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Comparing human exposure to emerging and legacy flame retardants from the indoor environment and diet with concentrations measured in serum

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ABSTRACT

This study investigates associations between serum concentrations of emerging and legacy halogenated flame retardants (HFRs) in 46 Norwegian women and measured indoor air and dust concentrations of the HFRs as well as detailed information on diet and household factors. Hexabromobenzene (median 0.03 ng/g lipid) and Dechlorane 602 (median 0.18 ng/g lipid) were detected in about 50% of the samples and Dechlorane Plus *syn* (median 0.45 ng/g lipid) and *anti* (median 0.85 ng/g lipid) in more than 78%. The most abundant polybrominated diphenyl ethers were 2,2′,4,4′,5,5′-hexabromodiphenyl ether (BDE-153; median 0.82 ng/g lipid) and 2,2′,4,4′-tetrabromodiphenyl ether (BDE-47; median 0.49 ng/g lipid) detected in more than 70% of the samples. In the bivariate analysis, no consistent associations were observed between the biomonitoring data and measured concentrations in indoor air and dust. On the other hand, consumption of specific food items (mainly lamb/mutton and margarine) correlated significantly with more than two HFR serum concentrations, while this was not the case for household factors (electronic appliances). Only the significant bivariate associations with diet were confirmed by multivariate linear regression analyses, which might indicate a higher contribution from food compared to the indoor environment to the variation of the body burden of these HFRs.

1. Introduction

Halogenated flame retardants (HFRs) are a group of chemicals used to provide fire resistance to a wide variety of consumer goods. The occurrence of the most frequently used HFRs, such as polybrominated diphenyl ethers (PBDEs) and 1,2,5,6,9,10-hexabromocyclododecane (HBCDD), has been recently detected in humans (Jakobsson et al., 2012; Rawn et al., 2014), even after they have been phased-out due to their toxic effects in animals, and reported associations between human body burden of HFRs and adverse health effects (Darnerud, 2008; Marvin et al., 2011; Turyk et al., 2008; Herbstman et al., 2010; Eskenazi et al., 2013). After the ban of these chemicals, other HFRs, such as hexabromobenzene (HBB) and dechloranes, have been increasingly detected in humans (Brasseur et al., 2014; Cequier et al., 2013; Ren et al., 2009). These new or "emerging" HFRs have similar physicochemical properties as the former flame retardants (FRs) and thus, they are also potentially hazardous for the environment and human health. The most studied sources of human exposure to HFRs are house dust and diet. The content of HFRs in dust may vary geographically due to different fire regulations and uses in different countries. In Europe, some studies suggest that exposure from house dust is lower than from the diet (Harrad et al., 2004; Roosens et al., 2009). However, in countries where indoor environments are highly contaminated, like the U.S.A., dust ingestion was estimated to account for 82% of the overall PBDE intakes in a modelling study (Lorber, 2008). This has been experimentally supported by later studies (Johnson et al., 2010; Stapleton et al., 2012; Watkins et al., 2011, 2012), which showed significant associations between concentrations of PBDEs in dust and in serum from the general population. The contamination of indoor dust has been surveyed to evaluate exposure to emerging and legacy HFRs through ingestion of dust (Cequier et al., 2014; Dodson et al., 2012). Nonetheless, most other studies have not found any significant associations between exposure to PBDEs from indoor dust and levels in human serum (Fromme et al., 2009; Imm et al., 2009; Roosens et al., 2009; Zheng et al., 2011). There is increasing awareness of short term exposures in micro-environments with high contamination of HFRs like in cars (Harrad et al., 2008). Such exposures could explain the lack of associations between human biomarkers and house dust.

On the other hand, the exposure to HFRs through diet is more likely because HFRs are lipophilic and tend to bioaccumulate in the food web. Diet has been reported as a significant source of human exposure to PBDEs (Fraser et al., 2009; Knutsen et al., 2008). Two studies from Scandinavia assessing the impact of fish consumption (Sjödin et al., 2000;

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Thomsen et al., 2008) and one study from U.S.A. (Anderson et al., 2008) reported fish as the food item that contributed most to the intake of PBDEs. In contrast, some studies reported a significant contribution of poultry and red meat to PBDE intake in the U.S.A. (Fraser et al., 2009; Rose et al., 2010). To the best of our knowledge, there are no studies assessing the relationship between dietary exposure and blood levels of emerging HFRs.

This work undertakes an experimental approach to elucidate the extent to which diet and dust and air from residential living rooms, as well as, several other household factors, contribute to the concentrations of emerging and legacy HFRs in the serum of 46 Norwegian women.

2. Methods and materials

2.1. Recruitment of participants, sampling and questionnaires

A Norwegian mother–child cohort comprising 48 women and 54 children was established in 2012 to measure concentrations of halogenated and organophosphate FRs in air and dust from the participants' living rooms as well as biomarkers of exposure in serum and urine. Detailed information about the cohort has been published elsewhere (Cequier et al., 2014). This paper covers the occurrence of persistent flame retardants in blood from the women in the study group (no blood was drawn from the children). Informed consent was received from all participants, and the study was approved by the Regional Committee for Medical Research Ethics.

The participants were asked to donate blood and to answer a food frequency questionnaire (FFQ) and a questionnaire related to household factors and demographic characteristics. A total of 46 blood samples were obtained from medical centres where venous blood was drawn into 10 mL BD Vacutainers® (Sarstedt, Nümbrecht, Germany), and serum was separated. The serum samples were shipped to the Norwegian Institute of Public Health and stored at −20 °C until analysis. Three lipid groups were enzymatically determined at the Oslo University Hospital and the total lipid content of the serum samples calculated according to Grimvall et al., 1997.

