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Legacy and alternative halogenated flame retardants in human milk in Europe: Implications for children's health

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ABSTRACT

In this study, 10 polybrominated diphenyl ethers (PBDEs) and 19 alternative halogenated flame retardants (AFRs) were determined in > 450 human milk samples across three European countries, representing northern, western and eastern Europe. This study provides first insights into the occurrence of selected AFRs in mother milk samples and compares them among three European countries. Sums of median concentrations of the most frequently detected PBDEs were 2.16, 0.88 and 0.45 ng g^{-1} lipid weight (lw) in Norway, the Netherlands and Slovakia, respectively. The sum of the concentrations of AFRs ranged from 0.14 to 0.25 ng g^{-1} lw in all countries, which was 2 to 15 times less compared to Σ_7PBDEs. The Penta-BDE replacement, bis(2-ethylhexyl) tetrabromophthalate, BEH-TEBP, was present at the greatest concentrations of any of the AFRs and in some samples exceeded concentrations of BDE 47 and BDE 153. Four AFRs including bromobenzenes (hexabromobenzene, pentabromobenzene, pentabromotoluene) and another Penta-BDE replacement (2-ethylhexyl-2,3,4,5-tetrabromobenzoate, EH-TBB) were detected in > 42% of all human milk samples. Because of the potential developmental neurotoxicity of the halogenated flame retardants, infant dietary intakes via breastfeeding were estimated; in four cases the intakes of BDE 47 exceeded the reference dose indicating that the present concentrations may pose a risk for children.

1. Introduction

Halogenated flame retardants (FRs) are added to manufactured materials, such as electronics, fabrics, plastics, coatings and polyurethane foams, and present about 25% of the total production of all flame retardants (Fink et al., 2008). Polybrominated diphenyl ethers (PBDEs) constitute an important group of FRs. They were introduced in the 1970s, but concerns over adverse health effects (EFSA, 2011) and environmental persistence led to bans or restrictions of uses of the PBDE commercial mixtures in the European Union (EU, 2004, 2010) and by the Stockholm Convention (UNEP, 2009). Despite the restrictions of most PBDEs more than a decade ago, PBDEs are still found to be ubiquitous in the environment and humans and a decreasing trend in the concentrations in humans for selected congeners in some European countries has not been clearly observed (Darnerud et al., 2015).

Because of the restrictions of PBDEs, the use of alternative halogenated flame retardants (AFRs) has increased. However, the environmental behaviour and toxicological properties of many AFRs are still not fully characterized (EFSA, 2012). Early evidence suggests that a number of them are persistent in the environment and may have adverse health effects similar to PBDEs (Dodson et al., 2012). A serious concern associated with the use of halogenated FRs is developmental neurotoxicity (Costa and Giordano, 2007; Fromme et al., 2016). For humans, the periods of life that are most vulnerable to FR exposure are prenatal and the first few years of life because the developing brain is more sensitive to neurotoxicants than the adult brain (Landrigan et al., 2004). Concentrations of FRs in mother milk provide important information for the assessment of the transfer of FRs to the infant. However, despite the toxic potential of the AFRs, there is currently little information regarding AFR concentrations in human matrices in the

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literature (Covaci et al., 2011; EFSA, 2012).

Concentrations of bromobenzene AFRs including hexabromobenzene (HBB) and pentabromotoluene (PBT) in human milk or serum are available from China, Japan and Norway and medians range between 0.03 and 0.33 ng g^{-1} lw (Cequier et al., 2013; Fujii et al., 2012; Shi et al., 2016). The concentrations in two mother milk samples from Sweden were below the limit of detection (LOD) (Sahlstrom et al., 2015). Another group of AFRs includes the Penta-BDE replacements 2-ethylhexyl-2,3,4,5-tetrabromobenzoate, EH-TBB, and bis(2-ethylhexyl) tetrabromophthalate, BEH-TEBP. Their concentrations have been reported in both human milk and serum in Canada (range < LOQ–164 ng g^{-1} for both milk and serum samples (Zhou et al., 2014b)), but in no European country. Concentrations of the Octa-PBDE replacement, 1,2-bis(2,4,6-tribromophenoxy)ethane (BTBPE), were measured in Norway, Sweden, China and Canada (0.08–16 ng g^{-1} lw (Cequier et al., 2013; Sahlstrom et al., 2015; Shi et al., 2016; Zhou et al., 2014b). High concentrations of dechloranes in humans in the range 2.79–180 ng g^{-1} were reported in e-waste dismantling regions in China (Ben et al., 2013; Ren et al., 2009; Yan et al., 2012). One or two orders of magnitude lower were the concentrations reported in Canada, Norway or France (Brasseur et al., 2014; Cequier et al., 2013; Zhou et al., 2014b). Concentrations of other halogenated AFRs in humans have not been reported although these compounds were shown to be present in the indoor environment, which can be an important exposure source for FRs (Cequier et al., 2014; Moya et al., 2004; Tao et al., 2016).

The aim of this study was to determine and compare concentrations of 10 PBDEs and 19 AFRs in > 450 human milk samples from 3 European countries, representing northern, western and central Europe (Norway, the Netherlands and Slovakia). The influence of the mothers' age and parity on the concentrations of FRs in all three countries was assessed. Additionally, infant exposure to FRs via mother milk, which is the main exposure pathway for infants, was estimated.

