Monitoring of PFOS in water – Africa region

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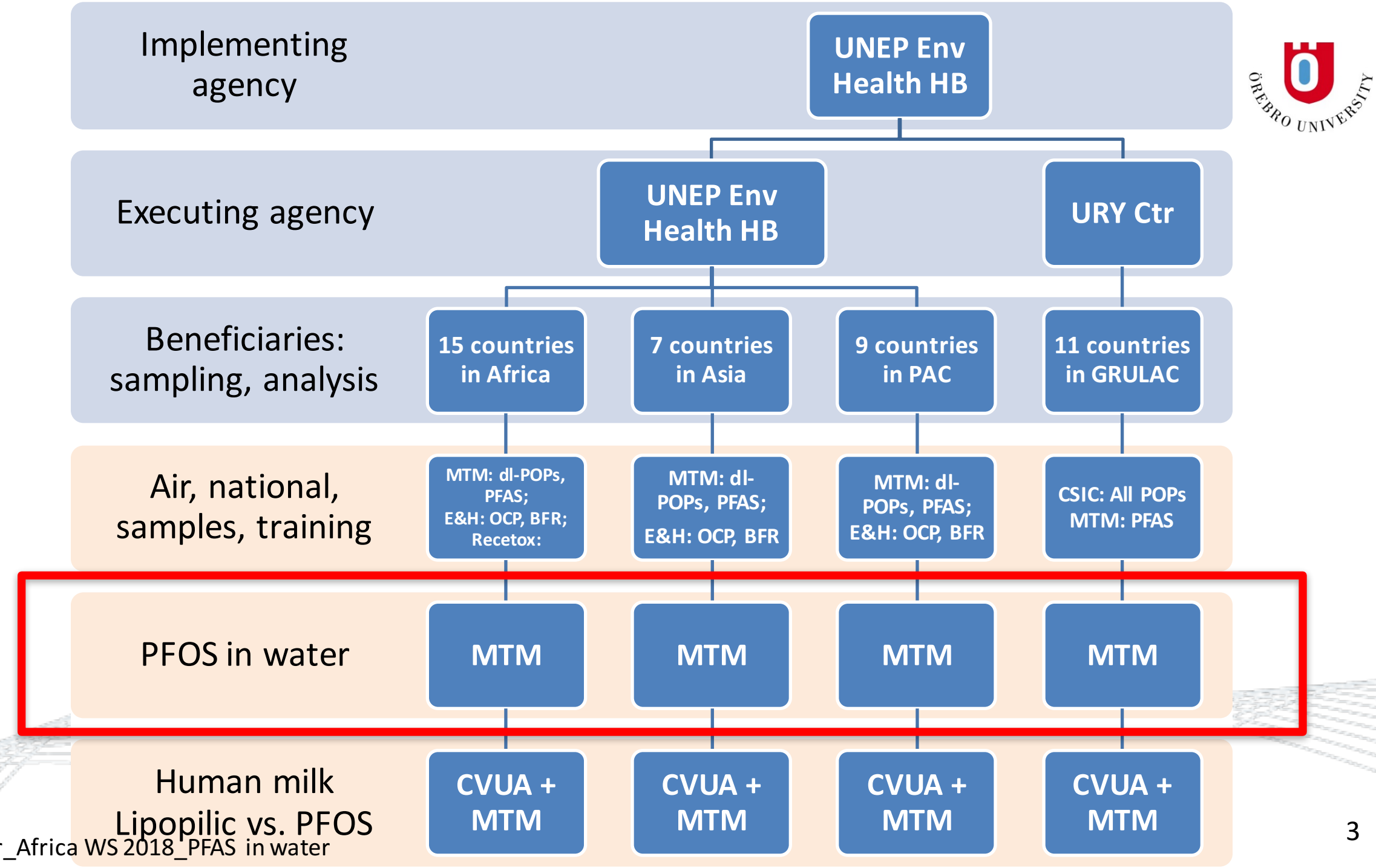
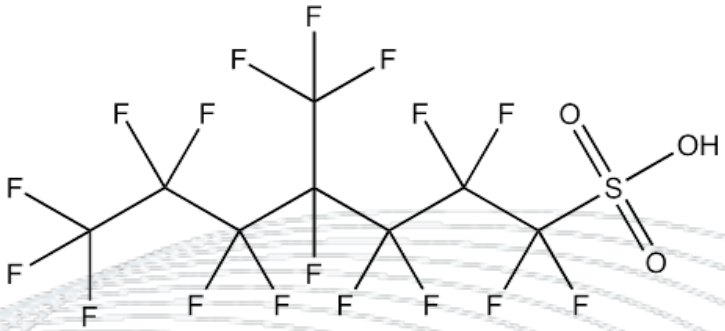
Content

- Context
- Sampling
  - Procedures and status of samples received
- Analysis
  - Sample preparation and instrumental analysis
- Results
- Proposal
- Conclusions

