

Mass transfer of PBDEs from plastic TV casing to indoor dust via three migration pathways - A test chamber investigation

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1 **TITLE**

2 Mass Transfer of PBDEs from plastic TV casing to Indoor Dust via Three Migration
3 Pathways - a Test Chamber Investigation

4
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22

23 **Abstract**

24 Polybrominated diphenyl ethers (PBDEs) are widely detected in humans with
25 substantial exposure thought to occur in indoor environments and particularly via
26 contact with indoor dust. Despite this, knowledge of how PBDEs migrate to indoor
27 dust from products within which they are incorporated is scarce. This study utilises an
28 in-house designed and built test chamber to investigate the relative significance of
29 different mechanisms via which PBDEs transfer from source materials to dust, using a
30 plastic TV casing treated with the Deca-BDE formulation as a model source.
31 Experiments at both room temperature and 60 °C revealed no detectable transfer of
32 PBDEs from the TV casing to dust via volatilisation and subsequent partitioning. In
33 contrast, substantial transfer of PBDEs to dust was detected when the TV casing was
34 abraded using a magnetic stirrer bar. Rapid and substantial PBDE transfer to dust was
35 also observed in experiments in which dust was placed in direct contact with the
36 source. Based on these experiments, we suggest that for higher molecular weight
37 PBDEs like BDE-209; direct dust:source contact is the principal pathway via which
38 source-to-dust transfer occurs.

39

40

41 **Keywords**

42 Brominated flame retardants, PBDEs, Migration pathways to dust, Test chambers

43

44 **Research Highlights**

- 45 • Transfer from a TV casing to dust of high molecular weight PBDEs examined
- 46 • Direct source:dust contact effected rapid and most substantial transfer
- 47 • Substantial source:dust transfer also occurred via abrasion of source

48 **1. Introduction**

49 Brominated flame retardants (BFRs) have numerous applications in indoor
50 environments and are found ubiquitously in indoor air and dust, leading to human
51 exposure and resultant concerns about adverse health impacts. As the majority of
52 BFRs in current use are incorporated into the product using an additive process they
53 are considered loosely bound to the product and are hence available for possible
54 migration from the treated product to dust in particular, via different mechanisms.
55 Hypothesised pathways of BFR migration to dust include: (1) volatilisation of BFRs
56 from the treated product with subsequent partitioning to dust; (2) abrasion via
57 physical wear and tear of the treated product, resulting in the transfer of particles or
58 fibres of the treated product directly to dust (Wagner et. al., 2013, Webster et. al.,
59 2009); and (3) transfer via direct contact between the treated product and dust
60 (Takigami et. al., 2008).

61
62 One of the principal classes of additive BFRs are polybrominated diphenyl ethers
63 (PBDEs), which have been in use since the 1970s (ATSDR, 2004) primarily as
64 additives in polyurethane foam (PUF); printed circuit boards and microprocessor
65 packaging in computers; thermoplastics, such as high impact polystyrene (HIPS) and
66 acrylonitrile-butadiene-styrene (ABS) copolymers; and textiles (La Guardia et. al.,
67 2006, Harrad et. al., 2008). Despite their presence at elevated concentrations in indoor
68 dust (up to 210 mg g⁻¹ of BDE-209 (Batterman et. al., 2009)), relatively little is
69 known about how PBDEs transfer to dust from goods within which they are
70 incorporated. Combined with evidence about the potential adverse health impacts of
71 PBDEs (USEPA 2008a, USEPA 2008b) this is of concern as dust has been shown to
72 be an important exposure pathway of PBDEs for toddlers who spend extended time
73 periods crawling over surfaces and display extensive hand-to-mouth contact ((Jones-
74 Otazo et. al., 2005); Stapleton et al., 2012). Moreover, it is estimated that US children
75 (1-5 years) have higher PBDE intakes than adults, and that a combination of ingestion
76 and dermal contact with indoor dust contributes 82% of overall total adult exposure of
77 tri to deca PBDEs (Lorber, 2008).

78
79
80

81 Emission chamber studies to date have focused largely on measurement of emissions
82 to air of BFRs and other semivolatile organic compounds (SVOCs) from treated
83 products (Rauert et. al., 2014c). The authors previous work has investigated the
84 migration of hexabromocyclododecane (HBCD) from a textile treated with the HBCD
85 technical formulation via migration pathways (1) and (2) (Rauert et. al., 2014a and
86 2014b), however to their knowledge the migration of PBDEs via any migration
87 pathway has yet to be studied. The mass transfer of phthalates, another class of semi-
88 volatile organic compound (SVOC), from wall paint and vinyl flooring to dust has
89 been investigated in modified chambers (Clausen et. al., 2004, Schripp et. al., 2010).
90 These studies demonstrated the migration of phthalates to dust occurred via both
91 volatilisation with subsequent partitioning to dust, and via direct transfer as a result of
92 contact between the source material and dust. This study for the first time investigates
93 experimentally, the migration of higher molecular weight PBDEs (particularly BDE-
94 209) from a model source to dust *via* three different migration pathways, using an in-
95 house test chamber. The contribution of each pathway to total PBDE dust
96 contamination is discussed, highlighting areas for future chamber experiments.

97

98 **2. Materials and Methods**

99 *2.1. PBDE treated plastic TV casing and low concentration dust procurement*

100 The model source used in this study consisted of plastic TV casing, treated with
101 PBDEs. It was received as small triangular pieces each weighing ~100 mg from the
102 National Institute for Environmental Studies (NIES), Tsukuba, Japan. The sample was
103 a composite of 50 cathode ray tube (CRT) back casings (high impact polystyrene) that
104 had been melted and remoulded to form a material for interlaboratory tests. Four
105 replicate analyses of the TV casing by NIES using methods reported previously
106 (Takigami et al, 2008), determined the concentrations of PBDEs in the sample, listed
107 in Table 1. The higher RSDs (> 20%) of some congeners suggest a degree of
108 inhomogeneity in the distribution of these compounds throughout the TV casing.

