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Perfluoroalkyl substances in Breast milk, infant formula and baby food from Valencian Community (Spain)

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ABSTRACT

Environmental and human exposures to perfluoroalkyl substances (PFASs) are of emerging concern since they are persistent and bioaccumulative. The present study reports PFASs levels in human milk, infant formulas and baby food (dry cereals and pots) from the Valencian Community (Spain) in order to evaluate the infant exposure to these substances through the diet. The results show that perfluorobutanoic acid (PFBA) and perfluorooctanoic acid (PFOA) were in all the samples of the four selected matrices (except PFOA in one sample of dry cereal baby food). Perfluoroheptanoic acid (PFHpA) and perfluorodecanoic acid (PFDA) were also detected in 70% of the breast milk samples. In infant formulas, PFDA and perfluorooctanesulfonate (PFOS) were detected in 75% and 69%, respectively. In dry cereals baby food, PFBA was in 100% of the samples while PFOA and PFOS in 92%. In baby food pots, PFDA was also detected in 83% of the samples. Estimated daily intakes (EDIs) of PFOA (maximum 32.2 ng kg^{-1} day^{-1}) and PFOS (9.0 ng kg^{-1} day^{-1}) are lower than tolerable daily intakes (TDIs) established for PFOA (1500 ng kg^{-1} day^{-1}) and PFOS (150 ng kg^{-1} day^{-1}).

1. Introduction

Perfluoroalkyl substances (PFASs) are a group of chemicals that include the perfluoroalkyl sulfonates, perfluoroalkyl carboxylates, perfluorosulfonamides and perfluorinated telomere alcohols as well as their derivatives (Ericson et al., 2008). Since the 1950s, PFASs have been manufactured for a wide range of consumer applications, such as coating in textiles, carpets and food packaging and to a lesser extend in industrial applications as antistatic additives because their unique properties as repellents of water and oil. They are also precursors of certain fluoropolymers such as polytetrafluoroethylene (PFTE). The strong carbon-fluorine bonds make them resistant to chemical and biological degradations (Onghena et al., 2012).

The reported global distribution and high environmental persistence of PFASs (Blum et al., 2015) together with the adverse health effects detected in laboratory animals (Bull et al., 2014), generate increasing concern about these compounds. From a regulatory point of view, PFASs fulfil the criteria to be considered as "persistent organic pollutants" (POPs). Indeed, PFOS, its salts and sulfonyl fluoride were classified as such in 2009 (UNEP, 2010). A recent study concluded that there was a significant decrease of cord blood immune globulin E with high maternal PFOA levels among female infants. However, there were no significant associations among maternal PFOS and PFOA levels and infant allergies or infectious diseases at age of 18 months (Okada et al., 2012). The mechanisms involved in thyroid homeostasis are complex and PFASs interact at several levels with this endocrine system. Consequently, higher concentrations of PFOA and PFOS in serum were associated with current thyroid disease in the U.S. general adult population (Melzer et al., 2010). The decrease of the thyroid hormone levels in serum of rats and monkeys after PFASs exposure (Lau et al., 2007) was also reported. These changes may affect foetal and neonatal development but more studies are needed to establish clinical significances (Wang et al., 2013; Webster et al., 2014). Therefore, a high scientific concern arises about how PFASs can influence human health at neonatal and early postnatal stages of life.

Several studies have suggested that diet is the primarily route of exposure to PFASs for the human being including newborns (Calafat et al., 2007; Picó et al., 2011). The first food normally given to an

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infant is breast milk. The World Health Organization (WHO) recognizes breast milk as the ideal food for the healthy growth and development of infants (WHO, 2015); breastfeeding is also an integral part of the reproductive process with important implications for the health and affectivity of both mother and child. As a counterpart, it could also be a potential excretion route for mothers that may contain toxic compounds due to the mother's exposure. During the last years, few studies have assessed the levels of PFASs in human breast milk (Al-sheyab et al., 2015; Antignac et al., 2013; Barbarossa et al., 2013; Croes et al., 2012; Fujii et al., 2012; Kadar et al., 2011; Lankova et al., 2013; Liu et al., 2010; Llorca et al., 2010; Motas Guzmàn et al., 2016; Sundström et al., 2011; Tao et al., 2008) reporting concentrations in wide range of scales from pg mL^{-1} to $\mu g\,L^{-1}$.

However, with changing lifestyles and the availability of commercially prepared formulae, these formula have become a popular alternative to be taken into account in the dietary studies as potential source of contaminants. The introduction of complementary foods by about 6 months is another potential source of contamination. Cereals are generally the first foods that are introduced into the infant's diet followed by fruits, meat, vegetables and fish. There is scarce information related to baby food and infant formulas. To our knowledge, there are only three previous studies on these types of food. One of them analyses 6 PFASs in 3 brands of commercial milk infant formulas and 2 brands of cereal baby food from Barcelona city (Llorca et al., 2010), the second determines 6 PFASs in infant formula and dairy milk from the USA (Tao et al., 2008), and the other determines 18 PFASs in infant formula from the Czech Republic (Lankova et al., 2013).

