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Concentration and correlations of perfluoroalkyl substances in whole blood among subjects from three different geographical areas in Korea

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HIGHLIGHTS

- Significant geographical differences in PFAS levels in whole blood were found in Korea.
- Gender was found to influence the concentrations of PFOA, PFNA, PFHxS and PFOSA.
- Significant positive associations between PFAS levels and age of subjects were found.
- Occupation was a determinant for PFNA and PFHxS concentrations.

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ABSTRACT

Toxicity and persistence of perfluorinated alkyl substances (PFASs) in human have raised considerable concern and several biomonitoring studies throughout the world reported the widespread occurrence of these compounds in human tissues. However, information regarding influence of geographic, lifestyle and demographic factor on PFAS levels in human blood tissues is limited. In this study, whole blood samples collected in 2006–2007 from 319 donors from suburban Seoul (Suwon and Yongin), Busan and Yeosu in Korea were analyzed for perfluorooctane sulfonate (PFOS), perfluorooctanoate (PFOA), perfluorononanoate (PFNA), perfluorohexane sulfonate (PFHxS) and perfluorooctane sulfonamide (PFOSA). Blood donors classified into seven age groups with ages ranging from 8 to 82 years, and different lifestyles and socio-economic status. PFOS (median = 4.15 ng/mL) was found at the highest concentration with a maximum concentration of 59.1 ng/mL. The concentrations of other PFASs were in the decreasing order of; PFOA (median = 1.30 ng/mL) > PFNA (median = 0.85 ng/mL) > PFHxS (median = 0.47 ng/mL) > PFOSA (median = 0.12 ng/mL). Geographical differences in the concentrations of five target PFASs were found. Significant positive relationships between PFAS concentrations and the age of the donors were found. Gender-related differences were found in the concentrations of PFOA, PFNA, PFHxS and PFOSA. No association was found between PFAS levels and several lifestyle factors and socio-economic status which included drinking habit, furniture/carpet in an indoor environment and monthly income. Occupation was an important determinant for PFNA and PFHxS concentrations in the whole blood. Except for PFOSA, significant associations were noted between PFASs concentrations and smoking habit. The results of this study provide information for further public health monitoring and safety management for PFASs in Korea.

1. Introduction

Perfluoroalkyl substances (PFASs) are a class of fully fluorinated chemicals which have unique properties including chemical stability and have been used in diverse commercial applications, since the 1950s (Banks et al., 1994). Among several PFASs, perfluorooctane sulfonate (PFOS) is an end-stage product of perfluoro chemicals produced using perfluorooctane sulfonyl fluoride (PFOSF) (Olsen et al., 2003). Since the late 1990s, PFOS has attracted considerable attention. Widespread global contamination by PFOS in humans and wildlife was reported in the early 2000s (Giesy and Kannan, 2001; Kannan et al., 2001, 2004). PFOS, its salts and PFOSF were listed in Annex B of the Stockholm Convention on May 2009 as persistent organic pollutants.

Several studies have examined toxicities of PFOS, PFOA and/or other PFASs in laboratory animals and humans. Some of these studies have shown hepatotoxicity and developmental toxicity in zebra fish (Du et al., 2009), immunotoxicity in human early childhood (Grandjean

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et al., 2012; Granum et al., 2013), and hormonal effects in ovoviparus swordtail fish (Han and Fang, 2010). Furthermore, many PFASs are highly persistent in the human body and half-lives were calculated to be in the range of 4–7 years (Olsen et al., 2007). Toxicity and persistence of PFASs in humans have raised considerable concern. Various biomonitoring studies throughout the world reported the widespread occurrence of these compounds in human tissues (Kannan et al., 2004; Inoue et al., 2004; Guruge et al., 2005; Tao et al., 2008; Harada et al., 2010; Kärrman et al., 2010). In Korea, several studies have examined exposure of humans to PFASs and these studies involved samples collected from Daegu (Kannan et al., 2004; Ji et al., 2012b), Siheung (Ji et al., 2012a), Busan (Harada et al., 2010; Kim et al., 2014), Gyeongbuk (Lee et al., 2013), and Seoul (Harada et al., 2010; Kim et al., 2011a). These earlier studies were sporadic in nature and focused on a single geographical location. Furthermore, the earlier studies did not examine the geographical, lifestyle and demographic factors that influence PFAS levels in humans. In the present study, concentrations of PFOS, perfluorooctanoate (PFOA), perfluorononanoate (PFNA), perfluorohexane sulfonate (PFHxS) and perfluorooctane sulfonamide (PFOSA) were measured in whole blood samples collected from three different geographical areas in Korea. The objectives of this study were to determine geographical differences in PFAS levels in humans in Korea and to assess associations between PFAS levels and demographic determinants such as gender, age and several selected lifestyle and socio-economic factors such as smoking habit, drinking habit, the use of sofa and carpet, occupation and monthly income.