109

110 In order to more easily detect increments in PBDE concentrations in dust as a result of
111 emissions from the model source, all experiments in this study used a dust sample
112 containing low concentrations of PBDEs (Σ PBDEs = 280 ng g⁻¹). This was derived
113 from a vacuum cleaner bag taken from a private residence in Belgium in 2012 and
114 stored at -18 °C thereafter. The dust was sieved at <500 μm before homogenisation

115 via vortexing. Concentrations of PBDEs in this dust, determined from repeat (n=9)
116 analyses are provided in Table 2. The low concentration dust showed a level of
117 inhomogeneity for BDE-209 (230 ± 180 ng g⁻¹) and this may pose a limitation to this
118 study, yet due to the low concentrations present, this dust was judged suitable for this
119 study.

120

121 *2.2. Test Chamber Experiments*

122 Chamber experimental designs for investigating the migration of HBCDs *via* the first
123 two proposed migration pathways have been reported previously (Rauert et. al.,
124 2014a, Rauert et. al., 2014b). The experimental details are summarised in the
125 following section.

126

127 *2.2.1 Experimental design for investigating volatilisation with subsequent* 128 *partitioning to dust.*

129 A cylindrical in-house designed and built test chamber was utilised for these
130 investigations; constructed from stainless steel with dimensions of 10 cm diameter
131 and 20 cm height to give a total chamber volume of 1570 cm³, and internal surface
132 area of 785 cm². Attachment of a Capex L2 Diaphragm Pump (Charles Austen Pumps
133 Ltd, Surrey, UK) provided a constant air flow of 10 L min⁻¹ through the chamber.
134 This air flow provided an air exchange rate (400 times per hour) that would exceed
135 that viewed in a 'real world' scenario (in general 4 times per hour) but was used due
136 to equipment restrictions. The higher air flow may have resulted in removal of more
137 volatile congeners before partitioning to dust, thereby leading to capture on the PUF
138 plug. Polyurethane foam (PUF) plugs (140 mm diameter, 12 mm thickness, 360.6 cm²
139 surface area, 0.07 g cm⁻³ density, PACS, Leicester, UK) were attached to the exit air
140 vent to collect analyte emissions in both the gas and suspended particulate phases.
141 The chamber was maintained at the desired temperature by immersion in a hot water
142 bath with chamber internal temperature monitored using a LogTag TRIX-8
143 temperature data logger (LoggerShop Technology, Dorset, UK). The chamber
144 configuration is illustrated in Figure 1. The inclusion of an aluminium mesh shelf
145 situated approximately 10 cm above the chamber floor, allowed physical separation of
146 a 2 cm x 2 cm portion of the model source placed on the shelf from an aliquot of low
147 concentration dust (200 mg) placed on a glass fibre filter (GFF, Whatman,

148 Loughborough, UK) on the chamber floor. The chamber was sealed, with air flow,
149 and experiments run for: (a) 24 hours at 60 °C, and (b) 1 week at room temperature
150 (22 ± 1 °C). The 60 °C maximum temperature scenario was chosen to represent a high
151 emission case of an electronic item heated during operation (Kemmlin et. al., 2003).
152 Post experiment, the dust was analysed for concentrations of PBDEs.

153

154 2.2.2 *Experimental design for investigating abrasion.*

155 The test chamber was next utilised to investigate migration via abrasion of particles to
156 dust. The experimental configuration employed for this purpose is illustrated in Figure
157 2. The removable aluminium shelf was placed 3 cm above the chamber floor and a
158 magnetic stirrer bar, 40 mm x 8 mm, (Fisher Scientific, Leicestershire, UK) placed on
159 the shelf to act as the abrading mechanism. The model source was placed on the shelf
160 and a known mass of low concentration dust (200 mg) placed on a glass fibre filter
161 (GFF), situated on the chamber floor. The chamber was sealed (with air flow attached
162 to collect emissions on polyurethane foam (PUF) plugs attached to the exit air vent)
163 and placed on a magnetic stirrer plate, operated at 200 rotations per minute. In this
164 way, abrasion was replicated via direct contact between the rotating stirrer bar and the
165 treated product, with any particles thus generated, falling through the mesh shelf and
166 incorporated into the dust sample below. This process was conducted at room
167 temperature (22 ± 1 °C) to minimise volatilisation, and repeated for four experimental
168 durations of 2, 3, 24, and 48 hours. This chamber abrasion process does not map
169 directly on to real time abrasion of rigid polymeric materials like TV casing; instead it
170 is aimed at mimicking long-term abrasion from repeated wiping/moving/bumping of
171 the source product; all of which processes are likely accentuated by weathering (e.g.
172 by sunlight) over time. Consequently, results from our chamber experiments were
173 extrapolated to ‘real world’ abrasion. It was assumed that the PBDE mass transferred
174 in 5 seconds of chamber abrasion equated to mass transfer occurring during 5 seconds
175 of ‘real world’ abrasion. A ‘maximum transfer’ scenario of 5 seconds of abrasion per
176 day was used in further calculations to determine the PBDE mass transferred per year
177 from abrasion.

178

179 Post experiment the dust aliquot was analysed for concentrations of BFRs.

180

181 *2.2.3 Experimental design for investigating transfer via direct contact between source*
182 *and dust particles*

183 The chamber experimental design was modified to investigate migration pathway (3)
184 and the experimental design is illustrated in Figure 3. The aluminium mesh shelf was
185 now placed 10 cm above the chamber floor. The model source was placed on top of a
186 clean GFF situated on the shelf, and a thin layer of dust (~150 mg) placed evenly on
187 the top surface of the BFR treated product. The dust was lightly and carefully
188 sprinkled over the surface of the product using laboratory tweezers. The chamber was
189 sealed (with no air flow, to minimise disturbance of the dust) and left at room
190 temperature (22 ± 1 °C) for either 24 hours or 1 week. Post experiment the dust was
191 removed by gently agitating the source, homogenised through vortex mixing, and
192 analysed. Each time period was repeated in duplicate with the entire dust sample
193 analysed for BFRs.

