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LEVELS OF SELECTED PER- AND POLYFLUORINATED ALKYL SUBSTANCES (PFAS) IN SWEDISH FIREFIGHTERS

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Introduction

Per- and polyfluorinated alkyl substances (PFAS) have been widely used in broad range of consumer and industrial products for their beneficial surfactant properties since their introduction in 1940s. PFAS have been used, among others, as lubricants, adhesives, surface coating materials and in firefighting foams. Knowledge on their toxicological and environmental properties has led to decrease in the use and voluntary phase out of some classes of these chemicals after 2000. Due to their physicochemical properties (persistency, stability) and wide global spread, they are still present in the environment and pose a significant risk of exposure to living organisms including humans. Additionally, certain compounds are still being used in firefighting foams.

The exposure in human population originates primarily through ingestion of contaminated food as well as drinking water. Perfluorinated carboxylic acids (PFCAs) and perfluorinated sulfonic acids (PFSAs) such as perfluorooctanoic acid (PFOA), perfluorononanoic acid (PFNA), perfluorooctane sulfonic acid (PFOS), and perfluorohexane sulfonic acid (PFHxS) are typically found in the highest concentrations in the general population.

As certain PFAS have been used as additives in firefighting aqueous film–forming foams (AFFFs), there is a risk of increased occupational exposure of certain professions, e.g. firefighters, to PFAS. The use of PFOS and other perfluoroalkyl acids (PFAAs) in AFFF formulations has been linked to environmental contamination related to handling, storage, and usage. Substantially elevated levels of PFOS have been reported in water and biological samples such as molluscs, turtles, wild mink, and fish downstream from airports with a history of firefighting training activities[1].

Information on occupational exposure among firefighters and teachers in Sweden are missing. In this study we analysed PFASs in blood serum samples obtained in 2015 from 50 professional firefighters and 11 professional firefighting teachers.

Materials and methods

Blood serum samples were collected from 50 professional firefighters from Helsingborg (southern Sweden), Sweden and 11 professional firefighting teachers from the Swedish Civil Contingencies Agency in Sandö (northern Sweden). The study was approved by the Ethics Committee of the University of Uppsala and the participants gave a written informed consent.

Samples were analysed using a previously published method[2], with minor modification. High throughput sample preparation method (96-well plates) was used. Each 96-well plate was considered as one run and consisted of a matrix matched calibration curve, certified reference material (NIST SRM 1957), and a set of samples, which in turn consisted of one method blank and one QC reference sample per ten authentic samples. The sample preparation procedure was performed as follows: serum samples were allowed to stabilize at room temperature overnight and then vortex mixed for 10 s before being sampled for the sample preparation procedure. Internal standards (10 μL of 0.2 ng/mL in methanol) and 150 μL serum were added to a 25 mg Ostro Protein Precipitation & Phospholipid Removal 96-well plate (Waters Corporation, Milford, USA) pre-conditioned with 450 μL acetonitrile. A 450 μL aliquot of acetonitrile (containing 1% formic acid) was added to all wells and mixed thoroughly with the sample by aspirating three times using an automated pipette. Samples were extracted using a vacuum manifold for approximately 5–7 min. Aliquots of 600 μL of the eluate from each collection plate insert were then transferred to glass LC-vials and evaporated down to 250 μL using nitrogen. The purified extracts were spiked with recovery standards (10 μL of 0.2 ng/mL in methanol) and diluted with 750 μL of 2 mM NH_4Ac in water. All samples and standards were ultrasonicated for 10 min prior to instrumental analysis.

Instrumental analyses were performed using UPLC–MS/MS system, Acquity UPLC coupled to a Xevo TQ-S (Waters Corporation, Milford, USA) with electrospray ionization operating in negative ion mode. 10 µL of sample was then injected on an Acquity UPLC BEH C18 2.1 mm × 100 mm, 1.7 μm (Waters Corporation, Milford, USA) analytical column (Waters Corporation, Milford, USA). A trap column (PFC Isolator column, Waters Corporation, Milford, USA) was installed between the pump and injector and used to retain fluorinated compounds originating from the UPLC system and the mobile phase. Target analytes were eluted using a programmed gradient of the eluents 2 mM NH_4Ac in water and methanol (9:1) and 2 mM NH_4Ac in methanol at a flow rate of 300 μL/min.

Results and discussions

Using the above described analytical technique, 10 PFAS were quantified in the studied serum samples. The summed PFAS concentrations for the firefighters ranged from 1.8 to 68.0 ng/mL, the summed PFAS concentrations for the firefighting teachers ranged from 8.0 to 19 ng/mL. Although the range of observed concentrations for firefighters was wider than for firefighting teachers, the median values were higher for firefighting teachers (14 ng/mL for firefighting teachers and 11 ng/mL for firefighters).

When comparing the compounds homologue profile (Figure 2) for the both groups, similar findings were observed for the both groups. For both groups PFOS was the most dominant homologue (median value 7.3 ng/mL for the firefighters and 8.9 ng/mL for the firefighting teachers). PFOA and PFHxS were the other most prominent compounds found in the serum samples with median values 1.6 ng/mL for firefighters and 2.0 ng/mL for firefighting teachers; and 1.2 ng/mL for firefighters and 1.7 ng/mL for firefighting teachers, respectively.

