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Perfluoroalkyl substances assessment in drinking waters from Brazil, France and Spain

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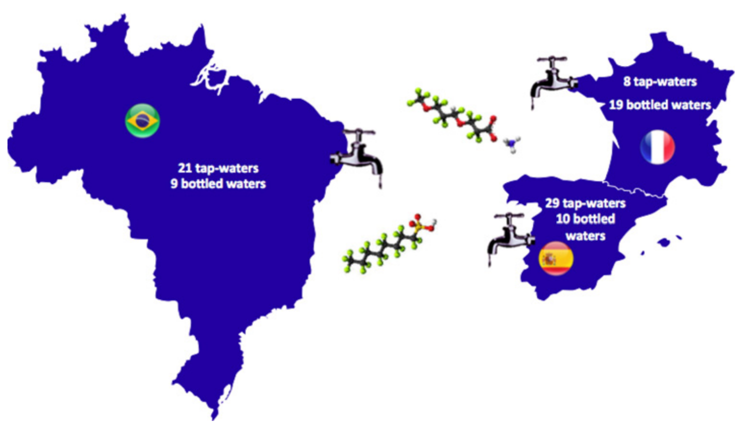
HIGHLIGHTS

- PFASs were assessed in 96 drinking waters from Brazil, France and Spain.
- The highest levels in tap and bottled waters were of 140 and 116 ng/l, respectively.
- The tolerable daily intake has been estimated for 16 PFASs.
- Drinking water did not pose imminent risk associated to PFASs.

GRAPHICAL ABSTRACT



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ABSTRACT

Human exposure to perfluoroalkyl substances (PFASs) occurs primarily via dietary intake and drinking water. In this study, 16 PFASs have been assessed in 96 drinking waters (38 bottled waters and 58 samples of tap water) from Brazil, France and Spain. The total daily intake and the risk index (RI) of 16 PFASs through drinking water in Brazil, France and Spain have been estimated.

This study was carried out using an analytical method based on an online sample enrichment followed by liquid chromatography coupled to tandem mass spectrometry (LC–MS/MS). The quality parameters of the analytical method were satisfactory for the analysis of the 16 selected compounds in drinking waters. Notably, the method limits of detection (MLOD) and method limits of quantification (MLOQ) were in the range of 0.15 to 8.76 ng/l and 0.47 to 26.54 ng/l, respectively.

The results showed that the highest PFASs concentrations were found in tap water samples and the more frequently found compound was perfluorooctanesulfonic acid (PFOS), with mean concentrations of 7.73, 15.33 and 15.83 ng/l in French, Spanish and Brazilian samples, respectively. In addition, PFOS was detected in all tap water samples from Brazil. The highest level of PFASs contamination in a single sample was 140.48 ng/l in a sample of Spanish tap water. In turn, in bottled waters the highest levels were detected in a French sample with

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116 ng/l as the sum of PFASs. Furthermore, the most frequent compounds and those at higher concentrations were perfluoroheptanoic acid (PFHpA) with a mean of frequencies in the three countries of 51.3%, followed by perfluorobutanesulfonic acid (PFBS) (27.2%) and perfluorooctanoic acid (PFOA) (23.0%).
Considering that bottled water is approximately 38% of the total intake, the total PFASs exposure through drinking water intake for an adult man was estimated to be 54.8, 58.0 and 75.6 ng/person per day in Spain, France and Brazil, respectively. However, assuming that the water content in other beverages has at least the same levels of contamination as in bottled drinking water, these amounts were increased to 72.2, 91.4 and 121.0 ng/person per day for an adult man in Spain, France and Brazil, respectively. The results of total daily intake in different gender/age groups showed that children are the most exposed population group through hydration with maximum values in Brazil of 2.35 and 2.01 ng/kg body weight (BW)/day for male and female, respectively. Finally, the RI was calculated. In spite of the highest values being found in Brazil, it was demonstrated that, in none of the investigated countries, drinking water pose imminent risk associated with PFASs contamination

1. Introduction

Perfluoroalkyl substances (PFASs) constitute an important synthetic group of chemicals, which are mostly found in protective coatings of fabrics, carpets and paper as well as in insecticides, paints and cosmetic formulations (Ericson et al., 2008a), fire-fighting foams, hydraulic fluids and waxes (Post et al., 2012) thanks to their amphiphilicity, stability and surfactant capacity (Perez et al., 2014). For these reasons, PFASs are widely distributed in the environment (Yamashita et al., 2008). Recently, perfluorooctanesulfonic acid (PFOS) was listed as a persistent organic pollutant (POP) under the Stockholm Convention on POPs (Wang et al., 2009).

