

# Test chamber investigation of the volatilization from source materials of brominated flame retardants and their subsequent deposition to indoor dust

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DOI:  
[10.1111/ina.12151](https://doi.org/10.1111/ina.12151)

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*Document Version*  
Early version, also known as pre-print

*Citation for published version (Harvard):*  
Rauert, C, Harrad, S, Stranger, M & Lazarov, B 2015, 'Test chamber investigation of the volatilization from source materials of brominated flame retardants and their subsequent deposition to indoor dust', *Indoor Air*, vol. 25, no. 4, pp. 393-404. <https://doi.org/10.1111/ina.12151>

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## Test chamber investigation of the volatilization from source materials of brominated flame retardants and their subsequent deposition to indoor dust

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1 **Research Highlights**

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- 3 • Uptake of BFRs by dust following volatilisation from a source shown  
4 experimentally
- 5 • Migration of HBCDs from curtains elevated concentrations in dust up to 10  
6 fold
- 7 • Test chamber design and sink effects are important considerations

8

1 **TITLE**

2 Test Chamber Investigation of the Volatilisation from Source Materials of  
3 Brominated Flame Retardants and their Subsequent Deposition to Indoor Dust

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22 **Abstract**

23 Numerous studies have reported elevated concentrations of brominated flame  
24 retardants (BFRs) in dust from indoor microenvironments. Limited information is  
25 available however on the pathways via which BFRs in source materials transfer to  
26 indoor dust. The most likely pathways hypothesised are: (a) volatilisation from the  
27 source with subsequent partitioning to dust, and (b) abrasion from everyday ‘wear and  
28 tear’ of the treated product that transfers microscopic fibres or particles to the dust.  
29 Test chambers are one method for investigating these pathways. This study reports on  
30 the development and application of an in-house test chamber for investigating BFR  
31 volatilisation from source materials and subsequent partitioning to dust. The  
32 performance of the chamber for such experiments was evaluated against that of a  
33 commercially available chamber, and inherent issues with such chambers were  
34 investigated, such as irreversible loss of BFRs to chamber surfaces (so-called “sink  
35 effects”). A sample of curtain fabric treated with hexabromocyclododecane (HBCD)  
36 was placed on a metal grid 10 cm above the chamber floor and subjected to emission  
37 testing. Concentrations of HBCD in dust placed on the chamber floor measured after  
38 the emission test, exceeded substantially those detected in the dust before the  
39 experiment. These results provide the first experimental evidence of HBCD  
40 volatilisation from a source material followed by deposition to dust.

41  
42 **Keywords**

43 Brominated flame retardants, HBCDs, PBDEs, test chambers, transfer to dust, test  
44 chamber sink effects

45

## 46 1. Introduction

47 Brominated flame retardants (BFRs) are a class of chemicals used in numerous foam,  
48 material and plastic products in a variety of indoor microenvironments (Harrad et al.,  
49 2010). Often they are incorporated via an additive process, so are loosely bound to the  
50 polymer and available for release during normal use of the product. Alternatively,  
51 some BFRs are covalently bound to the polymer matrix, and referred to as “reactive”  
52 BFRs. Elevated concentrations of BFRs have been reported in indoor air and dust,  
53 with consequent implications for human exposure (Batterman et al., 2009; Harrad et  
54 al., 2008). Correlations have been reported between putative BFR sources and BFR  
55 concentrations in indoor air and dust in several studies (Allen et al., 2008; de Wit et  
56 al., 2012; Harrad et al., 2004); however, little is known about the pathways via which  
57 BFRs migrate from treated consumer products into air and dust. The principal  
58 pathways of migration or mass transfer from treated materials into dust are  
59 hypothesised to comprise: volatilisation with subsequent deposition (or partitioning)  
60 to dust, abrasion (‘wear and tear’) of the treated product leading to direct particle or  
61 fibre transfer to dust (Wagner et al., 2013; Webster et al., 2009), and migration via  
62 direct contact between source material and dust (Takigami et al., 2008). Actual  
63 migration is likely to be a combination of these pathways, with the relative  
64 significance of each, dependent on factors such as the physicochemical properties of  
65 the BFR and the mode via which it is incorporated into the product. For example,  
66 while abrasion is likely a viable pathway for both additive and reactive BFRs; the  
67 other two pathways are likely far less facile for reactive BFRs. The use of test  
68 chambers is a potentially important strategy for investigating migration pathways of  
69 FRs to dust.

70  
71 Emission chambers have been utilised in studies for measurement of specific emission  
72 rates (SERs) of BFRs and organophosphorus flame retardants from consumer  
73 products, providing information on gas phase emissions (Rauert et al., 2014). In  
74 contrast, to the authors’ knowledge the migration of BFRs to particulates and dust has  
75 not been investigated via emission chambers; however the mass transfer of phthalates,  
76 another class of semi-volatile organic compound (SVOC), from wall paint and vinyl  
77 flooring to dust has been investigated in modified chambers (Clausen et al., 2004;  
78 Schripp et al., 2010). These studies demonstrated the migration of phthalates to dust

79 occurred via both volatilisation with subsequent deposition, and via direct transfer as  
80 a result of contact between the source material and dust.

81

82 The current study investigates the migration into dust *via* volatilisation and  
83 subsequent deposition of polybrominated diphenyl ethers (PBDEs) and  
84 hexabromocyclododecanes (HBCDs). An in-house test chamber was designed and  
85 built at the University of Birmingham. Experiments to evaluate the optimum  
86 configuration of this chamber are described, alongside its validation against a  
87 commercially available micro-emission chamber. Following validation, the in-house  
88 chamber was used to study the transfer of HBCDs from treated curtains into dust.

89

## 90 **2. Materials and Methods**

### 91 *2.1 Test chamber apparatus*

92 A cylindrical in-house designed and built test chamber was utilised at the University  
93 of Birmingham (UoB chamber), constructed from stainless steel with dimensions of  
94 10 cm diameter and 20 cm height to give a total chamber volume of 1570 cm<sup>3</sup>, and  
95 internal surface area of 785 cm<sup>2</sup>. Attachment of a Capex L2 Diaphragm Pump  
96 (Charles Austen Pumps Ltd, Surrey, UK) provided a constant air flow of 10 L min<sup>-1</sup>  
97 through the chamber, that led to an air change rate of 400 times per hour.  
98 Polyurethane foam (PUF) plugs (140 mm diameter, 12 mm thickness, 360.6 cm<sup>2</sup>  
99 surface area, 0.07 g cm<sup>-3</sup> density, PACS, Leicester, UK) were attached to the exit air  
100 vent to collect analyte emissions in both the gas and airborne particulate phases. The  
101 chamber was maintained at the desired temperature by immersion in a hot water bath  
102 with chamber internal temperature monitored using a LogTag TRIX-8 temperature  
103 data logger (LoggerShop Technology, Dorset, UK). The chamber configuration is  
104 illustrated in Figure 1. Note the inclusion of an aluminium mesh shelf situated  
105 approximately halfway down the chamber. As detailed later, this permitted separation  
106 of a BFR source from dust placed on the chamber floor.

