Emerging and legacy flame retardants in UK indoor air and dust

Tao, Fang; Abdallah, Mohamed Abou-Elwafa; Harrad, Stuart

DOI:

[10.1021/acs.est.6b02816](https://doi.org/10.1021/acs.est.6b02816)

License:

None: All rights reserved

Document Version

Peer reviewed version

Citation for published version (Harvard):

Tao, F, Abdallah, MA-E & Harrad, S 2016, 'Emerging and legacy flame retardants in UK indoor air and dust: evidence for replacement of PBDEs by emerging flame retardants?', *Environmental Science and Technology*.
<https://doi.org/10.1021/acs.est.6b02816>

[Link to publication on Research at Birmingham portal](#)

General rights

Unless a licence is specified above, all rights (including copyright and moral rights) in this document are retained by the authors and/or the copyright holders. The express permission of the copyright holder must be obtained for any use of this material other than for purposes permitted by law.

- Users may freely distribute the URL that is used to identify this publication.
- Users may download and/or print one copy of the publication from the University of Birmingham research portal for the purpose of private study or non-commercial research.
- User may use extracts from the document in line with the concept of 'fair dealing' under the Copyright, Designs and Patents Act 1988 (?)
- Users may not further distribute the material nor use it for the purposes of commercial gain.

Where a licence is displayed above, please note the terms and conditions of the licence govern your use of this document.

When citing, please reference the published version.

Take down policy

While the University of Birmingham exercises care and attention in making items available there are rare occasions when an item has been uploaded in error or has been deemed to be commercially or otherwise sensitive.

If you believe that this is the case for this document, please contact UBIRA@lists.bham.ac.uk providing details and we will remove access to the work immediately and investigate.

This document is confidential and is proprietary to the American Chemical Society and its authors. Do not copy or disclose without written permission. If you have received this item in error, notify the sender and delete all copies.

Emerging and legacy flame retardants in UK indoor air and dust: evidence for replacement of PBDEs by emerging flame retardants?

Journal:	<i>Environmental Science & Technology</i>
Manuscript ID	es-2016-02816t.R1
Manuscript Type:	Article
Date Submitted by the Author:	07-Oct-2016
Complete List of Authors:	Tao, Fang; University of Birmingham, Division of Environmental Health & Risk Management Abdallah, Mohamed; University of Birmingham, Division of Environmental Health & Risk Management Harrad, Stuart; University of Birmingham, Division of Environmental Health & Risk Management

SCHOLARONE™
Manuscripts

**Emerging and legacy flame retardants in UK indoor air and dust:
evidence for replacement of PBDEs by emerging flame retardants?**

Fang Tao¹, Mohamed Abou-Elwafa Abdallah^{1,2}, Stuart Harrad^{1}*

¹Division of Environmental Health and Risk Management,

School of Geography, Earth and Environmental Sciences,

University of Birmingham,

Birmingham, B15 2TT, UK.

²Department of Analytical Chemistry

Faculty of Pharmacy, Assiut University

71526 Assiut,

Egypt

* Corresponding author

E-mail: S.J.Harrad@bham.ac.uk

Tel.: +44 121 414 7298

fax: +44 121 414 3078.

Abstract

Concentrations of 27 emerging (EFRs) and legacy flame retardants (LFRs) were measured in samples of indoor air (n=35) and indoor dust (n=77) from UK homes and offices. All target compounds were detected in indoor air and dust samples. Relatively volatile EFRs (e.g. tetrabromoethylcyclohexane – DBE-DBCH) were more frequently detected in indoor air (detection frequencies > 60%), while less volatile EFRs (e.g. tetrabromobisphenolA-bis(2,3-dibromopropyl ether (TBBPA-BDBPE) and decabromodiphenyl ethane (DBDPE)) were predominant in dust. Concentrations of some EFRs (e.g. DBDPE) exceeded significantly those reported previously in UK dust ($p<0.05$), while concentrations of BDE-209 in office dust were significantly lower ($p<0.05$) than those reported previously in UK offices, consistent with the application of DBDPE as an alternative to the Deca-BDE formulation, of which BDE-209 is the principal constituent. Moreover, concentrations of BDEs 47 and 99 (both major constituents of the Penta-BDE product) in office air were significantly lower ($p<0.05$) than those in previous UK studies. Our results constitute important early evidence that restrictions on PBDEs have increased demand for EFRs in the UK, with the result that human exposure to PBDEs in UK homes and offices has decreased while exposure to EFRs has risen.

32 Introduction

33 Polybrominated diphenyl ethers (PBDEs) and hexabromocyclododecane (HBCDD) were among
34 the most extensively used brominated flame retardants (FRs) up to 2004.^{1,2} Since then, the Penta-
35 BDE and Octa-BDE commercial mixtures have been listed under the Stockholm Convention on
36 Persistent Organic Pollutants (POPs)³ and production and use of both commercial mixtures
37 phased out in Europe and North America.⁴ Additionally, use of Deca-BDE in the EU has been
38 banned in electrical and electronic applications since 1 July 2008⁵, and it is currently slated for
39 listing under the Stockholm Convention. Moreover, HBCDD has also been listed as a POP under
40 the same convention.⁶ Following these bans and restrictions on PBDEs and HBCDD
41 (collectively referred to as “legacy” flame retardants - LFRs), without concomitant relaxation of
42 flame retardancy regulations, there is potential for these products to be replaced by so-called
43 “emerging” flame retardants – EFRs – whose use is not restricted but that possess chemical
44 structures similar to those of LFRs.^{1,7} While this similarity is advantageous in the context of their
45 ability to impart flame retardancy; there are concerns it extends to their toxicity and adverse
46 environmental behavior – e.g. persistence and capacity for bioaccumulation.

47 While knowledge of environmental contamination with EFRs remains scant compared to our
48 understanding of LFRs like PBDEs; recent reports show a broad suite of EFRs including DBDPE,
49 1,2-bis(2,4,6-tribromophenoxy)ethane (BTBPE), 2-ethylhexyl-2,3,4,5-tetrabromobenzoate (EH-
50 TBB), bis(2-ethylhexyl)-tetrabromophthalate (BEH-TEBP), dechlorane plus (DDC-CO) and
51 TBBPA-BDBPE to be present in indoor dust from various countries including the USA⁸, China⁹,
52 Sweden¹⁰, Germany¹¹, Belgium¹² and the UK¹³. In a previous UK study, BTBPE and DBDPE
53 were detected in both office and home dust.¹³ However, very little is known about concentrations
54 of EFRs in indoor air. DBE-DBCH, pentabromotoluene (PBT), and hexabromobenzene (HBB)

were detected frequently in Swedish indoor air¹⁴, while Cequier et al.¹⁵ also found DBE-DBCH, PBT, HBB, DBDPE and pentabromobenzene (PBBz) in most indoor air samples from Norwegian households and primary schools.

EFRs like DBE-DBCH, BTBPE, DBDPE and DDC-CO display potential for persistence and bioaccumulation that exacerbates concern over their adverse human health effects.^{16–22} Moreover, animal studies suggest some EFRs pose health risks including: endocrine disruption (DBDPE, BTBPE, EH-TBB, BEH-TEBP and DBE-DBCH), neurodevelopmental and behavioural effects (EH-TBB, BEH-TEBP), hepatotoxicity (DBDPE), impaired reproductive physiology (DBDPE and DBE-DBCH), and gene expression (BTBPE); along with morphological abnormalities and mortality (DBE-DBCH), DNA damage (EH-TBB, BEH-TEBP and DBE-DBCH) and possibly cancer (DBE-DBCH).^{22–35}

This study measured 16 EFRs, 8 PBDEs, and 3 HBCDD diastereomers in indoor air and settled floor dust from UK homes and offices. Concentrations of EFRs and LFRs were compared with those in previous UK studies to evaluate whether restrictions on PBDEs and HBCDD have reduced concentrations in indoor environments. Moreover, given that unlike other EU member states, the UK has – since 1988 - flame retardancy regulations that apply to furniture and furnishings, we compared our concentrations of target FRs with those reported from other countries. In addition, we estimated exposure to our target FRs via inhalation and dust ingestion by UK adults and toddlers.

Materials and Methods

Sample collection

Air samples were collected from February to May 2015 in offices (n=20) and houses (n=15) in

Birmingham, UK using double-bowl passive air samplers containing a polyurethane foam disk (PUF) and a glass fiber filter (GFF) (further information in the Supporting Information (SI) section). Each sampler was deployed for ~45 days at a height of 1-2 m.³⁶ Sampling rates (m³/day) for PBDEs, HBCDDs and EFRs were derived from previously reported studies,³⁶⁻³⁸ with detailed information provided as SI. In summary, the air sampling rates used were: a uniform value of 1.677 m³/day for EFRs, and 1.74, 1.472, 0.992, 1.014, 0.685, 0.691, 0.55, 0.567, 0.807, 0.775, and 0.761 m³/day for BDEs-47, 99, 100, 153, 154, 183, and 209, plus α -, β -, and γ -HBCDD respectively.