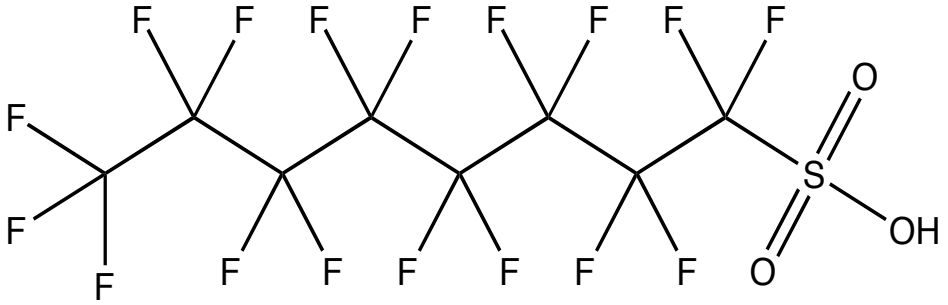

Implementing agency
UNEP Env Health HB
Executing agency
UNEP Env Health HB
URY Ctr
Beneficiaries: sampling, analysis
15 countries in Africa
7 countries in Asia
9 countries in PAC
11 countries in GRULAC
Air, national, samples, training
MTM: dl-POPs, PFAS; E&H: OCP, BFR; Recetox:
MTM: dl-POPs, PFAS; E&H: OCP, BFR
MTM: dl-POPs, PFAS; E&H: OCP, BFR
CSIC: All POPs MTM: PFAS
PFOS in water
MTM
MTM
MTM
MTM
Human milk Lipopilic vs. PFOS
CVUA + MTM
CVUA + MTM
CVUA + MTM
CVUA + MTM

PFOS was listed in annex B in 2009

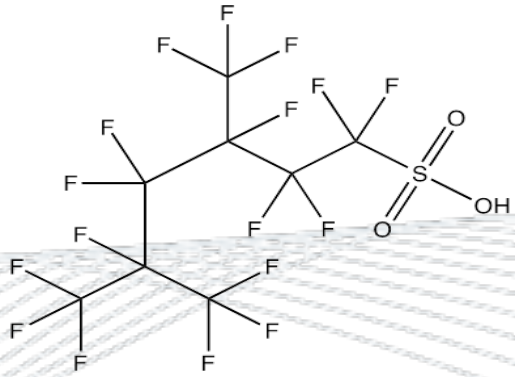
POP	Identity
Perfluorooctane sulfonic acid (PFOS)	• Single anionic compound with one linear (L-PFOS) and 89 branched isomers (theoretically; 11 found in the environment – status 2009) • Manufacture of PFOS via electrochemical fluorination generates mostly linear isomeric configuration, 21%-35% of the PFOS are branched isomers.



4-PFOS



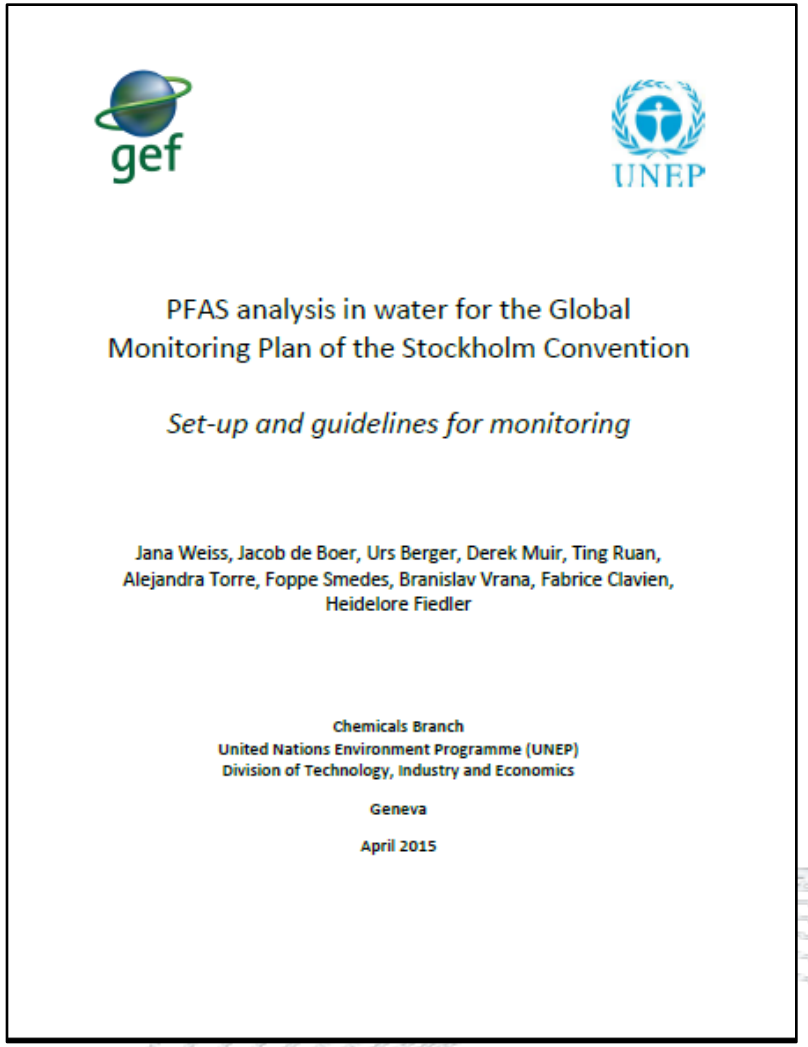
L-PFOS



3,5-PFOS

SOP for water sampling and PFAS analysis

- UNEP/GEF project 'Establishing the Tools and Methods to Include the Nine New POPs into the Global Monitoring Plan', GEF 4B97
- Laid down the frame:
  - Large rivers, estuaries
  - Dipping into water (no passive samplers)
  - 4-times per year
  - L- and br-PFOS for analysis



gef

UNEP

PFAS analysis in water for the Global Monitoring Plan of the Stockholm Convention

Set-up and guidelines for monitoring

Jana Weiss, Jacob de Boer, Urs Berger, Derek Muir, Ting Ruan, Alejandra Torre, Foppe Smedes, Branislav Vrana, Fabrice Clavien, Heidelore Fiedler