The observed levels of PFAS in firefighters and firefighting teachers were not significantly elevated (Table 1) when comparing to a large scale cohort of US population[3] and also not significantly increased when comparing to levels of PFASs in fifty 18 year old Swedish males sampled from 2009 to 2010[4]. When comparing the levels in this study (Table 2) and firefighter in other countries, the median levels in this study were several times lower than the reported levels for Australian firefighters[5] and similar range as reported for California firefighters[6].

To test if levels of PFAS are connected with the time of occupational exposure or age Spearman rank correlation analysis was performed. No correlation between years of occupational exposure or firefighter's age was observed in this case. However when the firefighters were grouped into 3 classes of occupational exposure time (<10 years, 10-20 years, >20years) an increase of the total PFAS levels could be observed between the <10 years group and the >10 years groups (figure 1). The firefighting teachers' average years of occupational exposure was 20 years. The levels in this group are similar to the firefighters with occupational exposure of 10-20 years.

The concentrations of PFAS in this study is within the range of the general population however elevated levels of PFOS and PFHxS in a few number of firefighters may be an indication of an occupational exposure. Since highly fluorinated substances eliminates slowly, historical exposure can be seen for many years and higher concentrations are therefore detected in individuals with highest number of working years. The historical usage of class B foams containing PFAS at the Helsingborg stations and MSB Sandö could not be properly elucidated.

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References

1. Houtz EF, Higgins CP, Field JA,Sedlak DL (2013); Environ Sci Technol. 47(15): 8187-8195; Jin C, Sun Y, Islam A, Qian Y,Ducatman A (2011); Journal of Occupational and Environmental Medicine. 53(3): 324-328; Laitinen JA, Koponen J, Koikkalainen J,Kiviranta H (2014); Toxicol Lett. 231(2): 227-232
2. Salihovic S, Kärrman A, Lindström G, Lind PM, Lind L,van Bavel B (2013); Journal of Chromatography A. 1305(164-170
3. NHANES, Fourth National Report on Human Exposure to Environmental Chemicals Update (2015), CDC National Center for Environmental Health, 1095, http://www.cdc.gov/biomonitoring/pdf/FourthReport_UpdatedTables_Feb2015.pdf
4. Borg D,Håkansson H Environmental and Health Risk Assessment of Perfluoroalkylated and Polyfluoroalkylated Substances (PFASs) in Sweden (2012), 139, https://www.naturvardsverket.se/Documents/publikationer6400/978-91-620-6513-3.pdf?pid=3822
5. Rotander A, Toms LM, Aylward L, Kay M,Mueller JF (2015); Environ Int. 82(28-34
6. Shaw SD, Berger ML, Harris JH, Yun SH, Wu Q, Liao C, Blum A, Stefani A,Kannan K (2013); Chemosphere. 91(10): 1386-1394

Table 1 Comparison of PFAS levels with US general population

geometric mean values, ng mL^{-1}	This study 2015 (n=50)	NHANES 2009-2010 (n=1075)
PFOS	7.9	11.5
PFHxS	1.3	1.6
PFOA	1.7	3.5
PFNA	0.64	1.37
PFDA	0.26	0.29
PFUnDA	0.27	0.18

Table 2 Comparison of PFAS levels in Helsingborg firefighters with other countries and a Swedish population of 18 years old males

median values, ng mL^{-1}	This study 2015 (n=50)	Firefighters Australia 2013 (n=149)	California firefighters 2009 (n=12)	Swedish males 2009-10 (n=50)
PFOS	7.3	66	9.0	6.9
PFHxS	1.2	25	1.0	0.78
PFOA	1.6	4.2	6.0	1.9
PFNA	0.66	0.69	2.0	0.96
PFDA	0.26	0.27	1.0	0.41
PFUnDA	0.25	0.14	0.20	<0.1