Dust was collected in offices (n=42) and houses (n=30) between June 2013 and May 2015. Samples were collected using a standard protocol under normal office and house use conditions to reflect actual human exposure.¹³ (detailed information provided as SI). All dust samples were sieved through a pre-cleaned 500 μ m mesh sieve, homogenized thoroughly, transferred to clean glass vials and stored at -20 °C until analysis. Details of the sampling methods are provided as SI.

Analytical protocols

Samples were spiked with internal standards (¹³C-BDE 209, ¹³C-BTBPE, ¹³C-BEH-TEBP, BDE 77, BDE 128) before extraction. Air samples (combined PUF and GFF) and aliquots of dust samples (typically between 50 and 200 mg) were extracted with hexane/acetone (3:1, v/v) using pressurized liquid extraction (Dionex, ASE 350). Crude extracts were purified by washing with 3-4 mL concentrated sulfuric acid before reconstitution in 200 μ L (dust) and 50 μ L (air) iso-octane containing 250 pg/ μ L PCB-129 as recovery determination standard for quality assurance/quality control (QA/QC) purposes.

FRs were analyzed on a Trace 1310 gas chromatograph coupled to an ISQ™ single quadrupole

mass spectrometer (Thermo Scientific, TX, USA) operated in electron capture negative ionization (ECNI) mode. Two μL of cleaned extract were injected onto a Thermo Scientific TraceGOLD (TG)- Standard Quality Control (SQC) column ($15\text{ m} \times 0.25\text{ mm} \times 0.25\text{ }\mu\text{m}$) using a programmable-temperature vaporizer injector in solvent vent mode.³⁹ After gas chromatography/mass spectrometry (MS) analysis, samples were evaporated and reconstituted in 200 μL of methanol containing $\text{d}_{18}\text{-}\gamma\text{-HBCDD}$ (25 $\text{pg}/\mu\text{L}$) as recovery determination standard for determination of HBCDDs by liquid chromatography (LC)-MS/MS.⁴⁰ Quality assurance included method and field blanks. Five-point calibration curves were constructed for each target compound with excellent linearity ($R^2 > 0.99$) over a concentration range relevant to those in samples. Average internal standard recoveries were: $113 \pm 17\%$ (BDE-77), $115 \pm 15\%$ (BDE-128), $98 \pm 21\%$ (^{13}C -BEH-TEBP), $108 \pm 27\%$ (^{13}C -BTBPE), and $95 \pm 28\%$ (^{13}C -BDE-209). Method accuracy and precision were evaluated via replicate analyses ($n=6$) of NIST SRM 2585 (organics in indoor dust). Detailed description of analytical methods and QA/QC measurements is provided as SI.

Statistical Analysis

Statistical analysis was conducted using Excel (Microsoft Office 2010) and IBM SPSS Statistics 21.0 (Chicago, IL, U.S.A.). Independent t-tests and ANOVA analyses were only conducted for target compounds with detection frequencies $\geq 60\%$. Where analyte peaks $< \text{LOQ}$, concentrations of target compounds were assumed to equal $\text{LOQ}/2$. Statistical analysis was performed on log-transformed concentrations, as concentrations in all data sets were revealed to be log-normally distributed using Kolmogorov-Smirnov test and visual inspection of quantile-by-quantile graphic plots. A p -value < 0.05 was considered significant.

Results and discussion

Levels of FRs in indoor air

All target FRs were detected in indoor air from UK homes and offices (Table 1).

EFRs

In both homes and offices, more volatile EFRs (DBE-DBCH, PBBz, PBT, HBB, tetrabromo-*o*-chlorotoluene (TBCT), 1,2,4,5-tetrabromo-3,6-dimethylbenzene (TBX), pentabromoethylbenzene (PBEB), and 2,3-dibromopropyl 2,4,6-tribromophenyl ether (TBP-DBPE)) showed higher detection frequencies in air (DF > 60%), while the less volatile DDC-CO and TBBPA-BDBPE were only detected in <20% of samples (Table 1). This is likely attributable to greater indoor use of these chemicals coupled with their relatively higher vapor pressures and lower K_{OA} values (Table S3). The most abundant compounds in air were α - and β -DBE-DBCH, which when summed as Σ DBE-DBCH account for 63% and 80% of Σ EFRs in home and office air respectively. Median concentrations of Σ DBE-DBCH in home and office air were 110 and 290 pg/m^3 respectively, which exceeds slightly those reported in Norwegian households (77.9 pg/m^3), classrooms (46.6 pg/m^3)¹⁵ and in Swedish indoor microenvironments (55 pg/m^3).¹⁴ We are aware of only one commercial DBE-DBCH formulation (Saytex BCL-462), which contains equal amounts of the two diastereomers, α - and β -DBE-DBCH.⁴¹ The ratio of β - to α -DBE-DBCH ($f_{\beta\text{-DBE-DBCH}}$) here ranged from 0.5 to 1.0, with a median value of 0.7, which is lower than in the commercial product. This is the first report of $f_{\beta\text{-DBE-DBCH}}$ in indoor air, which precludes comparison to other studies. Possible explanations for the different isomer distribution in air compared to the commercial product include: differences in physicochemical properties (e.g. vapour pressure) or atmospheric degradation between the two diastereomers and possible

isomerisation post-emission. The latter explanation appears unlikely, as thermal conversion of the DBE-DBCH isomers occurs ≥ 125 °C.⁴¹ However, such high temperatures could occur during incorporation of DBE-DBCH into polymers. Consequently, $f_{\beta\text{-DBE-DBCH}}$ values in indoor air in this study may reflect the pattern present in DBE-DBCH-treated items rather than that in the commercial formulation.

Other frequently detected EFRs in air were: EH-TBB, BEH-TEBP and BTBPE. EH-TBB and BEH-TEBP were major constituents of Firemaster 550 and Firemaster BZ-54.⁴² BEH-TEBP was also used in the flame retardant DP-45⁴² and as a plasticizer in polyvinyl chloride and neoprene.⁴³ The fraction of EH-TBB $f_{\text{EH-TBB}} = \text{EH-TBB}/(\text{EH-TBB} + \text{BEHTBP})$. The $f_{\text{EH-TBB}}$ value was 0.77 ± 0.03 in Firemaster 550 and 0.70 in Firemaster BZ-54.⁴³ The values of $f_{\text{EH-TBB}}$ in indoor air here are 0.03-0.99 (median=0.64) which is comparable to those reported in indoor air from Canada (0.3-0.99; median=0.83)⁴⁴, the USA (0.16-0.95; median=0.63)⁴⁴ and the Czech Republic (0.27-0.89; median=0.72)⁴⁴ and outdoor air from Toronto, Canada (0.69)⁴⁵ and Chicago, the USA (0.70)⁴⁶ but higher than outdoor air from the Great Lakes area (0.26-0.54)⁴² and Canada's Western Sub-Arctic (0.48)⁴⁷. Such variation in $f_{\text{EH-TBB}}$ ratios between studies may be attributable to different applications of BEH-TEBP across jurisdictions.

DFs of BTBPE, EH-TBB and BEH-TEBP exceed 70% in both microenvironment categories in this study (Table 1). This exceeded DFs (>33%, with BTBPE not detected at all) for the same compounds in Norwegian and Swedish air).^{14,15} This apparent greater detection of these EFRs in UK indoor air is at least partly attributable to the lower limits of quantitation (LOQs) in our study (BTBPE, EH-TBB and BEH-TEBP were 1.0, 0.1 and 0.1 pg/m³) compared to the Scandinavian studies for which LOQs for BTBPE, EH-TBB and BEH-TEBP were 31, 330 and 35 pg/m³ in the Swedish study and 15.7, 7.4 and 2.9 pg/m³ in the Norwegian study.^{14,15} While no

166 production information is available for the UK or the EU, both EH-TBB and BEH-TEBP are
167 reported replacements for Penta-BDE, and BTBPE a replacement for Octa-BDE.⁷ It is therefore
168 possible that following phase out of LFRs, these EFRs were more widely used in the UK than
169 Norway and Sweden as a result of the UK's 1988 Furniture and Furnishings (Fire) (Safety)
170 Regulations that differ substantially from those elsewhere in Europe.⁴⁸

171 *PBDEs*

172 BDEs-28, 47, 100, 99, and 209 were more frequently detected (DFs >85%) than other PBDEs
173 (Table 1). Concentrations of Σ PBDEs (defined as the sum of PBDEs-28, 47, 100, 99, 154, 153,
174 183 and 209) were 36-6400 pg/m³ (median=280 pg/m³) in UK homes. Notwithstanding slight
175 differences in the congeners constituting Σ PBDEs in different studies, the range of Σ PBDE
176 concentrations reported here, is comparable to studies conducted in the USA (210-3980 pg/m³)
177 and Sweden (72-1400 pg/m³), but higher than Germany (8.24-47 pg/m³), Australia (0.5-179
178 pg/m³) and Japan (17-55 pg/m³)⁴⁹⁻⁵³. Concentrations of Σ PBDEs were 22-600 pg/m³ (median=54
179 pg/m³) in UK offices, similar to Australia (15-487 pg/m³) but much lower than USA (21-17200
180 pg/m³) and Sweden (140-7300 pg/m³)⁴⁹⁻⁵⁴. BDE-209 predominated in homes and offices,
181 contributing 73% and 50% of the total atmospheric PBDEs, respectively. This dominance of
182 BDE-209 matches broadly that in Sweden⁵⁰, Germany⁵¹, Australia⁵², and Japan⁵³. In contrast,
183 BDE-47 and BDE-99 predominated in USA homes⁴⁹ and offices⁵⁴. This different pattern in the
184 USA is likely due the far more extensive use of Penta-BDE in USA (94.7% of global Penta-BDE
185 demand) than other countries⁵⁵.

