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The determination of perfluoroalkyl substances, brominated flame retardants and their metabolites in human breast milk and infant formula

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ABSTRACT

In the present study, a novel analytical approach for the simultaneous determination of 18 perfluoroalkyl substances (PFASs) and 11 brominated flame retardants (BFRs) including their hydroxylated metabolites and brominated phenols has been developed and validated for breast milk and infant formula. The sample preparation procedure based on extraction using acetonitrile and subsequent purification by dispersive solid-phase extraction (d-SPE) employing C18 sorbent is rapid, simple and high-throughput. Ultra-high performance liquid chromatography (UHPLC) interfaced with a tandem mass spectrometry (MS/MS) was employed for the identification/quantification of these compounds. The method recoveries of target compounds for both matrices ranged from 80% to 117% with relative standard deviations lower than 28% and quantification limits in the range of 3–200 pg/mL for milk and 5–450 pg/g for infant formula. Within the pilot study, the new method was used for the analysis of PFASs and BFRs in 50 human breast milks and six infant formulas. In the breast milk samples the total contents of PFASs and BFRs were in the range of 38–279 and 45–16,200 pg/mL, respectively. The most abundant PFASs detected in all tested breast milk samples were perfluorooctanoic acid (PFOA) and perfluorooctanesulfonate (PFOS), the latter contaminant was present not only as a linear form but also as a branched isomers. The incidence of BFRs was lower, the only representatives of this group, tetrabromobiphenol A (TBBPA) and α-hexabromocyclododecane (α-HBCD), were detected in less than 30% of breast milk samples. None of the infant formulas contained BFRs, traces of either PFOS, PFOA or PFNA were found in three samples.

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1. Introduction

A wide range of halogenated contaminants are present in the human environment. While most of the early monitoring studies focused on various chlorinated persistent organic pollutants (POPs), in recent decades, toxicological concerns emerged on the ubiquitous occurrence of fluorine and bromine containing compounds that may also accumulate in food chains. The high volume production of perfluoroalkyl substances (PFASs) and brominated flame retardants (BFRs), the latter represented mainly by polybrominated diphenyl ethers (PBDEs), hexabromocyclododecanes (HBCDs) and tetrabromobisphenol A (TBBPA), have led to their widespread distribution in the environment. As regards to PFASs, due to their unique characteristics such as chemical inertness, stability, hydrophobicity and lipophobicity, they are used in a variety of industrial and consumer applications while BFRs are used to reduce the flammability of treated materials [1,2].

Non-occupational human exposure to PFASs and BFRs, that may occur through a variety of pathways including inhalation of contaminated dust particles [3,4] or food [5,6]/drinking water ingestion [7], has been clearly documented by findings of these chemicals and their (bio)transformation products in human tissues and fluids including plasma and breast milk [8–10]. The latter matrix is a widely used bioindicator that can be used to assess the body burden of these environmental pollutants especially with regard to its importance as the first food for the newborn.

Recently, the European Food Safety Authority (EFSA) has outlined European Union (EU) framework and respective activities of the Panel on Contaminants in the Food Chain (CONTAM Panel) in the field of BFRs. Six Scientific Opinions on the main classes of these contaminants completed between October 2010 and October 2012 have been presented [11]. It is worthy to note that the very recent Scientific Opinion is also concerned with brominated phenols and their derivatives. With the exception of 2,4,6-tribromophenol (2,4,6-TBP), the data for risk assessment are lacking. In

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general, the requirement for the continuation of BFRs surveillance and the need to fill in the gaps in occurrence data on emerging/novel BFRs has been emphasized by EFSA [12]. Similarly, in the last few years, the CONTAM Panel has paid a great deal of attention to public health concerns for a wide range of PFASs entering human food chain [13]. The occurrence of PFASs in various food commodities and estimation of dietary exposure has been recently reviewed by EFSA within a comprehensive scientific report [14]. Nevertheless, the CONTAM Panel has acknowledged the limitation in information available on other PFASs and recommended further monitoring of food contamination. The use of analytical methods with improved sensitivity are needed to increase the proportion of quantified results and thereby the reliability of exposure assessments that has been highlighted.

In our study, we attempted to respond to the EFSA requirement and to implement a highly sensitive method for selected representatives of both the above discussed POP groups. Since the only data on exposure to halogenated POPs in the Czech Republic is available for organochlorine pesticides (OCPs) [15], polychlorinated biphenyls (PCBs) [16], polychlorinated dibenzo-p-dioxins and dibenzofurans (PCDD/Fs) [17] and PBDEs [18], we decided to provide a complementary information on two other groups of halogenated POPS. For this reason a set of breast milk samples for PFASs and polar BFRs represented by brominated phenols and hydroxylated derivatives of PBDEs (OH-PBDEs) was examined for the first time in the Czech Republic. Considering the fact that some newborns have to be fed by infant formula, we also included this matrix in our experiments as another potential exposure source to fluorine/bromine containing POPs.

