A possible influence of occupation and diet on level of perfluorinated acids in human

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Introduction

Perfluorooctane sulfonate (PFOS) and perfluorooctanoic acid (PFOA) are metabolites of several perfluorinated precursor compounds that are produced and used in a wide variety of consumer products. Their amphiphilic character and thermal, biological, and chemical stability made them temporarily useful for many purposes. In recent years have been evidenced that PFOS and PFOA are environmentally persistent and accumulate in the tissues of wildlife and humans [1,2]. Various international environmental agencies and bodies have appealed for more data regarding environmental distribution and human exposure to perfluorinated compounds (PFCs). PFOS has been found in body tissues and liquids of occupationally and non-occupationally exposed humans. The environmental distribution and human exposure pathways for PFCs are still under investigation, and therefore information on exposure rates to a larger number of poly- and perfluorinated compounds and their effects is urgently needed. The need of rigorous QA/QC in HPLC-MS/MS for PFCs analysis and reliable data is highly emphasized, too. To have a deeper insight into occurrence, sources and possible exposure pathways of PFCs to Poles, a blood of the city of Gdańsk region inhabitants in the northern part of Poland, and collected in 2003 for the purpose of the EU 5FP COMPRENDO project, was examined for 14 PFCs.

Materials and Methods

Extraction. The analytical procedure for the extraction of whole blood was similar to that described earlier [2].1 mL of whole blood, 1mL of 0.5 M tertrabytulammonium solution, and 2 mL of 0.25 M sodium carbonate buffer were added to a 15 mL polypropylene tube for extraction, and mixed. 5 mL of methyl -tert-butyl ether (MTBE) was added to the solution, the organic and aqueous layers were separated by centrifugation, and the former was removed from the solution. The aqueous mixture was rinsed with MTBE and separated twice. The solvent was evaporated under nitrogen, and the sample was reconstituted in 1mL of methanol. The particles that appeared in the final solution were removed by filtration using nylon syringe filters (Iwaki, Fukushima, Japan).

Instrumental Analysis and Quantification. Analysis of PFCs was performed using high performance liquid chromatograph-tandem mass spectrometer (HPLC -MS/MS), comprising an Agilent HP 1100 liquid chromatograph interfaced with Micromass® (Beverly, MA) Quattro Ultima mass spectrometer operated in the electrospray negative ionization mode. A 10 µL aliquot of the sample extract was injected into a guard column (XDB -C8, 2.1 mm i.d. x 12.5mm, 5 µm; Agilent Technologies, Palo Alto, CA) connected sequentially to a Betasil C18 column (2.1 mm i.d. x 50 mm length, 5 µm; Thermo Hypersil-Keystone, Bellefonte,PA) with 2 mM ammonium acetate aqueous solution and methanol as mobile phases, starting at 10% methanol. At a flow rate 300 µL/min, the gradient was increased to 30% methanol at 0.1 min, 75% methanol at 7 min, and 100% methanol at 10 min before reverting to original conditions at 12 min, at the 20 -min time point. The column temperature was maintained at 20 °C. The MS/MS parameters were optimized to transmit the $[M-K]^-$ or $[M-H]^-$ ions,whilecone-gas and desolvation-gas flows were kept at 60 and 750 L/hr, respectively. The ion source and desolvation temperatures were kept at 120 and 400 °C, respectively. Cone voltage and collision energies were optimized for each analyte. In all cases the capillary column was held at1.0kV.

Quantification was based on the response of the external standards that bracketed the concentration found in samples. The method limit of quantification (LOQ) was determined on the linear range of the calibration curve. For human blood samples, six calibration curve points prepared at 2, 10, 50, 200, 1000 and 2000 ppt (pg/mL) standard, injected at 10 µL, were used. Concentrations in samples that was at least 3 -fold greater than the lowest acceptable standard concentration were considered to be valid. A curve point was deemed acceptable if (1) it was back -

calculated to be within 30 % of the theoretical value, and (2) the peak area of the standard was at least 3 times greater than that in the blank. LOQ were between 2 and 50 ppt (pg/L) and depending on compound, and recovery ranged 57-106 % for 10 of 14 PFCs.

Results and Discussion

The results (arithmetic mean and range) of 60 whole blood samples examined are presented in Table 1. The method detection limit at the range of a few tens to hundreds of part -per-trillion (pg/mL) for a single compound could be achieved. Hence, detection of a wide range of PFCs was possible, and of the 14 PFCs searched 10 were found. A greatest mean PFOS concentration of 41 ng/mL was noted for the donors who declared elevated fish consumption rate, while for docker, farmer and general population groups were 12, 13 and 16 ng/mL, respectively. PFOA, PFHxS PFOSA, PFDoDA, PFUnDA, PFDA and PFNA concentrations of whole blood were relatively lower than those of PFOS. Nevertheless, these compounds were detected for each donor. PFHxA and PFHpA were less frequently found. Amongst of these three groups of blood donors examined a general population group determined by office workers remained somewhat more contaminated. Prolonged use of PFCs for paper and packing products, residential and mill -applied carpet spraying, stain -resistant textiles, and cleaners, may be an important source of exposure to these compounds. The accumulation rates of PFCs were similar in each group of donors, and they followed: PFOS>PFOA>PFHxS>PFNA>PFOSA>PFDA>