Their potential toxic effects and long half-life in humans (Bartell et al., 2010) are targets of many studies. The PFASs have been detected in human samples (Perez et al., 2012; Karrman et al., 2010; Sundstrom et al., 2011) and dietary intake is considered as one of the major routes of human exposure (Schecter et al., 2010). Furthermore, drinking water represents an important part of human nutrition, both by direct consumption as in food preparation (cooking) (Gellrich et al., 2013). Therefore, one of the main routes of human exposure to PFASs is drinking water (Noorlander et al., 2011; Thompson et al., 2011). The estimated human daily intake of PFOS or PFOA via drinking water can vary in the range <1% to 55% (Schecter et al., 2010; Gellrich et al., 2013; Noorlander et al., 2011; Thompson et al., 2011; Wilhelm et al., 2009). Moreover, serum concentrations are elevated in communities with highly contaminated drinking water (Wilhelm et al., 2009). However, drinking water occurrence studies have targeted PFOS and PFOA (Rahman et al., 2014), while some recent studies have detected a variety of PFASs including the replacement compounds in drinking water like perfluorobutanoic and sulfonate acids (Ahrens et al., 2010; Llorca et al., 2012). Despite the increasing use of short chain PFASs, there is still a lack of information about their presence, as well as their environmental fate and behaviour (Llorca et al., 2012). Furthermore, the possible degradation of products generated in the environment or during water treatment processes should be taken into account (Fromel and Knepper, 2010; Lee et al., 2010).

PFASs have been detected in wastewater (Stasinakis et al., 2013), surface water and groundwater. Surface waters are one of the main sources of drinking water (Thompson et al., 2011), but apart from the contamination of natural sources, some other events can occur during tap water production or water bottling that should be also considered (e.g. contamination from tubing, plastic containers, among others) (Llorca et al., 2012). In recent years, several studies assessed the presence of PFASs in drinking water, particularly in tap water (Gellrich et al., 2013; Llorca et al., 2012; Borg et al., 2013; Castiglioni et al., 2014). In turn, the expansion of the mineral water industry is a global trend. According to the European Federation of Bottled Waters (EFWB), France and Spain are among the largest consumers of bottled water in Europe. Already, Brazil has the largest reserve of fresh drinking water on the planet, and occupies fourth place in the world ranking of producers (Panorama do Mercado de Água Mineral). However, the environmental distribution of PFASs in Brazil is little known (Quinones and Snyder, 2009). In turn, due to the scarcity of data in this matrix the concentrations of PFASs found in mineral water are hard to rank (Gellrich et al., 2013).

The European Food Safety Authority (EFSA) based on the non-observable adverse effect levels (NOAELs), the lowest observed adverse effect levels (LOAELs), established that the tolerable daily intake (TDI) of PFOS and PFOA are 150 ng/kg/day and 1500 ng/kg/day, respectively (EFSA, 2008). The Office of Water (OW) of the Environmental Protection Agency (EPA) calculates the Provisional Health Advisory for PFOA at 400 ng/l and 200 ng/l for PFOS using the exposure scenario of 10-kg child consuming 1 l/day (Provisional Health Advisories for Perfluorooctanoic Acid (PFOA) and Perfluorooctane Sulfonate (PFOS)). However, very few guidelines are available for other PFASs in drinking water as Zushi et al. described (Zushi et al., 2012). Furthermore, these values are calculated for acute exposure while long-term exposures may be more suitable for drinking water. In addition to the individual concentrations, the total sum of compounds should also be considered (Pico et al., 2011). For these reasons, there is an urgent need for the continuous assessment of PFASs in drinking water (Llorca et al., 2012).

Due to the difficulties in the analysis of PFASs (e.g. cross contamination during samples manipulation from contact materials, and potential looses by adsorption to certain container materials), the study of the dietary exposure including short-chain compounds has not been fully addressed (Perez et al., 2014). Usually, the concentrations reported for PFASs in surface inland (i.e. river water or lake water) waters are from picograms to low-nanograms per litre. Therefore, sensitive and accurate analytical methods are essential to ensure reliable results. Online preconcentration in combination with liquid chromatography coupled to tandem mass spectrometry (LC–MS/MS) shows advantages such as the improved precision, an increased throughput capability and better sensitivity, and represents an advance for the rapid screening of PFASs in water, being of special relevance for the routine analysis of water (Llorca et al., 2012).

In order to calculate safety limits of exposure and improve health protection regulation, the Regulatory Organisms needs wider data sets on PFASs in drinking water and beverages. This paper reports the residue analysis of 16 PFASs in bottled water and tap water from Brazil, France and Spain. It must be clarified that bottled water samples in this study included bottled purified municipal waters, which will be referred along the text as "generic brands" and mineral, spring and artesian bottled waters which will be referred in this study under the common denomination of "gourmet brands". In order to represent the consumption in each country, the number of collected water samples from each sub-category was according to the estimated sales in each country.

A total number of 96 samples were analysed (30 from Brazil, 27 from France and 39 from Spain) using an analytical method based on automated on-line pre-concentration step followed by high performance