186 *HBCDDs*

187 In homes, concentrations of Σ HBCDDs were 19-1500 pg/m³ (median=110 pg/m³), comparable

to previously reported concentrations in UK houses (67-1300 pg/m³; median=180 pg/m³).⁵⁶ By comparison, Σ HBCDDs in our offices (median=41 pg/m³) were lower than those reported previously in UK offices (median=170 pg/m³).⁵⁶ Elsewhere, concentrations of Σ HBCDDs in offices, apartments, stores and two schools in Sweden (<1.3-19 pg/m³)¹⁴ were exceeded substantially by those reported here. On average, the HBCDD isomer distribution was 87% γ -HBCDD, 8% α -HBCDD, and 5% β -HBCDD in homes, and 71% γ -HBCDD, 18% α -HBCDD, and 11% β -HBCD in offices. This pattern is similar to previous reports for UK and Swedish indoor air^{14,56}.

Relative abundance of FRs in indoor air

PBDEs predominated in homes, contributing 44% Σ FRs, while EFRs predominated in offices, accounting for 83% Σ FRs. Σ HBCDDs contributed 18% and 8% Σ FRs in homes and offices, respectively (Figure S2, SI). The comparatively high abundance of EFRs in both offices (38%) and homes, suggests their widespread use in the UK. The far greater abundance of EFRs in offices could be attributable to different and greater numbers of sources in offices compared to homes, and also reflect a more rapid turnover of such source items in offices – i.e. putative FR sources such as foam filled office furniture and electronic and electrical equipment are more frequently replaced in offices. Such rapid “turnover” of old source items containing LFRs with new replacements containing EFRs, may explain the predominance of the latter in offices.

Levels of FRs in indoor dust

Table 2 summarises the concentrations of target FRs in UK homes and office dust.

208 *EFRs*

209 In contrast to air, less volatile compounds were more frequently detected in office and home dust.
210 These include: DDC-CO, TBBPA-BDBPE and DBDPE (DF>60%) (Table 2). Of note is the very
211 high concentration of 4,700,000 ng/g BTBPE detected in one office dust sample, which to the
212 authors' knowledge is the highest BTBPE level reported in indoor dust to date. We are unable to
213 explain this high concentration based on a survey of putative FR-treated items in the sampled
214 office. TBBPA-BDBPE was the most abundant compound, comprising 87% and 71% Σ EFRs in
215 homes and offices based on median concentrations, followed by BEH-TEBP, BTBPE, and
216 DBDPE. TBBPA-BDBPE was also the predominant EFR detected previously in UK classroom
217 dust, accounting for an average of 48% Σ EFRs,¹² indicating its extensive UK use. Concentrations
218 of TBBPA-BDBPE in this study exceeded those in Belgian homes and offices¹² and USA homes⁸.
219 In office dust, concentrations of BTBPE, BEH-TEBP, and DBDPE in this study were comparable
220 to those in offices in Beijing, China⁵⁷ but exceeded those in Belgian offices¹². For house dust, our
221 concentrations were comparable to those in Belgium, New Zealand, Germany, Sweden, and
222 Norway but lower than those found in USA and Canada.^{8,10-12,15,58-60} In studies not targeting
223 TBBPA-BDBPE; the most abundant EFRs in house dust from Norway, Germany, Sweden, USA
224 and China were DBDPE and BEH-TEBP^{8-11,15}. We observed a similar abundance of DBDPE and
225 BEH-TEBP. Our data also represent the first report of DDC-CO in UK indoor dust at median
226 concentrations of 5.7 and 73 ng/g in homes and offices, respectively. The contribution of *anti*-
227 DDC-CO to Σ DDC-CO (expressed as f_{anti}) in the technical mixture is 0.65–0.75.¹⁵ By
228 comparison, f_{anti} values in our indoor dust samples are 0.27-0.99. This wider range is similar to
229 previous studies of indoor dust from Canada, China and Sweden.^{14,60,61} Similar to DBE-DBCH in
230 air, plausible explanations include: isomer-specific degradation, variable environmental

behaviour arising from different physicochemical properties, as well as possible thermal isomerization during incorporation of DDC-CO into consumer products.

DBE-DBCH was detected in all indoor dust samples underlining its wide UK application. $f_{\beta\text{-DBE-DBCH}}$ in indoor dust was 0.32-2.88 (median=0.85). This median value is lower than in the commercial product. Interestingly, $f_{\beta\text{-DBE-DBCH}}$ values in indoor dust significantly exceed those in indoor air ($p<0.01$). Few studies have addressed isomer-specific aspects of DBE-DBCH. Wong et al.⁶³ reported the fate of DBE-DBCH in urban soil, with β -DBE-DBCH showing a slightly higher soil-air partition coefficient (K_{SA}) than α -DBE-DBCH, indicating β -DBE-DBCH to be less volatile than α -DBE-DBCH. This may provide a plausible explanation for the observed low $f_{\beta\text{-DBE-DBCH}}$ in indoor air and dust compared to the commercial formulation. Combined with the reported slightly faster degradation rate of α - compared to β -DBE-DBCH⁶³, this may contribute to the significantly lower $f_{\beta\text{-DBE-DBCH}}$ observed in indoor dust compared to air. The fate of DBE-DBCH isomers in the environment, the reasons for different isomeric profiles in various matrices and possible implications of such variations on exposed organisms are a research priority.

PBDEs

Each target PBDE was detected in >90% of indoor dust samples except for BDE-28 and BDE-47 (Table 2). In house dust, concentrations of Σ PBDEs were 180-370000 ng/g (median=4600 ng/g). This exceeds those reported in other countries like: Germany (36.6-1580 ng/g), Denmark (65-61524), Sweden (53-4000 ng/g), USA (920-17000 ng/g), Belgium (4-6509 ng/g), and China (132-3887 ng/g) but is comparable to Canada (170-170000 ng/g).^{51,52,64-68} In our office dust samples, concentrations of Σ PBDEs were 270-110000 ng/g (median=3000 ng/g). This is comparable to the USA, Sweden and China but higher than Belgium.^{51,55,67,69} Similar to previous

UK studies, BDE-209 predominated in dust, contributing 99% and 94% Σ PBDEs in homes and offices, respectively. This predominance of BDE-209 concurs with other countries in Europe and Asia, but is more marked than in North America, where greater use of Penta-BDE leads to a greater contribution from BDEs-47 and 99.^{51,52,55,64-67,69} The substantially higher concentrations of BDE-209 in UK indoor dust compared to other European countries, may be attributed to the extensive UK use of Deca-BDE in upholstery fabrics and textiles (1,000-1,200 tonnes/year out of an estimated 1,500 tonnes/year in the EU for this application) to comply with the UK Furniture and Furnishing Fire Safety Regulations 1988.⁷⁰

HBCDDs

HBCDDs were detected in all samples. Σ HBCDDs concentrations in homes were 50-110000 ng/g (median=610 ng/g) in homes, which compares closely with those previously detected in UK house dust (140-140000 ng/g)⁵⁷. In office dust, concentrations of Σ HBCDDs were 150-6400 ng/g (median=1700 ng/g). This is also in line with previous UK data (90-6600 ng/g).⁵⁷ Our Σ HBCDDs concentrations in office and house dust exceeded those in dust from offices, apartments, stores and two schools in Sweden (17-2900 ng/g).¹⁴ In our study, α -HBCDD was the dominant contributor to Σ HBCDD in home and office dust. The average isomer profile was 53% α -HBCDD, 29% γ -HBCDD, and 18% β -HBCDD in homes, while for offices; it was 56% α -HBCDD, 27% γ -HBCDD, and 17% β -HBCDD. This pattern differs from that in indoor air. To investigate whether the difference is statistically significant, fractional contributions of α -HBCDD and γ -HBCDD to Σ HBCDD detected in matched pairs (n=32) of indoor air and dust samples, i.e. collected from the same room at the same time were compared. Similar to a previous UK study, we found greater relative abundance of α -HBCDD in dust relative to air,

with the opposite observed for γ -HBCDD ($p < 0.001$). As previously, we attribute this to a post-depositional shift from γ -HBCDD to α -HBCDD, and/or preferential degradation of γ -HBCDD in indoor dust.⁵⁷

Relative abundance of FRs in indoor dust

Similar to indoor air, PBDEs predominated in house dust, contributing 66 % Σ FRs, while EFRs dominated in office dust, accounting for 51% Σ FRs. Σ HBCDDs contributed 9% and 17% Σ FRs in home and office dust, respectively (Figure S3).

