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

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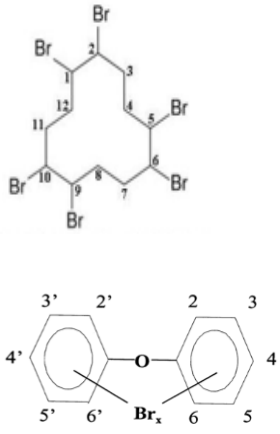
Accepted 27th February 2020

doi.org/10.1016/j.scitotenv.2020.137623

Abstract

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

Graphical abstract



Keywords

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

Highlights

- Br and BFRs measured in children's plastic toys
- HBCDD present in 4 toys at concentrations above the EU UTC limit value
- PBDE concentrations in 2 toys exceed proposed limit of 500 mg/kg
- TBBP-A detected in 11 samples
- Children's exposure via unintentional ingestion of toy plastic may be substantial

1. INTRODUCTION

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

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

, penta-, hexa-, hepta- and decaBDE of 10 mg/kg each to be introduced in July 2021 (European Commission, 2019).

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

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

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

2. MATERIALS AND METHODS

2.1. Sampling and screening for total Br via XRF

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

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

2.2. BFR measurement methods

2.2.1. Chemicals and reagents

HPLC-grade solvents were used for sample extraction and LC–MS/MS analysis (Fisher Scientific, Loughborough, UK). Concentrated sulphuric acid was purchased from Sigma–Aldrich (St. Louis, MA, USA). Individual α-, β- and γ-HBCDD standards, $^{13}C_{12}$ α-, β- and γ-HBCDD, d_{18}-γ-HBCDD, individual standards of PBDEs 17, 28, 47, 49, 77, 99, 100, 153, 154, 183,196, 197, 209 and 128, $^{13}C_{12}$-BDE-209,TBBP-A, $^{13}C_{12}$-TBBP-A, PBBz, PBT, PBEB, HBB, and $^{13}C_6$-HBB and DBDPE were purchased from Wellington Laboratories (Guelph, ON, Canada). Polychlorinated biphenyl (PCB)-129 was obtained from Qmx laboratories (Thaxted, UK). A certified reference material (CRM) for polypropylene (ERM-EC591), containing certified concentrations of PBDEs, was purchased from IRMM (Brussels, Belgium).

2.2.2. BFR extraction and extract purification

Samples were analysed for concentrations of BFRs using a validated in-house method (Abdallah et al., 2017). Briefly, accurately weighed 0.2 g aliquots of each sample where Br was detected by XRF were transferred into 15 mL glass centrifuge tubes and spiked with 20 ng of internal standards ($^{13}C_{12}$α-, β- and γ-HBCDD, $^{13}C_{12}$-BDE 77, $^{13}C_{12}$-BDE-128, $^{13}C_{12}$-TBBP-A and $^{13}C_6$-HBB) as well as 40 ng $^{13}C_{12}$-BDE 209. Samples were extracted with 3 mL CH_2Cl_2 by vortexing for 2 min and sonicating for 5 min. This was repeated with two further 3 mL aliquots of fresh CH_2Cl_2. Extracts were collected and combined in a separate centrifuge tube and evaporated to near dryness at 40 ˚C under a gentle stream of nitrogen before being reconstituted in 2 mL of hexane and vortexed to precipitate dissolved plastics. The hexane supernatant was collected and

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

2.2.3. Instrumental Analysis

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

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

^{13}C-labelled and d_{18}-labelled HBCD diastereomers, respectively and *m/z* 540.8→79, *m/z* 552.8→79 for the native and ^{13}C-labelled TBBP-A, respectively.

2.2.4. QA/QC

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

2.3. Data analysis

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

2.4. Exposure estimation methods

2.4.1. Exposure via oral ingestion

Exposure via oral ingestion ($E_{\text{oral ingestion}}$ in ng/kg body weight/day) was estimated using the following algorithm:

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

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

200

201 *2.4.2. Exposure via dermal uptake*

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

203 $$E_{dermal} = C_{toy}^{*} \times PSA \times IEF \times (AF/BW)$$

204 Here, C_{toy}^{*} is the BFR concentration of BFR in toy the (in ng/m^2) (C_{toy}* = 1.4 x 0.05 xC_{toy}

205 assuming a 0.05 cm depth of surface and a density of 1.4 g/cm^{3}equivlent to acrylonitrile

206 butadiene styrene) (Kuang et al., 2018), *PSA* is the palm surface area exposed dermally to the toy

207 (assumed to be 0.0986 m^2) (Chen et al., 2009), *IEF* is the indoor exposure fraction, or the

208 number of hours per day for which dermal contact with toys occurs (assumed to be 2; Chen et al.,

209 2009), and *AF* is the absorbed fraction. The latter is based on measured data for the dermal

210 uptake of PBDEs and HBCDD from fabrics over a 24 h contact (Abdallah and Harrad, 2018) and

211 measured data for 24 h contact with solutions of TBBP-A (Abdallah et al., 2015), and is

212 normalised for a 2 h period.

