

# Concentrations of legacy and emerging flame retardants in air and soil on a transect in the UK West Midlands

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1     **CONCENTRATIONS OF LEGACY AND EMERGING FLAME RETARDANTS IN**  
2             **AIR AND SOIL ON A TRANSECT IN THE UK WEST MIDLANDS**

3

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21

22

23 **Abstract**

24 Passive air samples were collected monthly for 6 months from 8 sites along a transect of  
25 Birmingham, United Kingdom between June 2012 and January 2013. Soil samples were  
26 collected once at each site. Average concentrations of BDE-209,  $\Sigma$ PBDEs<sub>17:183</sub> and  $\Sigma$ PBDEs  
27 in ambient air were 150, 49, and 180 pg m<sup>-3</sup>, respectively. Atmospheric concentrations of  
28 PBDEs were negatively correlated with distance from the city centre, exhibiting an “urban  
29 pulse”. The average  $\Sigma$ HBCDD air concentration was 100 pg m<sup>-3</sup>, however concentrations  
30 were not correlated with distance from the city centre. Several emerging flame retardants  
31 (EFRs) were identified in air and/or soil samples: 2,3,4,5-tetrabromo-bis(2-ethylhexyl)  
32 phthalate (BEH-TEBP), 1,2-dibromo-4-(1,2 dibromoethyl)cyclohexane (TBECH or DBE-  
33 DBCH), allyl 2,4,6-tribromophenyl ether (ATE), 2-bromoallyl 2,4,6-tribromophenyl ether  
34 (BATE), decabromodiphenyl ethane (DBDPE), and dechlorane plus (DP or DDC-CO).  
35 Average concentrations of BDE-209,  $\Sigma$ PBDEs<sub>17:183</sub> and  $\Sigma$ PBDEs in soil were 11, 3.6, and 15  
36 ng g<sup>-1</sup> soil organic matter. PBDE concentrations in soil were higher at sites closest to the city  
37 centre, however correlations with distance from the city centre were not significant. BDEs-  
38 47 and -99 contributed more to  $\Sigma$ PBDEs in soil samples than air samples, but in both, the  
39 predominant congener was BDE-209. BATE was more abundant in air than soil but ATE  
40 was abundant in soil but not air.

41

## 42 **1. Introduction**

43 Polybrominated diphenyl ethers (PBDEs) and hexabromocyclododecane (HBCDD) have  
44 been used extensively as flame retardants in textiles, plastics and electronic and electrical  
45 equipment. Concerns over their potential toxic nature have led to bans on Penta- and Octa-  
46 BDE technical products within Europe in 2003, and globally under the UNEP Stockholm  
47 Convention (SC) in 2009 (Stockholm Convention, 2009). Significant restrictions have been  
48 put on the DecaBDE technical product since 2008 (Deffree, 2008) and HBCDD was listed  
49 under the SC in 2013 (Health and Environment Alliance, 2013).

50

51 Previous studies of PBDEs in outdoor air along rural-urban transects of cities in Canada  
52 (Gouin et al., 2005; Harner et al., 2006; Melymuk et al., 2012) the UK (Harrad and Hunter,  
53 2006), Australia (Hearn et al., 2012) and Sweden (Newton et al., 2015) have found an “urban  
54 pulse” of higher concentrations within the city, decreasing with distance from the city centre.  
55 This urban pulse was also seen in soil samples in the UK study (Harrad and Hunter, 2006).  
56 Higher PBDE concentrations have been found in indoor air than outdoor air (Harner et al.,  
57 2006; Newton et al., 2015) and recent studies have shown that indoor air released via  
58 ventilation systems is a major pathway for outdoor air contamination with PBDEs (Björklund  
59 et al., 2012; Newton et al., 2015). Thus, the urban pulse for PBDEs seems to be directly  
60 linked to the higher density of buildings within a city, which contain flame-retarded goods  
61 that emit PBDEs to the indoor environment and subsequently to outdoor air. The possible  
62 urban pulse behaviour of HBCDDs has not been studied and measurements in urban outdoor  
63 air samples are limited (Remberger et al., 2004; Hoh and Hites, 2005; Abdallah et al., 2008;  
64 Yu et al., 2008; Takigami et al., 2009; Hu et al., 2011; Li et al., 2012)

65

66 PBDEs and HBCDDs are being replaced by a number of emerging flame retardants (EFRs).  
67 Firemaster<sup>®</sup> 550 has been used widely as a replacement for PentaBDE and contains 2-  
68 ethylhexyl-2,3,4,5-tetrabromobenzoate (EH-TBB), bis(2-ethylhexyl)tetrabromophthalate  
69 (BEH-TEBP), and triphenyl phosphate(TPhP)(Stapleton et al., 2008). Potential  
70 replacements/substitutions also include: bis(2,4,6-tribromophenoxy) ethane (BTBPE) and  
71 decabromodiphenyl ethane (DBDPE) for OctaBDE and DecaBDE respectively. Other EFRs  
72 in use include dechlorane plus (DP or DDC-CO), 1,2-dibromo-4-(1,2-  
73 dibromoethyl)cyclohexane (TBECH or DBE-DBCH), allyl 2,4,6-tribromophenyl ether  
74 (ATE), 2-bromoallyl 2,4,6-tribromophenyl ether (BATE), hexabromobenzene (HBB), 2,3-  
75 dibromopropyl-2,4,6-tribromophenyl ether (DPTE or TBP-DBPE) and pentabromotoluene  
76 (PBT) (Covaci et al., 2011; Bergman et al., 2012).

77

78 A number of EFRs have been found in outdoor air (Hermanson et al., 2010; Möller et al.,  
79 2010; Möller et al., 2011a; Möller et al., 2011b; Salamova and Hites, 2013; Salamova et al.,  
80 2014) and deposition samples (Meyer et al., 2012; Newton et al., 2014) from remote sites in  
81 the Arctic. HBCDDs have also been found in several air and deposition samples from the  
82 Arctic (Remberger et al., 2004; de Wit et al., 2010) (Hermanson et al., 2010; Meyer et al.,  
83 2012). This indicates that these FRs are released to the atmosphere from source regions and  
84 undergo long range atmospheric transport to the Arctic. Thus it may be that EFRs and  
85 HBCDDs in indoor air behave similarly to PBDEs and are emitted from flame-retarded  
86 products to indoor air and released from buildings to the outdoor environment. If this is the  
87 case, they should also show an urban pulse similar to that found for PBDEs. In support of  
88 this, Newton et al.(2015) recently found an urban pulse in outdoor air for several EFRs  
89 (DBDPE, EH-TBB, PBT,  $\alpha$ - and  $\beta$ -DBE-DBCH) in Stockholm, Sweden. However,  
90 concentrations of many EFRs were below the detection limits and their atmospheric

91 behaviour could therefore not be determined. Higher PBDE and HBCDD concentrations have  
92 been observed in UK compared to Swedish indoor environments (Harrad et al., 2010), and  
93 we hypothesise this will also be the case for EFRs. Thus, if HBCDD and EFRs are escaping  
94 from indoor environments to outdoor air from buildings, their atmospheric concentrations  
95 may be higher in Birmingham than Stockholm. The aim of this study was therefore to  
96 investigate the role of a city centre (Birmingham, UK) on concentrations of HBCDDs and  
97 EFRs in outdoor air and soil along a transect in the West Midlands conurbation of the UK, of  
98 which Birmingham is the major city. PBDEs were included for comparison with a previous  
99 such study carried out in 2003/2004 (Harrad and Hunter, 2006) in order to evaluate their  
100 response to the bans in 2003 (Penta- and OctaBDE) within the EU. BDE-209 is also included  
101 to evaluate its behaviour in outdoor air for this congener related to the use of the DecaBDE  
102 formulation. To our knowledge this study presents the first ambient air and soil data on EFRs  
103 for the UK.