194

195 *2.3. Determination of concentrations of PBDEs*

196 *2.3.1. Chemicals*

197 All solvents used for extraction and analysis were of HPLC grade quality (Fisher
198 Scientific, Loughborough, UK). Standards of PBDEs (BDE-47, 85, 99, 100, 153, 154,
199 183, 209), labelled ^{13}C -PBDEs (^{13}C -BDE 47, 99, 100, 153, 209), were acquired from
200 Wellington Laboratories (Guelph, ON, Canada). Florisil (60-100 mesh) and silica gel
201 (60Å, 60-100 mesh) were provided from Sigma Aldrich (Dorset, UK). Concentrated
202 sulfuric acid (95-97%) was obtained from Merck (Darmstadt, Germany). Glass fibre
203 filters (GFF, 12.5 cm diameter, 1 µm pore size, Whatman, UK) were purchased from
204 Agilent (UK).

205

206 *2.3.2. Sample analyses*

207 PUF and dust samples generated by test chamber experiments were extracted and
208 analysed using modified in-house methods as reported previously (Rauert et. al.,
209 2014a, Rauert et. al., 2014b). Briefly, samples were spiked with ^{13}C -PBDE analogues
210 as internal (surrogate) standards prior to pressurised liquid extraction (ASE, Dionex
211 Europe, UK, ASE 350) with hexane:dichloromethane (1:1 v/v). After clean-up of the
212 crude extracts via elution through sulfuric acid-impregnated silica (44% w/w), the
213 eluates were evaporated and made up to 100 µL using ^{13}C -BDE 100 in methanol, as a

214 recovery determination (or syringe) standard. Analyte separation was achieved with a
215 Varian Pursuit XRS3 (Varian, Inc., Palo Alto, CA) C18 reversed phase analytical
216 column (250 mm x 4.6 mm i.d., 3 μm particle size). Analysis was conducted with a
217 dual pump Shimadzu LC-20AB Prominence liquid chromatograph (Shimadzu, Kyoto,
218 Japan) equipped with a SIL-20A autosampler, and a DGU-20A3 vacuum degasser.
219 Mass spectrometric analysis was performed using a Sciex API 2000 triple quadrupole
220 mass spectrometer (Applied Biosystems, Foster City, CA) equipped with an APPI ion
221 source, operated in negative ion mode.

222

223 *2.4. Quality Assurance*

224 Samples were analysed using established QA/QC procedures. Method blanks were
225 conducted by extracting a pre-cleaned 66 mL cell filled with Hydromatrix and were
226 run with each batch of samples, and a clean PUF was extracted for a PUF blank.
227 Concentrations of all target PBDEs in all blanks were <LOQs. Method LOQs were
228 calculated assuming 0.2 g of dust (calculated as ng g^{-1}) or as ng per PUF/chamber
229 rinse and was calculated as the concentration relating to a 10:1 signal to noise ratio.
230 For ^{13}C BDE-47, 99, 153 and 209, average recoveries ranged from 80 to 85%.
231 Accuracy and precision of the analytical method was assessed via replicate analyses
232 ($n=15$) of NIST SRM 2585 (organics in house dust). The results of these analyses
233 compared with certified values as appropriate are supplied as supplementary data
234 (Table SD-1). Experimental data is presented as mean values of replicate experiments
235 \pm standard deviations.

236

237 **3. Results and Discussion**

238 *3.1. Test chamber experiments examining source-to-dust transfer via volatilisation* 239 *and subsequent partitioning to dust*

240 For the experiments conducted to examine transfer of PBDEs to dust via volatilisation
241 from the model source and subsequent partitioning to dust, concentrations of PBDEs
242 in the dust both pre and post experiment combined with masses detected on air exit
243 PUFs and in chamber inner surface solvent rinses are given in Table 2. A clear
244 increase in PBDE concentrations in dust, post experiment, was not observed in these
245 experiments, with the exception of experiment 2 conducted over 24 h at 60 $^{\circ}\text{C}$.
246 Moreover, PBDEs were not detected above LOQs (0.8 to 4.5 ng per PUF) on the PUF,

247 at either temperature, and only minor quantities were detected in the chamber surface
248 rinses. These PUF and chamber rinse results further suggest that the PBDEs are not
249 volatilising from the TV casing in this chamber configuration. We have previously
250 reported on experiments (Rauert et. al., 2014a) using the same experimental
251 configuration but in which the model source was a filter paper spiked with 100 ng
252 each of BDEs 47, 99 and 100. In contrast to our observations when TV casing
253 material was the model source, these earlier experiments revealed clear increments in
254 post-experiment concentrations of these congeners in dust, even though lower
255 concentrations were studied in the chamber in these filter paper experiments.
256 Specifically, the masses of BDE-47, 99 and 100 present in the model source in the
257 current experiments were 390, 960 and 330 ng respectively (up to ~10 times higher
258 concentration than in the spiked filter paper experiments). A plausible explanation for
259 these different outcomes is that PBDEs are more strongly bound to the TV casing than
260 they are to the GFF, and are hence less available for volatilisation. Moreover, the
261 melting and remoulding process used to produce the material tested may also have
262 influenced the strength with which the PBDEs are bound to the polymer. In addition,
263 the greater surface area:volume ratio of the GFF will likely contribute in more facile
264 volatilisation of PBDEs.