213

214 **3. RESULTS AND DISCUSSION**

215 *3.1. Concentrations of Br and BFRs in children's plastic toys*

216 Table 2 reports the average of the replicate measurements of total Br made by XRF for each toy,

217 including components thereof, while Table SI-3 lists each individual Br measurement for these

218 samples. In some cases, total Br appears to be uniformly distributed in the plastic, while in other

219 cases there is evidence for its heterogeneous dispersion in the toy. Table 2 also lists

220 concentrations of the target BFRs in each sample, as well as the median, arithmetic mean, and

221 maximum concentrations for the whole dataset.

222

223 BFRs were detected in all toys tested with summed concentrations ranging from 1.4 mg/kg to

224 about 6140 mg/kg. The principal BFRs detected in the toys were either PBDEs (in particular

225 BDE-209), HBCDD or TBBP-A, with only low concentrations detected of our target NBFRs.

226 The newest toys, purchased in 2017, contained < 20 mg/kg of BFRs but displayed a wide range
227 in compounds historical and new BFRs. Overall, the BFR pattern and absolute concentrations in
228 our samples are within the range of those previously reported for other studies of plastic items
229 containing recycled polymers, including toys and food contact articles (Chen et al., 2009;
230 Guzzonato et al., 2017; Ionas et al., 2014; Kuang et al., 2018; Puype et al., 2015, 2017).
231
232 If our study has quantified all of the Br-containing compounds in a sample, then the total Br and
233 ΣBFR concentrations should be broadly equal, with the latter slightly exceeding the former
234 because Br only constitutes a proportion of the mass of any BFR. Moreover, as we measured
235 BFRs in a single small aliquot of each toy or component thereof and our replicate XRF
236 measurements of Br revealed varying degrees of inhomogeneity of Br distribution within the
237 sample, Br and ΣBFR measurements will deviate in some instances. Specifically, the
238 heterogeneous distribution of Br and BFRs likely explains why ΣBFRs > average Br in sample #s
239 5 (ΣBFRs = 847 mg/kg c.f. Br = 90 mg/kg) and 6 (ΣBFRs = 468 mg/kg c.f. Br = 289 mg/kg);
240 thus, in sample #5, while Br was <LOQ at 2 measurement points, it was 269 mg/kg at a third,
241 and in sample #6, while Br was <LOQ at 1 measurement point, it was 578 mg/kg in the other.
242 Conversely, where Br exceeds ΣBFR substantially for a given sample (*e.g.*, sub-samples #15, 16
243 and 17 from the same toy) this implies that there is another source or sources of Br in that
244 sample. This may either be an organobromine compound, like the NBFR, BTBPE, which was
245 not measured here but was detected at 1,100 mg/kg in a UK plastic kitchen utensil (Kuang et al.,
246 2018), a polymeric BFR (Gouteux et al, 2008; Puype et al, 2017) or an inorganic Br compound.
247 Despite these discrepancies, however, there was a significant relationship between Br and ΣBFR
248 among the samples, with linear regression analysis returning a best fit line of Br = 1.39 ΣBFR +
249 208 (r^2 = 0.840, p< 0.05).
250