104

## 105 **2. Materials and Methods**

### 106 *2.1 Sampling & Site Selection*

107 Eight sampling sites were located on a 60 km transect along the prevailing wind direction  
108 from the south-west, through the city of Birmingham, to the north-east of the West Midlands  
109 conurbation (Figure 1, Table S1, Supporting Information (SI)) and reflected varying degrees  
110 of urbanisation (i.e. building density). Outdoor passive air samples (PAS) were collected  
111 monthly from each location between June 2012 and January 2013 (Table S2, SI) using the  
112 same configuration previously developed (Abdallah and Harrad, 2010).

113

114 Each PAS consisted of a polyurethane foam (PUF) disc (140 mm diameter, 12 mm thickness,  
115 360.6 cm<sup>2</sup> surface area, 0.07 g cm<sup>-3</sup> density, PACS, Leicester, UK) and a glass fibre filter

116 ((GFF) 125 mm diameter, 1  $\mu\text{m}$  pore size, Whatman, UK) as the sampling media. This  
117 configuration (Figure S1, SI) samples both the gaseous and particulate phases, thereby  
118 facilitating detection of higher molecular weight compounds such as BDE-209, and other  
119 compounds including HBCDDs, which are present in both phases (Harrad and Abdallah,  
120 2008; Abdallah and Harrad, 2010). This is important as if only the vapour phase was sampled  
121 concentrations of such compounds would be underestimated. The PUF disk and filter are  
122 sheltered between two stainless steel housings (top housing - 23 cm diameter, two litre  
123 volume; and bottom housing - 18 cm diameter, one litre volume). The GFF is suspended in  
124 the middle of the sampler, supported by a wire mesh. The sampler was designed so that air  
125 would flow over the GFF and the particulate phase would be sampled by the upper face of the  
126 GFF by a combination of gravitational settling and turbulent deposition. The GFF was lost  
127 from site 5 (Edgbaston) during sampling period 3 and so no BDE-209 data were available for  
128 that particular sample.

129

130 Soil sampling was performed at each site in January 2013 using the method of Evans (2007).  
131 Briefly, three sub-samples were taken at each location, at least 1 metre apart within a 1  $\text{m}^2$   
132 area from the top 5 cm of surface soil and were transferred using a stainless steel trowel into  
133 (dichloromethane (DCM) and *n*-hexane pre-rinsed) amber jars on site. The sub-samples were  
134 combined, sieved (<2 mm), homogenised, and stored at <4°C prior to extraction.

135

## 136 *2.2 Extraction and Clean-up*

137 Target compounds were extracted from PAS (PUF and GFF from each sample combined) at  
138 the University of Birmingham (UB) using pressurised liquid extraction (PLE). Samples were  
139 concentrated to near dryness and reconstituted in 100  $\mu\text{L}$  methanol. Full extraction  
140 parameters are provided as supplementary material. The final extract was sonicated for 30 s

141 and transferred to an inserted autosampler vial. After analysis via LC -MS/MS for HBCDDs  
142 and BDE-209, sample extracts were reconstituted in *n*-nonane for PBDE analysis via GC-  
143 EI/MS.

144

145 The extracts underwent further clean-up and fractionation for EFRs at Stockholm University  
146 (SU) as previously described (Sahlstrom et al., 2012; Newton et al., 2015) . Further detail is  
147 provided as supplementary material.

148

149 PBDEs were extracted from soil samples via complete in-cell extraction and clean-up at UB  
150 as previously described (Abdallah et al., 2013). More details are provided as supplementary  
151 material. The final volume was adjusted to 100  $\mu$ L in methanol. The sample was sonicated  
152 for 30 s and transferred into an inserted vial and analysed for BDE-209 via LC-APPI-  
153 MS/MS. The sample was then solvent exchanged into 50  $\mu$ L in *n*-nonane before analysis of  
154 tri-hepta PBDEs via GC-EI/MS. Organic matter (OM) content in soil samples was  
155 determined (gravimetrically) as the loss on ignition after heating the dried samples at 500  $^{\circ}$ C  
156 for 4 h.

157

158 A separate aliquot of 10 g of soil was taken for extraction, fractionation and analysis of EFRs  
159 and HBCDDs at SU.  $^{13}$ C-labelled BDEs -155, -183, -197, and -209, DDC-CO *syn*, DDC-CO  
160 *anti*,  $\alpha$ -,  $\beta$ -, and  $\gamma$ -HBCDD and  $^{13}$ C<sub>6</sub><sup>2</sup>H<sub>17</sub>-labelled EH-TBB and BEH-TEBP were used as  
161 surrogate standards. Samples were mixed with 8 mL water and 40 mL acetone, rotated on a  
162 mechanical rotator for 60 minutes, centrifuged and the supernatant was poured into a  
163 separation funnel containing 50 mL 0.2 M NaCl/0.1 M H<sub>3</sub>PO<sub>4</sub>. The soil samples underwent a  
164 second extraction in 40 mL of 3:1 *n*-hexane:acetone, rotation for 60 minutes, centrifugation  
165 and the supernatant was combined with that from the first extraction. Phases were allowed to



166 separate and the organic phase was removed. The aqueous phase was washed twice with 10  
167 mL *n*-hexane:diethylether (90:10). Samples were then solvent-exchanged to isooctane and  
168 the volume adjusted to approximately 2 mL. To remove sulfur, 2 mL 2-propanol, 2 mL  
169 TBA-reagent (tetrabutyl-ammonium hydrogen sulfate solution saturated with sodium sulfite)  
170 and one tip of a spatula of sodium sulfite were added to the samples. They were then shaken  
171 vigorously in a 50 °C water bath. 6 mL MilliQ water was added, samples were centrifuged,  
172 and the organic phase removed. Sample extracts then underwent the same fractionation and  
173 clean-up as described for air samples, with the addition of a third fraction eluted with 10 mL  
174 50:50 diethyl ether:*n*-hexane which contained HBCDDs (Sahlstrom et al., 2012).

### 175 *2.3 Instrumental Analysis*

176 Analysis of PBDEs in all air and soil samples and HBCDDs in air samples was performed at  
177 UB. Tri-heptaBDEs were determined via GC-EI/MS using an Agilent 5975 MS coupled with  
178 an Agilent 6850 GC with an Agilent DB-5ms column (30 m x 0.25 i.d. x 0.25 µm film  
179 thickness) (Drage et al., 2014). BDE-209 (all samples) and HBCDDs (air samples only) were  
180 analysed using LC-MS/MS. Full methods and temperature programmes can be found  
181 elsewhere (Abdallah et al., 2007; Abdallah et al., 2009; Drage et al., 2014).