2. Materials and methods

2.1. Human milk samples

Human milk samples were obtained from three European countries: Norway (n = 305, samples collected in years 2003–2006), the Netherlands (n = 116, years of collection 2011–14) and Slovakia (n = 37, 2011–12). Samples were collected and analyzed within the 7th FP project DENAMIC (DEvelopmental Neurotoxicity Assessment of Mixtures In Children) investigating links between levels of various environmental contaminants and the presence of developmental disorders in children. The participating mothers provided their informed consent and collected the samples between weeks 4 and 8 postpartum into pretreated bottles. The selection of mothers was made based on the examination of neurodevelopmental disorders of their children by means of the CBCL questionnaire (Child Behavioural Checklist) at the age of 24–36 months in each country and, therefore, neurocases presented 10–50% of the samples. Basic characteristics of the mothers are provided in Table 1. Milk samples were stored at −20 °C in the country of collection before sending aliquots to the RECETOX Trace Analytical Laboratories (Brno, Czech Republic).

2.2. Target compounds

The ten PBDE congeners analyzed in the human milk samples (BDE 28, 47, 66, 85, 99, 100, 153, 154, 183 and BDE 209) were chosen as they are representative of the three primary commercial mixtures, Penta-, Octa- and Deca-BDE and also represent the congeners most commonly detected in the environment or exhibit the greatest known toxicity. AFRs included hexabromobenzene (HBB), pentabromobenzene (PBBz), pentabromotoluene (PBT), EH-TBB, BEH-TEBP, BTBPE, TBCT, DBE-DBCH, allyl-2,4,6-tribromophenyl ether (TBP-AE), 2-bromoallyl-2,4,6-tribromophenyl ether (TBP-BAE), 1,2,5,6-tetrabromocyclooctane (TBCO), pentabromobenzyl acrylate (PBBA), pentabromoethylbenzene (PBEB), 2,3-dibromopropyl-2,4,6-tribromophenyl ether (TBP-DBPE), hexachlorocyclopentenyl-dibromocyclooctane (DBHCTD), 2,3,5,6-tetrabromo-p-xylene (TBX), Dechlorane Plus (DDC-CO), and Dechlorane Plus mono adduct (DDC-COMA).

Table 1
Demographics of the participating mothers from each group. Shown are medians and, in parentheses, 25th and 75th percentiles.

	Norway (n = 305)	The Netherlands (n = 120)	Slovakia (n = 37)	p-Value[b]
Years of sample collection	2003–2006	2011–2014	2011–2012	
Age (years)	30 (26–33)	31 (29–34)	30 (27–33)	0.001
Body mass index (kg m^{-2})[a]	23.4 (21.4–26.0)	23.2 (21.4–24.6)	21.9 (20.5–24.0)	0.079
% of lipids in human milk	3.0 (2.3–3.8)	3.8 (3.2–4.7)	4.0 (3.0–5.1)	0.001
Number of children, %				0.303
1	40	43	41	
2	39	38	47	
3 or more	21	19	11	
Not available			1	

[a] Before pregnancy.
[b] Differences between three countries evaluated with Kruskal–Wallis test for continuous variables and Chi-Square test for categorical variables.

2.3. Sample preparation and instrumental analysis

A detailed description of the method for the determination of PBDEs and AFRs has been previously published (Čechová et al., 2016). In brief, 10 ml of the sample were lyophilized and isotope-labelled internal standards were added. All native and ^{13}C–labelled standards were obtained from Wellington (Wellington laboratories, Canada). Pressurized liquid extraction (PLE) was followed by a two-stage clean-up: dialysis with semipermeable membrane (2 × 20 ml of hexane, 48 h duration with the exchange of the solvent after 24 h) and sorbent chromatography (basic alumina and C18, elution using 9 ml of acetonitrile). Prior to the instrumental analysis, 1 ng of the labelled recovery standards ($^{13}C_{12}$ BDE 77 and BDE 138) was added. Concentrations were normalized to lipid content, which was determined gravimetrically after PLE in each sample. The lipid content obtained by PLE was similar to the lipid content provided by the reference Röse-Gottlieb method for determination of lipids in milk (IDF, 1996), which was tested using whole cow's milk samples: 3.40 ± 0.15% of fat, n = 4, using the PLE method and 3.38 ± 0.18% of fat, n = 4, with the reference method.

The analyses of PBDEs and AFRs were performed using a 7890A (Agilent, USA) gas chromatograph coupled to a double-focusing high-resolution mass spectrometer (HRMS, AutoSpec Premier, Waters, UK) equipped with a 15-m × 0.25-mm × 0.10-μm Rtx-1614 column (Restek, USA). More details about the instrumental parameters are provided in the Supplementary Material.

2.4. Quality assurance/quality control

All measurements were performed in an ISO/IEC 17025 accredited laboratory. Verification of the FR method was carried out through participation in interlaboratory tests on PBDEs in human milk and AFR measurement (Interflab; Melymuk et al., 2015).

Quantification of PBDEs and selected AFRs was performed using the isotope dilution method where labelled internal standards were available ($^{13}C_{12}$ BDE 28, 47, 99, 100, 153, 154, 183 and 209, ^{13}C HBB, PBBz, EH-TBB, BEH-TEBP, BTBPE, *syn*- and *anti*-DDC-CO). The remaining AFR concentrations were corrected by the average recoveries obtained from the analysis of an in-house reference material (mother milk samples fortified with native standards) which was analyzed in a batch of every

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