Distribution pattern of legacy and "novel" brominated flame retardants in different particle size fractions of indoor dust in Birmingham, United Kingdom

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1   # Distribution pattern of legacy and "novel" brominated flame

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3   # Birmingham, United Kingdom

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9

10   **ABSTRACT**

11   This study investigates the particle size distribution of eight polybrominated diphenyl ethers

12   (PBDEs) and five "novel" brominated flame retardants (NBFRs) in settled house dust.

13   Elevated surface dust (ESD) and floor dust (FD) were collected from 5 homes in

14   Birmingham, UK, yielding a total of 10 samples. Each sample was fractionated into three

15   different particle sizes: 125-250 μm (P1), 63-125 μm (P2) and 25-63 μm (P3). Non-

16   fractionated bulk dust samples (BD) were also analysed. BDE-209 predominated, comprising

17   an average 74.3%, 77.3%, 69.2%, and 62.7% ΣBFRs of BD, P1, P2 and P3 respectively.

18   Σ_5NBFRs contributed 24.2%, 21.5%, 29.0% and 35.3% ΣBFRs, while $\Sigma_7$tri-hepta-BDEs

19   represented 1.5%, 1.2%, 1.7%, and 2.0% ΣBFRs. BEH-TEBP was the predominant NBFR

20   contributing 76.9%, 75.1%, 83.1%, and 83.9% ΣNBFRs in BD, P1, P2 and P3 respectively;

21   followed by DBDPE which contributed 20.1%, 21.9%, 14.1% and 13.9% ΣNBFRs. EH-TBB,

22   BTBPE and PBEB were the least abundant NBFRs. Concentrations of $\Sigma_7$tri-hepta-BDEs and

23   BEH-TEBP in P3 exceeded significantly ($P < 0.05$) those in P2, with those in P2 exceeding

24   significantly those in P1. In contrast, no significant differences were found between

25   concentrations of BDE-209, EH-TBB, BTBPE, and DBDPE in different particle size

26   fractions. Concentrations of $\Sigma_7$tri-hepta-BDEs, BDE-209, and BEH-TEBP in ESD exceeded

27   significantly those in FD ($P < 0.05$). Normalising BFR concentrations to organic carbon

28   content, did not alter these findings. This suggests that differences in BFR concentrations

29   between different particle size fractions are caused by variations in particle surface area to

30   volume ratio, rather than by variations in organic carbon content.

1. Introduction

Polybrominated diphenyl ethers (PBDEs) are a group of brominated flame retardants (BFRs) added to several polymers used in various consumer products such as electronics, textiles, and polyurethane foams. They are blended physically with – rather than chemically bound to - polymeric materials, which likely lead them to migrate into the environment (WHO, 1997; USEPA, 2010 Alaee et al., 2003). PBDEs are persistent and bioaccumulative toxicants, with available information suggesting that they affect negatively the nervous system, the liver and the thyroid system (NICNAS, 2007; USEPA, 2008; Shaw et al., 2009; Noyes et al., 2010; Yu et al., 2011; Johnson et al., 2013; Yang et al., 2014; Zhang et al., 2014; Fang & Stapleton, 2014). Hence, their manufacture and new use is now banned or severely restricted in many jurisdictions, and they are listed – or in the case of the Deca-BDE product nominated for listing - under the Stockholm Convention on Persistent Organic Pollutants (POPs) (UNEP, 2008; 2013a; b). Such bans and restriction on the use of established BFRs like PBDEs has resulted in increased production of several other BFRs collectively referred to here as novel brominated flame retardants (NBFRs). These NBFRs display physicochemical properties similar to those of established BFRs (Covaci 2011; EFSA, 2012), and there is growing concern about increasing environmental contamination with NBFRs (Shi et al., 2009; Shoeib et al., 2012; Ali et al., 2013; Fromme et al., 2014; Poma et al., 2014; Hassan et al., 2015; Al-Omran and Harrad in press; Newton et al., 2015) and their potential negative health effects (Johnson et al., 2013).