182

183 Analysis of HBCDDs in soil samples and EFRs in all air and soil samples was performed at  
184 SU. EFR analyses for fractions 1 and 2 were performed using a Trace GC Ultra fitted with a  
185 15 m TG-5HT column (Thermo Scientific, Waltham, USA, 0.25 mm i.d., 0.1 µm film  
186 thickness) except BEH-TEBP for which a 30 m TG-5SILMS column was used (Thermo  
187 Scientific, Waltham, USA, 0.25 mm i.d., 0.25 µm film thickness, see QA/QC section below  
188 for further explanation). The GC was coupled to a DSQ II MS (Thermo Scientific, Waltham,  
189 USA) operating in ECNI mode with ammonia as the moderating gas. HBCDDs were  
190 measured using ultra performance LC (ACQUITY™ UPLC) coupled to a tandem-

191 quadrupole MS (Xevo™ TQ-S). A UPLC column (ACQUITY UPLC® HSS C18; 1.8 µm;  
192 2.1×100 mm), with a pre-column (ACQUITY UPLC™ HSS C18; 1.8 µm VanGuard™; 2.1×  
193 5 mm) was used for separation. Temperature programs and other instrumental parameters can  
194 be found elsewhere (Sahlstrom et al., 2012).

195

#### 196 *2.4 Quality Assurance/Quality Control*

197 PAS were calibrated against active samplers for some PBDEs to determine the volume of air  
198 sampled and therefore the estimated concentrations (pg m<sup>-3</sup> air). The calibration used the  
199 same basic method as that used by Abdallah and Harrad (2010) for indoor air. Further  
200 information about how passive sampling rates were calculated is provided as supplementary  
201 material.

202 PUF disks were pre-extracted via PLE (ASE-350 (Dionex)) with 3:2 DCM:hexane (90°C and  
203 1500 psi; flush time – 5 minutes; static cycle – 4 minutes; purge time – 120 s; 1 static cycle).

204 GFFs were baked for 5 hours at 500 °C before the samplers were assembled and deployed.

205 Shelters were also thoroughly rinsed with n-hexane and acetone before each sampling period  
206 to avoid potential cross-contamination. The inner surface of the top housing of the PAS was

207 coated with aluminium foil and washed with n-hexane and acetone to try to minimise its

208 particle-scavenging potential (Abdallah and Harrad, 2010). PAS housing and PUFs were

209 cleaned within one day of being deployed and were subsequently stored and transported to

210 sampling sites in sealed plastic bags. One field blank was analysed with every five samples,

211 which consisted of one pre-extracted PUF and one GFF, stored in an airtight sealed bag for

212 the sampling campaign. The method limit of detection (mLOD) was defined as the average

213 blank level plus 3 standard deviations for compounds present in the blanks. In general,

214 blanks did not contain target compounds. However, BDE-209 was detected in the majority of

215 blanks at a level below 5% of all samples within the batch. Unstable ion ratios between the

216 quantifying and qualifying ions for BEH-TEBP (383.8 and 463.7, respectively) were  
217 observed. To rectify this, samples were rerun on a 30 m column to separate possible  
218 interferences and 512.9 was used as a qualifying ion, which resulted in less variability of ion  
219 ratios. For positive detection, ion ratios were allowed to deviate no more than 20% from the  
220 average ratio measured in the standards. Further to these criteria, recoveries of isotopically  
221 labelled internal standards were required to be between 25% – 150% for a value to be  
222 reported. The average recoveries of internal standards were 55% (<sup>13</sup>C-BDE-28), 68% (<sup>13</sup>C-  
223 BDE-47), 79% (<sup>13</sup>C-BDE-99), 53% (<sup>13</sup>C-BDE-153), 87% (<sup>13</sup>C-BDE-209) 52% (<sup>13</sup>C-DDC-CO  
224 *syn*), 38% (<sup>13</sup>C-DDC-CO *anti*), 41 % (<sup>13</sup>C- $\alpha$ -HBCDD), 73% (<sup>13</sup>C- $\beta$ -HBCDD) and 63% (<sup>13</sup>C-  
225  $\gamma$ -HBCDD).

226

227 All descriptive statistics were performed using Microsoft Excel 2007 or 2010, with statistical  
228 tests processed through SPSS for Windows (version 19.0 or 20). For statistical purposes, non-  
229 detects were replaced with zero. All confidence limits were set to 95% ( $p = 0.05$ ).

230

### 231 **3. Results and Discussion**

232 Mean concentrations of PBDEs, HBCDDs, and EFRs in air ( $\text{pg m}^{-3}$ , total concentrations) and  
233 concentrations in individual soil samples ( $\text{pg g}^{-1}$  OM) are given in Tables 1 and 2,  
234 respectively. Concentrations for individual air samples from each site as well as sampling  
235 rates ( $\text{pg day}^{-1}$ ) are given in Tables S4-S6 (SI).

236

#### 237 **3.1. Spatial variability in Ambient Air**

238 *PBDEs*

239 BDE-209 was detected in measurable concentrations in the majority of samples (39 out of  
240 48), highlighting its extensive use in the UK (Table S4, SI). At each site, BDE-209 comprised

241 61-92% of  $\Sigma$ PBDE ( $\Sigma$ PBDE = sum of BDEs -17, -28, -47, -49/71, -66, -85, -99, -100, -153, -  
242 154, -183, -209). Surprisingly, the highest  $\Sigma$ PBDE concentrations were found in Bromsgrove  
243 (site 3, a suburban site 20 km southwest of the Birmingham city centre) with an average of  
244  $490 \text{ pg m}^{-3}$  (92% BDE-209), more than double the concentrations of the most urban sites of  
245 Digbeth and Edgbaston (sites 6 and 5,  $180$  and  $210 \text{ pg m}^{-3}$  respectively). However, the mean  
246 concentration at Bromsgrove is skewed by one sample (June-July which contained  $1500 \text{ pg}$   
247  $\text{BDE-209 m}^{-3}$ ). There are no known sources of PBDEs close to the Bromsgrove sampling site,  
248 such as chemical companies or industries using thermal processes such as steel  
249 manufacturing or waste incineration.

250

251 After Bromsgrove, the highest  $\Sigma$ PBDE air concentrations found were close to the  
252 Birmingham city centre in Digbeth, Edgbaston and Bournville (averages of  $210$ ,  $170$  and  $180$   
253  $\text{pg m}^{-3}$ ) which are approximately  $0$ ,  $6$ , and  $8$  km from the city centre respectively. With  
254 Bromsgrove excluded, mean concentrations of BDE-209,  $\Sigma$ PBDE<sub>17:183</sub> ( $\Sigma$ PBDE<sub>17:183</sub> = sum  
255 of BDEs -17, -28, -47, -49/71, -66, -85, -99, -100, -153, -154, -183), and  $\Sigma$ PBDEs were more  
256 elevated close to the city centre (Digbeth, site 6) than they were further away. Correlations  
257 between concentrations and distance from the city centre during each individual sampling  
258 period were rarely statistically significant. However, when averaged over the full 6 months  
259 sampling period, significant negative correlations between concentrations in air and distance  
260 from the city centre were observed for BDE-209,  $\Sigma$ PBDE<sub>17:183</sub>, and  $\Sigma$ PBDEs ( $r = -0.842$ , -  
261  $0.872$ ,  $-0.946$ ;  $p = 0.018$ ,  $0.011$ , and  $0.001$ ; respectively; Bromsgrove excluded; Figure 2a).  
262 This is likely due to wide month-to-month variation (see section 3.2). These correlations  
263 confirm that the West Midlands conurbation is a source of PBDEs to the environment.

