

# Factors influencing leaching of PBDEs from waste cathode ray tube plastic housings

Stubbings, William A; Harrad, Stuart

DOI:

[10.1016/j.scitotenv.2016.06.107](https://doi.org/10.1016/j.scitotenv.2016.06.107)

License:

Creative Commons: Attribution-NonCommercial-NoDerivs (CC BY-NC-ND)

*Document Version*

Peer reviewed version

*Citation for published version (Harvard):*

Stubbings, WA & Harrad, S 2016, 'Factors influencing leaching of PBDEs from waste cathode ray tube plastic housings', *Science of the Total Environment*. <https://doi.org/10.1016/j.scitotenv.2016.06.107>

[Link to publication on Research at Birmingham portal](#)

**Publisher Rights Statement:**

Checked 28/7/2016

**General rights**

Unless a licence is specified above, all rights (including copyright and moral rights) in this document are retained by the authors and/or the copyright holders. The express permission of the copyright holder must be obtained for any use of this material other than for purposes permitted by law.

- Users may freely distribute the URL that is used to identify this publication.
- Users may download and/or print one copy of the publication from the University of Birmingham research portal for the purpose of private study or non-commercial research.
- User may use extracts from the document in line with the concept of 'fair dealing' under the Copyright, Designs and Patents Act 1988 (?)
- Users may not further distribute the material nor use it for the purposes of commercial gain.

Where a licence is displayed above, please note the terms and conditions of the licence govern your use of this document.

When citing, please reference the published version.

**Take down policy**

While the University of Birmingham exercises care and attention in making items available there are rare occasions when an item has been uploaded in error or has been deemed to be commercially or otherwise sensitive.

If you believe that this is the case for this document, please contact [UBIRA@lists.bham.ac.uk](mailto:UBIRA@lists.bham.ac.uk) providing details and we will remove access to the work immediately and investigate.

1           **FACTORS INFLUENCING LEACHING OF PBDEs FROM WASTE**  
2           **CATHODE RAY TUBE PLASTIC HOUSINGS**

3                           **William A. Stubbings<sup>1\*</sup>, Stuart Harrad<sup>1</sup>**

4           <sup>1</sup>School of Geography, Earth, & Environmental Sciences, University of Birmingham,  
5                           Birmingham, B15 2TT, UK.

6  
7                           \*Corresponding author: William A. Stubbings

8  
9                           Public Health Building,  
10                          School of Geography, Earth & Environmental Sciences,  
11                          University of Birmingham,  
12                          Birmingham, B15 2TT,  
13                          UK.

14                          william.a.stubbings@gmail.com  
15  
16  
17  
18  
19  
20  
21  
22  
23  
24  
25

26 **Abstract**

27 Samples of waste cathode ray tube (CRT) plastic housings were exposed to Milli-Q® water  
28 containing dissolved humic matter at concentrations of 0, 100 and 1000 mg L<sup>-1</sup> as leaching  
29 fluid under laboratory conditions, and polybrominated diphenyl ethers (PBDEs) determined  
30 in the resulting leachate. Despite the relatively hydrophobic physicochemical properties of  
31 PBDEs, concentrations of ΣPBDEs in the leachate from the leaching experiments in this study  
32 ranged from 14,000 – 200,000 ng L<sup>-1</sup>. PBDE leaching appears to be a second order process,  
33 whereby a period of initially intense dissolution of more labile PBDEs is followed by a slower  
34 stage corresponding to external diffusion of the soluble residue in the material. The bulk of  
35 transfer of PBDEs to the leaching fluid occurs within the first 6 hours of contact, during  
36 which time we suggest that the most labile PBDEs are “washed” off the surface of the CRT  
37 plastics. The predominant congeners in the chips were BDE-209 (2,600 mg kg<sup>-1</sup>) and BDE 183  
38 (220 mg kg<sup>-1</sup>). The impacts on PBDE leaching of leachate pH and temperature were also  
39 examined. Increasing the temperature of leaching fluids from 20 to 80 °C, enhances the  
40 leachability of BDE-209 and BDE-99 from plastics. In all cases, the alkaline pH 8.5 examined,  
41 resulted in the greatest PBDE concentrations in leachate. Agitation of the waste/leachate  
42 mixture enhances PBDE leaching from CRT plastics. Potential evidence for debromination of  
43 heavy congeners to the lower brominated and more bioavailable BDEs was observed.  
44 Specifically, BDEs-47, -85 and -100 were detected in the leachates, but were absent from  
45 the CRT plastics themselves.

46 **Keywords**

47 Polybrominated diphenyl ether;

48 E-waste;

49 Brominated flame retardants;

50 Leachate

51

## 52 1. Introduction

53 Polybrominated diphenyl ethers (PBDEs) are organic chemicals that historically were added  
54 to a plethora of consumer goods and materials such as electrical and electronic equipment  
55 (EEE) and textiles to impart flame retardancy. Total historic production of PBDEs (including  
56 Deca-BDE) has been estimated to amount to 1.3 million to 1.5 million tonnes between 1970  
57 and 2005 (UNEP, 2010a). Three commercial mixtures exist: Penta-BDE, Octa-BDE and Deca-  
58 BDE (marker congeners for each are: BDEs 47 & 99; BDE-183; and BDE-209, respectively).  
59 North America contributed 97.5 % of global Penta-BDE production (8,290 tonnes), 35.9 % of  
60 Octa-BDE (1,375 tonnes), and 44.3 % of Deca-BDE (24,300 tonnes) (Hale et al., 2003). In  
61 contrast, Asia contributed 53 % of global Octa-BDE production (2,030 tonnes) and 42 % of  
62 Deca-BDE (23,038 tonnes), but manufactured no Penta-BDE (Hale et al., 2003). Europe  
63 accounted for the remaining global production of 2.5 % Penta-BDE (213 tonnes), 12 % Octa-  
64 BDE (460 tonnes) and 13.7 % Deca-BDE (7,515 tonnes) (Hale et al., 2003). In 1999, it was  
65 reported that North America accounted for 50.6 % of total PBDE consumption.

66 CRT housings were conventionally produced using either acrylonitrile butadiene styrene  
67 (ABS) copolymers or high impact polystyrene (HIPS). Historically, around 95 % of Octa-BDE  
68 supplied in the EU was used in ABS (globally ~70 %), to which it was typically added at  
69 concentrations between 10-18 % by weight (EC, 2011). The main uses for BFR-treated ABS  
70 were predominantly in housings of EEE, particularly for cathode ray tube (CRT) housings  
71 (e.g. PC monitors and TVs), and office equipment (e.g. copying machines and business  
72 printers). The remaining ~5 % of minor uses of Octa-BDE were in HIPS, polybutylene  
73 terephthalate (PBT), and polyamide polymers, with typical concentrations between 12-15 %  
74 by weight (EC, 2011). Other possible uses were in: nylon, low density polyethylene,  
75 polycarbonate, phenolformaldehyde resins, and unsaturated polyesters, as well as in  
76 adhesives and coatings (UNEP, 2010a; 2010b).

77 While ABS was predominantly treated with Octa-BDE, HIPS was mainly treated with Deca-  
78 BDE typically added at concentrations between 13-15 % by weight (EC, 2011; BSEF, 2014).  
79 Widely used due to its relatively low cost, Deca-BDE was employed in a range of  
80 plastics/polymers and textiles. In plastics, Deca-BDE was used for EEE housings, in the

81 automotive and aeronautic sectors and in construction, in applications such as wires and  
82 cables, pipes and carpets (BSEF, 2014).

83 Despite their extensive use, acute toxicity studies have suggested that PBDEs can be  
84 hepatotoxic at relatively high doses (Zhou et al., 2002; Bruchajzer et al., 2011). Moreover,  
85 several studies have indicated that Penta- and Octa-BDE mixtures, as well as several of the  
86 major individual congeners present in wildlife and people, can alter liver enzymes, disrupt  
87 thyroid homeostasis, and are associated with early onset of puberty, reduced fertility, and  
88 impaired neurological development (Viberg et al., 2007). In general, the lower brominated  
89 congeners are more acutely toxic than the higher ones (Darnerud, 2003). Consistent with  
90 this, are reports that decabromodiphenyl ether (BDE-209) displays low acute toxicity when  
91 given by the oral, inhalation and dermal route (Kelly et al., 2008; Tomy et al., 2008; Wu et  
92 al., 2009). Moreover, some studies report that BDE-209 does not appear to be genotoxic, is  
93 not teratogenic, and does not seem to cause developmental toxicity (Hardy et al., 2009;  
94 Wang et al., 2010). In contrast however, work by Johansson et al., (2008) suggests that BDE-  
95 209 can be as potent as the lower brominated PBDEs in causing developmental neurotoxic  
96 defects.