Chemicals Branch
United Nations Environment Programme (UNEP)
Division of Technology, Industry and Economics

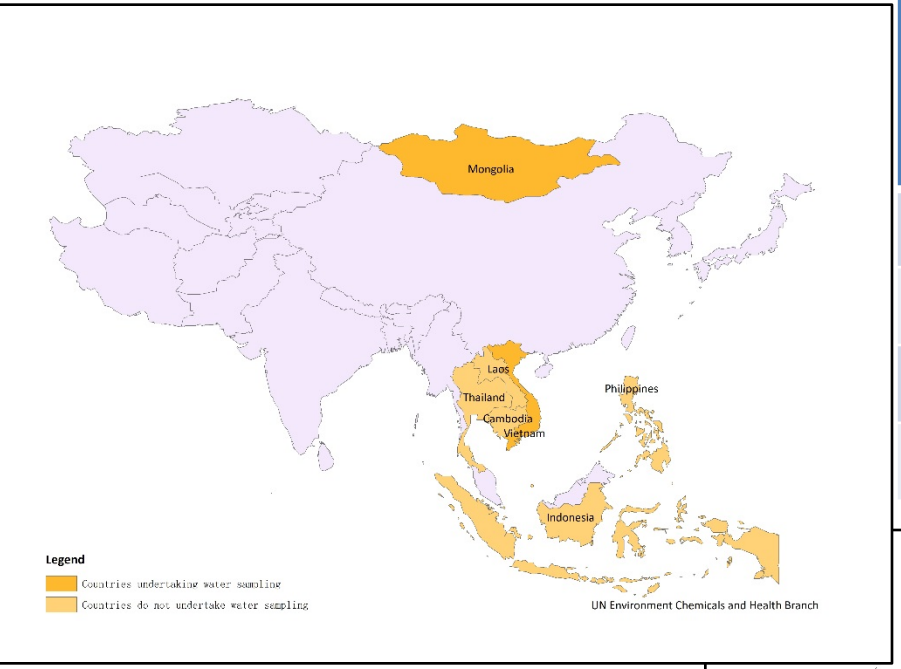
Geneva

April 2015

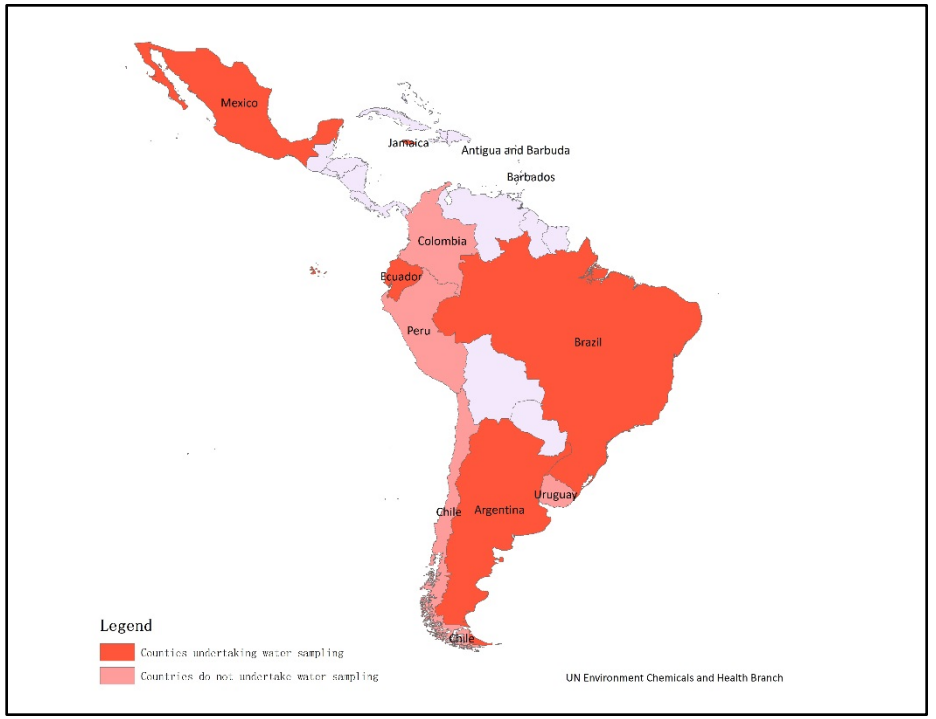
Surface water monitoring steps

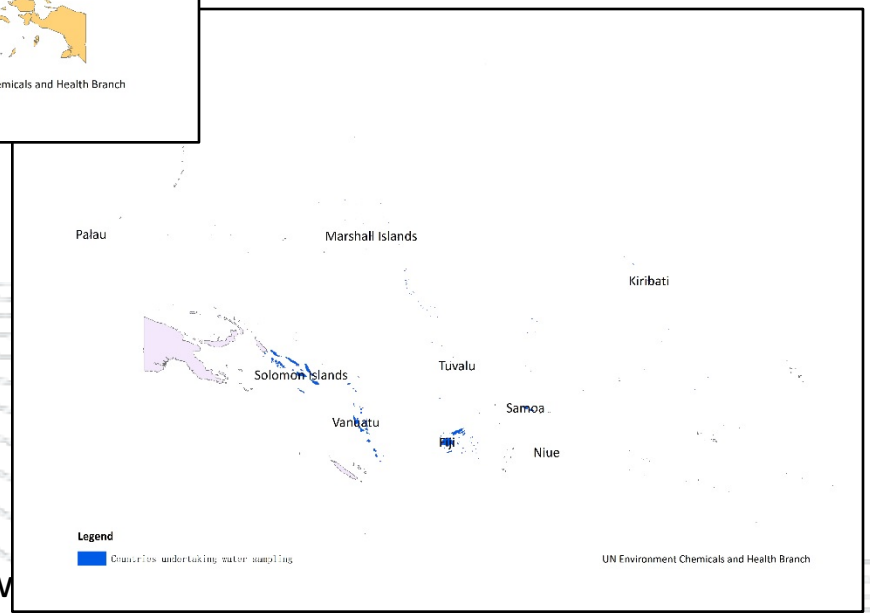
- SOP for water sampling prepared
- Highlight details in the script, and
- Verify presence of HDPE bottles in each country
  - Shipment of bottles by MTM
  - Storage of the bottles (kept in PS box and plastic bag)
  - Bucket, rope
  - Sampling on-site
  - Storage in fridge (not freezer)
  - Shipment of HDPE bottles