264

265 The strength of this pulse was calculated previously as the ratio of the sum of concentrations  
266 in Birmingham city centre to the average sum of concentration of all sites (Harrad and  
267 Hunter, 2006). Ratios for our study were 0.87 for BDE-209, 2.2 for  $\Sigma$ PBDEs<sub>17:183</sub>, and 1.1 for  
268  $\Sigma$ PBDEs. With Bromsgrove excluded, the pulse is stronger, 1.2, 2.1, and 1.4 for BDE-209,  
269  $\Sigma$ PBDEs<sub>17:183</sub>, and  $\Sigma$ PBDEs, respectively. It is unknown why the strength of the pulse for  
270 BDE-209 was lower in this study than it was for the lower brominated congeners, however it  
271 may be due to the proximity of domestic buildings to sampling sites. DecaBDE has been used  
272 extensively in the UK to meet strict flame retardancy regulations for furniture (Harrad et al.,  
273 2008). Using the same congeners as previously (2006), a ratio of 2.0 was found for  
274  $\Sigma$ PBDEs<sub>28:154</sub>, similar to the value of 2.2 calculated previously along a similar (but not  
275 identical) transect.

276

277 Concentrations of PBDEs in air in this study exceed slightly those found previously in  
278 Birmingham (Harrad and Hunter, 2006) and Toronto in 2000-2001 (Harner et al., 2006).  
279 Mean concentrations of  $\Sigma$ BDEs -47, -99, -100, -153, and -154 at each site in the current study  
280 ranged from 5.8-49  $\text{pg m}^{-3}$  compared to 2.8-23  $\text{pg m}^{-3}$  in the previous Birmingham study.  
281  $\Sigma$ PBDEs<sub>17:183</sub> ranged from 5.4 to 57  $\text{pg m}^{-3}$ , which were slightly higher, especially at urban  
282 sites, than those found in Toronto in 2000-2001, which ranged from about 10-30  $\text{pg m}^{-3}$   
283 (Harner et al., 2006). However, the largest increases in concentration between the current  
284 study and the previous two studies in Birmingham and Toronto were seen for BDEs-153 and  
285 -154 whereas concentrations of BDE-47 were often lower in this study (range from 1.6-7.9  $\text{pg}$   
286  $\text{m}^{-3}$  in the current study compared to 1.6-14  $\text{pg m}^{-3}$  in the previous Birmingham study). This  
287 could be due to the use of a GFF in the sampler used in the current study (thereby more  
288 efficiently sampling the less volatile BDEs-153 and -154), or because atmospheric half-lives  
289 of BDEs-153 and -154 may be longer than BDE-47. Compared to a more recent study using

290 high-volume samplers in Stockholm, Sweden, concentrations of BDEs-47 and -99 in  
291 Birmingham were one to two orders of magnitude greater and BDE-209 concentrations were  
292 about three orders of magnitude greater (Newton et al., 2015). For congeners measured in  
293 both studies (BDEs-47, -99, -100, -153, -154, and -209), this study found a much higher  
294 contribution from BDE-209 to  $\Sigma$ PBDEs (88%) than Stockholm (11%). By comparison, the  
295 Stockholm study saw a much larger contribution from lower brominated PBDEs like BDE-47  
296 (40% compared to 2.8% in Birmingham). This suggests substantially greater use and  
297 emissions of the DecaBDE formulation in the UK than in Sweden.

298

### 299 *HBCDDs*

300 HBCDDs were detected in the majority of air samples (44 out of 48) at similar levels to  
301 PBDEs when applying the same sampling rate for BDEs -99 and -100 ( $3.92 \text{ m}^3 \text{ day}^{-1}$ , Table  
302 1, Tables S5-S6, SI). Mean  $\Sigma$ HBCDD concentrations in air showed slightly increased levels  
303 near the city centre (Digbeth, site 6) compared to upwind rural/suburban sites (sites 1-4) but  
304 concentrations were not correlated with distance from the city centre (Figure 2a). This is  
305 likely due to sampling at several of the sites being in proximity to buildings possibly  
306 containing HBCDDs, which was heavily used as a flame retardant in building insulation.  
307 Very little spatial variation in isomer profiles was apparent. The  $\Sigma$ HBCDD concentration at  
308 the Edgbaston site (site 5, average =  $84 \text{ pg m}^{-3}$ , December to January =  $230 \text{ pg m}^{-3}$ ) was about  
309 twice that measured by Abdallah et al. (2008) using active sampling in December 2007 ( $37$   
310  $\text{pg m}^{-3}$ ) at the same site with this study displaying a considerably higher contribution from the  
311  $\alpha$ -isomer. The higher concentrations found in the current study could be due to ongoing  
312 emissions as no restrictions were placed on HBCDDs between the two studies. Alternatively,  
313 it may be attributed to differences in the two air sampling methods used, or to seasonal  
314 variations in atmospheric HBCDD concentrations; as the current study covers warmer

315 periods when concentrations of many POPs are known to be higher. The geometric mean  
316  $\Sigma$ HBCDD concentration ( $100 \text{ pg m}^{-3}$ ) was more than three orders of magnitude greater than  
317 that measured recently in Stockholm, Sweden ( $0.066 \text{ pg m}^{-3}$ ) (Newton et al., 2015).  
318 Concentrations of HBCDDs in air were similar to those of BDE-209. Given its recent listing  
319 under the Stockholm Convention (Health and Environment Alliance, 2013), HBCDD should  
320 be further monitored.

321

### 322 *EFRs*

323 Five EFRs were identified in air samples: BEH-TEBP, DDC-CO, DBE-DBCH, BATE, and  
324 DBDPE. Compounds sought but not detected were ATE, TBP-DBPE, HBB, DBHCTD,  
325 OBTMPI, PBT, TBCO, EH-TBB, and BTBPE. BEH-TEBP and DBDPE were detected in  
326 33% and 50% of air samples, respectively; however they were not quantified due to low  
327 recovery of the relevant internal standards ( $^{13}\text{C}$ -BTBPE and  $^{13}\text{C}$ -BDE-209) after the  
328 additional clean-up procedure that was performed for EFRs.  $\Sigma$ DDC-CO (sum *syn*- + *anti*-  
329 DDC-CO) was identified in 44% of samples with no spatial trends or discernible pattern in  
330 isomer ratios. Mean concentrations of  $\Sigma$ DDC-CO at each site ranged from  $0.57\text{-}21 \text{ pg m}^{-3}$   
331 (using the BDE-209 sampling rate as DDC-CO is expected to be particle bound). These  
332 concentrations are comparable to several measurements around the world including the Great  
333 Lakes ( $0.2\text{-}4 \text{ pg m}^{-3}$ , Venier and Hites, 2008) urban and rural areas of China ( $3.5\text{-}66 \text{ pg m}^{-3}$ ,  
334 Ren et al., 2008) and global background levels from the Arctic to Antarctica ( $0.05\text{-}4 \text{ pg m}^{-3}$ ,  
335 Möller et al., 2010). BATE and DBE-DBCH were detected in 77 % and 79 % of samples,  
336 respectively, with the highest levels of each found at Bournville (site 4), near a home which  
337 was completely refurbished shortly before sampling began (Figure S3, SI). A significant  
338 negative correlation with distance from site 4 was observed for DBE-DBCH ( $r=-0.726$ ,  
339  $p=0.041$ ) but not for BATE (Figure 2b). BATE concentrations were higher ( $0.86\text{-}17 \text{ pg m}^{-3}$ ,

340 median = 2.9) than those found at five sites in the Great Lakes region of the US using high-  
341 volume samplers (0.012 – 3.9 pg m<sup>-3</sup>, medians = 0.031 – 0.092 pg m<sup>-3</sup>, Ma et al. 2012).  
342 Concentrations of DBE-DBCH were 10-20 times higher (median = 7.2 pg m<sup>-3</sup>) than those  
343 found by high-volume sampling at several sites in Stockholm, Sweden (0.46 pg m<sup>-3</sup>) (Newton  
344 et al., 2015).

