

54 Hexabromocyclododecane (HBCDD) has been identified as an endocrine disrupting chemical
55 that induces enzymes and alters thyroid homeostasis with potential to cause adverse effects
56 in humans at relatively low exposure levels (Darnerud, 2003, 2008; van der Ven et al., 2006,
57 2009; Yamada-Okabe et al., 2005). This is compounded by evidence that its presence in the
58 environment is ubiquitous (de Wit, 2002; Gerecke et al., 2003; Janak et al., 2005; Remberger
59 et al., 2004; Tomy et al., 2004; Law et al., 2005, 2006; Covaci et al., 2006; de Wit et al., 2006;
60 Marvin et al., 2006; Kohler et al., 2008; Harrad et al., 2009; Harrad et al., 2010). In a
61 legislative context, HBCDD has been identified by the European Union as a Substance of
62 Very High Concern, meeting the criteria of a PBT (persistent, bioaccumulative and toxic)
63 substance (ECHA, 2014); while in Japan, HBCDD has been designated as a Monitoring
64 Chemical Substance under the Chemical Substances Control Law because of its persistence
65 and high bio-accumulation. Moreover, in 2013, HBCDD was listed as a persistent organic
66 pollutant (POP) by the United Nations Environment Programme (UNEP) under the
67 Stockholm Convention on POPs. In 2011, annual global production of HBCDD was an
68 estimated maximum of 28,000 tonnes (9,000 to 15,000 tonnes in China, 13,426 tonnes in
69 Europe and the US) (UNEP, 2011). Around 90% of HBCDD is used in the building industry,
70 typically added at ~3% by weight into extruded or expanded polystyrene foam in rigid
71 insulation panels/boards (EC, 2011; Marvin et al., 2011). Additionally, around 8% of HBCDD
72 was used as a textile coating agent in polymer dispersions applied to cotton or
73 cotton/synthetic blends for upholstery fabrics, e.g. residential and commercial upholstered
74 furniture and transportation seating, bed mattress ticking, draperies and wall coverings,
75 interior textiles, e.g. roller blinds, and vehicle interior textiles. HBCDD can also be used in
76 thermosol treatment of polyester, polypropylene and nylon fabrics, where it is applied as an
77 aqueous suspension or emulsion at a loading of 8-11% by weight (EC, 2011; UNEP, 2011;
78 Weil and Levchik, 2008). Currently, used furniture or textiles containing textiles treated with
79 HBCDD are widely treated as municipal rather than hazardous waste, and are thus landfilled
80 or incinerated. In the UK alone, WRAP (2012) estimated that in 2010/11 around 670,000
81 tonnes of furniture (an unknown fraction of which will consist of fabric coverings) and
82 310,000 tonnes of textiles are disposed of by householders annually. This reservoir of
83 HBCDDs within soft furnishings has and will continue to, gradually enter the waste stream,

84 and there is hence a pressing need to understand the fate of chemicals like HBCDD
85 associated with waste fabrics following disposal (Stubblings & Harrad, 2014). Potential
86 emission pathways for chemicals associated with landfill include contamination of leachate
87 and volatilisation. The physicochemical properties of HBCDD (water solubility = α -HBCDD
88 (41,000 ng L⁻¹), β -HBCDD (15,000 ng L⁻¹) and γ -HBCDD (2,400 ng L⁻¹) at 20 °C, vapour
89 pressure = 6.27×10^{-5} Pa at 21°C and Log K_{OW} = 5.625 (EC, 2008; Arnot et al., 2009)), suggest
90 that following disposal to landfill such leaching and volatilisation of HBCDD associated with
91 treated fabrics may not be extensive. However, other brominated flame retardants with
92 similar physicochemical properties like polybrominated diphenyl ethers (PBDEs), have been
93 reported in landfill leachate (Oliaei et al., 2002; Osako et al., 2004; Oliaei et al., 2010). In the
94 absence to our knowledge of empirical data related to the fate of HBCDD in landfill, this
95 study conducts a series of controlled laboratory experiments to test the hypothesis that
96 HBCDDs are capable of leaching from waste textiles.

97

98 **2. Materials and methods**

99 **2.1. Samples**

100 We investigated two types of flame-retardant-treated polyester upholstery textiles
101 (designated A and B) used to manufacture curtains. Each was made by a different Japanese
102 manufacturer, with all purchased in either August or September 2007. In previous studies
103 (Kajiwara et al., 2009; 2013; Kajiwara and Takigami, 2013), it was confirmed that both textiles
104 A and B had been treated with technical HBCDD.

105

106 **2.2. Leaching test methods**

107 Three distinct experimental scenarios were undertaken to examine the effects on the
108 leaching behaviour of HBCDD from curtain textile material of: (a) textile-leachate contact
109 time (single batch), (b) duration of serial or periodic wetting and draining of the textile
110 (serial batch), and (c) leachate temperature. In single batch experiments, textile samples
111 were contacted once only with the leaching fluid for either 6 h, 24 h or 48 h. In contrast, in
112 serial batch experiments, textiles were contacted with the leaching fluid for 168 h in total,

113 with leachate removed from the contact vessel and replenished with fresh leaching fluid at
114 intervals of 6 h, 24 h, 48 h, 72 h, 96 h, and 168 h. Finally, to examine the influence of the
115 temperature of the leaching fluid on leaching behaviour, single batch experiments were
116 conducted in which textiles were contacted with leaching fluid for 24 h at three different
117 temperatures (20, 50, and 80 °C). Fresh textile samples were used for each temperature.
118 The concentration of HBCDD was measured in each leachate sample generated. Conditions
119 employed in these experiments are summarised in Supplementary Information. All
120 experiments were conducted in PTFE bottles (500 mL). Curtain textile samples were first cut
121 into 5 x 5 cm squares and 10 grams weighed accurately before addition to the PTFE contact
122 vessel. In all experiments, the leaching fluid used was 250 mL of Milli-Q purified, deionised
123 water giving a liquid-solid ratio of 25:1 (v/w). Following addition of the sample and leaching
124 fluid, contact vessels were horizontally agitated on a mechanical shaker at 200 rpm for the
125 desired contact time. The exception was for experiments examining the influence of
126 temperature (20, 50, and 80 °C), which were not agitated and instead were maintained at
127 the desired temperature for 24 h by immersion of the contact vessel in a thermostatically
128 controlled water bath. Each experiment was conducted in duplicate.

129

130 **2.3. Sample preparation and chemical analysis**

131 Each leachate sample was filtered through a 0.50 µm size particle retention glass fibre filter
132 (Advantec, Japan) to remove any textile fibres from the leachate and then spiked with 60 ng
133 each of ¹³C₁₂-labelled α-, β-, and γ-HBCDDs as internal (or surrogate) standards. The filtrate
134 was then extracted in series using 2 x 50 mL dichloromethane (DCM) by liquid-liquid
135 extraction with mechanical shaking for 30 minutes each time. Approximately 5-10 mL 2%
136 NaCl solution was used to enhance separation after extraction. The combined DCM extracts
137 were dried via filtration through Na₂SO₄. The dried extract was concentrated with solvent
138 exchange to hexane before elution through a pre-cleaned acidified silica (1 g of 22%
139 concentrated sulfuric acid, w/w) and Na₂SO₄ column with 30 mL of n-hexane/DCM 9:1 (v/v).
140 The eluate was concentrated with solvent exchange to hexane before evaporation to
141 incipient dryness, addition of d₁₈-labelled α-, β-, and γ-HBCDD as recovery (or syringe)
142 standard and dilution in methanol prior to analysis via LC-ESI-MS/MS.

143 Concentrations of HBCDDs in test fabrics were determined in accordance with Kajiwara et
144 al. (2009). Briefly, a textile sample (~0.2 g) was added to 20 mL of DCM in a glass bottle with
145 a lid; the bottle was shaken by hand for 2 minutes and then kept in the dark at room
146 temperature for 2 days. A 200 μ L aliquot of the crude extract obtained by this method was
147 diluted with 20 mL toluene. A 50 μ L aliquot of the toluene was spiked with 50 ng each of
148 $^{13}\text{C}_{12}$ -labelled α -, β -, and γ -HBCDDs as internal standards prior to further dilution to 1 mL
149 with methanol. Each test fabric was analysed in triplicate.

150

151 **2.4 Determination of concentrations of HBCDDs**

152 For samples generated in single and serial batch experiments, HBCDDs were quantified
153 using an Alliance 2695 liquid chromatograph equipped with a Quattro Ultima triple
154 quadrupole mass spectrometer (Waters, Tokyo, Japan) (see supporting information for
155 additional details). Concentrations of HBCDDs in samples generated in experiments
156 examining the impact on leaching of variable leaching fluid temperature, were quantified
157 using a dual pump Shimadzu LC-20AB Prominence high pressure liquid chromatograph
158 (Shimadzu, Kyoto, Japan) equipped with a Sciex API 2000 triple quadrupole mass
159 spectrometer (Applied Biosystems, Foster City, CA, USA) (see supporting information for
160 additional details).

161

162 **2.5. Calculation of HBCDD leaching**

163 The percentage of HBCDDs present in the test textiles that was leached into each leachate
164 samples (PL) was calculated as follows (equation 1):

165 Equation 1:
$$PL = \left[\frac{C_{leachate} \times V}{C_{waste} \times W} \right] \times 100\%$$

166

167 PL = percentage leached (%)

168 $C_{leachate}$ = Conc. of HBCDD collected in leachate (mg/L)

169 V = volume of leachate (L)

170 C_{waste} = Conc. of HBCDD in waste sample (mg/kg)

171 W = total weight of waste sample (kg)

172 The percentage leached normalised to contact time (PLT , % h⁻¹) is expressed here as the
173 percentage of HBCDD leached from the textile per hour of contact time. PLT is calculated
174 according to equation 2.

175 Equation 2: $PLT = \frac{PL}{t}$

176 PL = percentage leached (%)

177 t = contact time (h)

178

179 **3. Results and discussion**

180 **3.1. Initial HBCDD concentrations and diastereomer profiles in the textile samples**

181 Table 1 displays the initial concentrations of HBCDD and individual diastereomers in the
182 treated textile samples used in this study. The textiles were analysed for α -, β -, γ -, δ - and ϵ -
183 HBCDD diastereomers. HBCDD is prepared commercially by bromination of *cis,trans,trans*-
184 cyclododecatriene (ctt-CDT) while δ - and ϵ - are formed by bromination of *trans,trans,trans*-
185 cyclododecatriene (ttt-CDT), a common contaminant in commercial ctt-CDT (Arsenault et al.,
186 2007). However, while traces of δ - and ϵ - were detected in our textile samples, their
187 concentrations were below the limit of quantitation (<500 mg kg⁻¹ and <300 mg kg⁻¹
188 respectively).

189 Depending on the manufacturer and the production method used, technical grade HBCDD
190 consists of 75-95 % γ -HBCDD, 3-13 % α - HBCDD and 0.5-12 % β -HBCDD (Becher, 2005; UNEP,
191 2011). In contrast, the HBCDD diastereomer pattern in the textiles used in this study was
192 roughly equally distributed between α - and γ - with a smaller proportion of β -HBCDD. The
193 difference between the diastereomer pattern observed in these samples and that reported
194 for technical grade HBCDD is likely due to the processes via which the textiles are flame-
195 retarded. HBCDD is applied via immersion of the textiles in a solution of technical HBCDD.
196 Following removal of the textile from the solution, the textile is desiccated at ~100-190 °C

197 (Johokiko, 2008). Thermal isomerisation of HBCDD towards a composition relatively
198 enriched in α -HBCD compared to the starting material has been demonstrated previously
199 (Köppen et al, 2008) and appears a plausible explanation for the pattern observed in our
200 textile samples.