Among the various human exposure pathways, ingestion of indoor settled dust appears to represent a major pathway for human exposure to BFRs in North America and Europe, particularly for young children as a result of normal hand-to-mouth activity (Besis and Samara 2012). Indoor settled dust refers to "particles in building interiors that have settled onto objects, surfaces, floors, and carpeting. These particles may include soil particles that have been tracked or blown into the indoor environment from outdoors as well as organic matter" (USEPA, 2011).

In general, indoor dust falls into a wide range of particle size fractions ranging from < 2.5 μm to over 2 mm and possessing organic contents between 5% and 95% (Morawska and Salthammer, 2003). However, for human exposure assessment, dust particles < 250 μm are considered of particular concern (USEPA, 2000; 2003), as these have been proposed as those

64   most likely to stick to hands and be ingested (Duggan and Inskip, 1985; Hee et al., 1985;

65   Edwards et al., 1999; Yamamoto et al., 2006).

66

67   A large and growing body of literature has investigated human exposure to BFRs via indoor

68   dust using a disparate range of particle sizes, for example, < 75 µm (Xu et al., 2015), < 100

69   (Kang et al., 2011), < 125 µm (Wu et al., 2007), < 150 µm (Wilford et al., 2005; Shoeib et

70   al., 2012; Whitehead et al., 2012), 25-250 µm (Al-Omran and Harrad, in press), < 500 µm

71   (Allen et al., 2008; Wang et al., 2010), 25-500 µm (Harrad et al. 2008a; 2008b; Muenhor et

72   al., 2010; Brommer et al., 2012), < 1000 µm (Suzuki et al., 2006), < 2000 µm (Gevao et al.,

73   20006) and all fractions (Takigami et al., 2008). Early studies on polycyclic aromatic

74   hydrocarbons (PAHs) and pesticides in indoor dust and airborne particles, indicate that, due

75   to the inverse relationship between particle size and specific surface area, levels of these

76   pollutants increase gradually with decreasing particle size (Lewis et al., 1999; Sygiyama et

77   al., 2000).

78

79   The first study to investigate PBDE concentrations as a function of dust particle size was ten

80   years later (Wei et al., 2009). By analysing four different dust fractions (250- 420 µm, 150-

81   250 µm, 75-150 µm, and < 75 µm) in indoor dust (1 car and 2 homes), Wei et al., (2009)

82   found that PBDE levels in car dust were inversely related to particle size, while they were

83   comparable in homes. Limited studies since, suggest BFR concentrations are influenced

84   significantly by dust particle size. Kefeni et al., (2014) reported that of the PBDEs detected in

85   dust particles < 250 µm from 2 homes and two offices; 93.4% were associated with particles

86   < 150 µm. In a similar study, Chao et al., (2014) found no significant difference in

87   concentrations of Σ_{28}PBDE in different particle sizes of house dust and electronic dust. Based

88   on analysis of office dust particle size fractions, Cao et al., (2013) reported some variation in

89   concentrations of PBDEs with particle size. Concentrations of tri-hexa PBDEs were highest

90   in the 74-100 µm and 100-200 µm particle size fractions, those of hepta-PBDEs were greatest

91   in 200-300 µm and 300-400 µm fractions, octa- and deca-PBDE concentrations peaked in

92   particles < 50 µm, while 2-bis (2,4,6-tribromophenoxy) ethane (BTBPE) was highest in the

93   50-74 µm and 75-100 µm size range. In a subsequent study by the same authors, Cao et al.,

94   (2014) found that in several non-domestic microenvironments, BDE-209 showed higher

95   levels in coarser particles in kindergartens (500-900 µm) and dormitories (900-2000 µm).

