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

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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^{-1} 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^{-1}. 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^{-1}) and BDE 183
38 (220 mg kg^{-1}). 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.

1. Introduction

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

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

While ABS was predominantly treated with Octa-BDE, HIPS was mainly treated with Deca-BDE typically added at concentrations between 13-15 % by weight (EC, 2011; BSEF, 2014). Widely used due to its relatively low cost, Deca-BDE was employed in a range of 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 21st 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.

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

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^{-1}, 100 mg L^{-1}

178   and 1000 mg L^{-1} 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

2.4. Chemical analysis of leachates

After contacting the leaching fluid, the leachate obtained from each of the different experimental conditions was filtered through a 0.45 μm pore size glass fibre filter (Advantec, Japan) to remove any small particles or fibres of the flame retarded material and then spiked with 50 ng each of $^{13}C_{12}$-labelled BDE-47, -99, -153 and -209, as internal (or surrogate) standards. The collected filtrate was then extracted in series using 3 x 50 mL dichloromethane by liquid-liquid extraction with mechanical shaking for 10 minutes each time. Approximately 5-10 mL 2 % NaCl solution was added post-experiment to leachates containing no DHM to enhance separation after extraction. When the NaCl solution was used on DHM containing leachates it produced an undesirable emulsion between the interface of the two layers and reduced PBDE recovery efficiencies. The combined dichloromethane extracts were dried via filtration through 5 g anhydrous Na_2SO_4.

The dried extract was concentrated to 0.5 mL using a Zymark Turbovap II (Hopkinton, MA, USA) with solvent exchange to n-hexane before elution through a pre-cleaned acidified silica (1 g of 44% concentrated sulfuric acid, w/w) and Na_2SO_4 column with 30 mL of n-hexane:DCM (9:1 v/v). The eluate was concentrated with solvent exchange to n-hexane before evaporation to incipient dryness, addition of $^{13}C_{12}$-labelled BDE-100 as recovery determination (or syringe) standard and dilution in methanol prior to analysis via LC-MS/MS equipped with an Atmospheric Pressure Photoionization source (APPI).

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

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: $PL = \left[\dfrac{C_{leachate} \times V}{C_{waste} \times W} \right] \times 100\%$

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^{-1}) 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: $PLT = \dfrac{PL}{t}$

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^{-1}, 13 ng g^{-1} and 12

258   ng g^{-1}.

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^{-1}, 100 mg L^{-1} and 1000 mg L^{-1}. Landfill site

278   leachates can contain a wide spectrum of dissolved organic matter concentrations, usually

279   in the range between ~100 mg L^{-1} up to ~50,000 mg L^{-1} (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^{-1}) 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^{-1} 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^{-1} 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

3.3. Leaching kinetics

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

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

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

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

While the small sample size (n=6) is acknowledged, this apparent fit with second order kinetics suggests initial rapid leaching followed by a slower second phase. This is consistent with our hypothesis that the most readily available PBDEs are "washed" off the CRT polymer 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^{-1} 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^{-1}) 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^{-1} DHM leaching fluid

369 when compared to the concentrations found in the 100 mg L^{-1} 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^{-1}) 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 ΣPBDE concentrations in the agitated experiments were 178 % greater than in the

397   equivalent non-agitated experiments at 0 mg L^{-1} DHM, 353 % greater at 100 mg L^{-1} DHM and

398   124 % greater at 1000 mg L^{-1} 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^{-1}) than leachates containing DHM.

410   PBDE concentrations, mean PL (%) and mean *PLT* values (% h^{-1}) in leachate from those

411   experiments examining leaching at different pH and at DHM concentrations of 0, 100, and

412   1,000 mg L^{-1} 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 MRLA

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 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 ΣPBDEs (14,000 – 200,000 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 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

490

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634

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

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

[a] Wania and Dugani (2003)   [b] Yue & Li (2013)   [c] Harner and Shoeib (2002)

[d] Wong et al., (2001)   [e] Tittlemier et al., (2002)

Table 2: Concentrations (ng L⁻¹) of PBDEs in leachate in duplicate experiments, together with mean PL (%) and mean PLT values (% h⁻¹) conducted on CRT plastics with different contact times and DHM concentrations.

DHM conc. (mg L⁻¹)	Contact time (h) / Congener	6				24				48			
		Conc. (ng L⁻¹)	Conc. (ng L⁻¹)	PL (%)	PLT (% h⁻¹)	Conc. (ng L⁻¹)	Conc. (ng L⁻¹)	PL (%)	PLT (% h⁻¹)	Conc. (ng L⁻¹)	Conc. (ng L⁻¹)	PL (%)	PLT (% h⁻¹)
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$_s$*)**

641 **obtained for PBDE congeners from CRT plastics[a].**

| Constant / Compound	Slope (min L ng^{-1}/min)	y-intercept (min L ng^{-1})	*Cs* (ng L^{-1})	*k* (L ng^{-1} min^{-1})	Two-tailed P value	Correlation Coefficient: r
0 mg L^{-1} DHM concentration.						
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
100 mg L^{-1} DHM concentration.						
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
1000 mg L^{-1} DHM concentration.						
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

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

642

Table 4: Concentrations (ng L^{-1}) of PBDEs in leachate in duplicate experiments, together with mean PL (%) and mean PLT values (% h^{-1})

conducted on CRT plastics with different temperatures and DHM concentrations.

