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Assessment of dietary exposure to organohalogen contaminants, legacy and emerging flame retardants in a Norwegian cohort

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ABSTRACT

Polychlorinated biphenyls (PCBs), organochlorine pesticides (OCPs), polybrominated diphenyl ethers (PBDEs), emerging halogenated flame retardants (EHFRs) and organophosphate flame retardants (PFRs) were detected in 24 h duplicate diet samples from a Norwegian cohort (n = 61), with concentrations ranging from <method limit of quantification (MLQ)-0.64 ng/g ww, <MLQ-0.70 ng/g ww, <MLQ-0.93 ng/g ww, <MLQ-0.14 ng/g ww, and <MLQ-150 ng/g ww, respectively. All studied contaminants were detected in the duplicate diet samples with detection frequencies (DF) ranging from 1.6 to 98%. The major contaminants were CB153 (median 0.042 ng/g ww), α-HCH (median 0.22 ng/g ww), BDE209 (median 0.45 ng/g ww), ethyl hexyl diphenyl phosphate (EHDPHP) (median 3.0 ng/g ww) and bis(2-ethylhexyl)-3,4,5,6-tetrabromo-phthalate (BEH-TEBP) (< MLQ-0.14 ng/g ww). Human dietary exposure assessment was conducted for each participant based on individual body weight and contaminant concentrations in their collected duplicate diet samples. The estimated median (95th percentile) dietary exposures for ΣPFR, ΣPCB, ΣOCP, ΣPBDE, and ΣEHFR were 87 (340), 5.8 (27), 11 (31), 1.3 (14), and <0.01 (3.4) ng/kg bw/day, respectively. The median and 95th percentile dietary exposures of most of the target analytes did not exceed the reference dose (RfD), except for PCBs where 16% of the participants exceeded the RfD. However, a relatively short period of such high intake is not expected to result in any adverse health effects. Participants of this cohort were exposed to higher levels of EHDPHP than any other FRs. Fish was the major dietary route for PCB, OCP and PBDE exposure, while meat was the main dietary exposure route for PFRs.

1. Introduction

Organochlorine pesticides (OCPs) and polychlorinated biphenyls (PCBs) were used worldwide until their restrictions in the late 1970s (Dirtu and Covaci, 2010). PCBs were produced in high tonnages during the 1950s to 1980s and were widely used as e.g. capacitor fluids and transformer coolants (Battershill, 1994). Due to their persistent, bioaccumulative and toxic properties, PCBs and OCPs are still among the most ubiquitous environmental pollutants. Flame retardants (FRs) are used in commercial products to reduce the fire risk and polybrominated diphenyl ethers (PBDEs) were the widely used organohalogen FRs in the past decades (van der Veen and de Boer, 2012, Frederiksen et al., 2009). The Stockholm Convention has listed PCBs, PBDEs (with the exception of Deca-BDE mixture) and some OCPs, including dichlorodiphenyltrichloroethane (DDT), hexachlorobenzene (HCB), alpha- and beta-hexachlorocyclohexane (α- and β-HCH), as persistent organic pollutants (POPs) for strict regulation globally. Deca-BDE was banned for usage in electrical and electronic products and has been completely phased out in Norway (Xu et al., 2016, Cequier et al., 2014). PBDEs are being replaced by alternative FRs, including organophosphate FRs (PFRs) and emerging halogenated FRs (EHFRs). Although there are no worldwide restrictions of alternative FRs, two PFRs, tris(1,3-dichloroisopropyl) phosphate (TDCIPP) and tris(2-chloroethyl) phosphate (TCEP), were recently banned for usage in children products and upholstered furniture by Washington State (Washington, 2016).

