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Concentrations of brominated flame retardants in indoor air and dust from Ireland reveal elevated exposure to decabromodiphenyl ethane

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1	Concentrations of Brominated Flame Retardants in
2	Indoor Air and Dust from Ireland reveal elevated
3	exposure to Decabromodiphenyl Ethane
4	
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14	KEYWORDS
15	BFRs, indoor dust, indoor air, cars, homes, offices, schools, human exposure, DBDPE,
16	PBDEs, HBCDD
17	ABSTRACT

Concentrations of decabromodiphenyl ethane (DBDPE), 13 polybrominated diphenyl ethers (PBDEs) and hexabromocyclododecane (HBCDD), were measured in indoor air and dust collected from Irish homes, cars, offices and primary schools during 2016-17. Median concentrations of DBDPE in air (88 pg/m³) and dust (6,500 ng/g) exceed significantly those previously reported internationally, with concentrations highest in offices and schools, suggesting DBDPE is widely used in Ireland. Median concentrations of BDE-209 in air (340

 pg/m^3) and dust (7,100 ng/g) exceed or are within the range of concentrations reported recently 24 for the same microenvironments in the UK, and exceed those reported in many other countries. 25 26 Concentrations of BDE-209 in cars exceeded significantly (p < 0.05) those in other micro-27 environments. HBCDD was detected in all dust samples (median: 580 ng/g), and in 81% of air 28 samples (median: 24 pg/m³) at concentrations similar to those reported recently for the UK and 29 elsewhere. Estimates of exposure to DBDPE of Irish adults (92 ng/day) and toddlers (210 ng/day) as well as to BDE-209 (220 ng/day and 650 ng/day for adults and toddlers respectively) 30 31 exceed substantially those reported for the UK population. Moreover, our estimates of exposure of the Irish population to Σ tri-deca-PBDEs exceed previous estimates for Ireland via dietary 32 33 exposure.

34

35 INTRODUCTION

3

Brominated flame retardants (BFRs) such as polybrominated diphenyl ethers (PBDEs) and 36 hexabromocyclododecane (HBCDD) were first marketed in the late 1960s¹ and subsequently 37 38 widely applied in many jurisdictions to a variety of soft furnishings, building insulation foams, 39 electrical and electronic equipment (EEE). There are three main commercial PBDE mixtures with varying degrees of bromination², namely Penta-BDE (primarily BDE-99 (45-50%) and 40 41 BDE-47 (38-42%), Octa-BDE (primarily BDE-183) and Deca-BDE (>90% BDE-209))³. Deca-42 BDE was mainly used in high impact polystyrene (HIPS) for electrical housings and in fabric and soft furnishing applications⁴. Penta-BDE was widely used in treatment of polyurethane 43 44 foam, especially for transport and for soft furnishings such as upholstery, mattresses and 45 textiles, as well as in circuit boards, packaging and textiles⁵; while Octa-BDE was used mainly 46 in hard plastic acrylonitrile butadiene styrene (ABS) casings, and to a lesser degree HIPS and EEE^{5,6}. 47

HBCDD has primarily been used as a flame retardant (FR) in expanded and extruded 48 polystyrene (EPS/XPS) used in building insulation foam, in textiles⁷ and in HIPS used for 49 EEE⁵. Both HBCDDs and PBDEs are categorised as additive BFRs and are therefore easily 50 released by volatilisation⁸⁻¹⁰ as well as abrasion and direct source-to-dust transfer^{11,12} from 51 treated products into the environment. Human exposure to BFRs is associated with many 52 53 adverse effects such as endocrine disruption, liver microsomal enzyme induction, immunotoxicity, neurotoxicity and carcinogenicity^{13,14}. Animal studies have further shown 54 55 neurodevelopmental and behavioural outcomes of exposure to PBDEs such as hepatic abnormality, endocrine disruption and possibly cancer^{13,15–17}. In animals, HBCDD was found 56 57 to induce hepatic cytochrome P450 enzymes and alter the normal uptake of neurotransmitters, while in humans it has been reported to trigger cancer through non-mutagenic mechanisms and 58 disruption of the thyroid hormone system^{13,18,19}. This evidence of their toxicity, combined with 59 60 their environmental persistence and bioaccumulation potential, has resulted in the listing of 61 Penta- and Octa-BDE (2009), HBCDD (2013) and Deca-BDE (2017) as persistent organic pollutants (POPs) under the Stockholm Convention²⁰ leading to restrictions on their 62 63 manufacture and use. Whilst banned in 2013, exemptions existed for HBCDD in Europe for 64 use in EPS/XPS insulation until August 2016²¹. The restrictions on PBDEs have created a market demand for replacement FRs, such as decabromodiphenyl ethane (DBDPE), marketed 65 as a replacement for Deca-BDE²². Limited toxicological data exists for DBDPE, however, it is 66 67 structurally very similar to BDE-209 and may therefore display comparable adverse effects²³. BFRs have been detected in human tissues such as breast milk, adipose tissue, blood, serum, 68 placenta and liver samples^{24–27}. Moreover, BFR concentrations in food products, household 69 dust and air have been recorded worldwide²⁷⁻³³. Results suggest multiple external exposure 70 pathways for BFRs including ingestion of dust, diet, dermal exposure and inhalation^{27, 29, 34}. 71 72 These data indicate non-occupational human exposure to HBCDDs and PBDEs occurs primarily by a combination of contact with indoor dust (dermal and/or ingestion), indoor air 73 and diet^{25, 31, 33} and dermal contact with flame-retarded fabrics³⁵. 74

75 Currently, knowledge of exposure of the Irish population to BFRs is confined to a single biomonitoring study using human breast milk conducted in 2010²⁷ and ongoing surveillance of 76 dietary exposure^{36,37}. Given the known importance in other countries of indoor exposures, this 77 78 study measures PBDEs, HBCDD and DBDPE in indoor air and settled floor dust samples 79 collected from Irish homes, cars, offices and schools. These data are used to calculate the first 80 exposure estimates for Irish adults and toddlers to PBDEs, HBCDD and DBDPE via inhalation 81 and ingestion of indoor dust. The European Union does not have a universal requirement for 82 upholstered furniture to be resistant to ignition³⁸. The UK and Ireland both have specific stringent fire safety legislation on the flammability of furniture, stating that filling materials 83 and upholstered covers must be resistant to various sources of ignition^{39–41}. This legislation is 84 specific to the UK and Ireland, and is not a requirement in other European countries³⁸. We 85 therefore tested the hypothesis that concentrations of DBDPE, PBDEs, and HBCDD in Ireland 86

87 would more closely resemble those in the UK than those in mainland Europe.

88 MATERIALS AND METHODS

89 Sampling strategy

90 Project ethical approval was obtained from the Research Ethics Committee of the National 91 University of Ireland, Galway (Ref 16/May/02). Project participants were recruited via the 92 project website (www.nuigalway.ie/elevate), through articles in the national press, and through 93 acquaintances of the authors. Paired samples of indoor air and dust were collected from 4 94 different microenvironment categories (homes (n=32), cars (n=32), offices (n=32) and primary 95 schools (n=32)) between August 2016 and January 2017 in 3 Irish counties (Galway, Limerick 96 and Dublin). Prior to the commencement of the study, participants completed a questionnaire 97 to collect information on the year of construction of the building, the age and presence of 98 putative sources like electrical items, car age and model etc.

99 Sampling methods

100 Indoor dust sampling - Project sampling protocols followed previously published 101 methodologies²⁹. Home and office participants were asked not to clean their cars for two weeks 102 or living rooms for two days, prior to sampling. Due to school policy, classroom floors are 103 cleaned on a daily basis, so samples were taken at the end of the school day from classrooms. 104 Further details of sample collection protocols are provided as Supplementary data.

105 *Air Sampling* - Air samples were collected by deploying passive air samplers for approximately 106 60 days in order to sample the maximum volume of air while remaining in the linear uptake 107 phase of the PUF disk samplers⁴². The sampling apparatus consisted of two parts: a sorbent 108 (XAD-3) impregnated polyurethane foam disk (PUF) (\emptyset : 140 mm, thickness: 12 mm, surface 109 area: 360.6 cm², density: 0.02 g cm⁻³; PACS Leicester, UK), pre-cleaned via Soxhlet extraction 110 with dichloromethane (DCM) for 8 hours⁴³. The PUF was partially enclosed in two stainless-111 steel housings (top \emptyset : 26 cm, bottom : \emptyset : 18 cm) and mounted according to previous studies⁴⁴. Samplers were placed on elevated surfaces in homes, offices, and schools, and on the floorbehind the passenger or driver's seat in cars.

114 Quality Assurance/Quality Control

115 A reagent blank was analysed with every batch of samples. Instrumental analysis is described 116 in detail in Supplementary data. None of the target compounds were detected in blank samples at concentrations above the limit of detection. Therefore, results were not corrected for blank 117 118 residues and method limits of detection (LOD) and limits of quantification (LOQ) were 119 estimated based on S/N = 3:1 and 10:1, respectively. Average LOQs ranged from 0.1 ng/g to 120 0.4 ng/g for PBDEs, 2.5 ng/g for BDE-209, 13 ng/g for DBDPE and 0.1 ng/g for HBCDDs in dust (Table SI-1). For air, LOQs were: 0.43 pg/m³ to 3.1 pg/m³ for PBDEs, 7.5 pg/m³ for BDE-121 209, 15 pg/m³ for DBDPE and 0.3 pg/m³ for HBCDDs (Table SI-2). For non-detects (nd) $\frac{1}{2}$ 122 123 LOQ was used for statistical analysis. Method accuracy and precision was determined by 124 analysis of an aliquot of standard reference material SRM-2585 (NIST) with every 10 samples. 125 Measured concentrations were close to the certified levels with a relative standard deviation (RSD) of <15% (Table SI -3). 126

127 Statistical Analysis

Statistical analysis was performed using SPSS 24.0. BFR concentration data was log normally 128 129 distributed (Kolmogorov-Smirnov test, (p>0.05)). A one-way ANOVA was used to test the significance of observed differences in BFR concentrations between microenvironment 130 131 categories and regional differences in BFR concentrations for different microenvironments 132 (p < 0.05). A two-tailed Pearson's correlation coefficient was used to investigate associations 133 between air and dust BFR concentrations in homes, cars, offices and schools and factors such 134 as year of building construction, car age, and number of electronics present. Differences in air 135 and dust concentrations in offices, schools and homes with electronic goods purchased before 136 and after 2009 or 2013 or in the presence or absence of room ventilation or presence or absence of carpets were examined using an independent sample t-test (p < 0.05). 137

138

139 RESULTS AND DISCUSSION

140 Concentrations of DBPDE, PBDEs and HBCDDs in indoor dust

- 141 All 13 PBDE congeners, DBDPE and HBCDD were detected in all microenvironments (Table
- 142 1, and Table SI-6, SI-7, SI-8). After BDE-209 (DF 100%), and HBCDD (99% DF) DBDPE
- 143 had the highest detection frequency (98%) (Table SI-9, SI-10).
- 144 **DBDPE**

145 DBDPE was detected in 98% of all dust samples analysed (n=120) across all 146 microenvironments ranging from <LOD to concentrations of 540,000 ng/g (median: 6500 147 ng/g). To the authors' knowledge, our data on concentrations of DBDPE in indoor dust are 148 both the most recent and contain the highest concentrations reported globally.