107

### 108 *2.2 Commercially-available micro-chamber*

109 A Micro-Chamber/Thermal Extractor<sup>TM</sup> (Markes International) located at VITO  
110 (Flemish Institute for Technological Research), Belgium consisting of 6 linked  
111 chambers (Figure 2) was used for comparison with the UoB chamber. Each linked  
112 chamber, internal surfaces constructed of electropolished stainless steel, had

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113 dimensions of 4.5 cm diameter and 2.8 cm height to give a total chamber volume of  
114 44 cm<sup>3</sup>, and internal surface area of 71 cm<sup>2</sup>. A uniform heating system (20-120°C)  
115 surrounded each chamber and adjustable airflow set at 0.5 L min<sup>-1</sup> (air change rate of  
116 682 times per hour) was provided to the chambers. The addition of a PUF plug (140  
117 mm diameter, 12 mm thickness, 360.6 cm<sup>2</sup> surface area, 0.07 g cm<sup>-3</sup> density, PACS,  
118 Leicester, UK) to the exit air line, facilitated collection of emitted analytes. The  
119 micro-chambers were also fitted with a shelf mid-way to facilitate separation of the  
120 BFR source from dust.

121

### 122 *2.3 HBCD treated curtains and low level dust procurement*

123 Fabric curtains treated with the HBCD technical formulation were obtained from the  
124 National Institute for Environmental Studies (NIES), Tsukuba, Japan. Concentrations  
125 of HBCDs in these curtains were 18,000 mg kg<sup>-1</sup> for  $\alpha$ -HBCD, 7,500 mg kg<sup>-1</sup> for  $\beta$ -  
126 HBCD, and 17,000 mg kg<sup>-1</sup> for  $\gamma$ -HBCD (Kajiwara et al., 2013).

127

128 Initial source-air-dust partitioning experiments were conducted using a bulk house  
129 dust sample obtained from a private residence in Birmingham. In common with many  
130 UK dust samples, this dust contained moderately elevated concentrations of HBCDs  
131 and of BDE-209, rendering it unsuitable for experiments studying these analytes. As a  
132 result, a further bulk dust sample containing lower concentrations of PBDEs and  
133 HBCDs was collected from a private residence in Belgium. Concentrations of PBDEs  
134 and HBCDs in both dusts are provided as supplementary data (Table SD-1).

135

### 136 *2.4 Chemicals*

137 All solvents used for extraction and analysis were of HPLC grade quality (Fisher  
138 Scientific, Loughborough, UK). Standards of individual PBDEs (BDEs 47, 85, 99,  
139 100, 153, 154, 183, 209), HBCDs ( $\alpha$ -HBCD,  $\beta$ -HBCD,  $\gamma$ -HBCD), labelled <sup>13</sup>C  
140 HBCDs ( $\alpha$ -,  $\beta$ -,  $\gamma$ -), d<sub>18</sub>  $\gamma$ -HBCD and labelled <sup>13</sup>C PBDEs (BDEs 47, 99, 100, 153,  
141 209) were purchased from Wellington Laboratories (Guelph, ON, Canada). Florisil  
142 (60-100 mesh) and silica gel (60Å, 60-100 mesh) were obtained from Sigma Aldrich  
143 (Dorset, UK) with concentrated sulfuric acid procured from Merck (Darmstadt,  
144 Germany). Large glass fibre filters (GFF, 12.5 cm diameter, 1  $\mu$ m pore size, Whatman,  
145 UK) and small GFFs (4.25 cm diameter, 0.7  $\mu$ m pore size, Whatman, UK) were  
146 purchased from Agilent (UK).



147

148 *2.5 Experimental Design for investigating BFR partitioning to dust after*  
149 *volatilisation*

150 The chamber configuration for these experiments is illustrated in Figure 1b. It consists  
151 of a known mass of pre-characterised dust (200 mg) weighed onto a GFF and placed  
152 on the chamber floor. A piece of material known to contain BFRs (e.g. HBCD-treated  
153 curtain) was placed on the mesh shelf located half way down the chamber. Post  
154 experiment, the chamber was cooled at room temperature for 5 hours (with air flow  
155 still attached) to minimise loss of volatiles when opening the chamber. The dust,  
156 PUFs and GFFs were then extracted and analysed separately. All chamber inner wall  
157 surfaces were washed with 200 mL of hexane:dichloromethane (1:1 v/v) and collected  
158 for separate analysis.

159

160 *2.6 Analytical protocols*

161 *2.6.1 Sample preparation and extraction*

162 Sample extraction and purification was performed using slight modifications of in-  
163 house published methods (Abdallah et al., 2009; Abdallah et al., 2008). Dust, PUFs  
164 and GFFs were extracted with pressurised liquid extraction (ASE-350, Dionex Europe,  
165 UK). PUFs and GFFs were packed into precleaned 66 mL cells using precleaned  
166 Hydromatrix (Varian Inc., UK) to fill the void. Dust samples were loaded into pre-  
167 cleaned 66 mL cells containing 1.5 g of pre-cleaned Florisil and Hydromatrix. Each  
168 cell was spiked with 4 ng each of <sup>13</sup>C-labelled α-, β-, and γ-HBCD; 40 ng of <sup>13</sup>C-  
169 PBDE 47; 10 ng each of <sup>13</sup>C-labelled PBDE-99 and PBDE-153; and 20 ng of <sup>13</sup>C-  
170 PBDE 209 as internal (surrogate) standards prior to extraction with  
171 hexane:dichloromethane (1:1 v/v) at 90 °C and 1500 psi. The cell was heated for 5  
172 min, held static for 4 min and purged for 90 s, with a flush volume of 50%, for 3  
173 cycles.

174

175 *2.6.2 Clean up*

176 The ASE extracts and chamber inner surface solvent rinses were combined and  
177 concentrated to 0.5 mL using a Zymark Turbovap II (Hopkinton, MA, USA), then  
178 purified by loading onto SPE cartridges filled with 8 g of pre-cleaned acidified silica  
179 (44% concentrated sulfuric acid, w/w). The analytes were eluted with 30 mL of  
180 hexane:dichloromethane (1:1, v/v), with the eluate evaporated to dryness under a

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181 gentle stream of nitrogen. Samples were reconstituted to 100  $\mu\text{L}$  with 2 ng of  $\text{d}_{18}\text{-}\gamma\text{-}$   
182 HBCD and 20 ng of  $^{13}\text{C}$ -PBDE 100 in HPLC grade methanol, used as recovery  
183 standards for internal standard recovery determination.

184

### 185 2.6.3 LC-MS/MS analysis

186 Target PBDEs and HBCDs were separated and analysed using modified, in-house  
187 published methods (Abdallah et al., 2009; Abdallah et al., 2008), using a dual pump  
188 Shimadzu LC-20AB Prominence liquid chromatograph (Shimadzu, Kyoto, Japan)  
189 equipped with a SIL-20A autosampler, and a DGU-20A3 vacuum degasser. Mass  
190 spectrometric analysis was performed using a Sciex API 2000 triple quadrupole mass  
191 spectrometer (Applied Biosystems, Foster City, CA) equipped with an APPI (PBDEs)  
192 or ESI (HBCDs) ion source, operated in negative ion mode.