97 Such evidence of toxicity is compounded by evidence that PBDEs are environmentally  
98 ubiquitous (de Wit, 2002; Law et al., 2006; de Wit et al., 2006; Kohler et al., 2008; Harrad et  
99 al., 2009). Concerns over the toxicology and persistence of these chemicals are exacerbated  
100 by evidence of PBDEs inside the human body. Numerous studies have reported the  
101 presence of PBDEs in human adipose tissue, blood serum, liver, placenta, cord blood and  
102 breast milk worldwide (Noren and Meironyte, 2000; Choi et al., 2003; Petreas et al., 2003;  
103 Covaci et al., 2008a; Toms et al. 2009). However, BDE-209 is considered relatively less  
104 persistent and bioaccumulative than the lower brominated congeners. These concerns  
105 about their adverse environmental impacts have meant that production of the Penta- and  
106 Octa-BDE commercial mixtures ceased in the EU and North America in 2004, and their use in  
107 all applications in 2006. Likewise, Deca-BDE was restricted severely in the EU in 2008. US  
108 manufacturers voluntarily committed to phase it out from most uses in the USA by the end  
109 of 2012, and ended all use by 31 December 2013 (BSEF, 2014).

110 As a further reflection of concern about their use, the Penta- and Octa-BDE commercial  
111 mixtures (tetra-, penta-, hexa- and hepta-BDEs) are listed as persistent organic pollutants  
112 (POPs) by the United Nations Environment Programme (UNEP) under the Stockholm  
113 Convention on POPs, while Deca-BDE is under active consideration for listing (UNEP, 2014).

114 Notwithstanding the bans and restrictions on manufacture of PBDEs, the reservoir of PBDEs  
115 present in waste EEE (WEEE) has and will continue to, gradually enter the waste stream, and  
116 there is hence a pressing need to understand the fate of chemicals like PBDEs associated  
117 with WEEE following disposal. While landfilling of WEEE is now restricted in many  
118 jurisdictions, in the early part of 21<sup>st</sup> century, Alcock et al. (2003) estimated that >80 % of  
119 total BFR-containing waste was landfilled in the UK and North America, leaving a substantial  
120 legacy. Potential emission pathways for chemicals associated with landfill include leaching  
121 and volatilisation. The physicochemical properties of PBDEs (Table 1), suggest following  
122 disposal to landfill, such leaching and volatilisation of PBDEs associated with treated WEEE  
123 may not be extensive. However, PBDEs have been reported in landfill leachate (Oliaei et al.,  
124 2002; Osako et al., 2004; Oliaei et al., 2010) and a study into PBDE leaching from WEEE  
125 demonstrated that PBDEs can be present in distilled water and landfill leachates at  
126 significant concentrations (Danon-Schaffer et al., 2013). This study conducts a series of  
127 controlled laboratory experiments to test the hypothesis that PBDEs are capable of leaching  
128 from waste CRT plastic housings. We further hypothesise that the leaching of PBDEs from  
129 the waste CRT plastic housings will be influenced by leachate temperature and pH, along  
130 with waste:leachate contact time and whether the waste is agitated during contact with the  
131 leachate.

132

## 133 **2. Materials and methods**

### 134 **2.1. Samples and sample preparation.**

135 The waste material studied in our experiments consisted of flame-retarded CRT plastic  
136 housings donated by Sims Recycling Solutions, UK. In 2013, a 1 kg grab sample of CRT  
137 housings taken from the PC and TV monitors waste plastic stream at a waste treatment  
138 plant was collected for this study. The CRT plastics had been subjected to a size reduction  
139 step at the waste treatment plant and were supplied as chips of ~ 5-25 mm diameter. The

140 chipped CRT plastic samples were manually separated from additional debris within the  
141 waste stream grab sample. Any wood, metal, or wires were removed prior to weighing.

## 142 **2.2. Chemical analysis of initial PBDE concentrations in CRT plastics.**

143 To assess the homogeneity of the starting material, five 30 mg aliquots of the homogenised  
144 plastic sample were analysed before conducting leaching experiments. PBDEs in hard plastic  
145 samples were extracted by means of a modified version of the combined ultrasound  
146 assisted extraction and vortexing method described by Ionas et al. (2012).

147 In order to improve the extraction, the hard plastics were subjected to a size reduction step  
148 to increase the contact surface area with the solvent. Due to the rigidity of the matrix and  
149 size of plastic chips obtained (approximately 2 mm × 5 mm × 5 mm) a Fritsch Pulverisette 0  
150 cryo-vibratory micro mill (Idar-Oberstein, Germany) was employed for this purpose. The  
151 samples along with one 25 mm diameter stainless steel ball were added to the stainless  
152 steel grinding mortar (50 mL volume) and submerged in liquid nitrogen until they reached  
153 the temperature of the surrounding liquid (-196 °C). It was then ground at a vibrational  
154 frequency of 30 Hz for 10 min and repeated 3-4 times. The resulting plastic particles varied  
155 in size, but typically passed through a 250 µm mesh aluminium sieve pre-rinsed with  
156 acetone, toluene and *n*-hexane.

157 The extraction process for the resulting homogenised plastic particles consisted of  
158 consecutive steps of vortexing for 1 min and ultrasonication for 15 min with 10 mL of *n*-  
159 hexane in pre-cleaned test tubes. This cycle of vortexing and ultrasonication was repeated 3  
160 times. The samples were left in solvent overnight to maximise recoveries. No destructive  
161 clean-up method was applied to minimise any degradation of PBDEs.

162

## 163 **2.3. Leaching test methods**

164 Three distinct experimental scenarios were undertaken to examine the effects on the  
165 leaching behaviour of PBDEs from CRT plastics: (a) plastic-leachate contact time, (b)  
166 leachate temperature, and (c) pH level of the leaching fluid. All scenarios employed single  
167 batch experiments where the CRT plastics were contacted once only with the leaching fluid.  
168 In scenario (a) experiments, CRT plastic samples were exposed to the leaching fluid for

169 either 6 h, 24 h or 48 h. Both scenarios (a) and (c) were conducted at the prevailing room  
170 temperature (20 °C). In scenario (b) experiments examining the influence of temperature of  
171 the leaching fluid on leaching behaviour, experiments were conducted in which CRT plastics  
172 were contacted with leaching fluid for 24 h at three different temperatures (20, 50, and 80  
173 °C). Finally, in scenario (c) experiments examining the influence of pH of the leaching fluid  
174 on leaching behaviour; experiments were conducted in which CRT plastics were contacted  
175 with leaching fluid for 6 h at three different pH levels (acidic 5.8, slightly acidic 6.5, and  
176 alkaline 8.5). In both scenarios (a) and (c), contact vessels were agitated at 200 rpm. In all  
177 three experiment scenarios, dissolved humic matter (DHM) solutions of 0 mg L<sup>-1</sup>, 100 mg L<sup>-1</sup>  
178 and 1000 mg L<sup>-1</sup> were employed as leaching fluids. Conditions employed in these  
179 experiments are summarised in Supplementary Information (SI).

180 Polytetrafluoroethylene (PTFE) bottles (500 mL) were used as contact vessels during  
181 controlled leaching experiments. The whole volume of the contact vessel was not  
182 completely filled with leaching fluid and as a result a headspace was present inside the  
183 contact vessel. In all experiments on CRT plastics, 5 g of sample was contacted with 125 mL  
184 of Type 1 ultrapure Milli-Q® water giving a liquid-solid ratio of 25:1 (v/w). Following addition  
185 of the sample and leaching fluid, contact vessels were horizontally agitated on a mechanical  
186 shaker at 200 rpm for the desired contact time. The exception was for experiments  
187 examining the influence of temperature, which were not agitated and instead were  
188 maintained at the desired temperature for 24 h by immersion of the contact vessel in a  
189 thermostatically controlled water bath. Each of the above leaching experiments were  
190 conducted in duplicate.

191 Leaching fluids were prepared using Milli-Q® water. The pH levels were determined before  
192 each experiment using a pH meter (Hanna, USA) and levels were corrected using either  
193 glacial acetic acid (Sigma-Aldrich) or sodium hydroxide (Sigma-Aldrich) solutions. In  
194 scenarios (a), (b) and (c), DHM solution was prepared by dissolving Aldrich humic acid  
195 (sodium salt) in Milli-Q® water. The solution was stirred for 5 minutes until total dissolution  
196 and then the pH was adjusted to the desired level, before finally it was centrifuged at 2000  
197 rpm for 1 min.

198



199 **2.4. Chemical analysis of leachates**

200 After contacting the leaching fluid, the leachate obtained from each of the different  
201 experimental conditions was filtered through a 0.45  $\mu\text{m}$  pore size glass fibre filter (Advantec,  
202 Japan) to remove any small particles or fibres of the flame retarded material and then  
203 spiked with 50 ng each of  $^{13}\text{C}_{12}$ -labelled BDE-47, -99, -153 and -209, as internal (or  
204 surrogate) standards. The collected filtrate was then extracted in series using 3 x 50 mL  
205 dichloromethane by liquid-liquid extraction with mechanical shaking for 10 minutes each  
206 time. Approximately 5-10 mL 2 % NaCl solution was added post-experiment to leachates  
207 containing no DHM to enhance separation after extraction. When the NaCl solution was  
208 used on DHM containing leachates it produced an undesirable emulsion between the  
209 interface of the two layers and reduced PBDE recovery efficiencies. The combined  
210 dichloromethane extracts were dried via filtration through 5 g anhydrous  $\text{Na}_2\text{SO}_4$ .

