



Monitoring of PFOS in water – Asia-Pacific region

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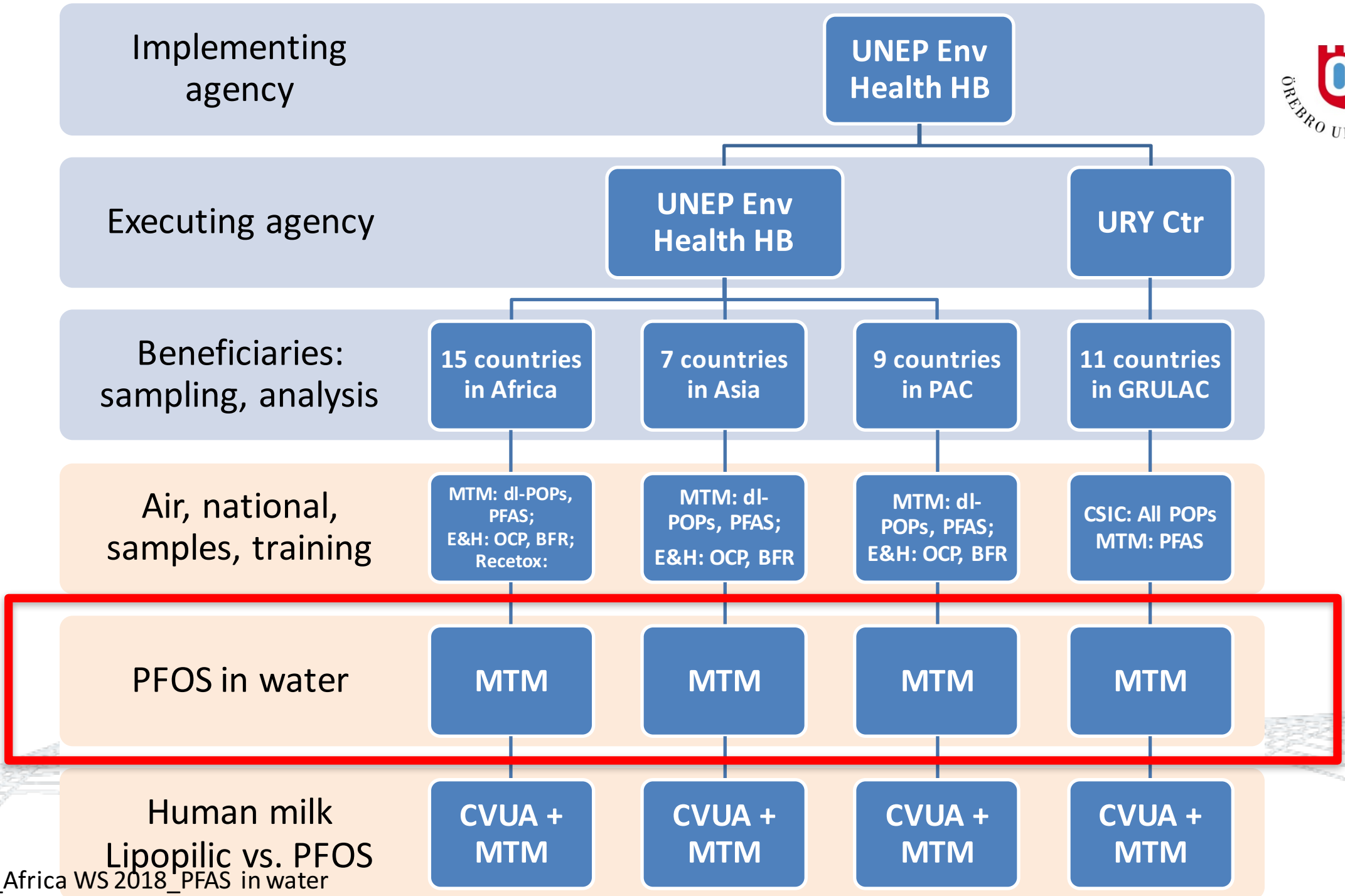
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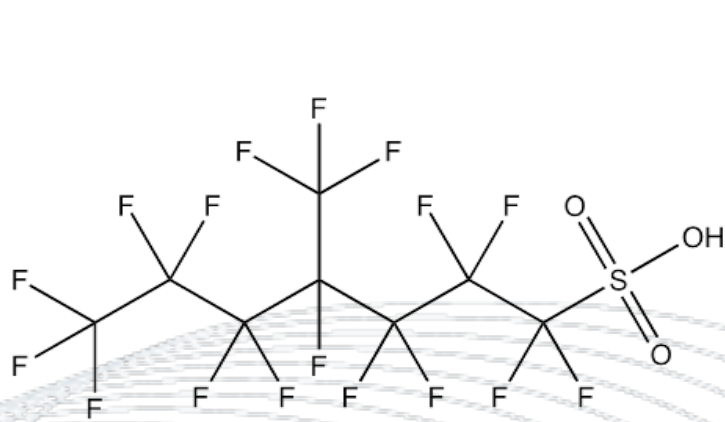
Content

