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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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KEYWORDS

BFRs, indoor dust, indoor air, cars, homes, offices, schools, human exposure, DBDPE, PBDEs, HBCDD

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/m^3) 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 for the same microenvironments in the UK, and exceed those reported in many other countries. Concentrations of BDE-209 in cars exceeded significantly (p<0.05) those in other micro-environments. HBCDD was detected in all dust samples (median: 580 ng/g), and in 81% of air samples (median: 24 pg/m^3) at concentrations similar to those reported recently for the UK and 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) exceed substantially those reported for the UK population. Moreover, our estimates of exposure of the Irish population to Σtri-deca-PBDEs exceed previous estimates for Ireland via dietary exposure.

INTRODUCTION

Brominated flame retardants (BFRs) such as polybrominated diphenyl ethers (PBDEs) and hexabromocyclododecane (HBCDD) were first marketed in the late 1960s[1] and subsequently widely applied in many jurisdictions to a variety of soft furnishings, building insulation foams, electrical and electronic equipment (EEE). There are three main commercial PBDE mixtures with varying degrees of bromination[2], namely Penta-BDE (primarily BDE-99 (45-50%) and BDE-47 (38-42%), Octa-BDE (primarily BDE-183) and Deca-BDE (>90% BDE-209))[3]. Deca-BDE was mainly used in high impact polystyrene (HIPS) for electrical housings and in fabric and soft furnishing applications[4]. Penta-BDE was widely used in treatment of polyurethane foam, especially for transport and for soft furnishings such as upholstery, mattresses and textiles, as well as in circuit boards, packaging and textiles[5]; while Octa-BDE was used mainly in hard plastic acrylonitrile butadiene styrene (ABS) casings, and to a lesser degree HIPS and EEE[5,6].

HBCDD has primarily been used as a flame retardant (FR) in expanded and extruded polystyrene (EPS/XPS) used in building insulation foam, in textiles[7] and in HIPS used for EEE[5]. Both HBCDDs and PBDEs are categorised as additive BFRs and are therefore easily released by volatilisation[8–10] as well as abrasion and direct source-to-dust transfer[11,12] from treated products into the environment. Human exposure to BFRs is associated with many adverse effects such as endocrine disruption, liver microsomal enzyme induction, immunotoxicity, neurotoxicity and carcinogenicity[13,14]. Animal studies have further shown 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 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 disruption of the thyroid hormone system[13,18,19]. This evidence of their toxicity, combined with their environmental persistence and bioaccumulation potential, has resulted in the listing of

Penta- and Octa-BDE (2009), HBCDD (2013) and Deca-BDE (2017) as persistent organic pollutants (POPs) under the Stockholm Convention[20] leading to restrictions on their manufacture and use. Whilst banned in 2013, exemptions existed for HBCDD in Europe for use in EPS/XPS insulation until August 2016[21]. The restrictions on PBDEs have created a market demand for replacement FRs, such as decabromodiphenyl ethane (DBDPE), marketed as a replacement for Deca-BDE[22]. Limited toxicological data exists for DBDPE, however, it is structurally very similar to BDE-209 and may therefore display comparable adverse effects[23]. BFRs have been detected in human tissues such as breast milk, adipose tissue, blood, serum, placenta and liver samples[24–27]. Moreover, BFR concentrations in food products, household dust and air have been recorded worldwide[27–33]. Results suggest multiple external exposure pathways for BFRs including ingestion of dust, diet, dermal exposure and inhalation[27, 29, 34]. 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 and diet[25, 31, 33] and dermal contact with flame-retarded fabrics[35].

Currently, knowledge of exposure of the Irish population to BFRs is confined to a single biomonitoring study using human breast milk conducted in 2010[27] and ongoing surveillance of dietary exposure[36,37]. Given the known importance in other countries of indoor exposures, this study measures PBDEs, HBCDD and DBDPE in indoor air and settled floor dust samples collected from Irish homes, cars, offices and schools. These data are used to calculate the first exposure estimates for Irish adults and toddlers to PBDEs, HBCDD and DBDPE via inhalation and ingestion of indoor dust. The European Union does not have a universal requirement for upholstered furniture to be resistant to ignition[38]. The UK and Ireland both have specific stringent fire safety legislation on the flammability of furniture, stating that filling materials and upholstered covers must be resistant to various sources of ignition[39–41]. This legislation is specific to the UK and Ireland, and is not a requirement in other European countries[38]. We therefore tested the hypothesis that concentrations of DBDPE, PBDEs, and HBCDD in Ireland would more closely resemble those in the UK than those in mainland Europe.

