

## Children's exposure to hazardous brominated flame retardants in plastic toys

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1 **Children's exposure to hazardous brominated flame retardants in plastic toys**

2

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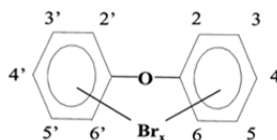
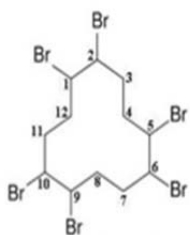
13 **Abstract**

14 We report concentrations of brominated flame retardants (BFRs) in 23 plastic samples from 20  
15 new and second-hand children's toys sourced from the UK that had been previously shown to be  
16 Br-positive by XRF. The results reinforce existing evidence that the recycling of BFR-treated  
17 electronic plastics has led to the unintentional BFR contamination of articles not required to be  
18 flame-retarded. The principal BFRs detected were PBDEs (and in particular BDE-209), HBCDD  
19 and TBBP-A. PBDEs were detected in all samples with a maximum concentration of BDE-209  
20 of 2500 mg/kg, and while TBBP-A was detected in 11 samples with a maximum concentration  
21 of 3100 mg/kg. HBCDD was detected in 14 cases and was present in four toys at concentrations  
22 (139-840 mg/kg) that would currently prevent their sale on the EU market. While estimated  
23 exposures to PBDEs via accidental ingestion of toy plastic fell well below USEPA reference  
24 doses, a child weighing 8.67 kg and ingesting 8 mg/day of a toy (the default assumption of the  
25 European Commission's Toy Safety Directive for scraped-off toy material) contaminated at our  
26 arithmetic mean concentration would be exposed to 0.2 ng/kg bw/day BDE-99. This compares  
27 closely to a health-based limit value (HBLV) proposed in The Netherlands of 0.23-0.30 ng/kg  
28 bw/day BDE-99. Of greater concern, the same child playing with a toy contaminated at the  
29 maximum concentration in this study would be exposed to 1.4 ng/kg bw/day BDE-99, thereby  
30 exceeding the HBLV. This paper is the first to consider BFR exposure via incidental ingestion of  
31 plastic from both contemporary and historical toys, revealing it to be considerable and for some  
32 children their most significant pathway of exposure.

33

34

35 **Graphical abstract**



36

37 **Keywords**

38 recycled plastics; human exposure; POPs; PBDEs; HBCDD; TBBP-A

39

40 **Highlights**

41 Br and BFRs measured in children's plastic toys

42 HBCDD present in 4 toys at concentrations above the EU UTC limit value

43 PBDE concentrations in 2 toys exceed proposed limit of 500 mg/kg

44 TBBP-A detected in 11 samples

45 Children's exposure via unintentional ingestion of toy plastic may be substantial

46

47 **1. INTRODUCTION**

48 Due to evidence of their adverse health effects, brominated flame retardants (BFRs) such as  
49 polybrominated diphenyl ethers (PBDEs) and hexabromocyclododecane (HBCDD) are subject to  
50 global bans and restrictions. As a consequence, reports of the presence of BFRs in plastic  
51 children's toys as a result of the use of recycled polymers containing such chemicals are of  
52 concern (Chen et al., 2009; Ionas et al., 2014; DiGangi et al., 2017; Guzzonato et al., 2017;  
53 Puype et al., 2019; Straková and Petrlík, 2017). Children are particularly vulnerable to the  
54 adverse health effects of contaminants because of their behavioural tendencies (*e.g.*, mouthing of  
55 objects and hand to mouth activities) that differ from adults and result in higher levels of  
56 exposure (Landrigan et al., 2011).

57

58 To protect children from migratable substances in toys, the Toy Safety Directive (TSD)  
59 2009/48/EC was introduced by the EU (European Commission, 2009). It stipulates that  
60 substances classified as carcinogenic, mutagenic, or toxic for reproduction (category 1A, 1B, or  
61 2 and referred to as CMRs) shall not be used in toys or components thereof. While Br and BFRs  
62 are not specified under the TSD, in an effort to prevent the contamination of new plastic articles  
63 with PBDEs and HBCDD, the EU introduced low persistent organic pollutant (POP)  
64 concentration limits (LPCLs). Waste articles, such as plastic casings of end-of-life electronic  
65 equipment, that contain HBCDD or PBDEs present in the Penta- and Octa- (and, since 2019,  
66 Deca-) BDE formulations at concentrations exceeding the LPCL of 1,000 mg/kg cannot be  
67 recycled until their PBDE and HBCDD content has been destroyed or irreversibly transformed  
68 (European Commission, 2014; 2016). However, the LCPL is currently being reviewed with the  
69 aim of adopting legislative limits that are lower than 500 mg/kg as quickly as possible and no  
70 later than 2021 (European Commission, 2019). Moreover, the EU has also introduced an  
71 Unintentional Trace Contaminant (UTC) limit for HBCDD of 100 mg/kg (European

72 Commission, 2016), with UTC limits for tetra-, penta-, hexa-, hepta- and decaBDE of 10 mg/kg  
73 each to be introduced in July 2021 (European Commission, 2019).