211 The dried extract was concentrated to 0.5 mL using a Zymark Turbovap II (Hopkinton, MA,  
212 USA) with solvent exchange to *n*-hexane before elution through a pre-cleaned acidified silica  
213 (1 g of 44% concentrated sulfuric acid, w/w) and  $\text{Na}_2\text{SO}_4$  column with 30 mL of *n*-  
214 hexane:DCM (9:1 v/v). The eluate was concentrated with solvent exchange to *n*-hexane  
215 before evaporation to incipient dryness, addition of  $^{13}\text{C}_{12}$ -labelled BDE-100 as recovery  
216 determination (or syringe) standard and dilution in methanol prior to analysis via LC-MS/MS  
217 equipped with an Atmospheric Pressure Photoionization source (APPI).

218 An additional extraction step was performed on the glass fibre filters used in the filtrate.  
219 After filtration of the leachate, filters were desiccated in a silica gel-containing glass  
220 desiccator covered with aluminium foil to prevent any potential photo-degradation of  
221 PBDEs. Any visible particles of plastic retained on the filters were carefully removed with  
222 tweezers prior to extraction. Filters were then extracted via five cycles of vortexing and  
223 ultrasonication. The individual filters for each experiment and 5 mL of a positive azeotropic  
224 mixture of *n*-hexane:acetone (3:2 v/v) were added to a pre-washed test tube, vortexed for 1  
225 min and sonicated for 5 mins. The supernatant was transferred to a clean tube, the  
226 extraction was repeated and both supernatants were combined (10 mL total) and vortexed  
227 for 1 min. The filter extract was then cleaned up in identical fashion to the leachate extracts.

228

229 **2.5 Determination of concentrations of PBDEs**

230 Concentrations of BDEs-47, -85, -99, -100, -153, -154, -183, and -209 in all samples  
231 generated from leaching experiments and pulverised homogenised plastics samples were  
232 quantified using a dual pump Shimadzu LC-20AB Prominence high pressure liquid  
233 chromatograph (Shimadzu, Kyoto, Japan) equipped with a Sciex API 2000 triple quadrupole  
234 mass spectrometer (Applied Biosystems, Foster City, CA, USA) (see SI for additional details).

235

236 **2.6. Calculation of PBDE leaching**

237 The percentage of PBDEs leached from the CRT plastic housing chips into each leachate  
238 sample (PL) was calculated as in equation 1:

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

240

241  $PL$  = percentage leached (%)

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

243  $V$  = volume of leachate (L)

244  $C_{waste}$  = Conc. of PBDEs in waste sample (mg/kg)

245  $W$  = total weight of waste sample (kg)

246 The percentage leached normalised to contact time ( $PLT$ , % h<sup>-1</sup>) is expressed here as the  
247 percentage of PBDEs leached from the CRT plastic chips per hour of contact time.  $PLT$  is  
248 calculated according to equation 2.

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

250  $PL$  = percentage leached (%)

251  $t$  = contact time (h)

252

253 **3. Results and discussion**

254 **3.1. Initial PBDE concentrations in CRT plastic samples**

255 Table 1 displays the mean initial concentrations and aqueous solubilities of individual PBDE  
256 congeners in the CRT plastics used in this study. Concentrations of BDE-47, BDE-85 and BDE-  
257 100 were below their respective limits of quantification (LOQs): 217 ng g<sup>-1</sup>, 13 ng g<sup>-1</sup> and 12  
258 ng g<sup>-1</sup>.

259 Deca-BDE was the predominant congener found in the samples followed by Octa-BDE. This  
260 may be due to HIPS being more prevalent in the grab sample of CRT chips, or because Deca-  
261 BDE, to some extent, replaced Octa-BDE in ABS plastics after the EU ban on Octa-BDE  
262 (Lassen et al., 2006). Concentrations of ΣPBDE are <1 % by weight suggesting that some  
263 dilution has occurred, indicating that some plastic chips within the CRT waste stream sample  
264 were likely not treated with PBDEs. It is likely that some of the chips were treated with  
265 Deca-BDE, a smaller fraction with Octa-BDE and some did not contain PBDEs. This is  
266 supported by the fact that hand-held XRF analysis of these chips revealed a heterogenous  
267 distribution of Br (pers. comm., Antonella Guzzonato, University of Birmingham, 2014).  
268 Further to this, according to Wäger et al., (2011), tetrabromobisphenol A (TBBPA) is the  
269 predominant BFR found in CRT monitors collected from Swiss WEEE recycling sites and it  
270 was also suggested by the authors that TBBPA was applied in ABS plastics.

271

272 **3.2. Effects of contact time and humic matter content of leaching fluid on PBDE leaching**  
273 **(single batch experiments).**

274 The liquid-solid ratio, contact durations and agitation speed were selected during method  
275 development after reviewing established standardised leaching protocols from North  
276 America, Europe and Japan and conducting initial experiments. Concentrations of DHM  
277 solutions used in experiments were 0 mg L<sup>-1</sup>, 100 mg L<sup>-1</sup> and 1000 mg L<sup>-1</sup>. Landfill site  
278 leachates can contain a wide spectrum of dissolved organic matter concentrations, usually  
279 in the range between ~100 mg L<sup>-1</sup> up to ~50,000 mg L<sup>-1</sup> (Kjeldsen et al., 2002).

280 Table 2 presents PBDE congener concentrations in duplicate samples, as well as mean PL (%)  
281 and mean PLT values (% h<sup>-1</sup>) in leachate from the single batch contact time experiments.

282 Relatively little change in PBDE concentrations in leachate are observed with increasing  
283 contact time for leaching fluids containing 0 and 100 mg L<sup>-1</sup> DHM. This suggests that the bulk  
284 of the transfer to the leaching fluid is occurring within the first 6 hours, during which time  
285 the most easily available PBDEs are “washed” off the surface of the CRT plastics. Therefore,  
286 serial batch experiments were not considered. However, the concentrations of ΣPBDEs in  
287 the leachate did increase slightly with longer contact times in the presence of the 1000 mg  
288 L<sup>-1</sup> DHM leaching fluid.

289 Contacting the CRT plastics with Milli-Q® water alone as the leaching fluid resulted in  
290 surprisingly high PBDE concentrations when considering the hydrophobicity of the higher  
291 brominated congeners (Table 1). We therefore suggest that dislodgement of fine dust from  
292 the surface of the CRT plastics was an important leaching mechanism for the more  
293 hydrophobic BDEs-153, -154, -183 and -209. Any dust that was present on the surface of the  
294 chips may be “washed” off when the leaching fluid was added to the chamber. If PBDEs had  
295 partitioned into this dust they would be more readily leached. These results are somewhat  
296 similar to those reported by Danon-Schaffer et al., 2013. An alternative mechanism would  
297 be abrasion of the CRT chips during agitation of the leaching chamber resulting in ultrafine  
298 particles of the flame retarded plastics being present in the leachate.

299 Aqueous solubility is likely to be more important for the relatively more soluble lower  
300 brominated PBDE congeners. These more soluble congeners are more readily dissolved in  
301 the aqueous leachate resulting in higher PLT values than observed for the higher  
302 brominated PBDEs. While BDE-47, BDE-85 and BDE-100 were not present at substantial  
303 concentrations in the CRT chips, they were detected in some of the leaching fluids, with the  
304 highest concentrations for these congeners in leachate detected in experiments with the  
305 longest contact times. This suggests either some debromination of the heavier PBDE  
306 congeners has occurred or reflects the relatively higher aqueous solubility of the lower  
307 brominated congeners. This is similar to our earlier work on hexabromocyclododecane  
308 (HBCDD; Stubbings et al., 2016), where ε-HBCDD was present in quantifiable concentrations  
309 in leachate after being contacted with HBCDD treated textiles, despite being <LOQ in the  
310 textile leached. These results are also to some extent similar to those reported by Danon-  
311 Schaffer et al., 2013.

312

### 313 3.3. Leaching kinetics

314 Ho et al., (2005) expressed the leaching of water-soluble organic components from sapwood  
315 in terms of a second-order rate equation and being somewhat analogous to the condition  
316 for our experiments, this equation was then applied to the leaching of PBDEs from CRT  
317 plastics as the following:

318 Equation 3: 
$$\frac{C_t}{t} = k(C_s - C_t)^2,$$

319 where  $k$  is the second-order leaching rate constant ( $L\ ng^{-1}\ min^{-1}$ ),  $C_s$  the leaching capacity,  
320 which is the concentration of PBDEs at saturation ( $ng\ L^{-1}$ ), and  $C_t$  is the concentration of  
321 PBDEs ( $ng\ L^{-1}$ ) in suspension at any given time,  $t$  (min). The leaching capacity,  $C_s$ , and the  
322 second-order leaching rate constant,  $k$ , can be determined experimentally from the slope  
323 and intercept by plotting  $t/C_t$  against  $t$ .

324 We generated plots of  $t/C_t$  against  $t$  for all single batch experiments ( $n = 6$ ) conducted at 20  
325 °C and agitated at 200 RPM. The slope, Y-intercept, saturated leaching capacity,  $C_s$ , the  
326 leaching rate constant,  $k$ , two-tailed  $p$  values, and Pearson's correlation coefficients,  $r$ , are  
327 given for individual PBDEs in Table 3. A positive and highly significant ( $p < 0.05$ ) linear  
328 correlation between  $t/C_t$  and  $t$  was observed for BDE-100 and BDE-209 with leaching fluids  
329 at  $0\ mg\ L^{-1}$  DHM (Milli-Q® water), while weaker correlations are observed for BDE-153 (90 %  
330 probability), -154 (84 % probability) and -183 (91 % probability). At  $100\ mg\ L^{-1}$  DHM only  
331 BDE-154 shows a highly significant correlation, while BDE-153 (90 % probability) and BDE-  
332 183 (82 % probability) show weaker correlations. With the  $1000\ mg\ L^{-1}$  DHM leaching fluid,  
333 BDE- 100, 153 and 183 are significantly correlated ( $p < 0.05$ ) and BDE-209 shows a weaker  
334 significance (93 % probability). Example plots of  $t/C_t$  versus  $t$  are provided for DHM  
335 concentrations 0, 100 and  $1000\ mg\ kg^{-1}$  in the SI (Fig. S2-4).