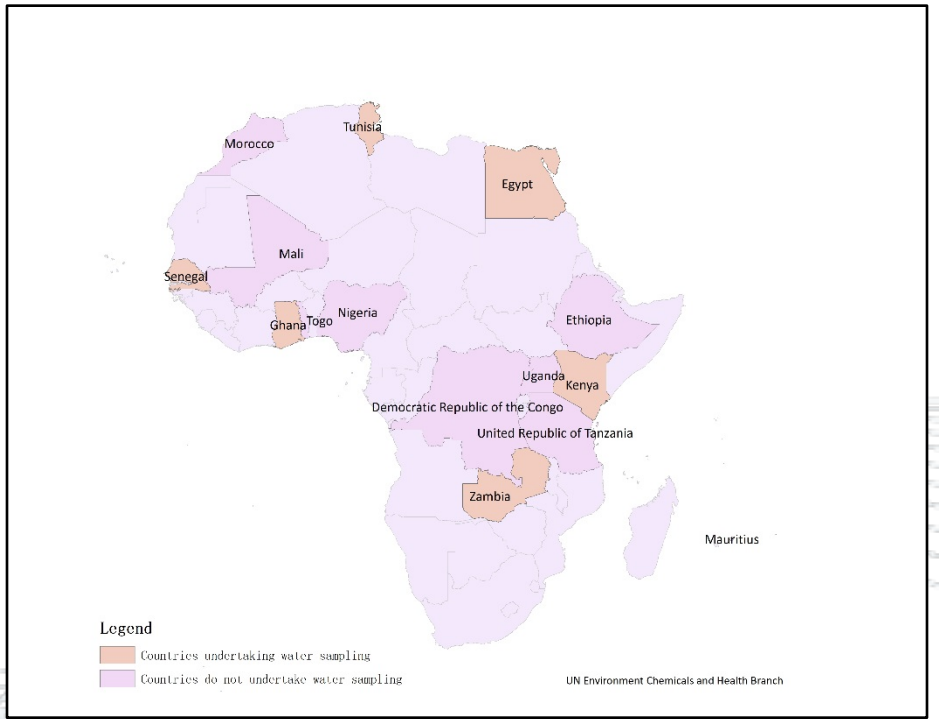
Water sampling in UNEP/GEF GMP2 projects



Project	# water sampling countries	# countries in project
Africa	6	15
Asia	2	7
Pacific Isl.	9	9
GRULAC	5	11







Sampling arrangements in 2017 (n=22) and 2018

Assignment of sampling bottles for each country			No. analyses per year
Bottle A:	Samples 1-8	For PFOS in expert back-up laboratory PFOS (L and br)	4
Bottle B	Samples 1-8	For PFOS in expert back-up laboratory PFOS (L and br)	4
bottle a:	Samples 1-8	For PFOS in national laboratory PFOS (L and br)	4
bottle b	Samples 1-8	For PFOS in national laboratory PFOS (L and br)	4
Codes:			
Green		Analysis in expert back-up laboratory	
No Fill		Analysis in national laboratory	
Yellow		Groups of chemicals recommended for analysis	
Bottle A/bottle a		For analysis in expert back-up/national laboratory	
Bottle B/bottle b		Retained sample to be kept in the national laboratory	

Arrangements in 2018:

- no Bottles B
- no bottles b
- 1 field blank

Africa: National analysis for PFOS anticipated in Egypt and Tunisia

- PFOS analysis training to be held in 2nd part of 2018

Water sampling procedures

- All water samples will be analysed by MTM Research Centre, Örebro University, Sweden;
- MTM Centre will:
  - Provide containers for sampling of surface water (1000 mL) and instructions
  - Clean the bucket by filling and emptying several times
  - Rinse the HDPE bottle two times with river/sea water
  - Fill one bottle (Bottle A) with water from the bucket
  - [Prepare one retained sample in Bottle B in the same way]
  - Analyse the water samples for L-PFOS, br-PFOS to report total PFOS

Example of HDPE bottles for water sampling

Custom's letter

Shipment was successful: All boxes/bottles received

Note

1 March 2017

To: Whom it may concern for customs clearance

From: Dr. Heidelore Fiedler, School of Science and Technology; Örebro University
Coordinator of UNEP/GMP2 project for water sampling

Re: Materials for UN capacity building project
Recipient: Ministry of National Resources and Environment - Samoa

Örebro University, MTM Research Centre is implementing a capacity building project for the United Nations Environment Programme (UNEP) and is shipping empty plastic bottles to the above-mentioned partner institution. The plastic bottles will be used for water sampling according to a UNEP-approved protocol.

