Perfluorinated compounds in human serum and seminal plasma from an urban and rural population in Sri Lanka

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Introduction

Fluorinated organic compounds (FOCs) have been used for variety of industrial applications such as surfactants, adhesives, insecticides, and their global production increase since 1970s. These compounds repel both water and oil. The high-energy carbon-fluorine covalent bonds in FOCs are strong enough to have high persistency in the environment. These compounds emerged as priory environmental pollutants since they are found in various biota throughout the world.[1-2] Human contamination of some FOCs was reported mostly in developed countries such as USA, Japan and from Europe.[3--7] In the present study, we report 10 FOCs in human serum including seminal plasma for the first time, collected from volunteers from Sri Lanka.

Methods and Materials

Human sera and seminal plasma from volunteer donors were collected in year 2003. They represented Colombo, an urban population (n = 11; 29-48 years), and Talawakele, a rural population (n=10; 24-61 years) in Sri Lanka. Sera and seminal plasma were prepared by centrifuging according to WHO criteria and kept –20C until FOCs analysis. Samples were analyzed for 10 FOCs: perfluorohexanesulfonate (PFHS), perfluorooctanesulfonate (PFOS), perfluoroheptanoic acid (PFHpA), perfluorooctanoic acid (PFOA), perfluorononanoic acid (PFNA), perfluorodecanoic acid (PFDA), perfluoroundecanoic acid (PFUnA), perfluorododecanoic acid (PFDoA), perfluorooctanesulfonylamide acid (PFOSA) and 1H,1H,2H,2H-perfluorooctanesulfonate (THPFOS). Extraction was carried out by an ion-pairing method, which described elsewhere.[3-4] One ml of serum or seminal plasma was mixed with 1ml of 0.5M tetrabutylammonium hydrogensulfate solution and 2ml of buffer (10 pH, 0.25M) in a polypropylene (pp) tube. The sample mixture was extracted with methyl *t*-butyl ether (MTBE) 5ml after shaking for 20 m followed by centrifugation. A 4ml of MTBE was removed from the solution and placed in a second pp tube. The extraction was performed for two more times and 5ml of MTBE was removed each time and combined in the second pp tube. The final extract was concentrated under nitrogen after adding 0.5ml of methanol. The sample was passed through a 0.1µm nylon filter and HPLC-MS/MS measurement was performed using a customized Agilent

HP1100 liquid chromatograph equipped with MS/MS (MICROMASS Co., Quatro Ultima Pt.). [4,5] The mean procedural recovery and blank of analytics are given in Table 1.

Table 1. Procedural recovery and blank detection of target FOCs

	PFOS	PFHS	PFDoA	PFUnA	PFDA	PFNA	PFOA	PFHpA	PFOSA	THPFOS
Rec. %	83	84	69	74	80	91	92	95	78	140
Blank pg/ml	10	10	4	5	9	11	120	30	10	3

Results and Discussion

The concentrations of FOCs in sera and seminal plasma are given in Figures 1 and 2. Mean blank value was subtracted from the sample data. For the calculation of mean, concentrations below blank were not included. The sample concentrations of PFOSA and THPFOS were similar or less than those for blank concentrations. Hence those data are not presented. The accumulation of FOCs in urban sera was in the order of PFOA > PFOS > PFHS > PFNA > PFHpA > PFUnA > PFDA > PFDoA. PFOA concentrations in 50% of the sera from the urban location were exceeded 10ng/ml. The accumulation trend of FOCs in seminal plasma was similar to that for sera in the urban population. The mean concentration of PFOA was (240 pg/ml) 2 folds greater than that of PFOS (130 pg/ml), while other detected FOCs were less than 50 pg/ml in Colombo seminal plasma.

PFOS and PFOA in sera from the urban area were detected in ng/ml levels with the highest values of 18 and 23 ng/ml respectively. These values were greater than those maximum concentrations reported for the sera from Italy and India. [7] PFOS in sera were within the range of that in Japan (2-20 ng/ml) and USA (6.7-82 ng/ml). [3,4,6] The highest PFOA concentration detected in Sri Lanka was to be in the upper limit reported for human sera in USA[3] However, the mean PFOS concentration in sera from Sri Lanka was lower than that of most of developed countries. [7] PFHS levels in sera from Sri Lankan male was less those concentrations in USA, however within the range of reported levels in Japan. [3, 7]