336 While the small sample size ( $n=6$ ) is acknowledged, this apparent fit with second order  
337 kinetics suggests initial rapid leaching followed by a slower second phase. This is consistent  
338 with our hypothesis that the most readily available PBDEs are "washed" off the CRT polymer  
339 surface early in the experiment. A second, slower stage follows, which corresponds

340 primarily to external diffusion and is related to the soluble remainder within the polymer  
341 matrix. This kinetics model seems especially relevant to the higher brominated PBDE  
342 congeners.

343 To further evaluate the hypothesis of second-order rate kinetics, the natural logarithms of  
344 the same PBDE leachate concentration data for single batch experiments conducted at 20  
345 °C, were plotted against contact time to check for linearity and negative slope intercepts  
346 that would suggest first order kinetics. The results are presented as SI (Fig. S5). The only  
347 congener to satisfy all first-order criteria was BDE-99 when the leaching fluid contained 100  
348 mg L<sup>-1</sup> DHM. A weaker correlation (92 % probability) was observed for BDE-100 at the same  
349 DHM concentration. This strongly supports the idea that leaching of PBDEs from CRT plastics  
350 in these experiments is predominantly governed by second-order leaching kinetics.

351

#### 352 **3.4. Effects of the temperature of leaching fluid on PBDE leaching from CRT plastics**

353 Within a landfill, temperatures can sometimes reach as high as 80-90 °C due to heat  
354 released during aerobic degradation (Kjeldsen et al., 2002). Therefore, the influence on  
355 PBDE leaching from CRT plastics of leachate temperatures of 20 °C, 50 °C and 80 °C was  
356 investigated. The only other study the author is aware of examining the effects of leachate  
357 temperature on PBDE leaching only examined differences between temperatures of 10 °C,  
358 20 °C and 25 °C (Danon-Schaffer et al., 2013).

359 Table 4 presents PBDE congener concentrations in duplicate experiments as well as mean PL  
360 (%) and mean PLT values (% h<sup>-1</sup>) in leachate from single batch temperature experiments. The  
361 highest concentrations of PBDEs were observed when Milli-Q® water was used as leaching  
362 fluid and contacted at 50 °C and 80 °C. Potential reasons for this could be related to reduced  
363 PBDE extraction efficiencies from DHM solutions, or from the filters in which DHM had  
364 passed through. This result is different from the findings of analogous studies contacting  
365 WEEE plastics with deionised water by Danon-Schaffer et al., (2013) and Choi et al., (2009).  
366 In these studies, PBDE concentrations were always significantly higher in leachate/DHM  
367 solutions, than those detected when deionised water was the leaching fluid. We note that  
368 concentrations of PBDEs were consistently higher in the 1000 mg L<sup>-1</sup> DHM leaching fluid

369 when compared to the concentrations found in the 100 mg L<sup>-1</sup> DHM leaching fluid. This is  
370 addressed further in section 3.7.

371 No agitation was used in these temperature experiments and this resulted in lower overall  
372 concentrations of PBDEs when compared with the agitated contact time experiments at 20  
373 °C. Because no agitation occurred in these temperature experiments it is very unlikely that  
374 abrasion of particles contributed to the concentrations of PBDEs in the leachate. BDE-85  
375 was not detected in the leachates in these temperature experiments.

### 376 **3.5. Effects of the pH of leaching fluid on PBDE leaching from CRT plastics.**

377 The pH levels used were based on real measured leachate pH levels that with only very few  
378 exceptions, lie in the range 5.8 to 8.5 (Renou et al. 2008). The influence of three pH levels,  
379 representing an acidic leachate (5.8), an alkaline leachate (8.5) and a mildly acidic leachate  
380 (6.5) on PBDE concentrations in leachate, were explored. PBDE congener concentrations in  
381 duplicate samples, as well as mean PL (%) and mean *PLT* values (% h<sup>-1</sup>) in leachate from  
382 these pH experiments are listed in Table 5.

383 There is very little variation in total PBDE concentrations in leachate at the different pH  
384 levels examined. Experiments with acidic pH (5.8) leaching fluids yield the lowest ΣPBDE  
385 concentrations of the three pH levels examined. The only other study of which we are aware  
386 that examined the influence of pH on PBDE leaching from WEEE (Danon-Schaffer et al.,  
387 2013) reported that acidic leaching fluids of pH 4-5 facilitated a greater leaching of PBDEs  
388 than those of pH 7 and 9, and that the enhancement of leaching at acidic pH was more  
389 marked for less brominated PBDEs.

390

### 391 **3.6. Effects of agitation on PBDE leaching from CRT plastics.**

392 By comparing the results of experiments conducted at 20 °C with contact times of 24 h in  
393 the agitated contact time experiment and the non-agitated experiment conducted at the  
394 same temperature and contact time, the effect of agitation on leaching of PBDEs from the  
395 CRT plastics can be examined (Figure 1).

396 The  $\Sigma$ PBDE concentrations in the agitated experiments were 178 % greater than in the  
397 equivalent non-agitated experiments at 0 mg L<sup>-1</sup> DHM, 353 % greater at 100 mg L<sup>-1</sup> DHM and  
398 124 % greater at 1000 mg L<sup>-1</sup> DHM. This illustrates that agitation has a considerable role in  
399 enhancing PBDE leaching from CRT plastics. The results of paired samples t-tests are  
400 presented in the SI (Table S5). There are highly significant differences ( $p < 0.05$ ) between  
401 BDE-153, BDE-183 and BDE-209 concentrations in the leachate generated in agitated and  
402 non-agitated experiments and a weaker significant difference observed for BDE-100 (90 %  
403 probability).

404

### 405 **3.7. Effects of DHM concentration of leaching fluid on PBDE leaching from CRT plastics**

406 It has been reported that the presence of DHM in leaching fluids enhances the leachability  
407 of PBDEs suspended in water (Choi et al., 2009). However, there are multiple instances in  
408 this study in which leachates from experiments containing no DHM have higher  
409 concentrations and *PLT* values (% h<sup>-1</sup>) than leachates containing DHM.

410 PBDE concentrations, mean PL (%) and mean *PLT* values (% h<sup>-1</sup>) in leachate from those  
411 experiments examining leaching at different pH and at DHM concentrations of 0, 100, and  
412 1,000 mg L<sup>-1</sup> are illustrated in Table 5.

413

### 414 **3.8 Statistical analysis of the whole data set**

415 A multiple linear regression analysis (MLRA) was performed for the entire data set for each  
416 PBDE congener. Leachate concentrations were used as the dependent variable, while DHM  
417 concentration, temperature, contact time, pH and whether the samples were agitated or  
418 not were used as independent variables. The independent variables for each PBDE congener  
419 are ranked by relative importance and significance and presented as SI (Table S6). The  
420 coefficients for each significant independent variable are also presented and can be used to  
421 predict how much the dependent variable is expected to increase when that independent  
422 variable increases by one, holding all the other independent variables constant.

423 However, we acknowledge that a degree of uncertainty is involved in performing an MLRA  
424 on the dataset due to the low number of data points compared to the number of influencing



425 variables. Additionally, the PBDE concentrations in the starting material likely vary between  
426 each experiment.

427 The effect of the length of contact time on BDE-209 concentrations was highly significant  
428 ( $p < 0.05$ ). The coefficients predict that BDE-209 concentrations increase by  $720 \text{ ng L}^{-1}$  for  
429 each additional hour of contact with the leaching fluid.

430 The effect of contact time also has a highly significant positive effect on leachate  
431 concentrations of the lower brominated congeners BDE-47 and BDE-85. They are more  
432 soluble and relatively hydrophilic than the heavier congeners so one would expect them to  
433 leach relatively quickly if they were present in the plastics to start with. A possible  
434 alternative explanation may be that external diffusion of these congeners is a slow process  
435 that requires greater than 24 h contact time.

436 Interestingly, the effect of agitation on PBDE leaching was highly significant and led to  
437 enhanced concentrations of BDEs -153, -100, -99, -85, and -47. This supports the hypothesis  
438 of a PBDE “wash off” effect.

439 The pH of the leaching fluid has a highly significant positive effect on the leaching of BDEs -  
440 154, -100, -99, -85, and -47. The largest effect was observed for BDE-154. In all cases, the  
441 alkaline 8.5 pH elicited the greatest concentrations.

442 The effect of the presence of DHM in the leachate elicits a significant positive effect on BDE-  
443 99 and BDE-100 leachate concentrations. However, this effect is ranked as least important  
444 when predicting the influence of the independent variables.