193

#### 194 2.6.3.1 PBDE Analysis

195 A Varian Pursuit XRS3 (Varian, Inc., Palo Alto, CA) C18 reversed phase analytical  
196 column (250 mm x 4.6 mm i.d., 3  $\mu\text{m}$  particle size) was used for separation of target  
197 PBDEs (47, 85, 99, 100, 153, 154, 183 and 209). A mobile phase programme based  
198 upon (mobile phase A) 1:1 methanol/water and (mobile phase B) 1:4  
199 toluene/methanol at a flow rate of 0.4  $\text{mL min}^{-1}$  was applied for elution of the target  
200 compounds; starting at 85% (mobile phase B), increased linearly to 100% (mobile  
201 phase B) over 20 min, and then held for 10 min. The column was equilibrated with  
202 85% (mobile phase B) for 5 min between runs. MS/MS detection, operated in MRM  
203 mode, was used for quantitative determination of the PBDE congeners based on  $m/z$   
204 420.8 $\rightarrow$ 78.8,  $m/z$  500.8 $\rightarrow$ 78.8,  $m/z$  578.8 $\rightarrow$ 78.8,  $m/z$  658.6 $\rightarrow$ 78.8,  $m/z$  486.6 $\rightarrow$ 78.8.  
205  $^{13}\text{C}$ -labelled analogues were determined based on  $m/z$  432.4 $\rightarrow$ 78.8, 512.4 $\rightarrow$ 78.8,  
206 590.6 $\rightarrow$ 78.8, and  $m/z$  494.7 $\rightarrow$ 78.8.

207

#### 208 2.6.3.2 HBCD Analysis

209 A Varian Pursuit XRS3 C18 reversed phase analytical column (150 mm x 4.6 mm i.d.,  
210 3  $\mu\text{m}$  particle size) was used for separation of target HBCDs ( $\alpha\text{-}$ ,  $\beta\text{-}$ ,  $\gamma\text{-}$ ). A mobile  
211 phase program based upon (mobile phase A) 1:1 methanol/water and (mobile phase  
212 B) methanol at a flow rate of 0.18  $\text{mL min}^{-1}$  was applied for elution of the target  
213 compounds; starting at 50% (mobile phase B), then increased linearly to 100%  
214 (mobile phase B) over 4 min, held for 5 min before decreasing linearly to 88%

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215 (mobile phase B) over 1 min. The column was equilibrated with 50% (mobile phase  
216 B) for 4 min between runs. MS/MS detection, operated in MRM mode, was used for  
217 quantitative determination of the HBCD diastereomers, <sup>13</sup>C-, and d<sub>18</sub>-labelled  
218 analogues based on *m/z* 640.4→79.0, *m/z* 652.4→79.0, and *m/z* 657.7→79 respectively.

#### 219 220 2.6.4 Quality Assurance

221 Samples were analysed using established QA/QC procedures. Method blanks were  
222 run with each batch of samples. For <sup>13</sup>C- $\alpha$ -,  $\beta$ -, and  $\gamma$ -HBCDs, average recoveries  
223 ranged from 64 to 97% while for <sup>13</sup>C-PBDE 47, 99, 153, and 209, average recoveries  
224 ranged between 69 and 80%. Accuracy and precision of the analytical method was  
225 assessed *via* replicate analyses (n=7) of NIST SRM 2585 (organics in house dust).  
226 The results of these analyses compared with indicative and certified values as  
227 appropriate are supplied as supplementary data (Table SD-2).

### 228 229 3. Results and Discussion

#### 230 3.1 Experimental design development

##### 231 3.1.1 Influence of exit air sampling train length

232 The influence of the length of polypropylene tubing carrying air exiting the chamber  
233 to the collection PUF was investigated in chamber experiments conducted at 60 °C for  
234 24 hours, to promote volatilisation. In both experiments the BFR “source” was a small  
235 GFF (4.25 cm diameter) spiked with 100 ng of each of the target BFRs. Reducing the  
236 tubing length (pictured in Figure 1a) from 15 cm to 2 cm increased the mass of all  
237 BFRs collected on the PUFs by up to 7 times. Figure 3 and Table SD-3 compare the  
238 masses collected on the PUF for both tubing lengths – with results the average of 3  
239 and 2 replicates for the 15 cm and 2 cm length tubing respectively. The substantially  
240 higher BFR masses detected on the PUF with shorter tubing length, suggests the  
241 analytes sorb strongly to the inner tubing surfaces thereby underestimating the extent  
242 of emissions via volatilisation. This is particularly relevant for chamber experiments  
243 conducted at above-ambient temperatures, which encourage volatilisation. Consistent  
244 with our data, Xu et al. (2012) reported that reducing the length of the stainless steel  
245 tube connecting their chamber to the sampling sorbent tube, increased apparent  
246 volatilisation of the phthalate DEHP from vinyl flooring. As a result of reducing the  
247 length of the connecting tube, Xu et al. (2012) found gas-phase concentrations

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248 reached steady state conditions in 20 rather than 40 days. We conclude therefore that  
249 the length of the connection between the chamber exit and the sampling sorbent  
250 should be kept to a minimum for studies of SVOCs like BFRs.

251

### 252 *3.1.2 PUF Breakthrough*

253 To test the sampling efficiency of the PUFs used to collect BFRs in chamber exit air;  
254 two PUFs were placed sequentially in a glass holder with the chamber-side end of the  
255 first collection PUF spiked with standards of native PBDEs and HBCDs  
256 (100 ng/analyte) before attachment to the chamber. The empty chamber was  
257 maintained at 60 °C to replicate an experimental scenario in which substantial losses  
258 might be expected (warm air passing through the system configuration), and air was  
259 pumped through the system for 24 hours. Post experiment, both PUFs were extracted  
260 separately and analysed. Analyte concentrations were below LOQs on the second  
261 “air-side” PUF while recoveries of analytes on the chamber-side PUF were 99±7 %.  
262 These data are clear evidence that there is no significant analyte loss via PUF  
263 breakthrough with the UoB chamber. Similar experiments were conducted with the  
264 micro-chamber and also revealed satisfactory analyte recoveries of 90±11 %.  
265 Recoveries of individual analytes are listed in Table 1.