2. Materials and methods

2.1. Survey population and blood sampling

The study area comprises of suburban Seoul (Suwon and Yongin), Busan and Yeosu (Fig. 1). Suwon and Yongin are industrialized and high traffic areas. Busan is the largest trading port and a metropolitan city. Yeosu is a small city. The approximate population and density of these cities at the sampling period were 1,100,000 and 8900/km^2 for Suwon, 900,000 and 1500/km^2 for Yongin, 3,600,000 and 4700/km^2 for Busan, and 295,000 and 587/km^2 for Yeosu. Children and adult volunteer participants were grouped into seven age groups as follows: 8–19 years, 20–29 years, 30–39 years, 40–49 years, 50–59 years, 60–69 years and over 70 years. Subjects belonged to both genders, and whole blood samples were randomly collected from February 2006 to June 2007 from people who visited hospitals for follow-up care for existing conditions. Information regarding any complaint or underlying disease of the subjects was not collected. The present study was approved by the Institutional Review Board of Pusan National University Hospital, Busan, Korea. The numbers of participants from Seoul suburban, Busan and Yeosu were 99, 110 and 110, respectively. The blood anticoagulant solution was not used to prevent interferences in the extraction procedure. Whole blood samples were kept at −20 °C until extraction. The whole blood samples were extracted within one month after the collection date.

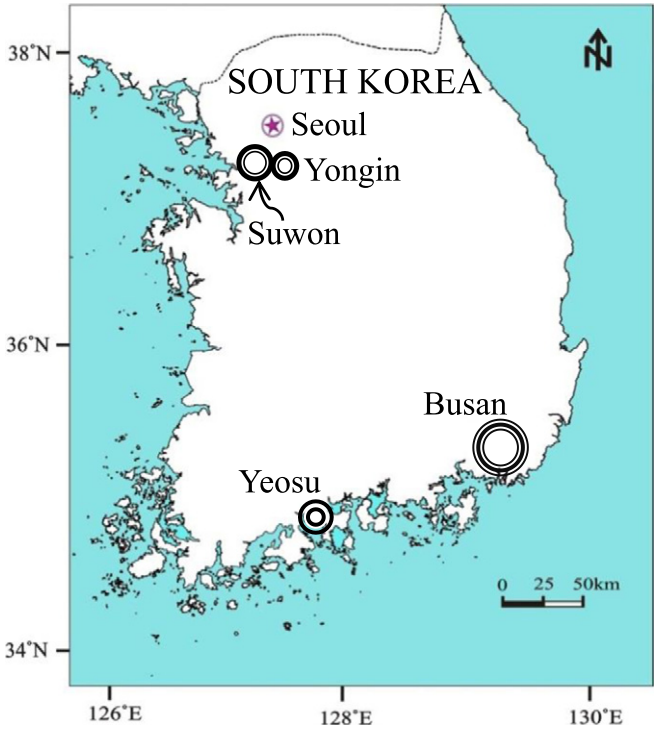

Fig. 1. Map of three blood sampling regions in South Korea including suburban Seoul (Yongin and Suwon), Busan and Yeosu.

2.2. Questionnaire surveys

On the day of blood collection, self-written questionnaires were used to collect information regarding participants including sex, age, education, marital status, socio-economic status such as income and occupation, lifestyle status such as smoking and drinking habits, and household conditions including the use of the sofa and carpet. The questionnaire was administered by trained investigators.

2.3. Chemicals and reagents

Two mass-labeled standards including $^{13}C_4$-PFOS (sodium perfluoro-1-[1,2,3,4-$^{13}C_4$] octane sulfonate) and $^{13}C_4$-PFOA (perfluoro-n-[1,2,3,4-$^{13}C_4$] octanoic acid) were purchased along with native perfluoroalkyl carboxylate acids (PFCAs) and perfluoroalkane sulfonates (PFSAs) from Wellington Laboratories (Guelph, ON, Canada). $^{13}C_4$-PFOS was used as a surrogate for PFSAs and PFOSA, and $^{13}C_4$-PFOA was used as a surrogate for PFCAs. Native standards of five target analytes (PFHxS, PFOS, PFOSA, PFOA and PFNA) were used for standard calibrations. High-performance liquid chromatography (HPLC) grade reagents including methanol (Kanto Chemical, Tokyo, Japan), water (J.T. Baker, USA) and ammonium acetate (Junsei, Japan) was obtained. Milli-Q water was prepared by a Barnstead Nanopure Infinity™ water purification system (Thermo Scientific, Waltham, MA, USA).

2.4. Extraction and analysis

Whole blood samples were extracted from the ion-pair extraction method reported in detail elsewhere (Hansen et al., 2001; Kannan et al., 2004). In brief, 1 mL of whole blood sample was taken in a 15 mL polypropylene (PP) tube and was homogenized by the addition of 2 mL of Milli-Q water and vortexed (Vortex Genie® 2, Scientific Industries, NY). Five nanograms of surrogate standards, 1 mL of tetra-n-butylammonium hydrogensulfate solution 0.5 M (adjusted to pH 10), 2 mL of 0.25 M sodium carbonate buffer and 5 mL of methyl-tert-butyl ether (MTBE) were then added to each tube. The mixture was vigorously shaken for 30 min. The organic and the aqueous layers were separated by centrifugation at 3000 ×*g* for 20 min, and the exact volume of the organic layer (4 mL) was transferred to another tube. The extraction procedure was repeated twice, and MTBE layers were transferred to the tube. The solvent was then evaporated under pure nitrogen to near dryness and reconstituted with 1 mL of methanol. The sample was then vortexed and transferred to a vial after filtration through a 0.2 μm nylon filter. Concentration of PFASs was determined by an Agilent 1100™ HPLC interfaced with an Applied Biosystems API 2000™ tandem mass spectrometer (MS/MS). Ten microliter aliquot of the extract was injected into a guard column connected serially to an analytical column (a Betasil C18, 100 × 2.1 mm, 5 μm particle size, Thermo Electron Corporation, Waltham, MA). The temperature of the