PERFLUORINATED ALKYL SUBSTANCES IN WHOLE BLOOD AND PLASMA; AN ASSESSMENT IN MATERNAL AND UMBILICAL CORD SAMPLES FROM INHABITANTS IN RUSSIA AND UZBEKISTAN

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Abstract

•In human biomonitoring, serum and plasma have been the preferred matrixes.
•The distribution between serum/plasma and whole blood for ionic PFAS are corrected in general with a factor of two.
•Neutral PFAS behave differently, and can be underestimated when they are measured in serum or plasma.

Introduction

In human biomonitoring of persistent organic pollutants serum and plasma has been the preferred matrix. Concentrations of perfluorinated alkyl substances (PFAS), have been reported for both serum, plasma, and whole blood,[1] where the first two are the most common. Results have shown that there are no differences in PFAS concentrations and distribution between these two matrixes [2]. When PFAS have been analysed in whole blood a factor of two has been applied to account for the volume displacements of red blood cells. Kärrman et al. [3] reported that for "neutral" PFAS compounds such as perfluorooctane sulfonamide (PFOSA) , this was not the case. When PFOSA concentrations are reported for serum or plasma, the results were underestimated.
PFOSA is regarded as a precursor for perfluorooctane sulfonate (PFOS), and can undergo metabolism and be converted to PFOS [4].

Objectives

Assess PFAS concentrations and distribution between whole blood and plasma from maternal and cord blood samples.

Study Population

•From Norilsk in Russia 7 paired maternal cord samples. Maternal age was 21-28 years.
•From Urgench in Uzbekistan 10 paired maternal-cord samples. Maternal age was 21-41 years.
•Sampling period was from January 2001 to July 2001.
•Blood was collected from mothers on the first to the third day after delivery. Cord blood was sampled immediately after the tying and cutting of the umbilical cord.

Materials and Methods

Sample preparation:
•Mass-labelled standards (Table 1[3]) was added to 0.5-1 mL whole blood or plasma.
•Samples were extracted for PFC using a modified method by Powley et al.[5].

Instrument:
•Thermo Scientific Accela 1250 pump (UPLC), and Thermo Scientific TSQ Vantage (MS/MS).
• Columns: **Trapping**; XBridge C18, 2.1 x 50mm, 5 µm, **Precolum;** Waters Van guard HSS T3, 2,1 x 5mm, 1.8 µm, **Analytical column**; Waters Acquity UPLC HSS 3T column 2,1 x 100 mm, 1,8 µm.
•Ionization mode: ESI negative (ESI-).

Results

The results are presented in Table 1. PFOS was the only compound above method quantification limit (MQL) in the samples from Urgench.
•In maternal plasma samples from Norilsk; PFOS > PFOA. In whole blood; PFOS > PFOSA.
•The ratio between maternal plasma and whole blood for samples with 100 % detection of ionic PFAS ranged from 1.6 to 1.8. For PFOSA it was 0.14.
•In umbilical cord samples the ratio between plasma and whole blood for ionic PFAS was 2.2 to 2.4. For PFOSA it was 0.95.
•The only correlation that were significant at 5 % was between PFHxS and PFNA in plasma.
•The correlation between PFOS and PFOSA was weak in plasma, however stronger in whole blood, but not significant.

Table 1 PFAS concentrations in whole blood and plasma from maternal and umbilical cord samples from inhabitants in Norilsk and Urgench. Median is only reported for samples where the PFAS concentration were above MQL[1,2].