266

### 267 *3.1.3 Sink Effects*

268 The lower vapour pressure of SVOCs affects their study in test chambers as it can  
269 lead to preferential sorption, following their volatilisation, to chamber surfaces rather  
270 than collection in gas phase emissions. The loss of analytes via sorption to chamber  
271 wall surfaces is referred to as sink effects and has been previously reported in  
272 chamber studies of SVOCs (Katsumata et al., 2008; Kemmlein et al., 2003; Uhde and  
273 Salthammer, 2006; Xu et al., 2012). We investigated the loss to such sink effects in  
274 both the UoB test chamber and the micro-chamber configurations. To do so, GFFs  
275 spiked with standards of the analytes (100 ng/analyte) were placed inside the  
276 completely sealed off chambers (no air flow), which were then heated to 60 °C for 24  
277 hours. Post experiment, whilst still sealed, both the UoB chamber and the micro-  
278 chamber were cooled to room temperature (22 °C) for 5 hours. The inner chamber  
279 surfaces were then rinsed as described in section 2.5 to assess the proportion of  
280 analytes reversibly deposited to such surfaces, and the GFF analysed to determine  
281 non-volatilised mass. Total mass recoveries of individual BFRs were then calculated

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282 as the sum of masses detected in the chamber solvent rinses, and the GFF; with the  
283 mass unaccounted for assumed to be due to loss to irreversible sorption to internal  
284 chamber surfaces (i.e. “sink effects”).

285  
286 Considerable levels of the more volatile analytes were recovered in the solvent  
287 washes of the chamber walls but 100% recovery was not obtained for any of the  
288 analytes. Table 2 lists the total % recovery of analytes in both the UoB and micro-  
289 chambers, with the proportions recovered from the chamber inner surface rinses and  
290 that remaining on the GFF reported separately. Liu et al. (2013) listed measures that  
291 can be undertaken to reduce such sink effects and minimise time for steady-state to be  
292 reached. These comprise: increasing the source surface area, decreasing the sink (i.e.  
293 chamber) surface area per volume ratio, using materials for chamber surfaces with  
294 lower sorptive capacity, and increasing the chamber air change rate. We therefore  
295 interpreted our data on loss to sink effects – which generally show a slightly greater  
296 loss for the micro-chamber - in this context.

297  
298 As the same size GFF was used in both chambers and both chamber internal surfaces  
299 were stainless steel, no differences exist in the source area or the sorptive capacity of  
300 the internal surfaces of the two chambers. In contrast, the lower surface area-to-  
301 volume ratio for the UoB chamber ( $0.5 \text{ m}^2 \cdot \text{m}^{-3}$ ) compared to the micro-chamber  
302 ( $1.6 \text{ m}^2 \cdot \text{m}^{-3}$ ) should lead to a lower sink effects loss for the UoB chamber. However,  
303 this is offset to some extent by the lower air change rate for the UoB chamber (400 air  
304 changes per hour) compared to the micro-chamber (682 air changes per hour). The  
305 ratio of the differences between these two parameters for the two chambers suggests  
306 the loss to sink effects in the micro-chamber be about twice that of the UoB chamber.  
307 Our data are broadly consistent with this, suggesting that the factors listed by Liu et al  
308 (2013) are the principal parameters governing losses to sink effects and should be  
309 taken into account in future chamber design. However, the greater losses of BDE-209  
310 in the UoB chamber highlights that other factors likely play a role.

311  
312 Other efforts were made to minimise sink effects for the UoB chamber. We first  
313 explored the impact of the sorptive capacity of the internal chamber surface. To do so,  
314 experiments were repeated in a blown glass tube (20 cm length, 3 cm diameter) to  
315 compare sink effects using glass and stainless steel surfaces, and the impact of coating

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316 the chamber interior with a Teflon spray to reduce active sorption sites was also  
317 evaluated. Improvements in analyte recovery were not observed using either glass or  
318 Teflon coated surfaces. In an attempt to reverse any sorption to chamber walls, the  
319 chamber was also heated post experiment to 80 °C for 6 hours, to volatilise analytes  
320 sorbed to chamber surfaces, but this yielded only minor improvements in analyte  
321 recovery from the chamber (an increase of 2-22%, see Table SD-4), and left up to  
322 60% of analyte mass still unaccounted for. Higher post-experiment temperatures were  
323 avoided to prevent analyte degradation or thermal stereoisomerisation of HBCDs  
324 (Heeb et al., 2008).

325  
326 To ascertain the full extent of sink effects from the stainless steel surfaces of the  
327 chamber, longer experiments of the order of months are required for attainment of  
328 steady state conditions inside the chamber, due to the slow emission rates and strong  
329 partitioning to chamber surfaces associated with SVOCs like BFRs (Xu et al., 2012).  
330 If steady state conditions are not reached then gas phase emissions and the rate of  
331 partitioning to dust may be underestimated. Our investigations suggest the UoB  
332 chamber is not constructed of low sorptive material and that over the experimental  
333 durations employed in this study, it is likely that steady state conditions are not  
334 attained. Therefore, our results are presented as an indicator of the importance of sink  
335 effects when determining SERs of BFRs and studying their migration to dust, and of  
336 the factors influencing sink effects; rather than a detailed study of partitioning to  
337 chamber interior surfaces.

### 338 339 *3.2 Partitioning of BFRs to dust using standards spiked on a GFF as the source*

340 Initial experiments evaluating the partitioning of BFRs to dust following their  
341 emission to air were conducted in both the UoB and the micro-chamber. In these  
342 experiments, a known mass of house dust (100-200 mg) was placed on a GFF on the  
343 chamber floor. Another GFF was spiked with standards of the analytes and placed on  
344 the wire mesh shelf, separated from the dust (by 5 cm in the UoB chamber and 1 cm  
345 in the micro-chamber), as the BFR ‘source’. To mimic operating conditions of  
346 electronic devices like PCs (Kemmler et al., 2003), the chamber was operated at  
347 60 °C for 24 hours; with the dust, spiked GFF and chamber surface rinses analysed  
348 separately post-experiment. BFR partitioning to dust was observed in both chambers  
349 and Figure 4 shows the post-experiment increase in PBDE concentrations in the dust.

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350 Data for the HBCDs and BDE-209 is not included as the UK house dust used in these  
351 initial experiments contained substantial concentrations of these analytes pre-  
352 experiment. The incremental concentration detected post-experiment in the dust is  
353 greater in the UoB chamber, likely due to the lower air change rate resulting in  
354 increased contact time compared to the micro-chamber. Conversely, as depicted in  
355 Figure 5, in the micro-chamber a greater proportion of the target analytes appear on  
356 the PUF with a lower proportion remaining on the GFF. Figure 5 also shows the  
357 proportion of the BFRs initially present in the “source” that is recovered in the various  
358 components of each experiment including the solvent chamber interior surface rinse.  
359 The micro-chamber was again more efficient at promoting volatilisation of BFRs  
360 which were subsequently collected on the PUF, rather than partitioning to dust, due to  
361 the micro-chamber’s comparatively higher air change rate (60% higher) and smaller  
362 volume. These result in a shorter distance between the “source” and air outlet leading  
363 to greater capture by the PUF. Note in Figures 4 and 5, the UoB chamber results are  
364 the average of 3 replicates and the micro-chamber data represent an average of 6  
365 replicates.

### 367 *3.3 Partitioning of HBCDs to dust using a HBCD treated curtain as the source*

368 Following our initial experiments using spiked GFFs as the BFR “source”,  
369 partitioning to dust was investigated as previously using a 2 x 2 cm square piece of  
370 HBCD treated curtain placed on the chamber shelf as the source. The curtains were  
371 not obtained ‘new’ from the manufacturer having been stored at -18 °C for 2-3 years  
372 prior to testing. This is relevant as other studies have reported that the age of the  
373 product tested can influence emissions of SVOCs, with emissions significantly  
374 reducing over time (Carlsson et al., 2000; Ni et al., 2007; Salthammer et al., 2003).  
375 Thus emissions from this small sub-sample may not be representative of this and  
376 similar materials generally.