Highest median concentrations were detected in schools (10,000 ng/g), followed by cars (7,700 ng/g), offices (6,100 ng/g) and homes (4,200 ng/g). Concentration data exceed markedly those
reported for similar microenvironments across Europe, China and Australia^{45–48}.

152 These substantially elevated DBDPE concentrations suggest that DBDPE may have been used 153 as a flame retardant in soft furnishings to meet Irish fire safety requirements for domestic furniture, which differ from other EU member states (except for the UK)³⁹⁻⁴¹. DBDPE is 154 155 thought to have replaced Deca-BDE in plastics and textiles with a wide range of uses in the transport, building, construction, and domestic sectors⁴⁹. DBDPE registrations under REACH⁵⁰ 156 157 now exceed in weight BDE-209 registrations; 13 importers or manufacturers report a combined annual tonnage of between 10,000 and 100,000 tonnes of DBDPE in 2018, compared to the 158 total range of 1,000 and 10,000 for BDE-209 in 2014⁴⁹. Concentrations of DBDPE in UK 159 indoor dust increased between 2006-07 and 2015^{47,51}. While no comparative Irish data exist, 160 161 we hypothesise similar increasing temporal trends are occurring in Ireland and thus compared 162 our Irish data with those in the most recent UK survey. Median DBDPE concentrations in Irish homes, cars, schools and offices exceed by 100, 77, 610 and 80 times those in UK homes in 163

164 2016^{47} , cars (sampled in 2003-2005)⁵¹, schools (sampled in 2007-2008)³¹ and offices (sampled 165 in 2016)⁴⁷ respectively.

Median concentrations of DBDPE reported here for Irish homes exceed those reported for Swedish homes⁵² Australian homes (also sampled in 2016)⁴⁸ and homes in Beijing⁵³. Median DBDPE concentrations reported for Irish cars also exceed those in Greece⁵⁴, while those in Irish offices exceed those in Australia⁴⁸. Moreover, median concentrations in Irish schools exceed those recently reported for low energy Swedish preschools (300 times higher)⁵⁵ and preschools in Stockholm (100 times higher)⁴⁶.

172 **PBDEs**

BDE-209 had a detection frequency (DF) of 100% while BDE-47 was detected in 98% of samples. The following PBDE congeners had DFs > 60%: -196, -197, -183 and -99, while congeners BDE-17, -28, -49, -66, -100, -154 and -153 had DFs between 3–50%. In terms of concentrations, BDE-209 was the most abundant congener in all dust samples, followed by BDE-99>BDE-47>BDE-183. The median concentration of Σ tri-octa BDEs (consisting of BDE-17, -28, -47, -49, -66, -99, -100, -153, -154, -183, -196 and -197) across all microenvironments was 43 ng/g dust.

In agreement with other international studies, BDE-209 was the most abundant PBDE 180 congener detected across all microenvironments^{28,32,33}, contributing to >99% of Σ PBDEs for 181 182 homes, cars and schools, and 98% in offices. This is unsurprising given BDE-209 was the most commonly used PBDE congener from 2000 until 2008⁵⁶ after which its use started to decline 183 following restrictions, its inclusion in the RoHs Directive and its classification as a SVHC 184 under REACH⁴⁹. An estimated 10% of the total Deca-BDE imported into the EU between 2000 185 and 2005, was imported into Ireland⁵⁶. Although no Irish statistics on use of Deca-BDE in 186 textiles exist, UK data is thought to closely represent usage patterns in Ireland, and an estimated 187 three quarters of the Deca-BDE used to treat UK textiles was used in domestic furniture⁵⁷ while 188 95% of all upholstered materials used in the UK were treated with flame retardants to comply 189

with the UKFFFSR (UK Furniture and Furnishings (Fire Safety) Regulation)⁵⁸. When compared with UK data^{31,47}, median BDE-209 concentrations in Irish homes (13,000 ng/g) are higher, while concentrations in Irish offices (3500 ng/g) and schools (8100 ng/g) are consistent with UK median concentrations reported in 2015 and 2007/08 respectively^{31,47}. In contrast, concentrations in UK cars⁵⁹ between 2003-2005 are four times higher than in Irish cars (median: 26,000 ng/g), perhaps reflecting a downward trend in Deca-BDE use in vehicle upholstery.

197 Comparisons with other countries reveal BDE-209 concentrations in Irish indoor environments 198 exceed those reported for Greece⁵⁴, Germany⁶⁰ and the Czech Republic²⁸. BDE-209 199 concentrations in Irish homes, offices and cars exceed recent values for Australia⁴⁸ as well as 190 those reported for Beijing homes and offices⁵³. BDE-209 median concentrations in Irish 191 schools also exceed those in Brazil (median: 420 ng/g)⁶¹.

Detection frequencies across all microenvironments for BDE-47 and BDE-99 (97% and 71%) were high but these congeners were present in lower concentrations than BDE-209. BDE-47 and BDE-99 are typically associated with the Penta-BDE mixture more widely used in North America⁷ than Europe. Concentrations of both congeners in Irish offices, homes and cars are exceeded by those in Australia, USA and Canada^{33,48} but are comparable to those for the Czech Republic and the UK^{33,59}.

208 With respect to Σ tri-octa BDEs, concentrations in Irish homes exceed slightly those in the UK, 209 Portugal and China^{47,62,63}, but are similar to those reported for Brazilian primary schools 210 (median: 41 ng/g)⁶¹.

211 HBCDDs

HBCDDs were detected in all samples, with concentrations in Irish homes (median: 490 ng/g) exceeding those for the UK (110 ng/g) in 2015 and in other international studies^{28,64,65}.

 Σ HBCDD concentrations in office, school and car dust (median: 380 ng/g, 800 ng/g, 490 ng/g)

respectively) are lower than those for the UK (median: 4,100 ng/g, 4,100 ng/g, 13,000 ng/g

respectively)^{31,47} for samples collected in 2015 and 2008, which may reflect a downward trend
in HBCDD use in response to recent restrictions.

218 \sum HBCDD median concentrations in office dust are exceeded by those in France in 2016 219 (median: 4,700 ng/g)⁶⁶. There are few published data on concentrations of HBCDD in schools; 220 results from this study (median: 800 ng/g) are consistent with those for Japan (510 ng/g)⁶⁷, but 221 the Japanese study was conducted before HBCDD's listing under the Stockholm Convention 222 in 2013. Concentrations in Irish cars are nearly 40 times higher than in the Czech Republic²⁸ 223 and 8 times higher than in Greece⁵⁴.

224 In this study, α -HBCDD was the dominant isomer in homes, offices and schools, with γ -

HBCDD dominant in cars. The average isomer profile for homes (46% α -HBCDD, 32% γ -

HBCDD and 22% β-HBCDD and offices (57% α-HBCDD, 26% β-HBCDD and 17% γ-HBCDD) is similar to that previously reported in the UK⁴⁷ and schools followed the same pattern (52% α-HBCDD, 24% γ-HBCDD and 24% β-HBCDD)³¹.

In contrast, similar to a Greek study⁵⁴ γ -HBCDD was the most abundant isomer in Irish cars for which the average profile was 45% γ -HBCDD, 38% α -HBCDD and 18% β -HBCDD. Previous researchers have also reported γ -HBCDD to dominate in car dust from the Czech Republic²⁸ and the UK⁵⁹.

233

234 Concentrations of DBPDE, PBDEs and HBCDDs in indoor air

There is a dearth of data regarding concentrations of BFRs in indoor air published over the last five years and so limited comparisons can be made with our data^{18,68,69}. Seven of our target PBDEs, along with DBDPE and HBCDD were detected in all MEs (Table 2, Table SI-11, SI-12, SI-13). BDE-209 had the highest detection frequency (DF 96%), followed by HBCDD (81% DF) and DBDPE (65 %) (Table SI-14, SI-15).

DBDPE

This study reports the most recent indoor air data anywhere for DBDPE in homes, schools and offices and the first data for cars. DBDPE was detected in 65% of air samples, lower than in Canada (85%)³³ but higher than the UK in 2016⁴⁷ (DF: 20%). Similar to our indoor dust data, concentrations in Irish indoor air are also mostly higher than those reported internationally. Concentrations of DBDPE in Irish home and offices are >10 and >30 times higher than 2016 UK data (cars and schools were not included in the UK study)⁴⁷.

247 Concentrations of DBDPE in Irish homes are comparable to those in US homes (median: 42 248 pg/m³), but exceed those reported for Canadian and Czech homes³³. Concentrations in Irish 249 offices exceed those in Spain⁷⁰, while those in schools exceed those reported for Swedish pre-250 schools in 2016-18⁵⁵ and Norwegian schools sampled in 2012 (median: 8.3 pg/m³)⁷¹.

251 **PBDEs**

BDE-209, -99 and -47 had DFs >90% in all microenvironments, whereas BDE-100, -28, -183, -154 and -153 were detected in <85 % of air samples, with BDE-197, -196, -49 and -17 not detected in any sample. The relative abundance of individual congeners in indoor air was: BDE-209>BDE-99>BDE-47>BDE-183. The median concentrations of PBDEs in indoor air for all microenvironments were 7.0 pg/m³ and 300 pg/m³ for Σ tri-octa BDE (consisting of BDE-17, -28, -47, -49, -66, -99, -100, -153, -154 -183, -196 and -197) and BDE-209 respectively.

BDE-209 was the predominant PBDE congener in all MEs representing 95, 97, 64 and 99% of
ΣPBDE for homes, cars, offices and schools respectively, similar to the UK⁴⁷, Sweden⁵² and
Germany⁷². Concentrations of BDE-209 in Irish homes are consistent with those for the UK in
2015⁴⁷, but those in Irish offices exceed by a factor of two those recently recorded in the UK⁴⁷.
Concentrations of BDE-209 in Irish homes and cars are lower than those in Sweden^{52,73}.