96   Moreover, BFR concentrations did not increase constantly with decreasing particle size.

97   Instead, the variation of concentrations with particle size was multi-modal, with the highest

98   levels associated with particle sizes around 900, 100, and 10 μm (Cao et al., 2014). A later

99   study revealed no significant variation in concentrations of HBCDs between different particle

100   size fractions (Cao et al., (2015). Other studies have used forensic microscopy to show that

101   the highest levels of BFRs are present in particles with different morphology, containing

102   more fibre-like material (Wei et al., 2009; Cao et al., 2013).

103

104   From the above, it is apparent that while concentrations of many BFRs vary according to the

105   dust particle size fraction, the exact nature of this variation remains unclear. Moreover, the

106   reasons for such variation have yet to be conclusively elucidated. A related issue is whether

107   BFR concentrations differ significantly between floor and elevated surface dust. We

108   hypothesised previously in a study of house dust from Basrah, Iraq, that the existence of such

109   differences would suggest a need to sample both dust sample types, in order to fully reflect

110   exposure of the room occupants (Al-Omran and Harrad, in press). In that same study, we

111   found that differences in the organic carbon content of dust samples, could not explain the

112   higher concentrations of PBDEs and NBFRs detected in elevated surface dust compared to

113   floor dust in the same rooms. It instead seems more plausible that BFR concentrations will be

114   greater in dust particles with a greater surface area to mass ratio, a hypothesis consistent with

115   the higher proportion of finer particles found in elevated surface compared to floor dust in

116   Basrah (Al-Omran and Harrad, in press).

117

118   This study therefore reports concentrations of eight PBDEs (BDE-28, BDE-47, BDE-99,

119   BDE-100, BDE-153, BDE-154, BDE-183 and BDE-209) and five NBFRs:

120   pentabromoethylbenzene (PBEB), 2-ethylhexyl-2,3,4,5-tetrabromobenzoate (EH-TBB), bis

121   (2-ethylhexyl) 3,4,5,6-tetrabromophthalate (BEH-TEBP), 2-bis (2,4,6-tribromophenoxy)

122   ethane (BTBPE), and decabromodiphenylethane (DBDPE) in both elevated surface dust and

123   floor dust from Birmingham, UK. Each dust sample is separated into three different particle

124   size fractions (125-250 μm, 63-125 μm, and 25-63 μm). BFR concentrations are reported

125   both as dry weight and normalised to dust organic carbon content. These data are used to test

126   our hypotheses that: (a) BFR concentrations in elevated surface dust will exceed those in

127   floor dust; (b) BFR concentrations will increase with decreasing particle size; and (c)

128   variations in dust organic carbon content cannot account for any variations in BFR

129   concentrations between different particle size fractions.

130

2. Materials and methods

2.1. Chemicals and standards

Native and labelled PBDEs (BDE-28, BDE-47, BDE-77, BDE-99, BDE-100, BDE128, BDE-153, BDE-154, BDE-183, BDE-209 and ^{13}C-BDE-209) and NBFRs (PBEB, EH-TBB, BTBPE, ^{13}C-BTBPE, BEH-TEBP, ^{13}C-BEH-TEBP and DBDPE) standards were purchased from Wellington Laboratories Inc. Guelph, Canada as stock solutions in iso-octane, except BDE-209 and ^{13}C-BDE-209 which were purchased as stock solutions in nonane. The recovery determination standard PCB-129 in hexane was purchased from Qmx Laboratories, UK. The purity of all standards is > 98%. Ethyl acetate (EA), Acetone (Ac), *n*-Hexane, dichloromethane (DCM), iso-octane, phosphoric acid and sulfuric acid were obtained from Fisher Scientific UK Ltd. All solvents used during analysis were of HPLC analytical grade. Silica gel (pore size 60 A˚, 70-230 mesh) was purchased from Sigma Aldrich, Switzerland, anhydrous sodium sulphate was obtained from Sigma Aldrich, USA, and Florisil® (particle size 60-100) acquired from Fluka, USA. Sodium bicarbonate was purchased from Nacalai Tesque, Japan, and sucrose (analytical reagent grade) was purchased from Fisher Scientific, UK. The standard reference material (SRM 2585, "Organic Contaminants in House Dust") was purchased from the National Institute of Standards and Technology (NIST) Gaithersburg, MD, USA. Finally, ISOLUTE amino propyl columns, SPE cartridges and frits were purchased from Biotage (Uppsala), Sweden.