	Maternal				Umbilical cord			
NORILSK (N=7)	Whole blood[3]		Plasma[3]		Whole blood[3]		Plasma[3]	
ng/mL	Median	Range	Median	Range	Median	Range	Median	Range
PFHpA	-	< MQL-0.10	-	< MQL-0.15	-	< MQL-0.12	-	< MQL-0.20
PFOA	0.89	0.33-1.40	1.61	0.63-2.48	0.49	0.15-1.12	1.00	0.36-2.32
PFNA	0.35	0.23-1.43	0.60	0.38-2.75	0.15	0.08-0.78	0.29	0.21-1.85
PFDcA	-	< MQL-0.26	-	< MQL-0.53	-	< MQL-0.08	-	< MQL-0.17
PFUnA	0.16	0.10-0.70	0.22	0.13-0.96	-	< MQL-0.23	-	< MQL-0.43
PFHxS	0.16	0.08-0.23	0.46	0.15-0.26	0.07	0.03-0.14	0.14	0.08-0.33
PFOS-sum	**5.79**	**3.61-8.38**	**11.0**	**5.56-14.5**	**1.88**	**0.49-3.89**	**4.11**	**1.75-6.27**
PFOS-linear	2.82	1.46-4.12	5.87	2.49-7.17	0.95	0.22-2.10	2.36	0.90-3.72
% linear	48.7	40.5-50.5	50.6	44.8-54.9	52.7	45.1-57.5	57.5	51.3-59.7
PFOSA-sum	**2.05**	**1.42-8.42**	**0.33**	**0.19-1.17**	**0.38[2]**	**<MQL-1.37**	**0.31**	**0.12-1.31**
URGENCH (N=10)								
PFOS-sum	**0.24**	**0.11-1.20**	**0.14**	**<MQL-0.89**	**-**	**<MQL-0.27**	**0.09**	**<MQL-0.69**

1) MQL: method quantification limit; PFHpA (0.05), PFOA (0.05), PFNA (0.08), PFDcA (0.1), PFUnA (0.05), PFHxS (0.03), PFOS (0.08), PFOSA (0.1).
2) calculated from 6 out of 7 samples.
3) Mass labelled internal standards: MPFOA, MPFNA, MPFDcA, MPFUnA, MPFHxS, MPFOS, MPFOSA

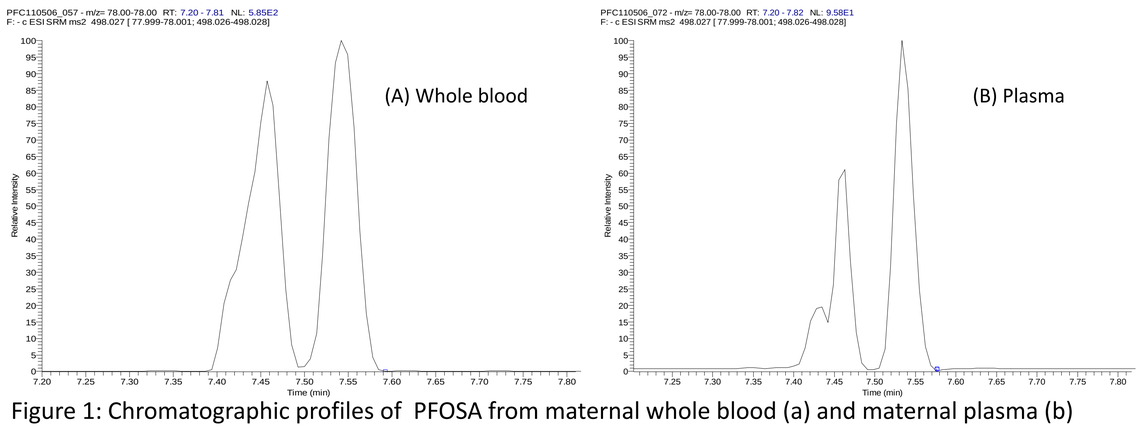

Figure 1: Chromatographic profiles of PFOSA from maternal whole blood (a) and maternal plasma (b)

Discussion and Conclusion

•One orders of magnitude higher concentrations of PFOS in Norilsk compared to Urgench.
•Ionic PFAS; plasma/whole blood ratio approximately two.
•Plasma/whole blood ratio for PFOSA was 0.14.
•Plasma/red blood cell ratios differ between pregnant women and the general population, and could explain the slight differences between this study and the study done by Ehresman et al [2] and Kärrman et al [3].
•PFOSA crosses the placenta to a lesser extent than ionic PFAS.
•Both in whole blood and plasma there were significant amounts of branched PFOSA, figure 1.

•Branched PFOSA could be a source to branched PFOS and be one of the explanations of the increased percentage of branched PFOS in human plasma and serum samples.

•In future human bio-monitoring, whole blood should be considered as the most sensitive and preferred matrix to be used.

References

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