It is difficult to make comparisons between the \sum tri-octa BDE concentrations reported here and elsewhere due to the different congener compositions studied. \sum tri-octa BDE median concentrations in Irish homes (5.6-330 pg/m³) were lower than those reported in the UK 267 (median: 13-2,600 pg/m³)⁴⁷, whereas those in Irish offices (median: 15 pg/m³, range 5.7-6200 268 pg/m³) exceed those in the UK (median: 20-150 pg/m³)⁴⁷. Lowest median concentrations in 269 this study were in schools (7.0-150 pg/m³), and were lower than those in South Korea (<dl-270 33,500 pg/m³)⁷⁴ and Norway (<dl-150 pg/m³)⁷¹.

271 Median concentrations of BDE-47 (2.1 pg/m³) and BDE-99 (6.1 pg/m³) are exceeded by those

in the US (median: 52 pg/m³, 15 pg/m³, respectively)³³. This likely reflects greater use of the

273 Penta BDE formulation in the US than Europe⁷.

274 **HBCDD**

HBCDDs were detected in 81% of all air samples. Σ HBCDD concentrations in Irish homes (median: 20 pg/m³) were 5 times lower than those in the UK (median: 110 pg/m³)⁴⁷. Concentrations in Irish cars (median: 25 pg/m³) are almost 500 times lower, and office samples (14 pg/m³) less than half those in the UK in 2008²⁹ (median: 13,000 pg/m³) and 2015⁴⁷ (median: 41 pg/m³) respectively, which may reflect a decreasing trend in HBCDD use. Nonetheless, median concentrations in all Irish microenvironments still exceed those in Sweden (<2 pg/m³) in 2006⁵².

282 Unlike the HBCDD isomer pattern in dust, the most abundant isomer in air samples was γ -

283 HBCDD across all microenvironments, followed by α -HBCDD. The HBCDD stereoisomer

284 concentration profile for homes (γ : 62%, α : 26%, β : 12%), cars (γ : 71%, α : 22%, β : 7%),

offices (γ : 66%, α : 27%, β : 7%) and schools (γ : 62%, α : 27%, β : 11%) is similar to the profiles in UK homes and offices⁴⁷.

287 Previous studies have also observed the γ -HBCDD isomer to make a greater contribution to 288 Σ HBCDD in air than in dust²⁹. This was shown to arise from a photolytically-mediated shift 289 from γ -HBCDD to α -HBCDD in dust⁷⁵.

290

291 Comparisons between microenvironments

292 Several studies observed differences in concentrations of BFRs between different 293 microenvironments^{47,48,73}. We therefore used one-way ANOVA to establish if there were any 294 significant (p<0.05) differences in BFR concentrations between the microenvironments (ME) 295 sampled followed by a SNK post-hoc test.

296 Indoor dust

There were no significant differences in DBDPE concentrations between different MEs. For 297 298 PBDEs, concentrations of BDE-209 were significantly lower in offices (median: 3,500 ng/g) 299 than in homes (median: 13,000 ng/g) (p<0.05), cars (median: 26,000 ng/g) (p<0.05) and schools (median: 8,100 ng/g) (p < 0.05). This may suggest declining use of this FR in offices 300 301 (and to a lesser extent schools), where faster turnover of electronic and electrical goods than in 302 homes is anticipated. Concentrations of BDE-99 in cars (median: 50 ng/g) exceed significantly 303 those in offices (p < 0.05) and schools (p < 0.05) but are statistically indistinguishable from those 304 in homes. Moreover, BDE-183 concentrations are significantly higher in cars (median: 4.1 ng/g) than in offices (median: 3.2 ng/g) (p < 0.05). Abdallah et al.²⁹ and McGrath et al.⁴⁸ made 305 306 similar observations. Higher concentrations of PBDEs have been associated with interiors of 307 vehicles, due to the increased volume of synthetic surfaces, increased volatilisation of BFRs 308 due to high temperatures in unoccupied cars as well as to smaller air volume within cars and reduced ventilation⁴⁸. No other significant differences were observed between MEs. 309

310 Indoor air

311 Differences in BFR concentrations in air were observed between the different 312 microenvironments studied. DBDPE and BDE-209 concentrations in schools were 313 significantly higher than in offices (p<0.05 for both). DBDPE concentrations in schools 314 (median: 220 pg/m³) exceeded significantly those in homes (median: 48 pg/m³) (p<0.05); while 315 BDE-209 concentrations (median: 410 pg/m³) in schools exceeded significantly those in cars 316 (median: 200 pg/m³) (p<0.05).

317 Concentrations of BDE-47 in homes (median: 2.1 pg/m³) were significantly lower compared

to those in offices (median: 3.4 pg/m³) (p<0.05). BDE-99 concentrations in homes (median: 6.1 pg/m³) exceeded significantly higher those in schools and cars (median: 3.1 pg/m³ and 2.1 pg/m³ respectively) (p<0.05).

The number of putative sources, the cleaning pattern and the location of the sampler relative to putative sources may influence the sample concentration^{29,48,75}. The contextual information recorded for participating schools, offices, homes and cars was thus examined but provided no insights into the concentration trends observed.

325

326 Regional differences between microenvironments

The study included samples collected from different regions (Limerick, Galway and Dublin) in Ireland. We examined our data to establish if there were any differences in BFR concentrations between each of the microenvironments (ME) between regions in sampled using one-way ANOVA followed by a Tukey post-hoc test.

331 Indoor dust

Concentrations of DBDPE in dust from Limerick schools (median: 24,000 ng/g) exceeded 332 333 significantly those in Galway schools (median: 1,500 ng/g; p < 0.001) but were not significantly 334 higher than in Dublin schools (median: 14,000 ng/g). Two notably high concentrations of 335 DBDPE (median: 230,000 ng/g and 540,000 ng/g) were found in two Limerick schools, however the density of electronic and electrical equipment like interactive white boards, 336 337 laptops, CD players and foam containing furniture within all participating schools were similar. 338 Moreover, the purchase of school furniture and electrical equipment is governed by Irish 339 national policy and not by individual schools or regions. We are therefore unable to explain 340 the significantly higher DBDPE concentrations in Limerick schools which may be attributable 341 to the small sample numbers involved (~10 schools from each region).

342 Indoor air

343 Some statistically significant regional differences in car and school BDE-209 concentrations were observed. In relation to cars, 10-12 cars were sampled in each region, Dublin car 344 345 concentrations (median: 3.8 pg/m^3) were significantly lower than Galway (median: 300 pg/m^3) 346 and Limerick (median: 530 pg/m³) cars (p < 0.001, p < 0.001), which could not be explained by 347 the contextual data. Most cars in this study were either manufactured in Germany or Asia. A recent survey of BFRs in Irish waste detected high BDE-209 concentrations in end of life 348 vehicles manufactured in both Germany and Asia⁷⁶. The cleaning pattern of the cars did not 349 350 influence the BDE-209 air concentration and neither did the presence of a child seat or air 351 conditioning.

Some significant (p < 0.05) regional differences were observed in concentrations of BDE-209 in schools. Significantly higher BDE-209 concentrations were detected in Galway schools (median: 930 pg/m³) and significant lower concentrations in Dublin schools (median: 150 pg/m³). Higher concentrations (not statistically significantly), were observed in Galway schools in older school buildings (built before 1983) whereas we could not see this trend in Limerick and Dublin. Nearly all classrooms contained one or more foam containing chairs, although the age of the chairs was difficult to establish.

359

360 Sources of BFRs in indoor air and dust

Our data was statistically analysed to explore associations between BFR concentrations and factors such as the number of electronics present in the room and type of floor surface etc. However, similar to several other international studies, few obvious trends were found^{28,30,66}. This is most likely due to the convenience sampling approach used and the likely variable BFR presence in putative sources.

366 Concentrations of HBCDD in office dust were positively correlated with the number of 367 electronics present (p<0.01). Higher air concentrations of Σ HBCDD (p<0.05) were found in 368 homes (13 out of 32) with carpets. Similar observations have been made in two UK studies^{29,47}. As HBCDD was not prevalent in Irish waste electronics or carpets⁷⁶, the cause of these correlations is unclear. A positive significant correlation (p<0.01) was found between concentrations of BDE-209 in air and the number of electronics in schools. BDE-209 was widely used in electronic and electrical items up until 2008, and high levels of this FR have also been detected in waste IT and telecommunication items in Ireland⁷⁶.

374

375 Temporal trends of BFR concentrations in air and dust data

376 This is the first study of BFR concentrations in Irish indoor air and dust, therefore no comparisons can be made with previous Irish data. Correlations between BFR concentrations 377 378 and year of building construction, car registration and the age of electronics present in the environment were examined (Pearson correlation, Table SI-16, SI-17). Furthermore, 379 380 independent t-tests were used to investigate differences in concentrations from different age 381 categories. Year of home construction was significantly negatively correlated with 382 concentrations of Σ HBCDD (p<0.01), which possibly reflects the impact of recent restrictions 383 on the use of HBCDD in building insulation materials.

384 Significantly higher concentrations in air of BDE-209 (p<0.05) were found in offices which

had electronics purchased after 2013 (n=16; 540 pg/m³) compared to pre 2013 (n=10: average:

 250 pg/m^3). Given the recent restictions on BDE-209 use, this observation is puzzling.

Less surprisingly, homes with a greater number of electronics purchased before 2009 (pre 2009 n=8, post 2009 n=21) had significantly higher concentrations of \sum tri-octa BDE, suggesting a positive impact from legislative restrictions on octa- and penta-BDE.

Year of car registration and concentrations in dust of BDE-47 (p<0.01), BDE-99 (p<0.05) and \sum tri-octa BDE (p<0.05) were negatively correlated. Moreover, concentrations in dust collected from cars (n=19) registered after the listing of Penta and Octa-BDE under the Stockholm Convention in 2009, were significantly lower than those in dust from cars registered pre 2009 (n=10) for congeners BDE-47 (p<0.01; average 42 ng/g, c.f. 8.6 ng/g), BDE-99 (p<0.01; 89 395 ng/g, c.f. 31 ng/g) and \sum tri-octa BDE (*p*<0.01; average concentration pre 2009: 255 ng/g, post 396 2009: 76 ng/g).