201

202 **3.2. Effects of contact time on leaching (single batch experiments)**

203 The influence of contact time on HBCDD concentrations in leachate in single batch
204 experiments conducted at 20 °C is illustrated by Figure 1, with leaching behaviour for the
205 same experiments provided in the Supplementary Information. Only a slight increase in
206 HBCDD concentrations detected in leachate was observed on increasing contact time from 6
207 to 24 and then 48 h. As a consequence, *PLT* decreases with increasing contact time. This
208 suggests the majority of HBCDD leaching occurs in the first six hours of contact between the
209 fabric source and the leaching fluid, thereafter, *PLT* diminishes. Moreover, in all experiments
210 conducted at 20 °C, α -HBCDD leached far more extensively than β -HBCDD or γ -HBCDD. We
211 believe that these diastereomer-specific variations in *PLT* are explicable in terms of the
212 aqueous solubility of HBCDD. Specifically, the aqueous solubility of α -HBCDD ($41 \mu\text{g L}^{-1}$),
213 exceeds that of both β -HBCDD ($15 \mu\text{g L}^{-1}$) and γ -HBCDD ($2.4 \mu\text{g L}^{-1}$) at 20 °C (EC, 2008; Arnot
214 et al., 2009).

215

216 Intriguingly, while ϵ -HBCDD was below the limit of quantitation in the curtain textile
217 samples (Table 1), it was detected in the leachate in both single (Figure 1) and serial batch
218 experiments (Figures 2 & 3). This suggests either that ϵ -HBCDD is present in the textile (but
219 below detection limit) and is substantially more water soluble than other HBCDD
220 diastereomers, and thus leached more efficiently; or that it is formed as a result of
221 isomerisation processes (Heeb et al, 2008; Köppen et al, 2008).

222

223 **3.3. Effect of cyclical wetting and draining on HBCDD concentrations and leaching** 224 **behaviour (serial batch experiments).**

225 Concentrations of HBCDDs (ng L^{-1}) detected in leachate and *PLT* values ($\% \text{ h}^{-1}$) obtained from
226 these experiments on both textiles A and B are presented in Figures 2 and 3. After 24 h
227 cumulative contact time, concentrations of HBCDD leached from both textiles in these serial
228 batch experiments diminish with increasing experimental duration. However, the decline in
229 concentration is not dramatic, and even after a cumulative 168 h of leaching, the ΣHBCDD
230 concentration >50% of that observed after just 6 h leaching. The observed decline in
231 leachate concentration with successive batches may be attributable to removal in the early
232 contact periods of less tightly bound HBCDD present on the surface of the textile. Overall –
233 although longer term experiments are required to confirm this - this serial batch experiment
234 indicates that replenishment of leaching fluid as would be expected in a landfill does not
235 result in diminished HBCDD leaching from textiles over long periods. Unfortunately,
236 insufficient material was available to us to conduct these longer term tests.

237

238 3.4. Leaching kinetics

239 Ho et al., (2005) expressed the leaching of water-soluble components from sapwood in
240 terms of the following second-order rate equation:

241 Equation 3:
$$\frac{Ct}{t} = k(Cs - Ct)^2,$$

242 where k is the second-order leaching rate constant ($\text{L ng}^{-1} \text{ min}^{-1}$), C_s the leaching capacity,
243 which is the concentration of HBCDD at saturation (ng L^{-1}), and C_t is the concentration of
244 HBCDD (ng L^{-1}) in suspension at any given time, t (min). The leaching capacity, C_s , and the
245 second-order leaching rate constant, k , can be determined experimentally from the slope
246 and intercept by plotting t/C_t against t .

247 We generated such plots for all our experiments conducted at 20 °C. We combined data at
248 that temperature for both single batch and serial batch experiments, by treating our serial
249 batch experiments as a series of single batch experiments. A positive and highly significant
250 linear correlation between t/C_t and t was observed in all instances. Plots are provided for
251 Textile A and B in Supplementary Information. This apparent fit with second order kinetics
252 confirms our observations above of initial rapid leaching followed by a slower second phase.

253 We suggest that initially there is intense dissolution in which maximum leaching takes place
254 as a result of removal from the fabric of HBCDD that is more loosely associated with easily
255 abraded fibres and present on the fabric surface rather than embedded within the fabric. A
256 second, slower stage follows, which corresponds primarily to external diffusion and is
257 related to the soluble remainder. The slope, Y-intercept, saturated leaching capacity, C_s , the
258 leaching rate constant, k , two-tailed p values, and Pearson's correlation coefficients, r , are
259 given for individual HBCDD diastereomers in [Table 2](#).

260

261 **3.5. Effect of temperature on leaching**

262 Within a landfill, temperatures can sometimes reach as high as 80-90 °C due to heat
263 released during aerobic degradation (Kjeldsen et al., 2002). Therefore, the influence on PLT
264 of leachate temperatures of 20 °C, 50 °C and 80 °C were investigated.

265 Concentrations and leaching behaviour of HBCDD from textiles A and B at different
266 temperatures are displayed in Figures 4 & 5, with the diastereomer pattern in leachate at
267 different temperatures shown in Supplementary Information. Note that while ϵ -HBCDD was
268 detected in leachate at 20 °C experiments (section 3.3), it was not found at quantifiable
269 levels in experiments run at higher temperatures. This suggests thermal instability of ϵ -
270 HBCDD. While concentrations of all diastereomers increased with increasing temperature,
271 raising the temperature from 20 °C to 80 °C increased leachate concentrations of γ -HBCDD
272 by a factor of 28 - 33, while α -HBCDD concentrations only increased by a factor of 4.3 - 4.8.
273 One possible explanation for this observation is that at higher temperatures the relatively
274 more hydrophobic isomers (β -HBCDD and γ -HBCDD) become more water soluble compared
275 to α -HBCDD and are therefore more readily leached. Alternatively, isomerisation may occur
276 at lower temperatures than hitherto documented.

277 **3.6. Effect of agitation on leaching**

278 By comparing the results of experiments conducted at 20 °C with contact times of 24 h in
279 the agitation time experiment and the temperature experiment the effect of agitation on
280 leaching of HBCDD from the textiles can be examined. The Σ HBCDD concentrations in the
281 agitated leachate samples were 36 times higher for Textile A and 20 times higher for Textile

282 B. This illustrates that agitation has a considerable role in enhancing HBCDD leachate
283 concentrations from treated textiles.

284

285 **4. Summary**

286 This study demonstrates that leaching of HBCDD from textiles using distilled deionised
287 water as a leaching fluid is a second order process. Following an initial period of
288 source:leaching fluid contact during which leaching is relatively facile, subsequent leaching
289 is slower. Leaching is higher for the more water soluble diastereomers and is substantially
290 greater at 80 °C compared to 20 °C. Our data, when combined with the plausibly enhanced
291 solubility of BFRs in leaching fluid containing dissolved organic matter (Choi et al, 2009), and
292 existing reports of measurable concentrations of HBCDD in landfill leachate (Morris et al.,
293 2004; Remberger et al., 2004; Suzuki and Hasegawa, 2006), suggests that leaching of HBCDD
294 from landfilled waste requires further study to elucidate its magnitude, the factors
295 influencing it, and its environmental impact.

296

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465

466

467

468 **Table 1: Mean Concentrations (mg kg⁻¹) of HBCDDs in textiles used in this study**

Diastereomer/ Sample	α -HBCDD	β -HBCDD	γ -HBCDD	δ -HBCDD	ϵ -HBCDD	Σ HBCDD
Textile A	11,000 \pm 55	4,500 \pm 130	10,000 \pm 160	<500	<300	26,000 \pm 170
Textile B	9,900 \pm 200	3,600 \pm 100	10,000 \pm 130	<500	<300	24,000 \pm 420

Material = polyester; Textile A colour = blue, Textile B colour = black; (n=3)

469

470

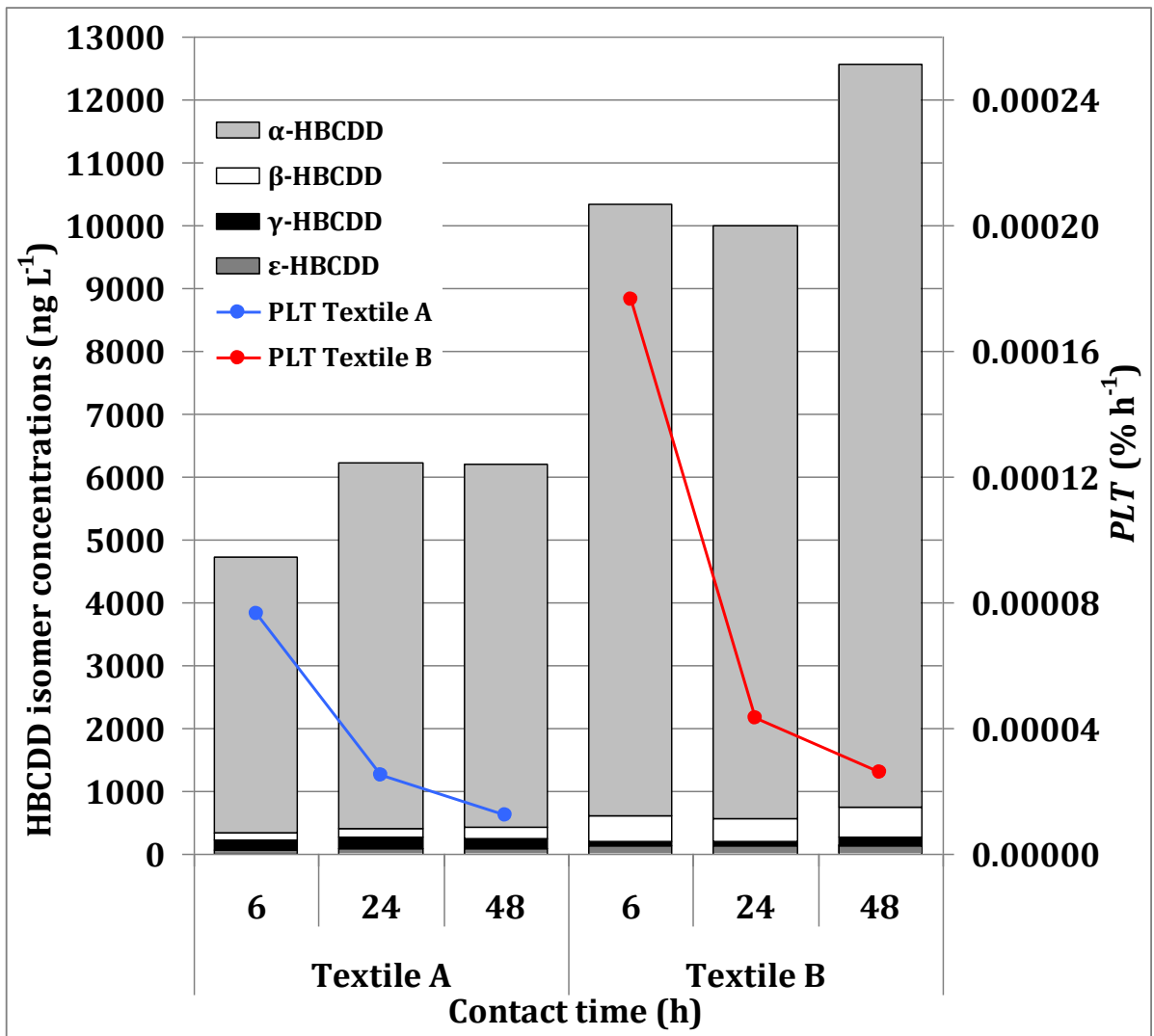
471 **Table 2: Second order leaching rate constants (k) and saturated leaching capacities (C_s)**
 472 **obtained for HBCDD diastereomers for Textiles A and B^a**

Constant / Compound	Slope	y-intercept	C_s (ng L ⁻¹)	Observed max. conc. (ng L ⁻¹)	k (L ng ⁻¹ min ⁻¹)	Two-tailed <i>P</i> value	Correlation coefficient: <i>r</i>
Textile A							
β-HBCDD	0.0056	0.9249	180	220	0.000012	.000	0.945
γ-HBCDD	0.0043	1.1723	230	410	0.000007	.000	0.832
Textile B							
γ-HBCDD	0.0082	3.5252	120	380	0.000019	.000	0.896

^aData not shown for plots for which y-intercept and thus k values were negative.