74

75 In addition to PBDEs and HBCDD, other BFRs have been used in a variety of applications to  
76 impart flame retardancy to polymers such as electrical items and fabrics. The most widely used  
77 of these is tetrabromobisphenol-A (TBBP-A) (Abdallah, 2016), while others such as  
78 decabromodiphenyl ethane (DBPDE), pentabromobenzene (PBBz), hexabromobenzene (HBB),  
79 pentabromotoluene (PBT), and pentabromoethylbenzene (PBEB) are also reported to have been  
80 used (Covaci et al., 2011). As use of the latter five BFRs is thought to have increased in recent  
81 years in response to restrictions on “legacy” BFRs like PBDEs and HBCDD, compounds such as  
82 DBDPE, PBBz, HBB, PBT, and PBEB are collectively referred to here as “novel” BFRs (or  
83 NBFRs). While TBBP-A and these NBFRs are not subject to restriction, their presence in, for  
84 example, indoor air has been demonstrated (Abdallah et al., 2008; Cequier et al., 2014; Newton  
85 et al., 2015), and concerns have emerged over their potential adverse health effects (Covaci et al.,  
86 2009; Nakari and Huhtala, 2009; Ezechiáš et al., 2012). Given the widespread use of such BFRs,  
87 similar concerns exist that they may be present in items containing recycled plastics, with  
88 DBDPE being reported to be present in children’s plastic toys purchased in China (Chen et al.,  
89 2009).

90

91 Previously, 200 second-hand plastic toys (encompassing plastic components from multi-material  
92 toys) sourced in the UK were analysed by X-ray fluorescence (XRF) spectrometry for the  
93 presence of hazardous elements (As, Ba, Cd, Cr, Hg, Pb, Sb, Se) regulated in children toys under  
94 the TSD, with Br as a proxy metric of BFRs also analysed and detected in many cases (Turner,  
95 2018a). A subsequent study also found Br in many plastic toys that had been purchased new,  
96 with the majority of Br-positive items black in colour and consistent with the recycling of

97 electronic waste plastic that is often black for cosmetic and economic purposes (Turner, 2018b).  
98 The overall aim of this study, therefore, was to measure concentrations of various legacy (*i.e.*  
99 PBDEs and HBCDD) and NBRs in a selection of toys sourced in the UK that had been shown  
100 to be Br-positive (Turner, 2018b), and to use these data to conduct an assessment of exposure of  
101 children playing with such toys and the associated health risk. As previous studies of this topic  
102 had not considered exposure via inadvertent ingestion of plastic particles, we further aimed to  
103 examine such exposure to test the hypothesis that this pathway is a significant source of exposure  
104 to infants. Subsidiary aims were to: (a) evaluate the extent to which measurements of elemental  
105 Br in toys are attributable to our target BFRs, and (b) identify any exceedances of the EU's  
106 current and impending LPCL and UTC limit values for PBDEs and HBCDD.

107

## 108 **2. MATERIALS AND METHODS**

### 109 *2.1. Sampling and screening for total Br via XRF*

110 Twenty three plastic components (samples) from 20 new and second-hand toys (Table 1)  
111 previously shown to contain Br that is believed to be derived in whole or in part from the  
112 recycling of electronic waste plastic (Turner, 2018a; 2018b) were selected for this study. Sample  
113 #s 4, 10, and 23 originated from new toys, with all other samples taken from second-hand items.  
114 Toys included game pieces, vehicles, parts of figures, items of jewellery and the handle of a  
115 dummy. As an additional check on the total Br content of each sample, and to assess the  
116 homogeneity of the distribution of Br, a NITON XL3t 700XRF spectrometer was used to make  
117 measurements at between two and four points on each sample (Table 1). Before analysis, the  
118 surface of each sample was wiped with a clean non-fibrillating tissue to remove any surface dust.  
119 The instrument window was then placed as flat as possible against the sample surface and a  
120 measurement of Br content conducted for 60 seconds. The limit of quantification for Br was 5  
121 mg/kg. Calibration of the XRF was performed by Niton UK using proprietary standards

122 containing varying concentrations of relevant inorganic compounds in a polymer matrix. The  
123 instrument was operated in a low density “plastics” mode and with thickness correction.

124

## 125 *2.2. BFR measurement methods*

### 126 *2.2.1. Chemicals and reagents*

127 HPLC-grade solvents were used for sample extraction and LC–MS/MS analysis (Fisher  
128 Scientific, Loughborough, UK). Concentrated sulphuric acid was purchased from Sigma–Aldrich  
129 (St. Louis, MA, USA). Individual  $\alpha$ -,  $\beta$ - and  $\gamma$ -HBCDD standards,  $^{13}\text{C}_{12}$   $\alpha$ -,  $\beta$ - and  $\gamma$ -HBCDD,  
130  $\text{d}_{18}$ - $\gamma$ -HBCDD, individual standards of PBDEs 17, 28, 47, 49, 77, 99, 100, 153, 154, 183,196,  
131 197, 209 and 128,  $^{13}\text{C}_{12}$ -BDE-209,TBBP-A,  $^{13}\text{C}_{12}$ -TBBP-A, PBBz, PBT, PBEB, HBB, and  $^{13}\text{C}_6$ -  
132 HBB and DBDPE were purchased from Wellington Laboratories (Guelph, ON, Canada).  
133 Polychlorinated biphenyl (PCB)-129 was obtained from Qmx laboratories (Thaxted, UK). A  
134 certified reference material (CRM) for polypropylene (ERM-EC591), containing certified  
135 concentrations of PBDEs, was purchased from IRMM (Brussels, Belgium).