Technical description of the materials:

- 2 sterile bottle made of high density polyethylene (HDPE) (1 L)

The content of this shipment does not pose any threat to human health. The total commercial value of the content is **EUR 5 maximum** (EUR 2.50 for each HDPE bottle).

To avoid further delays, my contact information is listed below.

Sincerely,

H. Fiedler

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E-mail: Heidelore.fiedler@oru.se

Sampling procedure

- Upon arrival at the sampling location, remove the aluminium foil from the bucket. Rinse the bucket at least three times with sea/lake/river water from the sampling site;
- Fill-up the first two bottles (labelled as Bottle 'A' and Bottle 'B') with water from the bucket and discard the water from the bottles;
- Repeat once more;
- Take a fresh new water sample with the bucket and this time fill the two plastic bottles (labelled as Bottle 'A' and Bottle 'B') until the neck of the bottle; keep these fillings as the sample, and seal the bottles carefully with the cap; put it bag in the PE plastic bag;
- Store the bottles in the plastic container and place the ice packs. Close the container until arrival at the laboratory;
- Repeat the above steps if samples are needed for the national laboratory (labelled as bottle 'a' and bottle 'b').
- After sampling, store the bucket in the PE bag it came in;
- Please record additional parameters such as in relation to location, sampling personnel, *etc*.

Sampling materials

Sampling equipment:

Metal bucket (20 L/10 L)
Clean plastic bottles, HDPE (1 L)
Plastic bag for sampling bottle
Plastic container for transport of bottles
PE plastic bag for transport of bucket
Ice (packs)
Rope/pole

Personnel / auxiliary materials:

Gloves
Log book
Water-proof pen

Preparation of bucket (by national laboratory in the laboratory)

10 L/20 L metal bucket (clean)

Wrap the mouth of the bucket with aluminium foil (see photo) and place the clean bucket into a PE plastic bag until use

Repeat this procedure before each sampling event

The label is a unique identifier for the following:

Country = Egypt

Sample to be analysed in the international expert laboratory (MTM) since all letters related to the country are capitalized and bottle is ‘A‘ (= for shipment and analysis)

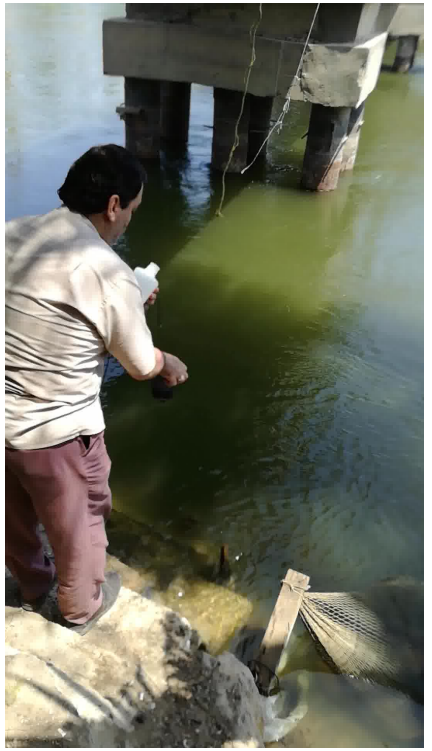
Sampling date = end of season 1 in the year 2017
= 31 March 2017

Practical issues - sampling

Jamaica

Tunisia

Egypt



- Water monitoring progresses well and smoothly;
- New HPDE sampling bottles were sent by MTM in April for 2018 campaign;
- No obstacles at customs;
- ”Issue”: requirement of ”open” water could not be maintained in Mongolia.

National information, e.*g*., Tunisia and Zambia

Sampling code	Site/Location	GPS coordinates of site (latitude/longitude)	Bottle	Weather observation	Water temperature (°C)	Name of persons who undertook sampling		Sampling date	Time - from:	Time - to:	Place where sample stored until analysis	Storage conditions	Shipment date to laboratory
ZMB-A (2017-1)	Kafue/Zambezi Confluence	15° 56' 60.2 S	A	Clear sky with few clouds, no rain	26.3	CHRISPIN SIMWANZA	CHRISTOPHER KANEMA	2-Apr-2017	14:30	15:00	ZAMBIA ENVIRONMENTAL MANAGEMENT	Fridge	5-Apr-2017
ZMB-B (2017-1)		28° 54' 85.6 E	B										
ZMB-A (2017-2)	Kafue/Zambezi Confluence		A					30-Jun-2017					
ZMB-B (2017-2)			B										

Nom de site	Type	Type d'échantillonnage	Longitude	Latitude	Altitude
Oued Madjerda Sur le pont de Kalaat Andalous	Eau de surface	Instantané	010° 08 ' 24.2 " E	37° 01' 16.6" N	± 4 m

Present status of water samples (2017)