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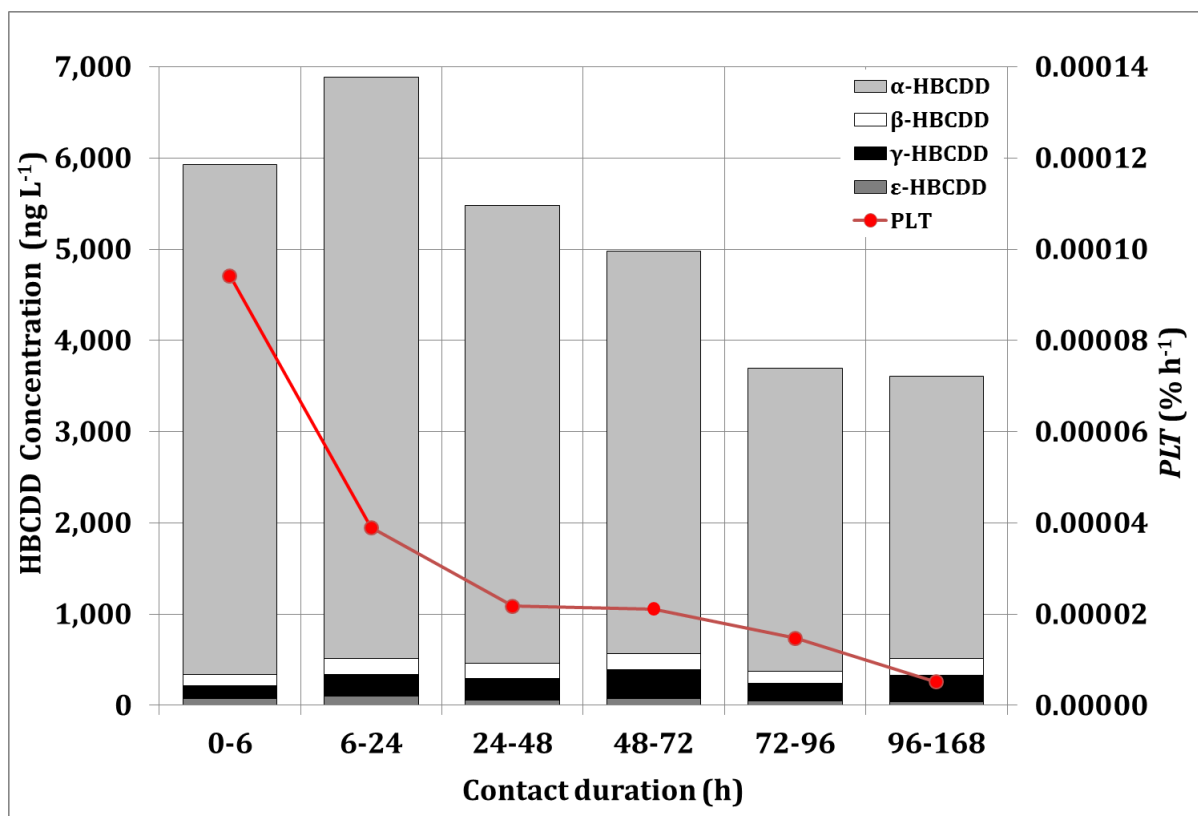
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477 Fig. 1: Mean (n=2) HBCDD concentrations (ng L⁻¹) and PLT values (% h⁻¹) in leachate
 478 produced from single batch experiments on Textiles A & B for different agitation times.

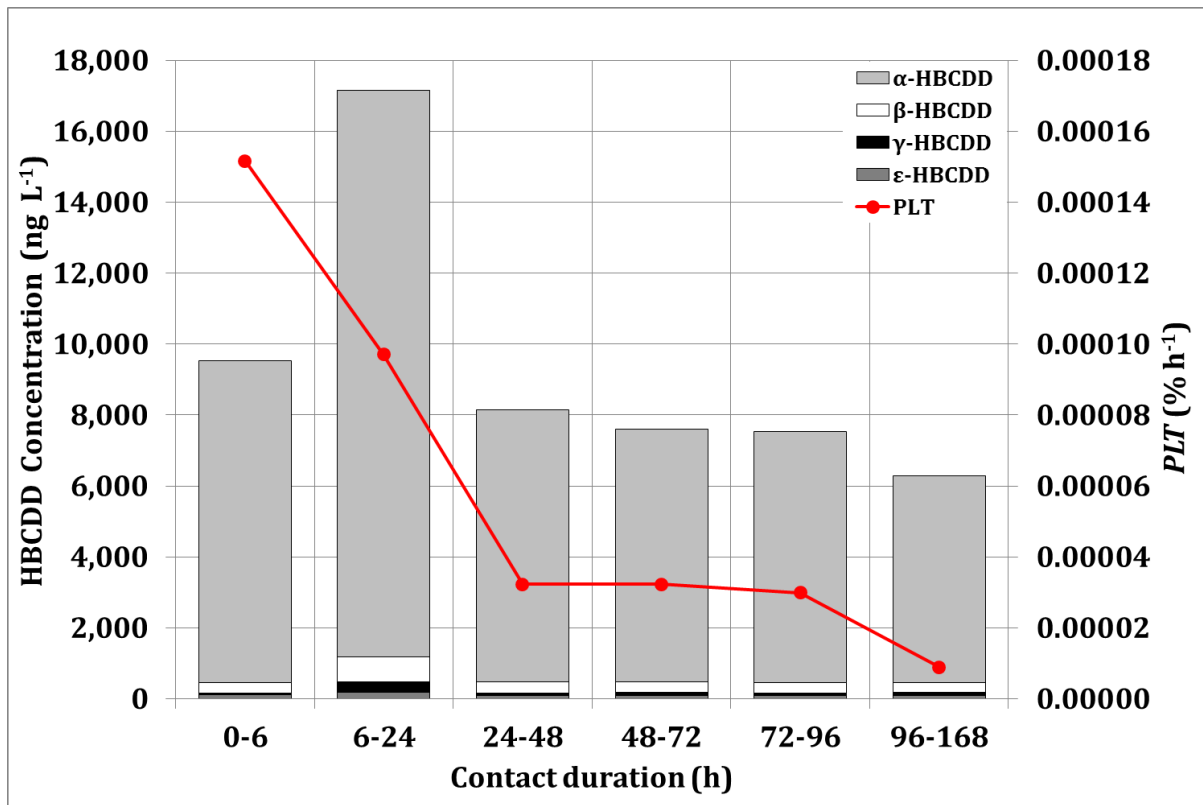
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480

481 **Fig. 2** Mean (n=2) HBCDD concentrations (ng L⁻¹) and *PLT* values (% h⁻¹) in leachate
 482 produced during serial batch experiments on Textile A examining the effect of cyclical
 483 wetting and draining.

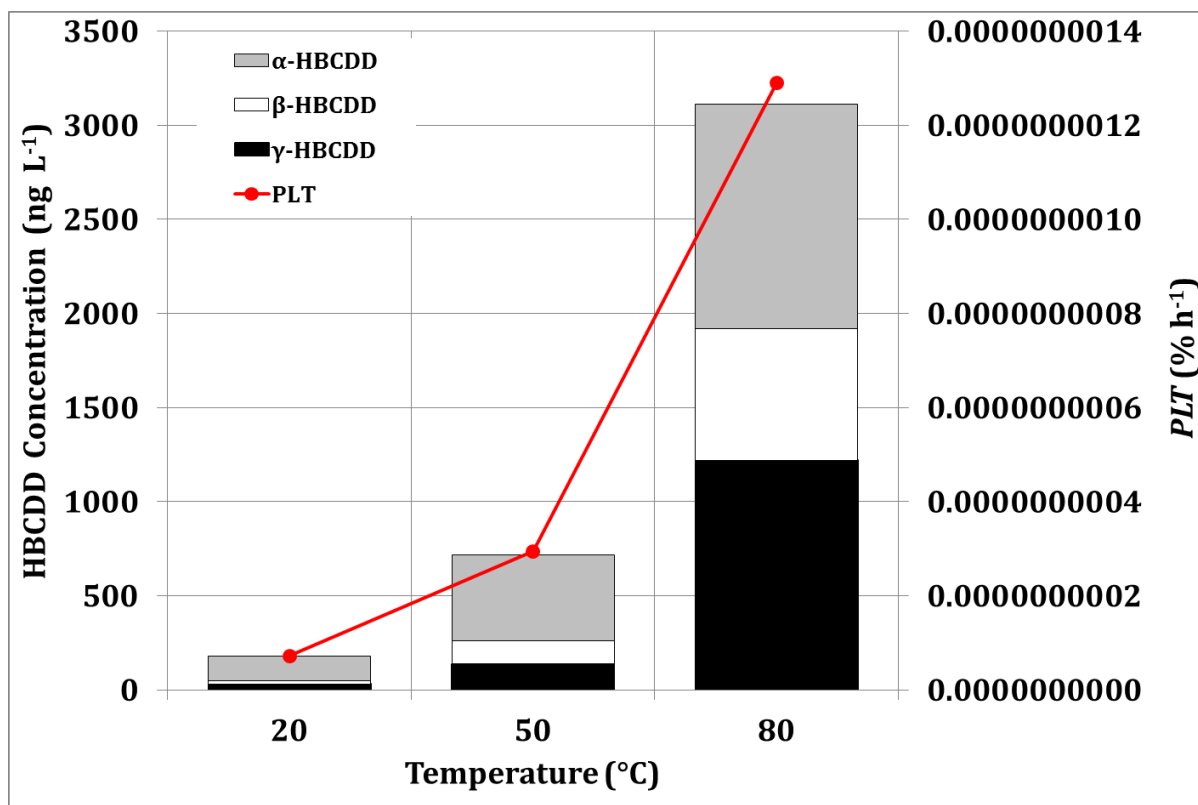
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486 **Fig. 3 Mean (n=2) HBCDD concentrations (ng L⁻¹) and PLT values (% h⁻¹) in leachate**
 487 **produced during serial batch experiments on Textile B examining the effect of cyclical**
 488 **wetting and draining.**

489

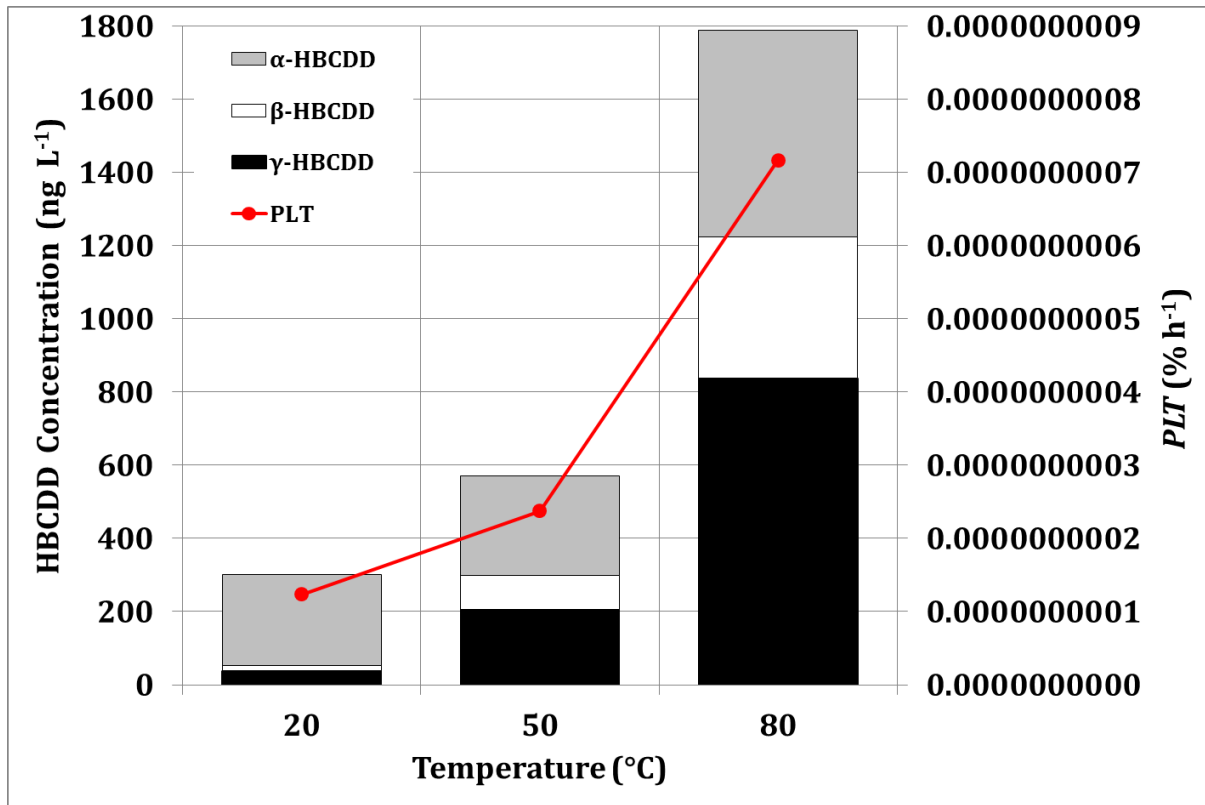


490

491 **Fig. 4 Mean (n=2) HBCDD concentrations (ng L⁻¹) and PLT values (% h⁻¹) from Textile A at**
 492 **different temperatures during 24h single batch experiments.**

