MONITORING OF PFAS IN CORE MATRICES OF THE STOCKHOLM CONVENTION

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Introduction

The Stockholm Convention on Persistent Organic Pollutants (POPs) (1-2) has adopted a global monitoring plan (GMP) of POPs to provide comparable monitoring information on the presence of POPs listed in Annexes A, B or C of the Convention and to follow changes over time and assess the effectiveness of the measures taken under the Convention (3). A regional approach based on the five regions of the United Nations was proposed and implemented on a regional basis (UN regions). Perfluoroalkane substances (PFAS) were not among the initial twelve POPs and although perfluorooctanesulfonic acid (PFOS) does not follow the typical pattern of the brominated and chlorinated POPs, the same core matrices – ambient air for environmental assessment and human milk for human exposure – are recommended for analysis. Due to the hydrophilicity of PFOS, surface water was added as a core matrix for the PFAS. The United Nations Environment Programme (UNEP) is assisting developing countries with capacity building and sampling in developing countries and analysis in expert laboratories to contribute with national data. Four regional projects were implemented in Africa, Asia (including the Pacific Islands countries, hereafter abbreviated as PAC) and the Latin American and Caribbean countries region (GRULAC) from 2016 to 2020. This paper summarizes the results generated by the PFAS laboratory that analyzed all samples for PFOS (4,5), perfluorooctanoic acid (PFOA) (6) and perfluorohexanesulfonic acid (PFHxS) (7), a compound not yet listed in the Stockholm Convention but agreed by countries to be included since was recommended for listing.

Materials and methods

All analyses were performed in the PFAS laboratory of MTM Research Center, Örebro University using a liquid chromatograph (LC) coupled to a triple quadrupole mass spectrometer detector (MS-MS, XEVO TQS Waters Corporation, Milford, USA) (8-10). Briefly, extraction was made using solid-phase extraction (SPE-WAX cartridge (6 mL, 150 mg, 30 µm; Waters Corporation Milford, USA); where necessary, a cleanup step with ENVI-Carb SPE tubes was added after the SPE cartridge during elution. Aliquots of 10 µL from the fractions after SPE were injected on a BEH (ethylene bridged hybrid) C_{18}-column (1.7 µm, 2.1 mm × 100 mm; Waters Corporation Milford, USA). Mobile phases used were methanol:water 70:30 (v/v) (A) and 100% methanol (B) with 2 mM ammonium acetate in both phases, for the human milk samples, methanol was replaced by acetonitrile (10). Two mass transitions (parent ion/product

ion) for each analyte were monitored. Branched isomers of PFOS were quantified using the potassium salt of a technical grade PFOS containing 78.8% perfluorooactane-1-sulfonate (linear PFOS, L-PFOS) and 21.2% of a mixture of branched isomers (br-PFOS) (Wellington, Guelph, ON, Canada). For ambient air, five PFOS precursors (perfluoro-1-octanesulfonamide (FOSA), methylperfluoro-1-octanesulfonamide (NMeFOSA), ethylperfluoro-1-octanesulfonamide (NEtFOSA), 2-(N-methylperfluoro-1-octanesulfonamido)-ethanol (NMeFOSE), and 2-(N-ethylperfluoro-1-octanesulfonamido)-ethanol (NEtFOSE)) were included (Wellington Laboratories, Guelph, ON, Canada). Details on analytical procedures, quality assurance/quality control, data handling and statistical methods are described in related publications (8-11).

Samples included 44 national pools of primipara mothers from 42 countries, 356 ambient air samples collected by passive air sampling (PAS) using pre-conditioned polyurethane foam disks (PUF) exposed for three months in 41 developing countries, and 144 surface water samples collected at the mouth of rivers or estuaries in 22 countries. Most sampling was done in 2017/2018. PFOS data shown here refer to the sum by addition of L- and br-PFOS determinations. PFOA and PFHxS refer to the linear isomers.