MATERIALS AND METHODS

Sampling strategy

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

Sampling methods

Indoor dust sampling - Project sampling protocols followed previously published methodologies[29]. Home and office participants were asked not to clean their cars for two weeks or living rooms for two days, prior to sampling. Due to school policy, classroom floors are cleaned on a daily basis, so samples were taken at the end of the school day from classrooms. Further details of sample collection protocols are provided as Supplementary data.

Air Sampling - Air samples were collected by deploying passive air samplers for approximately 60 days in order to sample the maximum volume of air while remaining in the linear uptake phase of the PUF disk samplers[42]. The sampling apparatus consisted of two parts: a sorbent (XAD-3) impregnated polyurethane foam disk (PUF) (ø: 140 mm, thickness: 12 mm, surface area: 360.6 cm^2, density: 0.02 g cm^{-3}; PACS Leicester, UK), pre-cleaned via Soxhlet extraction with dichloromethane (DCM) for 8 hours[43]. The PUF was partially enclosed in two stainless-steel housings (top ø: 26 cm, bottom : ø: 18 cm) and mounted according to previous studies[44].

Samplers were placed on elevated surfaces in homes, offices, and schools, and on the floor behind the passenger or driver's seat in cars.

Quality Assurance/Quality Control

A reagent blank was analysed with every batch of samples. Instrumental analysis is described 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 residues and method limits of detection (LOD) and limits of quantification (LOQ) were estimated based on S/N = 3:1 and 10:1, respectively. Average LOQs ranged from 0.1 ng/g to 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/m^3 to 3.1 pg/m^3 for PBDEs, 7.5 pg/m^3 for BDE-209, 15 pg/m^3 for DBDPE and 0.3 pg/m^3 for HBCDDs (Table SI-2). For non-detects (nd) ½ LOQ was used for statistical analysis. Method accuracy and precision was determined by analysis of an aliquot of standard reference material SRM-2585 (NIST) with every 10 samples. Measured concentrations were close to the certified levels with a relative standard deviation (RSD) of <15% (Table SI -3).

Statistical Analysis

Statistical analysis was performed using SPSS 24.0. BFR concentration data was log normally 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 categories and regional differences in BFR concentrations for different microenvironments ($p<0.05$). A two-tailed Pearson's correlation coefficient was used to investigate associations between air and dust BFR concentrations in homes, cars, offices and schools and factors such as year of building construction, car age, and number of electronics present. Differences in air and dust concentrations in offices, schools and homes with electronic goods purchased before 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 ($p<0.05$).

RESULTS AND DISCUSSION

Concentrations of DBPDE, PBDEs and HBCDDs in indoor dust

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

DBDPE

DBDPE was detected in 98% of all dust samples analysed (n=120) across all microenvironments ranging from <LOD to concentrations of 540,000 ng/g (median: 6500 ng/g). To the authors' knowledge, our data on concentrations of DBDPE in indoor dust are 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].

These substantially elevated DBDPE concentrations suggest that DBDPE may have been used 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 thought to have replaced Deca-BDE in plastics and textiles with a wide range of uses in the transport, building, construction, and domestic sectors[49]. DBDPE registrations under REACH[50] 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 total range of 1,000 and 10,000 for BDE-209 in 2014[49]. Concentrations of DBDPE in UK indoor dust increased between 2006-07 and 2015[47,51]. While no comparative Irish data exist, we hypothesise similar increasing temporal trends are occurring in Ireland and thus compared 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

2016[47], cars (sampled in 2003-2005)[51], schools (sampled in 2007-2008)[31] and offices (sampled in 2016)[47] respectively.

Median concentrations of DBDPE reported here for Irish homes exceed those reported for Swedish homes[52] Australian homes (also sampled in 2016)[48] and homes in Beijing[53]. Median DBDPE concentrations reported for Irish cars also exceed those in Greece[54], while those in Irish offices exceed those in Australia[48]. 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].

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 Σtri-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 congener detected across all microenvironments[28,32,33], contributing to >99% of ΣPBDEs for homes, cars and schools, and 98% in offices. This is unsurprising given BDE-209 was the most commonly used PBDE congener from 2000 until 2008[56] after which its use started to decline following restrictions, its inclusion in the RoHs Directive and its classification as a SVHC under REACH[49]. An estimated 10% of the total Deca-BDE imported into the EU between 2000 and 2005, was imported into Ireland[56]. Although no Irish statistics on use of Deca-BDE in textiles exist, UK data is thought to closely represent usage patterns in Ireland, and an estimated three quarters of the Deca-BDE used to treat UK textiles was used in domestic furniture[57] while 95% of all upholstered materials used in the UK were treated with flame retardants to comply 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 cars[59] 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.