Africa: All samples received

Country name	ISO_3	Campaign 1		Campaign 2		Campaign 3		Campaign 4		Blank	Subtotal	
		Sample ID	Date arrived	Sample ID	Date arrived	Sample ID	Date arrived	Sample ID	Date arrived	Date arrived	#	target
Africa		6	6	6	6	6	6	6	6	3	24	24
Egypt	EGY	EGY-A (2017-1)	2017-12-20	EGY-A (2017-2)	2017-12-20	EGY-A (2017-3)	2017-12-20	EGY-A (2017-4)	2018-01-05	2018-01-05	4	4
Ghana	GHA	GHA-A (2017-1)	2017-05-03	GHA-A (2017-2)	2017-07-12	GHA-A (2017-3)	2017-10-09	GHA-A (2017-4)	2018-01-15	2018-01-15	4	4
Kenya	KEN	KEN-A (2017-1)	2017-10-25	KEN-A (2017-2)	2017-10-25	KEN-A (2017-3)	2017-10-25	KEN-A (2017-4)	2018-06-14		4	4
Senegal	SEN	SEN-A (2017-1)	2017-06-31	SEN-A (2017-2)	2017-06-31	SEN-A (2017-3)	2017-12-28	SEN-A (2017-4)	2017-12-28		4	4
Tunisia	TUN	TUN-A (2017-1)	2018-01-11	TUN-A (2017-2)	2018-01-11	TUN-A (2017-3)	2018-01-11	TUN-A (2017-4)	2018-01-11	2018-01-11	4	4
Zambia	ZMB	ZMB-A (2017-1)	2017-04-10	ZMB-A (2017-2)	2017-07-12	ZMB-A (2017-3)	2017-10-13	ZMB-A (2017-4)	2018-01-08		4	4
Asia		2	1	2	1	2	2	2	2	1	6	8
Mongolia	MNG	MNG-A (2017-1)	2017-07-24	MNG-A (2017-2)	2017-07-24	MNG-A (2017-3)	2017-10-24	MNG-A (2017-4)	2018-05-16		4	4
Vietnam	VNM	VNM-A (2017-1)	Void	VNM-A (2017-2)	Void	VNM-A (2017-3)	2017-10-23	VNM-A (2017-4)	2018-01-15	2018-01-15	2	4
Pacific Islands		9	2	9	1	9	5	9	4	2	12	36
Fiji	FJI	FJI-A (2017-1)	Void	FJI-A (2017-2)	Void	FJI-A (2017-3)	Void	FJI-A (2017-4)	2018-01-24		1	4
Kiribati	KIR	KIR-A (2017-1)	2018-07-05	KIR-A (2017-2)	Void	KIR-A (2017-3)	2018-07-05	KIR-A (2017-4)	2018-07-05		3	4
Marshall Islands	MHL	MHL-A (2017-1)	Void	MHL-A (2017-2)	Void	MHL-A (2017-3)	Void	MHL-A (2017-4)			0	4
Niue	NIU	NIU-A (2017-1)	Void	NIU-A (2017-2)	Void	NIU-A (2017-3)	2017-12-08	NIU-A (2017-4)			1	4
Palau	PLW	PLW-A (2017-1)	2017-04-10	PLW-A (2017-2)	2017-07-24	PLW-A (2017-3)	2017-10-05	PLW-A (2017-4)			3	4
Samoa	WSM	WSM-A (2017-1)	Void	WSM-A (2017-2)	Void	WSM-A (2017-3)	Void	WSM-A (2017-4)			0	4
Solomon Islands	SLB	SLB-A (2017-1)	Void	SLB-A (2017-2)	Void	SLB-A (2017-3)	2018-05-11	SLB-A (2017-4)	2018-05-11	2018-05-11	2	4
Tuvalu	TUV	TUV-A (2017-1)	Void	TUV-A (2017-2)	Void	TUV-A (2017-3)	Void	TUV-A (2017-4)	2018-02-13	2018-02-13	1	4
Vanuatu	VUT	VUT-A (2017-1)	Void	VUT-A (2017-2)	Void	VUT-A (2017-3)	2017-11-15	VUT-A (2017-4)			1	4
GRULAC		5	5	5	5	5	5	5	5	1	20	20
Argentina	ARG	ARG-A (2017-1)	2017-04-03	ARG-A (2017-2)	2017-07-11	ARG-A (2017-3)	2017-10-24	ARG-A (2017-4)	2018-03-14		4	4
Brazil	BRA	BRA-A (2017-1)	2017-04-24	BRA-A (2017-2)	2017-07-18	BRA-A (2017-3)	2017-10-13	BRA-A (2017-4)	2018-01-26		4	4
Ecuador	ECU	ECU-A (2017-1)	2017-06-08	ECU-A (2017-2)	2017-09-04	ECU-A (2017-3)	2017-10-26	ECU-A (2017-4)	2018-02-06		4	4
Jamaica	JAM	JAM-A (2017-1)	2017-04-10	JAM-A (2017-2)	2017-07-11	JAM-A (2017-3)	2017-10-05	JAM-A (2017-4)	2018-01-10	2018-01-10	4	4
Mexico	MEX	MEX-A (2017-1)	2017-04-10	MEX-A (2017-2)	2017-07-11	MEX-A (2017-3)	2017-10-09	MEX-A (2017-4)	2018-01-08		4	4
		22	14	22	13	22	18	22	17	7	62	88
		Target	actual	Target	actual	Target	actual	Target	actual		70%	

Present status of water samples (2018)