Samples of air and dust were collected from the living room of the participants' residences. A comprehensive description of the collection of the samples and levels of HFRs in air and dust has been published previously (Cequier et al., 2014). In brief, air was passed through polyurethane foam (PUF) plugs with a quartz filter in front using pumps at a flow of 12 L/min for 24 h, and dust was collected vacuuming the entire floor of the living rooms. For air analysis, filter and PUFs were extracted together in an ultrasonic bath and total airborne HFRs determined by GC–MS (electron capture negative ionization mode). For dust analysis, coarse particles were removed and approximately 75 mg of non-sieved dust was extracted in an ultrasonic bath and HFRs determined by the same GC–MS technique.

Dietary exposure to HFR was assessed through the FFQ consisting of 340 questions organized in 42 food categories according to Norwegian dietary habits (Meltzer et al., 2008). The FFQs categorized consumption per day, week and month, and food intake expressed as g/day over the last year, were calculated. The FFQ has been subjected to a comprehensive validation in a pregnancy sub-cohort study (Brantsæter et al., 2008). In addition, participants answered a questionnaire covering demographic information and several household factors in order to assess likely sources of exposure to HFRs (see list in electronic supplementary material).

2.2. Analytical method

Regarding the abbreviation of the HFRs, this study follows the system proposed recently by Bergman et al. (2012) i.e., polybrominated diphenyl ethers (BDE-28, 47, 99, 153, 154 and 183), hexabromobenzene (HBB), Dechlorane Plus® (DDC-CO comprises two isomers *syn* and *anti*), 1,2-bis(2,4,6-tribromophenoxy) ethane (BTBPE), decabromodiphenyl ethane (DBDPE), hexachlorocyclopentadienyl-dibromocyclooctane (DBHCTD), Dechlorane 602 (DDC-DBF) and Dechlorane 603 (DDC-Ant). Detailed description of the analytical method and further information of the standards has been published elsewhere (Cequier et al., 2013). Briefly, 2 mL of serum was spiked with 300 pg of isotopically labelled internal standards and denatured with formic acid. Samples were applied on SPE columns (Oasis® HLB, Waters, Milford, MA, U.S.A.) followed by washing with 5% 2-propanol in water. Columns were dried and analytes eluted with DCM. Clean-up was performed on 33% sulphuric acid-silica (v/w) to remove lipids. Extracts were analysed on a GC HP 6890 series (Avondale, PA, U.S.A.) using a DB5-MS column of 15 m length, 0.25 mm I.D. and 0.1 μm film thickness (Agilent Technologies Inc. CA, U.S.A.). Quantification was performed with an HP 5973 mass selective detector working in electron capture negative ionisation mode.

The method was linear in the range from 0.1 to 1000 pg/μL, recoveries ranged from 36 to 122% with RSDs from 1 to 13%. No recovery correction for concentrations was needed because accuracies were within 88 and 122%, except for DBDPE (recovery 36% and accuracy 67%), but this FR was not detected in serum. The method limit of detection (MLD) ranged from 0.3 (HBB) to 20.2 (DBDPE) pg/g serum. As part of the quality control, twelve procedural blanks were included. When FRs were present in at least 50% of the procedural blanks, the content in the samples was corrected by subtracting the mean blank value. A quality control solution with known concentrations of predominant PBDE congeners was used to assure good performance of the GC–MS from batch to batch. The average accuracy of the determination of PBDE concentrations was 90% with RSD < 15%.

2.3. Statistical analysis

Statistical analyses were performed using SPSS v.20 (Chicago, IL, U.S.A.). Concentrations of HFRs in serum are presented as median, mean, minimum, maximum and number of samples above MLD for each compound. HFRs with detection frequencies < 48% were not subjected to statistical analysis. For HFRs with detection frequencies ≥ 48%, 48%, non-detects were replaced by half the MLD, and Spearman's rank correlation test was employed to calculate correlations among concentrations of different HFRs in serum, between HFRs in serum and in dust and air. Correlations with $p < 0.05$ were considered statistically significant. In order to assess the relationship between concentrations of HFRs in serum with daily consumption (g/day) of specific food categories, demographic information and household factors, a Spearman's rank correlation test was used. Factors correlated with serum concentrations ($p < 0.2$) in the bivariate analysis were further considered for inclusion in multivariable linear regression models of log transformed serum concentrations. All models were adjusted for body mass index (BMI) irrespectively of its significance because there are evidences that suggest likely associations between BMI and body burden of halogenated persistent pollutants (Knutsen et al., 2011). Factors that were found to be significant ($p < 0.05$), after removing the highest p-values following a backward selection procedure, were retained in the final multivariable linear regression models. In addition, serum concentrations and household factors alone were also evaluated in a regression model following the procedure mentioned above. Finally, the models were checked for concentrations of HFRs with high influence and for co-linearity. Multiple co-linearity was rejected when the variance inflation factor was <3 for all the variables in the model.

3. Results and discussions

3.1. Occurrence of HFRs in serum

3.1.1. Emerging HFRs

Five emerging HFRs were detected in the serum samples: HBB, DDC-DBF, DDC-CO (*syn* and *anti*), BTBPE and DDC-Ant (Table 1). HBB and