2.2. Sampling and sample preparation

Between September 2013 and February 2014, elevated surface dust (ESD) and floor dust (FD) was collected from the living room and two bedrooms in each of 5 homes in Birmingham, UK. ESD and FD was collected every month for 4 months in two homes (n = 16), and for 5 months in three (n = 30). In order to provide sufficient dust mass for fractionation (especially necessary for ESD for which dust mass loadings in these UK homes were very low), the ESD and FD samples from each home were then combined to yield two bulk dust samples (one ESD and one FD) from each of the 5 homes. Samples were collected using a handheld vacuum cleaner (DIRT DEVIL-DDMHH1-1100W), according to a clearly defined standard protocol (Harrad et al., 2008a). 1 m^2 of carpeted floor was vacuumed for 2 min and, in the case of bare floor, 4 m^2 for 4 min using 25 μm pore size nylon sample socks (Allied Filter Fabric Pty Ltd, Australia) that were mounted in the furniture attachment tube of the vacuum cleaner. Elevated surfaces (typically between 50-150 cm height) were vacuumed

164   for 2-4 min depending on the surface area. After sampling, socks were closed with a twist tie,

165   sealed in plastic bags and stored at −20 °C. Before sampling, the furniture attachment and the

166   vacuum tubing were cleaned thoroughly using an isopropanol-impregnated disposable wipe

167   and dried between collections. Information on the potential influences on BFR contamination

168   such as: the number and type of putative sources like electronic devices, foam-filled furniture

169   and floor material, ventilation system, house cleaning method was recorded.

170   Initially, to obtain bulk dust samples (referred to here as BD), all samples were sieved using a

171   pre-cleaned, n-hexane rinsed 250 μm mesh stainless testing sieve, covered with the lid and

172   shaken for 3-5 min. After weighing, BD samples were fractionated into three different

173   particle size fractions, 125-250 μm (referred to as large particle size - P1), 63-125 μm

174   (referred to as medium particle size - P2) and 25-63 μm (referred to as fine particle size –

175   P3). Fractionation was achieved by using 63 μm, 125 μm, and 250 μm stainless sieves which

176   were placed over each other and shaken by hand for 5-7 min. Following fractionation, the

177   mass of each fraction was recorded.

178

179   **2.3. Sample extraction and extract purification**

180   Analysis of PBDEs and NBFRs in fractionated and BD samples was conducted following the

181   same extraction and clean-up as reported elsewhere (Al-Omran and Harrad, in press).

182   Briefly, samples were spiked with internal standards (BDE-77, BDE-128, ^{13}C-BDE-209, [13]C-

183   BTBPE and ^{13}C-BEH-TEBP), extracted by ultrasonication with 3 x 2 mL n-hexane/acetone

184   (3:1, v/v), evaporated to incipient dryness under a gentle nitrogen stream and resolubilised in

185   1 mL n-hexane (Ali et al., 2011; van den Eede et al., 2012). For sample purification, the

186   extract was fractionated into two fractions (F1 and F2) using 2 g Florisil. F1 (containing

187   PBDEs and DBDPE) was eluted with 12 mL of hexane and F2 (containing the rest of the

188   targeted NBFRs) was eluted with 15 mL ethyl acetate. After evaporation to 1 mL, a second

189   purification step for F1 was conducted on 2 g acid silica (44% w/w) and eluted with 15 mL n-

190   hexane/DCM (1:1, v/v). F2 was evaporated to dryness, resolubilised in 3-5 mL of hexane,

191   then evaporated to 1 mL, and eluted with 12 mL n-hexane/DCM (1:1, v/v) using an

192   aminopropyl functionalised silica column (0.5 g). F1 and F2 were combined and evaporated

193   to incipient dryness, before resolubilisation in 100 μL of iso-octane containing PCB-129 at

194   250 pg/μL ready for GC/MS analysis (Al-Omran and Harrad, in press).