493

494



495

496 **Fig. 5 Mean (n=2) HBCDD concentrations (ng L⁻¹) and PLT values (% h⁻¹) from Textile B at**
497 **different temperatures during 24h single batch experiments.**

498

Highlights

- We study HBCDD leaching from contacting a treated textile with deionised water
- Leaching of HBCDD from textiles is shown to be a second order process
- α -HBCDD is preferentially leached compared to β - and γ -HBCDD at 20 °C
- At 80 °C γ -HBCDD is proportionally more readily leached than α -HBCDD
- While not detected in the textile, ϵ -HBCDD was detected in leachate
- A max. total HBCDD conc. of 20,000 ng L⁻¹ was detected in the leachate

26 **Abstract**

27 A series of laboratory experiments were conducted, whereby two HBCDD treated polyester
28 curtain samples were contacted with deionised Milli-Q water as leaching fluid and HBCDD
29 determined in the resulting leachate. As well as single batch (no replenishment of leaching
30 fluid), serial batch (draining of leachate and replenishment with fresh leaching fluid at
31 various time intervals) experiments were conducted. In single batch experiments at 20°C,
32 Σ HBCDD concentrations increased only slightly with increasing contact time (6 h, 24 h, and
33 48 h). This is supported by serial batch tests at 20 °C in which leaching fluid was replaced
34 after 6 h, 24 h, 48 h, 72 h, 96 h, and 168 h. Data from these experiments show that while
35 concentrations of HBCDD in leachate after 24 h cumulative contact time exceed those at 6
36 h; concentrations in samples collected at subsequent contact times remained steady at
37 ~50% of those in the 24 h sample. Consistent with this, leaching is shown to be second
38 order, whereby a period of initially intense dissolution of more labile HBCDD is followed by a
39 slower stage corresponding to external diffusion of the soluble residue within the textile. In
40 experiments conducted at 20°C, α -HBCDD is preferentially leached compared to β - and γ -
41 HBCDD. However, at higher temperatures, the relatively more hydrophobic diastereomers
42 are proportionally more readily leached, i.e. raising the temperature from 20°C to 80°C
43 increased concentrations of γ -HBCDD in the leachate by a factor of 28–33 while
44 corresponding α -HBCDD concentrations only increased by a factor of 4.3-4.8.

45

46 **Keywords**

47 Hexabromocyclododecane;

48 Waste soft furnishings;

49 Landfill;

50 Brominated flame retardants;

51 Leaching

52

53 1. Introduction

54 Hexabromocyclododecane (HBCDD) has been identified as an endocrine disrupting chemical
55 that induces enzymes and alters thyroid homeostasis with potential to cause adverse effects
56 in humans at relatively low exposure levels (Darnerud, 2003, 2008; van der Ven et al., 2006,
57 2009; Yamada-Okabe et al., 2005). This is compounded by evidence that its presence in the
58 environment is ubiquitous (de Wit, 2002; Gerecke et al., 2003; Janak et al., 2005; Remberger
59 et al., 2004; Tomy et al., 2004; Law et al., 2005, 2006; Covaci et al., 2006; de Wit et al., 2006;
60 Marvin et al., 2006; Kohler et al., 2008; Harrad et al., 2009; Harrad et al., 2010). In a
61 legislative context, HBCDD has been identified by the European Union as a Substance of
62 Very High Concern, meeting the criteria of a PBT (persistent, bioaccumulative and toxic)
63 substance (ECHA, 2014); while in Japan, HBCDD has been designated as a Monitoring
64 Chemical Substance under the Chemical Substances Control Law because of its persistence
65 and high bio-accumulation. Moreover, in 2013, HBCDD was listed as a persistent organic
66 pollutant (POP) by the United Nations Environment Programme (UNEP) under the
67 Stockholm Convention on POPs. In 2011, annual global production of HBCDD was an
68 estimated maximum of 28,000 tonnes (9,000 to 15,000 tonnes in China, 13,426 tonnes in
69 Europe and the US) (UNEP, 2011). Around 90% of HBCDD is used in the building industry,
70 typically added at ~3% by weight into extruded or expanded polystyrene foam in rigid
71 insulation panels/boards (EC, 2011; Marvin et al., 2011). Additionally, around 8% of HBCDD
72 was used as a textile coating agent in polymer dispersions applied to cotton or
73 cotton/synthetic blends for upholstery fabrics, e.g. residential and commercial upholstered
74 furniture and transportation seating, bed mattress ticking, draperies and wall coverings,
75 interior textiles, e.g. roller blinds, and vehicle interior textiles. HBCDD can also be used in
76 thermosol treatment of polyester, polypropylene and nylon fabrics, where it is applied as an
77 aqueous suspension or emulsion at a loading of 8-11% by weight (EC, 2011; UNEP, 2011;
78 Weil and Levchik, 2008). Currently, used furniture or textiles containing textiles treated with
79 HBCDD are widely treated as municipal rather than hazardous waste, and are thus landfilled
80 or incinerated. In the UK alone, WRAP (2012) estimated that in 2010/11 around 670,000
81 tonnes of furniture (an unknown fraction of which will consist of fabric coverings) and
82 310,000 tonnes of textiles are disposed of by householders annually. This reservoir of
83 HBCDDs within soft furnishings has and will continue to, gradually enter the waste stream,

84 and there is hence a pressing need to understand the fate of chemicals like HBCDD
85 associated with waste fabrics following disposal (Stubblings & Harrad, 2014). Potential
86 emission pathways for chemicals associated with landfill include contamination of leachate
87 and volatilisation. The physicochemical properties of HBCDD (water solubility = α -HBCDD
88 (41,000 ng L⁻¹), β -HBCDD (15,000 ng L⁻¹) and γ -HBCDD (2,400 ng L⁻¹) at 20 °C, vapour
89 pressure = 6.27×10^{-5} Pa at 21°C and Log K_{OW} = 5.625 (EC, 2008; Arnot et al., 2009)), suggest
90 that following disposal to landfill such leaching and volatilisation of HBCDD associated with
91 treated fabrics may not be extensive. However, other brominated flame retardants with
92 similar physicochemical properties like polybrominated diphenyl ethers (PBDEs), have been
93 reported in landfill leachate (Oliaei et al., 2002; Osako et al., 2004; Oliaei et al., 2010). In the
94 absence to our knowledge of empirical data related to the fate of HBCDD in landfill, this
95 study conducts a series of controlled laboratory experiments to test the hypothesis that
96 HBCDDs are capable of leaching from waste textiles.

97

98 **2. Materials and methods**

99 **2.1. Samples**

100 We investigated two types of flame-retardant-treated polyester upholstery textiles
101 (designated A and B) used to manufacture curtains. Each was made by a different Japanese
102 manufacturer, with all purchased in either August or September 2007. In previous studies
103 (Kajiwara et al., 2009; 2013; Kajiwara and Takigami, 2013), it was confirmed that both textiles
104 A and B had been treated with technical HBCDD.

105

106 **2.2. Leaching test methods**

107 Three distinct experimental scenarios were undertaken to examine the effects on the
108 leaching behaviour of HBCDD from curtain textile material of: (a) textile-leachate contact
109 time (single batch), (b) duration of serial or periodic wetting and draining of the textile
110 (serial batch), and (c) leachate temperature. In single batch experiments, textile samples
111 were contacted once only with the leaching fluid for either 6 h, 24 h or 48 h. In contrast, in
112 serial batch experiments, textiles were contacted with the leaching fluid for 168 h in total,

113 with leachate removed from the contact vessel and replenished with fresh leaching fluid at
114 intervals of 6 h, 24 h, 48 h, 72 h, 96 h, and 168 h. Finally, to examine the influence of the
115 temperature of the leaching fluid on leaching behaviour, single batch experiments were
116 conducted in which textiles were contacted with leaching fluid for 24 h at three different
117 temperatures (20, 50, and 80 °C). Fresh textile samples were used for each temperature.
118 The concentration of HBCDD was measured in each leachate sample generated. Conditions
119 employed in these experiments are summarised in Supplementary Information. All
120 experiments were conducted in PTFE bottles (500 mL). Curtain textile samples were first cut
121 into 5 x 5 cm squares and 10 grams weighed accurately before addition to the PTFE contact
122 vessel. In all experiments, the leaching fluid used was 250 mL of Milli-Q purified, deionised
123 water giving a liquid-solid ratio of 25:1 (v/w). Following addition of the sample and leaching
124 fluid, contact vessels were horizontally agitated on a mechanical shaker at 200 rpm for the
125 desired contact time. The exception was for experiments examining the influence of
126 temperature (20, 50, and 80 °C), which were not agitated and instead were maintained at
127 the desired temperature for 24 h by immersion of the contact vessel in a thermostatically
128 controlled water bath. Each experiment was conducted in duplicate.

129

130 **2.3. Sample preparation and chemical analysis**

131 Each leachate sample was filtered through a 0.50 µm size particle retention glass fibre filter
132 (Advantec, Japan) to remove any textile fibres from the leachate and then spiked with 60 ng
133 each of ¹³C₁₂-labelled α-, β-, and γ-HBCDDs as internal (or surrogate) standards. The filtrate
134 was then extracted in series using 2 x 50 mL dichloromethane (DCM) by liquid-liquid
135 extraction with mechanical shaking for 30 minutes each time. Approximately 5-10 mL 2%
136 NaCl solution was used to enhance separation after extraction. The combined DCM extracts
137 were dried via filtration through Na₂SO₄. The dried extract was concentrated with solvent
138 exchange to hexane before elution through a pre-cleaned acidified silica (1 g of 22%
139 concentrated sulfuric acid, w/w) and Na₂SO₄ column with 30 mL of n-hexane/DCM 9:1 (v/v).
140 The eluate was concentrated with solvent exchange to hexane before evaporation to
141 incipient dryness, addition of d₁₈-labelled α-, β-, and γ-HBCDD as recovery (or syringe)
142 standard and dilution in methanol prior to analysis via LC-ESI-MS/MS.

143 Concentrations of HBCDDs in test fabrics were determined in accordance with Kajiwara et
144 al. (2009). Briefly, a textile sample (~0.2 g) was added to 20 mL of DCM in a glass bottle with
145 a lid; the bottle was shaken by hand for 2 minutes and then kept in the dark at room
146 temperature for 2 days. A 200 µL aliquot of the crude extract obtained by this method was
147 diluted with 20 mL toluene. A 50 µL aliquot of the toluene was spiked with 50 ng each of
148 ¹³C₁₂-labelled α-, β-, and γ-HBCDDs as internal standards prior to further dilution to 1 mL
149 with methanol. Each test fabric was analysed in triplicate.

