ASSESSMENT OF PERFLUOROALKYL SUBSTANCES IN FOOD ITEMS AT GLOBAL SCALE

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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 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 (1).

As a consequence of their continues use for more than 60 years, residues of PFASs are widely spread in the environment (2-8). Some compounds can bioaccumulate and biomagnify in the food chain (9-15).

Dietary intake is considered as one of the major routes of human exposure to PFASs (16). Therefore, during the last years several studies have evaluated the occurrence of PFASs in food (17-24), mainly PFOS and PFOA (25).

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 to relevant PFASs in these diets.

Materials and Methods

Sampling collection. Between September 2011 and February 2013, samples were purchased from different supermarkets and retail stores in representative cities of Brazil, Saudi Arabia, Serbia and Spain. The selected foodstuff samples in this work were among the most consumed in each country. The samples were collected in same way that consumers use to do it. 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.

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 ºC until their analysis. The parts of the samples that were processed were those generally eaten by consumers.

Chemicals and standards Analyses were performed using the isotope dilution method. MPFAC-MXA (>98%) containing [13C4] -perfluorobutanoic acid (MPFBA (13C4)), Ion [18O2]-perfluorohexanesulfonate (MPFHxS (18O2)), [13C2]-perfluorohexanoic acid (MPFHxA (13C2)), Ion [13C4]-perfluorooctanesulfonate (MPFOS (13C4)), [13C4]-perfluorooctanoic acid (MPFOA (13C4)), [13C5]-perfluorononanoic acid (MPFNA (13C5)), [13C2]-perfluorododecanoic acid (MPFDoA (13C2)), [13C2]-perfluorodecanoic acid (MPFDA (13C2)), [13C2]-perfluoroundecanoic acid (MPFUdA (13C2)), MFTA-MXA (>98%) [13C2]-perfluorohexylethanoic acid (MFHEA(13C2)), [13C2]-perfluorooctylethanoic acid (MFOEA(13C2)), [13C2]-perfluorodecylethanoic acid (MFDEA(13C2)) analytical standards were obtained from Wellington Laboratories (Guelph, ON, Canada). Native standards used in this study were: PFAC-MXB (98% purity in methanol) containing perfluorobutanoic acid (PFBA), perfluoropentanoic acid (PFPeA), perfluorohexanoic acid (PFHxA), perfluoroheptanoic acid (PFHpA), perfluorooctanoic acid (PFOA), perfluorononanoic acid (PFNA), perfluorodecanoicacid (PFDA), perfluoroundecanoic acid (PFUdA), perfluorododecanoic acid (PFDoA), perfluorotridecanoic acid (PFTrA), perfluorotetradecanoic acid (PFTeA, perfluorohexadecanoic acid (PFHxDA), perfluorooctadecanoic acid (PFODA), perfluorobutanesulfonate (PFBS), perfluorohexanesulfonate (PFHxS),perfluorooctanesulfonate (PFOS), and perfluorodecanesulfonate (PFDS); and FTA (98% purity in isopropanol) including perfluorohexyl ethanoic acid (FHEA), perfluorooctyl ethanoic acid FOEA, perfluorodecyl ethanoic acid FDEA, were as well from Wellington Laboratories Inc., Canada.

Water, methanol, and acetonitrile, Chromasolv Plus for HPLC, ammonium acetate (AcNH4; MW 77.08; 98%), and formic acid (HFo) were obtained from Sigma–Aldrich, Steinheim, Germany.

Sample preparation Online extraction and instrumental analysis The preparation of the samples prior to analysis was as follows: Milk, dairy products and solid matrices were extracted by alkaline digestion using a previously protocol (6). Liquid samples as soups and juices were just filtered prior purification and analysis.

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 ionisation (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 fulfil the requirements specified in the Commission Recommendation 2010/161/EU.

TFC was performed using the Aria TLX-1 system (Thermo Fisher Scientific, Franklin, MA, USA), which comprised a PAL auto sampler (CTC Analytics, Zwingen, Switzerland), two mixing binary pumps (eluting pump and loading pump), and a three-valve switching device unit with six-port valve. The entire system

was controlled via Aria software, version 1.6. The purification of the target analytes was achieved using two extraction columns C_{18} XL (50 mm×0.5 mm, 60µm particle size, 60 Å pore size)) and Cyclone (50 mm×0.5 mm, 60 µm particle size, 60 Å pore size) connected in tandem. Liquid samples and extracts were loaded into the enrichment columns using ultrapure water acidified at pH 4.5 with formic acid.

LC was coupled to a triple quadrupole mass spectrometer Thermo Scientific TSQ Vantage (Thermo Fisher Scientific, San Jose, CA), equipped with a Turbo Ion Spray source, employed in the negative electrospray ionization (ESI (-)) mode. Acquisition was performed in selected reaction monitoring mode (SRM) to obtain enough identification points (IP) for confirmation of each analyte (European Commission Decision 2002/657/EC). Capillary and vaporizer temperatures were 270 °C and 300 °C, respectively. The scan time and width were set at 0.02 s and 0.02 m/z. Data was processed by the Xcalibur software version 1.4.

The method was based on a pre-treatment step, followed by on-line TFC coupled with LC-QqQ-MS using electrospray ionisation (ESI) in negative mode. It was validated for cereals, fish, fruit, milk, ready-to-eat foods, oil and meat. The MLOQs were in general at the pg/g level and pg/mL in solid samples and beverage, respectively. Recovery rates were in the range between 50 and 120 %, and the method presented the adequate precision and inter-day repeatability. For quantification purposes labelled internal standard addition was used.

The method was applied to the analysis of 283 food items (38 from Brazil, 35 from Saudi Arabia, 174 from Spain and 36 from Serbia).

Results and discussion

The analytical parameters of the method fulfil 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 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) was exceeded.

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