136

### 137 *2.2.2. BFR extraction and extract purification*

138 Samples were analysed for concentrations of BFRs using a validated in-house method (Abdallah  
139 et al., 2017). Briefly, accurately weighed 0.2 g aliquots of each sample where Br was detected by  
140 XRF were transferred into 15 mL glass centrifuge tubes and spiked with 20 ng of internal  
141 standards ( $^{13}\text{C}_{12}$  $\alpha$ -,  $\beta$ - and  $\gamma$ -HBCDD,  $^{13}\text{C}_{12}$ -BDE 77,  $^{13}\text{C}_{12}$ -BDE-128,  $^{13}\text{C}_{12}$ -TBBP-A and  $^{13}\text{C}_6$ -  
142 HBB) as well as 40 ng  $^{13}\text{C}_{12}$ -BDE 209. Samples were extracted with 3 mL  $\text{CH}_2\text{Cl}_2$  by vortexing  
143 for 2 min and sonicating for 5 min. This was repeated with two further 3 mL aliquots of fresh  
144  $\text{CH}_2\text{Cl}_2$ . Extracts were collected and combined in a separate centrifuge tube and evaporated to  
145 near dryness at 40 °C under a gentle stream of nitrogen before being reconstituted in 2 mL of  
146 hexane and vortexed to precipitate dissolved plastics. The hexane supernatant was collected and



147 washed with 2 mL of >98 % concentrated sulphuric acid before vortexing for 30 s. Samples  
148 were left for 2 h followed by centrifugation at 3000 rpm for 5 min to ensure complete separation  
149 of the organic layer. The clean supernatant hexane layer was collected in a glass tube and  
150 concentrated to near dryness before reconstitution in 200  $\mu$ L of toluene containing 0.1 ng/ $\mu$ L  
151 PCB-129 and d<sub>18</sub>- $\gamma$ -HBCDD for recovery determination (or syringe) standards. The extracts were  
152 transferred to auto-sampler vials with glass inserts for quantitative analysis of PBDEs, PBBz,  
153 and DBDPE on GC/MS. After GC-MS analysis, the same extracts were solvent-exchanged to  
154 methanol ready for determination of HBCDDs and TBBP-A via LC-MS/MS.

155

### 156 2.2.3. Instrumental Analysis

157 Determination of PBDEs and NBFs was conducted on a ThermoFisher Trace 1310 gas  
158 chromatograph coupled to a ThermoFisher ISQ mass spectrometer operated in electron  
159 ionization mode and using selective ion monitoring. With a programmable temperature  
160 vaporizer, 1  $\mu$ L of extracts were injected onto a Restek Rxi-5Sil MS column (15 m  $\times$  0.25 mm  $\times$   
161 0.25  $\mu$ m film thickness) with He as the carrier gas at a flow rate of 1.5 mL/min (Abdallah et al.,  
162 2017).

163

164 HBCDDs and TBBP-A were quantified on a Shimadzu LC-20AB prominence binary pump  
165 liquid chromatograph equipped with a SIL-20A auto-sampler, and a DGU-20A3 vacuum  
166 degasser coupled to an AB Sciex API 2000 triple quadrupole MS (Abdallah et al., 2017). An  
167 Agilent Pursuit XRS3 C18 column (150 mm  $\times$  2 mm id, 3  $\mu$ m particle size) eluted with a mobile  
168 phase of (i) 1:1 methanol/water with 2 mM ammonium acetate and (ii) methanol at a flow rate of  
169 180  $\mu$ L/min. The mass spectrometer was operated in negative ESI mode. MS/MS detection  
170 operated in the multiple reaction monitoring mode was used for quantitative determination of  
171 HBCDD isomers based on  $m/z$  640.6 $\rightarrow$ 79,  $m/z$  652.4 $\rightarrow$ 79, and  $m/z$  657.7 $\rightarrow$  79 for the native,

172 <sup>13</sup>C-labelled and d<sub>18</sub>-labelled HBCD diastereomers, respectively and *m/z* 540.8→79, *m/z*  
173 552.8→79 for the native and <sup>13</sup>C-labelled TBBP-A, respectively.

174

#### 175 2.2.4. QA/QC

176 Average recoveries of internal standards were between 65 % and 78 %. Table SI-1 shows that  
177 the concentrations of PBDEs detected in an aliquot of the certified reference material ERM-  
178 EC591 compared favourably with the certified values. Limits of quantification (LOQs) were  
179 estimated from a signal to noise ratio of 10:1; target compounds were not detected above LOQs  
180 in the blanks and results were therefore not corrected for blank residues. Table SI-2 gives the  
181 LOQs for all target compounds.

182

#### 183 2.3. Data analysis

184 For the purposes of calculating descriptive statistics, <LOQ values were replaced by *f* × LOQ,  
185 where *f* = the detection frequency of a given BFR expressed as a decimal fraction.

186

#### 187 2.4. Exposure estimation methods

##### 188 2.4.1. Exposure via oral ingestion

189 Exposure via oral ingestion (*E*<sub>oral ingestion</sub> in ng/kg body weight/day) was estimated using the  
190 following algorithm:

$$191 E_{\text{oral ingestion}} = C_{\text{toy}} \times m \times (BA/BW)$$

192 where *C*<sub>toy</sub> is the BFR concentration in the toy (in ng/g), *m* is the mass of toy ingested per day  
193 which, by default, is 8 mg/day according to the Toy Safety Directive (Lenzner et al., 2018), *BA* is  
194 the bioavailability of the BFR (%), assumed conservatively to equal the bioaccessibility of BFRs  
195 of dust in simulated gastrointestinal tract fluid (Abdallah et al., 2012), and *BW* is body weight  
196 (kg).

