Legacy and Alternative Flame Retardants in Norwegian and UK Indoor Environment: Implications of Human Exposure via Dust Ingestion

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Introduction

Penta-BDE and Octa-BDE commercial mixtures have been recently listed as persistent organic pollutants (POPs) for elimination under the Stockholm Convention[1,2], while the Deca-BDE mixture is currently under review. Due to legislative restrictions on their commercial use, PBDEs have been replaced with alternatives, known as "emerging" halogenated flame retardants (EHFRs)[3] and organophosphate flame retardants (PFRs)[4]. Various human health effects are associated with PBDEs exposure such as disruption of the endocrine and thyroid homeostasis[5] and neurodevelopmental growth of children[6]. In April 2016, the Washington State House Bill 2545 (Toxic-free Kids and Families Act) was approved to ban children's products and residential upholstered furniture from the market containing more than 0.1% of tris-(chloroethyl)-phosphate (TCEP), tris-(2,3-dichloropropyl)-phosphate (TDCIPP), Deca-BDE, hexabromocyclododecane (HBCD) and tetrabromobisphenol A (TBBPA) with an effective date set for June 2016. The implementation of this bill may potentially trigger the phasing out PBDE alternatives, thus initiate the development and use of newer FRs. In this study, we assessed the presence of legacy and alternative FRs in three different indoor environments from two European countries (the UK and Norway) in order to estimate and compare human intakes FRs via dust ingestion for non-working adults and toddlers in Norwegian and British houses, as well as for working adults in British stores and offices.

Materials and methods

Sampling

Ten indoor dust samples were collected from pre-existing vacuum cleaner bags (houses) in Norway (Oslo) as a part of the A-TEAM cohort sampling during November 2013 – April 2014 [7]. Twenty-two indoor dust samples from pre-existing vacuum cleaner bags (10 houses, 6 stores and 6 offices) were collected in Reading (UK) during August – December 2013. The UK house dust samples were collected from the houses of University of Reading employees, while UK office and store vacuum cleaner bags were collected in Reading. All dust samples were sieved to <250 μm and kept in hexane-washed amber glass bottles and stored at 4°C till analysis. Oven-baked Na_2SO_4 (granular) was also sieved as field blank.

Extraction and clean-up

The method was based on a previous study [8] with some modifications. Briefly, 30 mg of dust was extracted with 2.5 mL hexane:acetone (3:1) using ultra-sonication extraction for 10 min and vortexing for 1 min three times. The combined extract was concentrated on aminopropyl (NH_2) silica cartridges (500 mg, 3 mL, Agilent, USA) and further fractionated with 10 mL hexane (F1) and 12 mL of ethyl acetate (F2). F1 was further concentrated, following a clean-up on an acidified silica cartridge (5%, 1 g, 6 mL) and elution with 12 mL dichloromethane. F2 was equally aliquoted into two portions, F2a and F2b. Then, F1, F2a and F2b were evaporated, reconstituted with 100 μL of iso-octane (F1 & F2a) and methanol (F2b), respectively, and then filtered. Finally, the extracts were transferred to injection vials and analyzed on GC-ECNI-MS (F1, for PBDEs and EHFRs), GC-EI-MS (F2a, for m-PFRs, except TXP) and LC-QqQ-MS (F2b, for o-PFRs and TXP).

QA/QC and Data Analysis

SRM 2585 (n=2, NIST, USA) was used for QC testing, four Na_2SO_4 samples (30mg) were used as field blanks for background checking and results were blank corrected for all analytes by subtraction of the mean field blank values from the raw FR values (expressed in ng/g). GraphPad Prism® version

7.00 for Windows, (GraphPad Software, La Jolla CA, USA) was used for statistical analysis. All data were checked for normality using the D'agostino and Pearson tests, data that failed the normality test were log-transformed. Ordinary two-way ANOVA (Uncorrected Fisher's test, $p<0.05$) was performed to assess statistically significant differences of FRs between UK house and occupational concentrations and between UK and Norwegian houses.