Comparisons with other countries reveal BDE-209 concentrations in Irish indoor environments exceed those reported for Greece[54], Germany[60] and the Czech Republic[28]. BDE-209 concentrations in Irish homes, offices and cars exceed recent values for Australia[48] as well as those reported for Beijing homes and offices[53]. BDE-209 median concentrations in Irish 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 America[7] 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].

With respect to Σtri-octa BDEs, concentrations in Irish homes exceed slightly those in the UK, Portugal and China[47,62,63], but are similar to those reported for Brazilian primary schools (median: 41 ng/g)[61].

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].

$\sum$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.

∑HBCDD median concentrations in office dust are exceeded by those in France in 2016 (median: 4,700 ng/g)[66]. There are few published data on concentrations of HBCDD in schools; results from this study (median: 800 ng/g) are consistent with those for Japan (510 ng/g)[67], but the Japanese study was conducted before HBCDD's listing under the Stockholm Convention in 2013. Concentrations in Irish cars are nearly 40 times higher than in the Czech Republic[28] and 8 times higher than in Greece[54].

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 UK[47] and schools followed the same pattern (52% α-HBCDD, 24% γ-HBCDD and 24% β-HBCDD)[31].

In contrast, similar to a Greek study[54] 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 Republic[28] and the UK[59].

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 2016[47] (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].

Concentrations of DBDPE in Irish homes are comparable to those in US homes (median: 42 pg/m^3), but exceed those reported for Canadian and Czech homes[33]. Concentrations in Irish offices exceed those in Spain[70], while those in schools exceed those reported for Swedish pre-schools in 2016-18[55] and Norwegian schools sampled in 2012 (median: 8.3 pg/m^3)[71].

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/m^3 and 300 pg/m^3 for ∑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 UK[47], Sweden[52] and Germany[72]. Concentrations of BDE-209 in Irish homes are consistent with those for the UK in 2015[47], but those in Irish offices exceed by a factor of two those recently recorded in the UK[47]. 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 ∑tri-octa BDE concentrations reported here and elsewhere due to the different congener compositions studied. ∑tri-octa BDE median concentrations in Irish homes (5.6-330 pg/m^3) were lower than those reported in the UK (median: 13-2,600 pg/m^3)[47], whereas those in Irish offices (median: 15 pg/m^3, range 5.7-6200 pg/m^3) exceed those in the UK (median: 20-150 pg/m^3)[47]. Lowest median concentrations in this study were in schools (7.0-150 pg/m^3), and were lower than those in South Korea (<dl-33,500 pg/m^3)[74] and Norway (<dl-150 pg/m^3)[71].

Median concentrations of BDE-47 (2.1 pg/m^3) and BDE-99 (6.1 pg/m^3) are exceeded by those in the US (median: 52 pg/m^3, 15 pg/m^3, respectively)[33]. This likely reflects greater use of the Penta BDE formulation in the US than Europe[7].

HBCDD

HBCDDs were detected in 81% of all air samples. ∑HBCDD concentrations in Irish homes (median: 20 pg/m^3) were 5 times lower than those in the UK (median: 110 pg/m^3)[47]. Concentrations in Irish cars (median: 25 pg/m^3) are almost 500 times lower, and office samples (14 pg/m^3) less than half those in the UK in 2008[29] (median: 13,000 pg/m^3) and 2015[47] (median: 41 pg/m^3) respectively, which may reflect a decreasing trend in HBCDD use. Nonetheless, median concentrations in all Irish microenvironments still exceed those in Sweden (<2 pg/m^3) in 2006[52].

Unlike the HBCDD isomer pattern in dust, the most abundant isomer in air samples was γ-HBCDD across all microenvironments, followed by α-HBCDD. The HBCDD stereoisomer 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 offices[47].

Previous studies have also observed the γ-HBCDD isomer to make a greater contribution to ∑HBCDD in air than in dust[29]. This was shown to arise from a photolytically-mediated shift from γ-HBCDD to α-HBCDD in dust[75].