197

#### 198 2.4.2. Exposure via dermal uptake

199 We estimated exposure via dermal uptake ( $E_{\text{dermal}}$  in ng/kg body weight/day) as follows:

$$200 E_{\text{dermal}} = C_{\text{toy}}^* \times PSA \times IEF \times (AF/BW)$$

201 Here,  $C_{\text{toy}}^*$  is the BFR concentration of BFR in toy the (in ng/m<sup>2</sup>) ( $C_{\text{toy}}^* = 1.4 \times 0.05 \times C_{\text{toy}}$   
202 assuming a 0.05 cm depth of surface and a density of 1.4 g/cm<sup>3</sup> equivalent to acrylonitrile  
203 butadiene styrene) (Kuang et al., 2018),  $PSA$  is the palm surface area exposed dermally to the toy  
204 (assumed to be 0.0986 m<sup>2</sup>) (Chen et al., 2009),  $IEF$  is the indoor exposure fraction, or the  
205 number of hours per day for which dermal contact with toys occurs (assumed to be 2; Chen et al.,  
206 2009), and  $AF$  is the absorbed fraction. The latter is based on measured data for the dermal  
207 uptake of PBDEs and HBCDD from fabrics over a 24 h contact (Abdallah and Harrad, 2018) and  
208 measured data for 24 h contact with solutions of TBBP-A (Abdallah et al., 2015), and is  
209 normalised for a 2 h period.

210

### 211 3. RESULTS AND DISCUSSION

#### 212 3.1. Concentrations of Br and BFRs in children's plastic toys

213 Table 2 reports the average of the replicate measurements of total Br made by XRF for each toy,  
214 including components thereof, while Table SI-3 lists each individual Br measurement for these  
215 samples. In some cases, total Br appears to be uniformly distributed in the plastic, while in other  
216 cases there is evidence for its heterogeneous dispersion in the toy. Table 2 also lists  
217 concentrations of the target BFRs in each sample, as well as the median, arithmetic mean, and  
218 maximum concentrations for the whole dataset.

219

220 BFRs were detected in all toys tested with summed concentrations ranging from 1.4 mg/kg to  
221 about 6140 mg/kg. The principal BFRs detected in the toys were either PBDEs (in particular  
222 BDE-209), HBCDD or TBBP-A, with only low concentrations detected of our target NBFRs.

223 The newest toys, purchased in 2017, contained < 20 mg/kg of BFRs but displayed a wide range  
224 in compounds historical and new BFRs. Overall, the BFR pattern and absolute concentrations in  
225 our samples are within the range of those previously reported for other studies of plastic items  
226 containing recycled polymers, including toys and food contact articles (Chen et al., 2009;  
227 Guzzonato et al., 2017; Ionas et al., 2014; Kuang et al., 2018; Puype et al., 2015, 2017).

228

229 If our study has quantified all of the Br-containing compounds in a sample, then the total Br and  
230  $\Sigma$ BFR concentrations should be broadly equal, with the latter slightly exceeding the former  
231 because Br only constitutes a proportion of the mass of any BFR. Moreover, as we measured  
232 BFRs in a single small aliquot of each toy or component thereof and our replicate XRF  
233 measurements of Br revealed varying degrees of inhomogeneity of Br distribution within the  
234 sample, Br and  $\Sigma$ BFR measurements will deviate in some instances. Specifically, the  
235 heterogeneous distribution of Br and BFRs likely explains why  $\Sigma$ BFRs > average Br in sample #s  
236 5 ( $\Sigma$ BFRs = 847 mg/kg c.f. Br = 90 mg/kg) and 6 ( $\Sigma$ BFRs = 468 mg/kg c.f. Br = 289 mg/kg);  
237 thus, in sample #5, while Br was <LOQ at 2 measurement points, it was 269 mg/kg at a third,  
238 and in sample #6, while Br was <LOQ at 1 measurement point, it was 578 mg/kg in the other.  
239 Conversely, where Br exceeds  $\Sigma$ BFR substantially for a given sample (*e.g.*, sub-samples #15, 16  
240 and 17 from the same toy) this implies that there is another source or sources of Br in that  
241 sample. This may either be an organobromine compound, like the NBFR, BTBPE, which was  
242 not measured here but was detected at 1,100 mg/kg in a UK plastic kitchen utensil (Kuang et al.,  
243 2018), a polymeric BFR (Gouteux et al, 2008; Puype et al, 2017) or an inorganic Br compound.  
244 Despite these discrepancies, however, there was a significant relationship between Br and  $\Sigma$ BFR  
245 among the samples, with linear regression analysis returning a best fit line of  $\text{Br} = 1.39 \Sigma\text{BFR} +$   
246  $208$  ( $r^2 = 0.840$ ,  $p < 0.05$ ).

247

248 3.2. *Do concentrations of PBDEs and HBCDD in toys exceed LPCL and/or UTC limit values?*

249 Two of the samples analysed (#s 2 and 8) exceed the proposed LPCL value of 500 mg/kg for the  
250 summed concentrations of PBDEs (including Deca-BDE), and three additional samples (#s 6, 18  
251 and 20) exceed the UTC limit set for July 2021 of 10 mg/kg for Deca-BDE alone. With regard to  
252 HBCDD, four samples (#s 2, 5, 11 and 12) exceed the UTC limit of 100 mg/kg, although all  
253 were purchased before the limit was introduced (March 2016). Overall, eight out of the 23 sub-  
254 samples analysed exceed current or impending limit values for restricted BFRs. In all cases, the  
255 items exceeding limits were second-hand and manufactured before 2016. This may suggest that  
256 measures to eliminate BFRs from toys containing recycled plastic have been effective; however,  
257 we only studied three toys manufactured after these measures were introduced and a much larger  
258 study is required to fully evaluate the efficacy of these measures.

