

# Extent and mechanisms of brominated flame retardant emissions from waste soft furnishings and fabrics

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## Highlights

- Likely huge reservoir of BFRs associated with waste soft furnishings
- Little is known about mechanisms via which BFRs migrate from such waste materials
- Few studies exist of BFR emissions from regulated waste treatment activities
- BFR emissions from waste soft furnishings a potential serious environmental concern

1                   **EXTENT AND MECHANISMS OF BROMINATED FLAME**  
2                   **RETARDANT EMISSIONS FROM WASTE SOFT FURNISHINGS AND**  
3                   **FABRICS**

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32 **Abstract**

33 Use of BFRs in soft furnishings has occurred for over thirty years with the phase out of  
34 polybrominated diphenyl ethers (PBDEs) and hexabromocyclododecane (HBCD) only  
35 relatively recently begun. As products treated with BFRs reach the end of their lifecycle  
36 they enter the waste stream, thereby constituting an important and increasing  
37 reservoir of these chemicals. This review highlights the dearth of data on the extent  
38 and potential mechanisms of BFR emissions from waste soft furnishings. However,  
39 insights into what may occur are provided by scrutiny of the larger (though still  
40 incomplete) database related to BFR emissions from electronic waste (e-waste). In  
41 many countries, municipal landfills have historically been the primary disposal method  
42 of waste consumer products and therefore represent a substantial reservoir of BFRs.  
43 Published data for BFR emissions to both air and water from landfill and other waste  
44 disposal routes are collated, presented and reviewed. Reported concentrations of  
45 PBDEs in landfill leachate range considerably from  $<1 \text{ ng L}^{-1}$  to  $133,000 \text{ ng } \Sigma\text{PBDE L}^{-1}$ .  
46 As well as direct migration of BFRs from waste materials; there is evidence that some  
47 higher brominated FRs are able to undergo degradation and debromination during  
48 waste treatment, that in some instances may lead to the formation of more toxic and  
49 bioavailable compounds. We propose that waste soft furnishings be treated with the  
50 same concern as e-waste, given its potential as a reservoir and source of  
51 environmental contamination with BFRs.

52  
53 **Keywords**

54 Tetrabromobisphenol-A  
55 Hexabromocyclododecane  
56 Polybrominated diphenyl ethers  
57 Waste soft furnishings  
58 Migration  
59 Landfill

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## 63 1. Introduction

64 Brominated flame retardants (BFRs) are a group of synthetic chemical additives that  
65 over the last 30 years or so, have been applied to a wide range of consumer products  
66 such as: building materials, electronics and electrical goods, textiles and furnishings, to  
67 meet and comply with fire safety standards. Currently there are more than 75 different  
68 commercially-recognised BFRs. Moreover, BFRs have historically been the most widely  
69 used flame retardants (FRs) due to their low cost and high efficacy (Covaci et al., 2008).  
70 The five classes of BFR that have found most widespread use are  
71 tetrabromobisphenol-A (TBBP-A), hexabromocyclododecane (HBCD), and three  
72 technical mixtures of polybrominated diphenyl ethers (PBDEs): Penta-BDE, Octa-BDE,  
73 and Deca-BDE (Leonards et al., 2008). In an environmental context, BFRs are highly  
74 resistant to degradation whether through chemical, biological, or photolytic processes  
75 and are therefore capable of long range transport, bioaccumulation in human and  
76 animal tissues and potential trophic magnification. As a result, widespread  
77 contamination of air, water, soil, sediment, and terrestrial and marine biota by BFRs  
78 has been widely documented (Law et al., 2006; Law, 2010; Harrad et al., 2009b; Harrad  
79 et al., 2010a; Muir and de Wit, 2010).

80  
81 These considerations are exacerbated by evidence of the toxicity of some BFRs. HBCD  
82 has been identified as an endocrine disruptor that induces enzymes and alters thyroid  
83 homeostasis with potential to cause adverse effects in humans at relatively low  
84 exposure levels (Darnerud, 2003, 2008; Yamada-Okabe et al., 2005; van der Ven et al.,  
85 2006, 2009). With respect to PBDEs, acute toxicity studies have suggested that they  
86 can be hepatotoxic at relatively high doses (Zhou et al., 2002; Bruchajzer et al., 2011).  
87 Moreover, several studies have indicated that Penta- and Octa-BDE mixtures, as well  
88 as several of the major individual congeners present in wildlife and people, can alter  
89 liver enzymes, disrupt thyroid homeostasis, and are associated with early onset of  
90 puberty, reduced fertility, and impaired neurological development (Viberg et al., 2007).  
91 This latter effect is illustrated by a cohort study of 329 pregnancies in New York City, in  
92 which prenatal PBDE exposure (as indicated by cord blood PBDE levels) was associated  
93 with lower mental and physical development test scores for children aged 1, 4, and 6  
94 years (Herbstman et al., 2010). In general, the lower brominated congeners are more

1 95 acutely toxic than the higher ones (Darnerud, 2003). While BDE-209 is relatively less  
2 96 persistent and bioaccumulative than the lower brominated congeners, it has  
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4 97 nonetheless been shown to increase the incidence of adenomas and carcinomas  
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6 98 during chronic toxicity studies in rodents (Kelly et al., 2008; NTP, 1986, Tomy et al.,  
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8 99 2008; Wu et al., 2009). Moreover, work by Johansson et al., (2008) suggests that  
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10 100 decabromodiphenyl ether (BDE-209) can be as potent as the lower brominated PBDEs  
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12 101 in causing developmental neurotoxic defects. In contrast, TBBP-A is relatively less  
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14 102 persistent and bioaccumulative than most other BFRs (Domínguez et al., 2011).  
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16 103 Furthermore, it is not acutely toxic (WHO, 1995) and the toxicity and teratogenicity of  
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18 104 TBBP-A appeared low in experimental *in vivo* studies (Darnerud, 2003). However,  
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20 105 TBBP-A is a potential endocrine disruptor, acting as a thyroid hormone and oestrogen  
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22 106 agonist (Meerts et al., 2000; Kitamura et al., 2002, 2005), and additionally has been  
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24 107 reported to be immunotoxic as a result of its *in vitro* inhibition of a key T-cell receptor  
25  
26 108 (Mariussen and Fonnum, 2003).

27 109  
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29 110 Human exposure to BFRs occurs predominantly via indoor dust and food ingestion  
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31 111 (mainly oily fish, meat, dairy products, and the neonatal sources of human milk and  
32  
33 112 placental transfer), with a minor contribution from inhalation (Abdallah and Harrad,  
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35 113 2009; Covaci et al., 2009; Frederiksen et al., 2009). Concentrations of BFRs are higher  
36  
37 114 in indoor air than outdoor air; this is likely due to the usage and slow release of BFRs  
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39 115 from consumer products and building materials (Sjödin et al., 2001; Takigami et al.,  
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41 116 2007; Abdallah et al., 2008; Toms et al., 2011).

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44 118 These concerns about their adverse environmental impacts have meant that  
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46 119 production of the Penta- and Octa-BDE commercial mixtures ceased in the EU and  
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48 120 North America in 2004, and their use in all applications in 2006. Likewise, Deca-BDE  
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50 121 was restricted severely in the EU in 2008, with US manufacturers voluntarily  
51  
52 122 committing to phase it out from most uses in the USA by the end of 2012, and to end  
53  
54 123 all uses by 31 December 2013. As a further reflection of concern about their use, the  
55  
56 124 Penta- and Octa-BDE commercial mixtures (Tetra-, Penta-, Hexa- and Hepta-BDEs) and  
57  
58 125 HBCD are listed as persistent organic pollutants (POPs) under the UNEP Stockholm  
59  
60 126 Convention, while Deca-BDE is under active consideration for listing.

127

128 **1.1 BFR production and applications**

129 In 2005, the total annual usage of BFRs was estimated to be about 311,000 tonnes,  
130 130,000 tonnes of which was TBBP-A (Harju et al., 2008). HBCD annual production was  
131 estimated at up to 28,000 tonnes (9,000 to 15,000 tonnes in China, 13,426 tonnes in  
132 Europe and the US) (UNEP, 2011). Total historic production of PBDEs (including Deca-  
133 BDE) has been estimated to amount to 1.3 million to 1.5 million tonnes between 1970  
134 to 2005 (UNEP, 2010a).

