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Using hair, nail and urine samples for human exposure assessment of legacy and emerging *per*- and polyfluoroalkyl substances

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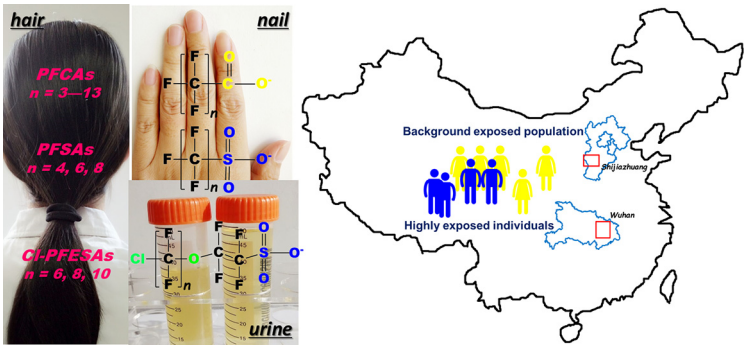
HIGHLIGHTS

- Urine is a suitable matrix to monitor exposure to short- and medium-chain PFASs.
- The levels of C8 Cl-PFESA and PFOS measured in hair and nails reflected internal exposure.
- C8 Cl-PFESA was ubiquitously detected in human hair, nails and urine indicating widespread human exposure.

GRAPHICAL ABSTRACT



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ABSTRACT

Non-invasive samples present ethical and practical benefits for investigating human exposure to hazardous contaminants, but analytical challenges and difficulties to interpret the results limit their application in biomonitoring. Here we investigated the potential for using hair, nail and urine samples as a measure of internal exposure to an array of legacy and emerging *per*- and polyfluoroalkyl substances (PFASs) in two populations with different exposure conditions. Paired urine-serum measurements of PFASs from a group of highly exposed fishery employees displayed strong correlations for PFASs with three to eight perfluorinated carbons ($\rho > 0.653$; $p < 0.01$). Consistent statistical correlations and transfer ratios in nails and hair from both populations demonstrated that these non-invasive samples can be used as a measure of internal exposure to perfluorooctane sulfonic acid and C8 chlorinated polyfluoralkyl ether sulfonic acid (C8 Cl-PFESA). Contrastingly, the infrequent detections and/or lack of consistent transfer ratios for perfluorooctanoic acid, perfluorononanoic acid and short-chain PFASs in hair and nail samples indicate passive uptake from the external environment rather than uptake and internal distribution. Collectively, the study supports the use of urine samples as a valid measure of internal exposure for a range of short- and medium-chain PFASs, while the validity of nail and hair samples as a measure of internal exposure may vary for different PFASs and populations. The ubiquitous detection of C8 Cl-PFESA in all sample matrices from both populations indicates widespread exposure to this contaminant of emerging concern in China.

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1. Introduction

Per- and polyfluoroalkyl substances (PFASs) is a class of man-made organic chemicals which fill many useful functions in society (Lindstrom et al., 2011; Paul et al., 2009; Arvaniti and Stasinakis, 2015; Dauchy et al., 2017). At the same time, their persistence and mobility make them problematic contaminants when released to the environment (Cousins et al., 2016; Naile et al., 2010; Groffen et al., 2018; Zhao et al., 2016). Particular attention has been directed to long-chain perfluoroalkyl carboxylic acids (PFCAs, with 7 or more perfluorinated carbons) and perfluoroalkyl sulfonic acids (PFSAs, with 6 or more perfluorinated carbons) which, in addition to being highly persistent, are classified as bioaccumulative and toxic (Conder et al., 2008; Lau et al., 2004). Given the phase-out of long-chain PFCAs, PFSAs and their respective precursors in Western countries, there is an increasing focus on PFAS alternatives which have not yet been regulated (Wang et al., 2014; Chen et al., 2018). One important example of such chemicals are the chlorinated polyfluoralkyl ether sulfonic acids (Cl-PFESAs), which are used as an alternative to perfluorooctane sulfonic acid (PFOS) for certain applications in China under the trade name F-53B (Ruan et al., 2015; Shi et al., 2015; Wang et al., 2013). Although emerging PFASs have similar physicochemical properties and are believed to pose similar hazards as their predecessors, data on exposure to humans remains limited (Shi et al., 2016; Wang et al., 2016).

Biomonitoring has been instrumental for characterizing exposure to legacy PFASs and unraveling links to adverse health effects in humans (Lam et al., 2014; Lopez-Espinosa et al., 2011; Okada et al., 2012; Shankar et al., 2011; Uhl et al., 2013; Winquist and Steenland, 2014). Whole blood, serum or plasma have typically been the preferred sample matrices for determining internal exposure to PFASs due to their proteinphilic properties (Alves et al., 2014; Beesoon et al., 2012; Shi et al., 2016). However, alternative non-invasive sampling techniques, including urine, nails and hair, have also been developed and applied in some studies (Guo et al., 2011; Liu et al., 2016; Zheng et al., 2016). The use of non-invasive biomonitoring techniques typically leads to lower costs of sample collection and reduction of discomfort for the study subjects (Kim et al., 2014; Li et al., 2012; Liu et al., 2011), which could help to increase the response frequency and sample size, particularly for toddlers and children, of biomonitoring studies (Winkens et al., 2017).