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

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

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

3.3. The presence of TBBP-A and NBFRs in toys

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

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

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

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

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

301 emission factors for TBBP-A and DBDPE do not appear to be available (Kemmlein et al., 2003).
302 Regarding mouthing exposure, Chen et al. (2009) based their estimates on experimentally-
303 derived measurements of BFR migration from two toy samples into human saliva. However, the
304 data obtained are expressed as pg/cm^2/minute rather than as a proportion of the BFR mass
305 present in these toys and cannot thus be extrapolated to estimate migration from toys containing
306 different BFR concentrations such as ours. More recently, exposure to a variety of organic
307 contaminants (but not BFRs) present in plastic children's toys has been evaluated, based on
308 inadvertent oral ingestion of small quantities of plastic and subsequent uptake via the
309 gastrointestinal tract (Lenzner et al., 2018).
310
311 Given the aforementioned considerations, we evaluate for the first time exposure to BFRs
312 measured in plastic children's toys for: (a) the oral ingestion of 8 mg/day of toy plastic (in line
313 with the default assumption of the Toy Safety Directive for scrapable toy material), and (b)
314 dermal uptake arising from a child handling toys. As Chen et al. (2009) identified infants aged
315 between 3 and 18 months (and of body weight 8.67 kg) to be at greatest risk, we have evaluated
316 exposure for this age group only.
317
318 Table 3 summarizes our estimates of typical and high-end exposure via both pathways identified
319 above ($E_{\text{oral ingestion}}$ and E_{dermal}) and obtained using both the arithmetic mean and the maximum
320 BFR concentrations, respectively, for the samples shown in Table 2. It is very clear that while
321 dermal exposure does occur for young children, exposure arising from accidental ingestion of
322 plastic from toys is orders of magnitude greater. Also shown in Table 2 are previously published
323 typical and high-end exposure estimates to BFRs for UK children arising from other pathways;
324 namely: diet (Tao et al, 2017), inhalation (Tao et al, 2016), dust ingestion (Tao et al, 2016),
325 dermal contact with BFR-containing fabrics and indoor dust (Abdallah and Harrad, 2018), and

breast milk consumption (Tao et al, 2017). Typical and high-end estimates arising from each pathway for ΣPBDEs and ΣHBCDDs are also compared in Figures 1 and 2, respectively.

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

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

4. Conclusions

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

SUPPORTING INFORMATION

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

ACKNOWLEDGEMENTS

This project has received funding from the European Union's Horizon 2020 research and innovation programme under the Marie Skłodowska-Curie grant agreement No 734522 (INTERWASTE) project.

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518 **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[a]	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[a]	Beads painted red	1997	2
14	Entry gate for garage	2004	3
15[a]	Bead from necklace	2005	3
16[a]	Link from necklace	2005	2
17[a]	Pendant from necklace	2005	4
18[a]	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

519 [a] sample #s 8 and 13, and 15, 16, and 17 are sub-samples from the same toys (beads and
520 necklace, respectively)

Table 2: Concentrations (mg kg^{-1}) 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[a]	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[a]	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[b]								500[b]									
UTC[c]								10									
UTC[d]										100							

<LOQ denotes not detected

[a] for purposes of calculating descriptive statistics, where concentration <LOQ the value has been replaced with f_x LOQ where f = detection frequency of BFR expressed as a decimal fraction

[b] Low POP Concentration Limit for ΣPBDEs – to be enforced from 2021
[c] Unintentional Trace Contaminant limit value for BDE-209 – to be enforced from 2021
[d] 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)[a]	0.2	0.2	21	35	64	0.0001
$E_{\text{oral ingestion}}$ (high-end)[a]	1.3	1.4	318	520	634	160
E_{dermal} (typical)[b]	0.001	0.001	-[i]	0.01	0.2	-[i]
E_{dermal} (high-end)[b]	0.007	0.006	-[i]	0.092	2.0	-[i]
Diet (typical)[c]	nr	nr	nr	4.8	1.0	3.0
Diet (high-end)[c]	nr	nr	nr	26	6.2	19
Breast milk (typical)[d]	17	5.9	0.65	35	17	18
Breast milk (high-end)[d]	41	10	2.8	80	34	350
Dermal contact with dust and fabrics[e]	nr	nr	-[j]	3.9	24	-[j]
Indoor air inhalation and dust ingestion (typical)[f]	0.10	0.17	31	33	2.9	32
Indoor air inhalation and dust ingestion (high-end)[f]	18	28	2200	2300	870	290
RfD[g]	100	100	7000	-	-	-
HBLV[h]	-	0.23-0.30	-	-	-	-

[a] assuming that child ingests 8 mg day^{-1} of toy plastic contaminated at arithmetic mean and maximum concentration for "typical" and high-end exposure

[b] assuming that dermal contact occurs with toys contaminated at the arithmetic mean and maximum concentration for "typical" and high-end exposure

[c] "typical" and high-end dietary exposures for UK toddlers (Tao et al., 2017)

[d] "typical" and high-end exposures for breast-fed UK infants (Tao et al., 2017)

[e] 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

[f] 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 95th percentile BFR concentration and high dust ingestion.