Temporal trends in UK indoor contamination

EFRs

To our knowledge, these are the first data about concentrations of EFRs in UK indoor air. Consequently, comparison with previous studies is not possible. With respect to indoor dust however, concentrations of BTBPE and DBDPE in dust taken from homes ($n=30$) and offices ($n=18$) in the West Midlands collected between July 2006 and June 2007 exist¹³. Following log-transformation of concentrations, we conducted a t-test to compare concentrations in these two studies. For house dust, concentrations of BTBPE in our study were statistically indistinguishable to the previous study ($p > 0.05$); in contrast, concentrations of DBDPE exceeded significantly ($p < 0.05$) those in the earlier study. Moreover, t-test comparison revealed concentrations of BTBPE and DBDPE in our office dust samples were both significantly higher than those reported previously ($p < 0.05$).¹³ While based on a relatively limited number of samples, these findings suggest restrictions on LFRs have led to a concomitant increase in concentrations in UK indoor dust of DBDPE and – to a lesser extent – BTBPE.

296 *PBDEs*

297 Two previous studies have reported concentrations of PBDEs in UK indoor air. The first reported
298 concentrations of BDE-47, 99, 100, 153, and 154 in air from offices and homes using high-
299 volume active air samplers from 2001-2002⁷¹; while the second - conducted between September
300 2003 and November 2005 - measured BDE-28, 47, 49, 66, 85, 99, 100, 153, and 154 using
301 double-bowl passive air samplers containing a PUF disk⁷². For home air, no significant
302 difference was observed between our study and the two previous studies^{71,72}. By comparison, for
303 office air, concentrations of BDE 47 and 99 were significantly lower than in previous studies
304 (ANOVA test of log transformed concentrations, $p < 0.05$)^{71,72}. We are aware of the potential
305 difficulties of comparing concentrations derived using different air sampler configurations. Two
306 studies that examined such difficulties are: (a) Melymuk et al. (2012), who found no major
307 differences between PBDE concentrations derived using passive air samplers and high volume
308 active samples; and (b) Abdallah and Harrad (2010), who found no significant difference
309 between indoor air concentrations of BFRs including PBDEs measured using both passive and
310 low volume active samplers. On the basis of these previous studies, we conclude the influence of
311 the different sampling methods used in the three studies compared here, should not overly
312 obscure the temporal trend.

313 Concentrations of BDE-209 in UK office dust were significantly lower ($p < 0.05$) than those
314 reported in a previous study of UK offices¹³; while for UK house dust, BDE-209 concentrations
315 were comparable ($p > 0.05$) to those reported previously¹³, perhaps indicating more rapid removal
316 of “legacy” PBDEs in offices than homes. No significant temporal differences were found for
317 other PBDEs in both home and office dust. We attribute the lack of a decline in BDEs- 47 and 99
318 in dust (in contrast to air) to the different sample populations for air and dust.

319 *HBCDDs*

320 We compared our data for HBCDDs in indoor air with those in the previous UK study⁵⁷ by
321 independent t-test. In domestic air, no significant differences were detected; in contrast,
322 concentrations of γ -HBCDD were significantly lower in office air in our study ($p < 0.001$)
323 (α -HBCDD and β -HBCDD were not compared as DFs were $< 60\%$). This may possibly indicate
324 replacement of HBCDDs by EFRs such as DBE-DBCH in expanded polystyrene for building
325 insulation¹⁴. For indoor dust, our concentrations of γ -HBCDD in house dust were significantly
326 lower ($p < 0.001$) than in the previous study⁵⁷ but not for other diastereomers and Σ HBCDDs. No
327 significant differences were observed for office dust.

328

329 **Comparisons between indoor microenvironments**

330 Previous studies of both air and dust revealed differences in concentrations of FRs between
331 offices and homes^{13,67,71,72}. Such differences are likely due to the different types and abundance
332 of FR sources in these two microenvironment categories. We therefore examined our data for
333 such differences.

334 *Indoor air*

335 We compared concentrations in home and office air using an independent t-test. For EFRs, DBE-
336 DBCH, PBBz and EH-TBB were significantly higher in offices than homes ($p < 0.001$ for DBE-
337 DBCH, $p < 0.05$ for PBBz and EH-TBB), with no significant differences between homes and
338 offices detected for other EFRs. For PBDEs, concentrations of BDE-209 were significantly
339 higher in homes than offices ($p < 0.005$); but no differences were found for other congeners. In

contrast, previous studies in West Midlands indoor air focusing on tri- to hexa-BDEs found concentrations in offices to exceed those in homes ($p < 0.05$).^{71,72} Finally, for HBCDDs, concentrations of γ -HBCDD were significantly higher ($p < 0.005$) in homes than offices. (α -HBCDD and β -HBCDD were not compared as their DFs were $< 60\%$).

Indoor dust

For indoor dust, statistical analysis revealed concentrations of DBE-DBCH, EH-TBB, BEH-TEBP, BTBPE, DDC-CO and DBDPE in offices exceeded significantly those in homes. No significant differences between offices and homes were found for other EFRs.

In contrast to our observations for air, BDE-209 concentrations in homes and offices were comparable ($p > 0.05$), while for BDE-47 and BDE-99, concentrations in offices exceeded significantly ($p < 0.001$) those in homes. This result concurs with previous studies of PBDEs in Belgian and UK home and office dust^{13,67}. We attribute the differences between air and dust (e.g. BDE-209 higher in homes than offices for air but dust) to the larger number of dust samples collected.

For HBCDDs, no significant differences were detected between concentrations of Σ HBCDDs in dust from homes and offices ($p > 0.05$); consistent with a previous study⁵⁷.

Correlations between FRs in the studied microenvironments

To investigate potential common sources of our FRs. Pearson correlation analysis was applied to assess relationships between the target compounds (Table S5 and 6). α -DBE-DBCH concentrations correlated significantly with those of β -DBE-DBCH in both air and dust samples ($p < 0.001$) with similar findings observed for HBCDD diastereomers. Significant correlations

between concentrations of tetra- to hexa-BDEs were observed in indoor air and dust ($p < 0.05$), with BDE-183 correlated with BDE-47 ($p < 0.005$), BDE-100 ($p < 0.05$), BDE-153 ($p < 0.01$) and BDE-154 ($p < 0.001$) in indoor dust. This probably reflects the presence of these congeners in Penta-BDE and Octa-BDE.

For EFRs, PBBz was correlated significantly with PBEB, TBP-DPTE and HBB in indoor air and dust. HBB also correlated with PBEB and TBP-DPTE in indoor air ($p < 0.001$), with HBB and PBBz correlated with BDE-28, 47 and 99 in air and dust ($p < 0.05$). While some of these observed correlations are hard to rationalise and may have occurred by chance; those between PBEB, HBB and PBBz may originate from a common source resulting from thermal degradation of polymeric FRs. Conditions that may favour such formation may be encountered during the process of incorporating these FRs into goods – i.e. the elevated temperatures experienced by FRs when incorporated into molten polymers.^{74–76}

Correlations between FR concentrations in air and dust

If semi-volatile organic compounds (SVOCs) partitioning between the gaseous and particulate phases have reached equilibrium under ideal conditions, their concentrations in air and dust should correlate.⁷⁷ To investigate this hypothesis, Pearson correlation analysis was conducted to investigate the relationship between FR concentrations in matched air and dust samples ($n=30$, Table S7). Significant correlations between concentrations of EFRs in air and dust were observed ($p < 0.005$), especially for the more volatile EFRs, e.g. DBE-DBCH and PBT. Moreover, concentrations of BDE-28 and 47 in air and dust were also significantly correlated ($p < 0.05$). The partition coefficient between dust and air is expressed as K_{DA} ($K_{DA} = C_{dust}/C_{air}$, where C_{dust} and C_{air} are the concentrations of FR in dust and air, respectively). Median values of Log K_{DA} in

homes and offices were linearly associated with K_{OA} values of the studied FRs (Figure S4), suggesting thermodynamic equilibrium to exist between air and dust for most target FRs. Similar relationships were reported by Cequier et al.⁴¹ for PFRs and PBDEs in Norwegian homes and classrooms who concluded knowledge of concentrations of FRs in either air or dust permits prediction of their levels in the other phase given the K_{OA} of the compound in question.⁴¹

No correlation between Log K_{DA} and K_{OA} of HBCDD diastereomers was found. This is consistent with the previously observed post-depositional transformation in dust of HBCDDs.^{57,78}

Exposure to FRs via inhalation and dust ingestion

Human exposure to FRs via inhalation and dust ingestion was estimated based on concentrations reported here. The algorithms and assumptions applied to estimate exposure via different routes are provided in SI. These data are important – especially for the EFRs – as they facilitate: (a) evaluation of the relative importance of inhalation as opposed to dust ingestion (and dietary exposure once such data are available) for different chemicals, and (b) future risk assessment by comparison of exposure with health-based limit values once set. Median estimated exposure for toddlers via air inhalation to Σ EFRs, Σ PBDEs and Σ HBCDDs was 0.66, 0.43 and 0.14 ng/day, respectively. For adults, estimated exposure via inhalation to Σ EFRs, Σ PBDEs and Σ HBCDDs was 4.3, 2.0 and 2.1 ng/day, respectively. Our estimated inhalation exposures to Σ tri-hexa BDEs (Table 3) were comparable to those reported previously for UK toddlers and adults (0.16 and 0.82 ng/day respectively)⁷². There are no previous estimates of human exposure to BDE-209 via inhalation in the UK. For Σ HBCDDs, Abdallah et al.⁵⁷ reported median daily intakes of 0.8 and 3.9 ng/day for UK toddlers and adults, slightly exceeding our estimates (Table 3).