397

398 Correlations between air and dust concentrations

399 We hypothesised concentrations of BFRs in air and dust correlate^{47,52,77}, as BFRs partition between the particulate and the gaseous phase⁷⁸. This hypothesis was tested by examining the 400 401 relationship between concentrations of BFRs in air and dust samples collected from the same 402 MEs using a Spearman's rho test (Table SI-18). Significant positive correlations were observed 403 for Σ HBCDD (in schools only) (p<0.01), for BDE-99 (in homes only) (p<0.05), and for BDE-404 209 (in homes only), (p < 0.01). It is unclear why correlations are only evident in certain microenvironments. This may be due to the limited number of samples in each individual 405 406 microenvironment, and therefore further sampling would be required for further investigation. 407

408 **Exposure assessment**

409 BFR concentrations in indoor air and dust were used to estimate exposures of Irish adults, 410 toddlers and school children, via inhalation of airborne BFRs and ingestion of BFRs in dust 411 (Table 3) (a summary of all the assumptions and algorithms used in exposure calculations are 412 presented in the supporting information). Two exposure scenarios were considered; a "typical" 413 exposure scenario using median BFR concentrations and the second a 'high-end exposure scenario', assuming ingestion/inhalation of the 95th percentile BFR concentrations. In addition, 414 415 a higher dust ingestion rate was used for the high-end scenario calculation. High-end exposure 416 scenario estimates for DBDPE (adult: 120 ng/kg bw/day, toddler: 2,500 ng/kg bw/day) and 417 BDE-209 (adult: 100 ng/kg bw/day, toddler 2,500 ng/kg bw/day) exceed the equivalent highend exposures reported recently for the UK⁴⁷ (adult: 3.4 ng/kg bw/day, 57 ng/kg bw/day; 418 419 toddler: 33 ng/kg bw/day, 1,900 ng/kg bw/day for DBDPE and BDE-209 respectively). By comparison, ∑HBCDD exposure estimates for adults (7.8 ng/kg bw/day) and toddlers (170 420

ng/kg bw/day) are below UK results (adult: 22 ng/kg bw/day, toddler: 750 ng/kg bw/day)⁴⁷.
The high-end exposure estimates (1,100 ng/kg bw/day) for BDE-209 and (86 ng/kg bw/day)
∑HBCDD calculated for school children (age 4-6), are below UK values of 330 ng/kg bw/day
and 1,300 ng/kg bw/day respectively³¹.

High-end estimates of exposure to BDE-209 for Irish adults, toddlers and school children (Table 3) are 100 ng/kg bw/day, 2,500 ng/kg bw/day and 1,100 ng/kg/day respectively and below the USEPA reference dose (RfD) value for adults of 7,000 ng/kg bw/day⁷⁹. Those for Octa-BDE (BDE-183), Penta-BDE (BDE-47 and BDE-99) and Σ HBCDD are also below USEPA guidelines^{79,80}. Our estimates of typical adult exposure via inhalation and dust ingestion exceed Irish dietary exposure estimates for BDE-209 (0.3 ng/kg bw/day) but fall below those for Σ PBDEs (2.4 ng/kg bw/day)⁸¹.

432

433 The limitations of this study are the convenience nature of the sampling that means that the 434 samples analysed are not necessarily representative of Ireland. Moreover, samples taken 435 represent a snapshot of contamination in time and space. Its strengths are that it reveals the presence of elevated concentrations of the legacy BFR BDE-209 and its replacement DBDPE 436 437 in air and dust from various Irish indoor environments. BDE-209 was the main PBDE congener 438 detected in homes and cars, suggesting substantial use of Deca-BDE to comply with fire safety 439 regulations. In striking contrast, DBDPE was the most abundant BFR detected in Irish offices 440 and school classrooms, suggesting widespread use in Ireland, likely as a replacement for BDE-441 209 – which is supported by the knowledge that DBDPE has been offered as a direct replacement for DecaBDE, with application at the same concentration of 10-15% by wt⁸². To 442 443 the authors' knowledge, concentrations of DBDPE in this study were the highest reported in 444 indoor environments anywhere to date. Detailed study of the health implications of exposure 445 to DBDPE are thus recommended.

