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Repeated measurements of per- and polyfluoroalkyl substances (PFASs) from 1979 to 2007 in males from Northern Norway: Assessing time trends, compound correlations and relations to age/birth cohort

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ABSTRACT

Background: Longitudinal biomonitoring studies can provide unique information on how human concentrations change over time, but have so far not been conducted for per- and polyfluoroalkyl substances (PFASs) in a background exposed population.
Objectives: The objectives of this study were to determine: i) serum PFAS time trends on an individual level; ii) relative compositions and correlations between different PFASs; and iii) assess selected PFAS concentrations with respect to periodic (calendar year), age and birth cohort (APC) effects.
Methods: Serum was sampled from the same 53 men in 1979, 1986, 1994, 2001 and 2007 in Northern Norway and analysed for 10 PFASs. APC effects were assessed by graphical and mixed effect analyses.
Results: The median concentrations of perfluorooctane sulphonic acid (PFOS) and perfluorooctanoic acid (PFOA) increased five-fold from 1979 to 2001 and decreased by 26% and 23%, respectively, from 2001 to 2007. The concentrations of PFOS and PFOA peaked during 1994–2001 and 2001, respectively, whereas perfluorohexane sulphonic acid (PFHxS) increased to 2001, but did not demonstrate a decrease between 2001 and 2007. Perfluorononanoic acid (PFNA), perfluorodecanoic acid (PFDA), and perfluoroundecanoic acid (PFUnDA) displayed increasing trends throughout the entire study period (1979–2007). Although PFOS comprised dominating and stable proportions of PFAS burdens during these years, the contributions from PFOA and PFHxS were considerable. The evaluation of APC effects demonstrated that calendar year was the dominating influence on concentrations of PFOA, PFUnDA, and PFOS, although time-variant and weaker associations with age/birth cohort were indicated.
Conclusions: The concentration changes of 10 PFASs in the repeated measurements from 1979 to 2007 demonstrated divergent time trends between the different PFASs. The temporal trends of PFASs in human serum during these 30 years reflect the overall trends in historic production and use, although global transport mechanisms and bioaccumulation potential of the different PFASs together with a varying extent of consumer exposure influenced the observed trends. Sampling year was the strongest descriptor of PFOA, PFUnDA and PFOS concentrations, and the calendar-year trends were apparent for all birth year quartiles. Discrepancies between the trends in this current longitudinal study and previous cross-sectional studies were observed and presumably reflect the different study designs and population characteristics.

Abbreviations: AIC, Akaike's Information Criterion; APC, age–period–cohort; FOSA, perfluorooctane sulfonamide; FTSA, fluorotelomer sulphonic acids; LOD, limit of detection; PFASs, poly- and perfluorinated alkyl substances; PFBA, perfluorobutanoic acid; PFBS, perfluorobutane sulphonic acid; PFCAs, perfluoroalkyl carboxylic acids; PFDA, perfluorodecanoic acid; PFDcS, perfluorodecane sulphonic acid; PFHpA, perfluoroheptanoic acid; PFHpS, perfluoroheptane sulfonic acid; PFHxA, perfluorohexanoic acid; PFHxS, perfluorohexane sulfonic acid; PFPeA, perfluoropentanoic acid; PFNA, perfluorononanoic acid; PFOA, perfluorooctanoic acid; PFOS, perfluorooctane sulfonic acid; PFSAs, perfluoroalkyl sulphonic acids; PFUnDA, perfluoroundecanoic acid; POP, persistent organic pollutant; SRM, standard reference material.

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1. Introduction

Production and use of per- and polyfluoroalkyl substances (PFASs) started in the 1950s and increased considerably during the 1970s (Paul et al., 2009; Prevedouros et al., 2006). PFASs continue to be in high demand today due to their widespread use in industrial and consumer product applications (Buck et al., 2011). Two major PFAS groups are the perfluoroalkyl carboxylic acids (PFCAs) and the perfluoroalkyl sulphonic acids (PFSAs) (Buck et al., 2011), of which perfluorooctanoic acid (PFOA) and perfluorooctane sulphonic acid (PFOS) have received most attention in studies of humans and the environment. Increasing concern for their persistency and bioaccumulative properties has led to voluntary and regulatory efforts restricting their use, including: i) phasing out PFOS and related compounds while providing shorter chain PFSAs as replacements during 2000–2002 by 3M, the major producer (US EPA, 2002); ii) inclusion of PFOS in the Stockholm Convention in 2009 (Stockholm Convention); and iii), initiation of a PFOA stewardship programme to phase out PFOA and longer chain PFCAs by 2015 (US EPA, 2006). As a consequence of these actions, the global production of PFOS and related chemicals decreased drastically after the peak between 1990 and 2000 (Paul et al., 2009), although production of PFOS has continued in China (Zhang et al., 2012) and it is likely that production of longer chain PFASs continued for some years after 2002 (Armitage et al., 2009).

