Human exposure to legacy and emerging halogenated flame retardants via inhalation and dust ingestion in a Norwegian cohort

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Introduction

Flame retardants (FRs) are substances added to a wide range of products, including textiles, plastics, foams and building insulation materials, to prevent fires or at least to make them more fire resistant. Occurrence of several FRs in the environment, including food and human biota, has raised the concern over the risks to human health and led to restriction on the production and the use of certain formulations of FRs, such as polybrominated diphenyl ethers (PBDEs) and hexabromocyclododecanes (HBCDDs) [1]. The phase out of these formulations has led to replacement by less well known and studied chemicals, known as emerging flame retardants (EFRs). These EFRs have been detected in e.g. indoor air and dust, outdoor air, soil and sediment [2-5].

Assessment of human exposure to FRs, particularly in the case of PBDEs, has focused on dietary intake and ingestion of contaminated household dust as the main exposure routes. Air inhalation was often reported as a minor pathway of exposure to these chemicals [6, 7]. Most of the studies have extrapolated human inhalation exposure from indoor stationary air data. However, in a study measuring inhalation exposure through stationary samplers and personal samplers worn by participants in Boston, USA, Allen et al. [8] concluded that personal air concentrations of less volatile PBDEs exceeded stationary air measurements, due to the presence of a 'personal cloud' of suspended particles generated by participant activities. On the other hand, lower levels of organophosphate FRs were observed in personal air samples compared to stationary air samples [9]. These results indicate that stationary indoor air concentrations might not fully represent what people are exposed to, due to time-activity patterns in several different microenvironments.

Therefore, this study aimed to estimate the daily inhalation and dust ingestion exposure of FRs in a Norwegian cohort. In order to also study the comparability of indoor air to personal air, simultaneous sampling of stationary air and personal air was done for a sub-sample of the participants.

Materials and methods

Settled dust and stationary air samples were collected from the living room of 61 households in Norway between November 2013 and April 2014 according to Papadopoulou et al. [10]. Personal air samples from people residing in these homes were collected simultaneously. Thirteen of the personal air samples were available for this study (the other personal air samples went to analysis of other analytes elsewhere). All samples were extracted with dichloromethane (DCM) in an ultrasonic bath for 30 min. The air and dust extracts were fractionated and clean-up according to Ionas and Covaci [11] and Sahlström et al. [12], respectively. PBDEs and EFRs were analysed by gas chromatography-mass spectrometry in electron capture negative ionization mode (GC-ECNI-MS), while HBCDDs

and tetrabromobisphenol A (TBBPA) were measured by ultra-performance liquid chromatography coupled to a tandem-quadrupole mass spectrometer (UPLC-MS). Inhalation and dust ingestion exposures were calculated for each participant using the concentrations found in samples.

Results and discussion

Results from the analysis are summarized in Figure 1. Individual FRs were detected in indoor dust, stationary air and personal air samples with concentrations ranging from <0.017-74000 ng/g, 0.012-720 pg/m^3 and <0.79-1200 pg/m^3, respectively. Less volatile FRs such as BDE-209, bis(2-ethylhexyl)-3,4,5,6-tetrabromophthalate (BEH-TEBP), decabromodiphenylethane (DBDPE), TBBPA and HBCDDs were frequently detected (DF≥93%) in dust at relatively high median concentrations (23-940 ng/g). More volatile FRs including 1,2-dibromoethyl)-1,2-dibromocyclohexane (DBE-DBCH) (median = 25 pg/m^3), 2-ethylhexyl-2,3,4,5-tetrabromobenzoate (EH-TBB) (152 pg/m^3) and BDE-47 (3.8 pg/m^3) were detected in at least 85% of the stationary air samples. These results are consistent with studies that showed that FRs with lower octanol-air partition coefficients (K_{OA}) tend to be less associated with dust particles [4, 5, 13]. Personal air samples were mainly dominated by BDE-209 (median=64 pg/m^3, DF 85%) and DBE-DBCH (median=110 pg/m^3, DF 54%). Statistical analysis (Related-samples Wilcoxon Signed Rank Test, p<0.05) showed that the concentrations of BDE-209 and DBE-DBCH were significantly higher in personal air compared to the corresponding stationary air (median = 25 and 2.5 pg/m^3, respectively).

