

## PERFLUOROALKYLATED COMPOUNDS IN HUMAN BLOOD

Kurunthachalam Kannan<sup>1</sup>, Kurunthachalam Senthil Kumar<sup>2</sup>, Simonetta Corsolini<sup>3</sup> and Kenneth M. Aldous<sup>1</sup>

<sup>1</sup>Wadsworth Center, New York State Department of Health, Empire State Plaza, P.O.Box 509, Albany, NY 12201-0509, USA

<sup>2</sup>Shimadzu Techno-Research Inc., 1, Nishinokyo-Shimoaicho, Nakagyo-ku, Kyoto 604-8436, Japan

<sup>3</sup>Dipartimento di Scienze Ambientali, Università di Siena, I-53100 Siena, Italy

### Introduction

Perfluorooctanesulfonate (PFOS) is known to be the end-stage metabolite of fluorochemicals produced using perfluorooctanesulfonylfluoride (POSF) as a precursor<sup>1</sup>. POSF-based fluorochemicals have been used in a wide variety of industrial and consumer products including protective coatings for carpets and apparel, paper coatings, insecticide formulations and surfactants<sup>2</sup>. PFOS has been reported to be widely distributed in the environment<sup>3</sup>. While studies investigating the occurrence of organofluorine compounds in human tissues date back to the late 1960s, only recently compound-specific analysis was performed of employees in the fluorochemical manufacturing industry, which identified PFOS and perfluorooctanoic acid (PFOA or C8) at concentrations of up to 12.8 and 114 µg/mL, respectively<sup>1</sup>. To date, little is known about the levels of PFOS in the general population<sup>4,5</sup>. Belisle and Hagen<sup>6</sup> reported the occurrence of organically bound fluorine in human blood in the US and China. In this study, concentrations of PFOS, perfluorohexanesulfonate (PFHxS), PFOA and perfluorooctanesulfonamide (PFOSA) were measured in the blood sera of the general population from the USA, Italy and India.

### Materials and Methods

Blood samples were collected from volunteer donations, during a blood drive organized by American Red Cross in Sanilac, Genesee and Chippewa Counties in Michigan, USA, on 9th June 2000 (n=75). Blood samples from Siena, Italy (n=50), and Coimbatore, India (n=45), were collected from local hospitals during 17-19 January 2001 and 21-26 January 2000, respectively. Serum was obtained from whole blood after clotting. Serum samples were kept at -20°C until analysis. Concentrations of PFOS, PFHxS, PFOA, and PFOSA were extracted using an ion-pairing extraction procedure and determined by use of high performance liquid chromatography (HPLC) interfaced with electrospray tandem mass spectrometer (ES-MS/MS)<sup>4</sup>.

Solvents, blood collection tubes, method and matrix blanks were checked for the presence of perfluorinated compounds. Rabbit serum (Pel-Freez, Brown Deer, WI) was used as a surrogate blank. Concentrations of target analytes in matrix and serum blanks were below the limit of quantitation (LOQ). Mean recoveries of PFOS, PFHxS, PFOA, and PFOSA spiked to the sera of donors at concentrations ranging from 10 to 250 ng/mL are shown in Table 1. Reported concentrations were not corrected for the recoveries. LOQ was determined based on the linear range of the calibration curve prepared at a concentration range of 1 to 1000 ng/mL, as was reported earlier<sup>4</sup>. LOQ for PFOS, PFHxS, PFOA, and PFOSA varied from 1 to 1.3, 1 to 1.3, 3 to 6 and 1.3 to 6 ng/mL, respectively.

**Table 1.** Recoveries (%) of target fluorochemicals spiked to human sera through the analytical procedure.

	PFOS	PFHxS	PFOA	PFOSA
USA	92±10	87±9	99±6	92±2
Italy	72±24	82±27	84±27	44±14
India	117±14	106±12	110±20	110±10

**Results and Discussion**

Concentrations of PFOS, PFHxS, PFOA, and PFOSA in sera samples collected from the USA, Italy, and India are shown in Table 2. For the calculation of mean and median, serum concentrations below the LOQ were not included. Therefore, the reported mean and median values may be conservative. Among the four fluorochemicals measured, PFOS was the most frequently detected compound in sera. Mean PFOS concentration in sera from the US donors was 32.6 ng/mL, which was less than those reported earlier (17.7 ng/mL)<sup>5</sup>. Mean PFOS concentration in sera from six different states in the USA was 34.9 ng/mL (n=645; range <4.3 – 1660 ng/mL)<sup>7</sup>, which was similar to that observed in this study. A comparison of PFOS concentrations in sera from different countries is shown in Figure 1. Mean PFOS concentration in the sera of US donors is similar to those reported for Canadians<sup>8</sup> and 4-fold greater than those reported for Japanese donors<sup>9</sup>.

