First results of PFOS monitoring in surface waters of three continents

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Introduction

At the fourth meeting of the Conference of the Parties to the Stockholm Convention on Persistent Organic Pollutants (POPs) in 2009, by decision SC-4/17 perfluorooctane sulfonic acid (PFOS), its salts and perfluorooctane sulfonyl fluoride was listed in the annex B of the Convention [1,2]. Listing in annex B allows production for certain uses associated with acceptable purposes and specific exemptions in accordance with Part III of Annex B [1]. With the listing of new POPs, such as PFOS and its precursors, the need for updating the guidance document for the "Global Monitoring Plan of POPs" (GMP) became evident [3]. Since water is the main transport medium for PFOS in the environment, surface water was added as a core matrix in the guidance document for the GMP for PFOS (but not for the other 26 POPs listed until 2015). In order to incorporate PFOS and related compounds into the GMP, a specific guidance was developed to determine the criteria for future monitoring of PFOS [4] and a standard operational procedure document was prepared to assist in the sampling of water for the analysis of PFOS (or PFAS) [5]. Direct sampling of water (also called "active sampling") is the most commonly used approach for PFAS analysis in water and therefore, is recommended for use in the Global Monitoring Plan projects. Although advances have been made with using passive samplers for POPs including PFOS, passive samplers have the major disadvantage in the complexity to determine the kinetics of the passive sampler material and design [5]. Since 2017, the sampling of surface water is underway in 22 countries in the framework of four UNEP-coordinated regional projects to support the Global Monitoring Plan on POPs using the recommended direct sampling approach. Here, we report the first results from the 1st year sampling.

Materials and methods

Sampling locations: Surface water samples were collected from up to 22 countries in Africa, Asia, Pacific Islands and Latin America/Caribbean regions with one sampling location *per* country. According to the guidance document [4], the sampling should be undertaken in the mixing zone, preferentially close to the mouth of major rivers, or in estuaries.

Sampling frequency: Samples were collected 4-times *per* year at quarterly intervals starting on 31 March 2017. Samples are labelled indicating the country by its ISO-alpha3 code, the sampling year and the sampling quarter (2017-1 to 2017-4). For the sampling, all participating countries have been provided with 1 L HDPE bottles placed in plastic bag and in polystyrene box. Such procedure enabled the countries to return the filled bottles after sampling in a safe manner.

Sampling procedure: Briefly, water was collected using a metal bucket, dipped three times into the water body and each time emptied into a 1 L HDPE bottle. Three times the water from the HDPE bottle was discarded. A fourth filling of the HDPE bottle was kept as a sample. The bottle was firmly closed with the cap and labelled according to a pre-assigned code indicating the sampling location and period. A second 1 L sample was taken at the same time and kept as a back-up. After sampling, the bottles were transferred to a fridge and kept at 4 °C to 6 °C until shipment to the analytical laboratory at MTM Research Centre, Örebro University where the samples were stored in the fridge until analysis. A travel blank has been collected once a year using one of the back-up bottles.

Chemical analysis: Water samples were first ultrasonicated for 10 min and transferred to a beaker. Then, 4 mL of methanol (MeOH) was added to the original bottle to remove any PFOS that might have adsorbed onto the wall of the bottle; the 4 mL of MeOH was collected and split equally to a polypropylene beaker (PP) containing 500 mL of the water sample for extraction and the original bottle contained the remaining 500 mL of the water samples. Solid phase extraction (SPE) cartridge with a weak anion exchange capacity (Oasis WAX cartridge,

150 mg, 30 µm, Waters, MA, USA) was used for extracting PFOS in the water samples. The extraction procedure followed ISO method (ISO25101) [6]. Before extraction, 0.1 pg of mass-labelled internal standard was spiked into the sample; whereas 0.1 pg of mass-labelled recovery standard was spiked into the sample before instrumental analysis.

Instrumental analysis: Separation and quantification of PFOS was performed on liquid chromatograph coupled to a tandem mass spectrometer (Acquity Ultra Performance Liquid Chromatograph (UPLC) and a Xevo TQ S mass spectrometer, Waters, MA, USA) in negative ionization mode. A reversed phase column (Waters BEH column, 100 x 2.1, 1.7 µm) was used for chromatographic separation; the column temperature was kept at 50 °C. Mobile phases were A: 2 mM ammonium acetate (70/30: Water/MeOH) and B: 2 mM ammonium acetate in MeOH. Standards of PFOS containing both branched and linear isomers were used for quantification. Internal calibrating method using mass-labelled standard was used to quantify the amounts of PFOS in the sample. The branched isomers included 3-/4-/5- and 6-/2- PFOS (Figure 1); L-PFOS is the linear PFOS; whereas br-PFOS is the sum of 3-/4-/5- and 6-/2- PFOS. Two procedure blanks were conducted in each batch of extraction and recoveries of PFOS in the samples were 90%±20%.