DHM conc. (mg L^{-1})	Temperature (°C) / Congener	20				50				80			
		Conc. (ng L^{-1})	Conc. (ng L^{-1})	PL (%)	*PLT* (% h^{-1})	Conc. (ng L^{-1})	Conc. (ng L^{-1})	PL (%)	*PLT* (% h^{-1})	Conc. (ng L^{-1})	Conc. (ng L^{-1})	PL (%)	*PLT* (% h^{-1})
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⁻¹) of PBDEs in leachate in duplicate experiments, together with mean PL (%) and mean PLT values (% h⁻¹)**

646 **conducted on CRT plastics with different pH levels and DHM concentrations.**

DHM conc. (mg L⁻¹)	pH / Congener	5.8				6.5				8.5			
		Conc. (ng L⁻¹)	Conc. (ng L⁻¹)	PL (%)	*PLT (% h⁻¹)*	Conc. (ng L⁻¹)	Conc. (ng L⁻¹)	PL (%)	*PLT (% h⁻¹)*	Conc. (ng L⁻¹)	Conc. (ng L⁻¹)	PL (%)	*PLT (% h⁻¹)*
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

647
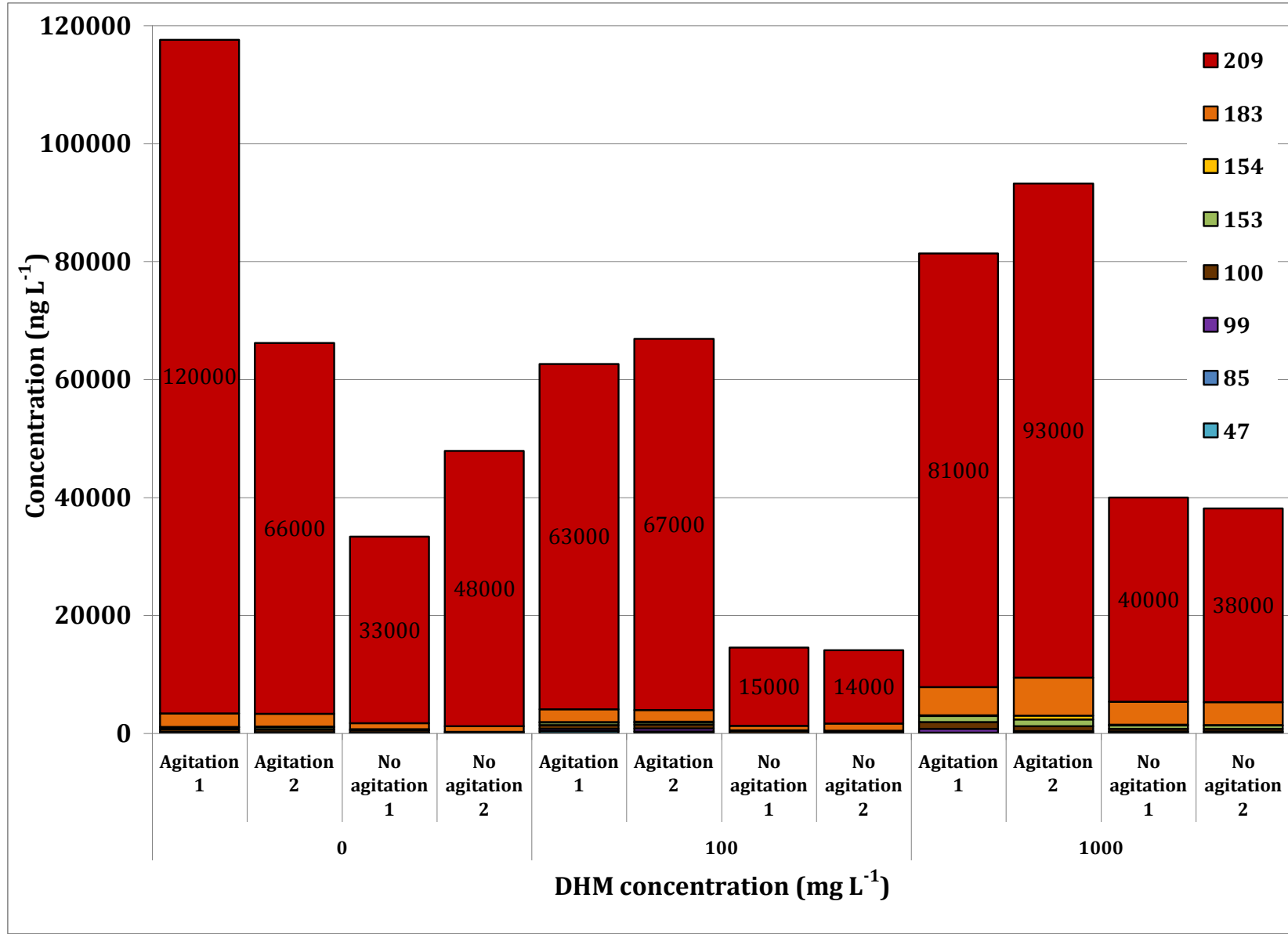
648   **Figure 1: PBDE concentrations (ng L^{-1}) in leachate produced during duplicate 24 h single batch experiments examining the effects of**

649   **agitation on leaching from CRT plastics using 0, 100 and 1000 mg L^{-1} dissolved humic matter (DHM) as leaching fluid. Data labels on bars are**

650   **for ΣPBDEs and rounded to two significant figures**

Supplementary material for on-line publication only

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