345

### 346 **3.2 Soils**

#### 347 *PBDEs*

348 Concentrations of PBDEs in soils (Table 2), expressed on an OM-normalised basis, follow a  
349 similar pattern to those in ambient air. The lowest ΣPBDE concentrations were found in the  
350 sites furthest from Birmingham city centre (Worcester (3.6 ng g<sup>-1</sup> OM) and Droitwich (2.3 ng  
351 g<sup>-1</sup> OM)), and the highest ΣPBDE concentration (besides Bromsgrove) was found in Digbeth  
352 (21 ng g<sup>-1</sup> OM – centre of Birmingham). The elevated ΣPBDE concentration found in soil  
353 from Bromsgrove (49 ng g<sup>-1</sup> OM) is consistent with the higher ambient air concentrations  
354 from the same location discussed above.

355

356 The soil samples were dominated by BDE-209, but displayed slightly higher contributions of  
357 BDE-47 and BDE-99 than in air (Figure 3). The mean contribution of BDEs -47 and -99 to  
358 total PBDE content increased from 2.4% and 2.0% in air to 7.9 and 8.1% in soil, respectively,  
359 while the contribution of BDE-209 decreased slightly (77% in air vs 72% in soil). This may  
360 be due to soil reflecting a longer term integral of releases of PBDEs to the environment as  
361 well as longer half-lives of PBDEs in soil than air (Palm et al., 2002), meaning that historic  
362 releases of lower brominated congeners prior to their bans are more likely reflected in soil  
363 concentrations. Furthermore, atmospheric half-lives of BDEs -47 and -99 (10 and 20 days



364 respectively), are considerably shorter than that of BDE-209 (318 days) meaning the former  
365 pair are likely to represent a lower proportion of total PBDE content in air (Palm et al., 2002).

366

367 While the relationship between concentrations in soil and distance from the city centre are not  
368 statistically significant ( $r = -0.518$ ,  $p = 0.234$  for BDE-209;  $r = -0.583$ ,  $p = 0.169$  for  
369  $\Sigma$ PBDEs<sub>17:183</sub>;  $r = -0.568$ ,  $p = 0.184$  for  $\Sigma$ PBDEs), urban pulses in soil are suggested.

370 Calculated in the same way as for air, and based on concentrations normalised to organic  
371 matter, these pulse ratios were: 1.4, 1.8, and 1.5 for BDE-209,  $\Sigma$ PBDEs<sub>17:183</sub>, and  $\Sigma$ PBDEs,  
372 respectively, with Bromsgrove included; and 3.2, 1.9, and 3.7, respectively, with Bromsgrove  
373 excluded. These urban pulses for soil, combined with the significant declines in air  
374 concentrations with increasing distance from the city centre, are consistent with the behaviour  
375 of an “urban pulse” of PBDEs (Harner et al., 2006; Harrad and Hunter, 2006).

376

377 Soil collected from the Edgbaston site had six times lower  $\Sigma$ PBDEs<sub>28:154</sub> concentrations (2.9  
378  $\text{ng g}^{-1}$  OM) than a soil sample taken from the same location in 2004 (19  $\text{ng g}^{-1}$  OM) (Harrad  
379 and Hunter, 2006). The decrease in concentrations during this time period is consistent with  
380 a study of Scottish soils which found increasing concentrations of BDEs-47 and -99 from  
381 1990-1999 but decreasing levels from 1999-2009 (Zhang et al., 2014). The authors attributed  
382 the observed trends to legislation banning the use of PentaBDE. This explanation may also be  
383 applicable to the differences observed between the BDE-47 concentrations in soil in this  
384 study (2013) and the soils from 2004 as well as the lower concentrations observed for BDE-  
385 47 in air discussed previously. However, given the heterogeneous nature of soil, more data  
386 are required to draw firm conclusions.

387

388 Concentrations as well as congener patterns of PBDEs in soils were roughly comparable to  
389 those reported in Stockholm recently (Newton et al., 2015). BDE-47 and -99 concentrations  
390 ranged from 0.58-2.1 and 0.55-1.6 ng g<sup>-1</sup> OM, respectively, compared to 0.24-1.7 and 0.20-  
391 1.7 ng g<sup>-1</sup> OM in Stockholm. BDE-209 concentrations ranged from 0.94-45 ng g<sup>-1</sup> OM  
392 compared to 0.31-31 ng g<sup>-1</sup> OM in Stockholm. The comparability between concentrations  
393 and congener patterns of PBDEs in soils in these two studies is in contrast to the findings in  
394 air, which were 1-3 orders of magnitude higher in Birmingham than Stockholm and exhibited  
395 very different congener patterns. This observation is consistent with the hypothesis that soil  
396 reflects a longer time period in terms of releases of PBDEs to the environment as well as to  
397 longer half-lives of PBDEs in soil than air.

398

399 *EFRs*

400 HBCDDs were found in all soil samples but were not quantified due to low recovery of the  
401 surrogate standards. BATE, which was found in most air samples, was found in soil only at  
402 site 8, Tamworth with a concentration of 0.049 ng g<sup>-1</sup> OM. However, a related compound  
403 (ATE) was found in all soil samples (Table 2). BATE and ATE are structurally related to  
404 DPTE (Ma et al., 2012) and are suspected to be biotransformation products of this compound  
405 (von der Recke and Vetter, 2007). These are the first reported levels of ATE in soil that the  
406 authors are aware of. DDC-CO and DBDPE were each found in all but one soil sample.  
407 BEH-TEBP and DBE-DBCH were not detected in soil. No significant correlations were  
408 found between soil and air for any EFRs nor were they significantly correlated with distance  
409 from the city centre. Median DBDPE concentrations (0.34 ng g<sup>-1</sup> OM) were in the lower  
410 range of those reported in Stockholm, Sweden (median of 0.91 ng g<sup>-1</sup> OM) (Newton et al.,  
411 2015). DBDPE concentrations on a dry weight basis ranged from <0.0059-0.24 ng g<sup>-1</sup> which

412 were within the range reported in sediments from the Great Lakes (0.11-2.8 ng g<sup>-1</sup> (Yang et  
413 al., 2012)) but much lower than agricultural soils in China (12-344 ng g<sup>-1</sup> (Zhu et al., 2014)).