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

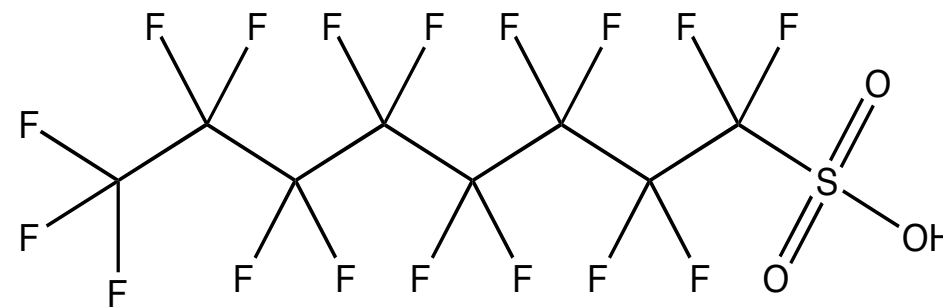


PFOS was listed in annex B in 2009

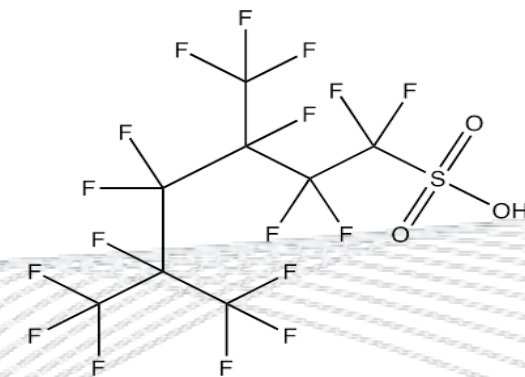
POP	Identity
Perfluorooctane sulfonic acid (PFOS)	<ul style="list-style-type: none">• Single anionic compound with one linear (L-PFOS) and 89 branched isomers (theoretically; 11 found in the environment – status 2009)• Manufacture of PFOS via electrochemical fluorination generates mostly linear isomeric configuration, 21%-35% of the PFOS are branched isomers.



