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Assessment of perfluoroalkyl substances in food items at global scale

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ABSTRACT

This study assessed the levels of 21 perfluoroalkyl substances (PFASs) in 283 food items (38 from Brazil, 35 from Saudi Arabia, 174 from Spain and 36 from Serbia) among the most widely consumed foodstuffs in these geographical areas. These countries were chosen as representatives of the diet in South America, Western Asia, Mediterranean countries and South-Eastern Europe.

The analysis of foodstuffs was carried out by turbulent flow chromatography (TFC) combined with liquid chromatography with triple quadrupole mass spectrometry (LC-QqQ-MS) using electrospray ionization (ESI) in negative mode. The analytical method was validated for the analysis of different foodstuff classes (cereals, fish, fruit, milk, ready-to-eat foods, oil and meat). The analytical parameters of the method fulfill the requirements specified in the Commission Recommendation 2010/161/EU. Recovery rates were in the range between 70% and 120%. For all the selected matrices, the method limits of detection (MLOD) and the method limits of quantification (MLOQ) were in the range of 5 to 650 pg/g and 17 to 2000 pg/g, respectively.

In general trends, the concentrations of PFASs were in the pg/g or pg/mL levels. The more frequently detected compounds were perfluorooctane sulfonic acid (PFOS), perfluorooctanoic acid (PFOA) and perfluorobutanoic acid (PFBA). The prevalence of the eight-carbon chain compounds in biota indicates the high stability and bioaccumulation potential of these compounds. But, at the same time, the high frequency of the shorter chain compounds is also an indication of the use of replacement compounds in the new fluorinated materials.

When comparing the compounds profile and their relative abundances in the samples from diverse origin, differences were identified. However, in absolute amounts of total PFASs no large differences were found between the studied countries. Fish and seafood were identified as the major PFASs contributors to the diet in all the countries. The total sum of PFASs in fresh fish and seafood was in the range from the MLOQ to 28 ng/g ww.

According to the FAO-WHO diets composition, the daily intake (DI) of PFASs was calculated for various age and gender groups in the different diets. The total PFASs food intake was estimated to be between 2300 and 3800 ng /person per day for the different diets.

Finally, the risk intake (RI) was calculated for selected relevant compounds. The results have indicated that by far in no case the tolerable daily intake (TDI) (150, 1500, 50,000, 1,000,000, 150, 1500 ng/kg body weight, for perfluorohexanesulfonate (PFHxS), fluorotelomer alcohol (FTOH), perfluorobutanesulfonic acid (PFBS), perfluorobutanoic acid (PFBA), PFOS and PFOA, respectively) was exceeded.

1. Introduction

Perfluoroalkyl substances (PFASs) are a group of chemicals characterized by their unique properties such as amphiphilicity and high resistance to degradation. Because of their unique

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features, PFASs are employed in a wide range of products and materials such as protective coatings for cloths and carpets, paper coatings, insecticides, paints, cosmetics and fire-fighting foams, among many others (Buck et al., 2011; Erik Kissa, 1994; Picó et al., 2011).

As a consequence of their continues use for more than 60 years, residues of PFASs are widely spread in the environment (Campo et al., 2014; De Silva et al., 2009; Delinsky et al., 2010; Giesy and Kannan, 2001; Lin et al., 2014; Llorca et al., 2012; Zhao et al., 2011). Some compounds can bioaccumulate and biomagnify in the food chain (Fang et al., 2014; Galatius et al., 2013; Jeon et al., 2010; Kannan et al., 2001; Vestergren et al., 2013; Xu et al., 2014; Yang et al., 2012), and have been detected in humans (Calafat et al., 2006; Llorca et al., 2010; Perez et al., 2012; Schecter et al., 2012).

Dietary intake is considered as one of the major routes of human exposure to PFASs (Schecter et al., 2010). Therefore, during the last years several studies have evaluated the occurrence of PFASs in food (D'Hollander et al., 2010; Domingo et al., 2012a; Ericson et al., 2008a; Eriksson et al., 2013; Haug et al., 2010a; Hlouskova et al., 2013; Jogsten et al., 2009; Ostertag et al., 2009), mainly PFOS and PFOA (Haug et al., 2010b). In these studies, high fish consumption rates were related to high PFASs exposure rates (D'Hollander et al., 2010; Haug et al., 2010b; Hlouskova et al., 2013).

PFASs are currently considered as emerging contaminants in the food chain. For this reason, the European Food Safety Authority (EFSA) has set the tolerable daily intakes (TDI) of PFOS and PFOA at150 ng/kg/day and 1500 ng/kg/day, respectively (EFSA, 2008), recommending as well the additional monitoring of PFASs of different chain lengths. On the other hand, in the Commission Recommendation 2010/161/EU urged to the Member States to monitor the occurrence of PFOS and PFOA, other PFAS with chain lengths between C4 and C15 and their precursors in food (EFSA, 2012).

Recent studies have indicated the prevalence of PFOS and PFOA and the presence of the longer chain homologs as well as the replacement compounds in food. For example, when analyzing samples from Faroe Islands, perfluoroundecanoic acid (PFUnDA) and PFOS were the most frequently detected in milk and drinking water, respectively (Eriksson et al., 2013).