TUN and ZMB already sent 2 samples

Country name	ISO_3	Campaign 1		Campaign 2		Campaign 3		Campaign 4		Blank	Subtotal	
		Sample ID	Date arrived	Sample ID	Date arrived	Sample ID	Date arrived	Sample ID	Date arrived	Date arrived	#	target
Africa		6	4	6	2	6	0	6	0	1	6	24
Egypt	EGY	EGY-A (2018-1)		EGY-A (2018-2)		EGY-A (2018-3)		EGY-A (2018-4)			0	4
Ghana	GHA	GHA-A (2018-1)	2018-04-09	GHA-A (2018-2)		GHA-A (2018-3)		GHA-A (2018-4)			1	4
Kenya	KEN	KEN-A (2018-1)	2018-06-14	KEN-A (2018-2)		KEN-A (2018-3)		KEN-A (2018-4)			1	4
Senegal	SEN	SEN-A (2018-1)		SEN-A (2018-2)		SEN-A (2018-3)		SEN-A (2018-4)			0	4
Tunisia	TUN	TUN-A (2018-1)	2018-05-09	TUN-A (2018-2)	2018-07-19	TUN-A (2018-3)		TUN-A (2018-4)		2018-07-19	2	4
Zambia	ZMB	ZMB-A (2018-1)	2018-04-09	ZMB-A (2018-2)	2018-07-10	ZMB-A (2018-3)		ZMB-A (2018-4)			2	4
Asia		2	2	2	0	2	0	2	0	0	2	8
Mongolia	MNG	MNG-A (2018-1)	2018-05-16	MNG-A (2018-2)		MNG-A (2018-3)		MNG-A (2018-4)			1	4
Vietnam	VNM	VNM-A (2018-1)	2018-04-26	VNM-A (2018-2)		VNM-A (2018-3)		VNM-A (2018-4)			1	4
Pacific Islands		9	3	9	2	9	0	9	0	1	5	36
Fiji	FJI	FJI-A (2018-1)		FJI-A (2018-2)		FJI-A (2018-3)		FJI-A (2018-4)			0	4
Kiribati	KIR	KIR-A (2018-1)		KIR-A (2018-2)		KIR-A (2018-3)		KIR-A (2018-4)			0	4
Marshall Islands	MHL	MHL-A (2018-1)		MHL-A (2018-2)		MHL-A (2018-3)		MHL-A (2018-4)			0	4
Niue	NIU	NIU-A (2018-1)		NIU-A (2018-2)		NIU-A (2018-3)		NIU-A (2018-4)			0	4
Palau	PLW	PLW-A (2018-1)		PLW-A (2018-2)		PLW-A (2018-3)		PLW-A (2018-4)			0	4
Samoa	WSM	WSM-A (2018-1)		WSM-A (2018-2)		WSM-A (2018-3)		WSM-A (2018-4)			0	4
Solomon Islands	SLB	SLB-A (2018-1)	2018-05-11	SLB-A (2018-2)		SLB-A (2018-3)		SLB-A (2018-4)			1	4
Tuvalu	TUV	TUV-A (2018-1)	2018-05-02	TUV-A (2018-2)	2018-07-10	TUV-A (2018-3)		TUV-A (2018-4)		2018-07-10	2	4
Vanuatu	VUT	VUT-A (2018-1)	2018-05-16	VUT-A (2018-2)	2018-07-18	VUT-A (2018-3)		VUT-A (2018-4)			2	4
GRULAC		5	5	5	3	5	0	5	0	0	8	20
Argentina	ARG	ARG-A (2018-1)	2018-04-23	ARG-A (2018-2)	2018-07-10	ARG-A (2018-3)		ARG-A (2018-4)			2	4
Brazil	BRA	BRA-A (2018-1)	2018-04-13	BRA-A (2018-2)		BRA-A (2018-3)		BRA-A (2018-4)			1	4
Ecuador	ECU	ECU-A (2018-1)	2018-07-05	ECU-A (2018-2)	2018-07-18	ECU-A (2018-3)		ECU-A (2018-4)			2	4
Jamaica	JAM	JAM-A (2018-1)	2018-04-13	JAM-A (2018-2)	2018-07-10	JAM-A (2018-3)		JAM-A (2018-4)			2	4
Mexico	MEX	MEX-A (2018-1)	2018-05-02	MEX-A (2018-2)		MEX-A (2018-3)		MEX-A (2018-4)			1	4
		22	14	22	7	22	0	22	0	2	21	88
		Target	actual	Target	actual	Target	actual	Target	actual		**24%**	

Chemical analysis

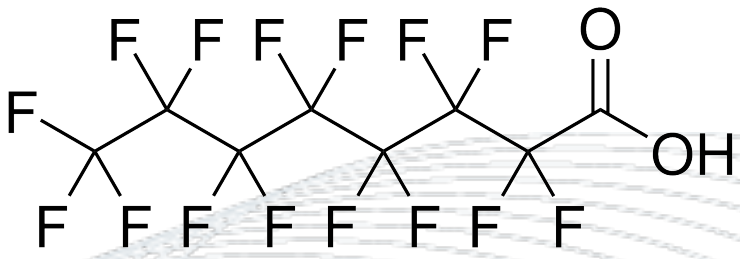
- Water samples were first ultrasonicated for 10 min and transferred to a beaker;
- 4 mL of methanol (MeOH) added to the original bottle to remove any PFOS that might have adsorbed onto the wall of the bottle;
- 4 mL of MeOH was collected and split equally to a polypropylene beaker (PP) containing 500 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 weak anion exchange capacity (Oasis WAX cartridge, 150 mg, 30 µm, Waters, MA, USA) was used for extracting PFOS in the water samples;
- Extraction procedure followed ISO method (ISO25101)
  - 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

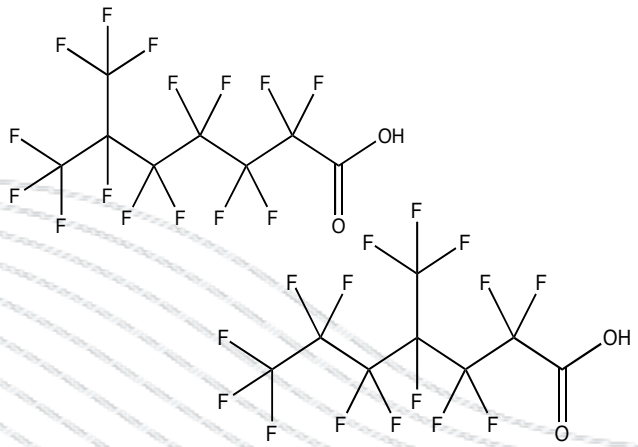
- Separation and quantification of PFOS was performed on liquid chromatograph coupled to a tandem mass spectrometer (Acquity Ultra Performance Liquid Chromatograph (UPLC) and a Xevo TQ S mass spectrometer, Waters, MA, USA) in negative ionization mode;
- Reversed phase column (Waters BEH column, 100 x 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 L- and br-PFOS (3,4,5-, 6,2 PFOS) used for quantification;
- Two procedure blanks were conducted in each batch of extraction and recoveries of PFOS in the samples were 90%±20%.