Environment and health concerns have been frequently reported for POPs and alternative FRs. They have been detected in various environmental matrices including in the outdoor environment (van der Veen

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and de Boer, 2012, Law et al., 2014), indoor environment (Cequier et al., 2014, Xu et al., 2016, Harrad et al., 2004), food (Labunska et al., 2015, Zheng et al., 2016, Tao et al., 2016, Grassi et al., 2010) and biota (Brandsma et al., 2015, Levin et al., 2016). They, or their metabolites, were also reported in human serum (Cequier et al., 2015, Zhao et al., 2016), breast milk (Antignac et al., 2016, Kim et al., 2014) and urine (Butt et al., 2014, Van den Eede et al., 2015). Many classes of POPs have been identified as threats to human health, linked to hormone-dependent cancer, reproductive disturbances, metabolic syndrome and obesity (Antignac et al., 2016); while some PFRs are considered carcinogenic and/or neurodevelopmental toxicants (van der Veen and de Boer, 2012, Butt et al., 2014). Tris(chloropropyl) phosphate (TCPP) and triphenyl phosphate (TPHP) were associated with reduced human semen quality (Meeker and Stapleton, 2010); rats fed with TDCIPP for 2 years were found to develop tumours in the liver, kidney and testes (van der Veen and de Boer, 2012); while prenatal exposure of rats to Firemaster 550, an FR commercial mixture containing 2-ethylhexyl-2,3,4,5-tetrabromobenzoate (EH-TBB), bis(2-ethylhexyl)-3,4,5,6-tetrabromo-phthalate (BEH-TEBP) and TPHP, led to early puberty, glucose sensitivity, and significant weight gain (Butt et al., 2014).

The occurrence of PCBs, OCPs and PBDEs in food is probably due to their high persistence and hydrophobicity, leading to bioaccumulation in the food chain (Frederiksen et al., 2009, Levin et al., 2016). Diet has been reported as the major source of human exposure to POPs in several market-basket studies (Fraser et al., 2009, Voorspoels et al., 2007, Lu et al., 2010, Törnkvist et al., 2011). In 2010, Dirtu and Covaci (2010) showed that the daily intake of DDTs, HCHs, PCBs and Σtri-hepta-BDEs for Romanian adults and toddlers was mainly due to food consumption (>94% and >70%, respectively) and not through dust ingestion. Similar findings had been reported by Roosens et al. (2009), Frederiksen et al. (2009) and Fromme et al. (2009) in comprehensive exposure studies, showing that dietary intake is the predominant exposure pathway for PBDEs. In a Swedish mother-toddler cohort study, Sahlström et al. (2015) found that diet was the main contributor for intake of ΣpentaBDE and α-tetrabromoethylcyclohexane (α-DBE-DBCH) for both mothers and toddlers. Dietary intake of ΣoctaBDE, hexabromocyclododecanes (ΣHBCDDs) and pentabromobenzene (PBBz) was more important for mothers. Diet contributed more than other external exposure pathways (indoor air, dust, household factors) to serum concentrations of PBDEs in a Norwegian cohort (Cequier et al. (2015).

There are few studies on the occurrence of PFRs and EHFRs in food. In previous studies, we detected PFRs, (including ethylhexyl-diphenyl phosphate (EHDPHP), used in food packaging), in some food samples (Poma et al., 2017, Xu et al., 2015). Whether the presence of PFRs in food is due to migration from food packaging, uptake from the agricultural environment, contamination during food processing or some other source is not clear. PFRs are less persistent than POPs. The structural differences among PFRs lead to a variety of physical and chemical properties within this class of compounds. For example, the accumulation of several PFRs including TPHP and EHDPHP in fish is not lipid dependent (Kim et al., 2011, Brandsma et al., 2015). Zheng et al. (2016) found low levels of chlorinated PFRs in free-range eggs from e-waste recycling areas in China, where extremely high levels of POPs and some persistent EHFRs were measured in the same eggs. There is also a lack of information on the occurrence of alternative FRs in food, as well as the resulting human exposure through diet.