377  
378 Initial experiments with the treated curtains were conducted in the UoB chamber for  
379 24 hours at 60 °C to promote volatilisation of the analytes (n=4). Further experiments  
380 (n=3) in this chamber were conducted at room temperature for 1 week, to better  
381 simulate ‘real-world’ conditions. The average increment in concentrations of HBCDs  
382 in dust under both scenarios (at 60 °C and room temperature) is depicted in Figure 6.  
383 Similarly substantial increases in HBCD concentrations in dust were observed at the

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384 end of both experiments, providing clear evidence of HBCD migration from the  
385 curtain to dust *via* volatilisation and subsequent partitioning.

386

387 Figure 6 also shows the pre- and post-experiment concentrations of HBCDs in dust  
388 when the 24 hour 60 °C experiments were conducted in the micro-chamber, using a  
389 sample of the same HBCD-treated curtain (n=6). Far greater variation in post-  
390 experiment concentrations was observed than those obtained under the same  
391 conditions using the UoB chamber. We believe this is because the source shelf in the  
392 micro-chamber placed the curtain only a very short distance (1 cm) from the entering  
393 airflow. Also the air change rate in the micro-chamber is 60% higher, resulting in a  
394 higher air velocity than in the UoB chamber. The resulting greater airflow turbulence,  
395 to which the curtain sample was exposed in the micro-chamber, caused abrasion of  
396 the curtain and the detection post-experiment of visible small fibres in the dust. Such  
397 abrasion was not reproducible and likely accounts for the more variable  
398 concentrations of HBCDs in the post-experiment dust samples. The importance of an  
399 appropriate experimental configuration is clearly shown by these results and the UoB  
400 chamber was more fit-for-purpose for these highly specific experiments.

401

#### 402 **4. Conclusions**

403 Migration of HBCDs and PBDEs from source materials to dust *via* volatilisation and  
404 subsequent deposition was demonstrated for the first time in test chamber experiments,  
405 confirming that this pathway is an important contributor to the concentrations of  
406 BFRs widely observed in indoor dust. Experimental evidence is provided that  
407 confirms sink effects are an important issue associated with chamber studies of BFRs.  
408 Moreover, this study demonstrates that chamber configuration, dimensions, and  
409 operating conditions exert substantial influences on experimental outcomes, and that a  
410 thorough understanding of such factors is essential to facilitate correct interpretation  
411 of data generated by chamber studies. Notwithstanding these issues, the ease with  
412 which volatilisation from a source followed by deposition to dust can be reproduced  
413 in test chambers, both underlines the validity of this migration pathway, and the  
414 potential for similar chamber experiments to study the migration to dust of BFRs and  
415 other SVOCs from a range of source materials *via* this and other hypothesised  
416 pathways.



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417 **Acknowledgements**

418 The research leading to these results has received funding from the European Union  
419 Seventh Framework Program (*FP7/2007-2013*) under grant agreement No 264600  
420 (INFLAME project). We also thank Natusuko Kajiwara and Hidetaka Takigami for  
421 supplying the HBCD-treated curtain samples.

422

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523 **Figures and Tables**

524

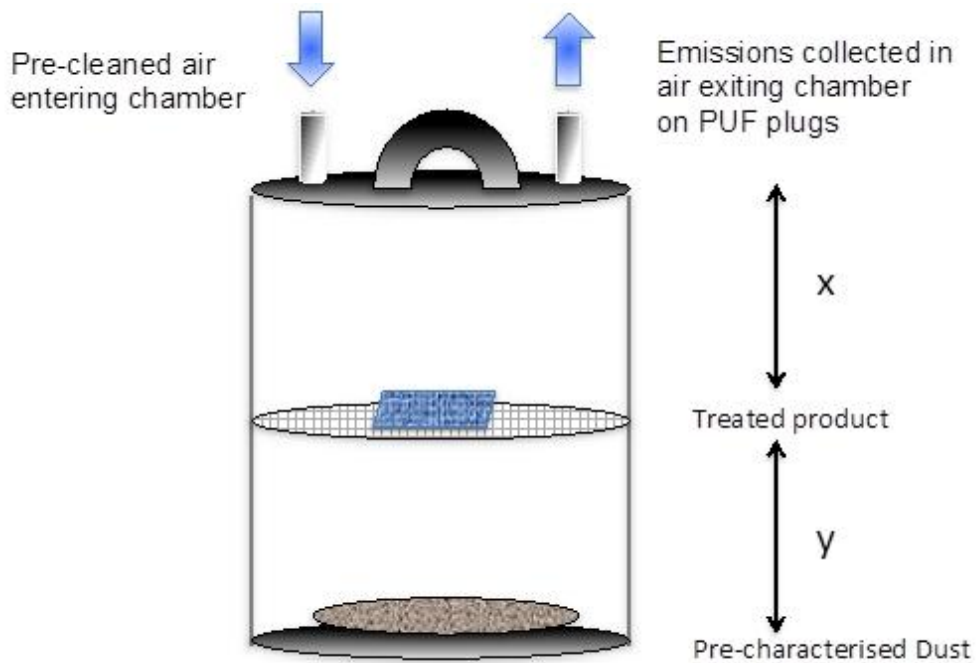
525 *Figure 1: (Top) Photograph of UoB test chamber configured for experiments*  
526 *monitoring emissions to air and (bottom) Schematic of experimental design for*  
527 *source-air-dust transfer experiments. For UoB chamber  $x,y = 10$  cm, for micro-*  
528 *chamber  $x = 1$  cm,  $y = 2$  cm.*

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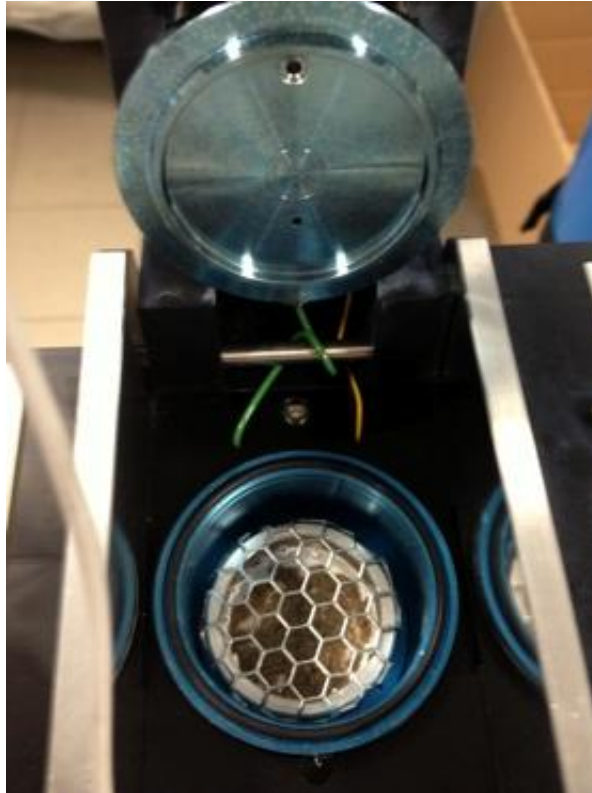