The main contributors to adult inhalation exposures were: α -DBE-DBCH, β -DBE-DBCH, BDE-209 and γ -HBCDD, contributing 21%, 14%, 17% and 24% to the median Σ FRs exposure, respectively. Similar findings were observed for toddlers (Figure 1 and Figure S5 and 6).

Estimates of “typical” exposure for toddlers (i.e. dust contaminated at the median concentration ingested at the mean dust ingestion rate) to Σ EFRs, Σ PBDEs and Σ HBCDDs were 38, 280 and 25 ng/day, respectively. For adults, “typical” exposures to Σ EFRs, Σ PBDEs and Σ HBCDDs were 27, 100 and 15 ng/day, respectively. Harrad et al.¹³ reported “typical” exposure of toddlers and adults to Σ PBDEs via dust ingestion to be 234.3 and 612.6 ng/day respectively, which in both instances exceeds our exposure estimates (Table 3). A previous study reported UK exposure to Σ HBCDDs via dust ingestion to be 86.9 and 32.5 ng/day for toddlers and adults respectively, which also exceeds our current estimates (Table 3)⁵⁷. For EFRs, our “typical” exposure estimates for UK adults and toddlers via dust ingestion exceed substantially those reported in a previous study¹² (Table 3). While this suggests UK exposure to LFRs via dust ingestion is decreasing, a substantial increase in exposure to EFRs is a potential cause for concern.

Under our “typical” exposure scenario, dust ingestion is a more significant contributor to human exposure to Σ EFRs, Σ PBDEs and Σ HBCDDs than air inhalation (Table 3). This is similar to the findings of previous studies on PBDEs and HBCDDs^{57,72}. For toddlers’ intake of FRs, dust ingestion was more important than air inhalation for all target compounds. However, for FRs with relatively high vapor pressures (e.g. DBE-DBCH and BDE-28), inhalation contributes more to UK adult exposure than dust ingestion (Table 3).

Acknowledgment

This research is supported by a Li Siguang scholarship to Fang Tao funded by the China

427 Scholarship Council and the University of Birmingham. We gratefully acknowledge all the
428 participants for their permission to collect air and dust samples in this study.

429 **Supporting Information**

430 Full details of the analytical protocols, QA/QC measurements and human exposure assessment
431 models are provided as supporting information. This material is available free of charge via the
432 Internet at <http://pubs.acs.org>.

Figures

Figure 1. Relative contribution (expressed as %) of different target FRs to the overall daily exposure (ng/day) of UK toddlers and adults via inhalation and dust ingestion.

Tables

Table 1. Descriptive Statistics for Concentrations (pg/m³) of target FRs in UK indoor air

Statistical Parameter	Homes					Offices				
	This study, n=15				UK previous studies	This study, n=20				UK previous studies
	DF	Mean	Median	Range	Range	DF	Mean	Median	Range	Range
α-DBE-DBCH	100%	99	64	17-350	--	100%	180	160	74-440	--
β-DBE-DBCH	100%	74	45	13-250	--	100%	140	120	41-300	--
TBX	100%	31	9.7	1.6-190	--	100%	16	14	2.6-38	--
PBBz	93%	6.6	5.3	<0.10-22	--	100%	16	11	3.1-47	--
TBCT	60%	22	9.9	<0.10-240	--	65%	1.6	<0.10	<0.10-11	--
PBT	100%	17	11	2.3-63	--	65%	15	4.7	<0.10-200	--
PBEb	100%	1.6	1.3	0.41-5.4	--	100%	4.2	1.7	0.31-35	--
TBP-DBPE	93%	3.5	2	<0.40-14	--	85%	18	1.9	<0.40-280	--
HBB	73%	11	4.2	<0.20-91	--	85%	19	9.4	<0.20-170	--
EH-TBB	100%	4.8	2	0.05-44	--	100%	22	5.3	0.67-240	--
BTBPE	73%	11	5	<1.0-50	--	100%	32	11	0.7-220	--
BEH-TEBP	93%	10	2.1	<0.10-130	--	90%	2.2	1.4	<0.10-11	--
syn-DDC-CO	7%	<2.0	<2.0	<2.0-4.6	--	5%	1.3	<2.0	<2.0-7.7	--
anti-DDC-CO	20%	2.2	<1.2	<1.2-20	--	5%	1.8	<1.2	<1.2-24	--
TBBPA-BDBPE	20%	13	<10	<10-87	--	5%	7.3	<10	<10-50	--
DBDPE	40%	26	<10	<10-97	--	5%	7.5	<10	<10-54	--
BDE28	100%	22	1.2	0.21-310	<dl-60.8 ^b	100%	4.3	2.7	0.81-13	<dl-43.5 ^b
BDE47	100%	120	13	0.15-1700	45-1330 ^a ; 1.9-106.9 ^b	100%	44	6	0.15-380	58-7140 ^a ; 4.0-567.6 ^b
BDE100	87%	44	1.5	<0.10-600	2.6-82 ^a ; <dl-26.5 ^b	85%	3	1.5	<0.10-17	4.1-1450 ^a ; <dl-142.4 ^b
BDE99	100%	130	12	0.05-1700	8.7-209 ^a ; <dl-80.4 ^b	100%	9.2	7.9	1.2-42	9.0-6510 ^a ; 3.9-633.5 ^b
BDE154	53%	14	1.2	<0.50-180	<1.0-6.0 ^a ; <dl-16.5 ^b	40%	0.78	<0.50	<0.50-6	<1.0-228 ^a ; <dl-12.8 ^b
BDE153	67%	24	1.8	<0.4-180	<1.0-6.1 ^a ; <dl-20.5 ^b	55%	0.6	<0.4	<0.4-3.6	<1.0-181 ^a ; <dl-7.0 ^b
BDE183	27%	2.8	<1.0	<1.0-12	--	10%	<1.0	<1.0	<1.0-3.8	--
BDE209	100%	660	170	23-3800	--	100%	74	26	2.3-350	--
α-HBCDD	40%	43	<2.6	<2.6-400	14-430 ^c	59%	8.8	5.4	<2.6-31	18-87 ^c
β-HBCDD	47%	17	<2.2	<2.2-160	5-54 ^c	53%	5.2	<2.2	<2.2-15	14-34 ^c
γ-HBCDD	100%	270	110	16-1400	39-710 ^c	100%	55	34	3.1-320	43-370 ^c
Σ HBCDDs	--	320	110	19-1500	67-1300 ^c	--	69	41	5.5-360	70-460 ^c

a) Harrad, S.; Wijesekera, R.; Hunter, S.; Halliwell, C.; Baker, R. Preliminary Assessment of UK Human Dietary and Inhalation Exposure to

441 Polybrominated Diphenyl Ethers. Environ. Sci. Technol. 2004, 38 (8), 2345; b) Harrad, S.; Hazrati, S.; Ibarra, C. Concentrations of
442 Polychlorinated Biphenyls in Indoor Air and Polybrominated Diphenyl Ethers in Indoor Air and Dust in Birmingham, United Kingdom:
443 Implications for Human Exposure. Environ. Sci. Technol. 2006, 40 (15), 4633.; c) Abdallah, M. A.-E.; Harrad, S.; Covaci, A.
444 Hexabromocyclododecanes and Tetrabromobisphenol-A in Indoor Air and Dust in Birmingham, UK: Implications for Human Exposure. Environ.
445 Sci. Technol. 2008, 42 (18), 6855.

446

447 **Table 2.** Descriptive Statistics for Concentrations (ng/g) of target FRs in UK indoor dust