135

136 There are essentially two modes via which BFRs are incorporated into polymers. One is  
137 referred to as additive; in this instance the BFR is added to the molten polymer. This  
138 “additive” mode means that the BFR is not tightly bound to the polymer and therefore  
139 its migration to the environment is relatively facile. The alternative approach is where  
140 the BFR is covalently-bound to the polymer via reaction. Release to the environment of  
141 BFRs incorporated via this “reactive” process is comparatively restricted (Law, 2010). A  
142 caveat however, is that during the process of incorporation into the treated product, a  
143 proportion of the reactive BFR used may not polymerise, and this residual fraction has  
144 potential to be released to the environment (de Wit, 2002). TBBP-A is primarily used as  
145 a reactive FR in epoxy, polycarbonate and phenolic resins in printed circuit boards  
146 (58%), but has also been used as an additive BFR in the manufacture of acrylonitrile-  
147 butadiene-styrene (ABS) resins (18%), and was “possibly” used as an additive in high  
148 impact polystyrene (HIPS) (BSEF, 2009; EFRA, 2007). Concentrations of TBBP-A  
149 commonly found in these applications are between 10% and 20% by weight,  
150 depending on the polymer (Covaci et al., 2009). Moreover, during the 1990s, TBBP-A  
151 was increasingly used as a replacement for Octa-BDE in ABS polymers (Watson et al.,  
152 2010).

153

154 The available data indicates that in general PBDEs (all congeners) were added at  
155 concentrations between ~3-30% by weight (WHO, 1994). The exact concentration  
156 applied was determined by several considerations such as the degree of flame  
157 retardancy required, the efficacy of the FR selected, whether it is applied in

158 conjunction with a synergist (e.g. antimony oxide), physical attributes of the end  
159 product (e.g. colour, density, stability, etc.), and its specific application (European  
160 Chemicals Bureau, 2000).

161  
162 In Europe approximately 95% of Penta-BDE was used in flexible polyurethane foam  
163 (PUF), mainly used for furniture upholstery and automotive applications (European  
164 Chemicals Bureau, 2000). The United Nations Environment Programme (UNEP) initially  
165 reported treated PUF to usually contain 10-18% by weight of Penta-BDE, however they  
166 have subsequently revised these estimates to be around 3-5% by weight for  
167 upholstery, cushions, mattresses, and carpet padding (UNEP, 2006a; UNEP 2010a). A  
168 similar concentration range of between 6-18% by weight of Penta-BDE in PUF was  
169 provided in the Plastics Additives Handbook (Zweifel, 2001; cited in EC, 2011). The  
170 remaining minor uses of Penta-BDE (totalling 5%) include: textiles, printed circuit  
171 boards, insulation foam, cable sheets, conveyor belts, lacquers, and possibly drilling  
172 oils (UNEP, 2007). UNEP reported that the approximate distribution of global Penta-  
173 BDE use was 60% in furniture and 36% in transport, with the remaining 4% deployed in  
174 other articles (UNEP, 2010b).

175  
176 Historically, around 95% of Octa-BDE supplied in the EU was used in ABS (globally  
177 ~70%), to which it was typically added at concentrations between 10-18% by weight  
178 (EC, 2011). The main uses for BFR-treated ABS were predominantly in housings of  
179 electrical and electronic Equipment (EEE), particularly for cathode ray tube (CRT)  
180 housings (e.g. PC monitors and TVs), and office equipment (e.g. copying machines and  
181 business printers). The remaining ~5% of minor uses were in HIPS, polybutylene  
182 terephthalate (PBT), and polyamide polymers, with typical concentrations between 12-  
183 15% by weight. Other possible uses were in: nylon, low density polyethylene,  
184 polycarbonate, phenolformaldehyde resins, and unsaturated polyesters, as well as in  
185 adhesives and coatings (UNEP, 2010a; 2010b).

186  
187 Widely used due to its relatively low cost, Deca-BDE was employed as a back coating  
188 on a wide range of fabrics, including: nylon, polypropylene, acrylics, and many other  
189 blends such as polyester-cotton (Weil and Levchik, 2008). Typically, Deca-BDE was



190 added at about 10-25% by weight in a 2:1 weight ratio with antimony oxide (Weil and  
191 Levchik, 2008). Important applications were in: automotive upholstery, draperies for  
192 hotels and public buildings, and institutional (e.g. office) upholstered furniture (Weil  
193 and Levchik, 2008).

194  
195 The principal use of HBCD (90%) is in the building industry, typically added at <3% by  
196 weight into extruded or expanded polystyrene foam in rigid insulation panels/boards  
197 (EC, 2011; Marvin et al., 2011), with a further ~2% deployed in HIPS used for electric  
198 and electronic equipment (distribution boxes for electrical lines and electrical  
199 housings) (EC, 2011). However, HBCD is also used as a textile coating agent in polymer  
200 dispersions applied to cotton or cotton/synthetic blends for upholstery fabrics, e.g.  
201 residential and commercial upholstered furniture and transportation seating, bed  
202 mattress ticking, draperies and wall coverings, interior textiles, e.g. roller blinds, and  
203 vehicle interior textiles. HBCD can also be used in thermosol treatment of polyester,  
204 polypropylene and nylon fabrics, where it is applied as an aqueous suspension or  
205 emulsion at a loading of 8-11% by weight (Weil and Levchik, 2008).

206  
207 The above underlines the extensive global use of BFRs in a wide range of applications,  
208 and demonstrates that while deployment in electronic and electrical equipment (EEE)  
209 is substantial; use in soft furnishings is extensive also. While attention to date has  
210 understandably focused largely on emissions during the production and use phases of  
211 the product life cycle; the fact that a considerable proportion of the BFR inventory has  
212 either entered or is moving towards the end-of-life phase, means that attention is  
213 increasingly turning towards the environmental implications of BFRs associated with  
214 waste materials. In particular, considerable interest has been aroused in potential BFR  
215 contamination from landfilled waste. At the beginning of the 21<sup>st</sup> century, the majority  
216 of BFR-containing consumer products ended up as untreated waste in landfill, with  
217 Alcock et al. (2003) estimating that >80% of total BFR-containing waste was landfilled  
218 in the UK and North America. The lifespans of the principal products containing TBBP-  
219 A, PBDEs, and HBCD are estimated to be ~10 years for soft furnishings and furniture,  
220 ~12 years for cars, but <10 years for EEE; with lifespans of EEE decreasing as the rate of  
221 obsolescence for these products hastens. Consequently, as European use of these BFRs

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222 in new goods peaked in the mid 1990s and has decreased substantially to zero since;  
223 many articles containing PBDEs (EEE in particular) have most likely already become  
224 waste and been treated by the existing waste management infrastructure. Essentially  
225 therefore, most products containing PBDEs in Europe have probably been landfilled  
226 already. This therefore represents a significant reservoir in landfilled waste. However,  
227 studies of emissions of BFRs from such waste are few.

228

### 229 **1.2 BFRs in waste soft furnishings and furniture**

230 In the UK alone, WRAP (2012) estimated that around 670,000 tonnes of furniture and  
231 310,000 tonnes of textiles are disposed of by householders annually. This estimate was  
232 extrapolated from data collected across the UK during 2010/11. Considering that these  
233 products were often treated with BFRs at percent levels by weight (UNEP, 2006a;  
234 UNEP 2010a; Weil and Levchik, 2008), it is apparent that they constitute a significant  
235 potential source of BFRs to the environment. Despite this, very little research has  
236 been undertaken that examines end of life management of BFRs associated with waste  
237 soft furnishings and furniture.

238

### 239 **1.3 Overview of UK landfills as a case study for the developed world**

240 Landfill has been the dominant waste management option in the UK for many years.  
241 Introduction of the European Directive 1999/31/EC on the Landfill of Waste (Landfill  
242 Directive) aimed to reduce the dependence on landfill as a disposal option. Its  
243 intention was to lessen the environmental impact of landfills and diminish the overall  
244 risk to human health. Before 2004, the UK disposed of both hazardous and non-  
245 hazardous wastes together at the same landfill, a practice known as co-disposal. Since  
246 July 2004, co-disposal is no longer practised and instead, landfills are divided into three  
247 distinct classes in which only specific waste types may be disposed of: landfills for  
248 hazardous waste, landfills for non-hazardous waste, and landfills for inert waste  
249 (Council of the European Union, 1999).

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251 From October 2007, it became a requirement that waste sent to landfill be pre-  
252 treated. This change aims to increase waste recycling and recovery and reduce  
253 pollutant emissions from landfills (Environment Agency, 2011). The process of

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- 254 treatment must change the characteristics of the waste, and it must do so in order to
- 255 substantially:
- 256 (a) Reduce its volume; or
- 257 (b) Reduce its hazardous nature; or
- 258 (c) Facilitate its handling; or
- 259 (d) Enhance its recovery potential.