Results and discussion

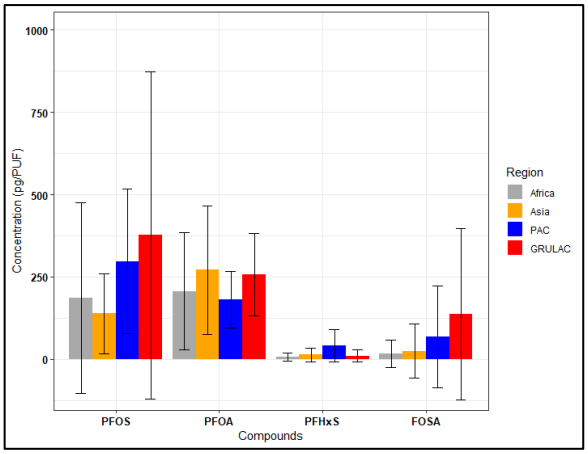
Ambient air

Chemical analysis of individual PUFs – samples from 2017 – often gave results below the limit of quantification (LOQ); therefore, for each country the extracts from the same year were combined, cleaned-up again, concentrated and analyzed again. These samples were named annual samples and the results divided by the number of PUFs to adjust the result to 1 PUF and allow comparison with the quarterly results. From 2018, a portion of the extract was used to generate the annual sample before ENVI Carb and SPE steps. Finally, 356 determinations were available whereby 39 samples did not pass the QA/QC so that no PFAS could be quantified; another nine PUFs (from one country) were analyzed and reported but not further included in regional or other assessments since the amounts of PFOS and PFHxS were many times higher than any other measurement. Remediation works at the airport were identified as the cause of the elevated levels (up to 36000 pg/PUF for ∑PFOS); these are not included in the following table and figure. Finally, 246 quarterly and 62 annual results were generated (9). The results from the 308 determinations, adjusted to one PUF and 3-month exposure is shown in Table 1. In Figure 1 and Table 1, it can be seen that median values of PFOA in all regions except for the Pacific Islands countries (PAC) were higher than for PFOS. For PFOS, high standard deviations (SD) were observed. Subsequently, the mean value for PFOS in the Group of Latin America and the Caribbean (GRULAC) was higher than the mean value for PFOA (Table 1). The median values for PFHxS and FOSA were at zero for three regions, each and only PAC had more than half of the PFHxS quantified and GRULAC for FOSA. It should be noted that FOSA could be quantified in only 46% of the samples; whereas the others had >90% detection frequency. The limit of quantification for the other PFOS precursors – NMeFOSA, NEtFOSA, NMeFOSE, and NEtFOSE was 200 pg/PUF and missing values were between 46.5% and 87.0% on a regional per compound basis. Overall, the PFOS precursors did

not play any role. For details, refer to (9).

Table 1. Descriptive statistics for PFAS concentrations according to region (concentrations in pg/PUF, adjusted to 1 PUF and 3 months) (n=308). SD = standard deviation

Region	Africa	Asia	GRULAC	PAC	Overall
Analytes	(N=118)	(N=46)	(N=101)	(N=43)	(N=308)
PFOS					
Mean (SD)	185 (289)	139 (122)	376 (497)	297 (219)	254 (357)
Median [Min, Max]	97.7 [0, 2480]	101 [27.3, 634]	192 [0, 2260]	266 [0, 827]	125 [0, 2480]
Missing	5 (4.2%)	1 (2.2%)	10 (9.9%)	3 (7.0%)	19 (6.2%)
PFOA					
Mean (SD)	207 (178)	271 (194)	257 (125)	181 (86.5)	230 (158)
Median	148 [0, 1190]	183 [83.1, 965]	233 [58.9, 655]	165 [0, 417]	188 [0, 1190]
Missing	10 (8.5%)	2 (4.3%)	5 (5.0%)	5 (11.6%)	22 (7.1%)
PFHxS					
Mean (SD)	7.00 (12.8)	13.4 (20.7)	9.72 (18.6)	41.6 (48.5)	13.7 (26.4)
Median	0 [0, 67.1]	0 [0, 96.1]	0 [0, 101]	34.7 [0, 206]	0 [0, 206]
Missing	2 (1.7%)	2 (4.3%)	1 (1.0%)	0 (0%)	5 (1.6%)
FOSA					
Mean (SD)	16.8 (40.9)	24.6 (81.8)	138 (260)	68.5 (155)	64.7 (171)
Median	0 [0, 251]	0 [0, 327]	34.9 [0, 964]	0 [0, 669]	0 [0, 964]
Missing	61 (51.7%)	30 (65.2%)	56 (55.4%)	20 (46.5%)	167 (54.2%)



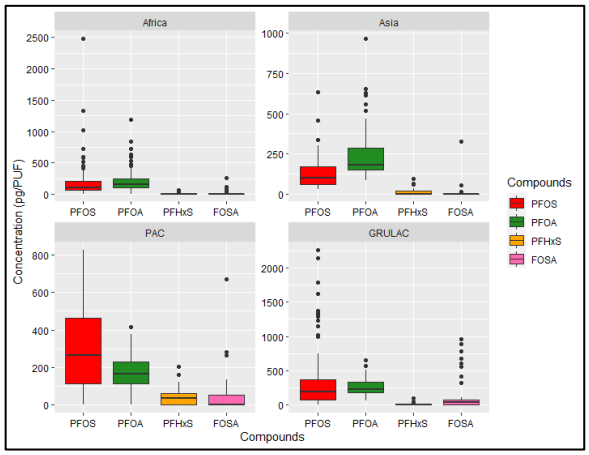
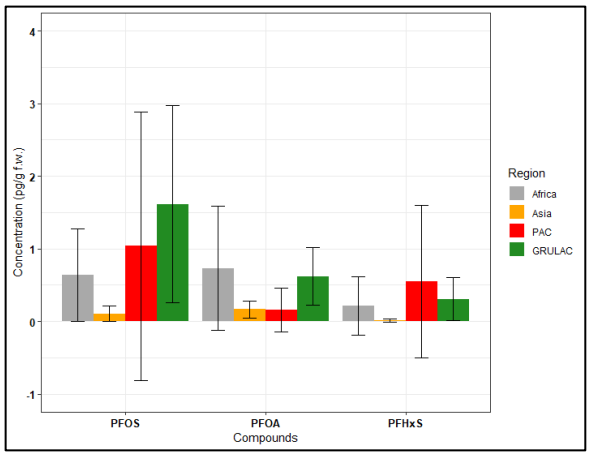