195

196   **2.4. Instrumental analysis**

197 Analysis of our target compounds was performed using a gas chromatograph (GC) (Trace
198 1310 Gas Chromatograph) coupled to a mass spectrometer (MS) (ISQ Quadrupole MS); both
199 (Thermo Fisher Scientific, USA). The GC was equipped with a programmable temperature
200 vaporiser (PTV) injector and fitted with a capillary fused silica column (RESTEK, USA, 15
201 m x 0.25 mm inner diameter, 0.25 μm film thickness). 2 μL of purified extract were injected
202 on the column. The inlet temperature was set at 92 °C. The GC oven temperature program
203 was set at 50 °C for 0.5 min, ramp 20 °C/min to 240 °C, hold 5 min, ramp 5 °C/min to 270 °C,
204 and ramp 20 °C/min to 305 °C, hold 19 min. Helium was used as a carrier gas with a flow
205 rate of 1.5 mL/min. The MS was operated in ECNI mode. The electron lens voltage was set
206 at 15 V and emission current set at 50 μA. The ion source and transfer line temperatures were
207 300 °C and 320 °C respectively. BDE-77 was used as internal standard for quantification of
208 BDE-28, PBEB, BDE-47, BDE-99, BDE-100; BDE-128 was used to quantify BDE-153,
209 BDE-154 and BDE-183; ^{13}C-BTBPE for BTBPE and EH-TBB; ^{13}C-BEH-TEBP for BEH-
210 TEBP; and ^{13}C-BDE-209 used for BDE-209 and DBDPE.

211 **2.5. QA/QC**
212 All glassware were cleaned by soaking in an alkali solution overnight, before rinsing with tap
213 water, followed by deionised water, baking at 450 °C for 4.5 h, cooling, washing with
214 acetone, and covering with aluminium foil until use. To assess any possible contamination
215 during sample preparation and analysis method, one laboratory blank was processed in
216 parallel with every set of 6 dust samples. In total 8 blanks were conducted. In none of these
217 were any of the target compounds detected, and hence data are not corrected for blank
218 concentrations. Similar results were obtained for field blanks (n=5). These consisted of
219 sodium sulphate that spread on aluminium foil, collected using the vacuum cleaner and
220 treated as a sample. For on-going evaluation of accuracy, an aliquot of SRM2585 was
221 analysed with every 15 samples (or part thereof). The obtained data compared favourably
222 with certified concentrations where provided and with previously reported data for this SRM
223 where certified concentrations were not available, (Tables S1 and S2, Supplementary Data).
224 Recoveries of internal standards ranged from 76 to 91 % in all dust samples (Table S3,
225 Supplementary Data). Limits of detection (LOD) were estimated based on a signal to noise
226 ratio 3:1, with limits of quantification (LOQ) estimated based on signal to noise ratio of 10:1,
227 (Table S4, Supplementary Data)

228 **2.6. Determination of organic carbon content in dust**

229   The total organic carbon (TOC) content of the dust samples was obtained by using a Total

230   Organic Carbon analyzer TOC-V$_{CSH/CSN}$ fitted with a Solid Sample Module SSM-5000, both

231   from SHIMADZU, Japan. The instrument provided measurements of Total Carbon (TC) and

232   Inorganic Carbon (IC), hence the TOC was deduced by subtracting the IC value from TC.

233   Due to the low dust mass available from H5 for fractionation and BFR analysis, TOC was not

234   determined in dust samples from this house.