260 The treatment of waste can be achieved by many methods depending on the aim of  
261 the treatment. These may include: manual sorting to change waste characteristics,  
262 physical (mechanical) treatment (crushing, grading, magnetic separation, eddy current  
263 separation, ballistic separation, trommeling (a revolving cylindrical sieve used for  
264 screening or sizing waste), and sorting, etc.), thermal treatment, and chemical or  
265 biological processes (anaerobic/aerobic digestion, biological stabilization of 'black bin'  
266 residues) (Environment Agency, 2011; Council of the European Union, 1999).

267 The Landfill Directive also places more stringent engineering and operation conditions  
268 on landfill operators. During the active phase and following closure of a site, a  
269 monitoring regime must be implemented to ensure groundwater quality is not  
270 compromised. Groundwater protection measures require that there is no discharge of  
271 a prescribed range of hazardous substances (including organohalogen compounds such  
272 as pesticides and herbicides, but not BFRs) to groundwater and that formal compliance  
273 points below a landfill have been established, where both leachate and groundwater  
274 composition must be monitored.

275

276 It is now mandatory for new landfills in developed nations to be engineered using a  
277 liner membrane barrier to separate the landfilled waste from the underlying ground.  
278 This membrane retards migration of leachate into surrounding groundwater. It  
279 generally comprises a layer of compacted clay with a minimum required thickness and  
280 a maximum allowable hydraulic conductivity, overlaid by a high-density polyethylene  
281 (HDPE) geomembrane. By doing so, the intention is that in the event of a hole  
282 developing, the impact of any leak will be minimised as there will also be clay below  
283 the HDPE as a further line of defence. All membranes are slightly porous and over time  
284 low volumes of leachate cross the membrane. The landfill membranes are designed

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285 such that at these low volumes the leachate should never have a measurable adverse  
286 impact on the quality of the receiving groundwater.

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288 However, the US EPA (1988) has voiced concerns that “once the unit is closed, the  
289 bottom layer of the landfill will deteriorate over time and, consequently, will not  
290 prevent leachate transport out of the unit.” Therefore it can be said that modern  
291 landfill designs delay, but do not wholly prevent ground and surface water pollution.  
292 Laid on top of the membrane is a series of leachate collection pipes to transport the  
293 leachate to a collection or treatment location. The failure or abandonment of the  
294 leachate collection system poses a more significant risk to groundwater. As landfills  
295 age they are prone to suffer large internal movements as waste decomposes unevenly.  
296 Consequently leachate collection systems are susceptible to internal failure and pipes  
297 can buckle and distort. Such failure causes leachate levels to slowly build within the  
298 landfill, and given time they may even rise sufficiently high to spill over the top of the  
299 containing membrane at uncapped sites. A positive feedback mechanism can then  
300 occur, in which further active decomposition and leachate generation can be triggered  
301 as leachate levels rise and rehydrate previously dried out waste masses. One of the  
302 many problems leachate collection systems can face, is clogging of the conduit pipes  
303 with mud or silt. The conditions in leachate collection systems are ideal for micro-  
304 organisms to multiply and this growth can exacerbate the clogging problem. Another  
305 mechanism via which clogging can occur is by chemical reactions within the leachate  
306 which in turn generates solid residues. Furthermore, the pipe walls may be weakened  
307 by the chemical composition of the leachate and cause them to fail. Simulations by  
308 Danon-Schaffer et al., (2013a) suggest that concentrations of PBDEs will continue to be  
309 significant in landfills beyond 2080, and that PBDEs contained in existing landfilled  
310 waste will persist to nearly 2070.

311

312 Within the UK, the waste electronic and electrical equipment (WEEE) Regulations came  
313 into force in July 2007. This requires collection of 65% of e-waste, and recovery of 85%  
314 of the collected material. This means that 35% of UK e-waste can still be disposed to  
315 landfill untreated, augmenting the already substantial quantity of e-waste residing in

1  
2 316 UK landfills. However, no regulations exist that address the disposal of waste soft  
317 furnishings.

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6 319 **2. Mechanisms of BFR migration from goods and materials and their behaviour**

7 320 The mechanisms via which BFRs transfer from waste products to the environment  
8  
9 321 remain an active field of investigation. PBDEs and HBCD are used primarily as additives  
10 322 and therefore migrate comparatively readily from the surface of products within which  
11 323 they are incorporated into the environment (Deng et al., 2007). In contrast, TBBP-A is  
12  
13 324 used predominantly (though not exclusively) as a reactive BFR and therefore its release  
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15 325 from treated goods is much less pronounced than for PBDEs and HBCD. This is  
16  
17 326 exemplified by the low concentrations of TBBP-A reported in indoor air, dust and food  
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19 327 (Covaci et al., 2009). In addition to migration from waste materials following disposal  
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21 328 to landfill, evidence also exists to suggest that transport of waste materials to disposal  
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23 329 sites and their subsequent storage before sorting or deposition may also prove to be  
24  
25 330 significant emission pathways for BFRs to the environment (Julander et al., 2005;  
26  
27 331 Muenhor et al., 2010). The following sections summarise current knowledge relevant  
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29 332 to our understanding of how BFRs are emitted to the environment as a result of waste  
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31 333 management.

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36 335 **2.1 Emissions to air**

37 336 Emission chamber experiments conducted by Kemmlein et al., (2003) documented  
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39 337 emissions of BFRs via volatilisation from a range of consumer products including  
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41 338 insulating materials, assembly foam, upholstery/mattresses, and electronics  
42  
43 339 equipment. An increase of temperature (from 23 to 60 °C) was found to cause a 500-  
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45 340 fold increase in emissions of BDE-47 from printed circuit boards. This has relevance for  
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47 341 emissions from waste, as within a landfill, temperatures can sometimes reach as high  
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49 342 as 80-90 °C due to heat released during aerobic degradation (Kjeldsen et al., 2002;  
50  
51 343 Environment Agency, 2002). Consequently, elevated volatile emissions of BFRs from  
52  
53 344 active landfills are plausible. However, the study of Kemmlein et al (2003) also showed  
54  
55 345 BFR emissions to vary between products, and of particular relevance to this review,  
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57 346 emissions of HBCD and Deca-BDE from the PUF and textile components of an  
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59 347 upholstered stool were not detected over a period of 170 days. Conversely, chamber  
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1 348 experiments by Wilford et al., (2003) showed that PBDEs volatilise from PUF at  
2 349 significant levels. Both studies showed that different PBDE congeners are released at  
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4 350 different rates, determined by their physical properties i.e. higher emissions observed  
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6 351 for congeners with higher vapour pressures (Table 1 - Kemmlin et al. 2003; Wilford et  
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8 352 al., 2003).

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11 354 More recently, Kajiwara and Takigami (2013) conducted emission chamber tests on  
12  
13 355 three curtain textile samples. Two of the samples were treated with technical HBCD  
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15 356 and one with technical Deca-BDE. Tests were conducted over a range of temperatures  
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17 357 (20, 40, 60, and 80 °C) for 120 hours. Both HBCD and BDE-209 (the least volatile PBDE)  
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19 358 were found to volatilise at 20 °C indicating that they are emitted from textiles even at  
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21 359 room temperature. At temperatures of 80 °C, HBCD emission rates were increased  
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23 360 twenty-fold compared to the rates at 60 °C, with those of Deca-BDE at 80 °C six times  
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25 361 greater than at 60 °C. There were no clear differences between the emission rates at  
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27 362 20, 40, and 60 °C for both BFRs.