Comparisons between microenvironments

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

Indoor dust

There were no significant differences in DBDPE concentrations between different MEs. For PBDEs, concentrations of BDE-209 were significantly lower in offices (median: 3,500 ng/g) 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 (and to a lesser extent schools), where faster turnover of electronic and electrical goods than in homes is anticipated. Concentrations of BDE-99 in cars (median: 50 ng/g) exceed significantly those in offices ($p<0.05$) and schools ($p<0.05$) but are statistically indistinguishable from those 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 similar observations. Higher concentrations of PBDEs have been associated with interiors of vehicles, due to the increased volume of synthetic surfaces, increased volatilisation of BFRs due to high temperatures in unoccupied cars as well as to smaller air volume within cars and reduced ventilation[48]. No other significant differences were observed between MEs.

Indoor air

Differences in BFR concentrations in air were observed between the different microenvironments studied. DBDPE and BDE-209 concentrations in schools were significantly higher than in offices ($p<0.05$ for both). DBDPE concentrations in schools (median: 220 pg/m^3) exceeded significantly those in homes (median: 48 pg/m^3) ($p<0.05$); while BDE-209 concentrations (median: 410 pg/m^3) in schools exceeded significantly those in cars (median: 200 pg/m^3) ($p<0.05$).

Concentrations of BDE-47 in homes (median: 2.1 pg/m^3) were significantly lower compared to those in offices (median: 3.4 pg/m^3) (p<0.05). BDE-99 concentrations in homes (median: 6.1 pg/m^3) exceeded significantly higher those in schools and cars (median: 3.1 pg/m^3 and 2.1 pg/m^3 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.

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.

Indoor dust

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

Indoor air

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 concentrations (median: 3.8 pg/m^3) were significantly lower than Galway (median: 300 pg/m^3) and Limerick (median: 530 pg/m^3) cars (p<0.001, p<0.001), which could not be explained by 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 vehicles manufactured in both Germany and Asia[76]. The cleaning pattern of the cars did not influence the BDE-209 air concentration and neither did the presence of a child seat or air 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/m^3) and significant lower concentrations in Dublin schools (median: 150 pg/m^3). 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.

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.

Concentrations of HBCDD in office dust were positively correlated with the number of electronics present (p<0.01). Higher air concentrations of ∑HBCDD (p<0.05) were found in 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 carpets[76], 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 Ireland[76].

Temporal trends of BFR concentrations in air and dust data

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 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, independent t-tests were used to investigate differences in concentrations from different age categories. Year of home construction was significantly negatively correlated with concentrations of ∑HBCDD (p<0.01), which possibly reflects the impact of recent restrictions on the use of HBCDD in building insulation materials.

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/m^3) 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 ∑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 ∑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

ng/g, c.f. 31 ng/g) and ∑tri-octa BDE (p<0.01; average concentration pre 2009: 255 ng/g, post 2009: 76 ng/g).

Correlations between air and dust concentrations

We hypothesised concentrations of BFRs in air and dust correlate[47,52,77], as BFRs partition between the particulate and the gaseous phase[78]. This hypothesis was tested by examining the relationship between concentrations of BFRs in air and dust samples collected from the same MEs using a Spearman's rho test (Table SI-18). Significant positive correlations were observed for ∑HBCDD (in schools only) (p<0.01), for BDE-99 (in homes only) (p<0.05), and for BDE-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 microenvironment, and therefore further sampling would be required for further investigation.

Exposure assessment

BFR concentrations in indoor air and dust were used to estimate exposures of Irish adults, toddlers and school children, via inhalation of airborne BFRs and ingestion of BFRs in dust (Table 3) (a summary of all the assumptions and algorithms used in exposure calculations are presented in the supporting information). Two exposure scenarios were considered; a "typical" 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, a higher dust ingestion rate was used for the high-end scenario calculation. High-end exposure scenario estimates for DBDPE (adult: 120 ng/kg bw/day, toddler: 2,500 ng/kg bw/day) and BDE-209 (adult: 100 ng/kg bw/day, toddler 2,500 ng/kg bw/day) exceed the equivalent high-end exposures reported recently for the UK[47] (adult: 3.4 ng/kg bw/day, 57 ng/kg bw/day; 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

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 respectively[31].
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/day[79]. Those for Octa-BDE (BDE-183), Penta-BDE (BDE-47 and BDE-99) and ∑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 ∑PBDEs (2.4 ng/kg bw/day)[81].