259

260 A recent report revealed the presence of HBCDD in various toys and Rubik's cubes purchased in  
261 the Czech Republic, up to a maximum of 91 mg/kg in a toy shoe (Straková et al., 2017). Of even  
262 greater concern, an earlier survey of 95 Rubik's cubes and 16 additional child-related items  
263 sourced from 26 countries around the world (DiGangi et al., 2017) revealed a maximum HBCDD  
264 concentration of 1,586 mg/kg, with two items exceeding the LPCL value at the time of 1,000  
265 mg/kg and seven exceeding the UTC limit value of 100 mg/kg.

266

267 3.3. *The presence of TBBP-A and NBRs in toys*

268 Relatively few reports exist of the presence of BFRs other than PBDEs and HBCDD in plastic  
269 toys, and we believe this study to be only the second report of TBBP-A in such products. Our  
270 data for concentrations of TBBP-A (range not detected to 3,140 mg/kg) suggest a broadly similar  
271 level of contamination to that observed in toys from the Czech Republic, Germany, and Italy  
272 (range 210 mg/kg – 7,800 mg/kg) (Guzzonato et al., 2017). Only trace quantities of the target

273 NBFRs were detected in our samples, providing reassurance that their presence in plastic toys is  
274 not currently of significant concern.

275

#### 276 *3.4. What are the human exposure implications of the presence of BFRs in toys?*

277 The potential for human exposure arising from the presence of PBDEs in toys has previously  
278 been evaluated (Chen et al., 2009; Ionas et al., 2014). These studies identified potential for  
279 exposure via inhalation arising from volatilization of PBDEs, mouthing, dermal contact and oral  
280 ingestion (transfer of PBDEs to hands and subsequent oral exposure). As both studies employed  
281 the same exposure assessment algorithms, the relative importance of the four exposure pathways  
282 was identical in both instances. In summary, exposure via mouthing was estimated to  
283 predominate for pre-school children, with exposures via the other pathways making relatively  
284 minor contributions. While the absolute estimated exposure levels varied due to the differences  
285 in BFR concentrations in toys between the two studies, neither study identified exposures via  
286 contact with toys to be of significant toxicological concern.

287

288 Detailed examination of the input data employed to estimate exposure via inhalation, dermal  
289 contact, and oral ingestion (Chen et al., 2009; Ionas et al., 2014) reveals the key input parameter  
290 in each case to be an emission factor derived for volatilization of PBDEs from flame-retarded  
291 items like television sets (Kemmlin et al., 2003). While constituting a useful approach to  
292 scoping exposure via these pathways, volatilization emission factors from source items  
293 containing PBDEs at concentrations well in excess of those present in plastic toys are predicted  
294 to overestimate inhalation exposures and are less appropriate when extrapolated to the estimation  
295 of dermal and oral ingestion pathways. Similar considerations apply to the volatilization  
296 emission factors reported previously (Kemmlin et al., 2003) for HBCDD (for which the  
297 emission factors are from flame-retarded expanded and extruded polystyrene), while published

298 emission factors for TBBP-A and DBDPE do not appear to be available (Kemmlein et al., 2003).  
299 Regarding mouthing exposure, Chen et al. (2009) based their estimates on experimentally-  
300 derived measurements of BFR migration from two toy samples into human saliva. However, the  
301 data obtained are expressed as  $\text{pg}/\text{cm}^2/\text{minute}$  rather than as a proportion of the BFR mass  
302 present in these toys and cannot thus be extrapolated to estimate migration from toys containing  
303 different BFR concentrations such as ours. More recently, exposure to a variety of organic  
304 contaminants (but not BFRs) present in plastic children's toys has been evaluated, based on  
305 inadvertent oral ingestion of small quantities of plastic and subsequent uptake via the  
306 gastrointestinal tract (Lenzner et al., 2018).

307

308 Given the aforementioned considerations, we evaluate for the first time exposure to BFRs  
309 measured in plastic children's toys for: (a) the oral ingestion of 8 mg/day of toy plastic (in line  
310 with the default assumption of the Toy Safety Directive for scrapable toy material), and (b)  
311 dermal uptake arising from a child handling toys. As Chen et al. (2009) identified infants aged  
312 between 3 and 18 months (and of body weight 8.67 kg) to be at greatest risk, we have evaluated  
313 exposure for this age group only.

314

315 Table 3 summarizes our estimates of typical and high-end exposure via both pathways identified  
316 above ( $E_{\text{oral ingestion}}$  and  $E_{\text{dermal}}$ ) and obtained using both the arithmetic mean and the maximum  
317 BFR concentrations, respectively, for the samples shown in Table 2. It is very clear that while  
318 dermal exposure does occur for young children, exposure arising from accidental ingestion of  
319 plastic from toys is orders of magnitude greater. Also shown in Table 2 are previously published  
320 typical and high-end exposure estimates to BFRs for UK children arising from other pathways;  
321 namely: diet (Tao et al, 2017), inhalation (Tao et al, 2016), dust ingestion (Tao et al, 2016),  
322 dermal contact with BFR-containing fabrics and indoor dust (Abdallah and Harrad, 2018), and

323 breast milk consumption (Tao et al, 2017). Typical and high-end estimates arising from each  
324 pathway for  $\Sigma$ PBDEs and  $\Sigma$ HBCDDs are also compared in Figures 1 and 2, respectively.