446 TABLES

locatio n	statistical parameter	DBDPE	BDE-209	BDE-47	BDE-99	BDE-183	∑tri-octa- BDEs	α-HBCDD	β–HBCDD	γ–HBCDD	∑-HBCDD
	n	29	29	29	29	29	29	26	26	26	26
	Median	4,200	13,000	7.6	13	1	49	200	100	200	490
homes (ng/g)	Range	410-460,000	140-650,000	0.6-240	<0.2-500	< 0.3-33	10-940	0.31-28,000	0.12- 12,000	0.83-5,600	1.3-43,000
× C C,	Mean	39,000	58,000	26	45	4.1	130	1,500	680	670	2900
ι	J K ^{47*}	<10 (<10-97)	4,500 (160- 370,000)	13 (0.15-1,700)	12 (0.05-1,700)	<1.0 (<1.0-12)		<2.6 (<2.6-400)	<2.2 (<2.2- 160)	110 (16- 1,400)	110 (19- 1,500)
US	SA ^{33,65*}	150 (nd-3,100)	2,200 (75-7,500)	270 (20-1,300)	340 (20-2,800)	11 (nd-37)		62 (17-910)	16 (7-230)	73 (13-790)	160 (39- 1,800)
Czech	Republic ^{28*}	140 (<20-1,700)	375 (41-5,500)	8.9 (<0.1-11)	11.6 (<0.1-95)	3.9 (<0.8-460)		26 (<0.3-280)	7.1 (<0.3- 57)	61 (<0.3- 740)	93 (<0.3-950)
Sw	eden ^{64*}	150 (943-1,500)	310 (140-310,000)	21 (6.5-460)	17 (<0.74-300)	-		56 (14-1,400)	18 (3.4-730)	37 (2.5- 4,000)	110 (20- 6,000)
Be	ijing ^{53*}	560 (220-3,100)	150 (69-410)	1.3 (0.67-4.2)	4.9 (1.2-25)	0.37 (0.21-3.7)	8.0 (5.1-37)	64 (34-510)	21 (9.8-120)	64 (30-370)	160 (74- 1,000)
Aus Bi	tralia ^{48*} *azil ^{61*}	1,600 (nd-9,000) 400 (150-740)	1,100 (290-13,000) 410 (160-1,200)	56 (nd-2,800) 8.0 (4.5-1,400	74 (16-58,000) 153 (20-290)	<mql (nd-26)<="" td=""><td>(18-11,000)</td><td></td><td></td><td></td><td></td></mql>	(18-11,000)				
n											
	п	28	28	28	28	28	28	29	29	29	29
cars	<i>n</i> Median	28 7,700	28 26,000	28 24	28 50	<i>28</i> 4.1	<i>28</i> 150	29 330	<i>29</i> 250	<i>29</i> 490	<i>29</i> 1,300
cars	<i>n</i> Median Range	28 7,700 <13-190,000	28 26,000 14-680,000	28 24 <0.1-130	28 50 <0.2-270	28 4.1 <0.3-92	28 150 0.094-690	29 330 3.4-3,700	29 250 4.8-2,600	29 490 2.4-17,000	29 1,300 2,400-20,000
cars (ng/g)	<i>n</i> Median Range Mean	28 7,700 <13-190,000 23,000	28 26,000 14-680,000 82,000	28 24 <0.1-130 31	28 50 <0.2-270 70	28 4.1 <0.3-92 9.8	28 150 0.094-690 200	29 330 3.4-3,700 650	29 250 4.8-2,600 410	29 490 2.4-17,000 180	29 1,300 2,400-20,000 2,800
cars (ng/g) U	n Median Range Mean K ^{32,51*}	28 7,700 <13-190,000 23,000 100 (<dl-2,900)<sup>51</dl-2,900)<sup>	28 26,000 14-680,000 82,000 100,000 (12,000- 2,600,000)	28 24 <0.1-130 31 54 (19-7,500)	28 50 <0.2-270 70 100 (23-80,00)	28 4.1 <0.3-92 9.8 7.8 (<dl-67)< td=""><td>28 150 0.094-690 200</td><td>29 330 3.4-3,700 650 20,00 (54- 88,00)²⁹</td><td>29 250 4.8-2,600 410 740 (16- 5,200)</td><td>29 490 2.4-17,000 180 9,600 (27- 56,000)</td><td>29 1,300 2,400-20,000 2,800 13,000 (190- 69,000)</td></dl-67)<>	28 150 0.094-690 200	29 330 3.4-3,700 650 20,00 (54- 88,00) ²⁹	29 250 4.8-2,600 410 740 (16- 5,200)	29 490 2.4-17,000 180 9,600 (27- 56,000)	29 1,300 2,400-20,000 2,800 13,000 (190- 69,000)
cars (ng/g) U Ger	n Median Range Mean K ^{32,51*} many ^{60*}	28 7,700 <13-190,000 23,000 100 (<dl-2,900)<sup>51 13,00 (110- 6,500)</dl-2,900)<sup>	28 26,000 14-680,000 82,000 100,000 (12,000- 2,600,000) 940 (220-3,100)	28 24 <0.1-130 31 54 (19-7,500) 17 (2.1-43)	28 50 <0.2-270 70 100 (23-80,00) 32 (1.3-88)	28 4.1 <0.3-92 9.8 7.8 (<dl-67) 3.7 (1.3-<0.2- 17)</dl-67) 	28 150 0.094-690 200	29 330 3.4-3,700 650 20,00 (54- 88,00) ²⁹	29 250 4.8-2,600 410 740 (16- 5,200)	29 490 2.4-17,000 180 9,600 (27- 56,000)	29 1,300 2,400-20,000 2,800 13,000 (190- 69,000)
cars (ng/g) U Ger Czech	n Median Range Mean K ^{32,51*} many ^{60*} Republic ^{28*}	28 7,700 <13-190,000 23,000 100 (<dl-2,900)<sup>51 13,00 (110- 6,500) 99 (<20-3,600)</dl-2,900)<sup>	28 26,000 14-680,000 82,000 100,000 (12,000- 2,600,000) 940 (220-3,100) 170 (<5-33,000)	28 24 <0.1-130 31 54 (19-7,500) 17 (2.1-43) 2.2 (<0.1-280)	28 50 <0.2-270 70 100 (23-80,00) 32 (1.3-88) <0.1 (<0.1-280)	28 4.1 <0.3-92 9.8 7.8 (<dl-67) 3.7 (1.3-<0.2- 17) <0.8 (<0.8-15)</dl-67) 	28 150 0.094-690 200	29 330 3.4-3,700 650 20,00 (54- 88,00) ²⁹ 9 (<0.3-45)	29 250 4.8-2,600 410 740 (16- 5,200) <0.3 (<0.3- 44)	29 490 2.4-17,000 180 9,600 (27- 56,000) 25 (<0.3- 240)	29 1,300 2,400-20,000 2,800 13,000 (190- 69,000) 33 (<0.3-240)
cars (ng/g) U Ger Czech	n Median Range Mean K ^{32,51*} many ^{60*} Republic ^{28*}	28 7,700 <13-190,000 23,000 100 (<dl-2,900)<sup>51 13,00 (110- 6,500) 99 (<20-3,600) 856 (33-5,200)</dl-2,900)<sup>	28 26,000 14-680,000 82,000 100,000 (12,000- 2,600,000) 940 (220-3,100) 170 (<5-33,000) 2,800 (110-38,000)	28 24 <0.1-130 31 54 (19-7,500) 17 (2.1-43) 2.2 (<0.1-280) 9.1 (0.63-9,000)	28 50 <0.2-270 70 100 (23-80,00) 32 (1.3-88) <0.1 (<0.1-280) 12 (1.4-11,000)	28 4.1 <0.3-92 9.8 7.8 (<dl-67) 3.7 (1.3-<0.2- 17) <0.8 (<0.8-15) 1.4 (LOD-1,200)</dl-67) 	28 150 0.094-690 200 (23-17,000)	29 330 3.4-3,700 650 20,00 (54- 88,00) ²⁹ 9 (<0.3-45) 90 (<loq- 1,300)</loq- 	29 250 4.8-2,600 410 740 (16- 5,200) <0.3 (<0.3- 44) 16 (<loq- 290)</loq- 	29 490 2.4-17,000 180 9,600 (27- 56,000) 25 (<0.3- 240) 46 (<loq- 260)</loq- 	29 1,300 2,400-20,000 2,800 13,000 (190- 69,000) 33 (<0.3-240) 155 (<loq- 1,800)</loq-
cars (ng/g) U Ger Czech Gr Bi	n Median Range Mean K ^{32,51*} many ^{60*} Republic ^{28*} reece ^{54*} razil ^{61*}	28 7,700 <13-190,000 23,000 100 (<dl-2,900)<sup>51 13,00 (110- 6,500) 99 (<20-3,600) 856 (33-5,200) 1,400 (420- 3,800)</dl-2,900)<sup>	28 26,000 14-680,000 82,000 100,000 (12,000- 2,600,000) 940 (220-3,100) 170 (<5-33,000) 2,800 (110-38,000) 1,600 (300-4,000)	28 24 <0.1-130 31 54 (19-7,500) 17 (2.1-43) 2.2 (<0.1-280) 9.1 (0.63-9,000) 31 (4.3-190)	28 50 <0.2-270 70 100 (23-80,00) 32 (1.3-88) <0.1 (<0.1-280) 12 (1.4-11,000) 100 (8.5-350)	28 4.1 <0.3-92 9.8 7.8 (<dl-67) 3.7 (1.3-<0.2- 17) <0.8 (<0.8-15) 1.4 (LOD-1,200)</dl-67) 	28 150 0.094-690 200 (23-17,000)	29 330 3.4-3,700 650 20,00 (54- 88,00) ²⁹ 9 (<0.3-45) 90 (<loq- 1,300)</loq- 	29 250 4.8-2,600 410 740 (16- 5,200) <0.3 (<0.3- 44) 16 (<loq- 290)</loq- 	29 490 2.4-17,000 180 9,600 (27- 56,000) 25 (<0.3- 240) 46 (<loq- 260)</loq- 	29 1,300 2,400-20,000 2,800 13,000 (190- 69,000) 33 (<0.3-240) 155 (<loq- 1,800)</loq-
cars (ng/g) U Ger Czech Gr Br locatio n	n Median Range Mean K ^{32,51*} many ^{60*} Republic ^{28*} reece ^{54*} reace ^{54*} statistical parameter	28 7,700 <13-190,000 23,000 100 (<dl-2,900)<sup>51 13,00 (110- 6,500) 99 (<20-3,600) 856 (33-5,200) 1,400 (420- 3,800) DBDPE</dl-2,900)<sup>	28 26,000 14-680,000 82,000 100,000 (12,000- 2,600,000) 940 (220-3,100) 170 (<5-33,000) 2,800 (110-38,000) 1,600 (300-4,000) BDE-209	28 24 <0.1-130 31 54 (19-7,500) 17 (2.1-43) 2.2 (<0.1-280) 9.1 (0.63-9,000) 31 (4.3-190) BDE-47	28 50 <0.2-270 70 100 (23-80,00) 32 (1.3-88) <0.1 (<0.1-280) 12 (1.4-11,000) 100 (8.5-350) BDE-99	28 4.1 <0.3-92 9.8 7.8 (<dl-67) 3.7 (1.3-<0.2- 17) <0.8 (<0.8-15) 1.4 (LOD-1,200) BDE-183</dl-67) 	28 150 0.094-690 200 (23-17,000) ∑tri-octa- BDEs	29 330 3.4-3,700 650 20,00 (54- 88,00) ²⁹ 9 (<0.3-45)	29 250 4.8-2,600 410 740 (16- 5,200) <0.3 (<0.3- 44) 16 (<loq- 290) β–HBCDD</loq- 	29 490 2.4-17,000 180 9,600 (27- 56,000) 25 (<0.3- 240) 46 (<loq- 260) γ–HBCDD</loq- 	29 1,300 2,400-20,000 2,800 13,000 (190- 69,000) 33 (<0.3-240) 155 (<loq- 1,800) Σ-HBCDD</loq-
cars (ng/g) U Ger Czech Gr Bi locatio n	n Median Range Mean K ^{32,51*} many ^{60*} Republic ^{28*} reece ^{54*} reacil ^{61*} statistical parameter n	28 7,700 <13-190,000 23,000 100 (<dl-2,900)<sup>51 13,00 (110- 6,500) 99 (<20-3,600) 856 (33-5,200) 1,400 (420- 3,800) DBDPE 31</dl-2,900)<sup>	28 26,000 14-680,000 82,000 100,000 (12,000- 2,600,000) 940 (220-3,100) 170 (<5-33,000) 2,800 (110-38,000) 1,600 (300-4,000) BDE-209 31	28 24 <0.1-130 31 54 (19-7,500) 17 (2.1-43) 2.2 (<0.1-280) 9.1 (0.63-9,000) 31 (4.3-190) BDE-47 31	28 50 <0.2-270 70 100 (23-80,00) 32 (1.3-88) <0.1 (<0.1-280) 12 (1.4-11,000) 100 (8.5-350) BDE-99 31	28 4.1 <0.3-92 9.8 7.8 (<dl-67) 3.7 (1.3-<0.2- 17) <0.8 (<0.8-15) 1.4 (LOD-1,200) BDE-183 31</dl-67) 	28 150 0.094-690 200 (23-17,000) ∑tri-octa- BDEs 31	29 330 3.4-3,700 650 20,00 (54- 88,00) ²⁹ 9 (<0.3-45) 90 (<loq- 1,300) α-HBCDD 32</loq- 	29 250 4.8-2,600 410 740 (16- 5,200) <0.3 (<0.3- 44) 16 (<loq- 290) β-HBCDD 32</loq- 	29 490 2.4-17,000 180 9,600 (27- 56,000) 25 (<0.3- 240) 46 (<loq- 260) γ-HBCDD 32</loq- 	29 1,300 2,400-20,000 2,800 13,000 (190- 69,000) 33 (<0.3-240) 155 (<loq- 1,800) Σ-HBCDD 32</loq-

447 **Table 1.** Summary of Concentrations of BFRs (ng/g) in Indoor Dust from Irish Homes, Cars, Offices and Schools, together with Median

448 Concentrations from selected other studies (*Median, **Mean).

offices (ng/g)	Range Mean	<13-1300,00 12,000	560-150,000 4,200	0.8-130 16	<0.2-160 26	<0.3-190 11	2.8-770 77	<0.1-4,400 520	18-710 160	8.8-3,300 170	84-5,200 850
UK47*		<10 (<10-54)	26 (2.3-350)	6 (0.15-380)	7.9 (1.2-42)	<1.0 (<1.0-3.8)		5.4 (<2.6-31)	<2.2 (<2.2-	34 (3.1-320)	41 (5.5-360)
Fra	ance ^{66*}							2,700 (540- 6,400)	440 (140- 1.500)	1,300 (312- 6,400)	4,700 (1,100-10,000)
Bei	jing ^{53*}	1,000 (580- 1,600)	490 (220-2,900)	1.5 (0.49-17)	1.6 (0.82-32)	0.69 (0.58-5.4)	10 (6.2-64)	100 (60-160)	35 (18-54)	93 (32-190)	260 (110- 390)
Aust	tralia ^{48*}	1,900 (nd- 10,000)	1,500 (nd-7,200)	220 (40- 540,0000	230 (46- 1,000,000)	<mql< td=""><td>(nd-920)</td><td></td><td></td><td></td><td>,</td></mql<>	(nd-920)				,
Br	azil ^{61*}	2000 (840-5000)	4200 (1800-25000)	13 (7.5-34)	30 (12-53)						
	п	32	32	32	32	32	32	30	30	30	3(
sabaala	Median	10,000	8,100	5	5.1	< 0.3	30	420	180	130	800
$(n\alpha/\alpha)$	Range	620-540,000	200-71,000	1.3-35	<0.2-240	<0.3-26	2.5-290	12-4,100	71-2,300	28-6,700	250-10,000
(ng/g)	Mean	48,000	17,000	9	20	2	50	680	350	620	1700
UK ^{31*}		98 (<20-2,500)	5,000 (49-88,000)	26 (1.6-120)	36 (1.1-270)	1.2 (<2-48)	100 (23- 1,000)	1,400 (24- 100,000	550 (14- 67,000	1,700 (34- 72,000)	4,100 (72- 89,000)
Japan ^{67**}		125 (9.0-800)	1,000 (200-4,800)	8.9 (0.68-73)	7.9 (0.58-60)	13 (0.22-110)		340 (18-1,700)	64 (2.4-340)	104 (0-500)	510 (20- 2,300)
Swe	eden ^{55*}	34 (<2.2-420)	54 (<4.1-1,200)								
Stock	kholm ^{46*}	150 (<0.58-300)	69 (<1.9-130)	30 (11-49)	44 (19-68)	5.7 (<2.2-<9.2)		310 (170-4,500)	72 (52-88)	129 (98-160)	510 (380- 640)
Br	azil ^{61*}	300 (210-700)	420 (94-1,200)	8.2 (3.2-30)	33 (30-36)						,