The aim of the present study is to evaluate infant exposure to 20 PFASs (perfluoroalkyl sulfonates and carboxylates) in 51 samples of different types of baby food (breast milk, infant formulas, dry cereals and baby food pots). The results of the occurrence combined with the dietary intake of these products attain a preliminary evaluation of the exposure through the estimated daily intake (EDI). The present study contributes new information being the first time that breast milk from the Valencian Community in Spain has been studied. Furthermore, the study covers cereal-based baby food, proteic baby-food and baby food based on fruit and vegetables that has been to the moment scarcely studied.

2. Materials and methods

2.1. Sample collection and preparation

Individual breast milk samples from 10 women from the province of Valencia (Spain) were taken in 2012. All women were healthy (body mass index between 18 and 25), of similar age, physic constitution and primiparous. Characteristics of the volunteer mothers are shown in Table 1. Informed consent was obtained of all volunteer mothers according to the rules of the local ethics committee. After signing the informed consent, the mothers were asked to complete a questionnaire about some topics and habits related to her breastfeeding and baby food until infants are two years old. The women collected their milk at home using their own breast – milk pump previously tested for blank values (data not shown). In the sampling, the breast was completely emptied because milk composition is not homogeneous during one feeding. Aliquots of 25–30 mL were stored at −20 °C into the pre-washed and tested 50 mL polypropylene (PP) tubes.

Table 1
Characteristics of the volunteer mothers (n = 10).

Characteristics	Mean ± SD
Mother age (year)	32 ± 2.36
Mother weight (kg)	64 ± 10.10
Mother height (cm)	167 ± 3.13
Time postpartum (month)	18 ± 5.79
Number of children in family	1 ± 0.00
Total mother breastfeeding duration (month)	18 ± 5.79
Present breastfeeding duration (week)	74 ± 5.66
Exclusive breastfeeding duration (month)	6 ± 0.84
Lactation frequency (feeds/24 h)	3 ± 1.64
Fish consume frequency (times/week)	2 ± 1.21

A wide range of industrial baby foods and infant formulas from retail – store, pharmacies and supermarket were included in this study. Industrial baby foods and infant formulas were supplied in different packaging (involving plastic, sealed containers, pouches, glass jars, boxes, tubs, aluminium bags, etc.). Detailed sample composition is given in Table 2. The wide range of infant formulas included in this study covers all the baby age segments for this kind of industrial food. The composition of these infant formulas depends on the age of the infant and the different brands, among other factors. Composition of carbohydrates ranges from 4.6% in dry cereals baby food to 18% in fruits and vegetables pots, for proteins from 0.6% in fruits and vegetables pots to 4.3% in pots considered as rich in proteins (e.g. meat) and for fats from 0.1% in fruits and vegetables pots to 5.9% in first and follow-on powdered infant formulas. Infant formulas were in powder (16 samples: 5 first, 9 follow on and 2 toddler formulas). Analysed formulas included milk, soy protein based, partially hydrolysed and extensively hydrolysed ("hypoallergenic") formulas.

Among the variety of dry-cereal baby food on the market, the samples for this study (n = 13) were chosen as representatives of the reality as possible (5 and 8 cereals, with honey, biscuits, honey and biscuits, without gluten, etc.). They comprised (i) simple cereals which are or have to be reconstituted with milk or other appropriate nutritious liquids; (ii) cereals added with high protein food which are or have to be reconstituted with water or other protein-free liquid and (iii) rusks and biscuits which are to be used either directly or after pulverisation, with the addition of water, milk or other suitable liquid.

The baby food pots (*n = 12*) can be distinguished into (i) proteics, in which the only or main ingredient is meat, poultry, fish, offal or other traditional source of protein constituting not less than 8% of the total product and (ii) non-proteics if the main ingredients are fruit or vegetables.

2.2. Chemicals and standards

A detailed list of chemicals and standards used in this study is given in the Supporting information (Section I). PFASs were from two groups: perfluoroalkyl carboxylates (PFCAs) and perfluoroalkyl sulfonates (PFSAs). Several isotopically labelled internal standards were used to ensure analytical quality of the results.

2.3. Sample extraction

Sample pre-treatment and extraction procedure was based on an alkaline digestion according to a protocol described elsewhere (Llorca et al., 2010). Briefly, solid samples (2 g) or liquid samples (15 mL), were transferred into a 50 mL PP tube. Then 2 mL of deionized water (only for solid samples) were added and shaken. Sample homogenates were fortified with the surrogate internal standards at 25 ng mL^{-1} (see Section I of the Supporting information) and digested with 8 mL of NaOH (10 mM in methanol) during 3 h at room temperature on an orbital shaker. After the orbital digestion, the samples were centrifuged during 15 min at 1810g and 3 mL of supernatant was taken, diluted with 27 mL of deionized water in a 50 mL PP tube and vortexed during 5 min. SPE was performed using Strata-X 33 μm Polymeric Reversed Phase 60 mg cartridges preconditioned with 5 mL of methanol and 5 mL of deionized water. Then,