265

266 Although BDE-209 was detected in dust post-experiment in each experiment; in 3 out
267 of 4 cases, concentrations were not substantially different to those present in the dust
268 pre-experiment. This suggests that migration of BDE-209 from the TV casing to dust
269 via this pathway was minimal. However, the second chamber experiment conducted
270 for 24 hours at 60 °C reveal a sizeable increment in the BDE-209 concentration in the
271 dust post-experiment (4800 ng g⁻¹) compared to the starting concentration (230 ± 180
272 ng g⁻¹). A possible explanation is that the dust in this experiment was contaminated as
273 a result of abrasion of the model source brought about by the air flow within the
274 chamber. Although an increment was only observed for BDEs 183 and -209 in this
275 specific experiment, this is likely because of the much lower concentrations of other
276 target PBDEs in the TV casing, such that any casing particles transferred would make
277 a negligible impact on dust concentrations. We have reported a similar effect in
278 chamber experiments examining HBCD transfer from a fabric source to dust (Rauert
279 et al., 2014b). However, we recognise that such air flow induced abrasion is less
280 likely for the TV casing studied here. In conclusion, these chamber experiments

281 suggest that migration from plastic TV casing to dust, of PBDEs consistent with
282 treatment with the Deca-BDE formulation via volatilisation and subsequent
283 partitioning to dust is minimal. We emphasise however, that our earlier work (Rauert
284 et al., 2014b) suggests strongly that such migration will likely be substantial from
285 source materials containing elevated concentrations of PBDEs more volatile than
286 those present in the material tested here, in which BDE-209 predominated.

287

288 *3.2. Test chamber experiments for abrasion of particles to dust*

289 Table 3 shows the concentrations of target PBDEs detected in dust following the
290 experiments described in section 2.1.2, in which source-to-dust transfer via source
291 abrasion was examined. Post experiment there was a clear increase in concentrations
292 of BDE-183 and BDE-209 in dust in each experiment conducted over all time
293 intervals studied. Discernible increases in concentration were also observed for BDEs-
294 153 and 154 in 2 out of 4 experiments. Concentrations of other target PBDEs were not
295 discernibly higher post-experiment in any instance.

296

297 In contrast to the outcome of our previously reported abrasion experiments using
298 HBCD treated curtains as the source (Rauert et. al., 2014b); there was no apparent
299 relationship between abrasion duration and concentration of either BDE-183 or -209.
300 This is likely attributable to the inherently inconsistent nature of the abrasion process.
301 Specifically, it was particularly difficult in our experiments to abrade the TV casing
302 pieces in a reproducible fashion, as they had a tendency to ‘flick’ around the chamber.
303 Evidence that the increment observed in concentrations of some PBDEs in dust during
304 these experiments is attributable to abrasion of the TV casing source is provided by
305 comparison of congener patterns in the TV casing and the dust both pre- and post
306 experiment. To facilitate this, the concentrations of PBDEs detected in each sample
307 were log-transformed (to permit clearer visual comparison of the contributions of less
308 abundant congeners) and expressed as percentage contributions to the sum of PBDEs
309 Figure 4 compares the relative contributions of BDE-209 and BDE-183 in each
310 sample in all four experiments, showing a similar pattern in the chamber generated
311 abrasion dust samples to that in the TV casing, that differs from that in the dust pre-
312 experiment. The similarity between congener profiles in the TV casing and post-
313 experiment dust samples, that both differ from that observed in the dust pre-

314 experiment, provide strong evidence that PBDEs have entered dust as a result of
315 abrasion of small particles of the TV casing.

316

317 Our results also indicate that abrasion of the plastic material will not result in a linear
318 relationship between abrasion time and PBDE concentration transferred to dust. The
319 resultant PBDE mass transferred will be highly dependent on the size and PBDE
320 concentration of the particles transferred during the abrasion process. As reported in
321 our previous findings (Rauert et. al., 2014b) BDE-209 containing polymer particles
322 observed in sampled indoor dust varied in measurable size from 30 to 250 μm in
323 length. When coupled with the forensic microscopy investigation of 'real' dust
324 samples reported previously (Rauert et. al., 2014b), our results suggest that abrasion
325 of plastic fragments into dust is a feasible and important migration pathway.

326

327 As highlighted earlier in 2.2.2, the abrasion induced in these test chamber experiments
328 does not represent realistic abrasion from e.g 24 hour use of a TV, as this method is
329 highly rigorous. However, we have interpreted these results as an acceleration test to
330 mimic long-term abrasion. To achieve this aim an estimate of possible abrasion time
331 of a TV casing needs to be made. Abrasion can occur from wiping/cleaning the
332 product but it is likely that for TV casing abrasion would be further encouraged from
333 degradation of the polymer due to high product operation temperatures (at least 60 $^{\circ}\text{C}$
334 (Kemmlin et. al., 2003)), or UV degradation encouraged by direct sunlight exposure,
335 hence relating chamber results to the 'real world' is difficult.

336

337 In the maximum PBDE mass transferred abrasion scenario, it was assumed TV
338 abrasion occurred for about 5 seconds a day, which included cleaning (such as
339 wiping) and enhanced polymer degradation leading to increased abrasion. The 2 hour
340 chamber abrasion experiment may thus represent house dust concentration increment
341 from abrasion over 1440 days (~4 years), where dust is contaminated with 22 000 μg
342 of BDE-209 (the mass transferred during the 2 hour abrasion experiment), equating to
343 5400 μg of BDE-209 contamination per year. Other product uses of BFR treated
344 plastics (such as computer keyboards) that have higher user contact time periods
345 would be expected to suffer even more extensive abrasion. There are many
346 uncertainties associated with these calculations, including the assumption that

347 abrasion via contact with a rotating stir bar is representative of ‘real world’ abrasion.
348 While acknowledging such uncertainties, the abrasion induced in these chamber
349 experiments represents a first attempt to imitate migration via abrasion from a product
350 treated with BFRs into dust and relate the migration to a ‘real world’ scenario.
351 Abrasion will also depend on factors such as: the product material (e.g. plastic or
352 fabric), how and how often the product is used, as well as its age and extent to which
353 it is exposed directly to UV light and consequent weathering. We conclude from our
354 studies that the ease with which abrasion can be replicated in these chamber
355 experiments, suggests it is a feasible migration pathway.