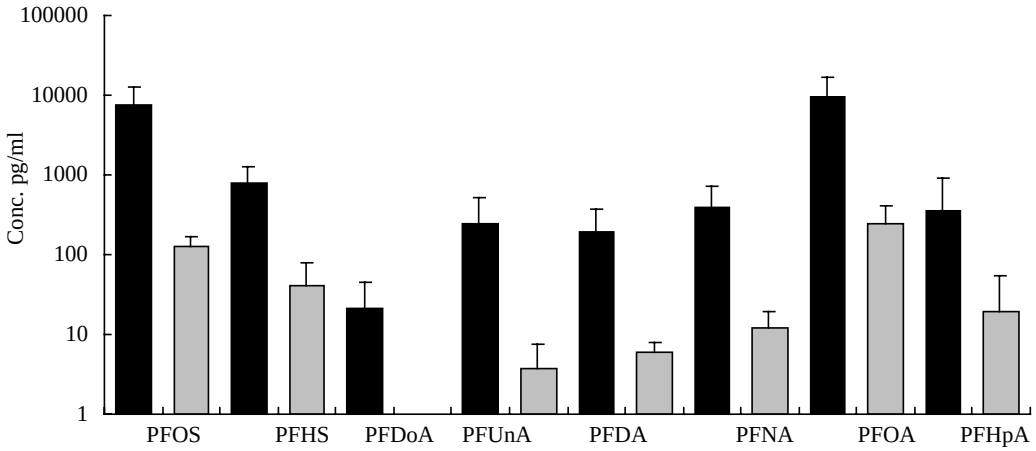

Figure 1. Concentrations of FOCs in human sera and seminal plasma from Colombo, an urban population in Sri Lanka. ND: less than blank, Sera: n=10, seminal plasma: n=11

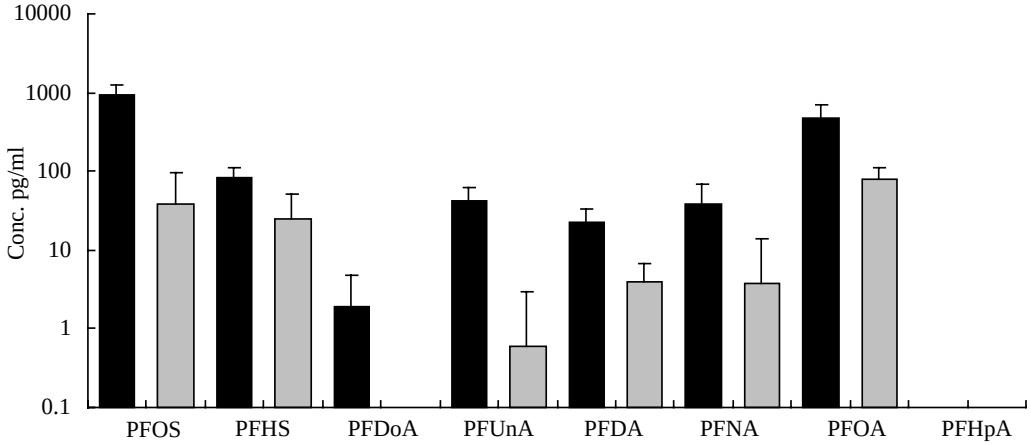

Figure 2. Concentrations of FOCs in human sera and seminal plasma from Talawakele, a rural population in Sri Lanka. ND: less than blank, Sera: n=10, seminal plasma: n=10

PFOS concentration (950 pg/ml) was 2 folds greater than PFOA (460 pg/ml) in the rural population, which was similar to mostly reported data for human sera. Only PFOA (78 pg/ml) and PFHS (25 pg/ml) detection frequency was 100% in rural seminal plasma. PFHpA was less than blank for both sera and seminal plasma in rural samples, while PFDoA was not found in seminal plasma from both populations.