150

151 **2.4 Determination of concentrations of HBCDDs**

152 For samples generated in single and serial batch experiments, HBCDDs were quantified
153 using an Alliance 2695 liquid chromatograph equipped with a Quattro Ultima triple
154 quadrupole mass spectrometer (Waters, Tokyo, Japan) (see supporting information for
155 additional details). Concentrations of HBCDDs in samples generated in experiments
156 examining the impact on leaching of variable leaching fluid temperature, were quantified
157 using a dual pump Shimadzu LC-20AB Prominence high pressure liquid chromatograph
158 (Shimadzu, Kyoto, Japan) equipped with a Sciex API 2000 triple quadrupole mass
159 spectrometer (Applied Biosystems, Foster City, CA, USA) (see supporting information for
160 additional details).

161

162 **2.5. Calculation of HBCDD leaching**

163 The percentage of HBCDDs present in the test textiles that was leached into each leachate
164 samples (PL) was calculated as follows (equation 1):

165 Equation 1: $PL = \left[\frac{C_{leachate} \times V}{C_{waste} \times W} \right] \times 100\%$

166

167 PL = percentage leached (%)

168 $C_{leachate}$ = Conc. of HBCDD collected in leachate (mg/L)

169 V = volume of leachate (L)

170 C_{waste} = Conc. of HBCDD in waste sample (mg/kg)

171 W = total weight of waste sample (kg)

172 The percentage leached normalised to contact time (PLT , % h⁻¹) is expressed here as the
173 percentage of HBCDD leached from the textile per hour of contact time. PLT is calculated
174 according to equation 2.

175 Equation 2: $PLT = \frac{PL}{t}$

176 PL = percentage leached (%)

177 t = contact time (h)

178

179 **3. Results and discussion**

180 **3.1. Initial HBCDD concentrations and diastereomer profiles in the textile samples**

181 Table 1 displays the initial concentrations of HBCDD and individual diastereomers in the
182 treated textile samples used in this study. The textiles were analysed for α -, β -, γ -, δ - and ϵ -
183 HBCDD diastereomers. HBCDD is prepared commercially by bromination of *cis,trans,trans*-
184 cyclododecatriene (ctt-CDT) while δ - and ϵ - are formed by bromination of *trans,trans,trans*-
185 cyclododecatriene (ttt-CDT), a common contaminant in commercial ctt-CDT (Arsenault et al.,
186 2007). However, while traces of δ - and ϵ - were detected in our textile samples, their
187 concentrations were below the limit of quantitation (<500 mg kg⁻¹ and <300 mg kg⁻¹
188 respectively).

189 Depending on the manufacturer and the production method used, technical grade HBCDD
190 consists of 75-95 % γ -HBCDD, 3-13 % α - HBCDD and 0.5-12 % β -HBCDD (Becher, 2005; UNEP,
191 2011). In contrast, the HBCDD diastereomer pattern in the textiles used in this study was
192 roughly equally distributed between α - and γ - with a smaller proportion of β -HBCDD. The
193 difference between the diastereomer pattern observed in these samples and that reported
194 for technical grade HBCDD is likely due to the processes via which the textiles are flame-
195 retarded. HBCDD is applied via immersion of the textiles in a solution of technical HBCDD.
196 Following removal of the textile from the solution, the textile is desiccated at ~100-190 °C

197 (Johokiko, 2008). Thermal isomerisation of HBCDD towards a composition relatively
198 enriched in α -HBCD compared to the starting material has been demonstrated previously
199 (Köppen et al, 2008) and appears a plausible explanation for the pattern observed in our
200 textile samples.

201

202 **3.2. Effects of contact time on leaching (single batch experiments)**

203 The influence of contact time on HBCDD concentrations in leachate in single batch
204 experiments conducted at 20 °C is illustrated by Figure 1, with leaching behaviour for the
205 same experiments provided in the Supplementary Information. Only a slight increase in
206 HBCDD concentrations detected in leachate was observed on increasing contact time from 6
207 to 24 and then 48 h. As a consequence, *PLT* decreases with increasing contact time. This
208 suggests the majority of HBCDD leaching occurs in the first six hours of contact between the
209 fabric source and the leaching fluid, thereafter, *PLT* diminishes. Moreover, in all experiments
210 conducted at 20 °C, α -HBCDD leached far more extensively than β -HBCDD or γ -HBCDD. We
211 believe that these diastereomer-specific variations in *PLT* are explicable in terms of the
212 aqueous solubility of HBCDD. Specifically, the aqueous solubility of α -HBCDD ($41 \mu\text{g L}^{-1}$),
213 exceeds that of both β -HBCDD ($15 \mu\text{g L}^{-1}$) and γ -HBCDD ($2.4 \mu\text{g L}^{-1}$) at 20 °C (EC, 2008; Arnot
214 et al., 2009).

215

216 Intriguingly, while ϵ -HBCDD was below the limit of quantitation in the curtain textile
217 samples (Table 1), it was detected in the leachate in both single (Figure 1) and serial batch
218 experiments (Figures 2 & 3). This suggests either that ϵ -HBCDD is present in the textile (but
219 below detection limit) and is substantially more water soluble than other HBCDD
220 diastereomers, and thus leached more efficiently; or that it is formed as a result of
221 isomerisation processes (Heeb et al, 2008; Köppen et al, 2008).

222

223 **3.3. Effect of cyclical wetting and draining on HBCDD concentrations and leaching** 224 **behaviour (serial batch experiments).**

225 Concentrations of HBCDDs (ng L^{-1}) detected in leachate and *PLT* values ($\% \text{ h}^{-1}$) obtained from
226 these experiments on both textiles A and B are presented in Figures 2 and 3. After 24 h
227 cumulative contact time, concentrations of HBCDD leached from both textiles in these serial
228 batch experiments diminish with increasing experimental duration. However, the decline in
229 concentration is not dramatic, and even after a cumulative 168 h of leaching, the ΣHBCDD
230 concentration >50% of that observed after just 6 h leaching. The observed decline in
231 leachate concentration with successive batches may be attributable to removal in the early
232 contact periods of less tightly bound HBCDD present on the surface of the textile. Overall –
233 although longer term experiments are required to confirm this - this serial batch experiment
234 indicates that replenishment of leaching fluid as would be expected in a landfill does not
235 result in diminished HBCDD leaching from textiles over long periods. Unfortunately,
236 insufficient material was available to us to conduct these longer term tests.

237

238 **3.4. Leaching kinetics**

239 Ho et al., (2005) expressed the leaching of water-soluble components from sapwood in
240 terms of the following second-order rate equation:

241 Equation 3:
$$\frac{Ct}{t} = k(Cs - Ct)^2,$$

242 where k is the second-order leaching rate constant ($\text{L ng}^{-1} \text{ min}^{-1}$), C_s the leaching capacity,
243 which is the concentration of HBCDD at saturation (ng L^{-1}), and C_t is the concentration of
244 HBCDD (ng L^{-1}) in suspension at any given time, t (min). The leaching capacity, C_s , and the
245 second-order leaching rate constant, k , can be determined experimentally from the slope
246 and intercept by plotting t/C_t against t .

247 We generated such plots for all our experiments conducted at 20 °C. We combined data at
248 that temperature for both single batch and serial batch experiments, by treating our serial
249 batch experiments as a series of single batch experiments. A positive and highly significant
250 linear correlation between t/C_t and t was observed in all instances. Plots are provided for
251 Textile A and B in Supplementary Information. This apparent fit with second order kinetics
252 confirms our observations above of initial rapid leaching followed by a slower second phase.

253 We suggest that initially there is intense dissolution in which maximum leaching takes place
254 as a result of removal from the fabric of HBCDD that is more loosely associated with easily
255 abraded fibres and present on the fabric surface rather than embedded within the fabric. A
256 second, slower stage follows, which corresponds primarily to external diffusion and is
257 related to the soluble remainder. The slope, Y-intercept, saturated leaching capacity, C_s , the
258 leaching rate constant, k , two-tailed p values, and Pearson's correlation coefficients, r , are
259 given for individual HBCDD diastereomers in Table 2.

260

261 **3.5. Effect of temperature on leaching**

262 Within a landfill, temperatures can sometimes reach as high as 80-90 °C due to heat
263 released during aerobic degradation (Kjeldsen et al., 2002). Therefore, the influence on PLT
264 of leachate temperatures of 20 °C, 50 °C and 80 °C were investigated.

265 Concentrations and leaching behaviour of HBCDD from textiles A and B at different
266 temperatures are displayed in Figures 4 & 5, with the diastereomer pattern in leachate at
267 different temperatures shown in Supplementary Information. Note that while ϵ -HBCDD was
268 detected in leachate at 20 °C experiments (section 3.3), it was not found at quantifiable
269 levels in experiments run at higher temperatures. This suggests thermal instability of ϵ -
270 HBCDD. While concentrations of all diastereomers increased with increasing temperature,
271 raising the temperature from 20 °C to 80 °C increased leachate concentrations of γ -HBCDD
272 by a factor of 28 - 33, while α -HBCDD concentrations only increased by a factor of 4.3 - 4.8.
273 One possible explanation for this observation is that at higher temperatures the relatively
274 more hydrophobic isomers (β -HBCDD and γ -HBCDD) become more water soluble compared
275 to α -HBCDD and are therefore more readily leached. Alternatively, isomerisation may occur
276 at lower temperatures than hitherto documented.

277 **3.6. Effect of agitation on leaching**

278 By comparing the results of experiments conducted at 20 °C with contact times of 24 h in
279 the agitation time experiment and the temperature experiment the effect of agitation on
280 leaching of HBCDD from the textiles can be examined. The Σ HBCDD concentrations in the
281 agitated leachate samples were 36 times higher for Textile A and 20 times higher for Textile

282 B. This illustrates that agitation has a considerable role in enhancing HBCDD leachate
283 concentrations from treated textiles.

284

285 **4. Summary**

286 This study demonstrates that leaching of HBCDD from textiles using distilled deionised
287 water as a leaching fluid is a second order process. Following an initial period of
288 source:leaching fluid contact during which leaching is relatively facile, subsequent leaching
289 is slower. Leaching is higher for the more water soluble diastereomers and is substantially
290 greater at 80 °C compared to 20 °C. Our data, when combined with the plausibly enhanced
291 solubility of BFRs in leaching fluid containing dissolved organic matter (Choi et al, 2009), and
292 existing reports of measurable concentrations of HBCDD in landfill leachate (Morris et al.,
293 2004; Remberger et al., 2004; Suzuki and Hasegawa, 2006), suggests that leaching of HBCDD
294 from landfilled waste requires further study to elucidate its magnitude, the factors
295 influencing it, and its environmental impact.