356

357

358 *3.3. Test chamber experiments for direct contact between source:dust*

359 Table 4 presents the concentrations of PBDEs detected in dust both before and after
360 experiments examining source-to-dust transfer as a result of direct contact (section
361 2.1.3). The average BDE-209 concentration present in dust after the two different
362 exposure durations examined, reveal greater mass transfer after 1 week (4,900 ng g⁻¹),
363 than after 24 hours (820 ng g⁻¹). This suggests that BDE-209 has not reached
364 source:dust equilibrium after 1 day of source:dust contact. While more detailed work
365 is required to characterise the kinetics of such transfer, this observation has practical
366 implications, as it implies that frequent cleaning to remove dust from source surfaces
367 will minimise contamination of dust. Also of interest, replicate experiments for each
368 exposure duration show large variations in concentrations of PBDEs in dust (590-
369 1000 and 1000-8700 ng g⁻¹ for 24 hours and 1 week of exposure respectively). This
370 may be due to an inhomogeneous distribution of PBDE concentration across the
371 surface of the source in contact with dust; and/or as a consequence of an
372 inhomogeneous distribution of the organic carbon content of the exposed dust.

373

374 Figure 5 shows the PBDE congener pattern (expressed as percentage contributions to
375 log-normalised Σ BDEs) in the dust post-experiment compared with that in the TV
376 casing and in the dust pre-experiment. Due to the lower concentrations in the second
377 24 hour duration experiment, only BDE-209 was detected, hence this experiment is
378 not included in this comparison. A similar congener profile was seen in post-
379 experiment dust and the TV casing, that differed from that in the dust pre-experiment.

380 These findings provide further evidence of substantial source-to-dust transfer of
381 PBDEs in these experiments.

382

383 The physical processes effecting migration of SVOCs between source and dust via
384 direct contact are not completely understood. However, Schripp et. al. (2010)
385 suggested SVOC transfer occurs as a result of contact between dust and gas phase
386 contaminants present in the boundary layer directly above the source. Compounds
387 with lower vapour pressures will be less abundant in this layer (and experience a
388 slower release into the boundary layer to replace mass sorbed by dust) leading to
389 lower mass transfer. Such a transfer mechanism would lead to congener ratios in post-
390 experiment dust that would be enriched in more volatile PBDEs compared to the
391 pattern present in the source. While more evidence is required to fully evaluate the
392 mechanisms via which source-to-dust transfer of PBDEs occurs via direct source:dust
393 contact, inspection of Figure 5 presents it is not consistent with the hypothesis of
394 Schripp et. al. (2010). An alternative explanation – advanced by Clausen et. al. (2004)
395 - is that transfer may occur as a consequence of direct contact between the source and
396 dust particles. In this scenario, the role of the boundary layer is replaced by the dust
397 particles, and the influence of vapour pressure is minimised. This explanation appears
398 more consistent with our experimental observations.

399

400 Only a few studies have investigated BFR concentrations in dust samples removed
401 from putative sources in indoor microenvironment studies. Prominent amongst these,
402 the study by Takigami et. al. (2008) reported elevated concentrations of BDE-209 in
403 dust sampled directly from the back casings of various TVs compared to that in the
404 surrounding floor dust. The components of the TV were also analysed for PBDEs,
405 with BDE-209 the dominant congener in the rear plastic cabinets of the TVs and in all
406 dust samples. As the congener profile in the dust sampled from the TV was similar to
407 that in the TV components it was strongly suggested that extensive PBDE transfer
408 occurred directly from the components in the TV casing to the dust, a similar finding
409 to that seen in these chamber experiments. The rapid transfer and high PBDE masses
410 transferred to dust further confirm that direct contact between dust and source
411 materials is a potentially important pathway of BFR migration to dust, particularly for
412 the low volatility BDE-209.

413

414 *3.4. Comparison of three migration pathways*

415 The migration of BDE-209 to dust in indoor microenvironments is strongly
416 influenced by the abrasion and direct contact migration pathways. In contrast,
417 volatilisation with subsequent partitioning to dust appears to exert little influence over
418 mass transfer. This result is expected as the very low vapour pressure of BDE-209
419 implies it will undergo minimal volatilisation. The abrasion chamber configuration
420 was successful in abrading a plastic matrix containing PBDEs, with elevated
421 concentrations detected in dust after as little as 2 hours of abrasion. The direct contact
422 experiments transferred highly elevated concentrations to dust and the majority of the
423 transfer was achieved in the first 24 hours of exposure.

424

425 In conclusion, while further experiments are required, this study provides evidence
426 that under ‘real world’ scenarios, migration of BDE-209 to dust is likely due to a
427 combination of the three migration pathways reported here. Our study highlights areas
428 requiring future research. We recognise that the experimental conditions examined
429 here do not necessarily represent ‘real-world’ scenarios and hence results are
430 presented as a preliminary indication of the relative importance of different pathways
431 via which BDE-209 undergoes source-to-dust transfer. Future studies should also
432 investigate a range of organic flame retardants, both those of higher volatility as well
433 as those incorporated reactively as the relative importance of the pathways examined
434 here will likely vary substantially from that observed here for additive, low volatility
435 PBDEs.

436

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441 the National Institute for Environmental Studies, Japan, for supplying the PBDE-
442 treated plastic TV casing.