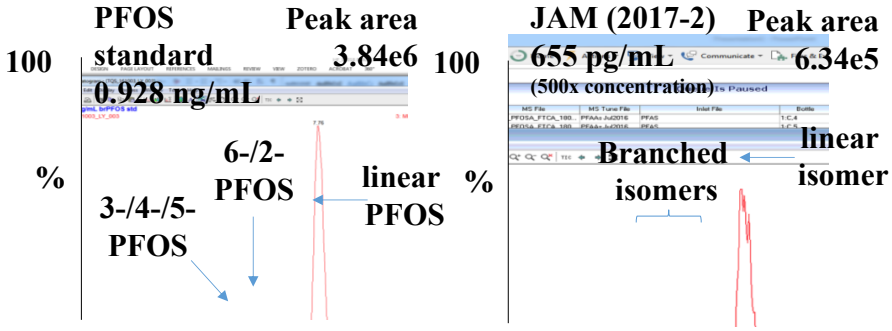

Figure 1: Chromatographic separation of PFOS isomers a) 0.928 ng/mL standard and b) water sample from Jamaica.

Results and discussion

The shipment of the filled water bottles has proven to be without problems during transportation or at customs. A summary of projected and actual number of samples received is shown in Table 1. 57 of 88 or 65% of all scheduled samples have been collected and arrived in the analytical laboratory. From GRULAC (Latin American and Caribbean region), all samples are available from the five GRULAC countries. From Africa, only one sample is missing. No samples have arrived from five of the nine Pacific Islands countries, namely Kiribati, Marshall Islands, Samoa, and Tuvalu.

Until present, 23 water samples from the three continents have been analyzed for linear and branched PFOS (L-PFOS, br-PFOS). In general, the concentrations were very low whereby the L-PFOS ranged from 0.036 ng/L to 2.46 ng/L and the br-PFOS from 0.008 ng/L to 0.77 ng/L. Table 2 shows for each region the number of results, the minimum, maximum and mean values for L-PFOS, br-PFOS and the sum PFOS. The highest mean value for the sum PFOS was found in the GRULAC region with 1.16 ng/L; in this region was also found the overall maximum so far (3.46 ng/L).

All samples had quantifiable concentrations of br-PFOS; L-PFOS was always dominating over br-PFOS, which ranged from 9% of the sum PFOS (sample from Palau in the Pacific Islands) to 41% (sample from Kenya in Africa) (Table 3). The majority of the samples had about 80% of L-PFOS and 20% of br-PFOS.

Table 1: Collection of water samples for PFOS analysis: planned vs. achieved

ISO_3	Campaign 1	Campaign 2	Campaign 3	Campaign 4	#Actual	#Target
Africa	**6**	**6**	**6**	**6**	**23**	**24**
EGY	EGY (2017-1)	EGY (2017-2)	EGY (2017-3)	EGY (2017-4)	4	4
GHA	GHA (2017-1)	GHA (2017-2)	GHA (2017-3)	GHA (2017-4)	4	4
KEN	KEN (2017-1)	KEN (2017-2)	KEN (2017-3)		3	4
SEN	SEN (2017-1)	SEN (2017-2)	SEN (2017-3)	SEN (2017-4)	4	4
TUN	TUN (2017-1)	TUN (2017-2)	TUN (2017-3)	TUN (2017-4)	4	4
ZMB	ZMB (2017-1)	ZMB (2017-2)	ZMB (2017-3)	ZMB (2017-4)	4	4
Asia	**2**	**2**	**2**	**2**	**5**	**8**
MNG	MNG (2017-1)	MNG (2017-2)	MNG (2017-3)		3	4
VNM			VNM (2017-3)	VNM (2017-4)	2	4
Pacific Isl	**9**	**9**	**9**	**9**	**9**	**36**
FJI				FJI (2017-4)	1	4
NIU			NIU (2017-3)		1	4
PLW	PLW (2017-1)	PLW (2017-2)	PLW (2017-3)	PLW (2017-4)	3	4
SLB			SLB (2017-3)	SLB (2017-4)	2	4
VUT			VUT (2017-3)		1	4
GRULAC	**5**	**5**	**5**	**5**	**20**	**20**
ARG	ARG (2017-1)	ARG (2017-2)	ARG (2017-3)	ARG (2017-4)	4	4
BRA	BRA (2017-1)	BRA (2017-2)	BRA (2017-3)	BRA (2017-4)	4	4
ECU	ECU (2017-1)	ECU (2017-2)	ECU (2017-3)	ECU (2017-4)	4	4
JAM	JAM (2017-1)	JAM (2017-2)	JAM (2017-3)	JAM (2017-4)	4	4
MEX	MEX (2017-1)	MEX (2017-2)	MEX (2017-3)	MEX (2017-4)	4	4