Figure 1. Bar plot (left) presenting mean values and error bars presenting the standard deviation (SD) and box plots (right) scaled for region in the air samples (n=308); all values refer to one PUF and 3 months exposure. The whiskers represent minimum and maximum concentrations without outliers. The lower border of the box represents the first quartile (25%), the line inside the box the median and the upper border is the third quartile (75%). The dots outside the whiskers are outliers, which were defined as all concentrations greater or smaller the interquartile range multiplied by 1.5

Water

A total of 144 water samples with 44 samples from Africa, 60 from PAC, and 40 from GRULAC. The values for (sum of L- and br- PFOS) ΣPFOS ranged 0.03 ng/L to 6.23 ng/L, for PFOA from 0.05 ng/L to 4.02 ng/L and from 0.03 ng/L to 3.51 ng/L for PFHxS. The results are visualized in Figure 2. Statistically significant differences between regions were found only for the PFOA concentrations in the Asia Pacific region (11 countries) in comparison to Africa (seven countries) and GRULAC (five countries).



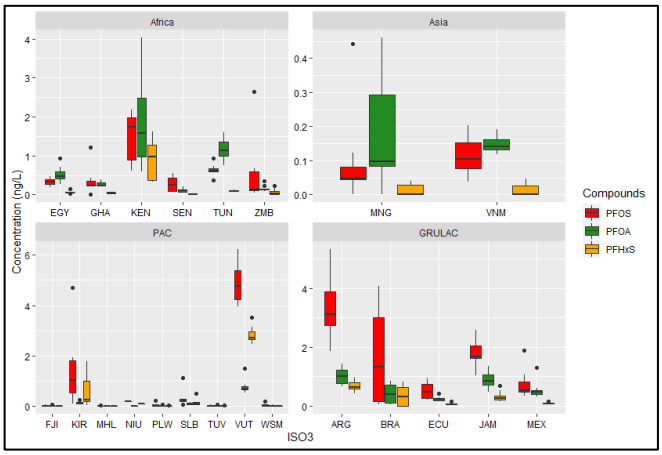
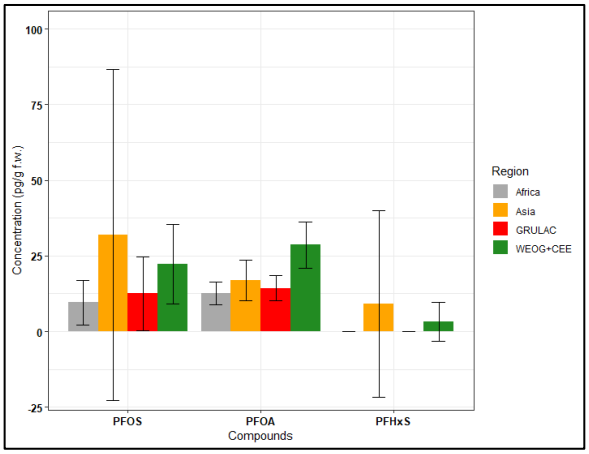


Figure 2. Bar plot (left) presenting mean values and error bars presenting the standard deviation (SD) and box plots (right) for each country scaled for region for the water samples (n=144)

Human milk

From 2016 to 2019, 44 human milk samples from primiparae were collected in 42 countries, pooled into one national sample and analyzed for PFOS, PFOA and PFHxS. PFOA was quantified in all samples between 6.20 pg/g f.w. and 37.4 pg/g f.w. PFOS was quantified in 36 samples but at a much wider range than PFOA (<6.2 pg/g f.w.-212 pg/g f.w.). PFHxS was quantifiable in only four samples with a maximum value of 111 pg/g f.w. (Figure 3). PFOS was highly correlated with PFHxS (Pearson correlation coefficient R=0.95) and weakly but still positively with PFOA (R=0.44). Statistical analysis (all on $p<0.05$) showed that PFOS and PFOA in European countries (WEOG+CEE) were significantly different from those in Africa and GRULAC.