Overall, biomonitoring of PFASs in human serum has demonstrated decreasing concentrations of PFOS and PFOA since the early 2000s, whereas trends for other PFASs have been variable (Calafat et al., 2007a; Glynn et al., 2012; Harada et al., 2004; Jin et al., 2007; Kannan et al., 2004; Kato et al., 2011; Olsen et al., 2005, 2012; Schröter-Kermani et al., 2012; Toms et al., 2009; Wang et al., 2011; Yeung et al., 2013a,b). A cross-sectional study of pooled sera from 40 to 50 year old men in Norway during 1976 to 2007 reported that many PFASs increased during the study period and that PFOS, PFOA and perfluoroheptane sulphonic acid (PFHpS) started declining around year 2000 (Haug et al., 2009). The observed time trends of PFOS and PFOA in human serum, to a large extent, mirror the changes in global production. However, the reasons for differing time trends for different PFAS homologues and between different studies are not well understood. Furthermore, the decline in human concentrations of PFOA and PFOS after the phase-out initiated in year 2000 was observed after a short time lag considering its relatively long human elimination half-life (Olsen et al., 2007) and the absence of consistent decreasing trends in wildlife for the same time period (Butt et al., 2010). Time trends in human biomonitoring primarily reflect a combination of the temporal changes in exposure (intensity, duration and intake rates), and elimination kinetics (Quinn and Wania, 2012; Ritter et al., 2009). With respect to exposure pathways, the body burden of PFASs is greatly influenced by dietary intake, although drinking water, inhalation of indoor air, ingestion of house dust, and direct contact with consumer/commercial products may also contribute to a varying extent (Egeghy and Lorber, 2011; Fromme et al., 2009; Haug et al., 2011; Lorber and Egeghy, 2011; Vestergren and Cousins, 2009). Consequently, temporality in human exposure depends on the response time of the major source media to changes in PFAS production. Furthermore, exposure to PFASs in human populations in Arctic regions may have a different response time to changes in production due to the time-lag of long-range transport of PFASs by air and ocean currents (Butt et al., 2010). Local or regional differences in contamination status together with life style differences and dietary habits may therefore result in different time trends between studies.

In addition to different population exposures, observed human time trends may also be affected by the study design and demographic characteristics of the study group. Previous studies on legacy persistent organic pollutants (POPs) have demonstrated that an improved understanding of age, period and birth cohort effects is needed to correctly interpret time trends in biomonitoring studies (Nøst et al., 2013; Quinn and Wania, 2012; Ritter et al., 2009). Generally, no association (Calafat et al., 2007a, b; Harada et al., 2007; Olsen et al., 2008; Yeung et al., 2006) and variable associations with age (Haug et al., 2009; Kato et al., 2011) have been reported for PFASs in cross-sectional studies. In one such study of pooled samples from Norwegian subjects, both positive and negative associations to age were reported, which varied between sampling years and the different PFASs (Haug et al., 2009).

The present study describes changes in PFAS concentrations and compositional patterns in repeated serum samples during 1979–2007 and, to the best of our knowledge, this is the first to report repeated measurements of a number of PFASs in a non-occupationally exposed population. The rare longitudinal study design allowed for an assessment of periodic time trends during nearly 30 years in addition to the age and birth cohort effects (APC effects) in concentrations of selected PFASs.

2. Subjects and methodology

2.1. Study population and subject selection

Five repeated population surveys called the Tromsø study (summarized by Jacobsen et al., 2012) took place in the municipality of Tromsø, Northern Norway in 1979, 1986–1987 (hereafter referred to as 1986), 1994–1995 (1994), 2001 and 2007–2008 (2007). Adult men ($n = 60$) were randomly selected from 1438 males who had participated and donated blood in all five surveys of the Tromsø study. Of these, 53 had sufficient sample volumes in ≥ 3 sampling years and the present analyses comprised 254 serum samples (11 samples randomly distributed across sampling years were missing). Birth year information was extracted from questionnaires, while individual dietary information was inadequate. The range in birth years was 1925–1950, and the median ages at the first and last sampling were 43 and 71. Serum samples were stored at −70 °C until analysis. The study was approved by the Regional Committees for Medical Research Ethics. Participation was voluntary and participants gave informed consents.

2.2. Analytical methodology

Analyses were performed at the laboratories of NILU — Norwegian Institute for Air Research, Fram Centre, Tromsø, Norway. All serum samples were quantified for 10 target analytes and a subset of 43 samples were initially quantified for 21 analytes (see Supplemental material, Table S1).

2.2.1. Extraction and clean up

Serum samples were analysed using the internal-standard method and sonication-facilitated liquid–liquid extraction in methanol, activated charcoal clean up, and analysed by ultrahigh pressure liquid chromatography triple-quadrupole mass spectrometry (Thermo Fisher Scientific Inc, Waltham, MA, USA).

Extraction was performed as per Hanssen et al. (2013) with the following changes; i) 100 μl serum was extracted in a 1.5 ml Eppendorf tube; ii) the internal standards (see Supplemental material, Table S2 for list); iii) the volume methanol (750 μl) added; and iv) amount of branched perfluorodecanoic acid (br-PFDA) recovery standard (20 μl of 0.102 ng/μl) used.

2.2.2. Instrumental analysis

The analytical specifications are described in Hanssen et al. (2013). The quantification was conducted with the LC Quan software, version 2.6.0 (Thermo Fisher Scientific Inc, Waltham, MA, USA). Of the 21 PFASs included in the analyses, 10 were detected in >20% of samples in a subset of 20 samples and the remaining samples were quantified for these 10 PFASs. The linear and branched PFOS isomers were chromatographically separated ("branched PFOS" was identified as one or several peaks eluting earlier than the linear PFOS; see Supplemental material, Fig. S1A). The mass-labelled internal standard for linear PFOS was also used for quantification of the branched isomers. Concentrations of