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Perfluorinated alkyl substances in Spanish adults: Geographical distribution and determinants of exposure

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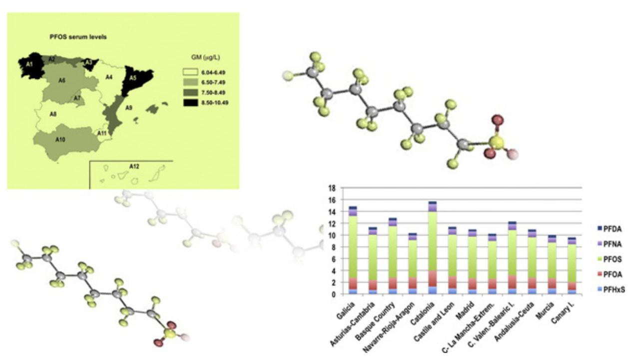
HIGHLIGHTS

- A new information has been reported for PFAS serum levels of Spanish adults.
- Exposure to PFAS was related with sex, age, diet and geographic area.
- Breast feeding decreases PFAS serum levels in women.
- Northeast Spain was the area with the highest exposure to PFAS levels.
- Spanish population has similar exposure levels than their European neighbours.

GRAPHICAL ABSTRACT



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ABSTRACT

Per- and polyfluoroalkyl substances (PFAS) are widely found in humans and the environment. Their persistence, bioaccumulation and toxicity make them a source of increasing public health concern. In this study, we analyzed the concentrations and geographical distribution of six PFAS in the serum of 755 Spanish adults aged 18–65.

The geometric mean concentrations (and P95 values) for PFOS (perfluoroctane sulfonate), PFOA (perfluorooctanoic acid), PFHxS (perfluorohexane sulfonate), PFNA (perfluorononanoic acid) and PFDA (perfluorodecanoic acid) were 7.67 (19.3), 1.99 (5.48), 0.91 (2.84), 0.96 (2.44) and 0.42 (0.99) µg/L, respectively. *N*-Methylperfluorooctane sulfonamide (*N*-MeFOSAA) was detected in only 3.3% of samples.

Residents in northeast (Catalonia) and northwest of Spain (Galicia) were found to have the highest serum values, whereas residents in the Canary Islands had the lowest values for almost all PFAS. Men presented higher levels than women, and we confirm that lactation (breastfeeding) contributes to a reduced body burden for all PFAS in women.

Our data provide new information on exposure to PFAS in a national cross section sample of Spanish adults, thus providing a proxy for reference values for the Spanish population and forming the base for following temporal trends in the future.

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1. Introduction

Perfluoroalkyl substances (PFAS) are a class of chemicals with both hydrophobic and oleophobic properties. They are resistant to thermal, chemical, and biological degradation due to their strong carbon—fluorine (C—F) bonds. These characteristics make them ideal for use in a variety of consumer products and industrial processes (Schultz et al., 2003). Their ubiquity, persistence and bioaccumulation result in their widespread presence in the environment as a result of direct emissions during manufacturing, use, or disposal of products as well as transformation of other precursors into PFAS (Armitage et al., 2009).

PFAS have been found in air, dust and drinking water, and in food items such as fish and dairy products. The contribution of individual pathways and sources to the body burden appears to depend on age, dose and substance. Food, drinking water and house dust are considered to be the main exposure sources for adults, while hand-to-mouth contact with consumer products and house dust is the most important source for children (Freberg et al., 2010; Jain, 2014; Mak et al., 2009). Furthermore, dermal absorption of PFAS occurs as a result of direct contact with consumer products, for example from all-weather clothing and other textiles (Trudel et al., 2008).

Four PFAS, namely perfluoroctane sulfonate (PFOS), perfluorooctanoic acid (PFOA), perfluorononanoic acid (PFNA), and perfluorohexane sulfonate (PFHxS), are commonly detected in humans (Calafat et al., 2007a; Fromme et al., 2007). The substances are metabolized slowly, and particularly long-chain PFAS are accumulating in the body (Perez et al., 2013). Elimination is species- and gender-dependent and particularly humans are slow eliminators of PFAS compared with other species (Olsen et al., 2009). For example, the half-life of PFOS, PFOA, and PFHxS in human serum is 5.4, 3.8, and 8.5 years respectively (Olsen et al., 2009). In general, the elimination is faster with decreasing carbon chain length (Freberg et al., 2010). The compounds have an affinity for proteins such as albumin and liver fatty acid-binding protein (Han et al., 2003). The highest concentrations in exposed animals are found in blood, liver, kidney and gall bladder (Peng et al., 2010).