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31 364 The few studies that have reported concentrations of BFRs in air at or near landfill sites  
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33 365 are summarised in Table 2. Weinberg et al., (2011) reported particulate phase  
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35 366 concentrations of BDE-183 at both active and closed landfill sites in Germany to fall  
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37 367 between 0.001 to 0.011 ng m<sup>-3</sup> and 0.001 to 0.003 ng m<sup>-3</sup> respectively. The authors  
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39 368 suggested that the significantly higher (p < 0.05) detection of BDE-183 at the active  
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41 369 landfill site compared to the closed site, indicates that BDE-183 might be emitted from  
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43 370 waste disposed at the active landfill. However, the study failed to detect PBDEs in the  
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45 371 vapour phase at either site, despite other European and UK background studies  
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47 372 reporting low concentrations in air, typically sub- to a few pg m<sup>-3</sup> (Gioia et al., 2006;  
48  
49 373 Lee et al., 2004). In Canada, St-Amand et al., (2008) reported concentrations of PBDEs  
50  
51 374 collected at a sanitary landfill near Ottawa. Vapour and particulate phase total PBDE  
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53 375 concentrations were generally below 0.002 and 0.02 ng m<sup>-3</sup> respectively and ranged  
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55 376 from 0.00036 to 0.0069 ng m<sup>-3</sup> and 0.00072 to 0.145 ng m<sup>-3</sup>, respectively. These  
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57 377 concentrations are in line with those detected at other locations not impacted directly  
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59 378 by point sources. In contrast, Oliaei et al., (2010) reported the total ΣPBDE  
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61 379 concentration of vapour and particulate phases combined in “ambient air of diffused  
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1 380 landfill gas" at a recently closed landfill in Minnesota, USA was 17.3 ng m<sup>-3</sup>. BDE-47 had  
2 381 the highest concentration (8.23 ng m<sup>-3</sup>), followed by BDE-209, -99, -28/33, and -100.  
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4 382 BDE-209 was found predominantly in the particulate phase, while lower brominated  
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6 383 BDEs were principally in the vapour phase. These data suggest strongly that the landfill  
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8 384 studied was a source of PBDEs.

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11 386 Given the paucity of data related to BFR concentrations in air in the vicinity of landfills;  
12  
13 387 Table 2 also summarises other data that illustrate the potential for emissions of BFRs  
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15 388 to air from waste products. In the UK, Harrad et al., (2010a) reported elevated  
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17 389 concentrations of HBCD in outdoor air sampled within the boundaries of an e-waste  
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19 390 treatment facility (22 ng  $\Sigma$ HBCDs m<sup>-3</sup>). Likewise, Julander et al., (2005) detected up to  
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21 391 214.3 ng m<sup>-3</sup>  $\Sigma_{24}$ PBDEs in airborne particulates sampled in the vicinity of an e-waste  
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23 392 recycling facility in Sweden. Moreover, in addition to the data summarised in Table 2,  
24  
25 393 other studies have reported elevated concentrations of PBDEs in indoor air and dust  
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27 394 within WEEE recycling facilities (Rosenberg et al., 2011; Sjödin et al., 2001; Takigami et  
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29 395 al., 2006).

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33 397 Emissions of BFRs are also plausible as a result of combustion of waste. Rupp and  
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35 398 Metzger (2005) qualitatively investigated the reaction of BDE-47 and BDE-153 between  
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37 399 250 °C and 500 °C. At such comparatively low temperatures, PBDEs are not destroyed  
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39 400 completely and thus may potentially act as precursors for the formation of e.g.  
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41 401 polybrominated dibenzo-*p*-dioxins and dibenzofurans (PBDD/Fs). Interestingly, the  
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43 402 same study revealed that thermal treatment of both BDE-47 and BDE-153 resulted in  
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45 403 the formation of monochlorinated polybrominated diphenyl ethers (CPBDEs) (Rupp  
46  
47 404 and Metzger, 2005).

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50 406 Such combustion emissions can occur either accidentally (as in landfill fires), or  
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52 407 intentionally via incineration of municipal solid waste (MSW). MSW is by nature a  
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54 408 heterogeneous mix of waste that will contain varying proportions of waste furniture  
55  
56 409 and fabrics. The concentration of  $\Sigma$ PBDEs outdoors at a MSW incineration plant in  
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58 410 Tagish, Yukon, Canada was reported as 2 ng m<sup>-3</sup> (Alaee, 2001). Agrell et al., (2004)  
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60 411 sampled air outside a MSW incineration plant in Malmö, Sweden. They reported

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412 concentrations of  $\Sigma$ PBDEs (BDE-28, -47, -66, -100, -153, -154, -183) for vapour and  
413 particulate phases combined that ranged between 0.00224 and 0.02132 ng m<sup>-3</sup>; with a  
414 median value of 0.0063 ng m<sup>-3</sup>. However, the authors note that the low concentrations  
415 were likely due to the sampling having taken place during cool periods (mean 8 °C, 17<sup>th</sup>  
416 October-9<sup>th</sup> November 2001 and 19<sup>th</sup> February-15<sup>th</sup> March 2002) when volatilisation  
417 from contaminated surfaces was less facile. Concentrations of  $\Sigma$ PBDEs and BDE-47  
418 were significantly higher at the MSW incineration plant compared to those at an urban  
419 background site. In Japan, PBDE output from incinerator stack emissions were  
420 reported as 65,000 ng/h, equivalent to an emission factor of 100 ng PBDE emitted per  
421 g waste incinerated) (Sakai et al., 2006). Investigations by Takigami et al., (in press) into  
422 the incineration of XPS and EPS insulation foams show that HBCD is destroyed almost  
423 entirely during the combustion process and resulting emissions are negligible  
424 (destruction efficiency of 99.9999%). It appears reasonable to assume that HBCDs in  
425 treated fabrics may exhibit similar behaviour during incineration. Finally, Tu et al.,  
426 (2011) reported emissions of  $\Sigma_{30}$ PBDEs measured in stack flue gas at two MSW  
427 incinerators in southern Taiwan. PBDE concentrations were 9.32 ng/Nm<sup>3</sup> and 7.62  
428 ng/Nm<sup>3</sup> again equating to an emission factor of 100 ng PBDE emitted per g waste  
429 incinerated.

430

## 431 **2.2 Leaching to groundwater**

432 Percolation of water through almost any material will cause soluble components to be  
433 dissolved out and enter the leachate. Insoluble liquids (such as oils) and small particles  
434 in the form of suspended solids may also be present in leachate (Environment Agency,  
435 2002). Leachate composition is primarily determined by the composition and solubility  
436 of the waste constituents. The composition of waste can be said to change over time  
437 as a landfill ages (for example due to weathering or biodegradation) and therefore the  
438 leachate composition also changes with time. This is particularly the case in landfills  
439 containing non-hazardous municipal waste. Generally, it is accepted that landfilled  
440 waste undergoes at least four phases of decomposition and therefore four stages in  
441 the generation of leachate. These are: (1) an initial aerobic phase, (2) an anaerobic acid  
442 phase, (3) an initial methanogenic phase, and (4) a stable methanogenic phase  
443 (Christensen and Kjeldsen, 1995).



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- 444 1. Leachate produced in the early stages of decomposition of waste is typically  
445 generated under aerobic conditions producing a complex solution with near  
446 neutral pH. This phase generally only lasts a few days or weeks because oxygen  
447 is not replenished once the waste is covered. It is relatively unimportant in  
448 terms of leachate quality, as most leachate produced during this phase results  
449 from the release of moisture during compaction and bypassing of precipitation  
450 through the buried refuse. However, because aerobic degradation produces  
451 heat, leachate temperatures can rise, sometimes as high as 80-90 °C, and if this  
452 heat is retained it can enhance the latter stages of leachate production  
453 (Kjeldsen et al., 2002; Environment Agency, 2002). Elevated temperatures are  
454 likely to enhance potential volatilisation and also the aqueous solubility of  
455 BFRs.
- 456 2. As decomposition processes develop and oxygen sources are depleted, the  
457 waste becomes anaerobic, supporting fermentation reactions. The anaerobic  
458 phase has two main stages in leachate generation; the acidogenic stage and the  
459 acetogenic stage. The acidogenic stage proceeds efficiently over a relatively  
460 narrow pH range around neutral. During the acetogenic stage, hydrolytic,  
461 fermentative, and acetogenic bacteria dominate, resulting in an accumulation  
462 of carboxylic acids, and a pH decrease. This acidic pH leachate is chemically  
463 aggressive and increases the solubility of many compounds (Kjeldsen et al.,  
464 2002; Environment Agency, 2002).
- 465 3. After several months or years, methanogenic conditions are established as the  
466 pH of the waste becomes sufficiently neutralised to permit at least limited  
467 growth of methanogenic bacteria. The leachate becomes neutral or slightly  
468 alkaline as the pH increases and acids are consumed. The overall volume of  
469 leachate is lower but still contains significant quantities of some pollutants (e.g.  
470 ammonium).
- 471 4. As biodegradation nears completion, the pH continues to increase and aerobic  
472 conditions may return. Some organic compounds are present in the leachate,  
473 mostly recalcitrant compounds such as humic and fulvic acids (Environment  
474 Agency, 2002; Kjeldsen et al., 2002). The implication of the continued presence