414

415

### 416 **3.3 Seasonal Variability in ambient air**

#### 417 *PBDEs*

418 Significant correlations between  $\Sigma$ PBDE<sub>17:183</sub> concentrations and average temperature  
419 (supplied by the UK Met Office, Figure S5), were not seen, however some seasonal  
420 observations were made. The previous study of West Midlands (Harrad and Hunter, 2006)  
421 also did not find any significant seasonal trends in  $\Sigma$ PBDE<sub>28:154</sub> concentrations. However,  
422 they did observe spring and summer increases in BDE-47 at sites close to the city centre,  
423 which was observed in this study also. As correlations between temperature and  
424 concentrations would indicate that secondary emissions from soils are a major source to the  
425 atmosphere, the lack of correlations, coupled with evidence of an urban pulse, indicate that  
426 ongoing primary emissions from consumer products are currently a more important source to  
427 the atmosphere than secondary emissions.

428

429 A tendency was seen for BDE-209 levels in air to be lower in warmer periods at Worcester,  
430 Droitwich, Bournville, Edgbaston, Digbeth, and Tamworth (Figure S6, SI). However, this  
431 was only statistically significant for Digbeth ( $r = -0.905$ ,  $p = 0.013$ ). This was also observed  
432 recently in Beijing, China, by Shi et al. (2013), who found BDE-209 concentrations in  
433 outdoor air to be more variable and overall lower in the spring and summer than autumn and  
434 winter. A potential explanation for this could be the photolytic debromination of BDE-209 as  
435 shown by Da Rosa et al. (2003) under laboratory conditions.

436

437 *EFRs and HBCDDs*

438 General trends of increasing concentrations with temperature were observed for DBE-DBCH  
439 and BATE. For individual sites, no correlations were statistically significant with the  
440 exception of BATE at site 4, Bournville ( $r=0.939$ ,  $p = 0.006$ ) and site 7, Sutton Coldfield  
441 ( $r=0.933$ ,  $p = 0.007$ ). However, when concentrations from all sites were averaged, BATE  
442 concentrations were strongly positively correlated with temperature ( $r=0.874$ ,  $p=0.023$ ,  
443 Figure S7, SI). DBE-DBCH and  $\Sigma$ EFR ( $\Sigma$ EFR =  $\alpha$ -DBE-DBCH +  $\beta$ -DBE-DBCH + BATE +  
444 DDC-CO *syn* + DDC-CO *anti*) showed higher concentrations in summer than winter but  
445 correlations with temperature were not significant (Figure S7, SI). No seasonal trends or  
446 correlations with temperature were observed for concentrations of HBCDDs, however, the  
447 contribution of  $\alpha$ -HBCDD to  $\Sigma$ HBCDDs increased steadily from 35% in July to 66% in  
448 December. This may be because of the higher volatility and lower octanol-air partition  
449 coefficient ( $K_{OA}$ ) of  $\alpha$ -HBCDD relative to  $\beta$ - and  $\gamma$ -HBCDD (Marvin et al., 2011), favouring  
450 partitioning to air even at lower temperatures.

451

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459

#### 460 **Supplementary material**

461 Additional description of sampling methods and locations, extraction and clean-up  
462 methodologies, individual sample ambient air concentrations for target compounds and  
463 figures demonstrating correlations and trends.

464

465

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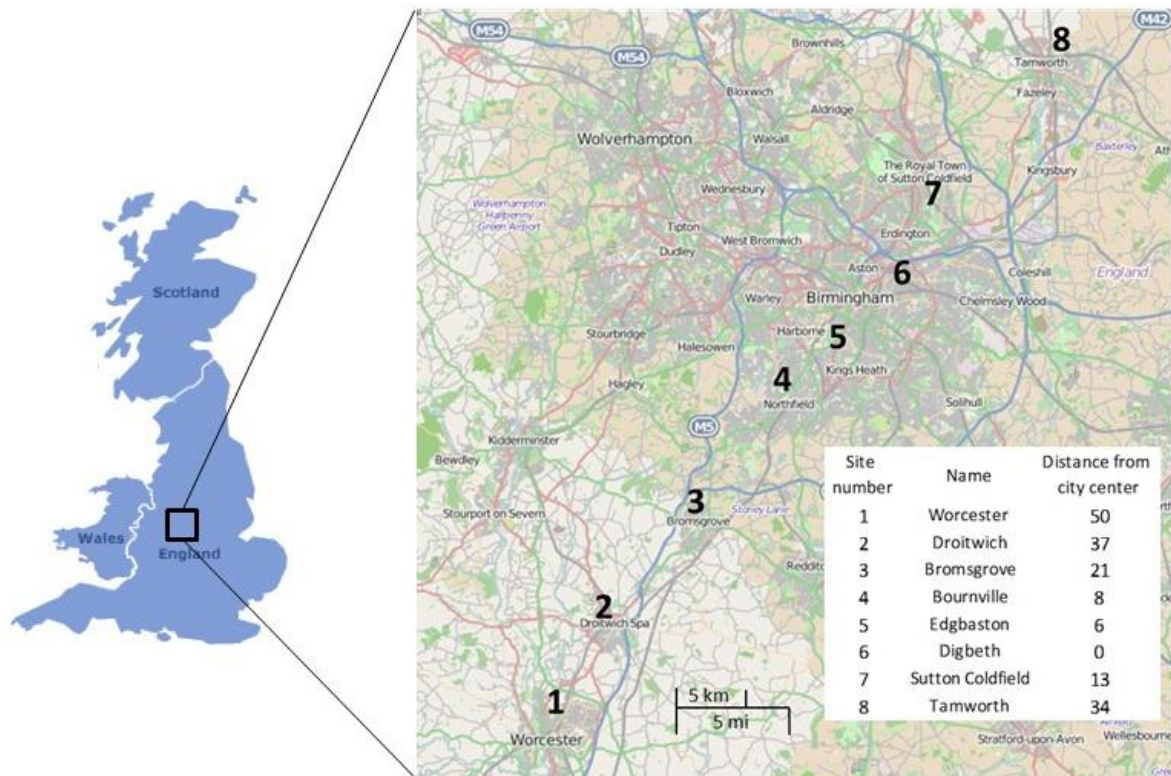
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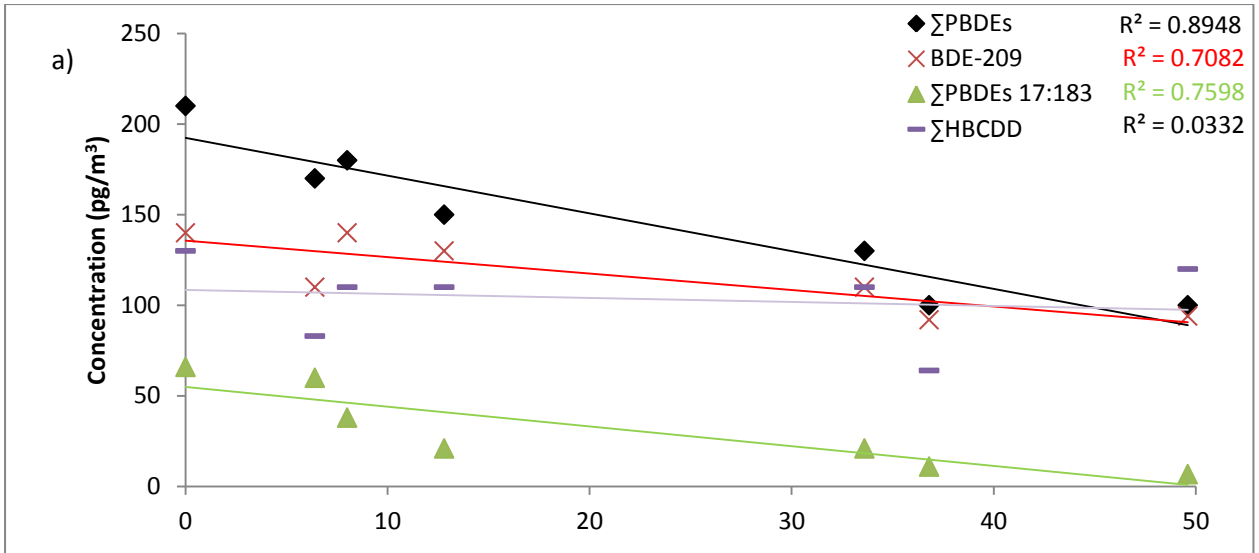