Although non-invasive samples present potential benefits for biomonitoring of contaminants, it is inherently difficult to determine the validity of hair and nail samples as a measure of internal exposure. This is illustrated in Fig. 1 by two principally different pathways leading to the presence of contaminants in non-invasive samples. In order for non-invasive samples to provide a valid biomarker of internal exposure, the concentrations detected in hair, nail and urine samples should reflect uptake from external exposure (Pathway 1, Fig. 1) followed by internal distribution from blood or serum to the non-invasive sample matrix (Pathway 2, Fig. 1). Such relationships for using hair and nails as a measure of internal exposure have been established for some metals, therapeutic and recreational drugs where the intake occurs primarily through the diet (McDowell et al., 2004; McLean et al., 2009; Soban'ska, 2005). There is, however, also a possibility that concentrations measured in hair and nail samples are a consequence of direct transfer from the surrounding environment e.g. air, dust and consumer products (Pathway 3, Fig. 1). Direct transfer may be particularly important for organic chemicals which have multiple uses in consumer products and are omnipresent in the indoor environment as exemplified by phthalate ester metabolites (Bui et al., 2017). Thus, it is important to evaluate the validity of hair and nail samples as markers of internal exposure for different chemical classes. In contrast to hair and nails, urine samples will not be affected by direct transfer from external exposure media and thus always provide a measure of internal exposure (Pathway 2, Fig. 1). The applicability of urine as a suitable biomonitoring matrix may, however, vary for different PFASs depending on the efficiency of renal excretion and analytical detection capability and may require normalization to simultaneously measured creatinine concentrations (Zhang et al., 2013b; Watkins et al., 2013).

The objective of this study was to investigate the applicability of hair, nail and urine samples as a measure of internal exposure to PFASs. Although there are a couple of studies providing measurements of PFASs in hair and nails, they display considerable variability in statistical associations and estimated nail to serum ratios and have generally included a limited number of analytes (Li et al., 2013; Liu et al., 2011; Wang et al., 2017). To address these short-comings, we analyzed an array of PFCAs (C4-C13), PFSAs (C4,C6 and C8) and Cl-PFESAs (C8, C10 and C12) in non-invasive samples from highly exposed fishery employees from Wuhan, China ($n = 8$) and a background exposed population in Shijiazhuang, China ($n = 41$). The underlying hypothesis for combining these sample sets was that the wide range in exposures would allow a more robust evaluation of processes between exposure media and different measures of internal exposure. In addition, passive uptake experiments were performed to determine if absorption in hair and nail matrices

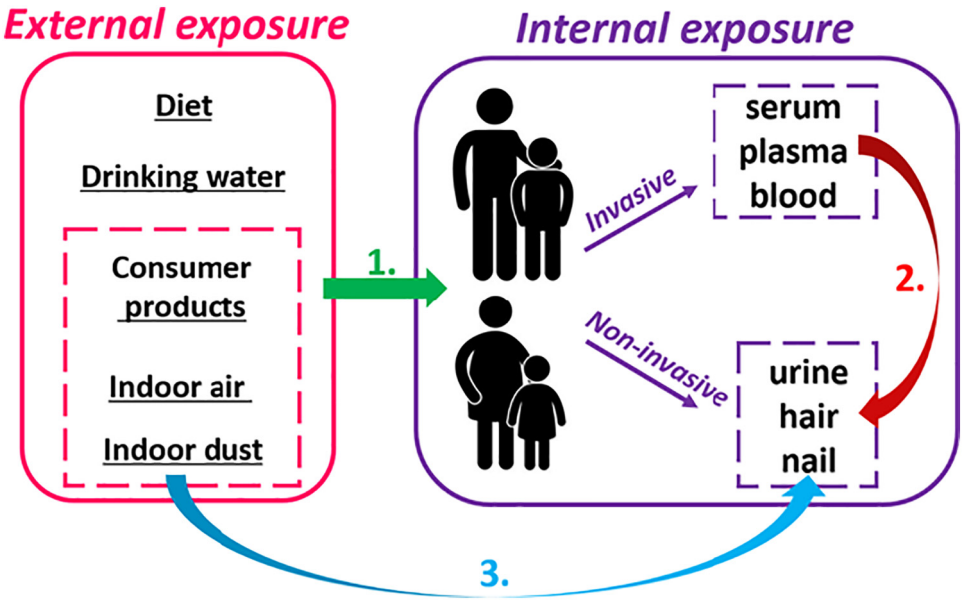

Fig. 1. Conceptual illustration of the pathways leading to of PFASs in non-invasive biomonitoring samples.