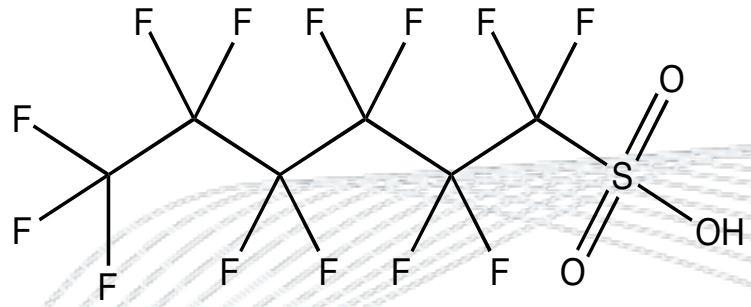
Next POPs? Analytes and matrices

	Air	Human Milk	Human Blood	Water
Perfluorooctanesulfonic acid (PFOS)	PFOS (linear and branched PFOS)			
POPs under review for listing				
Perfluorooctanoic acid (PFOA)	PFOA	PFOA	PFOA	PFOA
Perfluorohexanesulfonic acid (PFHxS)	PFHxS	PFHxS	PFHxS	PFHxS



Perfluorooctanoic acid





Perfluorohexane sulfonic acid

PFAS considered for listing in Stockholm Convention

- PFOA and PFHxS under review by the POPRC
- Listing into annexes A/B possible:
  - PFOA at COP-9 in 2019
  - PFHxS at COP-10 in 2021
- Proposal:
  - MTM Research Centre to expand the present analytes (L- and br-PFOS) by PFOA and PFHxS to have early information as to (possible) new POPs
  - Have input into the GMP guidance documents as to the congeners and isomers to be analyzed
  - To be included into future interlab assessments
  - Countries to make an informed decision at COPs.

Analytical standards

Native compounds

Solution A		Conc. g/mL	
Human milk *Water* *(others)*	BrPFOSK (L-PFOS)	1	For training and priority analysis, Stockholm Convention
	L-PFOSA	1	Extra package for human milk/biota and water
	L-PFOA	1	
	L-PFBS	1	
	L-PFHxS	1	
	L-PFDS	1	
	PFBA	1	
	PFPeA	1	
	PFHxA	1	
	PFHpA	1	
	PFNA	1	
	PFDA	1	
	PFUdA	1	
	PFDoA	1	
	PFTrDA	1	
	PFTDA	1	
	6:2 FTS	1	
Product Code:	UNEP-PFAS-SOLN. A		

Solution B		Conc. g/mL	
Air	N-MeFOSA	2	For training and analysis of air samples
	N-EtFOSA	2	
	N-MeFOSE	2	
	N-EtFOSE	2	
Product Code:	UNEP-PFAS-SOLN. B		

Labelled compounds

Extraction Mix A		Conc. g/mL
	M8PFOS	1
	M8FOSA-I	1
	M8PFOA	1
	M3PFBS	1
	M3PFHxS	1
	MPFBA	1
	M5PFPeA	1
	M5PFHxA	1
	M4PFHpA	1
	M9PFNA	1
	M6PFDA	1
	M7PFUdA	1
	MPFDoA	1
	M2PFTeDA	1
	M2-6:2 FTS	1
Product Code:	UNEP-PFAS-EXT. A	

Extraction mix B		Conc. g/mL
	d-N-MeFOSA	2
	d9-N-EtFOSE	2
Product Code:	UNEP-PFAS-EXT. B	

Labelled compounds

Injection mix A		Conc. g/mL
	MPFOS	1
	M2PFOA	1
	MPFHxS	1
	M3PFBA	1
	M3PFPeA	1
	MPFHxA	1
	MPFNA	1
	MPFDA	1
	MPFUdA	1
Product Code:	UNEP-PFAS-INJ.A	

Injection mix B		Conc. g/mL
	d-N-EtFOSA-M	2
	d7-N-MeFOSE	2
Product Code:	UNEP-PFAS-INJ.B	

Conclusions

- Proposed methods (as per guidance documents) proved successful and applicable;
- Water sampling – in Africa – progresses (very) well;
- No issues with customs, sample receipt at MTM Örebro University on-track;
- Analytical methods for L- and br-PFOS robust and established; amended to include more PFAS;
- Indicative water samples from all regions have been analyzed:
  - L- and br-PFOS were found in all samples
  - In general, concentrations are low with a maximum of 3.24 ng/L for total PFOS (2.46 ng/L for L-PFOS and 0.77 ng/L for br-PFOS)
- Last sampling date will be at/around 2018-12-31;
- Proposal to include the PFAS candidates – PFOA and PFHxS – into analysis at no additional costs for the Africa UNEP/GEF GMP2 project.

Thank you