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Legacy and alternative flame retardants in Norwegian and UK indoor environment: Implications of human exposure via dust ingestion

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ABSTRACT

Indoor dust has been acknowledged as a major source of flame retardants (FRs) and dust ingestion is considered a major route of exposure for humans. In the present study, we investigated the presence of PBDEs and alternative FRs such as emerging halogenated FRs (EHFRs) and organophosphate flame retardants (PFRs) in indoor dust samples from British and Norwegian houses as well as British stores and offices. BDE209 was the most abundant PBDE congener with median concentrations of 4700 ng g^{-1} and 3400 ng g^{-1} in UK occupational and house dust, respectively, 30 and 20 fold higher than in Norwegian house dust. Monomeric PFRs (m-PFRs), including triphenyl phosphate (TPHP), tris(chloropropyl) phosphate (TCPP) and tris(2-chloroethyl) phosphate (TCEP) dominated all the studied environments. To the best of our knowledge, this is the first report of isodecyldiphenyl phosphate (iDPP) and trixylenyl phosphate (TXP) in indoor environments. iDPP was the most abundant oligomeric PFR (o-PFR) in all dust samples, with median concentrations one order of magnitude higher than TXP and bisphenol A bis(diphenyl phosphate (BDP). iDPP and TXP worst-case scenario exposures for British workers during an 8 h exposure in the occupational environment were equal to 34 and 1.4 ng kg bw^{-1} day^{-1}, respectively. The worst-case scenario for BDE209 estimated exposure for British toddlers (820 ng kg bw^{-1} day^{-1}) did not exceeded the proposed reference dose (RfD) (7000 ng kg bw^{-1} day^{-1}), while exposures for sum of m-PFRs (Σm-PFRs) in British toddlers and adults (17,900 and 785 ng kg bw^{-1} day^{-1} respectively) were an order of magnitude higher than for Norwegian toddlers and adults (1600 and 70 ng kg bw^{-1} day^{-1}).

1. Introduction

Flame retardants (FRs) are widely used in everyday consumer products including carpets, electronic appliances, clothing and textiles, thermal insulation and cable coatings. Since the 1970s, polybrominated diphenyl ethers (PBDEs) have been widely used in consumer products as FRs (Alaee et al., 2003). Various human health effects are associated with PBDEs exposure such as disruption of the endocrine and thyroid homeostasis (Legler and Brouwer, 2003) and neurodevelopmental growth of children (Costa and Giordano, 2007). The commercial mixtures Penta-BDE and Octa-BDE have been listed as persistent organic pollutants (POPs) for elimination under the Stockholm Convention (Stockholm Convention, 2009a,b), while the Deca-BDE mixture is currently under review. The use of Deca-BDE was banned in Norway in 2008 (EBFRIP, 2008), while it was included by the EU in the amended Annex XVII of REACH (EC No 1907/2006), banning its production, use and marketing in the EU (European Commission, 2016). As a result of the REACH amendment, furniture and fire safety regulations in the UK are currently under review by the national competent authorities (UK Department for Business, Energy, and Industrial Strategy, 2016). Due to legislative restrictions on their commercial use, PBDEs have been replaced with alternatives, known as "emerging" halogenated flame retardants (EHFRs) including 2-ethylhexyl-2,3,4,5-tetrabromobenzoate (EH-TBB; Penta-BDE replacement), bis(2-ethylhexyl)-3,4,5,6-tetrabromophthalate (BEH-TEBP; Penta-BDE replacement), 1,2-bis(2,4,6-tribromophenoxy) ethane (BTBPE; Octa-BDE replacement), decabromodiphenyl ethane (DBDPE; Deca-BDE replacement) and Dechlorane Plus (DPs; Deca-BDE replacement) (Stapleton et al., 2008; Wang et al., 2011) and organophosphate flame retardants (PFRs) such as tris(2-chloroethyl) phosphate (TCEP) and tris(chloropropyl)phosphate (TCPP) (van der Veen and de Boer, 2012).

Abbreviations: EHFRs, emerging halogenated flame retardants; m-PFRs, monomeric PFRs; o-PFRs, oligomeric PFRs.

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Several studies have indicated that also EHFRs and PFRs may pose potential risks to humans. EH-TBB and BEH-TEBP, major components in the commercial product Firemaster 550®, have been proven to act as endocrine disruptors and obesogens when orally administered to rats (Patisaul et al., 2013) and can bind and activate the transcription of peroxisome proliferator-activated receptor γ (PPAR γ) ligands, while triphenyl phosphate (TPHP)-induced in vitro adipocyte differentiation and diverted osteogenic differentiation towards lipid accumulation has been reported (Pillai et al., 2014). DPs, EH-TBB, BEH-TEBP and PFRs, such as TCEP and tris(1,3-dichloro-2-propyl) phosphate (TDCIPP) have been detected in human breast milk and blood in Asian populations (Ben et al., 2013; Kim et al., 2014), as well as in blood, hair and nails in USA residents (Liu et al., 2016). TDCIPP has been linked with reduction in free thyroxine and increase in prolactin secretion in US men, while TPHP was associated with weakening sperm quality (Meeker and Stapleton, 2010). An in vitro estrogenic and *anti*-androgenic potency of TDCIPP, tris(2-butoxyethyl) phosphate (TBOEP), and TPHP on human osteosarcoma (U2OS) cell line exposed to indoor dust extracts has also been reported (Suzuki et al., 2013). In the EU, restrictions on the use of chlorinated PFRs, such as TDCIPP and TCPP, have been issued based on toxicological concerns related to their carcinogenic potency (ECHA, 2008a,b).