Statistical Parameter	Homes					Offices				
	This study, n=45				UK previous studies	This study, n=47				UK previous studies
	DF	Mean	Median	Range	Range	DF	Mean	Median	Range	Range
α -DBE-DBCH	100%	9.4	5.9	1.4-52	--	100%	23	15	2.5-130	--
β -DBE-DBCH	100%	12	6.2	1.5-77	--	100%	18	13	2.7-120	--
TBX	80%	18	1.4	<0.010-410	--	98%	3.2	2.1	<0.010-19	--
PBBz	87%	3.3	2.2	<0.010-12	--	91%	4.5	3.3	<0.010-23	--
TBCT	40%	21	<0.010	<0.010-300	--	67%	11	3.4	<0.010-68	--
PBT	67%	7.1	1.8	<0.010-90	--	87%	6	2.5	<0.010-59	--
PBEB	87%	2.3	0.78	<0.010-21	--	100%	2	1.4	0.36-10	--
TBP-DBPE	84%	6.6	1.8	<0.050-47	--	98%	24	4.7	<0.050-370	--
HBB	75%	1.8	<0.030	<0.030-12	--	91%	14	9.9	<0.030-84	--
EH-TBB	94%	21	10	<0.010-85	--	91%	120	31	<0.010-2000	--
BTBPE	100%	14	5.6	0.01-110	<dl-1900 ^a	100%	100000	160	0.019-4700000	<dl-40 ^a
BEH-TEBP	100%	240	65	16-3500	--	100%	1000	160	54-25000	--
<i>syn</i> -DDC-CO	63%	3.6	0.77	<0.26-28	--	98%	60	11	<0.26-640	--
<i>anti</i> -DDC-CO	84%	21	4.9	<0.15-170	--	98%	210	62	<0.15-2100	--
TBBPA-BDBPE	100%	5800	1000	71-49000	--	100%	3400	2300	310-14000	--
DBDPE	60%	240	41	<1.2-2300	<dl-3400 ^a	96%	1600	440	<1.2-17000	<dl-860 ^a
BDE28	57%	1.9	0.16	<0.03-15	<dl-2.1 ^a	82%	3.9	2.6	<0.03-22	<dl-11 ^a
BDE47	77%	14	13	<0.04-50	1.2-58 ^a	100%	83	37	7.1-660	2.6-380 ^a
BDE100	100%	4.2	3	0.75-16	<dl-17 ^a	100%	18	12	1.9-120	<dl-79
BDE99	100%	31	22	5-92	2.8-180 ^a	100%	100	77	15-480	4.2-490 ^a
BDE154	94%	2	1.2	<0.06-9.3	<dl-16 ^a	100%	7.7	3.9	0.8-68	<dl-38 ^a
BDE153	100%	4.8	3	0.025-24	<dl-110 ^a	100%	28	9.2	0.025-190	<dl-99 ^a
BDE183	90%	7.4	3.5	<0.13-51	<dl-550 ^a	100%	29	9.8	0.065-220	<dl-24 ^a
BDE209	100%	34000	4500	160-370000	<dl-2200000 ^a	100%	9100	2700	200-110000	620-280000 ^a
α -HBCDD	100%	2300	320	21-28000	22-66000 ^b	100%	1100	980	100-2800	15-2900 ^b
β -HBCDD	100%	1100	85	6.1-12000	9-26000 ^b	100%	300	330	22-590	11-1300 ^b
γ -HBCDD	100%	4900	93	23-71000	70-75000 ^b	100%	630	350	31-3700	36-3700 ^b
Σ HBCDDs	--	8300	610	50-110000	140-140000 ^b	--	2000	1700	150-6400	90-6600 ^b

448 a): Harrad, S.; Ibarra, C.; Abdallah, M. A.-E.; Boon, R.; Neels, H.; Covaci, A. Concentrations of Brominated Flame Retardants in Dust from

- 449 United Kingdom Cars, Homes, and Offices: Causes of Variability and Implications for Human Exposure. *Environ. Int.* **2008**, *34* (8), 1170.; b):
- 450 Abdallah, M. A.-E.; Harrad, S.; Covaci, A. Hexabromocyclododecanes and Tetrabromobisphenol-A in Indoor Air and Dust in Birmingham, UK:
- 451 Implications for Human Exposure. *Environ. Sci. Technol.* 2008, *42* (18), 6855.

Table 3. Estimates of exposure (ng/day) of UK Adults and Toddlers to FRs via air and dust, and relative significance (%) of each pathway under a typical exposure scenario ^a

Compounds	Intake (ng/day)			
	Toddlers		Adults	
	Air	Dust	Air	Dust
Σtri-hepta BDEs	0.11	10	0.6	2.1
BDE209	0.32	270	1.4	100
ΣHBCDDs	0.14	25	2.1	15
ΣEFRs	0.66	38	4.3	27
α-DBE-DBCH	0.24	0.31	1.7	0.16
β-DBE-DBCH	0.17	0.44	1.2	0.18
TBX	0.037	0.065	0.21	0.027
PBBz	0.02	0.11	0.13	0.047
TBCT	0.038	0.42	0.16	0.16
PBT	0.042	0.15	0.2	0.054
PBEB	0.005	0.017	0.028	0.009
TBP-DBPE	0.0075	0.058	0.039	0.031
HBB	0.016	0.083	0.11	0.07
EH-TBB	0.0075	0.35	0.053	0.19
BTBPE	0.019	0.31	0.13	1.5
BEH-TEBP	0.008	4.7	0.039	2.6
<i>syn</i> -DDC-CO	0.0038	0.014	0.02	0.058
<i>anti</i> -DDC-CO	0.0023	0.46	0.012	0.52
TBBPA-BDBPE	0.019	23	0.1	15
DBDPE	0.019	7.8	0.1	6.5

^a typical exposure scenario denotes adults and toddlers assumed to inhale air and ingest dust contaminated at the median concentration at the average ingestion rate (20 mg/day and 50 mg/day for adults and toddlers respectively)

References

- (1) Birnbaum, L. S.; Staskal, D. F. Brominated Flame Retardants: Cause for Concern? *Environ. Health Perspect.* **2004**, *112* (1), 9.
- (2) Ma, Y.; Salamova, A.; Venier, M.; Hites, R. A. Has the Phase-Out of PBDEs Affected Their Atmospheric Levels? Trends of PBDEs and Their Replacements in the Great Lakes Atmosphere. *Environ. Sci. Technol.* **2013**, *47* (20), 11457.
- (3) UNEP. *Stockholm Convention on Persistent Organic Pollutants*.
- (4) La Guardia, M. J.; Hale, R. C.; Harvey, E. Detailed Polybrominated Diphenyl Ether (PBDE) Congener Composition of the Widely Used Penta-, Octa-, and Deca-PBDE Technical Flame-Retardant Mixtures. *Environ. Sci. Technol.* **2006**, *40* (20), 6247.
- (5) Official Journal of the European Union, 9 May 2008, Judgment of the Court of 1 April 2008 (2008/C116/04).
- (6) UNEP. *Stockholm Convention on Persistent Organic Pollutants*. [Http://chm.pops.int/default.aspx](http://chm.pops.int/default.aspx) (Accessed November 19, 2014).
- (7) Covaci, A.; Harrad, S.; Abdallah, M. A. E.; Ali, N.; Law, R. J.; Herzke, D.; de Wit, C. A. Novel Brominated Flame Retardants: A Review of Their Analysis, Environmental Fate and Behaviour. *Environ. Int.* **2011**, *37* (2), 532.
- (8) Dodson, R. E.; Perovich, L. J.; Covaci, A.; Van den Eede, N.; Ionas, A. C.; Dirtu, A. C.; Brody, J. G.; Rudel, R. A. After the PBDE Phase-Out: A Broad Suite of Flame Retardants in Repeat House Dust Samples from California. *Environ. Sci. Technol.* **2012**, *46* (24), 13056.
- (9) Qi, H.; Li, W.-L.; Liu, L.-Y.; Zhang, Z.-F.; Zhu, N.-Z.; Song, W.-W.; Ma, W.-L.; Li, Y.-F. Levels, Distribution and Human Exposure of New Non-BDE Brominated Flame Retardants in the Indoor Dust of China. *Environ. Pollut.* **2014**, *195* (0), 1.
- (10) Sahlström, L. M. O.; Sellström, U.; de Wit, C. A.; Lignell, S.; Darnerud, P. O. Estimated Intakes of Brominated Flame Retardants via Diet and Dust Compared to Internal Concentrations in a Swedish Mother-Toddler Cohort. *Int. J. Hyg. Environ. Health* **2015**, *218* (4), 422.
- (11) Fromme, H.; Hilger, B.; Kopp, E.; Misserok, M.; Völkel, W. Polybrominated Diphenyl Ethers (PBDEs), Hexabromocyclododecane (HBCD) And “novel” brominated Flame Retardants in House Dust in Germany. *Environ. Int.* **2014**, *64*, 61.
- (12) Ali, N.; Harrad, S.; Goosey, E.; Neels, H.; Covaci, A. “Novel” brominated Flame Retardants in Belgian and UK Indoor Dust: Implications for Human Exposure. *Chemosphere* **2011**, *83* (10), 1360.
- (13) Harrad, S.; Ibarra, C.; Abdallah, M. A.-E.; Boon, R.; Neels, H.; Covaci, A. Concentrations of Brominated Flame Retardants in Dust from United Kingdom Cars, Homes, and Offices: Causes of Variability and Implications for Human Exposure. *Environ. Int.* **2008**, *34* (8), 1170.
- (14) Newton, S.; Sellström, U.; de Wit, C. a. Emerging Flame Retardants, PBDEs, and HBCDDs in Indoor and Outdoor Media in Stockholm, Sweden. *Environ. Sci. Technol.* **2015**, *49* (5), 2912.
- (15) Cequier, E.; Ionas, A. C.; Covaci, A.; Marcé, 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.
- (16) Tomy, G. T.; Palace, V. P.; Pleskach, K.; Ismail, N.; Oswald, T.; Danell, R.; Wautier, K.; Evans, B. Dietary Exposure of Juvenile Rainbow Trout (*Oncorhynchus Mykiss*) to 1,2-bis(2,4,6-Tribromophenoxy)ethane: Bioaccumulation Parameters, Biochemical Effects, and Metabolism. *Environ. Sci. Technol.* **2007**, *41* (14), 4913.
- (17) Muir, D. C. G.; Howard, P. H. Are There Other Persistent Organic Pollutants? A Challenge for Environmental Chemists. *Environ. Sci. Technol.* **2006**, *40* (23), 7157.
- (18) He, M. J.; Luo, X. J.; Chen, M. Y.; Sun, Y. X.; Chen, S. J.; Mai, B. X. Bioaccumulation of Polybrominated Diphenyl Ethers and Decabromodiphenyl Ethane in Fish from a River System in a Highly Industrialized Area, South China. *Sci. Total Environ.* **2012**.
- (19) de la Torre, A.; Sverko, E.; Alae, M.; Martínez, M. Á. Concentrations and Sources of Dechlorane