235   **2.7. Statistical analysis**

236   Statistical analysis of the data was performed using Microsoft Excel 2013 and IBM SPSS

237   statistics software (V. 20). The distribution of the concentration data for target pollutants was

238   tested using the Shapiro-Wilk test. This revealed concentrations of all our target BFRs to be

239   log normally distributed. Hence, data were log-transformed prior to comparison of means via

240   T-test and One-way Repeated Measures ANOVA for testing significant differences between

241   arithmetic means. For the purposes of statistical evaluation, all concentrations below LOQ

242   were assigned a value of 0.5 LOQ. A p value < 0.05 was taken to indicate statistical

243   significance.

244

245   **3. Results and discussion**

246   **3.1. Relationship between BFRs in different particle sizes**

247   In all dust samples analysed (n=40), BDE-47, BDE-99, BDE-153, BDE-209, BEH-TEBP,

248   and DBDPE were found with detection frequencies of 100 %, while the detection frequency

249   of other target compounds fell between 40-100%. Concentrations of BDE-28, BDE-100,

250   BDE-154, and PBEB were very low, and they are thus excluded from statistical analysis for

251   individual comparison. However, they were included in calculation of $\Sigma_7$tri-hepta-BDEs and

252   Σ_5NBFRs. $\Sigma_7$tri-hepta-BDEs refers to the summation of seven congeners (BDE-28, BDE-47,

253   BDE-99, BDE-100, BDE-153, BDE-154, and BDE-183), Σ_5NBFRs represent the sum of

254   PBEB, EH-TBB, BTBPE, BEH-TEBP, and DBDPE, with ΣBFRs equalling the sum of $\Sigma_7$tri-

255   hepta-BDEs, BDE-209 and Σ_5NBFRs. Of all target compounds, BDE-209 was the

256   predominant congener making average percentage contributions to ΣBFRs of 74.3%, 77.3%,

257   69.2%, and 62.7% in BD, P1, P2 and P3 dust samples respectively. Σ_5NBFRs contributed

258   24.2%, 21.5%, 29.1% and 35.3% ΣBFRs, while $\Sigma_7$tri-hepta-BDEs represented 1.5 %, 1.2 %,

259   1.7 %, and 2.0 % of ΣBFRs. Of the target NBFRs, BEH-TEBP predominated, with

260   corresponding mean percentage contributions to Σ_5NBFRs of 76.9%, 75.1%, 83.1%, and

261   83.9%, followed by DBDPE with percentages 20.1 %, 21.9 %, 14.1 % and 13.9 % in BD, P1,

262   P2 and P3 dust samples respectively. EH-TBB and BTBPE were the least abundant of the

263   target NBFRs, with EH-TBB comprising 0.95 %, 1.08 %, and 1.05 % and 0.79% Σ_5NBFRs,

264   and BTBPE 1.94%, 1.74%, 1.64% and 1.24% Σ_5NBFRs in BD, P1, P2 and P3 respectively.

265   Figure 1 shows average concentrations of $\Sigma_7$tri-hepta-BDEs, BDE-209, and Σ_5NBFRs in BD,

266   P1, P2 and P3, additionally, Figure 2 illustrates concentrations and profiles of tri-hepta-BDEs

267   and NBFRs.

268

269   As hypothesised and consistent with our previous study in Iraq (Al-Omran and Harrad, in

270   press), BFR concentrations in elevated surface dust exceeded those in floor dust. The t-test

271   analysis revealed that with the exception of DBDPE ($p = 0.978$), our target compounds in

272   elevated surface dust exceeded significantly those in floor dust with p values < 0.002 for each

273   of the three different particle size fractions and bulk dust. Average concentrations in ESD

274   exceeded those in FD by the following factors: for $\Sigma_7$tri-hepta-BDEs, 2.4, 2.5, 3.2 and 2.9, for

275   BDE-209, 1.4, 1.6, 1.4, and 1.3, and for Σ_5NBFRs, 2.9, 3.6, 4.7 and 4.6 in BD, P1, P2 and P3

276   respectively. Figure S1 (supplementary data) compares mean concentrations of $\Sigma_7$tri-hepta-

277   BDEs, BDE-209 and Σ_5NBFRs in three particle sizes and bulk dust for both floor dust (FD)

278   and elevated surface dust (ESD).