Results and discussion

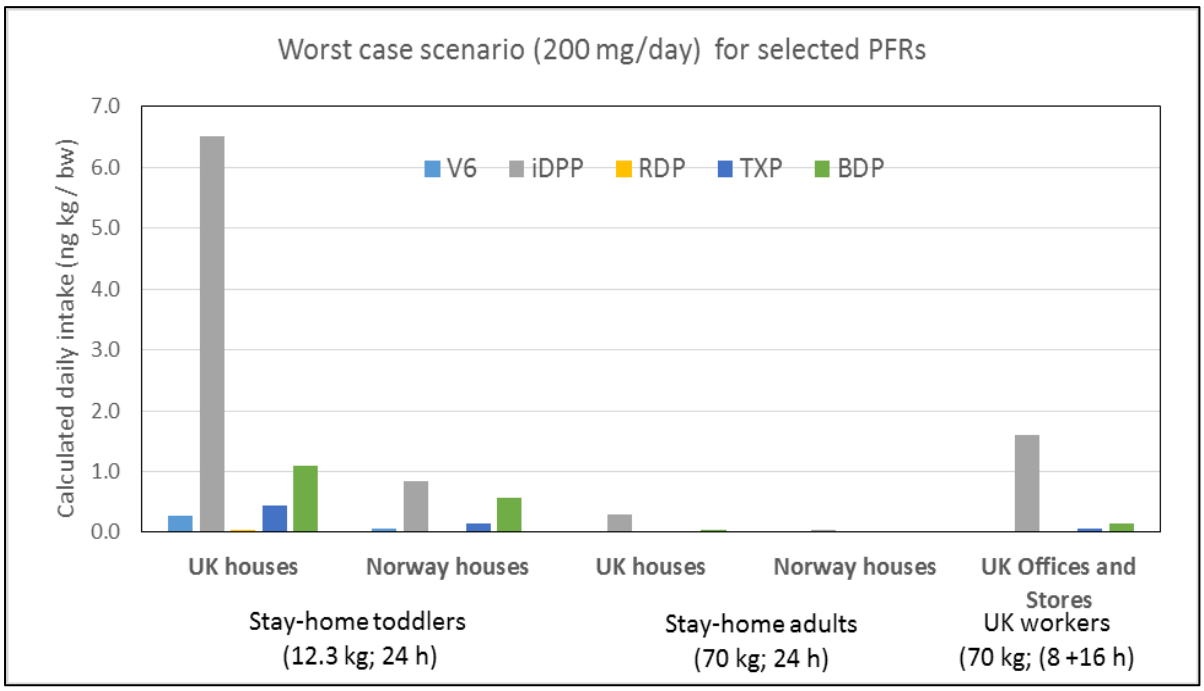
PBDEs, EHFRs and PFRs in dust

This study reports concentrations of four groups of FRs in dust from UK stores and offices (n=6 offices and n=6 stores), UK houses (n=10) and Norwegian houses (n=10). Overall, 28 and 31 compounds (out of 33) were detected in house and occupational dust samples, respectively. Studied chemicals included nine PBDE congeners, eight EHFRs, ten monomeric PFRs, and six oligomeric PFRs. In our study, monomeric PFRs presented the highest levels in total, followed by EHFRs, PBDEs and oligomeric PFRs. Overall, the UK occupational dust samples had the highest FR contamination, followed by UK and Norwegian house dust. In an attempt to define newly identified PFRs, this group is divided in monomeric (m-PFRs), including TPHP, TnBP, TCPP, TDCIPP etc., and oligomeric (o-PFRs), including V6, BDP and RDP, using the abbreviation nomenclature as suggested by Matsukami et.al. (2015)[9].

This is the first report of isodecyldiphenyl phosphate (iDPP) and trixylenyl phosphate (TXP) in the indoor environment. Most o-PFRs were detected in all three types of dust (DF>80%), apart from RDP (no detection in Norwegian house dust) and TDBPP (DF<50% in UK and Norwegian house dust samples). iDPP was the most abundant o-PFR in our dust samples, ranging from 600-145,000 ng g^{-1}, 110-1,700 ng g^{-1} and 6-260 ng g^{-1} in UK occupational dust, UK house dust and Norwegian house dust, respectively. Maximum values for iDPP and BDP were close to 145,000 ng g^{-1} and 6,000 ng g-^{1}, respectively, both found in dust from a toy store. In a personal computer (PC) store, the maximum concentration of TXP was near 6,000 ng g^{-1}. iDPP concentrations of UK house and occupational dusts were statistically significantly different ($p=0.019$).