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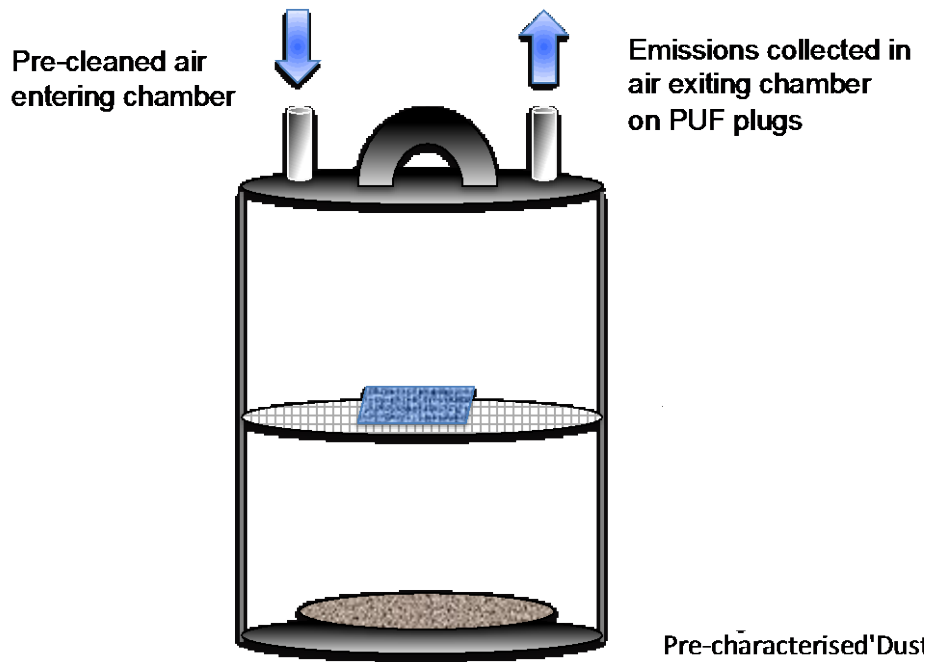
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511 **Figures and Tables**

512

513 *Figure 1: Schematic of test chamber configuration for volatilisation with subsequent*
514 *partitioning to dust experiments.*

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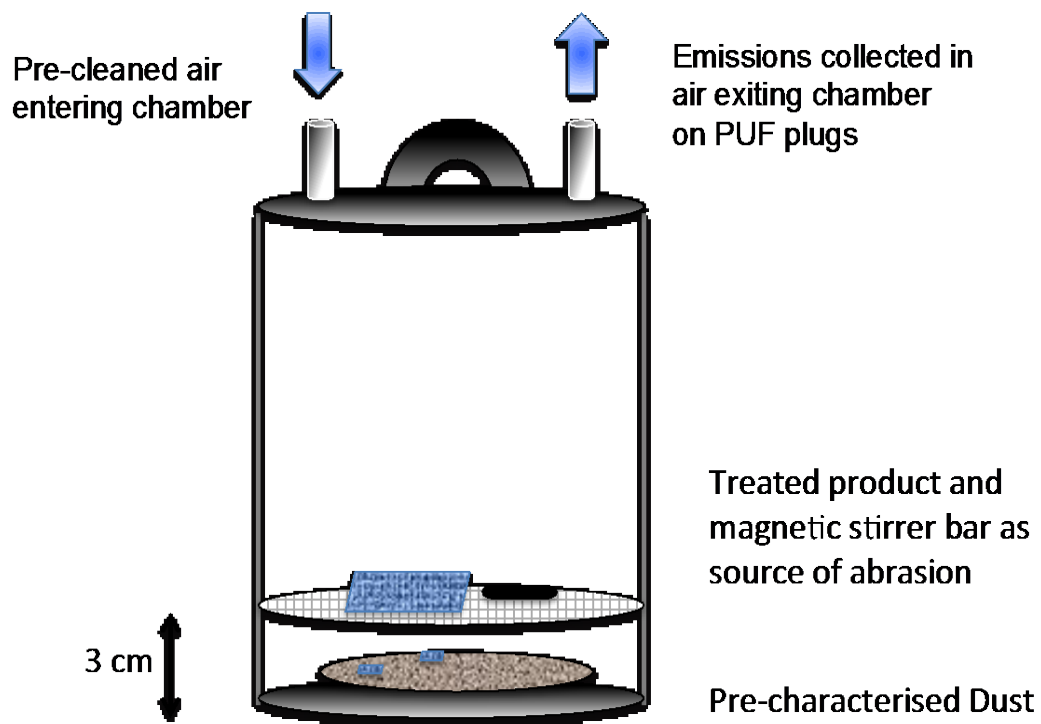
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Figure 2: Schematic of test chamber configuration for abrasion experiments

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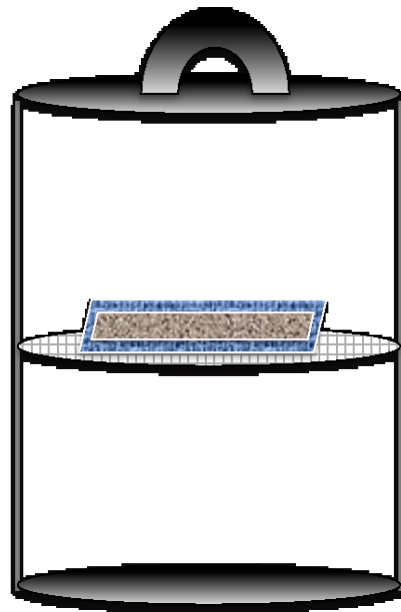


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522 *Figure 3: Schematic of test chamber configuration for direct contact between source*
523 *and dust experiments.*