445

#### 446 **4. Summary**

447 This study shows that substantial concentrations of PBDEs can be leached under laboratory  
448 conditions from CRT waste despite the low aqueous solubility of the higher brominated  
449 PBDEs. Concentrations observed here in leachate for  $\Sigma$ PBDEs ( $14,000 - 200,000 \text{ ng L}^{-1}$ ) are  
450 comparable to those reported in raw leachates from landfill (Öman and Junestedt, 2008;  
451 Odusanya et al., 2009; Kwan et al., 2013) and are 48 to 680 times higher than the highest  
452 reported BDE-209 concentration in a river system ( $295 \text{ ng L}^{-1}$ ) (Cristale et al., 2013). Our data

453 suggests that leaching of the higher brominated PBDEs from CRT plastics using Milli-Q®  
454 water as a leaching fluid is a second order process. Following an initial period of  
455 source:leaching fluid contact during which leaching is relatively facile, subsequent leaching  
456 is slower. This is perhaps not the case for lower brominated congeners BDE-47, BDE-85, and  
457 BDE-99 for which the kinetic process is less obvious due to low concentrations in the  
458 leachate and may potentially be formed by debromination.

459 Although attempts were made to ensure each 5 g aliquot of CRT plastic chips were  
460 representative of the bulk chipped sample, the heterogeneous mixture of the CRT plastics  
461 perhaps has a confounding effect on trends. It is likely that not all plastic chips present in  
462 the bulk sample used were flame retarded with PBDEs, while some were treated with Octa-  
463 BDE and others with Deca-BDE. Therefore, the starting concentrations of PBDE congeners in  
464 the different 5 g aliquot of the CRT plastic chips used in each leaching experiment may have  
465 been variable. Additionally, variability in the morphology of the CRT plastic chips such as the  
466 thickness, surface area, porosity and/or strength of the of the plastic may have influenced  
467 the potential for PBDEs to partition into the leaching fluid resulting in different leaching  
468 rates from chip to chip (Brandsma et al., 2013a).

469 These caveats aside, it appears that increasing the temperature of leaching fluids from 20 to  
470 80 °C, enhances the leachability of BDE-209 and BDE-99 from plastics. There is also some  
471 potential evidence for debromination of heavy congeners to the lower brominated and  
472 more bioavailable BDEs. Specifically, this relates to the detection of BDEs-47, -85 and -100 in  
473 the leachates, despite their absence from the CRT plastics themselves. This has implications  
474 for the potential for PBDEs to migrate into surface and ground waters due to the  
475 preferential physicochemical properties of lower brominated PBDEs.

476 Agitation of the sample during leaching has a significant impact on PBDE concentrations in  
477 the leaching fluid despite the issue of the inhomogeneity of the starting material. This  
478 perhaps suggests that the other factors evaluated are unlikely to exert a similarly strong  
479 influence on leaching of PBDEs, otherwise we would be able to detect it as we can for  
480 agitation.

481 The data presented here are preliminary and there are few comparable studies in the  
482 literature (Danon-Schaffer et al., 2013; Choi et al., 2009). Further work is required to fill

483 knowledge gaps and develop a greater understanding of PBDE leaching behaviour from  
484 WEEE polymers and other PBDE treated materials.

485

#### 486 **Acknowledgements**

487 The authors acknowledge gratefully the provision of an Open Competition CASE studentship  
488 award to WAS by the UK Natural Environment Research Council (NERC ref NE/I018352/1).  
489 Additional financial support to WAS from Ricardo-AEA is also acknowledged gratefully.

490

#### 491 **References:**

492 Alcock, R. E.; Sweetman, A. J.; Prevedouros, K.; Jones, K. C., 2003. Understanding levels and  
493 trends of BDE-47 in the UK and North America: an assessment of principal reservoirs and  
494 source inputs. *Environment International*, **29**, 691-698.

495 Brandsma, S.H.; de Boer, J.; Krystek, P.; Clarke, P.; Patel, P; Cusack, P.; Leonards, P.E., 2013.  
496 Leaching of halogen free and brominated flame retardants from plastics. *6th International  
497 Symposium on Brominated Flame Retardants*, San Francisco, 2013.

498 Bromine Science and Environment Forum (BSEF), 2014. Deca-BDE Applications. Available at:  
499 <http://www.bsef.com/our-substances/deca-bde/applications> [Accessed on 17 April 2014]

500 Bruchajzer, E.; Frydrych, B.; Sporny, S.; Szymanska, J. A., 2011. The effect of short-term  
501 intoxication of rats with pentabromodiphenyl ether (in mixture mimic commercial  
502 products). *Human and Experimental Toxicology*, **30**, 363-378.

503 Choi, K.-I.; Lee, S.-H.; Osako, M., 2009. Leaching of brominated flame retardants from TV  
504 housing plastics in the presence of dissolved humic matter. *Chemosphere*, **74**, 460-466.

505 Choi, J-W.; Fujimaki, S.; Kitamura, K.; Hashimoto, S.; Ito, H.; Suzuki, N.; Sakai, S-I.; Morita, M.,  
506 2003. Polybrominated dibenzo-p-dioxins, dibenzofurans, and diphenyl ethers in Japanese  
507 human adipose tissue. *Environmental Science & Technology*, **37**, 817-821.

508 Covaci, A Voorspoels, S.; Roosens, L.; Jacobs, W.; Blust, R.; Neels, H., 2008. Polybrominated  
509 diphenyl ethers (PBDEs) and polychlorinated biphenyls (PCBs) in human liver and adipose  
510 tissue samples from Belgium. *Chemosphere*, **73**, 170-175.

511 Cristale, J.; Katsoyiannis, A.; Sweetman, A.J.; Jones, K.C.; Lacorte, S., 2013. Occurrence and  
512 risk assessment of organophosphorus and brominated flame retardants in the River Aire  
513 (UK). *Environmental Pollution*, **179**, 194-200.

514 Darnerud, P. O., 2003. Toxic effects of brominated flame retardants in man and in wildlife.  
515 *Environment International*, **29**, 841-853.

516 Danon-Schaffer, M. N.; Mahecha-Botero, A.; Grace, J. R.; Ikonou, M. G., 2013. Transfer of  
517 PBDEs from e-waste to aqueous media. *Science of the Total Environment*, **447**, 458-471.

518 de Wit, C. A., 2002. An overview of brominated flame retardants in the environment.  
519 *Chemosphere*, **46**, 583-624.

520 de Wit, C.A.; Alae, M.; Muir, D.C.C., 2006. Levels and trends of brominated flame  
521 retardants in the Arctic. *Chemosphere*, **64**: 209-233.

522 European Commission, 2011. Final Report: Study on waste related issues of newly listed  
523 POPs and candidate POPs.

524 European Commission, (2011). Final Report: Study on waste related issues of newly listed  
525 POPs and candidate POPs.

526 Hale, R. C.; Alae, M.; Manchester-Neesvig, J. B.; Stapleton, H. M.; Ikonou, M. G., 2003.  
527 Polybrominated diphenyl ether flame retardants in the North American environment.  
528 *Environment International*, **29**, 771-779.

529 Hardy, M. L.; Banasik, M.; Stedeford T., 2009. Toxicology and human health assessment of  
530 decabromodiphenyl ether. *Critical Reviews in Toxicology*; **39**, 1-44.

531 Harner, T.; Shoeib, M., 2002. Measurements of Octanol-Air Partition Coefficients ( $K_{OA}$ ) for  
532 Polybrominated Diphenyl Ethers (PBDEs): Predicting Partitioning in the Environment. *Journal*  
533 *of Chemical Engineering Data*, **47**, 228-232.

534 Harrad, S.; Abdallah, M. A.-E.; Rose, N. L.; Turner, S. D.; Davidson, T. A., 2009. Current-use  
535 brominated flame retardants in water, sediment, and fish from English Lakes. *Environmental*  
536 *Science & Technology*, **43**, 9077-9083.

537 Ho, Y.-H.; Harouna-Oumarou, H. A.; Fauduet, H.; Porte, C., (2005). Kinetics and model  
538 building of leaching of water-soluble compounds of Tilia sapwood. *Separation and*  
539 *Purification Technology*, 45: 169-173.

540 Ionas, A.C.; Anthonissen, T.; Dirtu, A.C.; Covaci, A., 2012. Analysis of harmful organic  
541 chemicals in children's toys. *Organohalogen Compounds*, **74**, 1269-1272.

542 Johansson, N.; Viberg, H.; Fredriksson, A.; Eriksson, P., 2008. Neonatal exposure to deca-  
543 brominated diphenyl ether (PBDE 209) causes dose-response changes in spontaneous  
544 behaviour and cholinergic susceptibility in adult mice. *Neurotoxicology*, **29**, 911-919.

545 Kelly, B.; Ikonomou, M.; Blair, J.; Gobas, F., 2008. Bioaccumulation behaviour of  
546 polybrominated diphenyl ethers (PBDEs) in a Canadian Arctic marine food web. *Science of*  
547 *the Total Environment*, **401**, 60-72.

548 Kjeldsen, P.; Barlaz, M. A.; Rooker, A. P.; Baun, A.; Ledin, A.; Christensen, T. H., 2002. Present  
549 and Long-Term Composition of MSW Landfill Leachate: A Review. *Critical Reviews in*  
550 *Environmental Science and Technology*, **32**, 297-336.