279   **3.2 Distribution patterns of PBDEs and NBFRs with particle size**

280   The average mass percentage of dust fractions P1, P2 and P3 were about 20.6%, 32.7% and

281   46.6%, respectively. In other words, on average ~79% of the bulk dust mass was associated

282   with particles < 125 μm, which is comparable to the 80% figure reported for indoor dust

283   particles < 150 μm (Wei et al., 2009). Figure S2 (supplementary data) illustrates the mass

284   percentage contribution of dust fractions P1, P2 and P3 to BD.

285

286   Table 1 provides a statistical summary of concentrations of PBDEs in BD, P1, P2 and P3

287   respectively, with the equivalent data for NBFRs provided in Table 2. Following log

288   transformation of BFR concentrations (ng/g dw), one-way repeated measures ANOVA was

289   applied to test the hypothesis that concentrations of BFRs in P3 would exceed significantly

290   those in P2 and P1. This analysis revealed no significant differences ($p > 0.05$) between

291   concentrations in different dust particle size fractions of: BDE-209, BTBPE, DBDPE, and

292   EH-TBB. In contrast, in the finest particle size fraction (P3), concentrations of BDE-47 ($p =$

293   0.03), BDE-99 ($p = 0.004$), BDE-183 ($p = 0.046$), BEH-TEBP ($p = 0.001$), Σ_5NBFRs ($p =$

294   0.008), and $\Sigma_7$tri-hepta-BDEs ($p < 0.001$) exceeded significantly those detected in the

295   coarsest fraction (P1). Concentrations of BDE-99 (p = 0.009), BEH-TEBP (p = 0.017),

296   Σ_5NBFRs (p = 0.007), and $\Sigma_7$tri-hepta-BDEs (p < 0.001) in the finest particles (P3)

297   significantly exceeded those in the medium particle size fraction P2. In addition,

298   concentrations in P3 of BDE-183 (p = 0.053) were near-significantly elevated over those in

299   P2. Moreover, BDE-99 (p = 0.008), BDE-153 (p = 0.002) BHH-TEPB (p = 0.003), and Σtri-

300   hepta-BDEs (p = 0.003) in the medium particle size fraction (P2) exceeded significantly

301   those in the coarsest size fraction (P1). These findings show that for some BFRs,

302   concentrations will increase with decreasing particle size; while for other BFRs, such a

303   relationship does not exist. Figure 3 illustrates the distribution of $\Sigma_7$tri-hepta-BDEs, BDE-

304   209, BEH-TEBP and DBDPE in particle size fractions from elevated surface dust and floor

305   dust samples from five homes.

306

307   Interestingly, concentrations of our target BFRs in bulk dust (25-250 µm) exceeded

308   significantly those in one or more of the 3 particle size sub-fractions for BDE-153, BEH-

309   TEBP, and $\Sigma_7$tri-hepta-BDEs only. This suggests that the use in many past studies of a

310   relatively broad particle size range has likely not unduly influenced exposure assessment.

311

312   As semi-volatile organic compounds (SVOCs) and additive flame retardants, our target BFRs

313   can be released from the products via volatilisation into surrounding air, depending on their

314   vapour pressure (V_p). Such volatilised BFRs may then undergo deposition to both suspended

315   and settled indoor dust, with the relative partitioning between these two phases governed by

316   the octanol-air partition coefficient (K_{OA}) of the BFRs (Li et al., 2006; Weschler and

317   Nazaroff, 2010). This volatilisation with subsequent deposition process will be more

318   important for BFRs with higher vapour pressures/lower K_{OA} values. By comparison, the