1 475 of humic acids is that they enhance the leachability of BFRs from waste  
2 476 materials they contact.  
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6 478 Over time, leachate barrier systems are prone to degradation and ultimately failure.  
7  
8 479 When this occurs, pollution of groundwater becomes possible. Alternatively if leachate  
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10 480 is not removed for treatment at sufficiently high rates, seepage to both surface and  
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12 481 groundwater may occur (Slack et al., 2007). The processes via which BFRs leach from  
13  
14 482 landfilled waste are not yet understood. In order to understand these leaching  
15  
16 483 mechanisms, a full knowledge of the environmental partitioning mechanism at  
17  
18 484 aqueous/solid-phase interfaces is required, as well as the relevant physicochemical  
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20 485 properties of BFRs (Choi et al., 2009).  
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22 486  
23 487 PBDEs are hydrophobic, therefore their presence in leachate implies that other  
24  
25 488 constituents present in the leachate have enhanced their leachability. When wastes  
26  
27 489 come into contact with rainwater in a landfill, relatively hydrophilic BFRs such as TBBP-  
28  
29 490 A are more readily dissolved in the leachate (Osako et al., 2004). However, dissolved  
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31 491 humic matter (DHM) in the leachate interacts with hydrophobic BFRs such as the  
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33 492 higher brominated PBDEs in the waste and can enhance their leachabilities (Osako et  
34  
35 493 al., 2004).  
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39 495 Danon-Schaffer et al., (2013b) conducted a series of leaching experiments contacting  
40  
41 496 e-waste with distilled water and leachate from a major urban landfill in end-over-end  
42  
43 497 contactors at a rotational speed of 8 revolutions per minute. The authors found  
44  
45 498 greater transfer of PBDEs to the aqueous phase at lower pH levels (4 and 5). The  
46  
47 499 authors hypothesised that changes in pH affect the solubility and mechanical  
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49 500 properties of the plastic, influencing the dislodgement of fine particles from the  
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51 501 polymer. Compared to when e-waste was contacted with leachate, contacting e-waste  
52  
53 502 with distilled water resulted in a lower transfer of PBDE concentrations to the aqueous  
54  
55 503 phase. The duration of contact time (1 to 168 h) appeared to exert little influence on  
56  
57 504 the transfer of PBDEs to the distilled water. Likewise, when leachate was used (over  
58  
59 505 experimental durations of 1 to 654 h), relatively little PBDE was transferred to the  
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61 506 leachate after the first 24 h period and the last 630 h of contact appeared to have little  
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507 further effect on transfer. The authors suggested that there are two potential  
508 mechanisms responsible for the observed transfer rates; 1) dislodgement of ultra-fine  
509 particles of dust adhering to the surface of the plastic; or 2) abrasion occurring when  
510 the chipped e-waste material rubs against each other and against the walls of the  
511 columns during end-over-end contacting.

512  
513 Concentrations of BFRs in European landfill leachates have only been reported for  
514 Sweden (Table 3). Öman and Junestedt (2008) analysed leachate collected from  
515 Swedish municipal landfills containing household waste, industrial waste, construction  
516 and demolition waste, as well as ash, slag, sludge, lime, sediment and excavation  
517 material. The age of the waste in the landfills varied from a few years to 50 years.  
518 Concentrations of  $\Sigma$ PBDEs ranged from 10.2 ng L<sup>-1</sup> to 19,463 ng L<sup>-1</sup>, with those of TBBP-  
519 A reaching up to 20 ng L<sup>-1</sup>.

520  
521 In North America, Oliaei et al., (2002) reported concentrations of PBDEs in leachate  
522 sampled from five landfill sites with different waste characteristics (three municipal,  
523 one industrial, and one demolition) in Minnesota, USA. Concentrations of  $\Sigma$ PBDE  
524 ranged from 29 to 248 ng L<sup>-1</sup>. The demolition waste landfill had the highest total PBDE  
525 concentrations, suggesting that the fate of building material waste warrants serious  
526 consideration. BDE-209 was the dominant congener found in leachate, 60% to 98% of  
527 the total PBDE contamination (Oliaei et al., 2010). The second phase of this study  
528 reported total PBDE concentrations of 7.1 ng L<sup>-1</sup> in leachate from a recently closed  
529 landfill in Minnesota, USA (Oliaei et al., 2010). At this site, BDE-47 was the dominant  
530 congener found in leachate followed by BDE-99 and BDE-209 respectively. Water  
531 sampled from groundwater monitoring wells at the same site contained total PBDE  
532 concentrations of 0.052 ng L<sup>-1</sup> (sum of dissolved and particulate phases).

533  
534 In Japan (Osako et al., 2004), leachate samples were taken from seven different landfill  
535 sites and concentrations of PBDEs and TBBP-A determined. The study found  
536 substantial differences in the concentrations of BFRs in the raw leachate of each  
537 landfill site, with PBDE concentrations expressed as the sum of BDE-47, BDE-99 and  
538 BDE-100 ranging from <0.008 to 4 ng L<sup>-1</sup>. In particular, leachate from one section on a

1 539 site that contained both crushed fragments of bulk wastes such as WEEE, as well as  
2 540 sewage sludge containing a “large amount” of organic matter; showed an extremely  
3  
4 541 high concentration of PBDEs (e.g. 3.2 ng L<sup>-1</sup> tetra-BDE, 1.8 ng L<sup>-1</sup> penta-BDE, and 11 ng  
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6 542 L<sup>-1</sup> hepta-BDE). TBBP-A concentrations recorded in this study ranged from <1 to 620 ng  
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8 543 L<sup>-1</sup>, and it was even found in treated leachate at <1 to 11 ng L<sup>-1</sup>. Furthermore, relatively  
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10 544 high correlation coefficients were observed between concentrations of each PBDE  
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12 545 homologue group and chemical oxygen demand (COD) (R = 0.73, 0.90 and 0.92 for tri-,  
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14 546 tetra- and penta- BDE homologues respectively) and UV260 (R = 0.80, 0.93 and 0.93 for  
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16 547 tri-, tetra- and penta- BDE homologues respectively), both important indicators for  
17  
18 548 DHM. The authors stated that DHM has the potential to enhance leachability of  
19  
20 549 hydrophobic organic pollutants (HOPs) by complex interactions. The presence of DHM  
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22 550 was shown to significantly raise the leachability of HOPs, once DHM concentrations  
23  
24 551 exceed a critical micelle concentration. Hydrophobic single tail regions are sequestered  
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26 552 to the centre of the micelles leaving the hydrophilic head regions in contact with the  
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28 553 surrounding solvent. However, the study found no correlation between concentrations  
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30 554 of TBBP-A and either UV260 or COD. The authors hypothesised that more hydrophobic  
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32 555 HOPs have greater affinity to DHM and suggested that the relatively higher  
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34 556 hydrophobicity of PBDEs relative to TBBP-A, may account for the observed enhanced  
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36 557 leachability of PBDEs over TBBP-A. Osako et al., (2004) also suggested that this may be  
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38 558 one reason why TBBP-A does not correlate with UV260 and COD. However, as Table 1  
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40 559 shows, the water solubility of TBBP-A is very similar to that of the lower PBDE  
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42 560 homologues which did correlate with COD and UV260, and other factors are thus likely  
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44 561 involved.

45 562  
46 563 Choi et al. (2009) conducted leaching tests for PBDEs, polybrominated biphenyls,  
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48 564 polybrominated phenols and TBBP-A in plastic samples in the presence of DHM. Their  
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50 565 results clearly show that BFRs can be leached by organic matter. While their  
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52 566 experiments provide a valuable illustration of the importance of DHM in enhancing the  
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54 567 leachability of BFRs, the authors also highlight that conditions within MSW landfills are  
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56 568 more complicated, given the high organic matter loadings in leachate and complex  
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58 569 interactions between a wide range of heterogeneous BFR waste, non-FR waste, sludge,  
59  
60 570 etc..

571

572 Some plausible reasons why DHM has the ability to decrease pollutant/solid-phase  
573 interaction include: solubilisation, hydrolysis, catalysis, and photosensitisation  
574 mechanisms (Choi et al., 2009). Although it is logical to assume that only the BFRs  
575 distributed along the surface of a polymer can be leached by a solvent, other chemical  
576 engineering studies have reported sorption, diffusion, and permeation in the polymer  
577 matrix (Harogoppad and Aminabhavi, 1991; Gamst et al., 2003; Hansen, 2004; cited in  
578 Choi et al., 2009). Such interactions will likely involve multiple processes and vary in  
579 accordance with a variety of parameters such as temperature, solvent, and the  
580 molecular weight and morphology of the polymer (Choi et al., 2009).