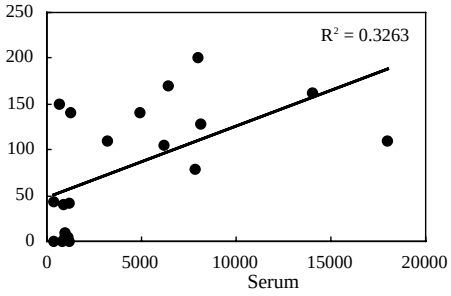

Figure 3. Relationship of PFOS concentrations in sera and seminal plasma from Sri Lanka

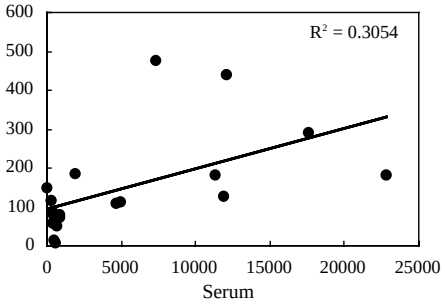

Figure 4. Relationship of PFOA concentrations in sera and seminal plasma from Sri Lanka

There were no FOCs data are reported for human seminal plasma. We observed an increasing trend of PFOS and PFOA accumulation between seminal plasma and sera (Figures 3 & 4), while no age trend.

The accumulation of PFOS in sera was positively correlated with PFHS, PFNA, PFUnA and PFOA suggesting that these compounds have similar accumulation properties (Figure 5) in human body fluids.

All the FOCs concentrations in sera and seminal plasma in urban location were significantly higher than those from the rural location. The greater exposure levels found in Colombo revealed that wide variety of applications with perfluoroalkylated compound such as paper, packing products, carpet spray, stain-resistant textiles, cosmetics, electronics and fire-fighting foams, are readily existing for urban community compared to the rural population in Sri Lanka

Overall, these data are indicated that human contamination of FOCs was widespread even in developing countries similar to those in industrialized ones. Exposure to organohalogen compounds may be associated with human reproductive failiers.[8] Several FOC compounds were found in seminal plasma have long half-lives (> 1 year) suggesting that those compounds might pose adverse health effects including male fertility associated with long-term exposure. Since these compound had greater accumulations in higher trophic positions, they should be considered in future risk assessments of chemical exposure in human.

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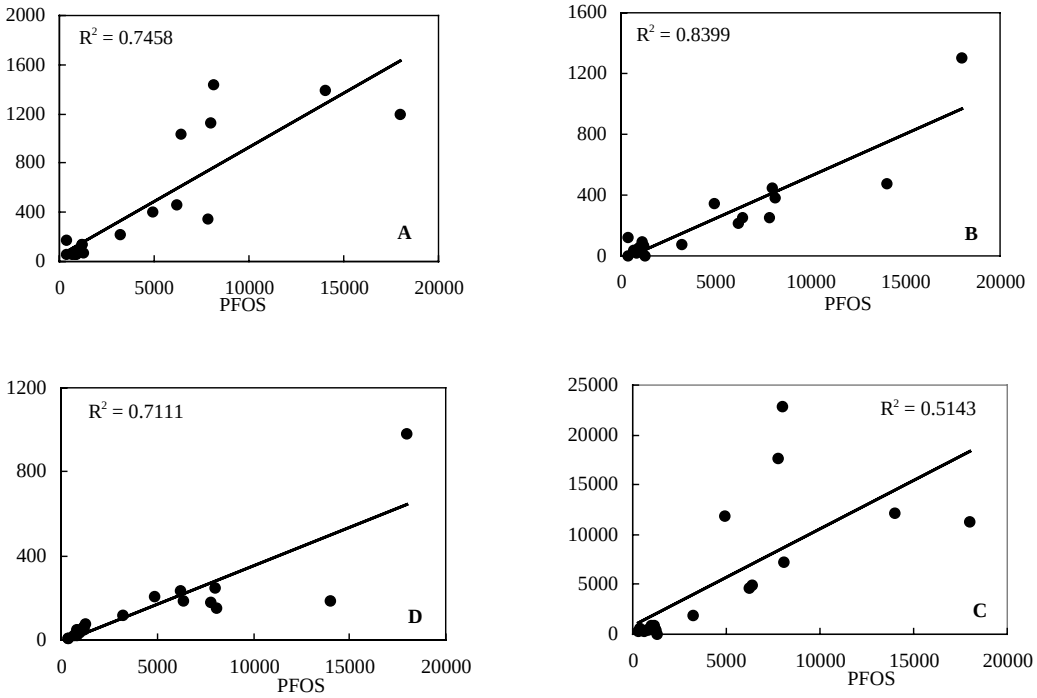

Figure 5. Relationship of PFOS and PFHS (A), PFNA (B), PFUnA (C) and PFOA (D) concentrations (pg/ml) in human sera from Sri Lanka.