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Occurrence of perfluoroalkyl substances in matched human serum, urine, hair and nail

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ABSTRACT

The purpose of this study was to determine perfluoroalkyl substances (PFASs) in human serum, urine, hair and nail from general populations, and to investigate the possibility for human urine, hair and nail used as the biomonitoring sample for PFASs exposure. We detected the concentrations of PFHxA, PFOA, PFNA, PFDA, PFUnDA, PFDoA, PFHxS and PFOS in 39 matched human serum, urine, hair and nail samples from Shenzhen in China. The detection frequency and the median level of PFOS were all higher than that of the other PFASs in four matrices. The median concentration of PFOS in serum, urine, hair, and nail were 9.24 ng/mL, 13.96 ng/L, 0.58 ng/g and 0.63 ng/g, respectively. The results of spearman correlation test indicated that nail was an ideal matrix for biomonitoring PFOS rather than human urine and hair in general populations for the non-invasive sampling.

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Introduction

Perfluoroalkyl substances (PFASs) are persistent organic pollutants (POPs) and persist in the environment. They are widely used in consumer and industrial products, such as surfactants, carpets, fire-retarding and food packaging (Hekster et al., 2003; Liu et al., 2009). Due to the multi-organ toxicity and potential health risk to humans (Guruge et al., 2006; Harada et al., 2005; Lau et al., 2006), perfluorooctanesulfonate (PFOS) and its salts had been included in Stockholm Convention on persistent organic pollutants since 2009 (Stockholm Convention on Persistent Organic Pollutants, 2009). As far as we know, PFASs are ubiquitous all over the world, which were frequently detected

in environment medium, human foodstuffs, human tissue and various animals, including soils (Wang et al., 2013), surface waters (Cai et al., 2012), tap water (Mak et al., 2009), fish and shell fish (Domingo et al., 2012; Munschy et al., 2013; Shi et al., 2010; Zhao et al., 2011), foods (Guerranti et al., 2013; Zhang et al., 2010), foodstuff packing (Zafeiraki et al., 2014), human blood (Guo et al., 2011; Ji et al., 2012) and human milk (Barbarossa et al., 2013; Liu et al., 2010). Moreover PFASs have been verified associated with breast cancer (Siddique et al., 2016), obesogenic effects (Karlsen et al., 2017), allergic diseases (Goudarzi et al., 2016) and asthma (Humblet et al., 2014) in recent years.

So far, human blood and breast milk are the most common biomonitoring matrices for human exposure to PFASs in

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general populations (Kim et al., 2014; Stubleski et al., 2016). However, the collection of human samples like serum is very difficult from some persons, especially neonates and young children, because of ethics and humanity. Non-invasive samples like nails, hairs are therefore imminently required (Li et al., 2013). Human hair and nail, as the most common non-invasive samples, is easily available, stored, transported and ethically not prioritized, which could be used as a biomonitoring sample for human exposure to some POPs associates with environmental or occupational exposure (Król et al., 2013; Appenzeller and Tsatsakis, 2012; Li et al., 2013; J. Liu et al., 2011; W. Liu et al., 2011; Schramm, 2008; Xu et al., 2010). Besides, nail and hair are mainly composed of keratin which quite suitable for monitoring the exposure for PFASs. Recently some studies have already developed the method for determining PFASs in human hair and nail with the lower limit of detection (LOD) (Alves et al., 2015; Li et al., 2012; J. Liu et al., 2011; W. Liu et al., 2011; Perez et al., 2012; Xu et al., 2010). Moreover urine is the primary elimination pathway of PFASs, and the association between blood concentrations and urine concentrations for PFASs has been found by few researches (Zhang et al., 2013a, 2015). Although our laboratory has already discussed the possibility for human urine, hair and nail to be used as the biomonitoring sample of human exposure to PFASs (Li et al., 2013), it is essential to investigate comprehensively in different locations and populations.

In this study, we detected the PFASs concentrations in 39 matched human serum, urine, hair and nail samples from Shenzhen, one of most developed cities in south China. We contrasted the concentrations of PFASs in other countries and assessed the gender and age effect for PFASs in the four matrices. We also validated the possibility again for human urine, hair and nail used as the biomarker of human exposure to PFASs.