581

582 Odusanya et al., (2009) reported concentrations of PBDEs in leachate collected from  
583 five landfill sites in South Africa. Expressed as the sum of BDEs-28, -47, -66, -71, -75, -  
584 77, -85, -99, -100, -119, -153, -154 and -183, concentrations ranged from 8.4 to 54.8 ng  
585  $\Sigma$ PBDEs L<sup>-1</sup> across the five sites. The dominant congeners found in the leachate were  
586 BDEs-28, -47, -71 and -75. The site with the highest concentrations of PBDEs also had  
587 the highest COD value, further supporting the influence of DHM on leaching. More  
588 recently Daso et al., (2013) reported PBDE concentrations from leachate at three  
589 landfill sites in Cape Town, South Africa. Leachate was collected on six occasions at bi-  
590 monthly intervals. Concentrations of the sum of BDEs-28, -47, -99, -100, -153, -154, -  
591 183 and -209 ranged from 45 to 17,953 ng  $\Sigma$ PBDEs L<sup>-1</sup>, 2.25 to 164 ng  $\Sigma$ PBDEs L<sup>-1</sup> and  
592 13.3 to 9,360 ng  $\Sigma$ PBDEs L<sup>-1</sup> for the three landfills.

593

594 PBDEs were detected in leachate from 26 out of 28 landfill and dumpsites across  
595 Canada (Li et al., 2012). While 59 PBDE congeners were monitored in all samples, only  
596 BDEs-47, -99, -100, -153, -154, -183, -206, -207, and -209 were detected frequently.  
597 The sum of these 9 congeners constituted more than 99% of the total PBDEs  
598 measured. Concentrations ranged substantially from 0.03 to 1,020 ng  $\Sigma$ PBDEs L<sup>-1</sup>, with  
599 an average of 166 ng  $\Sigma$ PBDEs L<sup>-1</sup>. The dominant congener was BDE-209 with a mean  
600 contribution of 52%.

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602 Recently, Zhou et al., (2013) reported BFR concentrations from raw ( $\Sigma$ PBDEs 5.67 ng L<sup>-1</sup>;  
603 TBBP-A 15.4 ng L<sup>-1</sup>) and treated ( $\Sigma$ PBDEs <6.1 ng L<sup>-1</sup>; TBBP-A <4.5 ng L<sup>-1</sup>) landfill  
604 leachates from Laogang landfill site, Shanghai, China. Elsewhere in Asia, Kwan et al.,  
605 (2013) reported PBDEs in leachate from ten MSW dumping sites located within eight  
606 tropical countries viz: Laos, Cambodia, Vietnam, India, Indonesia, Thailand, the  
607 Philippines, and Malaysia. Concentrations ranged from 3.7 to 133,000 ng  $\Sigma$ PBDEs L<sup>-1</sup>.  
608 Debromination of PBDE technical mixtures (including BDE-209) is implied by the  
609 presence in leachate of congeners that are either absent from or present only in trace  
610 concentrations in commercial formulations (e.g., BDEs-208, -207, -206, -202, -188, -  
611 179, -49, -17/25, -8, and -1). Further discussion of such debromination follows in  
612 section 2.3.

613

### 614 **2.3 Debromination and degradation**

615 There is strong evidence that BDE-209 debrominates over time, forming lower  
616 brominated PBDEs with stronger bioaccumulation characteristics and higher toxicity  
617 (Danon-Schaffer, 2010; Kajiwara et al., 2008, 2013; Schenker et al., 2008; Stapleton  
618 and Dodder, 2008). Little information is available in the literature on the degradation  
619 pathways/kinetics of PBDEs. Work by Danon-Schaffer and Mahecha-Botero (2010)  
620 details a simplified degradation/debromination pathway based on stepwise  
621 debromination of each homologue group of congeners to the next (lower) one,  
622 beginning with BDE-209 and extending ultimately to low molecular weight congeners  
623 (tri-BDEs, di-BDEs and mono-BDEs). PBDE congeners lose bromines due to reductive  
624 debromination, photolysis, and microbial degradation in anaerobic environments  
625 (Danon-Schaffer and Mahecha-Botero, 2010). Reported BDE-209 photodegradation  
626 half-lives range between <15 minutes up to 408 days, depending on the matrix with  
627 which it is associated and the radiation wavelengths (Stapleton, 2008). It is unclear to  
628 what extent degradation occurs in the natural environment as shielding effects likely  
629 limit the amount of UV light to which the PBDEs are exposed (Domínguez et al., 2011).  
630 Also of concern, Kajiwara et al. (2013) showed that exposure to natural sunlight of  
631 textiles treated with Deca-BDE, resulted in the formation of polybrominated  
632 dibenzofurans (PBDFs) as products of photodecomposition. A maximum total PBDF  
633 concentration of 27,000 ng g<sup>-1</sup> was reached after 329 days of exposure. This was

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634 approximately 10 times the initial concentration. The authors also reported that di- to  
635 hexa-BDF congener concentrations increased continuously throughout the study.  
636 Interestingly, textiles that contained approximately 4% HBCD by weight showed no  
637 substantial loss of any HBCD diastereomers during the entire exposure period (371  
638 days). This suggested that debromination and isomerisation of HBCD diastereomers  
639 did not occur and that HBCD is resistant to sunlight. However, this contrasts with the  
640 work of Harrad et al., (2009a) in which dust samples were exposed to light indoors for  
641 different periods of time with a control sample kept in darkness. Within the first week  
642 of exposure there was a significant shift from  $\gamma$ -HBCD to  $\alpha$ -HBCD and evidence of HBCD  
643 degradation in the presence of light. The experimental data suggested a rapid  
644 photolytically mediated shift in the diastereomer profile and a slower degradative loss  
645 of HBCDs via elimination of HBr to degradation products pentabromocyclododecenes  
646 (PBCDs) and tetrabromocyclododecadienes (TBCDs). The difference between the two  
647 studies may be an indication of the influence of the material with which the HBCD is  
648 associated.

649

650 Analysis of dust samples from inside TV casings detected elevated concentrations of  
651 PBDEs. In one television studied, lower brominated homologues displayed elevated  
652 concentrations in dust relative to those in the plastic components (Takigami et al.,  
653 2008). While one explanation for this is that lower congeners transfer more efficiently  
654 via volatilisation and subsequent deposition to dust, another suggestion proposed by  
655 the authors was that the PBDEs detected in the dust might be transformed (e.g.,  
656 through debromination and oxidation) during the transfer from components to dust. In  
657 a similar vein, Harrad et al., (2009a) reported that dust collected from within the casing  
658 of a HBCD flame retarded TV showed a substantially higher ratio of  $\gamma$ -HBCD to  $\alpha$ -HBCD  
659 than dust sampled at increasing distances from the source. This is consistent with a  
660 photolytically mediated shift in the diastereomer profile. Chen et al., (2010) reported  
661 elevated ratios of BDE-208:BDE-183 and BDE-208:BDE-209 in TV/PC display casings,  
662 and PC components sampled in South China. The authors attributed these ratios to the  
663 decomposition of higher brominated PBDEs during the process of manufacturing, use  
664 and/or recycling of PBDE-containing products, in addition to degradation in the  
665 environment. Elevated values of such ratios were also reported by Muenhor et al.,

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666 (2010) in dust samples taken from e-waste storage facilities in Thailand. The authors  
667 suggest that debromination of BDE-209 to BDE-208 had taken place during the lifetime  
668 of the e-waste and further hypothesised that the elevated abundances of BDE-208 and  
669 of the other nona-BDEs (BDE-206 and BDE-207) found in their dust samples arose  
670 largely as a result of direct migration of such congeners from stored e-waste.

671  
672 Finally, reductive debromination of deca-, nona- and octa-BDEs, to lower brominated  
673 congeners can occur in anaerobic environments (akin to landfill conditions) *via*  
674 microbial activity (Gerecke et al., 2005; He et al., 2006; Robrock et al., 2008). Gerecke  
675 et al., (2006) found that TBBP-A and HBCD also underwent microbially mediated  
676 degradation under anaerobic conditions in digested sewage sludge, with the half-life of  
677  $\alpha$ -HBCD almost twice that of  $\beta$ -HBCD and  $\gamma$ -HBCD. Additionally, it has been reported  
678 that BDE-209 and nona-BDEs can be debrominated by anaerobic sediment microbes  
679 (Parsons et al., 2004; Tokarz et al., 2008).