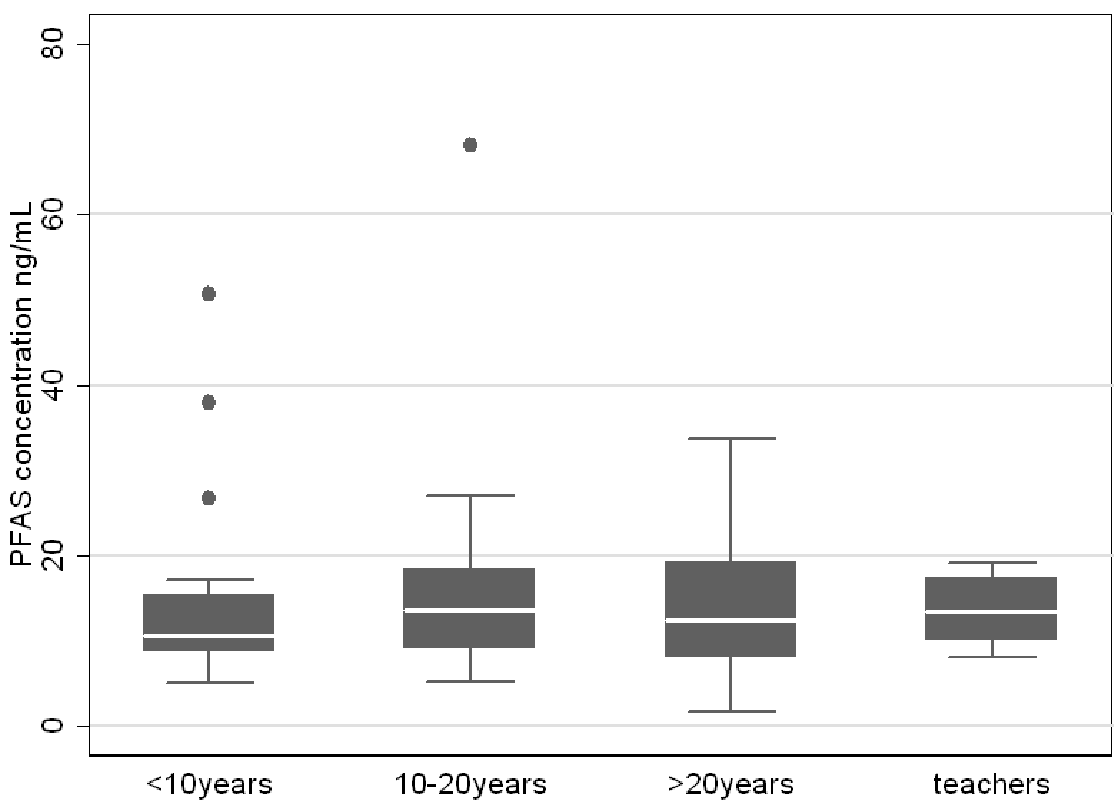

Figure 1 PFAS median levels in firefighters (sorted by years of occupational exposure) and in firefighting teachers

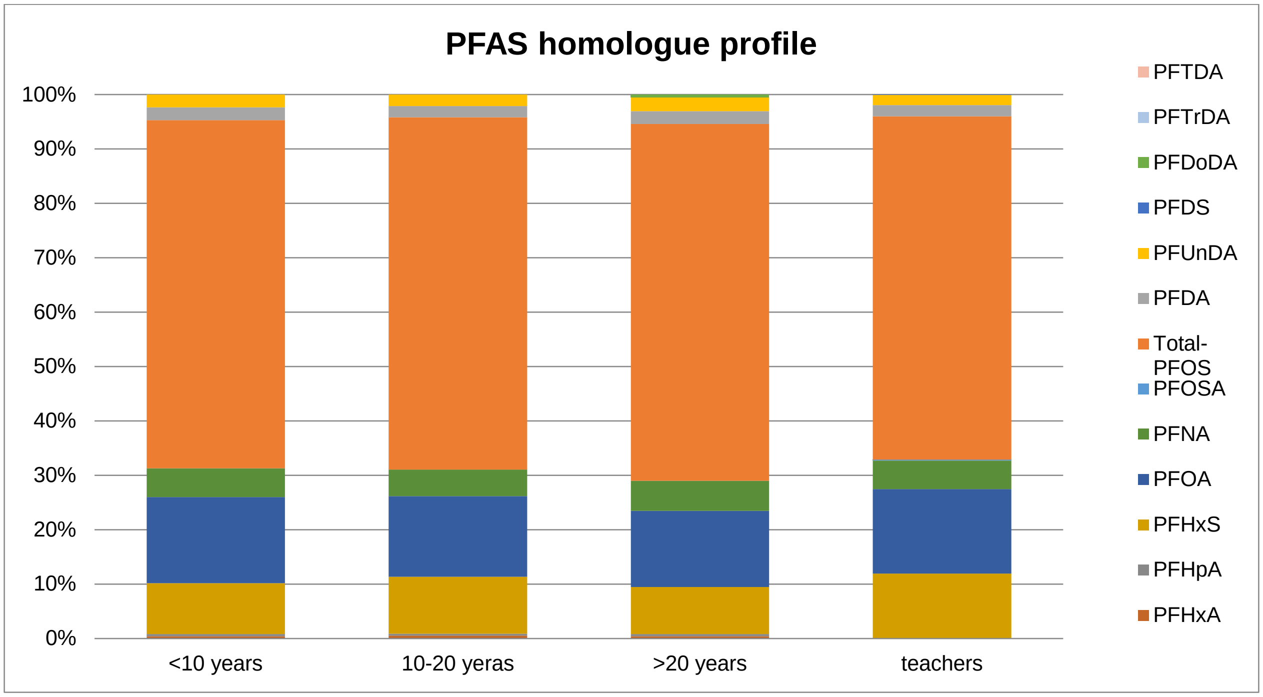

Figure 2 PFAS homologue profile in firefighters (sorted by years of occupational exposure) and firefighting teachers