- Plus in Sewage Sludge. *Chemosphere* **2011**, 82 (5), 692.
- (20) Howard, P. H.; Muir, D. C. G. Identifying New Persistent and Bioaccumulative Organics among Chemicals in Commerce. *Environ. Sci. Technol.* **2010**, 44 (7), 2277.
- (21) Brominated Flame Retardants (BFRs) in Food.
- (22) Johnson, P. I.; Stapleton, H. M.; Mukherjee, B.; Hauser, R.; Meeker, J. D. Associations between Brominated Flame Retardants in House Dust and Hormone Levels in Men. *Sci. Total Environ.* **2013**, 445–446, 177.
- (23) Egloff, C.; Crump, D.; Chiu, S.; Manning, G.; McLaren, K. K.; Cassone, C. G.; Letcher, R. J.; Gauthier, L. T.; Kennedy, S. W. In Vitro and in Ovo Effects of Four Brominated Flame Retardants on Toxicity and Hepatic mRNA Expression in Chicken Embryos. *Toxicol. Lett.* **2011**, 207 (1), 25.
- (24) Nakari, T.; Huhtala, S. In Vivo and in Vitro Toxicity of Decabromodiphenyl Ethane, a Flame Retardant. *Environ. Toxicol.* **2009**, 25 (4), 333.
- (25) Wang, F.; Wang, J.; Dai, J.; Hu, G.; Luo, X.; Mai, B. Comparative Tissue Distribution, Biotransformation and Associated Biological Effects by Decabromodiphenyl Ethane and Decabrominated Diphenyl Ether in Male Rats after a 90-Day Oral Exposure Study. *Environ. Sci. Technol.* **2010**, 44 (14), 5655.
- (26) Ezechiáš, M.; Svobodová, K.; Cajthaml, T. Hormonal Activities of New Brominated Flame Retardants. *Chemosphere* **2012**, 87 (7), 820.
- (27) Bearr, J. S.; Stapleton, H. M.; Mitchelmore, C. L. Accumulation and DNA Damage in Fathead Minnows (*Pimephales Promelas*) Exposed to 2 Brominated Flame-Retardant Mixtures, Firemaster 550 and Firemaster BZ-54. *Environ. Toxicol. Chem.* **2010**, 29 (3), 722.
- (28) Saunders, D. M. V.; Higley, E. B.; Hecker, M.; Mankidy, R.; Giesy, J. P. In Vitro Endocrine Disruption and TCDD-like Effects of Three Novel Brominated Flame Retardants: TBPH, TBB, & TBCO. *Toxicol. Lett.* **2013**, 223 (2), 252.
- (29) Mankidy, R.; Ranjan, B.; Honaramooz, A.; Giesy, J. P. Effects of Novel Brominated Flame Retardants on Steroidogenesis in Primary Porcine Testicular Cells. *Toxicol. Lett.* **2014**, 224 (1), 141.
- (30) Noyes, P. D.; Haggard, D. E.; Gonnerman, G. D.; Tanguay, R. L. Advanced Morphological - Behavioral Test Platform Reveals Neurodevelopmental Defects in Embryonic Zebrafish Exposed to Comprehensive Suite of Halogenated and Organophosphate Flame Retardants. *Toxicol. Sci.* **2015**, 145 (1), 177.
- (31) Park, B. J.; Palace, V.; Wautier, K.; Gemmill, B.; Tomy, G. Thyroid Axis Disruption in Juvenile Brown Trout (*Salmo Trutta*) Exposed to the Flame Retardant β -Tetrabromoethylcyclohexane (β -TBECH) via the Diet. *Environ. Sci. Technol.* **2011**, 45 (18), 7923.
- (32) Larsson, A.; Eriksson, L. a; Andersson, P. L.; Ivarson, P.; Olsson, P.-E. Identification of the Brominated Flame Retardant 1,2-Dibromo-4-(1,2-Dibromoethyl)cyclohexane as an Androgen Agonist. *J. Med. Chem.* **2006**, 49, 7366.
- (33) Khalaf, Hazem, Anders Larsson, Håkan Berg, Robert McCrindle, Gilles Arsenault, and P.-E. O. Diastereomers of the Brominated Flame Retardant 1,2-Dibromo-4-(1,2 dibromoethyl)cyclohexane Induce Androgen Receptor Activation in the HepG2 Hepatocellular Carcinoma Cell Line and the LNCaP Prostate Cancer Cell Line <http://ehp.niehs.nih.gov/0901065/> (accessed Oct 9, 2015).
- (34) McGregor, D. B.; Brown, A. G.; Howgate, S.; McBride, D.; Riach, C.; Caspary, W. J.; Carver, J. H. Responses of the L5178Y Mouse Lymphoma Cell Forward Mutation Assay. V: 27 Coded Chemicals. *Environ. Mol. Mutagen.* **1991**, 17 (3), 196.
- (35) Pradhan, A.; Kharlyngdoh, J. B.; Asnake, S.; Olsson, P.-E. The Brominated Flame Retardant TBECH Activates the Zebrafish (*Danio Rerio*) Androgen Receptor, Alters Gene Transcription and Causes Developmental Disturbances. *Aquat. Toxicol.* **2013**, 142–143, 63.
- (36) Abdallah, M. A.-E.; Harrad, S. Modification and Calibration of a Passive Air Sampler for Monitoring Vapor and Particulate Phase Brominated Flame Retardants in Indoor Air: Application to Car Interiors. *Environ. Sci. Technol.* **2010**, 44 (8), 3059.
- (37) Hazrati, S.; Harrad, S. Calibration of Polyurethane Foam (PUF) Disk Passive Air Samplers for

- Quantitative Measurement of Polychlorinated Biphenyls (PCBs) and Polybrominated Diphenyl Ethers (PBDEs): Factors Influencing Sampling Rates. *Chemosphere* **2007**, 67 (3), 448.
- (38) Wilford, B. H.; Harner, T.; Zhu, J.; Shoeib, M.; Jones, K. C. Passive Sampling Survey of Polybrominated Diphenyl Ether Flame Retardants in Indoor and Outdoor Air in Ottawa, Canada: Implications for Sources and Exposure. *Environ. Sci. Technol.* **2004**, 38 (20), 5312.
- (39) Ali, N.; Harrad, S.; Muenhor, D.; Neels, H.; Covaci, A. Analytical Characteristics and Determination of Major Novel Brominated Flame Retardants (NBFRs) in Indoor Dust. *Anal. Bioanal. Chem.* **2011**, 400 (9), 3073.
- (40) Harrad, S.; Abdallah, M. A. E.; Rose, N. L.; Turner, S. D.; Davidson, T. A. Current-Use Brominated Flame Retardants in Water, Sediment, and Fish from English Lakes. *Environ. Sci. Technol.* **2009**, 43 (24), 9077.
- (41) Arsenault, G.; Lough, A.; Marvin, C.; McAlees, A.; McCrindle, R.; MacInnis, G.; Pleskach, K.; Potter, D.; Riddell, N.; Sverko, E.; et al. Structure Characterization and Thermal Stabilities of the Isomers of the Brominated Flame Retardant 1,2-Dibromo-4-(1,2-Dibromoethyl)cyclohexane. *Chemosphere* **2008**, 72 (8), 1163.
- (42) Ma, Y.; Venier, M.; Hites, R. A. 2-Ethylhexyl Tetrabromobenzoate and Bis(2-Ethylhexyl) Tetrabromophthalate Flame Retardants in the Great Lakes Atmosphere. *Environ. Sci. Technol.* **2012**, 46 (1), 204.
- (43) WHO (1997) *Flame Retardants: A General Introduction. Environmental Health Criteria 192. WHO, Geneva.*
- (44) Venier, M.; Audy, O.; Vojta, Š.; Bečanová, J.; Romanak, K.; Melymuk, L.; Krátká, M.; Kukučka, P.; Okeme, J.; Saini, A.; et al. Brominated Flame Retardants in the Indoor Environment — Comparative Study of Indoor Contamination from Three Countries. *Environ. Int.* **2016**, 94, 150.
- (45) Shoeib, M.; Ahrens, L.; Jantunen, L.; Harner, T. Concentrations in Air of Organobromine, Organochlorine and Organophosphate Flame Retardants in Toronto, Canada. *Atmos. Environ.* **2014**, 99, 140.
- (46) Peverly, A. A.; Ma, Y.; Venier, M.; Rodenburg, Z.; Spak, S. N.; Hornbuckle, K. C.; Hites, R. A. Variations of Flame Retardant, Polycyclic Aromatic Hydrocarbon, and Pesticide Concentrations in Chicago's Atmosphere Measured Using Passive Sampling. *Environ. Sci. Technol.* **2015**, 49 (9), 5371.
- (47) Yu, Y.; Hung, H.; Alexandrou, N.; Roach, P.; Nordin, K. Multiyear Measurements of Flame Retardants and Organochlorine Pesticides in Air in Canada's Western Sub-Arctic. *Environ. Sci. Technol.* **2015**, 49 (14), 8623.
- (48) 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.
- (49) Johnson-Restrepo, B.; Kannan, K. An Assessment of Sources and Pathways of Human Exposure to Polybrominated Diphenyl Ethers in the United States. *Chemosphere* **2009**, 76 (4), 542.
- (50) Thuresson, K.; Björklund, J. A.; de Wit, C. A. Tri-Decabrominated Diphenyl Ethers and Hexabromocyclododecane in Indoor Air and Dust from Stockholm Microenvironments 1: Levels and Profiles. *Sci. Total Environ.* **2012**, 414, 713.
- (51) 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.
- (52) Toms, L. L.; Bartkow, M. E.; Symons, R.; Paepke, O.; Mueller, J. F. Chemosphere Assessment of Polybrominated Diphenyl Ethers (PBDEs) in Samples Collected from Indoor Environments in South East Queensland , Australia. *Chemosphere* **2009**, 76 (2), 173.
- (53) Takigami, H.; Suzuki, G.; Hirai, Y.; Sakai, S. I. Brominated Flame Retardants and Other Polyhalogenated Compounds in Indoor Air and Dust from Two Houses in Japan. *Chemosphere* **2009**, 76 (2), 270.