Monomeric PFR (m-PFRs), including TDCIPP, TCPP and TCEP, are routinely used as FRs in flexible polyurethane foams (PUFs) and textiles (Ali et al., 2012; Cao et al., 2014b). TPHP can be used as a plasticiser and a FR in PVC, thermoplastics and synthetic polymers, while TBOEP is exclusively used as a plasticiser in floor polish and rubber products (Marklund et al., 2003; Stapleton et al., 2009; van der Veen and de Boer, 2012). The use of EHFRs and m-PFRs in consumer products has thus increased and this is reflected by their high abundance in indoor dust in the UK (Brommer and Harrad, 2015), China (Cao et al., 2014a), Japan (Tajima et al., 2014), Sweden (Newton et al., 2015) and Norway (Cequier et al., 2014). PFRs such as TCPP, TCEP and TBOEP dominate house, office and hotel environments, with levels in hotel dust six fold higher than office dust from China (Cao et al., 2014b). A few studies have reported oligomeric PFRs (o-PFRs) in considerable amounts in dust, such as tetraekis(2-chlorethyl)-dichloroisopentyl diphosphate (V6), an alternative of Penta-BDE, TCPP and TDCIPP (ECHA, 2008c), along with resorcinol bis(diphenyl phosphate (RDP) and bisphenol A bis(diphenyl phosphate (BDP) as Deca-BDE alternatives in electronic and plastic consumer products (Ballesteros-Gómez et al., 2014; Brandsma et al., 2013; Matsukami et al., 2015). Since house dust acts as a repository sink for EHFRs and PFRs, dust originating from indoor environments (e.g. houses, offices, stores) is considered as a major source of human exposure to FRs (Alves et al., 2014; Jones-Otazo et al., 2005).

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 TCEP, TDCIPP, Deca-BDE, hexabromocyclododecane (HBCD) and tetrabromobisphenol A (TBBPA) with an effective date set for June 2016. Additional six FRs, including TPHP, TCPP, V6, EH-TBB, BEH-TEBP, and isopropylated triphenyl phosphate (IPTPHP) will be evaluated and recommended to the Legislature for possible restriction in consumer products (State of Washington, 2016). The implementation of this bill may potentially trigger the phasing out PBDE alternatives, thus initiate the development and use of newer FRs. 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.

To bridge this knowledge gap, the main objectives of the present study are:

a) To assess the presence of legacy and alternative FRs in three different indoor environments from two European countries (the UK and Norway)
b) To estimate and compare human intakes to a wide range of FRs via dust ingestion using the same dust samples for non-working adults and toddlers in Norwegian and British houses, as well as for working adults in British stores and offices.

2. Materials and methods

2.1. 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 (Papadopoulou et al., 2016). Twenty-two indoor dust samples from pre-existing vacuum cleaner bags (10 houses, 6 stores and 6 offices; Table SI-1) 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 with respect to the participant's approval and willingness to cooperate in the present study. All dust samples were sieved to <250 μm using a methanol-washed metallic sieve; this size fraction of dust is likely to be ingested according to (Yu et al., 2012). Oven-baked Na_2SO_4 (granular) was also sieved as field blank. All dust samples were kept in hexane-washed amber glass bottles and stored at 4 °C till analysis.

2.2. Extraction and clean-up

The method was based on a previous study (Van den Eede et al., 2012) 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 isooctane (F1 & F2a) and methanol (F2b), respectively, and then filtered. Finally, the extracts were transferred to injection vials and analysed 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). More details about sample preparation and instrumental analysis are found in SI.

2.3. QA/QC and data analysis

Overall, 28 and 31 compounds (out of 33) were detected in house and occupational dust samples, respectively (Tables SI-2, SI-3, SI-4, and SI-5). SRM 2585 ($n = 2$, NIST, USA) was used for QC testing and the results were in line with the literature (Table SI-6). Four Na_2SO_4 samples (30 mg) 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^{-1}) according to (Abdallah and Covaci, 2014). Method limits of detection (mLOD) were calculated as three times the standard deviation of the field blanks. For non-detected analytes, mLOD was calculated based on signal-to-noise-ratio 3:1 (Table SI-7). GraphPad Prism® version 7.00 for Windows, (GraphPad Software, La Jolla CA, USA) was used for statistical analysis. Compounds with detection frequencies (DF) lower than 40% were excluded from statistical analysis. Where needed, non-detections were replaced by half of mLOD 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 and checked for normality again. Not all data were normally distributed after log-transformation. Ordinary two-way ANOVA (Uncorrected