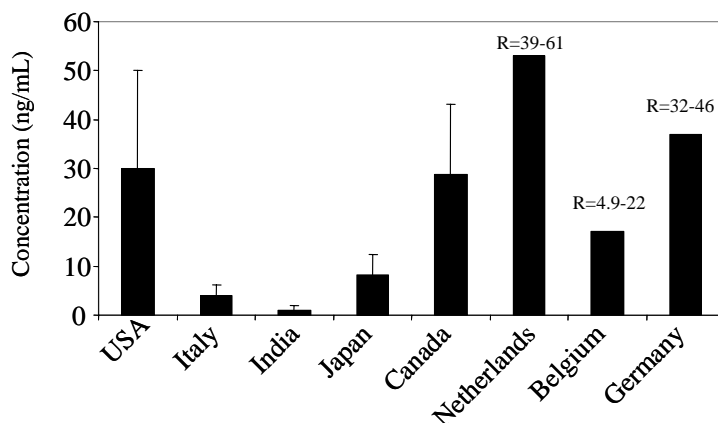
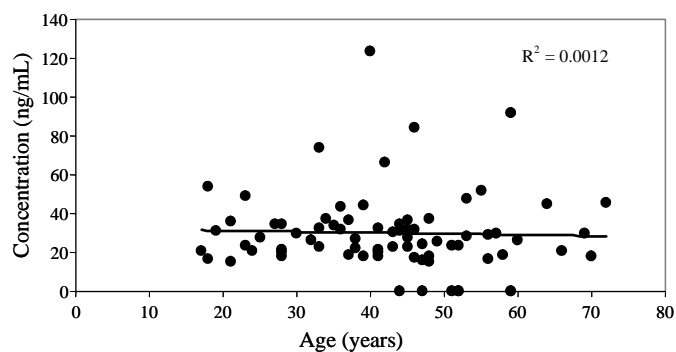


Figure 1. Concentrations of PFOS in human sera from various countries. Data for the Netherlands, Belgium and Germany are from OECD, 2002; Data for Canada are from Kubwabo et al., 2003. R= range.

PFOS was frequently detected in Italian sera as it was in the sera of US donors. However, PFOS concentrations in Italian sera were 7.5-fold lower than those found in the sera of US donors. Only 51% of the sera samples collected from India contained PFOS at concentrations greater than 1 ng/mL. When the values below the LOQ were treated as zero, mean PFOS concentration in Indian sera was 1 ng/mL, which was approximately 20 to 30-fold lower than those found in the sera of the US donors. These results suggest that the patterns of exposure to perfluorochemicals in India and Italy are different from that in the USA. Prolonged use of these chemicals for a wide variety of applications such as paper and packing products, residential and mill applied carpet spraying, stain-resistant textiles and cleaners may be a major source of human exposure to perfluorochemicals.

**Table 2.** Perfluorochemical concentrations in sera (ng/mL); values below the detection limits were not included in the calculation of mean and median.

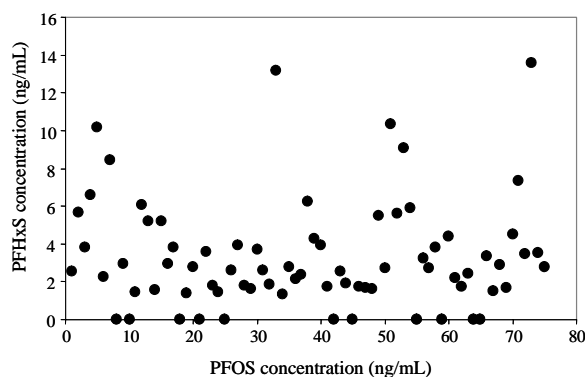
Country/Sex		PFOS	PFHxS	PFOA	PFOSA	
<b>USA</b>	Mean	32.5	3.6	4.7	3.7	
	Female (n=46)	Median	28.9	2.8	4.4	2.2
		Range	<1.3-91.7	<1.3-13.2	<3-7.3	<1.3-23.5
		% positive	91	85	46	44
	Male (n=29)	Mean	32.9	4.3	5.7	3.0
	Median	26.2	3.3	4.4	2.9	
	Range	<1.3-124	<1.3-13.6	<3-14.7	<1.3-6.1	
	% positive	93	76	45	52	
<b>Italy</b>	Mean	4.4	1.3	<3	1.7	
	Female (n=8)	Median	3.5	1.3	<3	1.7
		Range	<1-8	<1-1.4	<3	<1.3-1.7
		% positive	87.5	37.5	0	12.5
	Male (n=42)	Mean	4.3	1.7	<3	1.8
	Median	4.2	1.7	<3	1.6	
	Range	<1-10.3	<1-2.1	<3	<1.3-2.3	
	% positive	90.5	33.0	0	9.5	
<b>India</b>	Mean	2.3	1.6	<3	<3	
	Female (n=11)	Median	2.5	1.6	<3	<3
		Range	<1-3	<1-1.8	<3	<3
		% positive	55	36	0	0
	Male (n=34)	Mean	1.7	1.6	3.5	<3
	Median	1.3	1.5	3.5	<3	
	Range	<1-3.1	<1-2.9	<3-3.5	<3	
	% positive	50	41	3	0	

**Figure 2.** Relationship of PFOS concentrations in sera from US donors and age.

PFHxS was the next most frequently detected compound in human sera. Concentrations of PFHxS in the sera of US donors were 8 to 10-fold less than those of PFOS concentrations. PFHxS was found in 30 to 40% of the sera samples collected from Italy and India. Mean PFHxS concentration in the sera of Italian donors was 2-fold less than that of PFOS concentration, whereas those in Indian donors, the mean concentrations of PFHxS and PFOS were similar. These results further suggest that the patterns of exposures in India and Italy are different from that in the USA. PFOA and PFOSA were found more frequently in the sera of the US donors than the samples from Italy and India. We also measured perfluorononanoic acid (PFNA) and perfluorodecanoic acid (PFDA) in the blood sera of US donors and the concentrations were between 0.5 and 1 ng/mL.

Mean serum PFOS concentrations were similar between male and female donors. No associations were observed between measured PFOS concentrations and age (Figure 2). Similarly, no significant relationship was observed between PFOS and PFHxS concentrations in the sera of US donors (Figure 3). These results may suggest that the sources of exposures of fluorochemicals measured in this study are independent of each other.

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**Figure 3.** Relationship between PFOS and PFHxS concentrations in sera from US donors.

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