296

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468 **Table 1: Mean Concentrations (mg kg⁻¹) of HBCDDs in textiles used in this study**

Diastereomer/ Sample	α -HBCDD	β -HBCDD	γ -HBCDD	δ -HBCDD	ϵ -HBCDD	Σ HBCDD
Textile A	11,000 \pm 55	4,500 \pm 130	10,000 \pm 160	<500	<300	26,000 \pm 170
Textile B	9,900 \pm 200	3,600 \pm 100	10,000 \pm 130	<500	<300	24,000 \pm 420

Material = polyester; Textile A colour = blue, Textile B colour = black; (n=3)

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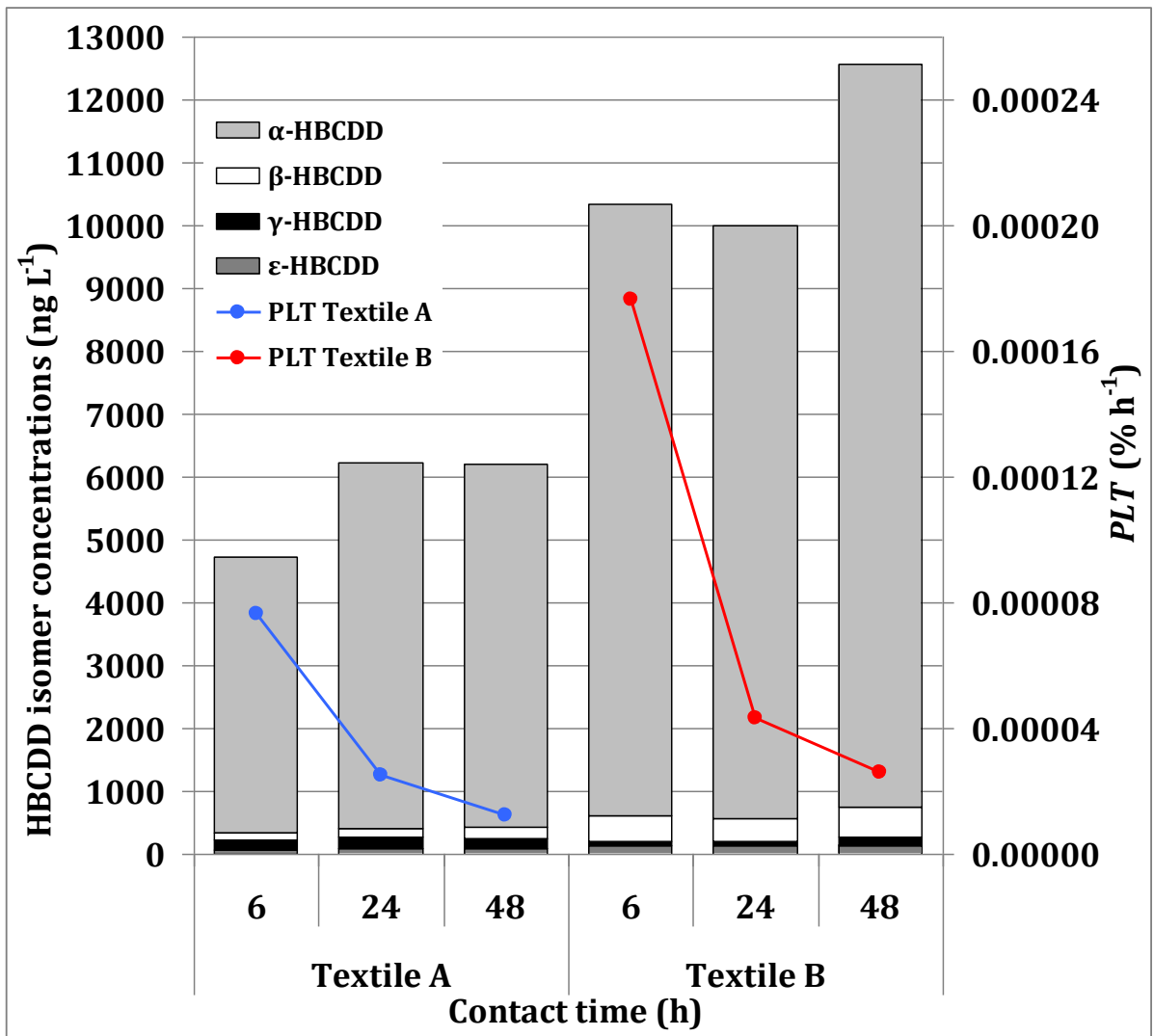
471 **Table 2: Second order leaching rate constants (k) and saturated leaching capacities (C_s)**
 472 **obtained for HBCDD diastereomers for Textiles A and B^a**

Constant / Compound	Slope	y-intercept	C_s (ng L ⁻¹)	Observed max. conc. (ng L ⁻¹)	k (L ng ⁻¹ min ⁻¹)	Two-tailed <i>P</i> value	Correlation coefficient: <i>r</i>
Textile A							
β-HBCDD	0.0056	0.9249	180	220	0.000012	.000	0.945
γ-HBCDD	0.0043	1.1723	230	410	0.000007	.000	0.832
Textile B							
γ-HBCDD	0.0082	3.5252	120	380	0.000019	.000	0.896

^aData not shown for plots for which y-intercept and thus k values were negative.

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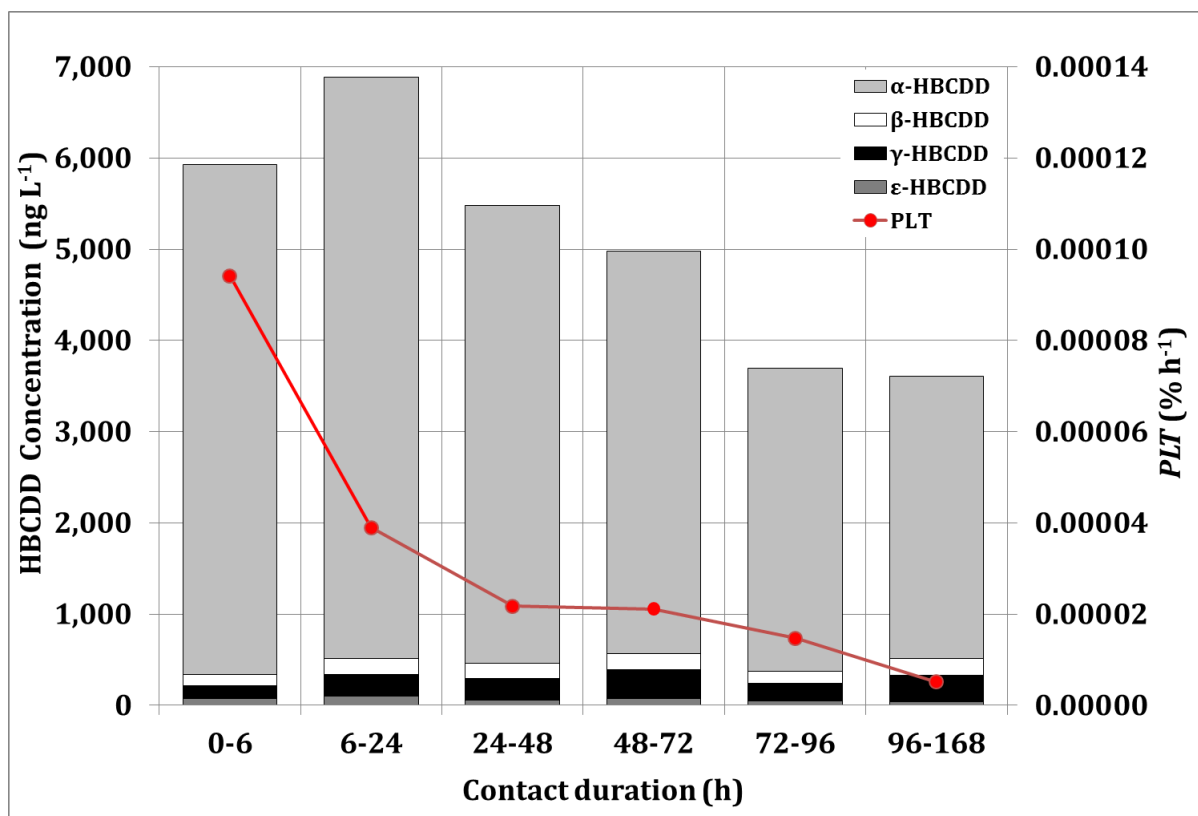
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477 Fig. 1: Mean (n=2) HBCDD concentrations (ng L⁻¹) and PLT values (% h⁻¹) in leachate
 478 produced from single batch experiments on Textiles A & B for different agitation times.

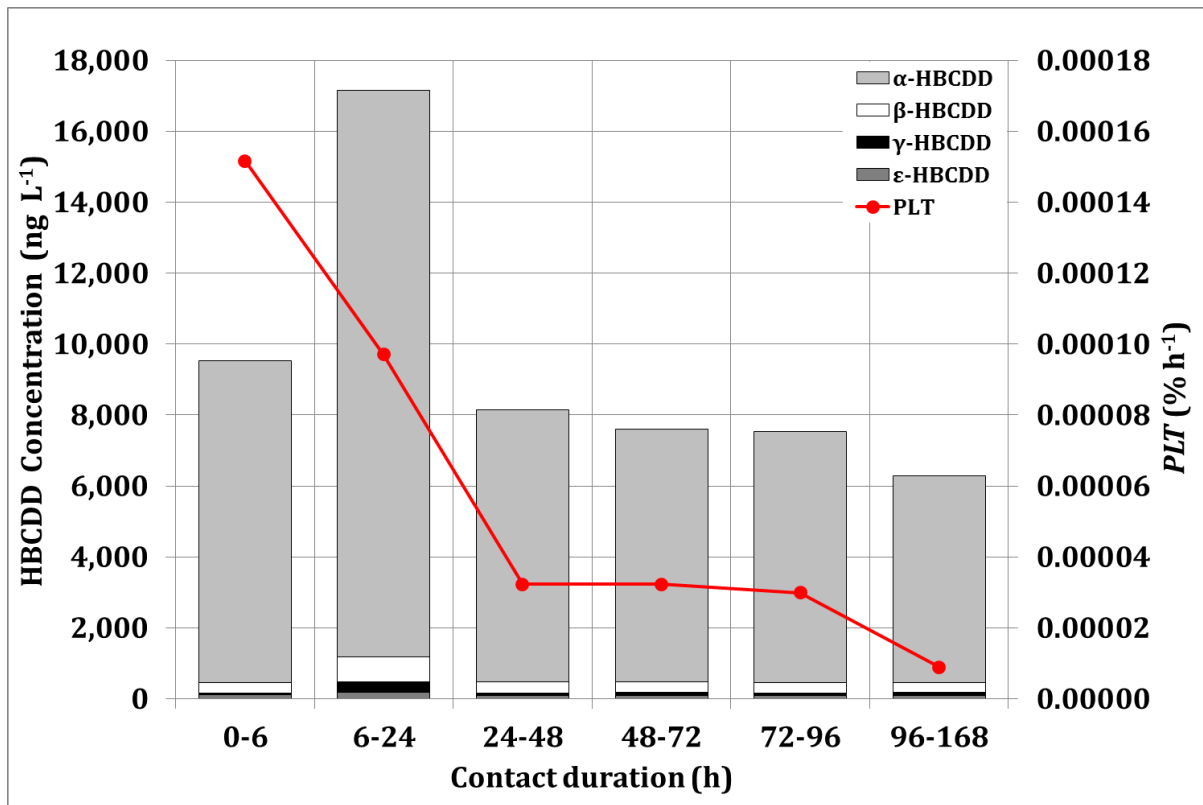
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481 **Fig. 2** Mean (n=2) HBCDD concentrations (ng L⁻¹) and *PLT* values (% h⁻¹) in leachate
 482 produced during serial batch experiments on Textile A examining the effect of cyclical
 483 wetting and draining.