325

326 It is evident that exposure via incidental oral ingestion of toy plastic can make a very substantial  
327 contribution to overall exposure of young children to our target BFRs. Specifically, under the  
328 typical scenarios (where the plastic ingested is assumed to contain BFRs at the arithmetic mean  
329 concentration determined in this study, along with typical estimates for other pathways),  
330 ingestion contributes 31.8 % of overall exposure to  $\Sigma$ PBDEs and 58 % of overall exposure to  
331  $\Sigma$ HBCDD. Under the high-end exposure scenarios (where the plastic ingested is assumed to  
332 contain the maximum BFR concentration determined, along with high-end estimates for other  
333 pathways), the contribution made by ingestion of toy plastic to overall exposure falls to 17.7 %  
334 and 41 % of  $\Sigma$ PBDEs and  $\Sigma$ HBCDD, respectively.

335

336 We also compared exposures to PBDEs via oral ingestion of and dermal uptake from plastic toys  
337 with the reference doses (RfDs) promulgated by the USEPA for BDEs 47 and 99 (= 100 ng/kg  
338 bw/day) and BDE 209 (= 7,000 ng/kg bw/day) (US EPA, 2019a; 2019b; 2019c). Reassuringly,  
339 even under the maximum exposure scenario estimated exposures arising from toys alone or the  
340 combined pathways are well below the respective RfD values. However, our maximum exposure  
341 estimate arising from toys alone for BDE-99 (1.4 ng/kg bw/d) exceeds the health-based limit  
342 value (HBLV) proposed in the Netherlands (Bakker et al., 2008) of 0.23-0.30 ng/kg bw/day.  
343 Moreover, the typical exposure estimate from toys (0.2 ng/kg bw/day) is very close to this  
344 HBLV.

345

346 **4. Conclusions**



347 This study provides the first evidence of the presence of a range of BFRs in both new and  
348 second-hand toys sourced from the UK. These data add to previous evidence from elsewhere in  
349 the world that suggest that recycling of BFR-treated plastics has led to the unintentional but  
350 widespread contamination of articles not required to meet flame retardancy regulations. Eight out  
351 of the twenty plastic toys examined contained concentrations of PBDEs or HBCDD that would  
352 now or in the near future prevent their sale on the EU market. Exposure of young children to  
353 BFRs via incidental ingestion of plastic from toys has also been evaluated for the first time.  
354 Exposure via this route appears to be considerable and for some individuals and BFRs may  
355 represent the most significant pathway via which they are exposed.

356

#### 357 **SUPPORTING INFORMATION**

358 Tables showing: (1) concentrations of PBDEs detected in a certified reference material compared  
359 to certified values, (2) limits of quantification for target BFRs, and (3) concentrations of total Br  
360 detected in replicate measurements made for each toy.

361

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513

514

515 **Table 1: Plastic toy samples selected for analysis**

Sample #	Toy Description	Approximate Date of Purchase or manufacture	# total Br measurements (by XRF)
1	Wind-up bug	2005	3
2	Big Eyes spectacles	2005	2
3	Tic Tac Toe game box	2001	2
4	Black Fidget Spinner with metallic Finish	2017	2
5	Motorcycle	2004	3
6	Magnetic compass	2005	2
7	Car chassis I	2004	3
8 <sup>a</sup>	Beads painted gold	1997	2
9	Action Man Binoculars	2006	2
10	Black Fidget spinner	2017	2
11	Circular dice	2005	2
12	Othello games counter	1997	2
13 <sup>a</sup>	Beads painted red	1997	2
14	Entry gate for garage	2004	3
15 <sup>a</sup>	Bead from necklace	2005	3
16 <sup>a</sup>	Link from necklace	2005	2
17 <sup>a</sup>	Pendant from necklace	2005	4
18 <sup>a</sup>	Wheels of jeep	2007	3
19	Car chassis II	2005	4
20	Wheels of airplane	2004	4
21	Piece from board game	2006	4
22	Case of board game	2006	4
23	Handle of child's dummy	2017	3

516 <sup>a</sup> sample #s 8 and 13, and 15, 16, and 17 are sub-samples from the same toys (beads and  
517 necklace, respectively)