4-PFOS



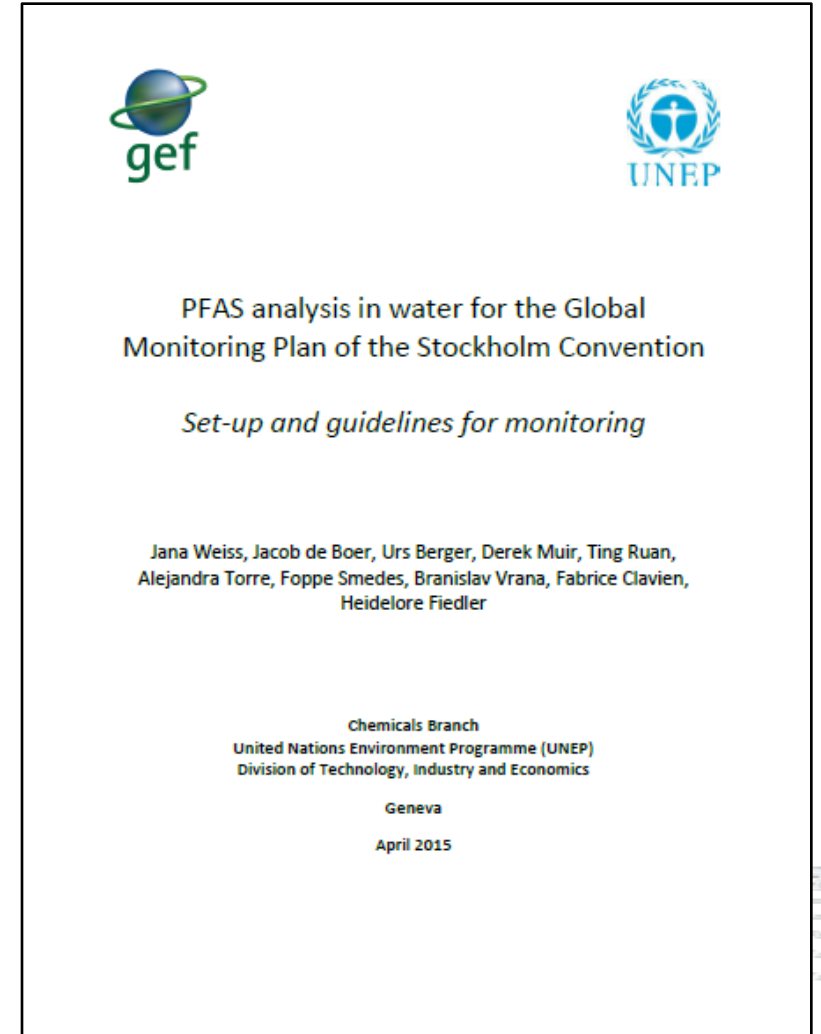
L-PFOS



3,5-PFOS

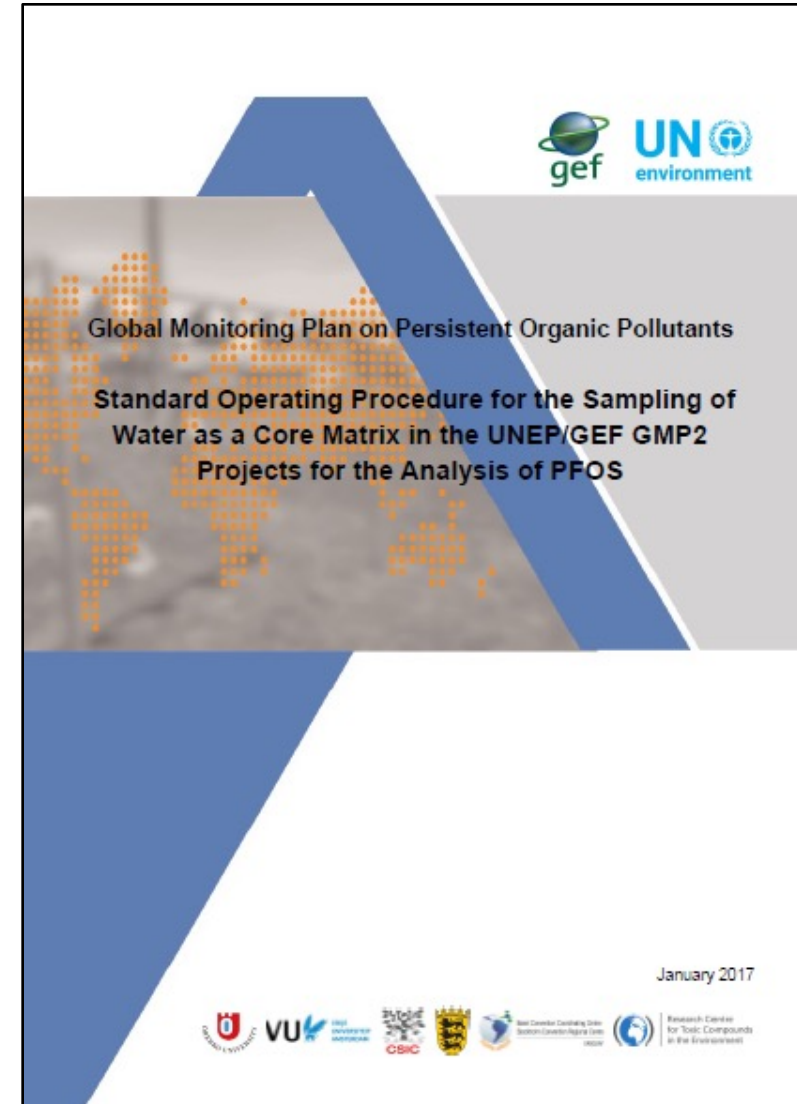
SOP for water sampling and PFAS analysis