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534 *Figure 2: Photographs of the micro-chamber showing (top) Chamber modifications*  
535 *for the dust experiments, and (bottom) Experimental configuration of the 6 linked*  
536 *chambers configured for monitoring emissions to air.*



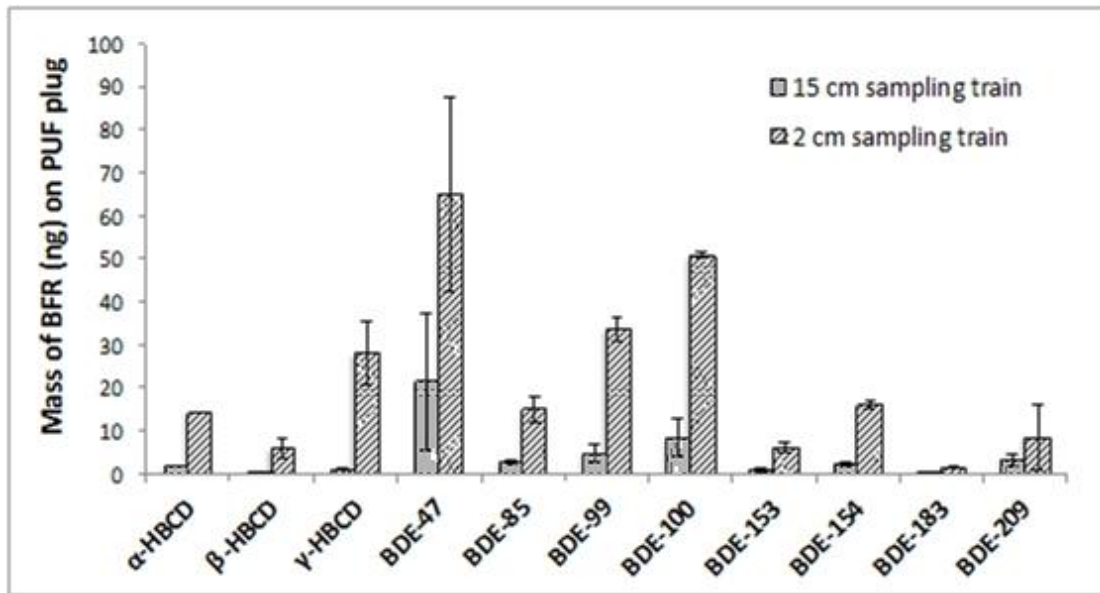
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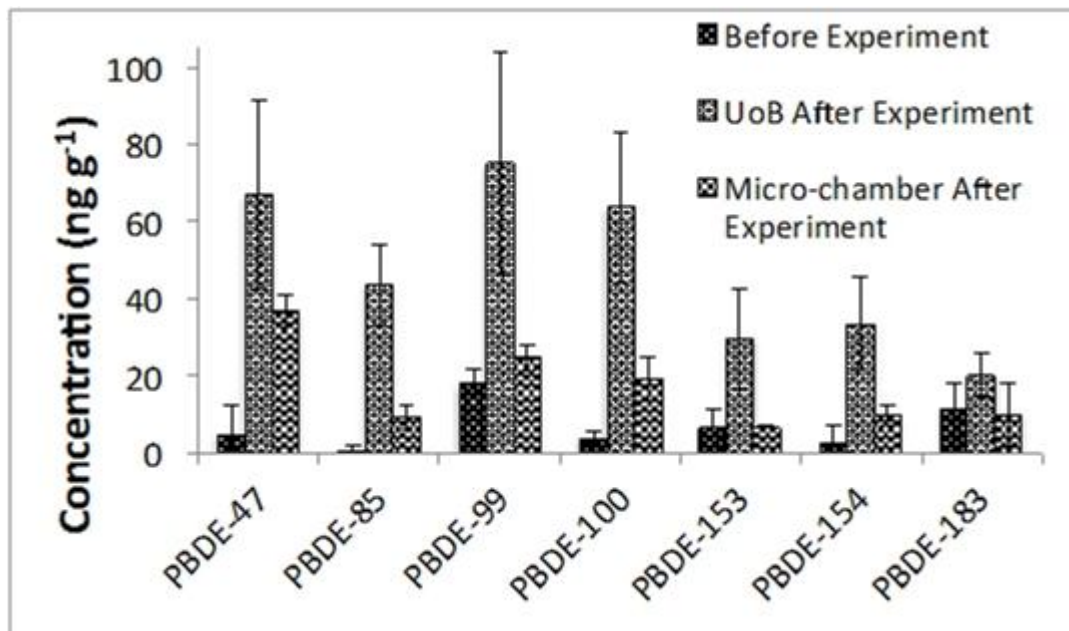
541 *Figure 3: Mass of BFR (ng) collected on PUF plugs sampling chamber exit air for*  
542 *different exit air sampling train lengths*