The limitations of this study are the convenience nature of the sampling that means that the samples analysed are not necessarily representative of Ireland. Moreover, samples taken 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 in air and dust from various Irish indoor environments. BDE-209 was the main PBDE congener detected in homes and cars, suggesting substantial use of Deca-BDE to comply with fire safety regulations. In striking contrast, DBDPE was the most abundant BFR detected in Irish offices and school classrooms, suggesting widespread use in Ireland, likely as a replacement for BDE-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 wt[82]. To the authors' knowledge, concentrations of DBDPE in this study were the highest reported in indoor environments anywhere to date. Detailed study of the health implications of exposure to DBDPE are thus recommended.

TABLES

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

location	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*
homes (ng/g)	**Median**	4,200	13,000	7.6	13	1	49	200	100	200	490
	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
	Mean	39,000	58,000	26	45	4.1	130	1,500	680	670	2900
UK[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)
USA[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)
Sweden[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)
Beijing[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)
Australia[48*]		1,600 (nd-9,000)	1,100 (290-13,000)	56 (nd-2,800)	74 (16-58,000)	<MQL (nd-26)	(18-11,000)				
Brazil[61*]		400 (150-740)	410 (160-1,200)	8.0 (4.5-1,400	153 (20-290)						
	n	*28*	*28*	*28*	*28*	*28*	*28*	*29*	*29*	*29*	*29*
cars (ng/g)	**Median**	7,700	26,000	24	50	4.1	150	330	250	490	1,300
	Range	<13-190,000	14-680,000	<0.1-130	<0.2-270	<0.3-92	0.094-690	3.4-3,700	4.8-2,600	2.4-17,000	2,400-20,000
	Mean	23,000	82,000	31	70	9.8	200	650	410	180	2,800
UK[32,51*]		100 (<dl-2,900)[51]	100,000 (12,000-2,600,000)	54 (19-7,500)	100 (23-80,00)	7.8 (<dl-67)		20,00 (54-88,00)[29]	740 (16-5,200)	9,600 (27-56,000)	13,000 (190-69,000)
Germany[60*]		13,00 (110-6,500)	940 (220-3,100)	17 (2.1-43)	32 (1.3-88)	3.7 (1.3-<0.2-17)					
Czech Republic[28*]		99 (<20-3,600)	170 (<5-33,000)	2.2 (<0.1-280)	<0.1 (<0.1-280)	<0.8 (<0.8-15)		9 (<0.3-45)	<0.3 (<0.3-44)	25 (<0.3-240)	33 (<0.3-240)
Greece[54*]		856 (33-5,200)	2,800 (110-38,000)	9.1 (0.63-9,000)	12 (1.4-11,000)	1.4 (LOD-1,200)	(23-17,000)	90 (<LOQ-1,300)	16 (<LOQ-290)	46 (<LOQ-260)	155 (<LOQ-1,800)
Brazil[61*]		1,400 (420-3,800)	1,600 (300-4,000)	31 (4.3-190)	100 (8.5-350)						
location	statistical parameter	**DBDPE**	**BDE-209**	**BDE-47**	**BDE-99**	**BDE-183**	**∑tri-octa-BDEs**	**α–HBCDD**	**β–HBCDD**	**γ–HBCDD**	**∑-HBCDD**
	n	*31*	*31*	*31*	*31*	*31*	*31*	*32*	*32*	*32*	*32*
	Median	6,100	3,500	7.7	7	3.2	30	220	96	630	380

offices (ng/g)	**Range**	<13-1300,00	560-150,000	0.8-130	<0.2-160	<0.3-190	2.8-770	<0.1-4,400	18-710	8.8-3,300	84-5,200
	Mean	12,000	4,200	16	26	11	77	520	160	170	850
UK[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)
France[66]*								2,700 (540-6,400)	440 (140-1,500)	1,300 (312-6,400)	4,700 (1,100-10,000)
Beijing[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)
Australia[48]*		1,900 (nd-10,000)	1,500 (nd-7,200)	220 (40-540,0000	230 (46-1,000,000)	<MQL	(nd-920)				
Brazil[61]*		2000 (840-5000)	4200 (1800-25000)	13 (7.5-34)	30 (12-53)						
	n	*32*	*32*	*32*	*32*	*32*	*32*	*30*	*30*	*30*	*30*
schools (ng/g)	**Median**	10,000	8,100	5	5.1	<0.3	30	420	180	130	800
	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
	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)
Sweden[55]*		34 (<2.2-420)	54 (<4.1-1,200)								
Stockholm[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)
Brazil[61]*		300 (210-700)	420 (94-1,200)	8.2 (3.2-30)	33 (30-36)						