[g] USEPA Reference dose (US EPA, 2019a; 2019b; 2019c)

[h] Health based limit value proposed by Bakker et al. (2008)

[i] 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 ΣPBDEs under (a) typical and (b) high-end scenarios (note no high-end estimate available of dermal exposure via dust and fabrics)

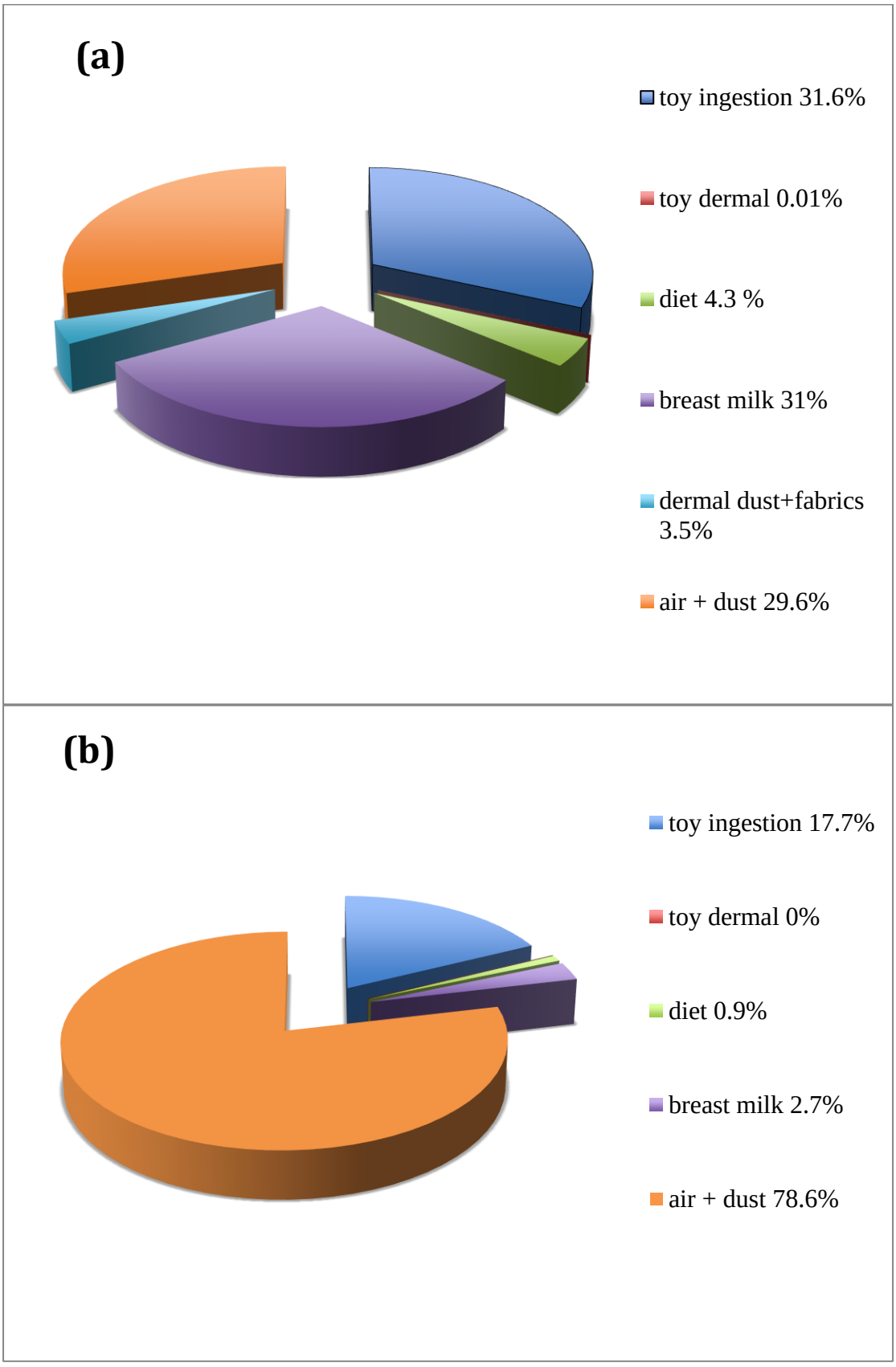

Figure 2: Relative contribution (expressed as %of total exposure) of selected pathways to exposure of UK young children to ΣHBCDD under (a) typical and (b) high-end scenarios (note no high-end estimate available of dermal exposure via dust and fabrics)