**Table 2: Concentrations (mg kg<sup>-1</sup>) of selected BFRs and total Br (obtained using XRF) in the plastic toys**

Sample #	BDE-47	BDE-100	BDE-99	BDE-153	BDE-183	BDE-197	BDE-196	BDE-209	TBBP-A	HBCDD	PBBz	PBT	PBEB	HBB	DBDPE	ΣBFRs	Average Br
1	0.19	<LOQ	0.21	0.89	4.3	1.8	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	0.0002	0.0028	7.5	27
2	0.28	<LOQ	0.32	74	97	43	20	570	15	130	0.0003	<LOQ	<LOQ	0.0002	<LOQ	950	1700
3	0.30	<LOQ	0.15	<LOQ	0.21	0.15	<LOQ	2.2	<LOQ	25	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	28	52
4	0.30	0.13	0.39	<LOQ	0.46	<LOQ	<LOQ	2.0	2.3	9.1	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	15	590
5	2.40	0.72	3.7	0.46	0.50	<LOQ	<LOQ	1.8	<LOQ	840	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	850	90
6	0.26	<LOQ	0.31	2.0	13	6.3	4.3	250	190	1.1	0.0004	<LOQ	<LOQ	<LOQ	0.02	470	290
7	0.34	<LOQ	0.66	<LOQ	0.37	<LOQ	<LOQ	<LOQ	<LOQ	0.25	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	1.6	21
8	1.4	0.93	2.3	63	360	180	91	290	2500	9.6	0.0022	<LOQ	<LOQ	0.0039	0.22	3500	8100
9	<LOQ	<LOQ	0.49	<LOQ	0.39	<LOQ	<LOQ	<LOQ	<LOQ	0.52	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	1.4	78
10	0.66	<LOQ	0.73	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	5.5	1.2	0.0003	<LOQ	0.0004	<LOQ	<LOQ	8.0	33
11	0.35	0.26	0.41	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	11	360	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	380	380
12	0.56	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	550	0.0003	<LOQ	<LOQ	<LOQ	0.0005	550	510
13	2.0	0.64	3.2	110	<LOQ	280	140	2500	3100	<LOQ	0.0023	<LOQ	<LOQ	<LOQ	0.25	6100	7300
14	0.64	<LOQ	0.74	<LOQ	0.22	<LOQ	<LOQ	<LOQ	28	20	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	49	9
15	<LOQ	<LOQ	<LOQ	<LOQ	7.4	<LOQ	<LOQ	<LOQ	1.9	<LOQ	<LOQ	0.33	<LOQ	0.23	<LOQ	10	960
16	<LOQ	<LOQ	<LOQ	<LOQ	2.7	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	0.30	0.07	<LOQ	0.12	<LOQ	3.2	840
17	<LOQ	<LOQ	<LOQ	<LOQ	5.2	<LOQ	<LOQ	<LOQ	1.6	<LOQ	0.49	0.13	<LOQ	0.22	<LOQ	7.8	1000
18	<LOQ	<LOQ	<LOQ	<LOQ	2.5	0.35	0.39	12	<LOQ	<LOQ	1.5	<LOQ	<LOQ	<LOQ	0.19	17	76
19	<LOQ	<LOQ	<LOQ	<LOQ	2.0	<LOQ	<LOQ	<LOQ	<LOQ	2.7	0.36	0.04	<LOQ	0.09	<LOQ	5.5	4.3
20	<LOQ	<LOQ	<LOQ	0.24	3.6	1.5	1.3	112	84	1.9	0.61	0.07	<LOQ	0.15	<LOQ	210	850
21	<LOQ	<LOQ	<LOQ	<LOQ	2.2	<LOQ	<LOQ	0.42	<LOQ	<LOQ	0.07	<LOQ	<LOQ	<LOQ	<LOQ	2.8	4.5
22	<LOQ	<LOQ	<LOQ	<LOQ	1.2	0.33	0.56	<LOQ	<LOQ	<LOQ	0.11	<LOQ	<LOQ	<LOQ	<LOQ	2.3	4.0
23	<LOQ	<LOQ	<LOQ	<LOQ	2.4	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	0.28	<LOQ	<LOQ	0.09	<LOQ	3.0	0.0
Median <sup>a</sup>	0.26	0.00027	0.21	0.0005	2.0	0.0009	0.0007	0.1	0.8	1.1	0.0004	0.0002	0.00002	0.00004	0.0008	15	90
Average <sup>a</sup>	0.42	0.12	0.59	11	22	23	11	160	260	85	0.16	0.03	0.00003	0.04	0.03	570	1000
Maximum	2.4	0.93	3.7	110	360	280	140	2500	3100	840	1.5	0.33	0.0004	0.23	0.25	6100	8100
LPCL <sup>b</sup>								500 <sup>b</sup>									
UTC <sup>c</sup>								10									
UTC <sup>d</sup>										100							

<LOQ denotes not detected

<sup>a</sup> for purposes of calculating descriptive statistics, where concentration <LOQ the value has been replaced with  $f \times \text{LOQ}$  where  $f$  = detection frequency of BFR expressed as a decimal fraction

- <sup>b</sup> Low POP Concentration Limit for  $\Sigma$ PBDEs – to be enforced from 2021
- <sup>c</sup> Unintentional Trace Contaminant limit value for BDE-209 – to be enforced from 2021
- <sup>d</sup> Unintentional Trace Contaminant limit value for HBCDD – current since 2016

**Table 3: Estimated exposures (ng/kg bw/day) to BFRs of young children associated with plastic toys and other pathways**

Exposure pathway/scenario	BDE-47	BDE-99	BDE-209	ΣPBDEs	ΣHBCDD	ΣNBFRs
$E_{\text{oral}}$ ingestion (typical) <sup>a</sup>	0.2	0.2	21	35	64	0.0001
$E_{\text{oral}}$ ingestion (high-end) <sup>a</sup>	1.3	1.4	318	520	634	160
$E_{\text{dermal}}$ (typical) <sup>b</sup>	0.001	0.001	- <sup>i</sup>	0.01	0.2	- <sup>i</sup>
$E_{\text{dermal}}$ (high-end) <sup>b</sup>	0.007	0.006	- <sup>i</sup>	0.092	2.0	- <sup>i</sup>
Diet (typical) <sup>c</sup>	nr	nr	nr	4.8	1.0	3.0
Diet (high-end) <sup>c</sup>	nr	nr	nr	26	6.2	19
Breast milk (typical) <sup>d</sup>	17	5.9	0.65	35	17	18
Breast milk (high-end) <sup>d</sup>	41	10	2.8	80	34	350
Dermal contact with dust and fabrics <sup>e</sup>	nr	nr	- <sup>j</sup>	3.9	24	- <sup>j</sup>
Indoor air inhalation and dust ingestion (typical) <sup>f</sup>	0.10	0.17	31	33	2.9	32
Indoor air inhalation and dust ingestion (high-end) <sup>f</sup>	18	28	2200	2300	870	290
RfD <sup>g</sup>	100	100	7000	-	-	-
HBLV <sup>h</sup>	-	0.23-0.30	-	-	-	-

<sup>a</sup> assuming that child ingests 8 mg day<sup>-1</sup> of toy plastic contaminated at arithmetic mean and maximum concentration for “typical” and high-end exposure

<sup>b</sup> assuming that dermal contact occurs with toys contaminated at the arithmetic mean and maximum concentration for “typical” and high-end exposure