- 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

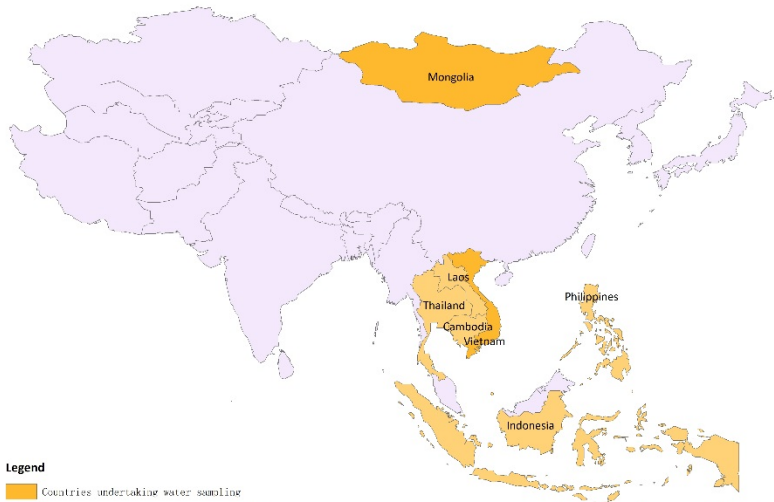


Surface water monitoring steps

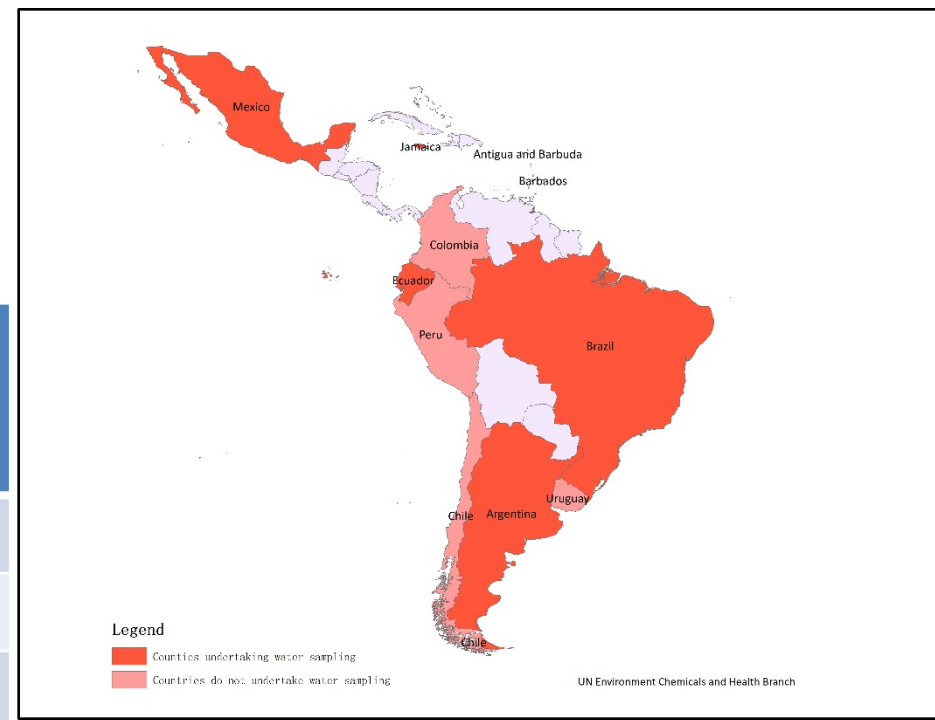
- SOP for water sampling prepared
- Highlight details in the script, and
- Verify presence of HDPE bottles in each country
 - Shipment of bottles by MTM
 - Storage of the bottles (kept in PS box and plastic bag)
 - Bucket, rope
 - Sampling on-site
 - Storage in fridge (not freezer)
 - Shipment of HDPE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