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location	statistical parameter	DBDPE	BDE-209	BDE-47	BDE-99	BDE-183	∑tri-octa- BDEs	α-HBCDD	β-HBCDD	γ-HBCDD	∑- HBCDD
	п	28	28	28	28	28	28	32	32	32	32
	Median	48	410	2.1	6.1	<1.1	19	< 0.3	< 0.3	10	20
Homes	Range	15-7,000	<7.5-5,500	< 0.43-28	< 0.43-330	<1.1-7.5	5.6-330	< 0.3-57	< 0.3-34	< 0.3-3,500	0.9-25,00
(pg/m ³)	Mean	390	880	4.9	37	0.8	50	10	3.5	100	110
ι	U K ⁴⁷	<10 (<10-97)	170 (23-3,800)	13 (0.15-1,700)	12 (0.05-1,700)	<1.0 (<1.0-12)		<2.6 (<2.6- 400)	<2.2 (<2.2- 160)	110 (16- 1,400)	110 (19- 1,500)
Sw Cat Cz U	reden ⁵² nada ³³ zech ³³ JSA ³³	9.2 (na-74) - 42 (nd-71)	310 (43-1,100) 49 (nd-220) 9.4 (nd-15) 260 (nd-5,500)	39 (54-760) 1.6 (0.56-16) 52 (4.5-820)	5.3 (1.3-73) 0.29 (0.16-1.4) 15 (nd-1,300)	1.3 (nd-1.6) 0.12 (nd-0.23) 2.5 (nd-5)					2 (<1.6-33)
	n	29	29	29	29	29	29	32	32	32	32
Cars	Median	160	200	1.9	2.1	<1.1	11	8.9	< 0.3	18	25
(ng/m^3)	Range	<15-3,200	<7.5-7,100	0.79-19	<0.43-150	<1.1	6.5-200	0.3-170	0.3-62	0.3-2,300	0.9-2,300
(98)	Mean	340	660	3.2	9.1	0.58	19	13	6.2	180	200
U	K ^{44,51}			14.8 (2.9-4,700) ⁵¹	12 (0.0-2,300) ⁵¹			2,000 (54- 8,800)	740 (16- 5,200)	9,600 (27- 56,000)	$ \begin{array}{r} 13,000 \\ (190- \\ 69,000)^{44} \end{array} $
Sw	veden ⁵²		400 (160- 2,500)								0.0 (<1.6)
	п	31	31	31	31	31	31	32	32	32	32
Offices	Median	<15	240	3.4	4.2	0.55	15	< 0.3	< 0.3	9.6	14
(pg/m^3)	Range	<15-2,800	<7.5-1,600	<0.43-4,800	< 0.43-880	<1.1	5.7-6,200	0.3-1,500	0.3-710	0.3-1,500	0.9-2,800
	Mean	240	420	160	48	0.54	230	86	42	90	220
ι	U K ⁴⁷	<10 (<10-54)	26 (2.3-350)	6 (0.15-380)	7.9 (1.2-42)	<1.0 (<1.0-3.8)		5.4 (<2.6-31)	<2.2 (<2.2-15)	34 (3.1-320)	41 (5.5-360)
Sw	veden ⁵²		3,200 (68- 5,800)					,	,		0.0 (<1.6)
	п	31	31	31	31	31	31	32	32	32	32
Schools	Median	220	410	2.3	3.1	<1.1	12	16	< 0.3	22	38
(ng/m^3)	Range	<15-3,800	<7.5-21,000	1.5-29	< 0.43-99	<1.1-1.4	7.0-150	0.3-210	0.3-4,600	0.3-1,500	0.9-6,300
(PS/III)	Mean	460	1,600	5.2	9.5	0.54	21	33	160	96	280
Sw	reden ⁵⁵	<7.6	<32	17	<14	<2.1	100	< 0.57	<0.41	<1.0	<2.0
No	rway ^{/1}	8.3	< <u>MLD</u>	130	23	<mld< th=""><th>180</th><th></th><th></th><th></th><th></th></mld<>	180				
South	1 Korea/4	-	0.21 (nd-3.6)	0.40 (nd-17)	0.28 (nd-13)	0.015 (nd-0.15)					

Table 2. Summary of Concentrations of BFRs (pg/m³) in Indoor Air from Irish Homes, Cars, Offices and Schools and Median Concentrations
 from selected previous studies

			α-HBCDD	β-HBCDD	γ-HBCDD	∑-HBCDD	DBDPE	BDE-209	BDE-47	BDE-99	BDE-183	∑tri-octa-BDEs
adult	air	median	0.00035	0.00025	0.0039	0.0071	0.016	0.13	0.0010	0.0022	0.00040	0.0067
		high	0.073	0.037	0.34	0.46	1.2	1.7	0.012	0.10	0.0023	0.10
	dust	median	0.075	0.029	0.085	0.14	1.3	3.1	0.0023	0.0036	0.00045	0.013
		high	2.4	0.83	4.1	7.4	120	99	0.13	0.14	0.017	0.35
	total	median	0.075	0.029	0.088	0.14	1.3	3.2	0.0033	0.0058	0.00084	0.020
		high	2.5	0.87	4.4	7.8	120	100	0.14	0.25	0.020	0.45
UK^{47}	total	high	6.1	3.4	13	22	3.4	57	0.64	0.81	0.093	1.7
toddlar	air	median	0.00019	0.000055	0.0037	0.0073	0.010	0.14	0.0008	0.0021	0.00020	0.0067
touuici	an	high	0.00019	0.000055	0.0037	0.0075	0.019	1 0	0.0008	0.0021	0.00020	0.0007
	dust	median	0.020	0.0000	1.0	2.5	21	64	0.0083	0.11	0.0023	0.11
	dust	high	49	18	98	170	2,500	2,500	3.2	3.3	0.31	7.6
	total	modian	0.08	0.51	1.0	2.5	21	64	0.040	0.071	0.0056	0.26
	iotai	high	0.98	18	1.0	170	2500	2 500	0.040	3.4	0.0030	0.20
UK^{47}	total	high	200	120	430	750	2,500	1.900	15	24	2.3	100
school	air	median	0.0008	0.00003	0.0028	0.0052	0.019	0.090	0.00048	0.0012	0.00012	0.0039
child		high	0.017	0.074	0.17	0.25	0.62	1.2	0.0042	0.044	0.0010	0.045
	dust	median	0.61	0.30	0.47	1.42	14	29	0.018	0.030	0.0022	0.12
		high	25	11	48	86	1,400	1,100	1.3	1.4	0.14	3.6
	total	median	0.61	0.30	0.47	1.4	14	30	0.019	0.031	0.0023	0.12
		high	25	11	48	86	1,400	1,100	1.3	1.4	0.14	3.7
UK^{31}	dust	high				330		13,000		4.3		

458 Table 3. Estimates of exposure (ng/kg bw/day) of Irish adults, toddlers and school children to FRs via indoor air, inhalation and dust ingestion
 459 under typical^a and high-end^b exposure scenarios^c.

460

^a Typical exposure scenario suggests adult and toddler exposure to air inhalation and dust ingestion at the median concentration at the average ingestion rates (air: $20 \text{ m}^3/d^{29}$ for adults and $3.8 \text{ m}^3/d$ toddlers and school children; dust: 20 m/day for adults and 50 m/day for toddlers and school children.

^b High-end exposure scenario suggests adult and toddler exposure to air and dust ingestion at the 95th percentile concentration using high ingestion rates (adult 50 mg/day, toddlers and school children 200 mg/day²⁹).

^c All values expressed as ng/kg/bw/day, assuming body weight of 70 kg for adults, 10 kg for toddlers, and 20 kg for school children.

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481 SUPPORTING INFORMATION

- 482 Full details of sampling (including air sampling rates), analytical (including QA/QC data),
- 483 and exposure assessment methods; alongside detailed information about BFR concentrations

- 485 locations in Ireland are provided as supporting information. This material is available free of
- 486 charge via the Internet at <u>http://pubs.acs.org</u>
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488 REFERENCES

- 489 (1) Secretariat of the Stockholm Convention. *Guidance for the inventory, identification and*490 *substitution of Hexabromocyclododecane (HBCD) under the Stockholm Convention on*491 *Persistent Organic Pollutants, Draft*; 2015.
- 492 (2) Kirk, R.; Othmer, D. *Kirk-Othmer encyclopedia of chemical technology*, 5th ed.; Wiley:
 493 New York, 2007.
- 494 (3) WHO (World Health Organisation). *Environmental Health Criteria 192. Flame*495 *retardants: a general introduction*; Geneva, 1997.
- 496 (4) Weil, E.; Levchik, S. Polystyrenes and Thermoplastic Styrene Copolymers. In *Flame*497 *Retardants for Plastics and Textiles: Practical Applications*; Hanser Publishers:
 498 Munich, 2009; pp 35–57.
- 499 (5) European Comission. *Final report: Study on waste related issues of newly listed POPs*500 *and candidate POPs*; Munich, 2011; Vol. 2011.
- 501 (6) UNEP. Technical review of the implications of recycling commercial penta and 502 octabromodiphenyl ethers. *Unep/Pops/Poprc.6/2 1.* **2010**, *August 201* (August), 3–41.
- 503 (7) Bromine Science and Environmental Forum (BSEF); BSEF. Major Brominated Flame
 504 Retardants Volume Estimates. Total Market Demand by Region in 2001. www.bsef.com
 505 (accessed Feb 12, 2019).
- 506 (8) Alaee, M.; Arias, P.; Sjödin, A.; Bergman, Å. An overview of commercially used
 507 brominated flame retardants, their applications, their use patterns in different
 508 countries/regions and possible modes of release. *Environ. Int.* 2003, 29 (6), 683–689.
- 509 (9) Darnerud, P. Toxic effects of brominated flame retardants in man and in wildlife.