1. Materials and methods

1.1. Chemicals and reagents

PFAC-MXB and MPFAC-MXA were purchased from Wellington Laboratories with purities $\geq 98\%$. PFAC-MXA is a mixture standard, which consists of perfluorohexanoic acid (PFHxA), perfluorooctanoic acid (PFOA), perfluorononanoic acid (PFNA), perfluorodecanoic acid (PFDA), perfluoroundecanoic acid (PFUnDA), perfluorododecanoic acid (PFDoA), perfluorohexanesulfonate (PFHxS) and perfluorooctanesulfonate (PFOS). As well as MPFAC-MXA is a mixture internal standards of above mentioned PFASs. Methanol (LC-MS grade) and acetonitrile (HPLC grade) were obtained from Fisher Scientific (USA), while acetone was purchased by J.T. Baker (Phillipsburg, USA). Tetra-*n*-butylammonium hydrogen sulfate (TBA) was obtained from J&K chemical company, and methyl-*tert*-butyl ether (MTBE) and ammonium hydroxide (analytical grade) was achieved from Sigma-Aldrich. Moreover ammonium acetate (HPLC grade) and formic acid (HPLC grade) were supplied from Dikma Pure (Richmond Hill, USA). Sodium carbonate (analytical grade) was purchased from the Jinke Institute of Fine Chemicals. Weak anion exchange solid phase extraction (SPE) cartridges (Oasis@Wax, 150 mg, 6 mL, 30 μm) were provided by Waters (Milford, Ireland).

1.2. Sample collection

We collected matched human serum, urine, hair and nail samples from 15 males and 24 females in 2015 with non-occupation exposure in Shenzhen, China. The ages of the donors ranged from 20 to 53 years old with the average age of 38 years old. All the donors were fully told the purpose and content of this investigation and signed the consent forms. According to the sampling method used in our laboratory, about 2 mL serum, 50 mL urine, 0.5 g hair and 0.5 g nail samples for each donor were gathered (Li et al., 2012). The individual samples were then stored in a polypropylene centrifuge tube pre-cleaned by water and methanol successively. The serum and urine samples were frozen at -20°C immediately until the analysis (Li et al., 2012, 2013).

1.3. Sample preparation

The sample preparation methods were described in detail in our previous publications (Li et al., 2012, 2013). To remove the external contamination, about 20 mL of water was added to each of the individual hair or nail sample and let soaked for 10 min to remove any surface dirt that may have interfered with the analysis. The water was then discarded and the samples were washed twice with acetone, and then air-dried. Before extraction, the hair and nail samples were ground to powder employed a Mini-mill Grinder (FRITSCH, "Pulverisette 23", Germany). The serum samples were extracted by ion-pair extraction developed by Hansen et al. (2001). For urine, hair and nail samples, PFASs were extracted by various organic solvent. Then the extracts were all cleaned by the WAX cartridge. After that the target were eluted with 9% ammonium hydroxide in methanol, which was concentrated to dryness under nitrogen gas and reconstituted by 200 μL solution of water/methanol (V/V; 1/1). Finally the particles were removed by filtration using 0.2 μm nylon filter.

1.4. Instrumental analysis

The instrumental analysis methods were also depicted in detail in our previous studies (Guo et al., 2011; Li et al., 2012, 2013; Liu et al., 2009, 2010; J. Liu et al., 2011; Wu et al., 2012). PFASs were performed employing ultra-performance liquid chromatography coupled with tandem mass spectrometry in negative-ion pattern with electrospray ionization source and multiple-reaction-monitoring mode. A 20- μL extract was injected to a 50°C ACQUITY UPLC BEH C18 column (2.1 mm i.d. \times 50 mm length, 1.7 μm ; Waters, USA) in full loop model. Methanol and 2 mM ammonia acetate were used for the gradient program, with the flow rate of 0.4 mL/min. The particular mass transitions are summarized in Table S1.

1.5. Quality assurance/quality control (QA/QC)

The blanks of various solvents in the experiment are firstly examined, and no PFAS solvents were used for sample preparation and instrumental analysis. Two method blank samples were extracted with each batch of samples to examine the background concentrations (Li et al., 2013; Wu et al., 2012). The five-point standard calibration was run before and after instrumental analysis to affirm the accuracy of each sample, which

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