319   presence of less volatile BFRs may be governed more by other processes such as direct

320   contact between BFR source and dust and abrasion of BFR source materials (Rauert and

321   Harrad, 2015; Suzuki et al., 2009; Webster et al., 2009). These factors, combined with the

322   fact that atmospheric deposition of BFRs to dust particles will be greater for finer particle

323   sizes due to their greater surface area to volume ratio (Lewis et. al., 1999; Wei et al., 2009;

324   Mercier et al., 2011); means that significantly higher concentrations on finer dust particles

325   would be anticipated for more volatile BFRs, with this likely less influential for their less

326   volatile counterparts. With the exception of BEH-TEBP – for which the available data on its

327   vapour pressure suggests it would behave in the same way as BDE-209, BTBPE, and

328   DBDPE (see table S5 listing available data for key physicochemical properties of our target

329   BFRs) - this is consistent with our data, that show higher concentrations of BDEs 47, 99, and

330   BEH-TEBP in finer dust particles, but no particle size preference for BDE-153, BDE-209,

331   BTBPE, DBDPE, and EHTBB.

332

3.3 Influence of organic carbon content of dust on BFR particle size distribution

334   In addition to the particle surface area to volume/mass ratio, variations in organic carbon

335   content between ESD and FD and between different particle size fractions could potentially

336   influence BFR concentrations in both ESD versus FD and in different particle size fractions.

337   Figure S3 illustrates TOC contents of different particle size fractions in both FD and ESD.

338   That this is feasible, is underlined by the fact that significant positive linear correlations were

339   observed between BFR concentrations in all samples and their corresponding total organic

340   carbon (TOC) content, with R values ranging between 0.883 and 0.979 ($p < 0.001$). We

341   therefore examined our data to check whether normalising BFR concentrations to the organic

342   carbon content of the dust fraction analysed, exerted any influence on our observations. We

343   found that doing so, made no difference to our findings based on concentrations normalised

344   to dry weight of dust alone. This is consistent with our previous findings comparing BFRs in

345   ESD and FD in Iraq (Al-Omran and Harrad, in press), that differences in organic carbon

346   content of dust cannot explain either the differences in BFR concentrations in ESD and FD,

347   or the variation in BFR concentrations with particle size fraction. Figure S4 (Supplementary

348   Data) shows BFR concentrations and their corresponding total organic carbon (TOC) content

349   in different particle sizes in elevated surface dust and floor dust from the four homes for

350   which this was possible.

351

4. Conclusions

353   While based on a small number of homes, our findings suggest that BFR concentrations

354   recorded in indoor dust samples are influenced by the particle size fraction analysed.

355   However, there is substantial variation between different BFRs. Specifically, while

356   concentrations of more volatile BFRs like Σtri-hepta-BDEs are significantly higher in dust

357   particles of 25-63 μm diameter than in those of 125-250 μm and 63-125 μm diameter;

358   concentrations of less volatile BFRs such as BDE-209, BTBPE, EH-TBB, and DBDPE do

359   not differ significantly between different dust particle size fractions. This is consistent with

360   hypotheses that less volatile BFRs enter dust predominantly via mechanisms that do not

361 display clear preference for any one particle size fraction, such as abrasion of and direct
362 contact with flame retarded materials, Consistent with our previous research in Iraq,
363 concentrations of most of our target BFRs in elevated surface dust exceed significantly those
364 in floor dust from the same UK microenvironments. Variations in the organic carbon content
365 of dust explain neither the higher concentrations of BFRs in elevated surface compared to
366 floor dust, nor the higher concentrations of some BFRs in finer dust particles. Instead, our
367 data suggest that it is the greater surface area to volume ratio of finer dust particles that
368 accounts for their higher BFR concentrations. Despite our small sample size precluded
369 meaningful human exposure assessment, the results of this research support the idea that
370 human exposure assessment could be affected by the dust particle size fractions analysed, and
371 more detailed study of this issue is recommended.
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