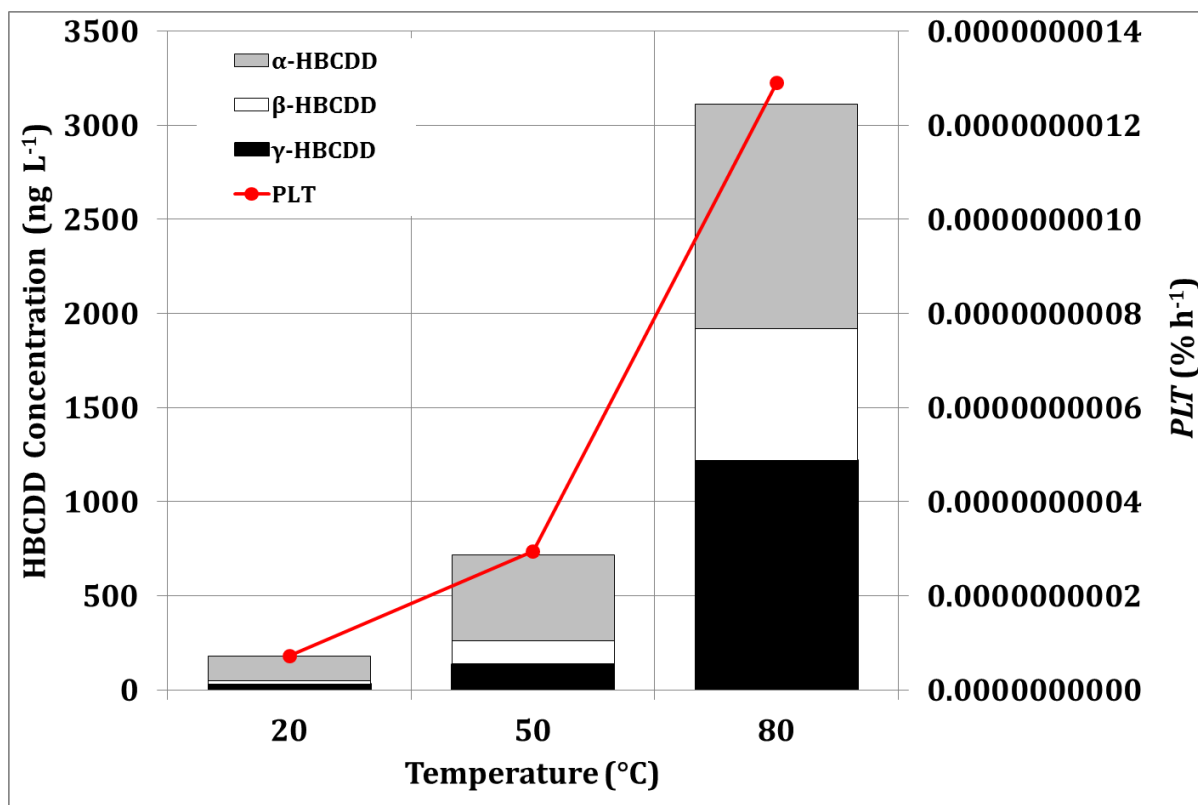
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486 **Fig. 3** Mean (n=2) HBCDD concentrations (ng L⁻¹) and *PLT* values (% h⁻¹) in leachate
 487 produced during serial batch experiments on Textile B examining the effect of cyclical
 488 wetting and draining.

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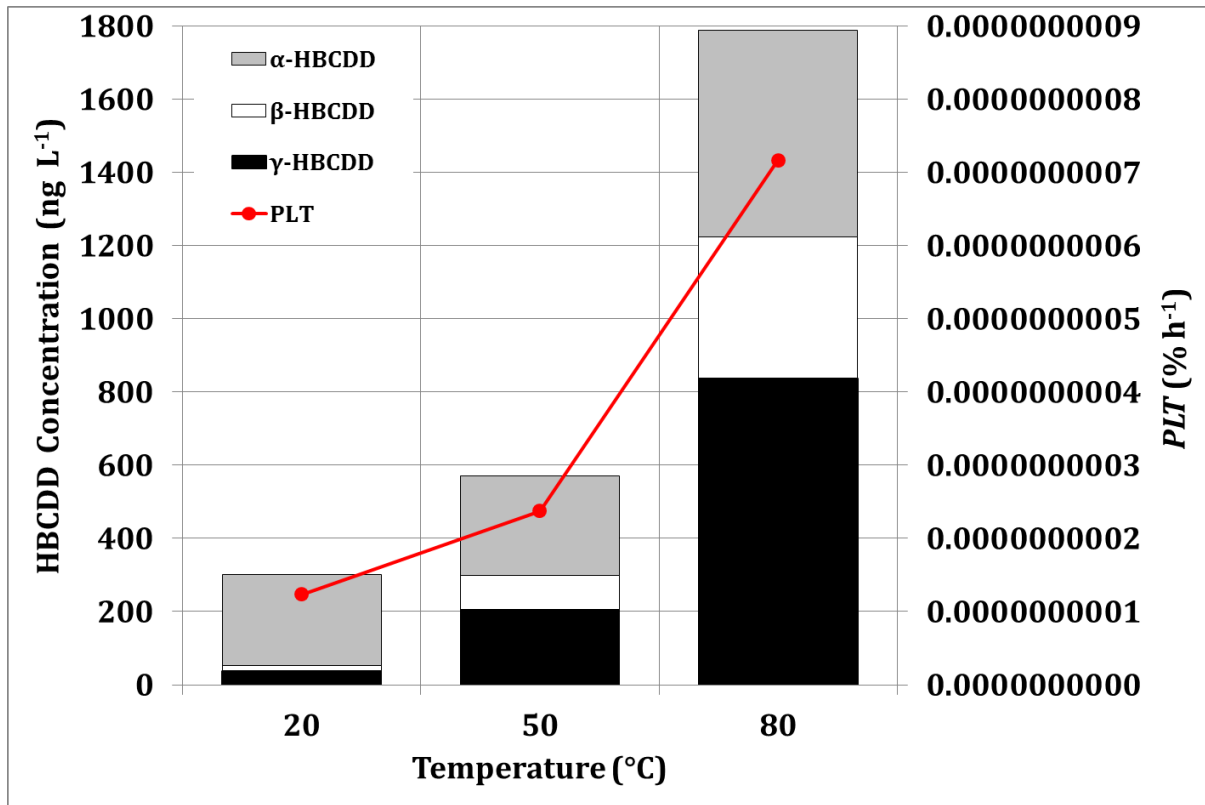


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491 **Fig. 4** Mean (n=2) HBCDD concentrations (ng L⁻¹) and *PLT* values (% h⁻¹) from Textile A at
 492 different temperatures during 24h single batch experiments.

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495

496 **Fig. 5 Mean (n=2) HBCDD concentrations (ng L⁻¹) and PLT values (% h⁻¹) from Textile B at**
497 **different temperatures during 24h single batch experiments.**

498

1 **Table 1: Mean Concentrations (mg kg^{-1}) of HBCDDs in textiles used in this study**

Diastereomer/ Sample	α -HBCDD	β -HBCDD	γ -HBCDD	δ -HBCDD	ϵ -HBCDD	Σ HBCDD
Textile A	11,000 \pm 55	4,500 \pm 130	10,000 \pm 160	<500	<300	26,000 \pm 170
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Material = polyester; Textile A colour = blue, Textile B colour = black; (n=3)

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4 **Table 2: Second order leaching rate constants (k) and saturated leaching capacities (C_s)**
 5 **obtained for HBCDD diastereomers for Textiles A and B^a**

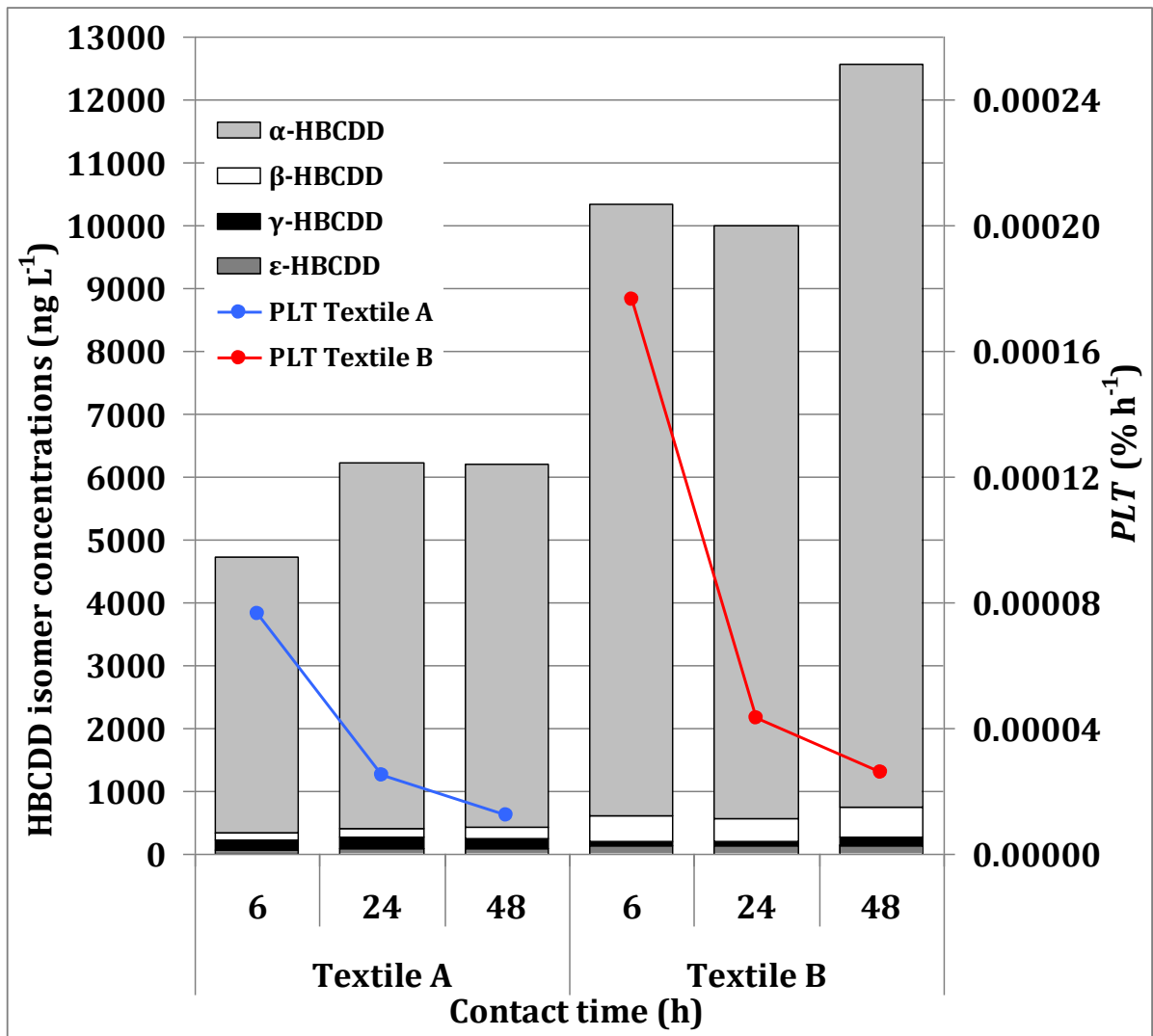
Constant / Compound	Slope	y-intercept	C_s (ng L ⁻¹)	Observed max. conc. (ng L ⁻¹)	k (L ng ⁻¹ min ⁻¹)	Two-tailed <i>P</i> value	Correlation coefficient: <i>r</i>
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^aData not shown for plots for which y-intercept and thus k values were negative.