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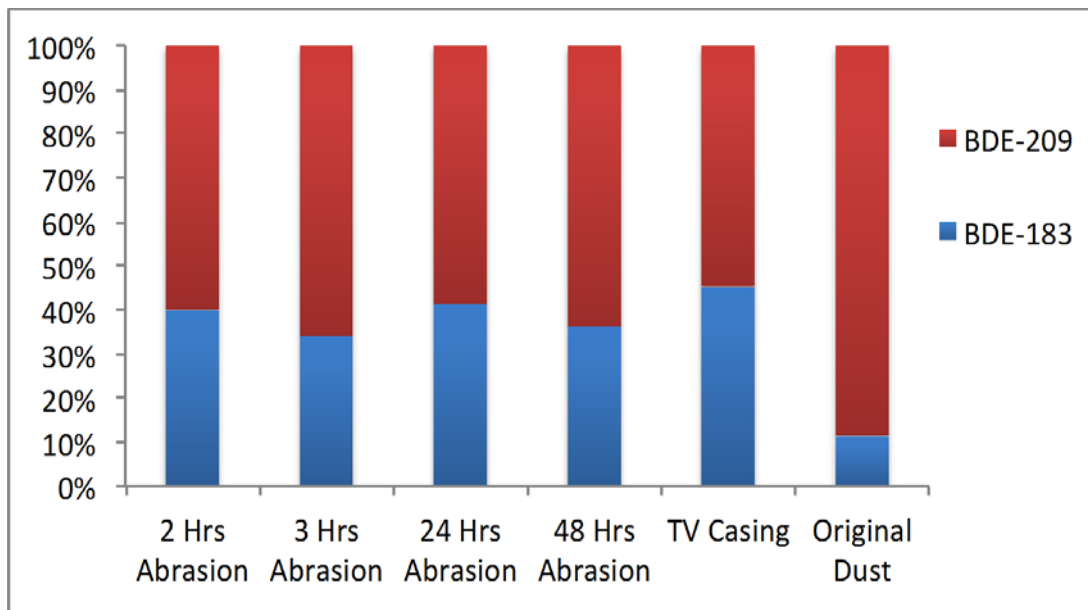
**Pre characterised dust
layered on top of BFR
source material**

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528 *Figure 4: Relative contributions (%) of BDE-209 and 183 in the four chamber*
529 *generated abrasion dust samples, the original TV casing and the low concentration*
530 *dust pre-experiment, derived from log-normalised concentrations*



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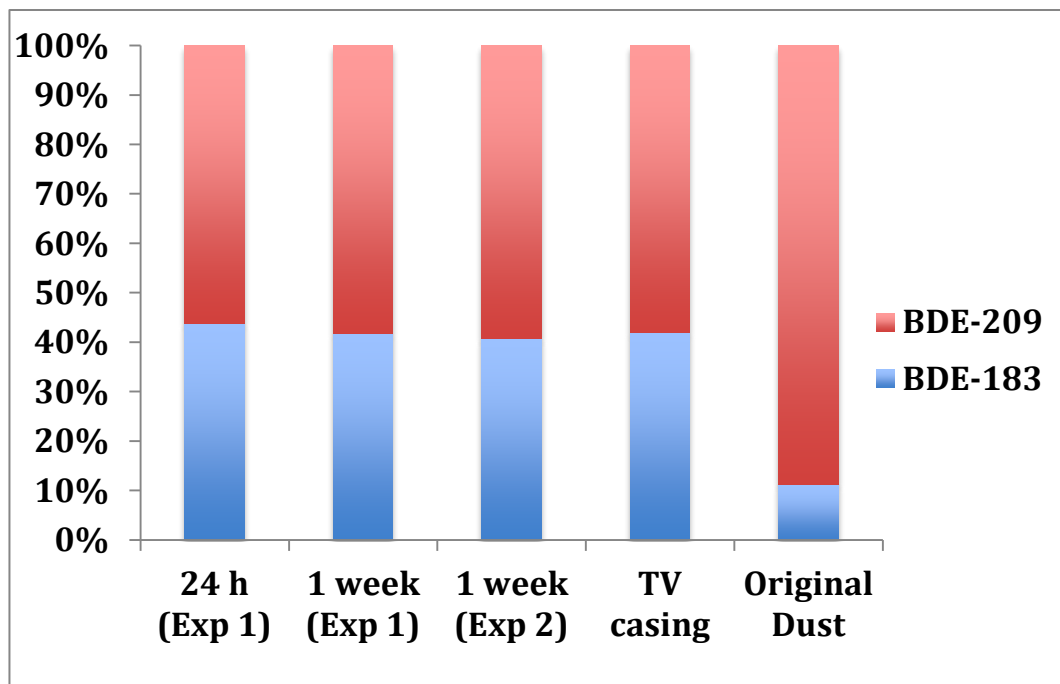
Figure 5: Relative contributions (%) of BDE-209 and 183 in direct contact

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experiment generated dust samples, the original TV casing and the low concentration

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dust pre-experiment, derived from log-normalised concentrations



541

542 *Table 1: PBDE concentrations ($\mu\text{g g}^{-1}$) and %RSD of 4 analyses of the Plastic TV*
543 *back casing used as the model source in this study*

544

| Analyte | Concentration ($\mu\text{g g}^{-1}$) | %RSD |
|----------------|--|-------------|
| BDE-47 | 1.3 | 15 |
| BDE-85 | N/A | N/A |
| BDE-99 | 3.2 | 27 |
| BDE-100 | 1.1 | 39 |
| BDE-153 | 520 | 26 |
| BDE-154 | 59 | 22 |
| BDE-183 | 3 700 | 21 |
| BDE-209 | 90 000 | 19 |