There is evidence that perfluorinated compounds may pose a risk to human health. In September 2016, the Persistent Organic Pollutants Review Committee (POPRC) to the Stockholm Convention on Persistent Organic Pollutants reached a consensus agreement that PFOA is likely to lead to significant adverse human health and environmental effects such that global action is warranted. Current regulatory actions within the European Union, and elsewhere, mainly concern PFOS and PFOA, while other widely used PFAS are still under evaluation. PFOA has been added to the European Candidate List for authorization within REACH (ED/69/2013) as a substance of very high concern (Kennedy et al., 2004). PFOS and PFOA are classified as suspected carcinogenic (WHO-IARC, 2016), presumed reprotoxic, harmful to breast-fed children and specifically toxic to target organs. It is currently not known if non-regulated PFAS exert similar toxicity. SAICM (Strategic International Chemicals Management Actions, http://www.saicm.org) recognizes PFAS as an emerging policy issue.

When assessing human exposure, the measurement of PFAS levels in body fluids is the most reliable tool for establishing individual exposure associated with environment and lifestyle. In this regard, the human biomonitoring studies that have been performed since the early 2000s (Calafat et al., 2007a; Schroeter-Kermani et al., 2013) have demonstrated that populations worldwide are exposed to several PFAS and that these chemicals are accumulating in the body (Sturm and Aherns, 2010; Vestergren and Cousins, 2009). The findings have demonstrated how different regulatory and non-regulatory actions have affected human exposure. For example, the voluntary restrictions on PFOA and PFOS resulted in decreasing levels in human samples, while the presence of non-regulated PFAS, used to replace PFOS and PFOA increased (Sturm and Aherns, 2010; Vestergren and Cousins, 2009).

In 2008, the Spanish Ministry of Agriculture, Food and the Environment promoted a national Human Biomonitoring program (HBM). The purpose of this program was to enhance the current understanding of the distribution of priority environmental pollutants, such as metals, pesticides, flame retardants, perfluorinated compounds, and polychlorinated biphenyls (PCB), in the Spanish population and to establish reference values (Bartolomé et al., 2015; Cañas et al., 2014; Huetos et al., 2014; López-Herranz et al., 2016; Ramos et al., 2016). In this regard, we designed BIOAMBIENT.ES project, a nationwide cross-sectional study, aimed at obtaining a representative sample of the Spanish occupied population. A subsample of Bioambient.es was selected to analyze PFAS. Here we present baseline serum values for six PFAS in a national cross-section of Spanish occupied adults.

2. Materials and methods

2.1. Study population

BIOAMBIENT.ES is a nationwide cross-sectional epidemiological study with a stratified cluster sampling designed to cover all geographical areas, sex and occupational sectors, and aimed to obtain a representative sample of the Spanish active workforce. The complex design of the study is detailed elsewhere (Perez-Gomez et al., 2013). In brief, volunteers had to be consecutively selected among occupied people older than 16 years, residents in Spain for 5 years or more, which underwent their annual occupational medical check-up between March 2009 and July 2010 in the health facilities of the Societies for Prevention of IBERMUTUAMUR, MUTUALIA, MC-PREVENCIÓN, MUGATRA, UNIMAT PREVENCIÓN, and PREVIMAC, which were distributed across Spain.

A total amount of 113 Prevention Health Centers were available for the project. Those centers are distributed across the whole country; they provide their services to >436,000 companies in Spain in all activity sectors, with 3,600,000 workers employed within a large spectrum of occupations and occupational categories, and perform >650,000 occupational health exams per year. This high number of annual surveys, as well as its wide geographical coverage could allow us to obtain a fairly representative sample of the Spanish workforce. A total of 38 Health Prevention Centers were randomly selected across 12 previously predefined geographical areas, following a proportional distribution according to data from the Spanish Active Population Survey 2007 (Instituto Nacional de Estadística, 2012). Sampling was undertaken in four quarterly recruitment periods to take into account seasonal variability and, was also stratified by sex and by economical sector (two groups: "Service activities" and "Agriculture, Industry & Construction" as defined on the National Classification of Economic Activities for 2009 (Instituto Nacional de Estadística, 2011). Individual information on socio-demographic aspects, lifestyle and environmental conditions, including specific questions on tobacco exposure, diet and food frequency, was obtained using a self-administered questionnaire. Of the total 1880 blood samples collected within Bioambient.es, a subset of 755 serum samples was used to study PFAS exposure. They were obtained by random sampling within each area-gender-occupational sector combination. A set of weights was defined, assigning each participant the inverse of his probability of selection relative to the distribution of occupied people in Spain by autonomous community, sex, and economic activity sector, in accordance with the information provided by the last Spanish Active Population Survey (Instituto Nacional de Estadística, 2009).

2.2. Ethical approval

The study was performed in accordance with legal/ethical principles and regulations concerning research involving individual information and biological samples, including the Organic Law 15/1999 on Personal Data protection and its Regulations, Law 41/2002 on the Autonomy of Patients and rights and obligations relating to health information and