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546 *Figure 4: Concentrations (ng g<sup>-1</sup>) of PBDEs in dust, pre and post partitioning*  
547 *experiment in the UoB chamber (n=3) and micro-chamber (n=6) using a spiked GFF*  
548 *as the source*  
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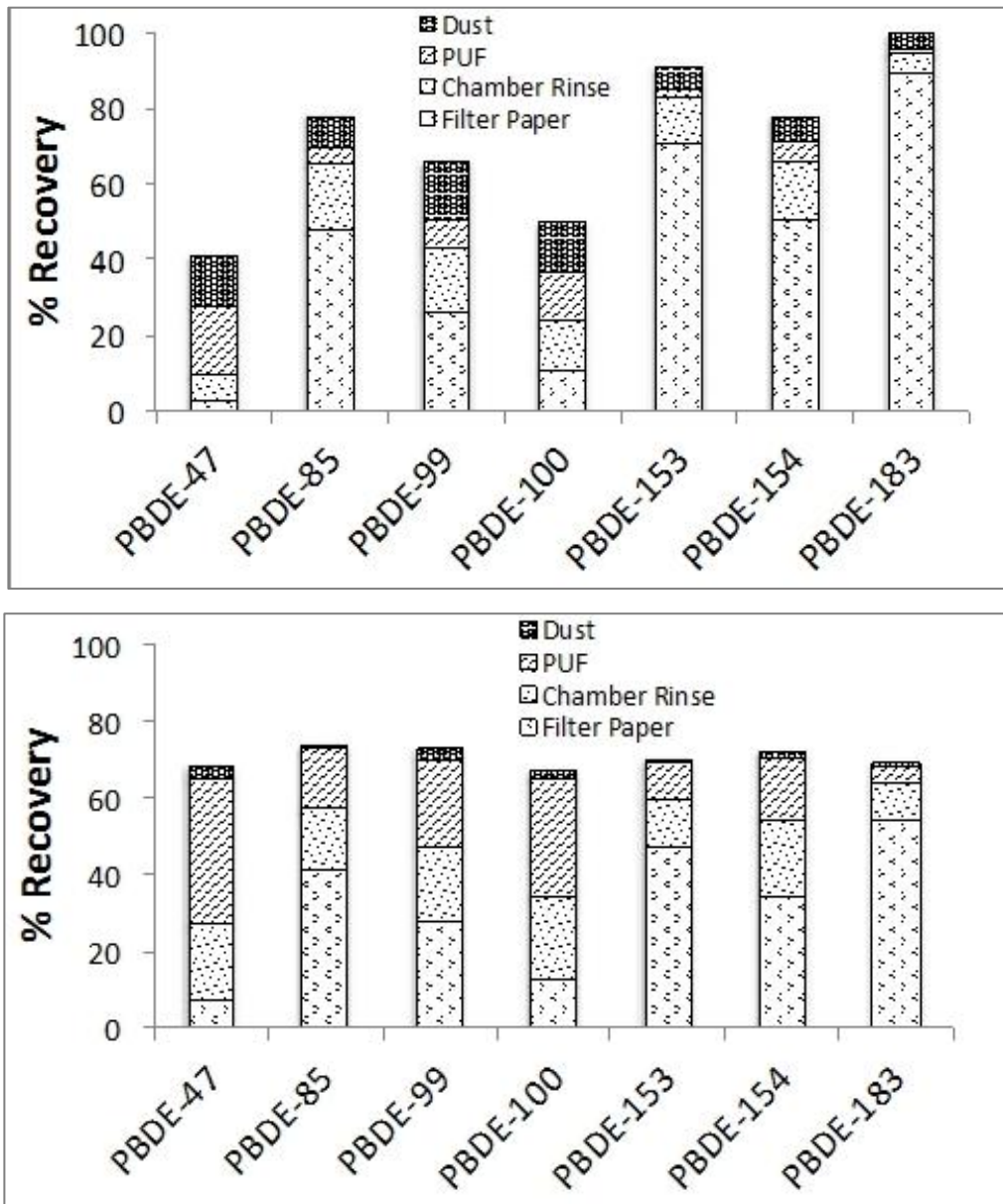


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551 Figure 5: Average recovery (%) of PBDEs in various components in (top) the UoB  
 552 chamber (n=3) and (bottom) the micro-chamber (n=6) using a spiked GFF as the  
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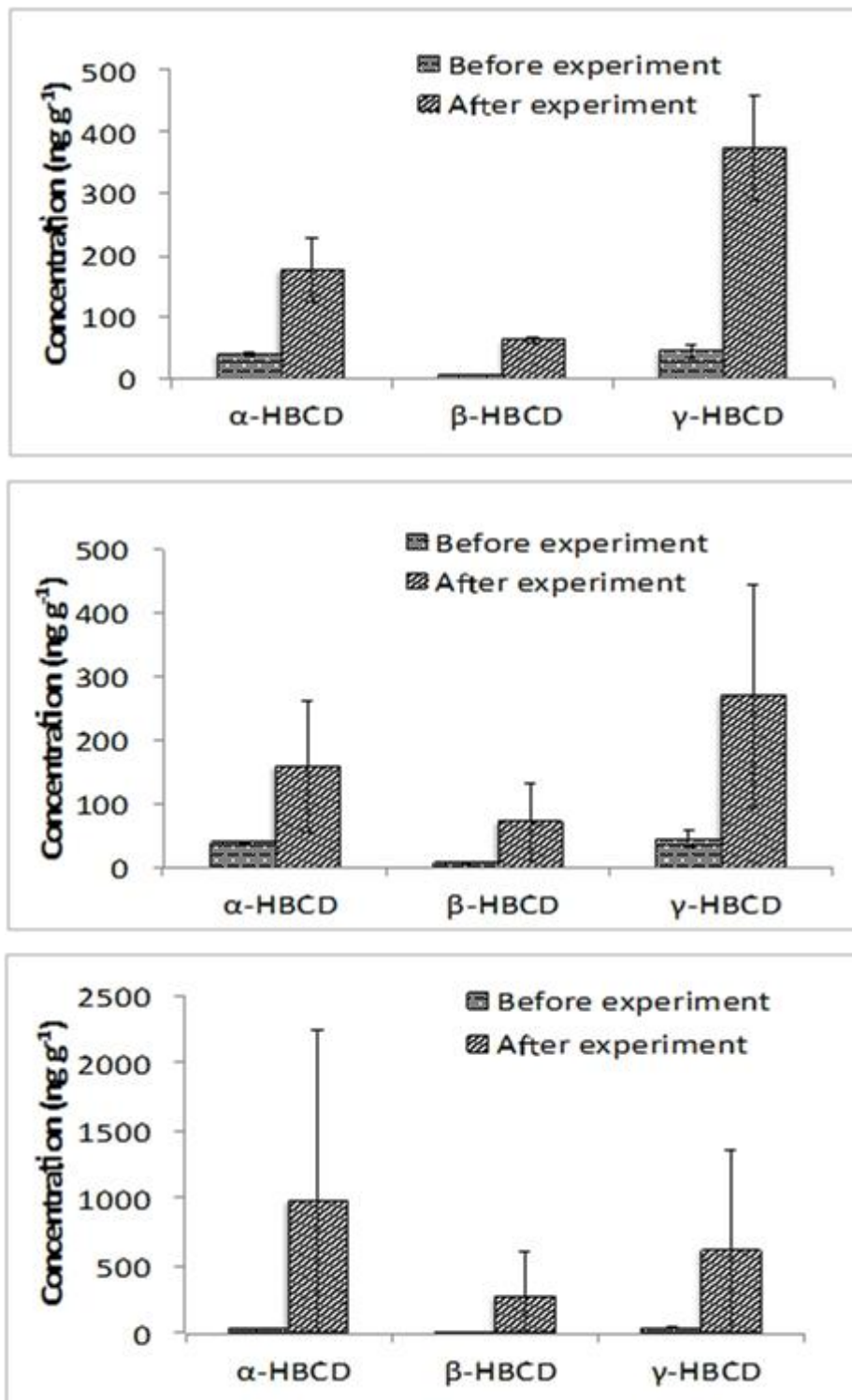
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560 *Figure 6: Concentrations of HBCDs in dust (ng g<sup>-1</sup>) pre- and post-experiments using*  
 561 *a HBCD-treated curtain as the source after: (top) 24 hours at 60 °C in the UoB*  
 562 *chamber (n=4); (middle) 1 week at room temperature in the UoB chamber (n=3), and*  
 563 *(bottom) 24 hours at 60 °C in the micro-chamber (n=6)*



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569 *Table 1: Recoveries (%) of BFRs from PUF breakthrough experiments*

