Perfluorinated compounds in serum from Australian urban and rural regions

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Introduction

Perfluorooctanesulfonate (PFOS) and perfluorooctanoate (PFOA) belong to a group of organic perfluorinated chemicals (PFCs), which have physico-chemical properties that make them highly persistent. They are man-made and used e.g. as surfactants in textile and paper protection and in the telomer industry ^{1, 2}. As a result from many years of production and their persistence, PFCs are ubiquitous in the environment and have been found in blood samples of humans from various countries as well as in biota collected in relatively remote locations ³⁻⁵. PFOS and PFOA are biologically active and potentially toxic to humans and the environment ^{6, 7}. Therefore distribution and exposure pathways are currently under investigation.

To date no information is available on the concentration of PFCs in humans from the Southern Oceanic region. This study aimed to evaluate the level of PFCs in serum from the population of two regions in Australia and evaluate trends in the PFC levels related to gender, age and region.

Materials and methods

Samples

Serum samples were collected by a Brisbane based private pathology company, Sullivan and Nicolaides Pathology, from stored sera that had been collected as part of their routine testing procedures. The samples were obtained from males and females from the following age groups: < 16, 16-30, 31-45, 46-60 and > 60 years. The urban samples were obtained from the Southeast of Australia (Sydney, Canberra, Wollongong, Newcastle and other major population centres from New South Wales) and the rural samples from rural areas from all States and the Northern Territory. Rural areas were defined as those postcodes outside metropolitan or major regional centres. For both regions there were 100 samples in each pool constructed by taking about 1 mL of each individual serum sample.

The project was submitted to The University of Queensland Medical Research Ethics Committee Approval and approval was obtained on the 20th September 2002. The project was allocated Clearance Number 2002000656.

Analysis

An SPE-LC/MS method for analysis of PFCs in whole blood, described in detail elsewhere was used for the serum samples ⁸. Briefly, a number of PFCs were analysed in 0.75 mL serum by first adding formic acid/water followed by solid-phase extraction on a C18 sorbent (BondEluteHF. Varian,Harbor City CA, USA). Separation and detection was performed with LC-MS (HP 1100 LC/MSD, Waldbronn, Germany) using internal standard quantification. However, using 200 mg C18 material in the solid-phase extraction, as described for whole blood, resulted in low recovery (20-50%) of the internal standard perfluoroheptanoic acid (PFHpA) and other PFCs added to serum. Reducing the material weight to 100 mg increased the recoveries in serum to 70% for PFOS and PFOA and 80% for PFHpA and perfluorohexanesulfonate (PFHxS). The instrumental limit of detection (LOD) was defined as the concentration needed to produce a signal to noise ratio of 3:1 and was 0.1-0.5 ng/mL for PFOS, PFOA and PFHxS. Quality control and blank samples were included for quality assurance.

Results and Discussion

PFCs including PFOS, PFOA and PFHxS were detected in all serum sample pools ranging in concentration from 13-29 ng/mL for PFOS, 5.0-9.9 ng/mL for PFOA and 2.7-19 ng/mL for PFHxS.

Regions

Given in Table 1 are median, variability, range and geometric mean for PFOS, PFOA and PFHxS concentrations in

serum from urban and rural regions. Only a marginal difference between serum levels in rural and urban regions can be seen. Higher PFHxS median especially for women living in the urban region (rural 5.5, urban 8.0 ng/mL) was observed as well as slightly higher PFOS median in the urban region for both men and women. Generally, no systematic differences or other factors indicate that the exposure for PFOS and PFOA in the Australian general population differs between urban and rural regions.

Table 1. Descriptive statistics for 3 PFCs (ng/mL) in Australian serum sample pools from urban (n=20) and rural (n=18) regions.