551 Kohler, M.; Zennegg, M.; Bogdal, C.; Gerecke, A.C.; Schmid, P.; Heeb, N.V.; Sturm, M.;  
552 Vonmont, H.; Kohler, H.-P.; Giger, W., 2008. Temporal trends, congener patterns, and  
553 sources of octa-, nona-, and decabromodiphenyl ethers (PBDE) and  
554 hexabromocyclododecanes (HBCD) in Swiss lake sediments. *Environmental Science and*  
555 *Technology*, **42**, 6378-6384.

556 Kwan, C. S.; Takada, H.; Mizukawa, K.; Torii, M.; Koike, T.; Yamashita, R.; Rinawati; Saha, M.;  
557 Santiago, E. C., 2013. PBDEs in leachates from municipal solid waste dumping sites in  
558 tropical Asian countries: phase distribution and debromination. *Environmental Science and*  
559 *Pollution Research*, **20**, 4188-4204.

560 Lassen, C.; Havelund, S.; Leisewitz, A.; Maxon, P., 2006. Deca-BDE and Alternatives in  
561 Electrical and Electronic Equipment. Danish Ministry of the Environment. Environmental

562 Project No. 1141 2006 Miljøprojekt. Available at:  
563 [www2.mst.dk/Udgiv/publications/2007/978.../978-87-7052-350-9.pdf](http://www2.mst.dk/Udgiv/publications/2007/978.../978-87-7052-350-9.pdf) [Accessed 17 March  
564 2016].

565 Law, K.; Halldorson, T. H.; Danell, R. W.; Stern, G. A.; Gerwutz, S.; Alaei, M.; Marvin, C.;  
566 Whittle, D.M.; Tomy, G.T., 2006. Bioaccumulation and trophic transfer of some brominated  
567 flame retardants in a Lake Winnipeg (Canada) food web. *Environmental Toxicology and*  
568 *Chemistry*, **25**, 2177-2186.

569 Noren, K.; Meironyte, D., 2000. Certain organochlorine and organobromine contaminants in  
570 Swedish human milk in perspective of past 20–30 years. *Chemosphere* **40**, 1111-1123.

571 Odusanya, D. O.; Okonkwo, J. O.; Botha, B., 2009. Polybrominated diphenyl ethers (PBDEs)  
572 in leachates from selected landfill sites in South Africa. *Waste Management*, **29**, 96-102.

573 Oliaei, F.; Weber, R.; Watson, A., 2010. PBDE contamination in Minnesota landfills, waste  
574 water treatment plants and sediments as PBDE sources and reservoirs. *Organohalogen*  
575 *Compounds*, **72**, 1346-1349.

576 Oliaei, F.; King, P.; Phillips, L., 2002. Occurrence and concentrations of polybrominated  
577 diphenyl ethers (PBDEs) in Minnesota environment. *Organohalogen Compounds*, **58**, 185-  
578 188.

579 Öman, C. B.; Junestedt, C., 2008. Chemical characterization of landfill leachates – 400  
580 parameters and compounds. *Waste Management*, **28**, 1876-1891.

581 Osako, M.; Kim, Y.-J.; Sakai, S., 2004. Leaching of brominated flame retardants in leachate  
582 from landfills in Japan. *Chemosphere*, **57**, 1571-1579.

583 Petreas, M.; She, J.; Brown, F.R.; Winkler, J.; Windham, G.; Rogers, E.; Zhao, G.; Bhatia, R.;  
584 Charles, M.J., 2003. High body burdens of 2, 20, 4, 40-tetrabromodiphenyl ether (BDE-47) in  
585 California women. *Environmental Health Perspectives*, **111**, 1175-1180.

586 Renou, S.; Givaudan, J.G.; Poulain, S.; Dirassouyan, F.; Moulin, P., 2008. Landfill leachate  
587 treatment: Review and opportunity. *Journal of Hazardous Materials*, **150**, 468-493.

588 Stubbings W. A., Kajiwara N., Takigami H., Harrad S., 2016. Leaching behaviour of  
589 Hexabromocyclododecane from treated curtains. *Chemosphere*, 144: 2091-2096.

590 Tittlemier, S. A.; Halldorson, T.; Stern, G. A.; Tomy, G. T., 2002. Vapor pressures, aqueous  
591 solubilities and Henry's law constants of some brominated flame retardants. *Environmental*  
592 *Toxicology and Chemistry*, **21**, 1804-1810.

593 Toms, L.-M.; Sjödin, A.; Harden, F.; Hobson, P.; Jones, R.; Edenfield, E.; Mueller, J. F., 2009.  
594 Concentrations of polybrominated diphenyl ethers (PBDEs) in pooled human serum are  
595 higher in children (aged 2-5 years) than in infants and adults. *Environmental Health*  
596 *Perspectives*, **117**, 1461-1465.

597 Tomy, G.T.; Pleskach, K.; Oswald, T.; Halldorson, T.; Helm, P.A.; Macinnis, G.; Marvin, C. H.,  
598 2008. Enantioselective bioaccumulation of hexabromocyclododecane and congener-specific  
599 accumulation of brominated diphenyl ethers in an eastern Canadian Arctic marine food  
600 web. *Environmental Science & Technology*, **42**, 3634-3639.

601 United Nations Environment Programme (UNEP), 2014. Stockholm Convention website.  
602 Available at: [www.pops.int/](http://www.pops.int/) [Accessed 17 April 2014].

603 United Nations Environment Programme (UNEP), 2010a. Technical review of the  
604 implications of recycling commercial Penta and Octabromodiphenyl ethers. Stockholm  
605 Convention document for 6th POP Reviewing Committee meeting (UNEP/POPS/POPRC.6/2).  
606 Available at: [http://chm.pops.int/Portals/0/Repository/POPRC6/UNEP-POPS-POPRC.6-](http://chm.pops.int/Portals/0/Repository/POPRC6/UNEP-POPS-POPRC.6-2.English.pdf)  
607 [2.English.pdf](http://chm.pops.int/Portals/0/Repository/POPRC6/UNEP-POPS-POPRC.6-2.English.pdf) [Accessed 24 June 2013].

608 United Nations Environment Programme (UNEP), 2010b. Technical review of the  
609 implications of recycling commercial Penta and Octabromodiphenyl ethers. Annexes.  
610 Stockholm Convention document for 6th POP Reviewing Committee meeting

611 Viberg, H., Fredriksson, A. & Eriksson, P., 2007. Changes in spontaneous behaviour and  
612 altered response to nicotine in the adult rat, after neonatal exposure to the brominated  
613 flame retardant, decabrominated diphenyl ether (PBDE 209). *Neurotoxicology*, **28**, 136-142.

614 Wäger, P.A.; Schluep, M.; Müller, E.; Gloor, R., 2012. RoHS regulated Substances in Mixed  
615 Plastics from Waste Electrical and Electronic Equipment. *Environ. Sci. Technol.*, **46**, 628-635.

616 Wang, F.; Wang, J.; Dai, J.; Hu, G.; Wang, J.; Luo, X.; Mai, B., 2010. Comparative tissue  
617 distribution, biotransformation and associated biological effects by decabromodiphenyl  
618 ethane and decabrominated diphenyl ether in male rats after a 90-day oral exposure study.  
619 *Environmental Science & Technology*, **44**, 5655-5660.

620 Wania, F.; Dugani, C. B., 2003. Assessing the long-range transport potential of  
621 polybrominated diphenyl ethers: a comparison of four multimedia models. *Environmental*  
622 *Toxicology and Chemistry*, **22**, 1252-1261.

623 Wong, A.; Lei, Y. D.; Alaei, M.; Wania, F., 2001. Vapor Pressures of the Polybrominated  
624 Diphenyl Ethers. *Journal of Chemical Engineering Data*, **46**, 239-242.

625 Wu, J.; Luo, X.; Zhang, Y.; Yu, M.; Chen, S.; Mai, B.; Yang, Z., 2009. Bio-magnification of  
626 polybrominated diphenyl ethers (PBDEs) and polychlorinated biphenyls in a highly  
627 contaminated freshwater food web from South China. *Environmental Pollution*, **157**, 904-  
628 909.

629 Zhou, T.; Ross, D. G.; DeVito, M. J.; Crofton, K. M., 2001. Effects of short-term in vivo  
630 exposure to polybrominated diphenyl ethers on thyroid hormones and hepatic enzyme  
631 activities in weanling rats. *Toxicological Sciences*, **61**, 76-82.

632 Yue, C.; Li, L. Y., 2013. Filling the gap: Estimating physicochemical properties of the full array  
633 of polybrominated diphenyl ethers (PBDEs). *Environmental Pollution*, **180**, 312-323.