PFUnDA>PFHpA>PFHxA>PFDoDA. Similar profile and concentration range of PFCs quantified were reported recently for blood of donors from the Warsaw of Poland (WWF Detox report) and USA [3]. On the contrary to Asian and several European countries other than Poland, PFHxS content was greater than that of PFOSA. A recent study suggested that exposure to long -alkyl-chain perfluorocarboxylates other than PFOA may be widespread, as they were frequently found in mammals of Canadian Arctic [4]. Although only a few data are available for PFNA in human blood a somewhat wider range was noted in this study when compared to that noted recently for the citizens of Atlanta in Georgia (USA) and Sweden [3] PFOS, PFHxS and PFNA concentration noted for donors declaring enhanced fish consumption rate is evidently greater when compared to three other donor group (Fig. 1) or data reported previously for Poland, United States, Sweden, and Belgium. A good correlation between PFOS and PFOA concentration of whole blood of the donors sampled was noted (Fig. 2). As fishes are suggested to be important sources of PFCs for the Gdańsk region citizens more information of their residue concentration in seafood would be valuable.

Table 1. PFCs concentration in human blood (ng/mL) in the Gdańsk region

	Dockers		Farmers		Frequent fish cons.		General population	
Compound	Range	Mean	Range	Mean	Range	Mean	Range	Mean
PFOS	5.2-24	12	6.6-25	13	14-84	41	6.7-46	16
PFHxS	0.17-1.0	0.51	0.22-1.4	0.57	0.49-3.66	1.4	0.17-1.5	0.47
PFOSA	0.06-1.1	0.37	0.11-1.0	0.3	0.28-2.6	0.99	0.053-0.9	0.44
PFDoDA	0.004-0.023	0.01	0.006-0.033	0.02	0.011-0.38	0.06	0.006-0.038	0.02
PFUnDA	0.029-0.2	0.09	0.041-0.16	0.09	0.073-1.1	0.36	0.040-0.3	0.11
PFDA	0.062-0.34	0.15	0.11-0.26	0.19	0.15-1.4	0.54	0.090-0.51	0.20
PFNA	0.16-0.82	0.40	0.30-0.81	0.56	0.41-3.8	1.7	0.3-1.5	0.61
PFOA	1.2-5.8	2.7	1.2-6.2	3.4	1.7-8.7	4.1	1.3-5.2	3.0
PFHpA	0.005-0.57	0.07	0.007-0.15	0.06	0.033-0.79	0.19	0.017-0.47	0.17
PFHxA	0.001-0.016	0.01	0.005-0.063	0.03	0.014-0.24	0.06	0.004-0.065	0.03

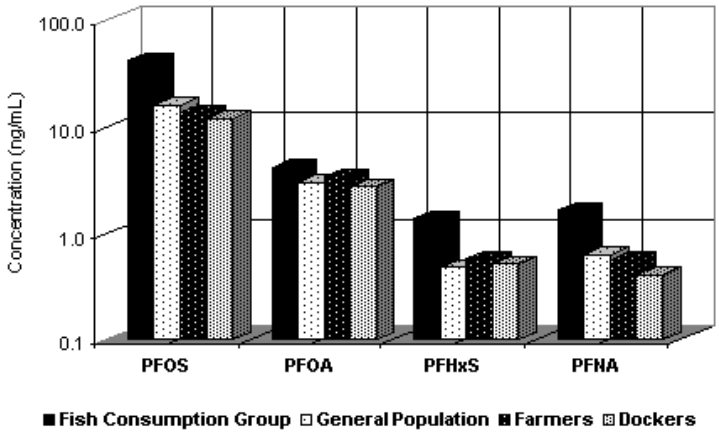

Fig.1. The means of PFOS, PFOA, PFHxS and PFNA for donor groups.

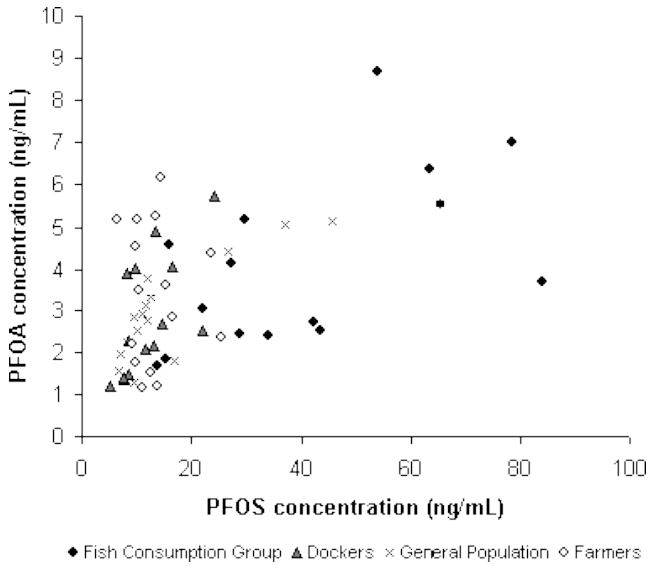

Fig. 2. Relationship between PFOS and PFOA for blood donors.

Previously reported studies on human exposure have mainly been focused on serum. Further studies have shown that PFOS and PFOA bind to plasma proteins. Studies on the distribution of long alkyl chain PFCs and sulfonamides in blood have been examined recently, nevertheless, more information about concentration in whole blood is useful. This is the first study to report the occurrence of a wide range of perfluorinated acids in blood of Poles. Further studies are being conducted to examine the sources and the exposure pathways of these compounds.

References

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