	PFOS		PFOA		PFHxS	
	Urban	Rural	Urban	Rural	Urban	Rural
Median	22	20	7.1	8.1	7.3	5.7
IQR ^a	20 - 24	17 - 25	6.7 - 8.1	6.6 – 9.1	5.7 - 9.6	4.5 - 6.5
Range	16 - 29	13 - 28	5.1 – 9.6	5.0 - 9.9	3.5 – 19	2.7 – 11
Geometric mean	22	20	7.2	7.7	7.6	5.4

^aInterquartile range

Age and gender

The influence of age and gender on median levels is shown in Figure 1. Each stratum consists of two pooled samples, each with 100 individuals. The reproducibility between the two pools can also be seen in Figure 1. Only small differences can be seen between PFOS median for women and men (20 and 23 ng/mL respectively). The trend for PFHxS is reproducible between the pools and different compared to PFOS and PFOA. Levels for women >60 years and men <16 years, both in the urban region are higher when compared to the other age groups.Furthermore, age and gender do not seem to be clear determining factors for the levels of studied PFCs in serum.



Figure 1. Results for PFOS, PFOA and PFHxS in pooled serum samples from rural and urban regions in Australia, divided in different age groups and gender. Each stratum consists of 2 pools.

Since this is the first report on Australian levels of PFCs a comparison with other countries is interesting. Highest

PFOS levels in the general population serum have been reported from North America with median range 26-54 ng/mL. The PFOS median in Australian serum (21 ng/mL) is just below the North American range but higher than for example Belgium and Japan. Australian PFOA concentrations (7.6 ng/mL) as well as the PFHxS median concentrations(6.7 ng/mL) are high compared to studies in other countries. To the best of our knowledge, the Australian PFHxS median is the highest reported so far in a general population. The highest concentration found here (19 ng/mL) is however not as high as some serum samples from USA (highest 66.3 ng/mL) ^{4, 9, 10}. Possible causes for observed elevated median concentrations for the pools are unknown and need to be further confirmed by determining individual levels.



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Figure 2. Comparison between median levels (ng/mL) in serum from different countries.

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References

1. 3M. (1999). Fluorochemical Use, Distribution and Release Overview. U.S. EPA public docket AR226-0550.

2. EPA.(2003).U.S. EPA public docket AR 226. Washington, DC.

3. Martin, J. W.; Smithwick, M. M.; Braune, B. M.; Hoekstra, P. F.; Muir, D. C.; Mabury, S. A. (2004) *Environ SciTechnol.* 38: 373-380.

4. Kannan, K.; Corsolini, S.; Falandysz, J.; Fillman, G.; Kumar, K. S.; Loganathan, B. G.; Mohd, M. A.; Olivero, J.; van Wouwe, N.; Yang, J. H.; Aldous, K. M. (2004) *Environ SciTechnol.* 38: 4489-4495.

5. Giesy, J. P.; Kannan, K. (2001) Environ SciTechnol. 35: 1339-1342.

6. 3M. (2003). Health and environmental assessment of perfluorooctanesulfonic acid and its salts. St. Paul, MN.

7. Kennedy, G. L.; Butenhoff, J. L.; Olsen, G. W.; O'Connor, J. C.; Seacat, A. M.; Perkins, R. G.; Biegel, L. B.; Murphy, S. R.; Farrar, D. G. (2004) *Crit Rev Toxicol*. 34: 351-384.

8. Kärrman, A.; van Bavel, B.; Järnberg, U.; Hardell, L.; Lindström, G. (2005) Anal Chem. 77: 864-870.

9. Olsen, G. W.; Church, T. R.; Miller, J. P.; Burris, J. M.; Hansen, K. J.; Lundberg, J. K.; Armitage, J. B.; Herron, R. M.; Medhdizadehkashi, Z.; Nobiletti, J. B.; O'Neill, E. M.; Mandel, J. H.; Zobel, L. R. (2003) *EnvironHealthPerspect.* 111: 1892-1901.

10. Olsen, G. W.; Church, T. R.; Larson, E. B.; van Belle, G.; Lundberg, J. K.; Hansen, K. J.; Burris, J. M.; Mandel, J. H.; Zobel, L. R. (2004) *Chemosphere*. 54: 1599-1611.

11. Kuklenyik, Z.; Reich, J. A.; Tully, L. L.; Needham, L. L.; Calafat, A. M. (2004) *Environ SciTechnol.* 38: 3698-3704.

12. Kubwabo, C.; Vais, N.; Benoit, F. M. (2004) J Environ Monitor. 6: 540-545.