634



635 **Table 1: Mean ± standard deviation concentrations (mg kg<sup>-1</sup>) of PBDEs in CRT plastics used in this study (n=5) and selected physicochemical**  
 636 **properties data**

Congener	Concentration (mg kg <sup>-1</sup> )	% RSD	log K <sub>ow</sub>	Aqueous Solubility (mg L <sup>-1</sup> )	log K <sub>OA</sub>	Vapour Pressure (Pa)
BDE-99	0.36 ± 0.025	7.1	6.76 <sup>a</sup>	0.077 <sup>b</sup>	11.31 <sup>c</sup>	5.00×10 <sup>-5</sup> <sup>d</sup>
BDE-153	14 ± 2.0	14	7.08 <sup>a</sup>	0.031 <sup>b</sup>	11.82 <sup>c</sup>	5.80×10 <sup>-6</sup> <sup>d</sup>
BDE-154	0.73 ± 0.065	9.0	7.82 <sup>b</sup>	-	11.92 <sup>c</sup>	3.80×10 <sup>-6</sup> <sup>b</sup>
BDE-183	220 ± 19	8.7	8.27 <sup>b</sup>	-	11.96 <sup>c</sup>	4.68×10 <sup>-7</sup> <sup>e</sup>
BDE-209	2600 ± 120	4.5	9.97 <sup>b</sup>	0.002 <sup>b</sup>	15.73 <sup>b</sup>	1.43×10 <sup>-8</sup> <sup>b</sup>

<sup>a</sup> Wania and Dugani (2003)      <sup>b</sup> Yue & Li (2013)      <sup>c</sup> Harner and Shoeib (2002)  
<sup>d</sup> Wong et al., (2001)      <sup>e</sup> Tittlemier et al., (2002)



638 **Table 2: Concentrations (ng L<sup>-1</sup>) of PBDEs in leachate in duplicate experiments, together with mean PL (%) and mean PLT values (% h<sup>-1</sup>)**  
 639 **conducted on CRT plastics with different contact times and DHM concentrations.**

DHM conc. (mg L <sup>-1</sup> )	Contact time (h) / Congener	6				24				48			
		Conc. (ng L <sup>-1</sup> )	Conc. (ng L <sup>-1</sup> )	PL (%)	PLT (% h <sup>-1</sup> )	Conc. (ng L <sup>-1</sup> )	Conc. (ng L <sup>-1</sup> )	PL (%)	PLT (% h <sup>-1</sup> )	Conc. (ng L <sup>-1</sup> )	Conc. (ng L <sup>-1</sup> )	PL (%)	PLT (% h <sup>-1</sup> )
0	BDE-47	140	150			81	31			380	380		
	BDE-85					9.4				26	29		
	BDE-99	430	410	3.0	0.021	150	160	1.1	0.045	690	820	5.3	0.11
	BDE-100	730	650			440	460			660	830		
	BDE-153	7,700	7,600	7.4	0.0034	370	400	0.24	0.010	890	920	0.64	0.013
	BDE-154	2,200	2,100	1.3	0.0012	65	74	0.066	0.0028	190	180	0.16	0.0033
	BDE-183	28,000	25,000	0.30	0.00048	2,300	2,200	0.026	0.0011	5,000	5,300	0.059	0.0012
	BDE-209	44,000	46,000	0.043	0.0015	110,000	63,000	0.084	0.0035	79,000	76,000	0.073	0.0015
	ΣPBDEs	83,000	81,000	0.072	0.012	120,000	66,000	0.080	0.0033	86,000	84,000	0.074	0.0015
100	BDE-47	290	340			350	340			180	550		
	BDE-85	11	12								18		
	BDE-99	650	760	5.0	0.83	430	500	3.3	0.14	210	410	2.2	0.046
	BDE-100	1,000	1,300			640	630			740	540		
	BDE-153	1,200	1,400	2.3	0.38	410	410	0.34	0.014	1,200	760	0.58	0.012
	BDE-154	660	660	0.23	0.039	99	99	0.071	0.0030	200	140	0.17	0.0035
	BDE-183	5,600	5,700	0.065	0.011	2,200	2000	0.024	0.0010	6,100	5,100	0.064	0.0013
	BDE-209	64,000	62,000	0.060	0.010	58,000	63,000	0.058	0.0024	48,000	63,000	0.053	0.0011
	ΣPBDEs	73,000	73,000	0.064	0.011	63,000	67,000	0.056	0.0024	56,000	71,000	0.055	0.0012
1000	BDE-47	130	130			120	120			760	690		
	BDE-85									31			
	BDE-99	410	470	3.1	0.52	640	300	3.3	0.14	940	1,000	6.8	0.14
	BDE-100	920	760			1,200	790			930	1,100		
	BDE-153	1,200	1,600	1.0	0.17	1,000	1,200	1.2	0.049	1,100	1,400	1.6	0.034
	BDE-154	430	150	0.24	0.040	92	580	0.19	0.0079	250	710	0.22	0.0046
	BDE-183	4,500	4,700	0.052	0.0087	4,800	6,500	0.065	0.0027	6,500	7,200	0.079	0.0016
	BDE-209	60,000	62,000	0.058	0.010	74,000	84,000	0.075	0.0031	80,000	190,000	0.13	0.0027
	ΣPBDEs	68,000	70,000	0.060	0.010	81,000	93,000	0.076	0.0032	91,000	200,000	0.13	0.0027

640 **Table 3: Second order leaching rate constants (*k*) and saturated leaching capacities (*C<sub>s</sub>*)**  
 641 **obtained for PBDE congeners from CRT plastics<sup>a</sup>.**

Constant / Compound	Slope (min L ng <sup>-1</sup> /min)	y-intercept (min L ng <sup>-1</sup> )	C <sub>s</sub> (ng L <sup>-1</sup> )	k (L ng <sup>-1</sup> min <sup>-1</sup> )	Two-tailed P value	Correlation Coefficient: r
<b>0 mg L<sup>-1</sup> DHM concentration.</b>						
BDE-47	0.0010	13	1,000	0.000000078	.901	0.066
BDE-99	0.00092	3.3	1,100	0.00000026	.114	0.267
BDE-100	0.0013	0.51	770	0.0000033	.013	0.905
BDE-153	0.0012	0.54	870	0.0000025	.096	0.725
BDE-154	0.0055	3.6	180	0.0000086	.103	0.648
BDE-183	0.00020	0.092	5,000	0.00000044	.164	0.743
BDE-209	0.000012	0.0027	85,000	0.000000051	.091	0.965
<b>100 mg L<sup>-1</sup> DHM concentration.</b>						
BDE-153	0.0011	0.66	950	0.0000017	.100	0.729
BDE-154	0.0066	0.68	150	0.000063	.020	0.881
BDE-183	0.00016	0.17	6,100	0.00000016	.177	0.634
<b>1000 mg L<sup>-1</sup> DHM concentration.</b>						
BDE-47	0.00011	6.2	8,900	0.0000000020	.959	0.028
BDE-99	0.00079	1.2	1,300	0.00000051	.224	0.584
BDE-100	0.0010	0.10	1,000	0.0000089	.001	0.976
BDE-153	0.00080	0.052	1,300	0.000012	.001	0.978
BDE-154	0.0023	2.6	430	0.0000020	.394	0.431
BDE-183	0.00013	0.044	7,400	0.00000042	.001	0.977
BDE-209	0.0000076	0.0047	130,000	0.000000012	.068	0.779

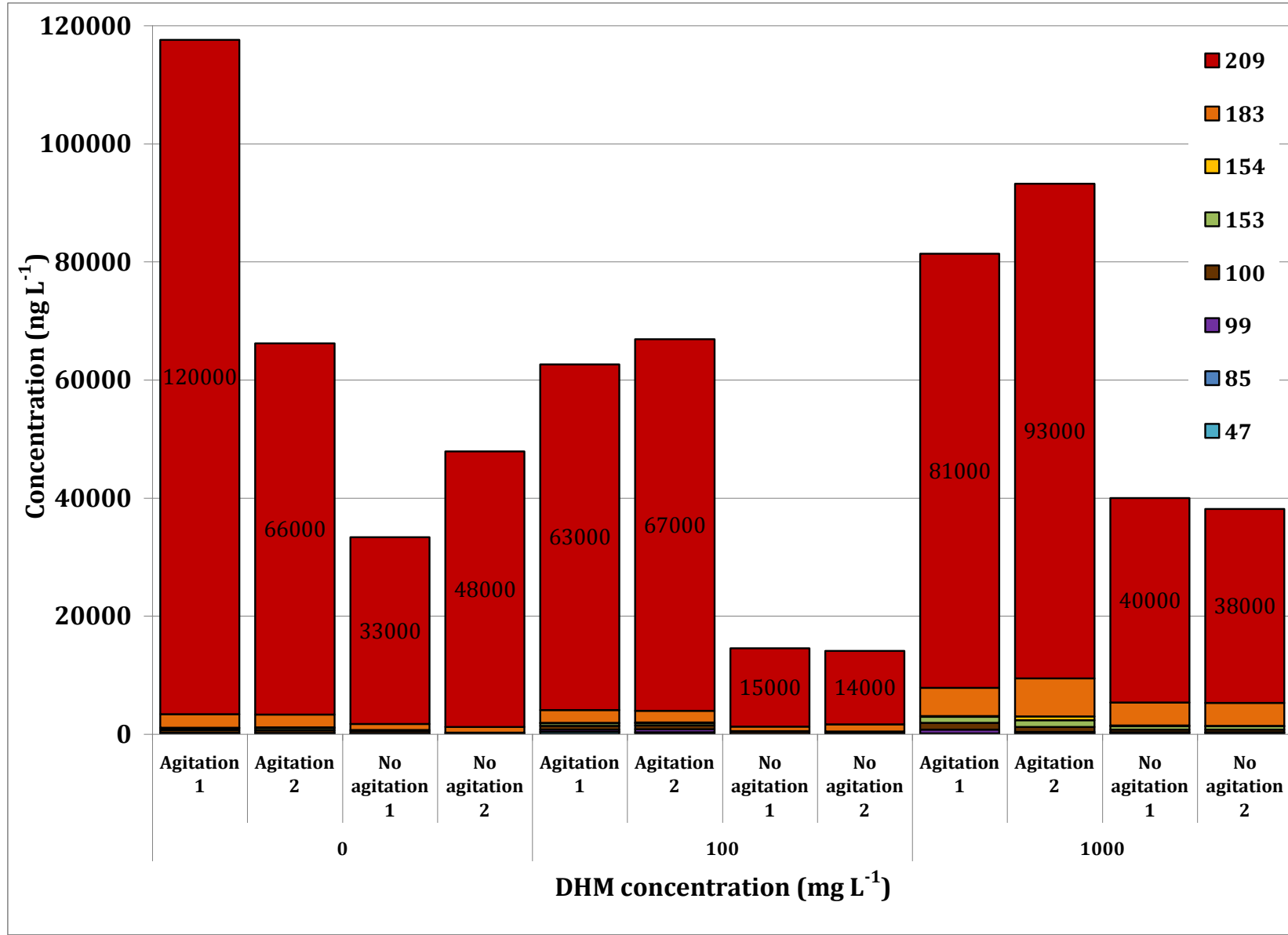
<sup>a</sup>Data not shown for plots for which y-intercept and thus k values were negative.  
 p-values highlighted red = significant (p<0.10).