- 510 *Environ. Int.* **2003**, *29* (6), 841–853.
- (10) Covaci, A.; Voorspoels, S.; Ramos, L.; Neels, H.; Blust, R. Recent developments in the
 analysis of brominated flame retardants and brominated natural compounds. *Journal of Chromatography A*. 2007, pp 145–171.
- (11) Rauert, C.; Harrad, S.; Stranger, M.; Lazarov, B. Test chamber investigation of the
 volatilization from source materials of brominated flame retardants and their subsequent
 deposition to indoor dust. *Indoor Air* 2015, 25 (4), 393–404.
- 517 (12) Rauert, C.; Harrad, S. Mass transfer of PBDEs from plastic TV casing to indoor dust via
 518 three migration pathways A test chamber investigation. *Sci. Total Environ.* 2015, *536*,
 519 568–574.
- 520 (13) Darnerud, P. O. Brominated flame retardants as possible endocrine disrupters. *Int. J.*521 *Androl.* 2008, *31* (2), 152–160.
- 522 (14) Vonderheide, A. P.; Mueller, K. E.; Meija, J.; Welsh, G. L. Polybrominated diphenyl
 523 ethers: Causes for concern and knowledge gaps regarding environmental distribution,
 524 fate and toxicity. *Sci. Total Environ.* 2008, *400* (1–3), 425–436.
- 525 (15) Hakk, H. Different HBCD stereoisomers are metabolized differently. *Toxicol. Lett.*526 2010, *196*, S33–S34.
- 527 (16) Wikoff, D. S.; Birnbaum, L. Human Health Effects of Brominated Flame Retardants. In
 528 Brominated Flame Retardants; Eljarrat, E., Barceló, D., Eds.; Springer Berlin
 529 Heidelberg: Berlin, Heidelberg, 2011; pp 19–53.
- 530 (17) Birnbaum, L. S.; Staskal, D. F. Brominated flame retardants: Cause for concern?
 531 *Environ. Health Perspect.* 2004, *112* (1), 9–17.
- 532 (18) Covaci, A.; Gerecke, A. C.; Law, R. J.; Voorspoels, S.; Kohler, M.; Heeb, N. V.; Leslie,
 533 H.; Allchin, C. R.; De Boer, J. Hexabromocyclododecanes (HBCDs) in the environment
- 534 and humans: A review. *Environ. Sci. Technol.* **2006**, *40* (12), 3679–3688.
- 535 (19) Law, R. J.; Kohler, M.; Heeb, N. V; Gerecke, A. C.; Schmid, P.; Voorspoels, S.; Covaci,

- A.; Becher, G.; Janák, K.; Thomsen, C. Hexabromocyclododecane challenges scientists
 and regulators. *Environ. Sci. Technol.* 2005, *39* (13), 281A-287A.
- 538 (20) Secretariat of the Stockholm Convention. *Stockholm Convention on Persistent Organic* 539 *Pollutants*; United Nations Environment Programme, 2010.
- 540 (21) European Commission. Commission Regulation (EU) 2016/293. Off. J. Eur. Union
 541 2016.
- 542 (22) Arias, P. A. Brominated flame retardants- An overview. The Second International
 543 Workshop on Brominated Flame Retardants, BFR 2001. In *The Second International*544 *Workshop on Brominated Flame Retardants, BFR 2001*; Stockholm, 2001; pp 17–19.
- 545 (23) Hardy, M. L.; Margitich, D.; Ackerman, L.; Smith, R. L. The subchronic oral toxicity
 546 of ethane, 1,2-bis(pentabromophenyl) (Saytex 8010) in rats. *Int. J. Toxicol.* 2002, *21* (3),
 547 165–170.
- 548 (24) Abdallah, M. A. E.; Harrad, S. Tetrabromobisphenol-A, hexabromocyclododecane and
 549 its degradation products in UK human milk: Relationship to external exposure. *Environ*.
 550 *Int.* 2011, *37* (2), 443–448.
- 551 (25) Abdallah, M. A. E.; Harrad, S. Polybrominated diphenyl ethers in UK human milk:
 552 Implications for infant exposure and relationship to external exposure. *Environ. Int.*553 2014, 63, 130–136.
- 554 (26) Frederiksen, M.; Thomsen, C.; Frøshaug, M.; Vorkamp, K.; Thomsen, M.; Becher, G.;
 555 Knudsen, L. E. Polybrominated diphenyl ethers in paired samples of maternal and
 556 umbilical cord blood plasma and associations with house dust in a Danish cohort. *Int. J.*557 *Hyg. Environ. Health* 2010, *213* (4), 233–242.
- Pratt, I.; Anderson, W.; Crowley, D.; Daly, S.; Evans, R.; Fernandes, A.; Fitzgerald, M.;
 Geary, M.; Keane, D.; Morrison, J. J.; Reilly, A.; Tlustos, C. Brominated and fluorinated
 organic pollutants in the breast milk of first-time Irish mothers: is there a relationship to
 levels in food? *Food Addit. Contam. A, Chem. Anal. Control. Expo. risk Assess.* 2013,

562 30

- *30* (10), 1788–1798.
- 563 (28) Kalachova, K.; Hradkova, P.; Lankova, D.; Hajslova, J.; Pulkrabova, J. Occurrence of
 564 brominated flame retardants in household and car dust from the Czech Republic. *Sci.*565 *Total Environ.* 2012, *441* (441), 182–193.
- 566 (29) Abdallah, M. A. E.; Harrad, S.; Covaci, A. Hexabromocyclododecanes and
 567 Tetrabromobisphenol-A in in Indoor Air and Dust in Birmingham, UK: Implications
 568 for Human Exposure. *Environ. Sci. Technol.* 2008, 42 (18), 1–7.
- 569 (30) Cunha, S. C.; Kalachova, K.; Pulkrabova, J.; Fernandes, J. O.; Oliveira, M. B. P. P.;
 570 Alves, A.; Hajslova, J. Polybrominated diphenyl ethers (PBDEs) contents in house and
- 571 car dust of Portugal by pressurized liquid extraction (PLE) and gas chromatography-572 mass spectrometry (GC-MS). *Chemosphere* **2010**, *78* (10), 1263–1271.
- 573 (31) Harrad, S.; Goosey, E.; Desborough, J.; Abdallah, M. A. E.; Roosens, L.; Covaci, A.
 574 Dust from U.K. primary school classrooms and daycare centers: The significance of dust
 575 as a pathway of exposure of young U.K. children to brominated flame retardants and
 576 polychlorinated biphenyls. *Environ. Sci. Technol.* 2010, *44* (11), 4198–4202.
- 577 (32) Harrad, S.; Ibarra, C.; Abdallah, M. A. E.; Boon, R.; Neels, H.; Covaci, A.
 578 Concentrations of brominated flame retardants in dust from United Kingdom cars,
 579 homes, and offices: Causes of variability and implications for human exposure. *Environ.*580 *Int.* 2008, *34* (8), 1170–1175.
- (33) Venier, M.; Audy, O.; Vojta, Š.; Bečanová, J.; Romanak, K.; Melymuk, L.; Krátká, M.;
 Kukučka, P.; Okeme, J.; Saini, A.; Diamond, M. L.; Klanova, J. Brominated flame
 retardants in the indoor environment Comparative study of indoor contamination
 from three countries. *Environ. Int.* 2016, *94*, 150–160.
- 585 (34) Abdallah, M. A. E.; Pawar, G.; Harrad, S. Effect of Bromine Substitution on Human
 586 Dermal Absorption of Polybrominated Diphenyl Ethers. *Environ. Sci. Technol.* 2015,
 587 49 (18), 10976–10983.

- (35) Abdallah, M. A. E.; Harrad, S. Dermal contact with furniture fabrics is a significant
 pathway of human exposure to brominated flame retardants. *Environ. Int.* 2018, *118*(May), 26–33.
- (36) (FSAI) Food Safety Authority of Ireland. Monitoring and surveillance series.
 Investigation into levels of chlorinated and brominated organic pollutants in carcass fat, offal, eggs and milk produced in Ireland; Dublin, January 2010.
- 594 (37) Tlustos, C.; McHugh, B.; Pratt, I.; Tyrell, L.; McGovern, E. Investigation into Levels of
 595 Dioxins, Furans, Polychlorinated Biphenyls and Brominated Flame Retardants in
 596 Fishery Products in Ireland. *Mar. Environ. Heal. Ser.* 2006, *26*, 1–58.
- 597 (38) Alliance for Flame Retardant Free Furniture in Europe. Competitiveness
 598 http://www.safefurniture.eu/competitiveness.html (accessed Jun 14, 2019).
- 599 (39) Hagen, R.; Karemaker, M.; Larsson, I.; Hörnqvist, A.; Brants, D.; Elorza, J.; Watts, D.;
- Van Mierlo, E.; Maloziec, D.; Paloluoma, P.; de Witte, L. *Fire safety of upholstered furniture and mattresses in the domestic area: European fire services recommendations on test methods*; 2017.
- 603 (40) Fire Safety Advice Center. Furniture and Furnishings (Fire Safety) Regulations
 604 1988/1989,1993 and 2010 http://www.firesafe.org.uk/furniture-and-furnishings-fire605 safety-regulations-19881989-and-1993/ (accessed Feb 25, 2019).
- 606(41)Irish Statute Book (eISB). S.I. No. 316/1995 Industrial Research and Standards (Fire607Safety)(DomesticFurniture)Order,1995608http://www.irishstatutebook.ie/eli/1995/si/316/made/en/print# (accessed Jul 19, 2018).
- 609 (42) Hazrati, S.; Harrad, S. Calibration of polyurethane foam (PUF) disk passive air samplers
- 610 for quantitative measurement of polychlorinated biphenyls (PCBs) and polybrominated
- diphenyl ethers (PBDEs): Factors influencing sampling rates. *Chemosphere* 2007, 67,
 448–455.
- 613 (43) Shoeib, M.; Harner, T.; Sum, C. L.; Lane, D.; Zhu, J.; Lee, S. C.; Lane, D.; Zhu, J.