- 614 (54) Batterman, S.; Godwin, C.; Chernyak, S.; Jia, C.; Charles, S. Brominated Flame Retardants in
615 Offices in Michigan, USA. *Environ. Int.* **2010**, *36* (6), 548.
- 616 (55) Bromine Science and Environmental Forum (BSEF). Major Brominated Flame Retardants
617 Volume Estimates: Total Market Demand By Region in 2001, 21 January 2003. downloaded from
618 www.bsef.com
- 619 (56) Abdallah, M. A.-E.; Harrad, S.; Covaci, A. Hexabromocyclododecanes and Tetrabromobisphenol-
620 A in Indoor Air and Dust in Birmingham, UK: Implications for Human Exposure. *Environ. Sci.*
621 *Technol.* **2008**, *42* (18), 6855.
- 622 (57) Cao, Z.; Xu, F.; Covaci, A.; Wu, M.; Yu, G.; Wang, B.; Deng, S.; Huang, J. Differences in the
623 Seasonal Variation of Brominated and Phosphorus Flame Retardants in Office Dust. *Environ. Int.*
624 **2014**, *65*, 100.
- 625 (58) Ali, N.; Dirtu, A. C.; Eede, N. Van den; Goosey, E.; Harrad, S.; Neels, H.; 't Mannetje, A.;
626 Coakley, J.; Douwes, J.; Covaci, A. Occurrence of Alternative Flame Retardants in Indoor Dust
627 from New Zealand: Indoor Sources and Human Exposure Assessment. *Chemosphere* **2012**, *88*
628 (11), 1276.
- 629 (59) Stapleton, H. M.; Allen, J. G.; Kelly, S. M.; Konstantinov, A.; Klosterhaus, S.; Watkins, D.;
630 McClean, M. D.; Webster, T. F. Alternate and New Brominated Flame Retardants Detected in U.S.
631 House Dust. *Environ. Sci. Technol.* **2008**, *42* (18), 6910.
- 632 (60) Shoeib, M.; Harner, T.; Webster, G. M.; Sverko, E.; Cheng, Y. Legacy and Current-Use Flame
633 Retardants in House Dust from Vancouver, Canada. *Environ. Pollut.* **2012**.
- 634 (61) Wang, J.; Tian, M.; Chen, S.-J.; Zheng, J.; Luo, X.-J.; An, T.-C.; Mai, B.-X. Dechlorane Plus in
635 House Dust from E-Waste Recycling and Urban Areas in South China: Sources, Degradation, and
636 Human Exposure. *Environ. Toxicol. Chem.* **2011**, *30* (9), 1965.
- 637 (62) Wong, F.; Kurt-Karakus, P.; Bidleman, T. F. Fate of Brominated Flame Retardants and
638 Organochlorine Pesticides in Urban Soil: Volatility and Degradation. *Environ. Sci. Technol.* **2012**,
639 *46* (5), 2668.
- 640 (63) Harrad, S.; Ibarra, C.; Diamond, M.; Melymuk, L.; Robson, M.; Douwes, J.; Roosens, L.; Dirtu, A.
641 C.; Covaci, A. Polybrominated Diphenyl Ethers in Domestic Indoor Dust from Canada, New
642 Zealand, United Kingdom and United States. *Environ. Int.* **2008**, *34* (2), 232.
- 643 (64) Wilford, B. H.; Shoeib, M.; Harner, T.; Zhu, J.; Jones, K. C. Polybrominated Diphenyl Ethers in
644 Indoor Dust in Ottawa, Canada: Implications for Sources and Exposure. *Environ. Sci. Technol.*
645 **2005**, *39* (18), 7027.
- 646 (65) Vorkamp, K.; Thomsen, M.; Frederiksen, M.; Pedersen, M.; Knudsen, L. E. Polybrominated
647 Diphenyl Ethers (PBDEs) in the Indoor Environment and Associations with Prenatal Exposure.
648 *Environ. Int.* **2011**, *37* (1), 1.
- 649 (66) D'Hollander, W.; Roosens, L.; Covaci, A.; Cornelis, C.; Reynders, H.; Campenhout, K. Van;
650 Voogt, P. De; Bervoets, L. Brominated Flame Retardants and Perfluorinated Compounds in Indoor
651 Dust from Homes and Offices in Flanders, Belgium. *Chemosphere* **2010**, *81* (4), 478.
- 652 (67) Yu, Y.-X.; Pang, Y.-P.; Li, C.; Li, J.-L.; Zhang, X.-Y.; Yu, Z.-Q.; Feng, J.-L.; Wu, M.-H.; Sheng,
653 G.-Y.; Fu, J.-M. Concentrations and Seasonal Variations of Polybrominated Diphenyl Ethers
654 (PBDEs) in in- and out-House Dust and Human Daily Intake via Dust Ingestion Corrected with
655 Bioaccessibility of PBDEs. *Environ. Int.* **2012**, *42* (0), 124.
- 656 (68) Kang, Y.; Wang, H. S.; Cheung, K. C.; Wong, M. H. Polybrominated Diphenyl Ethers (PBDEs) in
657 Indoor Dust and Human Hair. *Atmos. Environ.* **2011**, *45* (14), 2386.
- 658 (69) EU Risk Assessment Report. European Union Risk Assessment Report on
659 BIS(PENTABROMOPHENYL) ETHER. *Eur. Comm. Jt. Res. Centre, Eur. Chem. Bur.*
660 *EUR20402EN, 2002.* **2002**, Vol. 17.
- 661 (70) Harrad, S.; Wijesekera, R.; Hunter, S.; Halliwell, C.; Baker, R. Preliminary Assessment of UK
662 Human Dietary and Inhalation Exposure to Polybrominated Diphenyl Ethers. *Environ. Sci.*
663 *Technol.* **2004**, *38* (8), 2345.
- 664 (71) Harrad, S.; Hazrati, S.; Ibarra, C. Concentrations of Polychlorinated Biphenyls in Indoor Air and

- Polybrominated Diphenyl Ethers in Indoor Air and Dust in Birmingham, United Kingdom: Implications for Human Exposure. *Environ. Sci. Technol.* **2006**, *40* (15), 4633.
- (72) Melymuk, L.; Robson, M.; Helm, P. a.; Diamond, M. L. PCBs, PBDEs, and PAHs in Toronto Air: Spatial and Seasonal Trends and Implications for Contaminant Transport. *Sci. Total Environ.* **2012**, *429*, 272.
- (73) Gouteux, B.; Alae, M.; Mabury, S. a.; Pacepavicius, G.; Muir, D. C. G. Polymeric Brominated Flame Retardants: Are They a Relevant Source of Emerging Brominated Aromatic Compounds in the Environment? *Environ. Sci. Technol.* **2008**, *42* (24), 9039.
- (74) Buser, H. R. Polybrominated Dibenzofurans and Dibenzo-P-Dioxins: Thermal Reaction Products of Polybrominated Diphenyl Ether Flame Retardants. *Environ. Sci. Technol.* **1986**, *20* (4), 404.
- (75) Thoma, H.; Hutzinger, O. Pyrolysis and GC/MS-Analysis of Brominated Flame Retardants in on-Line Operation. *Chemosphere* **1987**, *16* (6), 1353.
- (76) Bergh, C.; Torgrip, R.; Emenius, G.; Östman, C. Organophosphate and Phthalate Esters in Air and Settled Dust - a Multi-Location Indoor Study. *Indoor Air* **2011**, *21* (1), 67.
- (77) 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.

For table of contents only (TOC art)