680  
681 In summary, the available evidence suggests that the BFR content of landfilled waste  
682 will likely change over time, as a result of a variety of degradation processes.

683

#### 684 **2.4 Abrasion and weathering**

685 Hale et al. (2002) conducted weathering experiments on BFR-treated PUF for several  
686 weeks under full sunlight conditions in summer. Typical daytime temperatures were as  
687 high as 30-35 °C and humidity generally exceeded 80%. Disintegration of the surface of  
688 the PUF occurred within four weeks and resulted in small, low-density fragments easily  
689 dispersed by precipitation or wind. Moreover, weathered PUF fragments appeared to  
690 preserve the original constituent pattern of Penta-BDE.

691

692 Work by Webster et al. (2009) using environmental forensic microscopy, suggests that  
693 physical abrasion is a viable mechanism via which BDE-209 can migrate from consumer  
694 products to indoor dust. BDE-209 has a very low vapour pressure, therefore the  
695 authors hypothesised that abrasion is a more plausible transfer mechanism than  
696 volatilisation – particularly in dust samples containing highly elevated concentrations  
697 of BDE-209. This was supported by the heterogeneous distribution of the bromine in



1 698 the dust samples. Furthermore, bromine-rich particles were not observed free in the  
2 699 dust but appeared to be embedded in a polymeric/organic matrix and associated with  
3  
4 700 calcium. Calcium carbonate is a very common additive in plastics. This evidence  
5  
6 701 supports the abrasion hypothesis in that BDE-209 is primarily present in dust samples  
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8 702 containing highly elevated concentrations of this congener as inclusions in plastic  
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10 703 particles. Given the conditions prevalent in landfills, it is not unreasonable to  
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12 704 hypothesise that similar abrasive mechanisms will be at work on landfilled waste and  
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14 705 thereby facilitate BFR emissions.  
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16 706

### 17 707 **3. Analysis and discussion**

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19 708 Currently there appear little or no data on emissions of BFRs from waste soft  
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21 709 furnishings in the literature. Indeed only a few data exist concerning the emissions of  
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23 710 BFRs from landfill sites or during the incineration of MSW; as well as the potential for  
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25 711 emissions during transport of waste to landfills or incinerators. The absence of data on  
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27 712 these aspects constitute major research gaps. Fig. 1 illustrates the various potential  
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29 713 pathways via which BFRs may migrate from waste during transport to and storage at  
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31 714 waste treatment facilities as well as during the treatment process itself. The bulk of  
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33 715 research into BFR emissions from waste focuses on primitive e-waste dismantling and  
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35 716 recycling conducted in areas such as Taizhou, Zhejiang province and Guiyu, Guangdong  
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37 717 province in China (Chen et al., 2008; Chen et al., 2009; Han et al., 2009) and is  
38  
39 718 therefore not immediately relevant to disposal of waste soft furnishings under  
40  
41 719 controlled conditions.  
42

43 720

44 721 A small number of emission chamber experiments have shown that volatilisation of  
45  
46 722 BFRs from a range of products including soft furnishings are amplified significantly at  
47  
48 723 temperatures above 80 °C (Kajiwara and Takigami, 2013; Kemmlein et al., 2003).

49  
50 724 However, despite evidence that temperatures within landfills can reach up to 80-90 °C;  
51  
52 725 to the authors' knowledge there have been no experiments conducted that examine  
53  
54 726 the effect of temperature on the leachability of BFRs from waste.  
55

56 727

57  
58 728 As well as volatilisation and leaching, an additional migration pathway from waste of  
59  
60 729 BFRs such as BDE-183 and BDE-209, is via fugitive emissions of dust to air by abrasion  
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1 730 during waste unloading and/or compacting by on site vehicles. However, there appear  
2 731 no studies to date that have measured the extent to which this occurs. Likewise, there  
3  
4 732 exist no studies to date that examine the potential for fugitive (largely, but not  
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6 733 exclusively particle-bound) emissions of BFRs as a result of the landfilling of residual  
7  
8 734 bottom and fly ash generated by waste incineration.

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11 736 As well as limited data on the extent and pathways of BFR emissions during waste  
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13 737 treatment, our understanding of the factors influencing such emissions is hampered by  
14  
15 738 our limited knowledge of environmentally-relevant physicochemical properties of  
16  
17 739 some BFRs, e.g., aqueous solubility, and partition coefficients like  $K_{OW}$ ,  $K_{OC}$ , and Henry's  
18  
19 740 constant. While such physicochemical properties for lower brominated PBDEs are  
20  
21 741 relatively well-characterised, those of BDE-209, TBBP-A, HBCD, and "novel" BFRs like  
22  
23 742 decabromodiphenyl ethane (DBDPE) are subject to greater uncertainty. Enhanced  
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25 743 understanding of these properties – and of factors like climate - is needed to facilitate  
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27 744 understanding of how BFRs are leached from waste materials in a landfill setting. For  
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29 745 example, while Odusanya et al (2009) reported higher concentrations of PBDEs in  
30  
31 746 landfill leachate in winter compared to summer; it still appears likely that hotter  
32  
33 747 climates will enhance the leachability of BFRs in landfill. As a result, compared to much  
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35 748 of North America and northern Europe; subtropical and tropical regions such as  
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37 749 southern China, Laos, Cambodia, Vietnam, India, Indonesia, Thailand, the Philippines,  
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39 750 and Malaysia are unlikely to display similar BFR concentrations in landfill leachate.

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42 752 Further international variability in BFR concentrations in landfill leachate will likely  
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44 753 arise due to different waste management practices. For example, the low  
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46 754 concentrations detected in leachate from Japanese landfills may well be attributable to  
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48 755 the fact that 80% of MSW is incinerated in Japan. Hence, the proportion of Japanese  
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50 756 landfill that is incinerator ash is high, and direct extrapolation of Japanese landfill  
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52 757 leachate data to countries such as the UK where incineration is far less prevalent and  
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54 758 BFR-containing waste is more likely landfilled untreated, appears unwise.

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58 760 Given that in many (though not all) studies, BDE-209 is the dominant PBDE congener  
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60 761 found in landfill leachates, this suggests that water solubility alone is not the primary

1 762 factor driving BFR leaching from landfilled waste. Understanding what does drive BFR  
2 763 leaching is important; while there are no reported measurements of HBCD  
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4 764 concentrations in landfill leachates, the evidence for PBDEs suggests that leaching  
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6 765 could constitute an appreciable pathway via which HBCD and related BFRs migrate into  
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8 766 the environment. Specifically, Li et al., (2012) estimated average annual emissions  
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10 767 from a single urban landfill in Canada to be 3.5 tonnes  $\Sigma$ PBDEs /year.

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13 769 Moreover, evidence for reductive debromination of BFRs by microbes under anaerobic  
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15 770 conditions suggests this could also occur in landfill, resulting in some instances in more  
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17 771 toxic and bioavailable compounds, particularly during phase 2 and 3 of landfill leachate  
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19 772 generation (Parsons et al., 2004; Gerecke et al., 2005, 2006; He et al., 2006; Robrock et  
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21 773 al., 2008; Tokarz et al., 2008). While this hypothesis has yet to be verified fully; it is  
22  
23 774 supported by the relatively higher abundances in landfill leachate of PBDE congeners  
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25 775 that are absent from the commercial formulations (Kwan et al., 2013).