- 614 Sorbent-Impregnated Polyurethane Foam Disk for Passive Air Sampling of Volatile
 615 Fluorinated Chemicals. *Anal. Chem.* 2008, *80* (3), 675–682.
- 616 (44) Abdallah, M. A. E.; Harrad, S. Modification and calibration of a passive air sampler for
 617 monitoring vapor and particulate phase brominated flame retardants in indoor air:
 618 Application to car interiors. *Environ. Sci. Technol.* 2010, 44 (8), 3059–3065.
- 619 (45) Qi, H.; Li, W.; Liu, L.; Zhang, Z.; Zhu, N.; Song, W.; Ma, W.; Li, Y. Levels, distribution
- and human exposure of new non-BDE brominated fl me retardants in the indoor dust of
 China. *Environ. Pollut.* 2014, *195*, 1–8.
- 622 (46) Persson, J.; Wang, T. Temporal trends of decabromodiphenyl ether and emerging
- brominated flame retardants in dust, air and window surfaces of newly built low energy
- 624 preschools. *Indoor Air* **2019**, *00*, 1–13.
- (47) Tao, F.; Abdallah, M. A.-E.; Harrad, S. Emerging and Legacy Flame Retardants in UK
 Indoor Air and Dust: Evidence for Replacement of PBDEs by Emerging Flame
 Retardants? *Environ. Sci. Technol.* 2016, *50* (23), 13052–13061.
- (48) McGrath, T. J.; Morrison, P. D.; Ball, A. S.; Clarke, B. O. Concentrations of legacy and
 novel brominated flame retardants in indoor dust in Melbourne, Australia: An
 assessment of human exposure. *Environ. Int.* 2018, *113*, 191–201.
- 631 (49) European Chemical Agency (ECHA). Bis(pentabromophenyl) ether
 632 https://echa.europa.eu/registration-dossier/-/registered-dossier/14217/1# (accessed Feb
 633 12, 2019).
- 634 (50) European Chemical Agency (ECHA). 1,1'-(ethane-1,2-diyl)bis[pentabromobenzene]
 635 https://echa.europa.eu/registration-dossier/-/registered-dossier/15001 (accessed Feb 12,
 636 2019).
- 637 (51) Harrad, S.; Hazrati, S.; Ibarra, C. Concentrations of Polychlorinated Biphenyls in Indoor
 638 Air and Polybrominated Diphenyl Ethers in Indoor Air and Dust in Birmingham, United
 639 Kingdom: Implications for Human Exposure. *Environ. Sci. Technol.* 2006, 40 (15),

640 4633–4638.

- 641 (52) Thuresson, K.; Björklund, J. A.; de Wit, C. A.; Wit, C. A. De. Tri-decabrominated
 642 diphenyl ethers and hexabromocyclododecane in indoor air and dust from Stockholm
 643 microenvironments 1: Levels and profiles. *Sci. Total Environ.* 2012, *414* (1), 713–721.
- 644 (53) Wang, J.; Wang, Y.; Shi, Z.; Zhou, X.; Sun, Z. Legacy and novel brominated flame
 645 retardants in indoor dust from Beijing, China: Occurrence, human exposure assessment
 646 and evidence for PBDEs replacement. *Sci. Total Environ.* 2018, *618*, 48–59.
- 647 (54) Besis, A.; Christia, C.; Poma, G.; Covaci, A.; Samara, C. Legacy and novel brominated
 648 flame retardants in interior car dust Implications for human exposure. *Environ. Pollut.*649 2017, 230, 871–881.
- (55) Larsson, K.; Wit, C. A. De; Sellstro, U.; Sahlstro, L.; Lindh, C. H.; Berglund, M.
 Brominated Flame Retardants and Organophosphate Esters in Preschool Dust and
 Children's Hand Wipes. *Environ. Sci. Technol.* 2018, *52*, 4878–4888.
- 653 (56) European Chemical Agency (ECHA). *Annex XVI consultant report decabde*; London,
 654 2014.
- 655 (57) European Chemicals Bureau. European Union risk assessment report: Diphenyl ether,
 656 octabromo derivative; 2003.
- 657 (58) European Chemical Agency (ECHA). Annex XV dossier Proposal for Identification of
 658 a PBT / vPvB Substance; 2012.
- (59) Harrad, S.; Abdallah, M. A. E. Brominated flame retardants in dust from UK cars Within-vehicle spatial variability, evidence for degradation and exposure implications. *Chemosphere* 2011, 82 (9), 1240–1245.
- 662 (60) Brommer, S.; Harrad, S.; Van Den Eede, N.; Covaci, A. Concentrations of
 663 organophosphate esters and brominated flame retardants in German indoor dust
 664 samples. J. Environ. Monit. 2012, No. 14, 2482.
- 665 (61) Cristale, J.; Aragão Belé, T. G.; Lacorte, S.; Rodrigues de Marchi, M. R. Occurrence

- and human exposure to brominated and organophosphorus flame retardants via indoor
 dust in a Brazilian city. *Environ. Pollut.* 2018, 237, 695–703.
- 668 (62) Coelho, S. D.; Sousa, A. C. A.; Isobe, T.; Kim, J.-W.; Kunisue, T.; Nogueira, A. J. A.;
- Tanabe, S. Brominated, chlorinated and phosphate organic contaminants in house dust
 from Portugal. *Sci. Total Environ.* 2016, *569–570*, 442–449.
- 671 (63) Peng, C.; Tan, H.; Guo, Y.; Wu, Y.; Chen, D. Emerging and legacy flame retardants in
 672 indoor dust from East China. *Chemosphere* 2017, *186*, 635–643.
- 673 (64) Sahlström, L. M. O.; Sellström, U.; De Wit, C. A.; Lignell, S.; Darnerud, O. Estimated
 674 intakes of brominated flame retardants via diet and dust compared to internal
 675 concentrations in a Swedish mother–toddler cohort. *Int. J. Hyg. Environ. Health* 2015,
 676 218, 422–432.
- 677 (65) Dodson, R. E.; Perovich, L. J.; Covaci, A.; Dirtu, A. C.; Brody, J. G.; Rudel, R. A. After
 678 the PBDE Phase-Out: A Broad Suite of Flame Retardants in Repeat House Dust Samples
 679 from California. *Environ. Sci. Technol.* 2012, *46*, 13056–13066.
- 680 (66) Abou-Elwafa Abdallah, M.; Bressi, M.; Oluseyi, T.; Harrad, S. 681 Hexabromocyclododecane and tetrabromobisphenol-A in indoor dust from France, 682 Kazakhstan and Nigeria: Implications for human exposure. Emerg. Contam. 2016, 2, 683 73–79.
- 684 (67) Mizouchi, S.; Ichiba, M.; Takigami, H.; Kajiwara, N.; Takamuku, T.; Miyajima, T.;
 685 Kodama, H.; Someya, T.; Ueno, D. Exposure assessment of organophosphorus and
 686 organobromine flame retardants via indoor dust from elementary schools and domestic
 687 houses. *Chemosphere* 2015, *123*, 17–25.
- 688 (68) Covaci, A.; Voorspoels, S.; Abdallah, M. A. E.; Geens, T.; Harrad, S.; Law, R. J.
 689 Analytical and environmental aspects of the flame retardant tetrabromobisphenol-A and
 690 its derivatives. *Journal of Chromatography A*. 2009, pp 346–363.
- 691 (69) Frederiksen, M.; Vorkamp, K.; Thomsen, M.; Knudsen, L. E. Human internal and

- 692 external exposure to PBDEs A review of levels and sources. *Int. J. Hyg. Environ.*693 *Health* 2009, 212 (2), 109–134.
- (70) Reche, C.; Viana, M.; Querol, X.; Corcellas, C.; Barceló, D.; Eljarrat, E. Particle-phase
 concentrations and sources of legacy and novel flame retardants in outdoor and indoor
 environments across Spain. *Sci. Total Environ.* 2019, *649*, 1541–1552.
- (71) Cequier, E.; Ionas, A. C.; Covaci, A.; Marc, R. M.; Becher, G.; Thomsen, C.; Marce, R.
 M.; Becher, G.; Thomsen, C. Occurrence of a broad range of legacy and emerging flame
 retardants in indoor environments in Norway. *Environ. Sci. Technol.* 2014, *48* (12),
 6827–6835.
- (72) Fromme, H.; Körner, W.; Shahin, N.; Wanner, A.; Albrecht, M.; Boehmer, S.; Parlar,
 H.; Mayer, R.; Liebl, B.; Bolte, G. Human exposure to polybrominated diphenyl ethers
 (PBDE), as evidenced by data from a duplicate diet study, indoor air, house dust, and
 biomonitoring in Germany. *Environ. Int.* 2009, *35* (8), 1125–1135.
- 705 (73) Newton, S.; Sellström, U.; de Wit, C. A.; Sellstro, U.; Wit, C. A. De. Emerging Flame
 706 Retardants, PBDEs, and HBCDDs in Indoor and Outdoor Media in Stockholm, Sweden.
 707 *Environ. Sci. Technol.* 2015, *49*, 2912–2920.
- (74) Lim, Y.-W.; Kim, H.-H.; Lee, C.-S.; Shin, D.-C.; Chang, Y.-S.; Yang, J.-Y. Exposure
 assessment and health risk of poly-brominated diphenyl ether (PBDE) flame retardants
 in the indoor environment of elementary school students in Korea. *Sci. Total Environ.*2014, 470–471, 1376–1389.
- (75) Harrad, S.; Abdallah, M. A. E.; Covaci, A. Causes of variability in concentrations and
 diastereomer patterns of hexabromocyclododecanes in indoor dust. *Environ. Int.* 2009, *35* (3), 573–579.
- 715 (76) Drage, D. S.; Sharkey, M.; Abdallah, M. A. E.; Berresheim, H.; Harrad, S. Brominated
 716 flame retardants in Irish waste polymers: Concentrations, legislative compliance, and
 717 treatment options. *Sci. Total Environ.* 2018, 625, 1535–1543.

- (77) Shoeib, M.; Harner, T.; Ikonomou, M.; Kannan, K. Indoor and Outdoor Air
 Concentrations and Phase Partitioning of Perfluoroalkyl Sulfonamides and
 Polybrominated Diphenyl Ethers. *Environ. Sci. Technol.* 2004, *38* (5), 1313–1320.
- 721 (78) Bennett, D. H.; Scheringer, M.; McKone, T. E.; Hungerbühler, K. Predicting long-range
- transport: A systematic evaluation of two multimedia transport models. *Environ. Sci. Technol.* 2001, *35* (6), 1181–1189.
- (79) United States Environmental Protection Agency (US EPA). Technical Fact Sheet –
 Polybrominated Diphenyl Ethers (PBDEs) and Polybrominated Biphenyls (PBBs).
 2012, No. May, 1–5.
- (80) National Research Council (US). Hexabromocyclododecane. In *Toxicological Risks of Selected Flame-Retardant Chemicals*; The National Academies Press: Washington,
 D.C., 2000; pp 53–71.
- 730 (81) Trudel, D.; Tlustos, C.; Von Goetz, N.; Scheringer, M.; Hungerbühler, K. PBDE
 731 exposure from food in Ireland: Optimising data exploitation in probabilistic exposure
 732 modelling. *J. Expo. Sci. Environ. Epidemiol.* 2010, *21* (6), 565–575.
- 733 (82) Dungey, S.; Akintoye, L. Environmental risk evaluation report: 1,1'- (Ethane-1,2734 diyl)bis[penta-bromobenzene], CAS: 84852-53-9; Bristol, 2007.
- 735

736