However, the difficulties associated with the ultra-trace analysis of PFASs in food have hampered the study of the dietary exposure. As a result, few studies till now have evaluated the PFASs dietary exposure (Clarke et al., 2010; Domingo et al., 2012b; Ericson et al., 2008b; Kärrman et al., 2009; Noorlander et al., 2011; Tittlemier et al., 2007; Vestergren et al., 2012).

In one of the first studies in Canada (Tittlemier et al., 2007), the average of the dietary intake of total perfluorocarboxylates and PFOS was 250 ng/day. In 2008, (Ericson et al., 2008b) assessed the total PFASs daily intake in Catalonia (Spain). In this work, the average dietary intake for a standard adult man (70 kg of body weight) was found to be around 74.2 ng/day. In a more recent study by the same group, (Domingo et al., 2012a) this value has set around 1100 and 1700 ng/day fresh weight (fw), children being the most exposed population group. These rates corresponded to an amount of PFOA and PFOS between 290 and 450 ng/day.fw and between 80 and 150 ng/day.fw, respectively. Comparing these results with those from another study in the Netherlands (Noorlander et al., 2011), it can be seen that the total daily intake for PFOS was much higher in The Netherlands than in Spain due to a well-known higher consumption of dairy products in the Netherlands. In spite of that, it should be noted that in both cases the intake was below the tolerable intake values established by the EFSA.

Based on 21 measurements and consumption data for the general Norwegian population, a rough estimatimation of the TDI of PFASs was performed by Haugh et al. around 100 ng per day and PFOA and PFOS contributed to about 50% of the total intake (Haug et al., 2010a).

In the US, Schecter et al. (2010) studied the presence of PFAS among other persistent organic pollutants (POPs) in 31 types of samples collected in supermarkets from Dallas. PFOA was present in 17 of the 31 type of samples analyzed, ranging from 0.07 ng/g in potatoes to 1.80 ng/g in olive oil. In terms of dietary intake, PFOA was consumed at a higher level in comparison to other PFASs.

Recently, (Hlouskova et al., 2013) studied the occurrence of PFASs in 15 food commodities consumed in various European markets. In this study, PFOS followed by PFOA, PFBA, and PFNA were the most frequently detected compounds. Whilst PFHxA, PFHpA, PFHxDA were detected in only a few samples. About the different food commodities studied, seafood followed by pig and bovine liver were the samples that showed the highest levels.

In another recent study, (Herzke et al., 2013) the PFASs content in foods and vegetables collected in four countries (Belgium, Czech Republic, Italy and Norway), were studied. I20 different types of vegetables were sampled in Belgium, Czech Republic, Italy and Norway. Perfluorinated carboxylic acids were the main group of detected PFASs, with PFOA as the most abundant one in general followed by perfluorinated hexanoic acid and perfluorinated nonanoic acid. Dietary intake estimates for PFOA show only low human exposure due to vegetable consumption for adults and children, mostly governed by high intake of potatoes.

Should be pointed out that differences between different studies and countries can be attributed, at least in part, to the different analytical methods used by the different research groups. In addition, other factors contributing to these differences are the time between sampling and analysis (since the levels of some compounds can decrease along the time), conservation and temporal trends.

The main objectives of this study were (i) to expand market basket surveys and study the presence of 21 PFASs in common consumed food items in 283 food items (38 from Brazil, 35 from Saudi Arabia, 174 from Spain and 36 from Serbia); (ii) to assess the total daily PFASs intake in the diet of these countries, which have been selected as representatives of the diets in South America, Western Asia, the Mediterranean area and the South-Eastern Europe, and (iii) to assess the dietary risks associated with relevant PFASs in these diets.

2. Materials and methods

2.1. Sampling collection

Between September 2011 and February 2013, samples were purchased from different supermarkets and retail stores in representative cities of Brazil (Sao Paulo, Sao Sebastian, Pereque-Ilhabela, Porto Alegre), Saudi Arabia (Riyadh), Serbia (Belgrade and Novi Sad) and Spain (Barcelona, Girona and Madrid). The selected foodstuff samples in this work were among the most consumed in each country. The samples were collected as a regular consumer does. A total number of 283 food items (35 from Arabia, 38 from Brazil, 174 from Spain and 36 from Serbia) were studied. The 283 food items corresponded to 849 individual samples, 3 different individual samples for each food item. A summary of the samples is presented in Table S1 of the Supplemental Material.

Foodstuffs were pertaining to the following categories: (1) cereals, (2) pulses and starchy roots, (3) tree-nuts, oil crops and vegetable oils, (4) vegetables and fruits, (5) meat and meat products, (6) milk, animal fats, dairy products and eggs, (7) fish and seafood, and (8) other such as candies or coffee.

Immediately after sampling perishable samples were frozen at −80 °C before shipping on dry ice to the IDAEA-CSIC laboratory (Barcelona, Spain) for chemical analysis. Non-perishable samples were stored and shipped at room temperature. After reception at IDAEA-CSIC laboratory, individual units were melt, combined, homogenized and store in polypropylene tubes freeze at −20 °C until their analysis. The parts of the samples that were processed were those generally eaten by consumers.