643 **Table 4: Concentrations (ng L<sup>-1</sup>) of PBDEs in leachate in duplicate experiments, together with mean PL (%) and mean PLT values (% h<sup>-1</sup>)**  
 644 **conducted on CRT plastics with different temperatures and DHM concentrations.**

DHM conc. (mg L <sup>-1</sup> )	Temperature (°C) / Congener	20				50				80			
		Conc. (ng L <sup>-1</sup> )	Conc. (ng L <sup>-1</sup> )	PL (%)	PLT (% h <sup>-1</sup> )	Conc. (ng L <sup>-1</sup> )	Conc. (ng L <sup>-1</sup> )	PL (%)	PLT (% h <sup>-1</sup> )	Conc. (ng L <sup>-1</sup> )	Conc. (ng L <sup>-1</sup> )	PL (%)	PLT (% h <sup>-1</sup> )
0	BDE-47	76				93				160		120	
	BDE-85												
	BDE-99	78	65	0.51	0.021	81	75	0.55	0.23	290	260	1.9	0.080
	BDE-100	380				270		230		550		520	
	BDE-153	160	160	0.082	0.0034	290	440	0.13	0.0053	320	380	0.29	0.012
	BDE-154	25	22	0.028	0.0012	32	42	0.063	0.0026	83	86	0.061	0.0026
	BDE-183	1,000	980	0.012	0.00048	2,200	2,700	0.028	0.0012	2,100	2,100	0.024	0.0010
	BDE-209	32,000	47,000	0.037	0.0015	94,000	110,000	0.095	0.0040	140,000	120,000	0.12	0.0052
	ΣPBDEs	33,000	48,000	0.035	0.0015	97,000	110,000	0.090	0.0038	140,000	130,000	0.12	0.0049
100	BDE-47					280		190		42		72	
	BDE-85												
	BDE-99	25	21	0.16	0.0062	160	150	1.09	0.045	81	87	0.59	0.025
	BDE-100	340		310		530		520		940		1,000	
	BDE-153	130	98	0.066	0.0079	1,200	690	1.7	0.071	240	250	0.12	0.0049
	BDE-154	22	17	0.020	0.0024	870	110	0.16	0.0069	32	37	0.043	0.0018
	BDE-183	720	1,200	0.011	0.0013	8,600	4,200	0.073	0.0030	2,000	21,000	0.13	0.0054
	BDE-209	13,000	12,000	0.012	0.00049	16,000	19,000	0.017	0.00071	63,000	39,000	0.048	0.0020
	ΣPBDEs	15,000	14,000	0.012	0.00052	28,000	25,000	0.023	0.0010	66,000	61,000	0.055	0.0023
1000	BDE-47	170		170		210		200				5.4	
	BDE-85												
	BDE-99	130	130	0.94	0.039	330	320	2.3	0.096	140	150	1.0	0.042
	BDE-100	440		440		630		620		480		220	
	BDE-153	630	600	0.33	0.014	550	580	0.42	0.018	410	410	0.24	0.0099
	BDE-154	98	95	0.11	0.0044	120	120	0.099	0.0041	68	71	0.072	0.0030
	BDE-183	3,900	3,800	0.044	0.0018	3,100	3,300	0.037	0.0015	6,900	23,000	0.17	0.0071
	BDE-209	35,000	33,000	0.032	0.0013	36,000	38,000	0.035	0.0014	68,000	59,000	0.060	0.0025
	ΣPBDEs	40,000	38,000	0.034	0.0014	41,000	43,000	0.036	0.0015	76,000	83,000	0.069	0.0029

645 **Table 5: Concentrations (ng L<sup>-1</sup>) of PBDEs in leachate in duplicate experiments, together with mean PL (%) and mean PLT values (% h<sup>-1</sup>)**  
 646 **conducted on CRT plastics with different pH levels and DHM concentrations.**

DHM conc. (mg L <sup>-1</sup> )	pH / Congener	5.8				6.5				8.5			
		Conc. (ng L <sup>-1</sup> )	Conc. (ng L <sup>-1</sup> )	PL (%)	PLT (% h <sup>-1</sup> )	Conc. (ng L <sup>-1</sup> )	Conc. (ng L <sup>-1</sup> )	PL (%)	PLT (% h <sup>-1</sup> )	Conc. (ng L <sup>-1</sup> )	Conc. (ng L <sup>-1</sup> )	PL (%)	PLT (% h <sup>-1</sup> )
0	BDE-47	190	190			140	150			140	140		
	BDE-85	9.0	22							11	11		
	BDE-99	220	350	2.0	0.34	430	410	3.0	0.49	250	250	1.8	0.29
	BDE-100	350	630			730	650			1,700	820		
	BDE-153	680	860	0.41	0.068	7,700	7,600	7.4	1.2	3,300	6,000	25	4.2
	BDE-154	110	120	0.13	0.022	2,200	2,100	1.3	0.22	3,300	11,000	0.81	0.14
	BDE-183	4,300	4,800	0.052	0.0086	28,000	25,000	0.30	0.051	4,100	5,200	0.053	0.0089
	BDE-209	49,000	52,000	0.048	0.0080	44,000	46,000	0.043	0.0071	77,000	78,000	0.074	0.012
	ΣPBDEs	55,000	59,000	0.050	0.01	83,000	81,000	0.072	0.012	90,000	100,000	0.083	0.014
100	BDE-47	160	99			290	340			610	220		
	BDE-85					11	12			11	11		
	BDE-99	520	560	3.8	0.63	650	760	5.0	0.83	760	670	5.1	0.84
	BDE-100	880	1,400			1,000	1,300			1,100	890		
	BDE-153	940	1,000	5.5	0.92	1,200	1,400	2.3	0.38	1,500	2,600	5.6	0.93
	BDE-154	1,900	1300	0.17	0.028	660	660	0.23	0.039	350	2,900	0.36	0.059
	BDE-183	4,300	4,400	0.050	0.0083	5,600	5,700	0.065	0.011	4,000	3,800	0.044	0.0074
	BDE-209	44,000	45,000	0.042	0.0070	64,000	62,000	0.060	0.010	54,000	55,000	0.052	0.0086
	ΣPBDEs	52,000	53,000	0.046	0.0077	73,000	73,000	0.064	0.011	63,000	66,000	0.056	0.0093
1000	BDE-47	98	100			130	130			390	260		
	BDE-85									23	20		
	BDE-99	240	300	1.9	0.32	410	470	3.1	0.52	1,400	1,200	9.2	1.4
	BDE-100	960	900			920	760			1,900	1,600		
	BDE-153	820	1,400	4.6	0.77	1,200	1,600	1.0	0.17	2,300	1,900	3.8	0.97
	BDE-154	1,200	1,500	0.19	0.032	430	150	0.24	0.040	510	1,700	0.36	0.055
	BDE-183	2,400	2,900	0.030	0.0050	4,500	4,700	0.052	0.0087	5,400	4,700	0.058	0.0089
	BDE-209	40,000	43,000	0.039	0.0066	60,000	62,000	0.058	0.0096	60,000	59,000	0.056	0.0093
	ΣPBDEs	46,000	50,000	0.042	0.0070	68,000	70,000	0.060	0.010	72,000	70,000	0.062	0.010



648 **Figure 1: PBDE concentrations ( $\text{ng L}^{-1}$ ) in leachate produced during duplicate 24 h single batch experiments examining the effects of**  
649 **agitation on leaching from CRT plastics using 0, 100 and 1000  $\text{mg L}^{-1}$  dissolved humic matter (DHM) as leaching fluid. Data labels on bars are**  
650 **for  $\Sigma$ PBDEs and rounded to two significant figures**



**Supplementary material for on-line publication only**

**[Click here to download Supplementary material for on-line publication only: Supporting information PBDEs CRT waste.doc](#)**