Water sampling in UNEP/GEF GMP2 projects

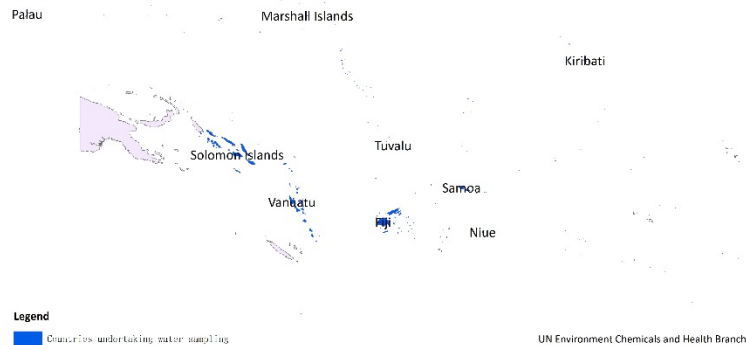


Project	# water sampling countries	# countries in project
Africa	6	15
Asia	2	7
Pacific Isl.	9	9
GRULAC	5	11

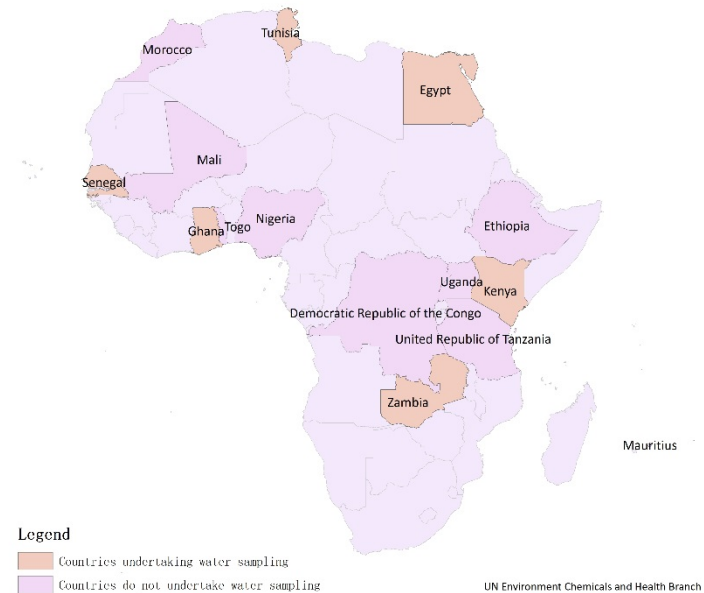


UN Environment Chemicals and Health Branch

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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

Asia: National analysis for PFOS anticipated in Vietnam (and Thailand but does not participate in the water sampling network – **needs adjustment?**)

- PFOS analysis training to be held in Thailand in 2nd part of 2018
- Visit of Vietnam to Örebro in August 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

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 3 maximum (EUR 2.50 for each HDPE bottle).

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

Sincerely,

Dr. Heidelore Fiedler
Professor of Chemistry
Örebro University, School of Science and Technology
MTM Research Center
Fakultetsgatan 1
SE-701 82 Örebro, Sweden
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E-mail: Heidelore.fiedler@oru.se

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



Hfiedler_Africa WS 2018_PFAS in water

- 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.

Present status of water samples (2017 and 2018)



Country name	ISO_3	Campaign 1		Campaign 2		Campaign 3		Campaign 4		Blank Date arrived	Subtotal	
		Sample ID	Date arrived	Sample ID	Date arrived	Sample ID	Date arrived	Sample ID	Date arrived		#	target
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

		Sample ID	Date arrived	Sample ID	Date arrived	Sample ID	Date arrived	Sample ID	Date arrived	Date arrived	#
Asia		2	2	2	0	2	0	2	0	0	2
Mongolia	MNG	MNG-A (2018-1)	2018-05-16	MNG-A (2018-2)		MNG-A (2018-3)		MNG-A (2018-4)			1
Vietnam	VNM	VNM-A (2018-1)	2018-04-26	VNM-A (2018-2)		VNM-A (2018-3)		VNM-A (2018-4)			1

- From Mongolia: all scheduled water samples received
- From Vietnam: 2 samples missing from 2017-1 and 2017-2
- Mongolia: to send one travel blank for 2018

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 μ m, 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