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#### 28 29 777 **4. Conclusions**

30 778 There has been very little research into the extent of emissions of BFRs from waste  
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32 779 soft furnishings. The mechanisms via which BFRs migrate from such waste materials  
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34 780 remain far from completely understood, and current understanding is almost entirely  
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36 781 based on the larger – but still far from complete – database on emissions from WEEE  
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38 782 and in-use materials. While – in addition to the burgeoning database on BFR emissions  
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40 783 resulting from informal e-waste recycling activities - evidence exists of elevated  
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42 784 airborne concentrations of HBCDs in the vicinity of a UK e-waste treatment facility  
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44 785 together with the presence of BFRs (specifically PBDEs and TBBP-A) in landfill leachate;  
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46 786 other studies of BFR emissions from regulated waste treatment activities remain few.  
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48 787 Although BFRs are hydrophobic, evidence exists that their leachability from waste  
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50 788 materials is substantially enhanced when DHM is present in the leachate. There is a  
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52 789 need to enhance understanding of the factors influencing emissions and of the  
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54 790 potential for BFR degradation under landfill conditions. Landfill sites already constitute  
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56 791 an enormous reservoir of BFR-containing materials and commercial goods e.g. e-  
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58 792 waste, building materials, carpets, furniture and upholstery fabrics. As a result, without  
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60 793 careful management, such landfills will continue to act as substantial sources of BFRs

1 794 to the global environment, and the wisdom of continued landfilling of BFR-containing  
2 795 waste is questionable. For instance, Weber et al. (2011) suggest that such products  
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4 796 should be destroyed or managed in an environmentally sound manner before they  
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6 797 enter the waste stream, and that such BFR waste should not be landfilled or recycled  
7  
8 798 in view of its toxicity and associated environmental concerns. While hitherto, scientific  
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10 799 and societal focus has been on e-waste, this review highlights that many of the same  
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12 800 concerns exist regarding emissions from waste soft furnishings, and that studies to  
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14 801 enhance our currently scant understanding of BFR emissions from this important  
15  
16 802 waste stream constitute an urgent research priority.  
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18 803

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27 808 acknowledged gratefully.  
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**Table 1: Selected physicochemical properties of brominated flame retardants**

Compound	Log $K_{OW}$	Aqueous Solubility (mg/L)	Log $K_{OA}$	Vapour Pressure
BDE-15	5.48 <sup>a</sup>	0.821 <sup>b</sup>	8.72 <sup>g</sup>	8.80×10 <sup>-3</sup> <sup>i</sup>
BDE-28	5.80 <sup>a</sup>	0.421 <sup>b</sup>	9.50 <sup>h</sup>	1.57×10 <sup>-3</sup> <sup>i</sup>
BDE-47	6.39 <sup>a</sup>	0.112 <sup>b</sup>	10.53 <sup>h</sup>	2.50×10 <sup>-4</sup> <sup>i</sup>
BDE-85	7.37 <sup>b</sup>	0.097 <sup>b</sup>	11.69 <sup>b</sup>	9.86×10 <sup>-6</sup> <sup>j</sup>
BDE-99	6.76 <sup>a</sup>	0.077 <sup>b</sup>	11.31 <sup>h</sup>	5.00×10 <sup>-5</sup> <sup>i</sup>
BDE-100	6.53 <sup>a</sup>	0.085 <sup>b</sup>	11.13 <sup>h</sup>	2.86×10 <sup>-5</sup> <sup>j</sup>
BDE-153	7.08 <sup>a</sup>	0.031 <sup>b</sup>	11.82 <sup>h</sup>	5.80×10 <sup>-6</sup> <sup>i</sup>
BDE-183	8.27 <sup>b</sup>	-	11.96 <sup>h</sup>	4.68×10 <sup>-7</sup> <sup>j</sup>
BDE-209	9.97 <sup>b</sup>	0.002 <sup>b</sup>	15.73 <sup>b</sup>	1.43×10 <sup>-8</sup> <sup>b</sup>
HBCD	5.60 <sup>c</sup>	0.030 <sup>e</sup>	10.46 <sup>e</sup>	6.27×10 <sup>-5</sup> <sup>k</sup>
TBBP-A	5.90 <sup>d</sup>	0.099 <sup>f</sup>		4.72×10 <sup>-9</sup> <sup>f</sup>

<sup>a</sup> Wania & Dugani (2003)      <sup>g</sup> Li et al., (2006)  
<sup>b</sup> Yue & Li (2013)              <sup>h</sup> Harner & Shoeib (2002)  
<sup>c</sup> MacGregor & Nixon (1997)    <sup>i</sup> Wong et al., (2001)  
<sup>d</sup> MacGregor & Nixon (2001)    <sup>j</sup> Tittlemier et al., (2002)  
<sup>e</sup> Marvin et al., (2011)            <sup>k</sup> USEPA (2008)  
<sup>f</sup> Kuramochi et al., (2008)      Nb : estimated values used where not measured

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**Table 3: Concentrations of brominated flame retardants in landfill leachate and related aqueous samples**

Compound	Aqueous medium	Site Category	Concentration (ng L <sup>-1</sup> )	Country
ΣPBDEs	Raw Leachate	Active landfill	10.2 – 19,463	Sweden <sup>a</sup>
TBBP-A	Raw Leachate	Active landfill	<1 – 20	Sweden <sup>a</sup>
ΣPBDEs	Raw Leachate	Active landfill	29 – 248	USA <sup>b</sup>
ΣPBDEs	Raw Leachate	Closed landfill	7.1	USA <sup>c</sup>
ΣPBDEs	Groundwater	Closed landfill	0.052	USA <sup>c</sup>
Σ <sub>3</sub> PBDEs	Raw Leachate	Active landfill	<0.008 – 4	Japan <sup>d</sup>
TBBP-A	Raw Leachate	Active landfill	<1 – 620	Japan <sup>d</sup>
TBBP-A	Treated Leachate	Active landfill	<1 – 11	Japan <sup>d</sup>
Σ <sub>13</sub> PBDEs	Raw Leachate	Active landfill	8.392 – 54.761	S. Africa <sup>e</sup>
Σ <sub>8</sub> PBDEs	Raw Leachate	Active landfill	2.25 – 17,953	S. Africa <sup>f</sup>
Σ <sub>59</sub> PBDEs	Raw Leachate	Active landfill	0.03 – 1,020	Canada <sup>g</sup>
Σ <sub>30</sub> PBDEs	Raw Leachate	Active landfill	5.67	China <sup>h</sup>
Σ <sub>22</sub> PBDEs	Treated Leachate	Active landfill	<6.10	China <sup>h</sup>
TBBP-A	Raw Leachate	Active landfill	15.41	China <sup>h</sup>
TBBP-A	Treated Leachate	Active landfill	<4.50	China <sup>h</sup>
Σ <sub>46</sub> PBDEs	Raw Leachate	Active waste dump	3.7 – 133,000	S.E. Asia <sup>i</sup>
<sup>a</sup> Öman and Junestedt, (2008)			<sup>f</sup> Daso et al., (2013)	
<sup>b</sup> Oliaei et al., (2002)			<sup>g</sup> Li et al., (2012)	
<sup>c</sup> Oliaei et al., (2010)			<sup>h</sup> Zhou et al., (2013)	
<sup>d</sup> Osako et al., (2004)			<sup>i</sup> Kwan et al., (2013)	
<sup>e</sup> Odusanya et al., (2009)				

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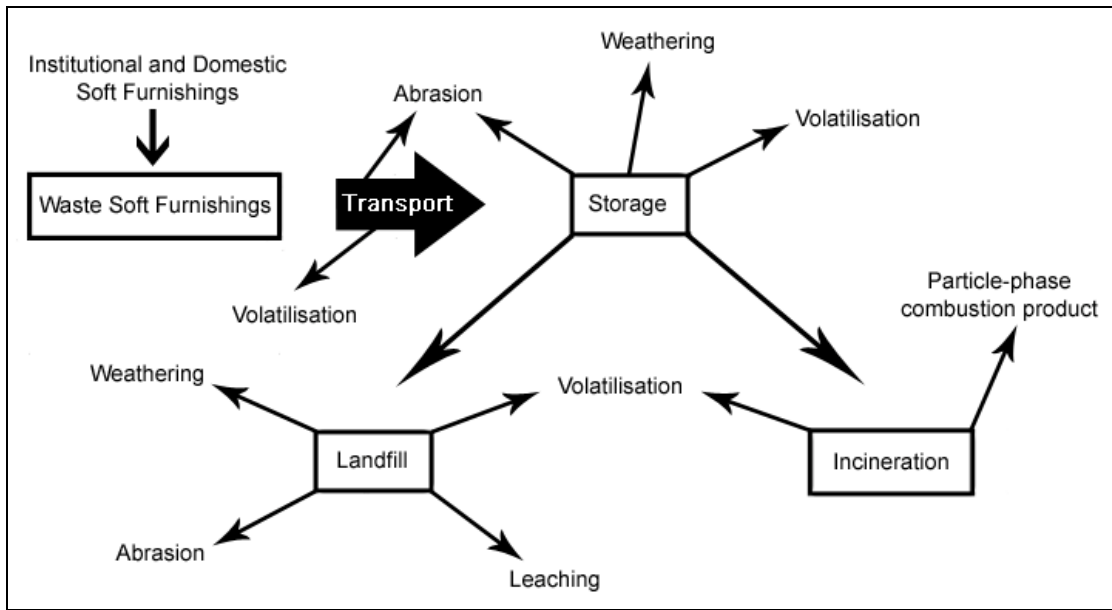
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Figure 1: Potential BFR migration pathways from waste soft furnishings

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