	<b>BDE-47</b>	<b>BDE-85</b>	<b>BDE-99</b>	<b>BDE-100</b>	<b>BDE-153</b>	<b>BDE-154</b>	<b>BDE-183</b>	<b>BDE-209</b>	<b>α-HBCD</b>	<b>β-HBCD</b>	<b>γ-HBCD</b>
<i>Birmingham Chamber</i>	93	106	105	106	101	100	92	107	92	93	100
<i>Micro-chamber</i>	102	80	94	92	88	89	82	92	82	87	83

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571 *Table 2: Average (± standard deviation) recoveries of PBDEs and HBCDs from various components during experiments testing sink*  
572 *effects for the UoB and micro-chambers*

	<b>BDE-47</b>	<b>BDE-85</b>	<b>BDE-99</b>	<b>BDE-100</b>	<b>BDE-153</b>	<b>BDE-154</b>	<b>BDE-183</b>	<b>BDE-209</b>	<b>α-HBCD</b>	<b>β-HBCD</b>	<b>γ-HBCD</b>
<i>Total recovery (%) UoB chamber (n=1)</i>	43	52	54	51	89	78	76	90	89	70	65
<i>Total recovery (%) Micro-chamber (n=8)</i>	47 ± 14	50 ± 6.1	49 ± 8.9	46 ± 13	53 ± 9.1	51 ± 12	60 ± 6.0	97 ± 14	55 ± 22	36 ± 21	25 ± 26
<i>Recovery (%) GFF-UoB</i>	5.3	21	13	10	59	35	71	85	86	69	63
<i>Recovery (%) GFF-Micro</i>	6.2 ± 5.9	13 ± 6.0	10 ± 5.4	8.0 ± 5.2	25 ± 14	15 ± 13	45 ± 11	96 ± 14	45 ± 21	32 ± 20	20 ± 23
<i>Recovery (%) surface rinse - UoB</i>	38	32	41	41	30	43	5.6	4.3	2.6	1.0	1.8
<i>Recovery (%) surface rinse - Micro</i>	41 ± 9.8	37 ± 4.0	39 ± 5.5	38 ± 8.5	28 ± 5.7	36 ± 5.0	15 ± 5.3	1.4 ± 0.8	10 ± 3.1	4.4 ± 1.5	5.1 ± 2.9

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6 **575 Supplementary Data**

7 *576 Table SD-1: Average starting concentrations of BFRs (ng g<sup>-1</sup>) in bulk dust used for chamber experiments from 6 and 7 repeat analyses*  
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9 *577 respectively*

	<b>BDE-47</b>	<b>BDE-85</b>	<b>BDE-99</b>	<b>BDE-100</b>	<b>BDE-153</b>	<b>BDE-154</b>	<b>BDE-183</b>	<b>BDE-209</b>	<b>α-HBCD</b>	<b>β-HBCD</b>	<b>γ-HBCD</b>
<i>Birmingham House Dust (n=6)</i>	4.6 ± 7.8	0.6 ± 1.0	17 ± 4.1	4.1 ± 1.6	6.6 ± 4.6	2.5 ± 4.9	11 ± 6.7	2036 ± 551	393 ± 106	180 ± 45	2609 ± 3238
<i>Belgian House Dust (n=7)</i>	9.9 ± 11	2.0 ± 1.8	27 ± 31	4.6 ± 4.7	5.9 ± 6.1	3.1 ± 3.0	1.9 ± 2.1	230 ± 176	46 ± 19	13 ± 10	50 ± 39

16 *578*  
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18 *579 Table SD-2: Average concentrations (ng g<sup>-1</sup>) in 7 analyses of SRM 2585 and the reported certified PBDE (Stapleton et al., 2006) and*  
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20 *580 indicative HBCD values (Keller et al., 2007)*

	<b>BDE-47</b>	<b>BDE-85</b>	<b>BDE-99</b>	<b>BDE-100</b>	<b>BDE-153</b>	<b>BDE-154</b>	<b>BDE-183</b>	<b>BDE-209</b>	<b>α-HBCD</b>	<b>β-HBCD</b>	<b>γ-HBCD</b>
<i>SRM Measured Value (n=7)</i>	347 ± 39	35.1 ± 4.6	730 ± 93	133 ± 13	126 ± 13	78.6 ± 13	44.4 ± 5.0	2460 ± 400	19 ± 5.7	5.6 ± 2.2	98 ± 35
<i>Certified/Indicative Values</i>	498 ± 46	43.8 ± 1.6	892 ± 53	145 ± 11	119 ± 11	83.5 ± 2.0	43.0 ± 3.5	2510 ± 190	19 ± 3.7	4.3 ± 1.1	120 ± 22

27 *581*  
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29 *582 Table SD-3: BFR mass collected on PUFs with different air sampling train lengths and analytes recovered (%) by heating the chamber*  
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31 *583 post experiment*

	<b>BDE-47</b>	<b>BDE-85</b>	<b>BDE-99</b>	<b>BDE-100</b>	<b>BDE-153</b>	<b>BDE-154</b>	<b>BDE-183</b>	<b>BDE-209</b>	<b>α-HBCD</b>	<b>β-HBCD</b>	<b>γ-HBCD</b>
<i>PUF mass (ng) 15 cm tubing (n=3)</i>	21 ± 16	2.8 ± 0.6	4.9 ± 1.9	8.4 ± 4.5	1.0 ± 0.3	2.3 ± 0.5	0.4 ± 0.1	3.2 ± 1.4	1.9 ± 0.2	0.7 ± 0.1	1.2 ± 0.4
<i>PUF mass (ng) 2 cm tubing (n=2)</i>	65 ± 23	15 ± 2.9	34 ± 2.6	51 ± 0.8	6.3 ± 1.0	16 ± 0.7	1.5 ± 0.2	8.4 ± 7.7	14 ± 0.1	5.9 ± 2.3	28 ± 7.7

38 *584*  
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40 *585 Table SD-4: BFR recovery (%) on chamber exit PUF achieved by heating UoB chamber post-experiment to 80 °C for 6 hours*

<i>Recovery (%) (n=3)</i>	2.1 ± 1.7	8.8 ± 4.7	9.0 ± 4.9	5.6 ± 3.3	4.5 ± 1.7	6.9 ± 3.5	1.7 ± 0.9	3.0 ± 1.0	12 ± 13	4.6 ± 6.3	22 ± 29
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## Conflict of Interest Declaration

We wish to confirm that there are no known conflicts of interest associated with this publication and there has been no significant financial support for this work that could have influenced its outcome.

We confirm that the manuscript has been read and approved by all named authors and that there are no other persons who satisfied the criteria for authorship but are not listed. We further confirm that the order of authors listed in the manuscript has been approved by all of us.

We confirm that we have given due consideration to the protection of intellectual property associated with this work and that there are no impediments to publication, including the timing of publication, with respect to intellectual property. In so doing we confirm that we have followed the regulations of our institutions concerning intellectual property.

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Signed by all authors as follows:

Cassandra Rauert

 13/3/14

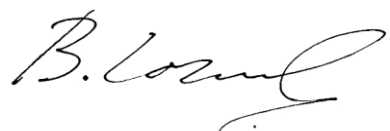
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Marianne Stranger

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Borislav Lazarov

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