Table 2: Results of PFOS in surface water from the first year of the GMP2 project (sampling in 2017)

Region	Africa				Asia			
Unit		ng L^{-1}				ng L^{-1}		
PFAS	#	Min	Max	Mean	#	Min	Max	Mean
L-PFOS	9	0.07	1.70	0.57	2	0.04	0.30	0.17
br-PFOS	9	0.01	0.71	0.19	2	0.01	0.05	0.03
Sum PFOS	9	0.01	1.70	0.38	2	0.04	0.36	0.20

Region	Pacific Islands				GRULAC			
Unit		ng L^{-1}				ng L^{-1}		
PFAS	#	Min	Max	Mean	#	Min	Max	Mean
L-PFOS	2	0.06	0.19	0.12	14	0.12	2.46	0.93
br-PFOS	2	0.008	0.016	0.012	14	0.020	0.77	0.23
Sum PFOS	2	0.07	0.20	0.13	14	0.14	3.24	1.16

Table 3: Distribution between L-PFOS and br-PFOS in water samples according to UN region (%)

	L-PFOS			br-PFOS		
	Average	Min	Max	Average	Min	Max
Africa	79%	59%	90%	21%	10%	41%
Asia	84%	82%	86%	16%	15%	18%
Pacific Islands	91%	89%	92%	9%	8%	11%
GRULAC	81%	72%	93%	19%	7%	28%

Data for comparison are scarce since most environmental programmes do not differentiate between L- and br-PFOS. In an initial survey when testing the methodology in 2012, we analyzed for L-PFOS only and collected samples in four developing countries and in the Netherlands (Table 4). The concentrations are within one order of magnitude and the higher concentrations were found in the developed, industrialized country.

Table 4: Concentrations of L-PFOS in surface waters (2012 sampling)

Country	Fiji	Kenya	Mali	Uruguay	The Netherlands	
Site name	Waimanu River	Sabaki River Mouth	Sotuba River	Río de la Plata	Kampen, IJssel	Rotterdam, Nieuwe Maas
Unit	ng L^{-1}	ng L^{-1}	ng L^{-1}	ng L^{-1}	ng L^{-1}	ng L^{-1}
L-PFOS anion	1.1	4.6	5.7	<1.0	9.9	11

The project will continue with sampling in the 22 countries through 2018. Adding these samples and with informatoin over two years, it is envisaged to draw some conclusions as to the presence of PFOS in surface waters but also as to the seasonal variation over two year; although not at all sampling points. It is also envisaged to analyze for a wider spectrum of perfluorinated compounds.

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References
1. UNEP, Decision SC-4/17: Listing of perfluorooctane sulfonic acid (PFOS), its salts and perfluorooctane sulfonyl fluoride in annex B. 2009, United Nations Environment Programme: New York, NY, USA.
2. UNEP, Stockholm Convention on persistent organic pollutants (POPs), as amended in 2009. Text and annexes. 2010, United Nations Environment Programme.
3. UNEP, Guidance on the Global Monitoring Plan for Persistent Organic Pollutants, UNEP, 2015. p. 168.
4. Weiss, J., et al., PFAS analysis in water for the Global Monitoring Plan of the Stockholm Convention Set-up and guidelines for monitoring, in United Nations Environment Programme (UNEP) Division of Technology, Industry and Economics, Geneva. 2015.
5. UN Environment, Global Monitoring Plan on Persistent Organic Pollutants: Standard Operational Procedure for the Sampling of Water as a Core Matrix in the UNEP/GEF GMP2 Projects for the Analysis of PFOS, Heidelore Fiedler and Leo Yeung, Örebro University, Editor. 2017, UN Environment, Environment and Health Branch: Geneva, Switzerland. p. 11.
6. ISO. ISO25101. Water quality — Determination of perfluorooctanesulfonate (PFOS) and perfluorooctanoate (PFOA) — Method for unfiltered samples using solid phase extraction and liquid chromatography/mass spectrometry; 2009.