Human exposure assessment

In all scenarios much higher intakes from dust ingestion have been calculated for m-PFRs than for PBDEs, EHFRs and o-PFRs. This is the first study reporting human exposure via dust ingestion for most o-PFRs. Among all o-PFRs, in most scenarios, the highest intakes via dust ingestion were calculated for iDPP, followed by BDP or TXP (Fig.1). Considering 8h of exposure during a workday, British employees were found to have higher estimated exposure of individual o-PFRs than British and Norwegian stay-home adults (24 h) (Table 1). In the worst case scenario for toddlers, Norwegian toddlers may have an exposure of equal to 11.3 ng kg bw^{-1} day^{-1} for BDP, while British toddlers have TXP exposure equal to 8.7 ng kg bw^{-1} day^{-1}. Toddler estimated intakes for o-PFRs were found to be higher than stay-home adults in both countries. In the worst case scenario, iDPP estimated intake for employees in a British-based toy store was considerably higher than for other o-PFRs, together with TDBPP and TXP. This is the first study reporting considerable concentrations of iDPP and TXP in the indoor environment of Norway and the UK. However, only dust ingestion was investigated as an exposure pathway in the present study, while inhalation has been also proposed as an alternative route of exposure for several m-PFRs. Therefore, the continuous and rigorous assessment of legacy and alternative FRs, especially oligomeric PFRs (o-PFRs), in the indoor environment is essential due to their potential adverse effects on human health.



Acknowledgments

The research leading to these results has received funding from the European Union Seventh Framework Programme FP7/2007–2013 under grant agreement n° 316665 (A-TEAM project). The authors would like to acknowledge Dr. Eleni Papadopoulou from NIPH (Norway) for her help during the ATEAM sampling campaign. Walid Maho and Dr. Alin Ionas are acknowledged for the support on instrumental analysis. Katerina Kademoglou would like to acknowledge the financial support from the Mediterranean Scientific Association of Environmental Protection (MESAEP) during her PhD studies by means of the Emmanuel Lahaniatis Award for Young Scientists.

References

1. Stockholm Convention. UNEP/POPS/POPRC.4/14 Listing of hexabromodiphenyl ether and heptabromodiphenyl ether. (2009).
2. Stockholm Convention. UNEP/POPS/POPRC.4/18 Listing of tetrabromodiphenyl ether and pentabromodiphenyl ether. (2009).
3. Covaci, A. *et al.* Novel brominated flame retardants: A review of their analysis, environmental fate and behaviour. *Environ. Int.* **37,** 532–556 (2011).
4. van der Veen, I. & de Boer, J. Phosphorus flame retardants: Properties, production, environmental occurrence, toxicity and analysis. *Chemosphere* **88,** 1119–1153 (2012).
5. Legler, J. & Brouwer, A. Are brominated flame retardants endocrine disruptors? *Environ. Int.* **29,** 879–885 (2003).
6. Costa, L. G. & Giordano, G. Developmental neurotoxicity of polybrominated diphenyl ether (PBDE) flame retardants. *NeuroToxicology* **28,** 1047–1067 (2007).
7. Papadopoulou, E. *et al.* Sampling strategy for estimating human exposure pathways to consumer chemicals. *Emerg. Contam.* (2016). doi:10.1016/j.emcon.2015.12.002
8. Van den Eede, N., Dirtu, A. C., Ali, N., Neels, H. & Covaci, A. Multi-residue method for the determination of brominated and organophosphate flame retardants in indoor dust. *Talanta* **89,** 292–300 (2012).
9. Matsukami, H., Suzuki, G. & Takigami, H. Compositional Analysis of Commercial Oligomeric Organophosphorus Flame Retardants Used as Alternatives for PBDEs: Concentrations and Potential Environmental Emissions of Oligomers and Impurities. *Environ. Sci. Technol.* **49,** 12913–12921 (2015).