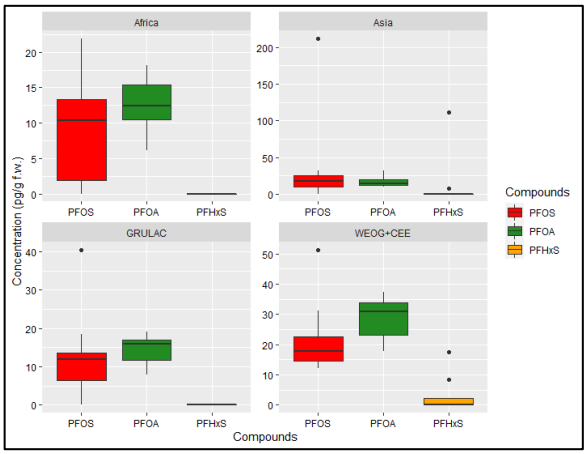


Figure 3. Bar plot (left) presenting mean values and error bars presenting the standard deviation (SD) and box plots (right) scaled for region for human milk national pools (n=44)

Pattern

Three very different core matrices as recommended by the Stockholm Convention have been analyzed for the two listed and one recommended perfluoroalkane substances. In order to assess differences on regional or matrix basis, the pattern of these three PFAS were subject to statistical and multivariate analysis. Due to the narrow time period, no temporal trends could be analysed. From the 496 samples analyzed, 435 had at least two PFAS quantified and were used for pattern analysis by using the percentage of each of the PFAS to the sum of the three PFAS. The box whisker plots in Figure 4, left, show a comprehensive picture of the pattern of the three matrices in each of the regions. It can be seen that for all sample types and in all regions the median values of the measurements were greater for PFOS than for PFOA; PFHxS did not play a role at all. The overall largest difference was for human milk (median PFOS = 73%, median PFOA= 23%), the smallest for air (PFOS=53%; PFOA=47%). There were some differences in the regions but Spearman correlation had very high coefficients>0.98; thus no significant differences could be determined. As expected, there is a significant negative correlation between PFOS and PFOA (r=-0.91; with very high significance $p=2.2 \cdot 10^{-16}$). Principal component analysis for the 435 samples shows an almost complete overlap of the three core matrices patterns along the new two main dimensions (PC1=64%, PC2=36%), which explain 100% of the variation (Figure 4, right)

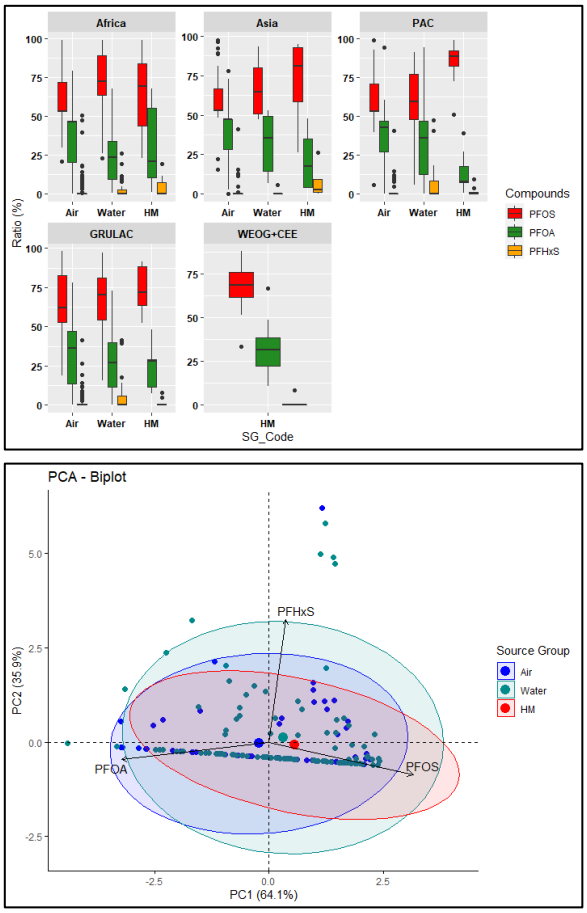


Figure 4. Box plots of PFAS measurements in air, water and human milk (HM) as ratio of PFOS, PFOA or PFHxS to the sum of these three PFAS (left). PCA with ellipses around the matrices (right)

To conclude:

- Air samples with PAS/PUFs: Low sorption capacity of PUFs hamper analysis and quantification of PFAS; where quantified, PFOS and PFOA dominated over PFHxS and PFOS precursors.
- Surface water: Using the standardized sampling protocol (12) and analyzing for three PFAS, these data may serve as a baseline for future monitoring activities and the starting point for trend assessment.
- Human milk: PFOA was found in al samples and in relatively low range; PFHxS was rarely detected.

Acknowledgements

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