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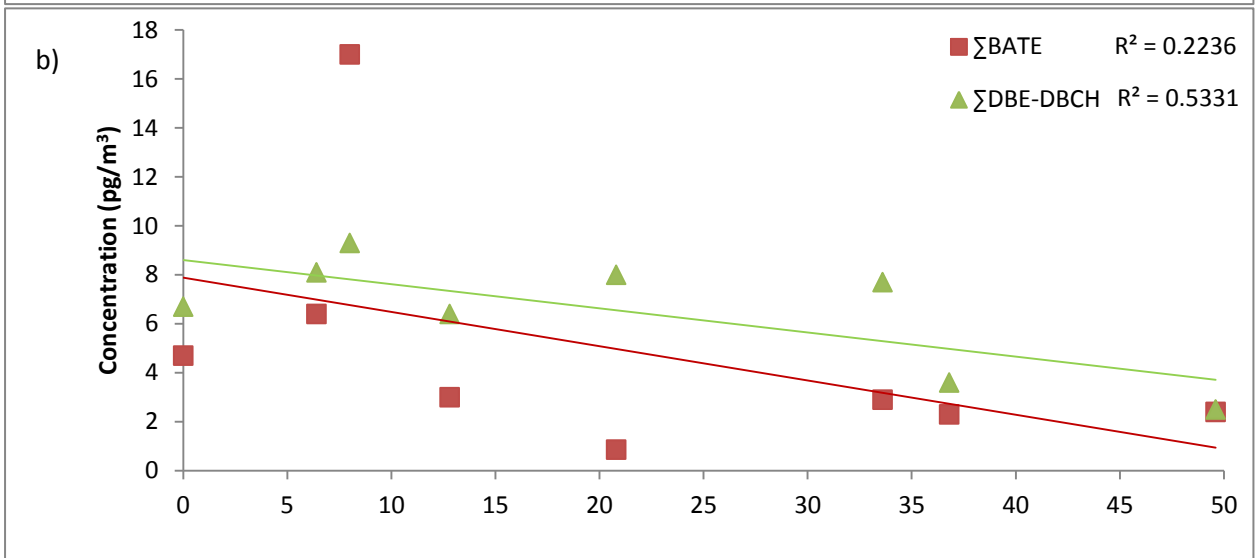
608 Figure 1 - Passive air and soil sampling locations for the urban-rural transect.

609

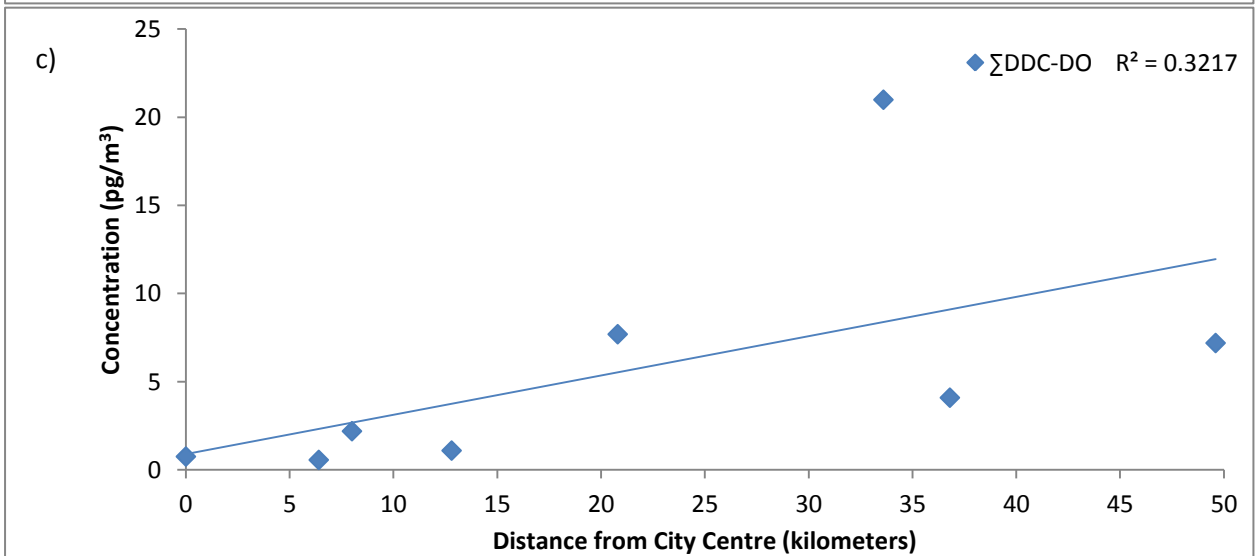
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<sup>a</sup>(Bromsgrove and August to October samples (all sites) excluded)

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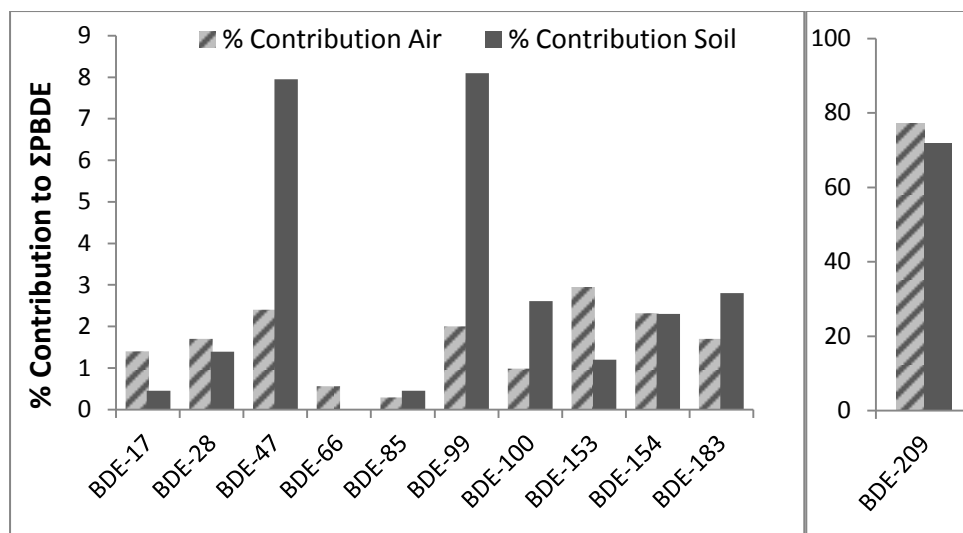
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Figure 2 Correlations between mean concentrations and distance from city centre for a) BDE-209<sup>a</sup>, ΣPBDEs<sup>a</sup>, ΣPBDEs<sub>17:183</sub><sup>a</sup> and ΣHBCDD, b) ΣBATE and ΣDBE-DBCH; and c) ΣDDC-DO