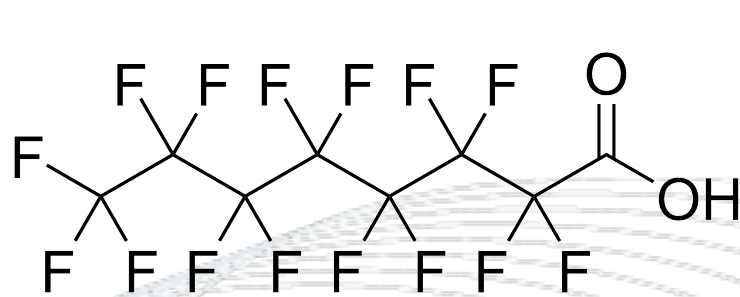
- Separation and quantification of PFOS was performed on liquid chromatograph coupled to a tandem mass spectrometer (Acquity Ultra Performance Liquid Chromatograph (UPLC) and a Xevo TQ S mass spectrometer, Waters, MA, USA) in negative ionization mode;
- Reversed phase column (Waters BEH column, 100 x 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% \pm 20%.

Results in 2012 pilot survey

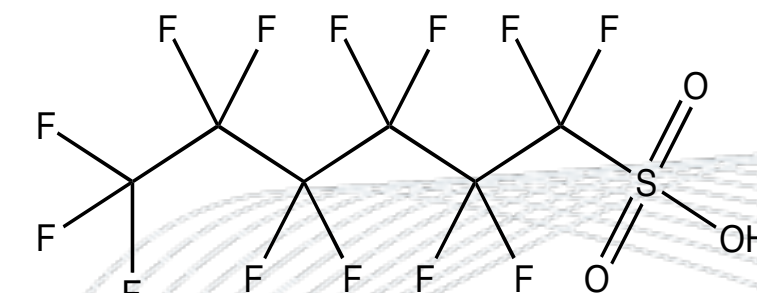
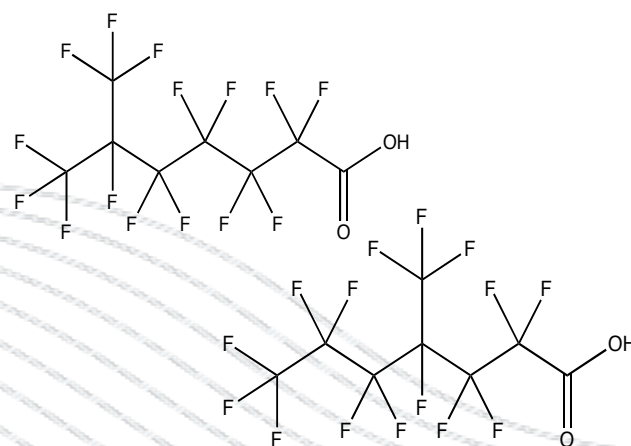
Country	Fiji	Kenya	Mali	Uruguay	Netherlands	
Site name	Waimanu River	Sabaki River Mouth	Sotuba/Mali	Río de la Plata	Kampen, IJssel	Rotterdam, Nieuwe Maas
Unit	ng L ⁻¹	ng L ⁻¹	ng L ⁻¹	ng L ⁻¹	ng L ⁻¹	ng L ⁻¹
L-PFOS	1.1	4.6	5.7	<1.0	9.9	11

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

Drinking water regulations

PFAS

	Drinking Water Limits (µg/L)										
	CARBOXYLATES							SULFONATES			PRECURSOR
	C4	C5	C6	C7	C8	C9	C10	C4	C6	C8	
	PFBA	PFPeA	PFHxA	PFHpA	PFOA	PFNA	PFDA	PFBS	PFHxS	PFOS	6:2FTS
USA: EPA					0.07					0.07	
USA: MN	7				0.035			7		0.027	
USA: NJ					0.014	0.013					
USA: VT					0.02						
USA: ME					0.1						
MRL				0.01	0.02	0.02		0.09	0.03	0.04	
Canada (Health)					0.2					0.6	
New Zealand					0.55					0.7	
Australia					0.55					0.7	
Sweden	Health-based guideline: 0.9 for 11 PFAS; action Level 0.09 for 11 PFAS										
Denmark										0.1	
Germany					0.3					0.3	
UK					0.3					0.3	
WHO					0.4					0.04	
EU (proposal 2/2018)	0.1 for individual PFAS and 0.5 for PFASs in total										

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	BrPFOSK (L-PFOS)	1	For training and priority analysis, Stockholm Convention
Water			
(others)			
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 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 Asia UNEP/GEF GMP2 project.

Thank you