Although the current trend in food contaminants control is to integrate various contaminants groups into a single procedure, the review of the available scientific literature did not reveal a procedure that was applied for analysis of BFRs and PFASs in breast milk/infant formula. In some studies, both groups of contaminants were monitored [19–21] by using two alternative methods for each compound class. As regards BFRs, gas chromatography coupled to mass spectrometry (GC–MS) is the method of choice for the most often monitored representatives-PBDEs [22]. This approach can also be employed for the determination of other widely used BFRs, nevertheless, some limitations need to be taken into consideration: the separation of HBCD isomers is hardly feasible by common GC capillaries [23], and in the case of rather more polar TBBPA, derivatization of the hydroxyl group is needed prior to injection [24]. Similarly, brominated phenols or OH-PBDEs are not amenable to GC–MS analysis without derivatization [25]. As a result, high performance liquid chromatography (HPLC) based methods represent a more convenient option. Several methods have been recently published describing the use of this approach for examination of polar BFRs, their metabolites [26], HBCD isomers or TBBPA in body fluids [27,28]. Regarding PFASs, the other group of contaminants involved in our study, HPLC–MS(/MS) is also the key technique used for their quantification in biotic matrices [9].

The objectives of our study were: (i) to implement an solution for the simultaneous analysis of PFASs and BFRs including several metabolites amenable to LC–MS analysis in milk and infant formulas and (ii) to apply a new method for the examination of breast milk and infant formula samples.

2. Materials and method

2.1. Samples collection

The samples of human breast milk were obtained from 50 Czech women living in the Olomouc region (located in the north-east part of the Czech Republic) from April to August 2010 thanks to co-operation with the Gyneacological-maternity Clinic, Faculty Hospital in Olomouc. The age of participating mothers ranged from 20 to 43 years (mean and median age was 30 years). To acquire information that could be relevant to the estimation of contamination pathways, patients completed a questionnaire about their age, body weight, current area of residence (rural/urban), number of children (primapara/multipara), occupation, and dietary habits. Approximately 50 mL of each breast milk sample was collected by hand expressing into a pre-cleaned glass bottle and samples were stored at −20 °C until analysis. The lipid content of the human breast milk samples was determined gravimetrically (results ranging from 0.5–4.9%, mean 2.4%); for this purpose the liquid–liquid extraction (LLE) with hexane and diethyl ether followed by filtration of organic phase through anhydrous sodium sulfate was used [18].

In addition, 6 different types of infant formula from the Czech retail market were examined in this study: (i) one powdered infant and two toddler milk formulas, and (ii) one special formula for babies with lactose intolerance, one formula for premature babies and one soya based formula for babies with non-milk diets.

(i) Milk formulas were supplied in 800 g paper packages and the content of proteins, fats and carbohydrates were in the range of 9.3–10.4, 2.9–3.1 and 55.8–59.1 g in 100 g of formula, respectively.
(ii) Special formulas were obtained in 400 g tin packaging with the composition in proteins, fat and carbohydrates in the range of 10.8–12.8, 10.9–27.3 and 46.1–56 g in 100 g of formula, respectively.

2.2. Standards and chemicals

The individual standards of PFASs and HBCD isomers as well as isotopically labeled internal standards of PFASs and HBCD isomers were purchased from the Wellington Laboratories (Guelph, ON, Canada). PFOS standard supplied by Wellington Laboratories contained 78.8% linear (L-PFOS) and 21.2% branched isomers (Br-PFOS), thus separate quantification of L- and Br-PFOS was possible. Individual standards of OH-PBDEs: 6-hydroxy-2,2′,4,4′-tetrabromodiphenylether (6-OH-BDE-47), 2′-hydroxy-2,3′,4,5′-tetrabromodiphenylether (2′-OH-BDE-68), 4′-hydroxy-2,2′,4,5′-tetrabromodiphenylether (4′-OH-BDE-49), 6-hydroxy-2,2′,4,4′,5-pentabromodiphenylether (6-OH-BDE-99), and brominated phenols: 2,4-dibromophenol (2,4-DBP), 2,4,6-TBP, pentabromophenol (PBP), were purchased from AccuStandard (New Haven, CT, USA). The standard of TBBPA was obtained from Cambridge Isotope Laboratories (Andover, MA, USA). The purity of individual standards was at least 98%. Working standard mixtures of all analytes were prepared in methanol (MeOH) and stored in the refrigerator (5 °C); PFASs and OH-PBDEs were at concentrations 0.25; 0.5; 1; 5; 10; 50 and 100 ng/mL, the concentrations of HBCD isomers, TBBPA and brominated phenols were five times higher. Calibration was prepared by mixing 30 μL of particular working standard mixture with 270 μL of blank matrix extract prepared as described below (without addition of isotopically labeled internal standards) to obtain matrix-matched standards corresponding to the relevant concentration levels: 0.025; 0.05; 0.1; 0.5; 1; 5 and 10 ng/mL for PFASs and OH-PBDEs, and 0.125; 0.25; 0.5; 2.5; 5; 25 and 50 ng/mL for HBCD isomers, TBBPA and brominated phenols.

High performance liquid chromatography (HPLC) grade MeOH was supplied by Merck (Darmstadt, Germany). Acetonitrile (MeCN), anhydrous magnesium sulfate and HPLC grade ammonium acetate (99.99%) were obtained from Sigma-Aldrich (Taufkirchen, Germany). Water purified by a Milli-Q® Integral system (no PFASs containing polymers), supplied by Merck (Darmstadt, Germany), was used throughout the study. Sodium chloride was supplied by Lach-Ner

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