<sup>c</sup> “typical” and high-end dietary exposures for UK toddlers (Tao et al., 2017)

<sup>d</sup> “typical” and high-end exposures for breast-fed UK infants (Tao et al., 2017)

<sup>e</sup> sum of exposures via dermal contact with indoor dust and BFR-containing fabrics (Abdallah and Harrad, 2018). Note ΣPBDE exposure for this estimate covers only those congeners present in the Penta-BDE formulation detected in a fabric covering from a US sofa

<sup>f</sup> sum of estimates of exposure of UK toddlers via indoor air inhalation and dust ingestion (Tao et al., 2016). For dust ingestion, “typical” exposure assumes median BFR concentration and mean dust ingestion, high-end exposure assumes 95<sup>th</sup> percentile BFR concentration and high dust ingestion.

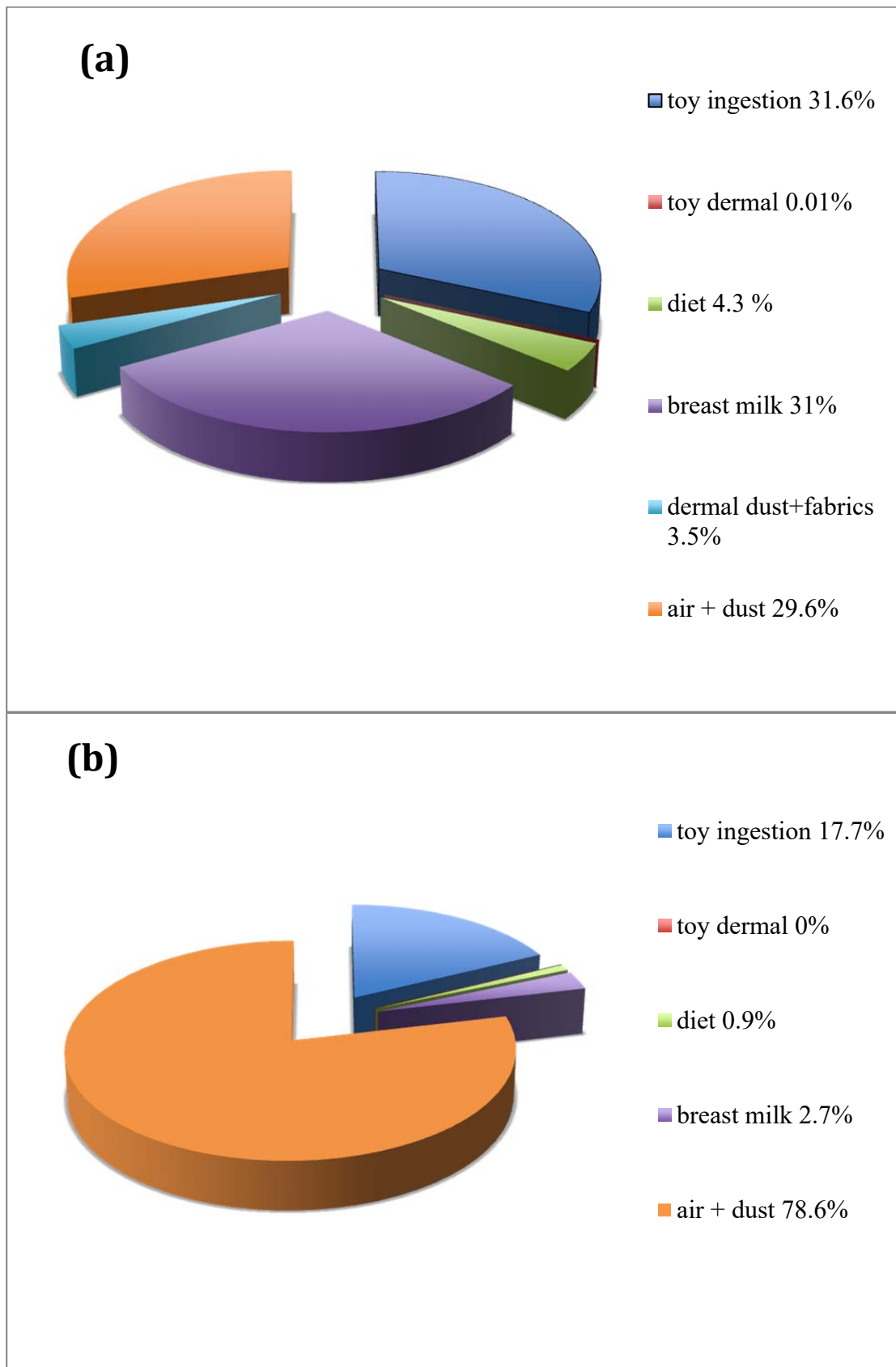
<sup>g</sup> USEPA Reference dose (US EPA, 2019a; 2019b; 2019c)

<sup>h</sup> Health based limit value proposed by Bakker et al. (2008)

<sup>i</sup> dermal absorption not detected for BDE-209 and not studied for our target NBFRs

nr = not reported

**Figure 1: Relative contribution (expressed as % of total exposure) of selected pathways to exposure of UK young children to  $\Sigma$ PBDEs under (a) typical and (b) high-end scenarios (note no high-end estimate available of dermal exposure via dust and fabrics)**



**Figure 2: Relative contribution (expressed as %of total exposure) of selected pathways to exposure of UK young children to  $\Sigma$ HBCDD under (a) typical and (b) high-end scenarios (note no high-end estimate available of dermal exposure via dust and fabrics)**