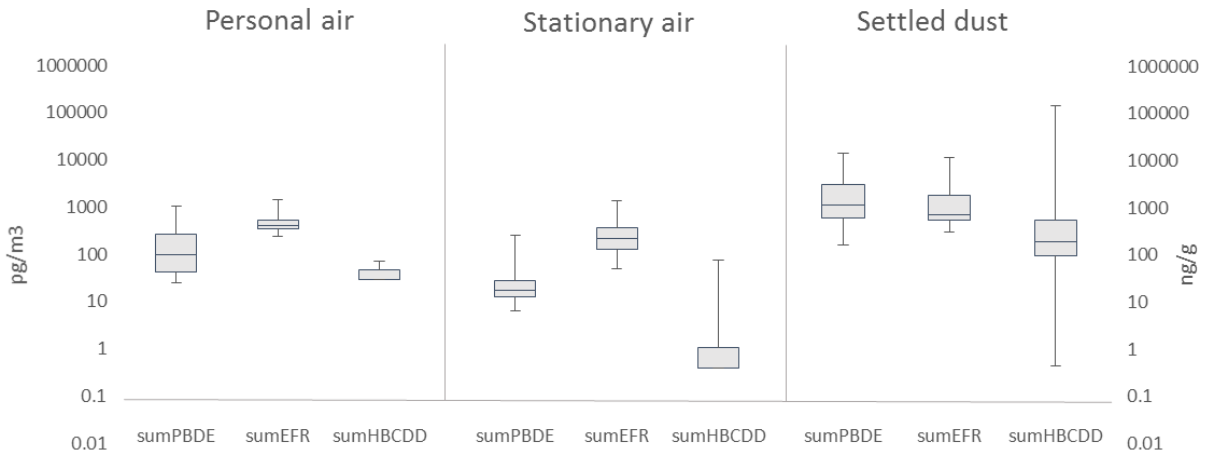

Figure 1: Concentrations of sumBDE, sumEFR and sumHBCDD in personal air, stationary air (pg/m^3) and indoor dust (ng/g) samples.

The measured concentrations of FRs in indoor dust and air were used to calculate the human exposure from dust ingestion and air inhalation. Dust ingestion was the main route of exposure to most of the FRs. The daily exposure through dust ingestion was highest for sumPBDE, followed by sumEFR and sumHBCDD (medians = 450, 290 and 83 pg/kg bw/d, respectively) (Figure 2). Daily inhalation exposure estimated using stationary air data found EFRs, such as DBE-DBCH and EH-TBB to be predominant. However, the inhalation exposure values obtained were lower compared to those estimated with personal air data (sumEFR: 8.6 versus 94 pg/kg bw/d; sumPBDE: 0.66 versus 24

pg/kg bw/d; sumHBCD: 0.022 vs 8.1 pg/kg bw/d). Statistical analysis showed no significant correlations between corresponding stationary air and personal air.