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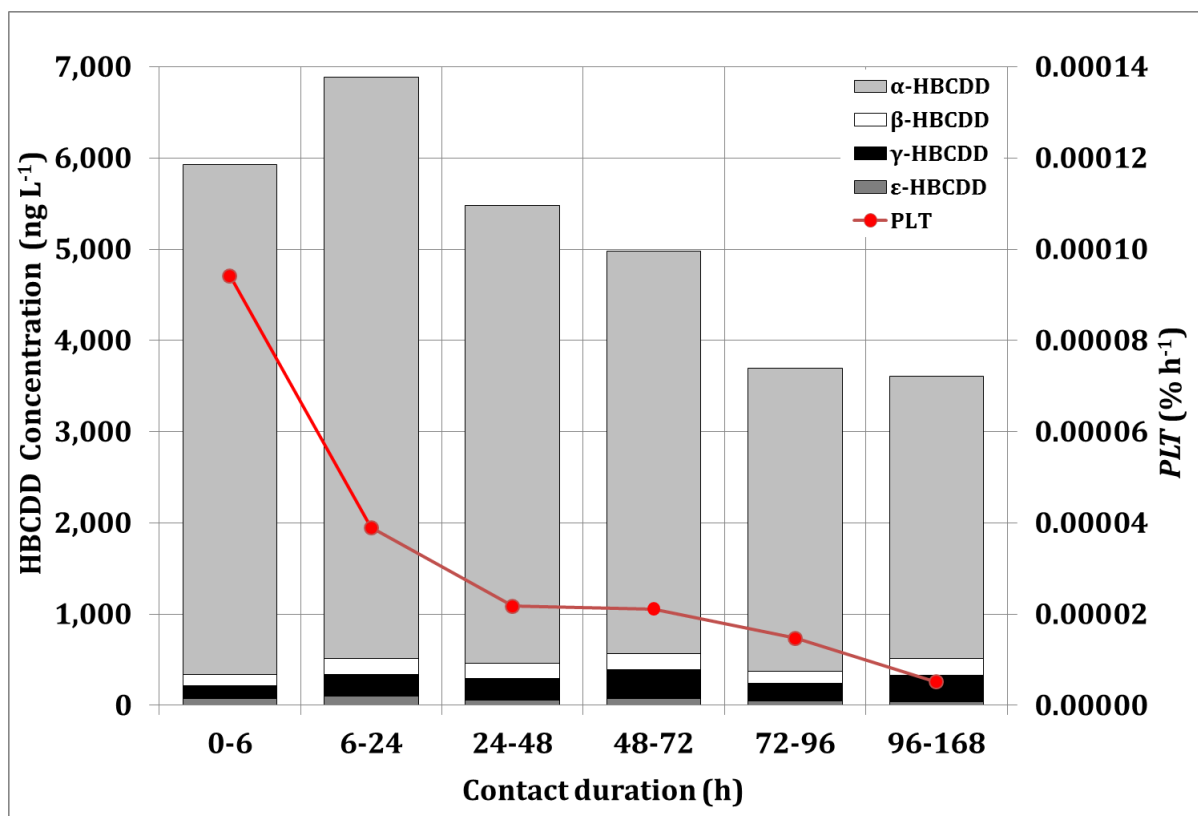
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3 Fig. 1: Mean ($n=2$) HBCDD concentrations (ng L^{-1}) and PLT values ($\% \text{ h}^{-1}$) in leachate
4 produced from single batch experiments on Textiles A & B for different agitation times.

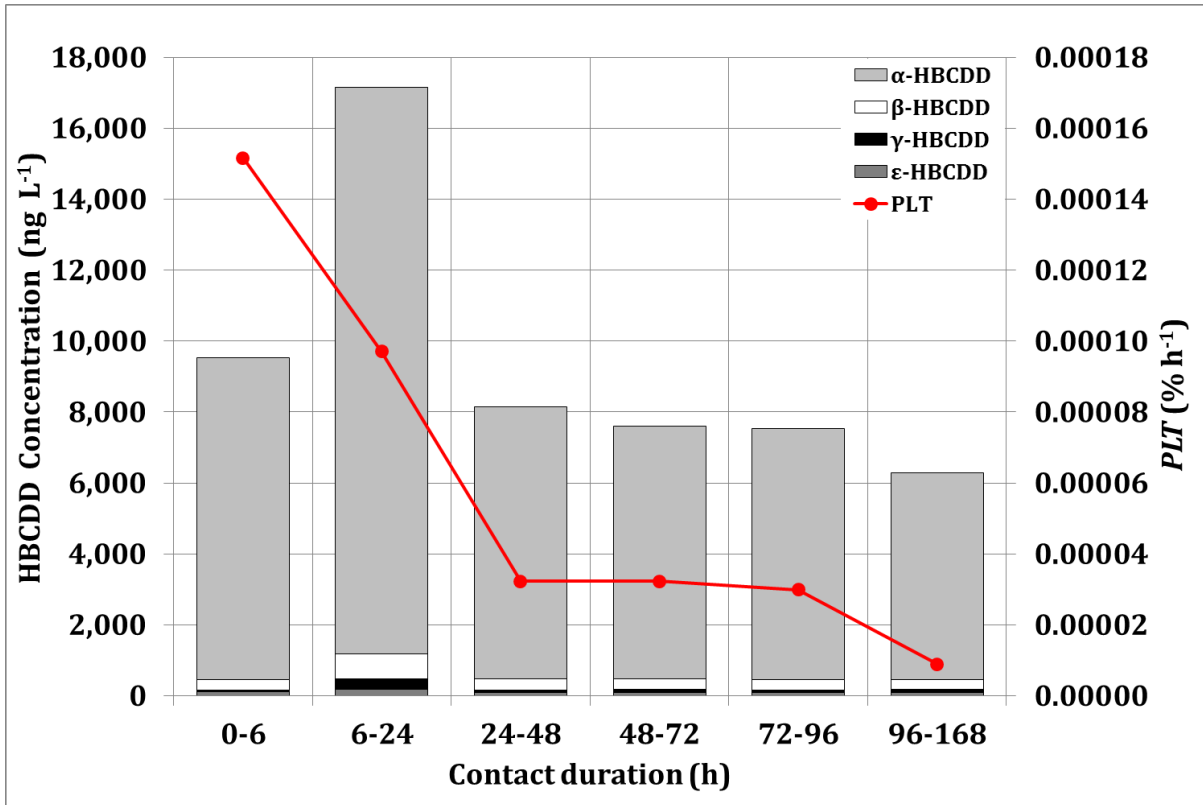
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7 Fig. 2 Mean (n=2) HBCDD concentrations (ng L⁻¹) and *PLT* values (% h⁻¹) in leachate
 8 produced during serial batch experiments on Textile A examining the effect of cyclical
 9 wetting and draining.

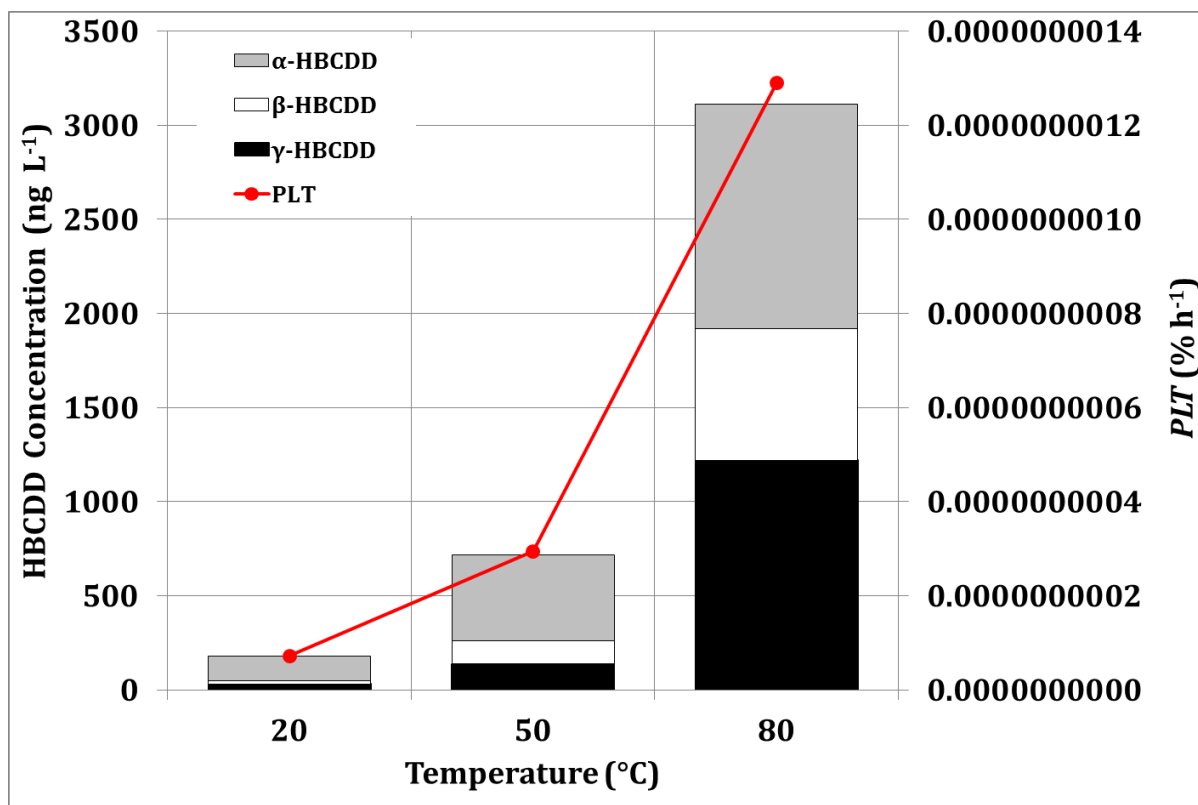
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12 **Fig. 3 Mean (n=2) HBCDD concentrations (ng L⁻¹) and PLT values (% h⁻¹) in leachate**
 13 **produced during serial batch experiments on Textile B examining the effect of cyclical**
 14 **wetting and draining.**

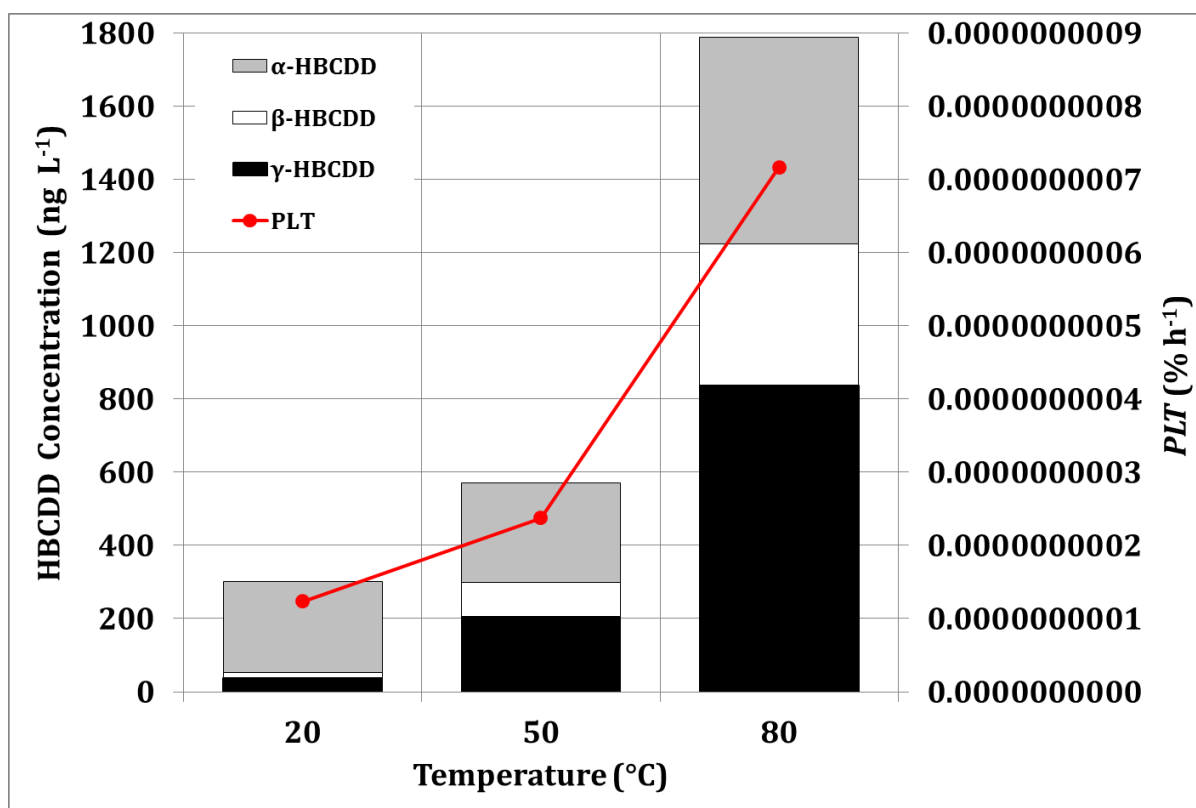
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17 Fig. 4 Mean (n=2) HBCDD concentrations (ng L⁻¹) and PLT values (% h⁻¹) from Textile A at
 18 different temperatures during 24h single batch experiments.

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22 **Fig. 5 Mean (n=2) HBCDD concentrations (ng L⁻¹) and *PLT* values (% h⁻¹) from Textile B at**
 23 **different temperatures during 24h single batch experiments.**

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Supplementary Material

[Click here to download Supplementary Material: Supplementary Information2.doc](#)