Several methods have been applied to estimate human dietary exposure to environmental contaminants. A combination of food item analysis together with food frequency questionnaires (FFQs) is the most common method used. FFQs provide an approximation of the habitual diet over a designated period of time but they might not be able to produce reliable estimates of true intake at the individual level, since the information about the exact amount of each food ingredient consumed during that period is rarely recorded. Furthermore, potential contamination introduced in the kitchen or during cooking or food storage might be missed (Melnyk et al., 2014). Measurements of duplicate diet samples can bypass many of the unknowns and assumptions that must be made when estimating dietary intake from separately collected consumption surveys (Lu et al., 2010). Important aspects including cooking, storing and packaging at home, and meal composition, are incorporated in duplicate diet methods (Papadopoulou et al., 2016). Collection of duplicate diet samples combined with accurate food consumption data provides more accurate dietary exposure estimation for both a cohort and individuals. However, this method is more costly, burdensome to the participants and labour-intensive in large sampling campaigns. It is also difficult to retrieve which food ingredients are the major contamination sources since the analysis is performed on composite samples.

In this study, human exposure to PCBs, OCPs, PBDEs, EHFRs, and PFRs through dietary intake was determined. Each participant provided one duplicate diet sample where they collected duplicate portions of everything they ate and drank over a 24-hour sampling period, together with a weighed food record. To the best of our knowledge, this is the first study on PFR and EHFR exposure using a duplicate diet approach.

2. Materials and methods

2.1. Targets compounds

This study investigated sixteen PCBs (CB 99, 101, 105, 118, 138, 153, 156, 170, 171, 177, 180, 183, 187, 194, 206 and 209); nine OCPs, including oxychlordane (OxC), *trans*-nonachlor (TN), *cis*-nonachlor (CN), HCB, dichlorodiphenyltrichloroethane (*p,p′*-DDT), dichlorodiphenyldichloroethylene (*p,p′*-DDE), α-, β- and γ-HCH; nine PBDEs (BDE 28, 47, 66, 85, 100, 153, 154, 183 and 209); six EHFRs, including 1,2-bis(2,4,6- tribromophenoxy)ethane (BTBPE), EH-TBB, BEH-TEBP, dechlorane plus (*syn*- and *anti*-DDC-CO) and decabromdiphenyl ethane (DBDPE); and six PFRs, including TCEP, TDCIPP, TCPP, EHDPHP, TPHP and tris(butoxyethyl) phosphate (TBOEP). PCB 143 was used as the internal standard (IS) for PCB and OCP analysis. BDE 103, BE 128 and $^{13}C_{12}$-BDE-209 were used as IS for PBDE analysis. Isotope-labeled standards were used for EHFRs and PFRs analysis. More details about chemicals and materials are found in the supplementary information (SI).

2.2. Sample collection

The participants (n = 61) from a Norwegian cohort collected duplicate portions of all foods consumed over one 24-h period in a sampling campaign carried out between November 2013 and May 2014 as described in Papadopoulou et al. (2016). Food samples were collected in pre-cleaned polypropylene (PP) bottles and weights, types of food and packaging material were recorded in a food record. More details can be found in the SI and in Papadopoulou et al. (2016).

2.3. Analytical method optimisation

Sample extraction and clean-up was performed according to Xu et al. (2015) with some modifications. In short, 2 g of freeze-dried food sample were spiked with IS, extracted with 5 mL acetonitrile: toluene (9:1, v:v) in an ultrasonic bath for 20 min. Instead of using ultrasonication and vacuum assisted extraction (UVAE) as previously described (Xu et al., 2015), syringe filtration was applied, which significantly simplified and speeded-up the extraction process (Fig. 1). This was followed by a multi-stage clean-up procedure involving Florisil, aminopropyl silica (APS) and acid silica cartridges and dispersive solid phase extraction (d-SPE) (Fig. 1). In the present method, fraction A (FA) from the Florisil column and fraction C (FC) from the APS column were combined to a fraction D (FD), which was further cleaned-up through an acid silica column. This resulted in better removal of interferences in FD and smoothing of the previous occasional baseline