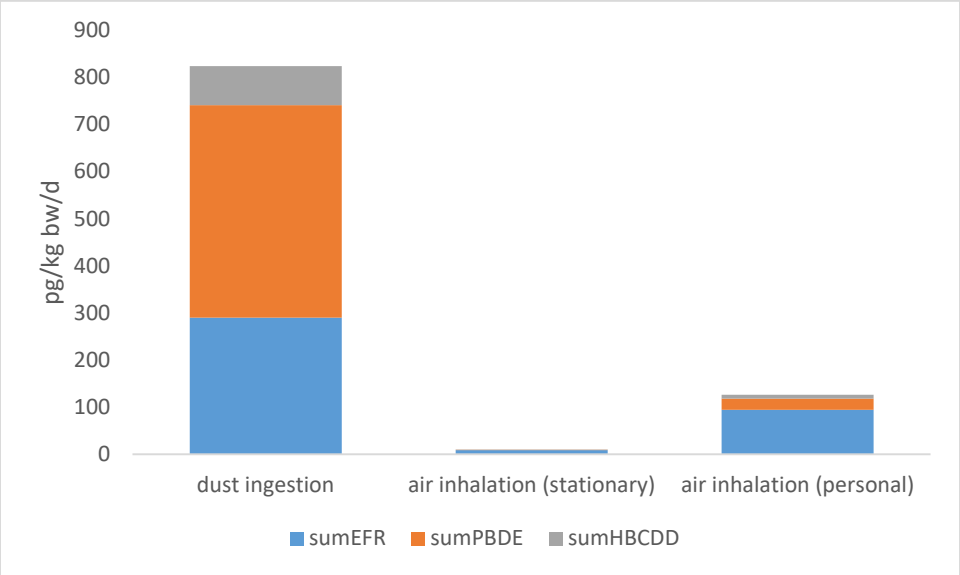

Figure 2: Comparison of the median estimated exposure to FRs through dust ingestion and air inhalation (pg/kg bw/d).

Spearman rank correlation analysis showed that FR concentrations found in air and dust were positively correlated to the number of electronic equipment (such as TVs, videos, DVD players, desktops, laptops and PC screens) in the living room ($0.26 < r < 0.53$). No significant correlations were observed between personal air concentrations and any indoor parameter. Although this study was limited to a small number of personal air samples, our data indicate that sampling of living room air only cannot capture the whole exposure profile for a person.

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References

1. UNEP. *Stockholm Convention on Persistent Organic Pollutants*. [cited 2016 January 13]; Available from: http://chm.pops.int/TheConvention/ThePOPs/ListingofPOPs/tabid/2509/Default.aspx.
2. Drage, D.S., et al., *Concentrations of legacy and emerging flame retardants in air and soil on a transect in the UK West Midlands.* Chemosphere, 2016. **148**: p. 195-203.
3. Yang, R., et al., *Emerging brominated flame retardants in the sediment of the Great Lakes.* Environmental Science & Technology, 2012. **46**(6): p. 3119-3126.

4. Cequier, E., et al., *Occurrence of a Broad Range of Legacy and Emerging Flame Retardants in Indoor Environments in Norway.* Environmental Science & Technology, 2014. **48**(12): p. 6827-6835.
5. Newton, S., U. Sellström, and C.A. de Wit, *Emerging Flame Retardants, PBDEs, and HBCDDs in Indoor and Outdoor Media in Stockholm, Sweden.* Environ Sci Technol, 2015. **49**(5): p. 2912-20.
6. Cequier, E., et al., *Comparing human exposure to emerging and legacy flame retardants from the indoor environment and diet with concentrations measured in serum.* Environment International, 2015. **74**(0): p. 54-59.
7. Fromme, H., et al., *Human exposure to polybrominated diphenyl ethers (PBDE), as evidenced by data from a duplicate diet study, indoor air, house dust, and biomonitoring in Germany.* Environment International, 2009. **35**(8): p. 1125-1135.
8. Allen, J.G., et al., *Personal exposure to Polybrominated Diphenyl Ethers (PBDEs) in residential indoor air.* Environmental Science & Technology, 2007. **41**(13): p. 4574-4579.
9. Xu, F., et al., *Comprehensive Study of Human External Exposure to Organophosphate Flame Retardants via Air, Dust, and Hand Wipes: The Importance of Sampling and Assessment Strategy.* Environmental Science & Technology, 2016. **50**(14): p. 7752-7760.
10. Papadopoulou, E., et al., *Sampling strategy for estimating human exposure pathways to consumer chemicals.* Emerging Contaminants, 2016. **2**(1): p. 26-36.
11. Ionas, A.C. and A. Covaci, *Simplifying multi-residue analysis of flame retardants in indoor dust.* International Journal of Environmental Analytical Chemistry, 2013. **93**(10): p. 1074-1083.
12. Sahlström, L., U. Sellström, and C.A. de Wit, *Clean-up method for determination of established and emerging brominated flame retardants in dust.* Analytical and Bioanalytical Chemistry, 2012. **404**(2): p. 459-466.
13. Wong, F., et al., *Dioxin-like activities, halogenated flame retardants, organophosphate esters and chlorinated paraffins in dust from Australia, the United Kingdom, Canada, Sweden and China.* Chemosphere, 2017. **168**: p. 1248-1256.