Table 2. Summary of Concentrations of BFRs (pg/m^3) in Indoor Air from Irish Homes, Cars, Offices and Schools and Median Concentrations from selected previous studies

location	statistical parameter	**DBDPE**	**BDE-209**	**BDE-47**	**BDE-99**	**BDE-183**	**∑tri-octa-BDEs**	**α-HBCDD**	**β-HBCDD**	**γ-HBCDD**	**∑-HBCDD**
	n	*28*	*28*	*28*	*28*	*28*	*28*	*32*	*32*	*32*	*32*
Homes (pg/m^3)	**Median**	48	410	2.1	6.1	<1.1	19	<0.3	<0.3	10	20
	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
	Mean	390	880	4.9	37	0.8	50	10	3.5	100	110
UK[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)
Sweden[52]			310 (43-1,100)								2 (<1.6-33)
Canada[33]		9.2 (na-74)	49 (nd-220)	39 (54-760)	5.3 (1.3-73)	1.3 (nd-1.6)					
Czech[33]		-	9.4 (nd-15)	1.6 (0.56-16)	0.29 (0.16-1.4)	0.12 (nd-0.23)					
USA[33]		42 (nd-71)	260 (nd-5,500)	52 (4.5-820)	15 (nd-1,300)	2.5 (nd-5)					
	n	*29*	*29*	*29*	*29*	*29*	*29*	*32*	*32*	*32*	*32*
Cars (pg/m^3)	**Median**	160	200	1.9	2.1	<1.1	11	8.9	<0.3	18	25
	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
	Mean	340	660	3.2	9.1	0.58	19	13	6.2	180	200
UK[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)	13,000 (190-69,000)[44]
Sweden[52]			400 (160-2,500)								0.0 (<1.6)
	n	*31*	*31*	*31*	*31*	*31*	*31*	*32*	*32*	*32*	*32*
Offices (pg/m^3)	**Median**	<15	240	3.4	4.2	0.55	15	<0.3	<0.3	9.6	14
	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
UK[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)
Sweden[52]			3,200 (68-5,800)								0.0 (<1.6)
	n	*31*	*31*	*31*	*31*	*31*	31	*32*	*32*	*32*	*32*
Schools (pg/m^3)	**Median**	220	410	2.3	3.1	<1.1	12	16	<0.3	22	38
	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
	Mean	460	1,600	5.2	9.5	0.54	21	33	160	96	280
Sweden[55]		<7.6	<32	17	<14	<2.1		<0.57	<0.41	<1.0	<2.0
Norway[71]		8.3	<MLD	130	23	<MLD	180				
South Korea[74]		-	0.21 (nd-3.6)	0.40 (nd-17)	0.28 (nd-13)	0.015 (nd-0.15)					

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 under typical[a] and high-end[b] exposure scenarios[c].

			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*
toddler	air	median	0.00019	0.000055	0.0037	0.0073	0.019	0.14	0.0008	0.0021	0.00020	0.0067
		high	0.020	0.0066	0.35	0.37	1.4	1.9	0.0083	0.11	0.0025	0.11
	dust	median	0.98	0.51	1.0	2.5	21	64	0.039	0.069	0.0054	0.25
		high	49	18	98	170	2,500	2,500	3.2	3.3	0.31	7.6
	total	median	0.98	0.51	1.0	2.5	21	64	0.040	0.071	0.0056	0.26
		high	49	18	99	170	2,500	2,500	3.2	3.4	0.31	7.7
UK[47]	*total*	*high*	*200*	*120*	*430*	*750*	*33*	*1,900*	*15*	*24*	*2.3*	*100*
school child	air	median	0.0008	0.00003	0.0028	0.0052	0.019	0.090	0.00048	0.0012	0.00012	0.0039
		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*		
RfDs[79,80]						**200,000**		**7,000**	**2,000**	**100**	**3,000**	

[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 m^3/d[29] for adults and 3.8 m^3/d toddlers and school children; dust: 20 mg/day for adults and 50 mg/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/day[29]).
[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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SUPPORTING INFORMATION

Full details of sampling (including air sampling rates), analytical (including QA/QC data), and exposure assessment methods; alongside detailed information about BFR concentrations in samples of indoor air and dust from different microenvironment categories in different locations in Ireland are provided as supporting information. This material is available free of charge via the Internet at http://pubs.acs.org

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