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620 Figure 3 - Mean PBDE congener profile of all soil and air samples for all sites along the  
621 rural-urban transect in the West Midlands, UK. n=48 for air samples, n=8 for soil sample

**Table 1 – Mean ( $\pm$ standard deviation) concentrations ( $\text{pg m}^{-3}$ ) of selected PBDEs and EFRs in air for each sampling site. “<” indicates a compound was below the detection limit.**

Location	Site #	BDE-28	BDE-47	BDE-99	BDE-100	BDE-153	BDE-154	BDE-183	BDE-209	$\Sigma$ PBDEs	$\Sigma$ tri-hepta PBDEs	$\Sigma$ HBCDD	BATE	$\Sigma$ DDC-DO	$\Sigma$ DBE-DBCH
<b>Worcester</b>	<b>1</b>	1.2 $\pm$ 1.4	1.8 $\pm$ 1.3	0.62 $\pm$ 1.4	0.53 $\pm$ 0.83	0.67 $\pm$ 0.96	0.92 $\pm$ 0.99	<1.5	94 $\pm$ 99	100 $\pm$ 97	6.8 $\pm$ 3.2	120 $\pm$ 120	2.4 $\pm$ 1.9	7.2 $\pm$ 16	2.5 $\pm$ 3.5
<b>Droitwich</b>	<b>2</b>	2.0 $\pm$ 2.0	1.6 $\pm$ 2.1	0.22 $\pm$ 0.48	<0.45	1.6 $\pm$ 3.5	1.5 $\pm$ 3.2	1.8 $\pm$ 4.1	92 $\pm$ 130	100 $\pm$ 130	11 $\pm$ 16	64 $\pm$ 69	2.3 $\pm$ 1.5	4.1 $\pm$ 7.6	3.6 $\pm$ 5.5
<b>Bromsgrove</b>	<b>3</b>	3.6 $\pm$ 3.4	4.9 $\pm$ 6.0	6.0 $\pm$ 13	2.5 $\pm$ 5.6	6.5 $\pm$ 11	4.1 $\pm$ 7.3	4.8 $\pm$ 11	370 $\pm$ 520	490 $\pm$ 590	37 $\pm$ 65	95 $\pm$ 95	0.86 $\pm$ 1.2	7.7 $\pm$ 12	8.0 $\pm$ 15
<b>Bournville</b>	<b>4</b>	3.7 $\pm$ 2.3	5.2 $\pm$ 3.6	3.5 $\pm$ 4.8	1.9 $\pm$ 3.7	5.9 $\pm$ 9.4	3.8 $\pm$ 6.6	4.9 $\pm$ 7.9	140 $\pm$ 170	180 $\pm$ 150	38 $\pm$ 47	110 $\pm$ 140	17 $\pm$ 9.4	2.2 $\pm$ 3.0	9.3 $\pm$ 14
<b>Edgbaston</b>	<b>5</b>	5.4 $\pm$ 9.3	7.6 $\pm$ 11	7.5 $\pm$ 16	5.2 $\pm$ 11	11 $\pm$ 23	12 $\pm$ 20	<1.5	110 $\pm$ 92	170 $\pm$ 100	60 $\pm$ 110	83 $\pm$ 90	6.4 $\pm$ 5.8	0.57 $\pm$ 0.81	8.1 $\pm$ 12
<b>Digbeth</b>	<b>6</b>	5.9 $\pm$ 9.1	7.9 $\pm$ 9.0	6.0 $\pm$ 9.6	2.4 $\pm$ 5.2	14 $\pm$ 25	8.4 $\pm$ 15	11 $\pm$ 21	140 $\pm$ 120	210 $\pm$ 110	66 $\pm$ 110	130 $\pm$ 130	4.7 $\pm$ 3.9	0.76 $\pm$ 0.86	6.7 $\pm$ 5.5
<b>Sutton Coldfield</b>	<b>7</b>	1.7 $\pm$ 1.3	3.1 $\pm$ 2.6	3.0 $\pm$ 3.9	0.53 $\pm$ 0.77	2.5 $\pm$ 4.1	4.5 $\pm$ 5.4	2.8 $\pm$ 6.3	130 $\pm$ 130	150 $\pm$ 130	21 $\pm$ 22	110 $\pm$ 110	3.0 $\pm$ 2.6	1.1 $\pm$ 1.3	6.4 $\pm$ 12
<b>Tamworth</b>	<b>8</b>	2.8 $\pm$ 3.3	5.1 $\pm$ 4.4	3.9 $\pm$ 3.7	2.0 $\pm$ 2.9	3.0 $\pm$ 5.1	0.37 $\pm$ 0.82	<1.5	110 $\pm$ 150	130 $\pm$ 140	21 $\pm$ 19	110 $\pm$ 110	2.9 $\pm$ 2.9	21 $\pm$ 46	7.7 $\pm$ 10

**Table 2 – Concentrations of selected PBDEs and EFRs in soil (ng g<sup>-1</sup> organic matter).**

Location	Site #	BDE-28	BDE-47	BDE-99	BDE-100	BDE-153	BDE-154	BDE-183	BDE-209	∑PBDEs	∑tri-hepta PBDEs	ATE	∑DDC-CO	DBDPE
<b>Worcester</b>	<b>1</b>	0.18	0.68	0.58	0.19	<0.15	<0.12	<0.19	1.5	3.6	2.1	0.076	1.2	0.21
<b>Droitwich</b>	<b>2</b>	0.085	0.58	0.55	0.12	<0.082	<0.064	<0.11	0.94	2.3	1.4	0.30	<0.016	<0.022
<b>Bromsgrove</b>	<b>3</b>	<0.026	2.1	1.6	0.45	<0.13	<0.10	<0.17	45	49	4.2	0.10	2.1	0.34
<b>Bournville</b>	<b>4</b>	0.50	0.95	0.77	0.26	0.30	1.6	<0.11	1.7	6.2	4.4	0.47	1.4	0.35
<b>Edgbaston</b>	<b>5</b>	0.26	0.84	0.95	0.31	0.28	0.28	0.62	5.7	9.4	3.7	0.045	1.9	0.36
<b>Digbeth</b>	<b>6</b>	0.31	1.4	1.1	0.31	0.44	<0.077	1.6	15	21	5.8	0.18	4.5	0.62
<b>Sutton</b>	<b>7</b>	<0.0085	0.76	0.88	0.51	<0.043	<0.034	<0.056	8.7	11	2.2	0.010	2.0	0.15
<b>Coldfield</b>	<b>8</b>	0.14	1.9	1.5	0.15	0.18	0.28	0.76	10	15	4.9	0.69	2.0	0.99

**Supplementary Material**

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