545

* N/A = not analysed

546

547 *Table 2: Concentrations of PBDEs (ng g⁻¹) in dust pre (n=9) and post volatilisation experiments and mass of PBDEs (ng) collected on PUFs*
 548 *and in chamber solvent rinses, under two temperature scenarios*

| | | BDE-47 | BDE-85 | BDE-99 | BDE-100 | BDE-153 | BDE-154 | BDE-183 | BDE-209 |
|--------------------------|---|----------------|---------------|----------------|----------------|----------------|----------------|----------------|------------------|
| | <i>Pre experiment (ng g⁻¹)</i> | <i>10 ± 11</i> | <i>2 ± 2</i> | <i>27 ± 31</i> | <i>5 ± 5</i> | <i>6 ± 6</i> | <i>3 ± 3</i> | <i>2 ± 2</i> | <i>230 ± 180</i> |
| 24 Hours at 60 °C | | | | | | | | | |
| Experiment 1 | Dust (ng g ⁻¹) | <4.5 | <0.8 | 1.8 | <0.7 | 4.1 | <1.8 | 14 | 210 |
| | PUF (ng) | <4.5 | <0.8 | <0.8 | <0.7 | <1.3 | <1.8 | <1.0 | <1.2 |
| | Chamber Rinse (ng) | <4.5 | <0.8 | 2.2 | <0.7 | 3.8 | <1.8 | 11 | 270 |
| Experiment 2 | Dust (ng g ⁻¹) | <4.5 | <0.8 | 2.1 | <0.7 | <1.3 | <1.8 | <1.0 | 4800 |
| | PUF (ng) | <4.5 | <0.8 | <0.8 | <0.7 | <1.3 | <1.8 | <1.0 | <1.2 |
| | Chamber Rinse (ng) | <4.5 | <0.8 | <0.8 | <0.7 | 1.8 | <1.8 | 5.6 | 55 |
| 1 week at 22 °C | | | | | | | | | |
| Experiment 1 | Dust (ng g ⁻¹) | <4.5 | <0.8 | 1.5 | <0.7 | <1.3 | <1.8 | <1.0 | 230 |
| | PUF (ng) | <4.5 | <0.8 | <0.8 | <0.7 | <1.3 | <1.8 | <1.0 | <1.2 |
| | Chamber Rinse (ng) | <4.5 | <0.8 | <0.8 | <0.7 | <1.3 | <1.8 | 6.8 | 340 |
| Experiment 2 | Dust (ng g ⁻¹) | <4.5 | <0.8 | 1.5 | <0.7 | <1.3 | <1.8 | 2.0 | 120 |
| | PUF (ng) | <4.5 | <0.8 | <0.8 | <0.7 | <1.3 | <1.8 | <1.0 | <1.2 |
| | Chamber Rinse (ng) | <4.5 | <0.8 | <0.8 | <0.7 | <1.3 | <1.8 | 3.7 | 150 |

549 *NB: LOQs calculated as the concentration relating to a 10:1 signal:noise ratio*

550 *Table 3: Concentrations (ng g⁻¹) in dust pre experiment and post experiment for four*
 551 *different abrasion experimental durations*

| | Pre-experiment (ng g ⁻¹) | 2 hours (ng g ⁻¹) | 3 hours (ng g ⁻¹) | 24 hours (ng g ⁻¹) | 48 hours (ng g ⁻¹) |
|----------------|--|---|---|--|--|
| BDE-47 | 10 ± 11 | <4.5 | <4.5 | <4.5 | <4.5 |
| BDE-85 | 2 ± 2 | <0.8 | <0.8 | <0.8 | <0.8 |
| BDE-99 | 27 ± 31 | 3.2 | 1.9 | 17 | 2.5 |
| BDE-100 | 5 ± 5 | <0.7 | <0.7 | <0.7 | <0.7 |
| BDE-153 | 6 ± 6 | 120 | <1.3 | 520 | 7.5 |
| BDE-154 | 3 ± 3 | 12 | <1.8 | 93 | <1.8 |
| BDE-183 | 2 ± 2 | 1100 | 41 | 3100 | 240 |
| BDE-209 | 230 ± 180 | 37 000 | 1300 | 91 000 | 15 000 |

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554 *Table 4: Mean ± SD concentrations (ng g⁻¹) of PBDEs in dust pre experiment and*
 555 *maximum and minimum concentrations (ng g⁻¹) in dust post direct contact experiment*
 556 *for 24 hours and 1 week exposure (n=2)*

| | Pre experiment (ng g⁻¹) | 24 hours (ng g⁻¹) | 1 week (ng g⁻¹) |
|----------------|---|-------------------------------------|-----------------------------------|
| BDE-47 | 10 ± 11 | <4.5 | <4.5 |
| BDE-85 | 2 ± 2 | <0.8 | <0.8 |
| BDE-99 | 27 ± 31 | <0.8 | <0.8 |
| BDE-100 | 5 ± 5 | <0.7 | <0.7 |
| BDE-153 | 6 ± 6 | (<1.3, 20) | (29, 65) |
| BDE-154 | 3 ± 3 | <1.8 | <1.8 |
| BDE-183 | 2 ± 2 | (<1.0, 220) | (140, 500) |
| BDE-209 | 230 ± 180 | (590, 1000) | (1000, 8700) |

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*Table SD-1: Mean ± standard deviation of PBDEs in SRM 2585, %RSD and
Certified values*

| Analyte | Measured mean ± Standard Deviation (n = 15) | % RSD | Certified Value (SRM2585, NIST) |
|----------------|--|--------------|--|
| BDE-47 | 438 ± 59 | 13.6 | 498 ± 46 |
| BDE-85 | 37.7 ± 5.0 | 13.3 | 43.8 ± 1.6 |
| BDE-99 | 817 ± 61 | 7.4 | 892 ± 53 |
| BDE-100 | 140 ± 12 | 8.6 | 145 ± 11 |
| BDE-153 | 124 ± 15 | 12.0 | 119 ± 1 |
| BDE-154 | 76.7 ± 10 | 13.6 | 83.5 ± 2.0 |
| BDE-183 | 42.4 ± 5.9 | 14.0 | 43.0 ± 3.5 |
| BDE-209 | 2410 ± 300 | 12.3 | 2510 ± 190 |

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Reference:

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