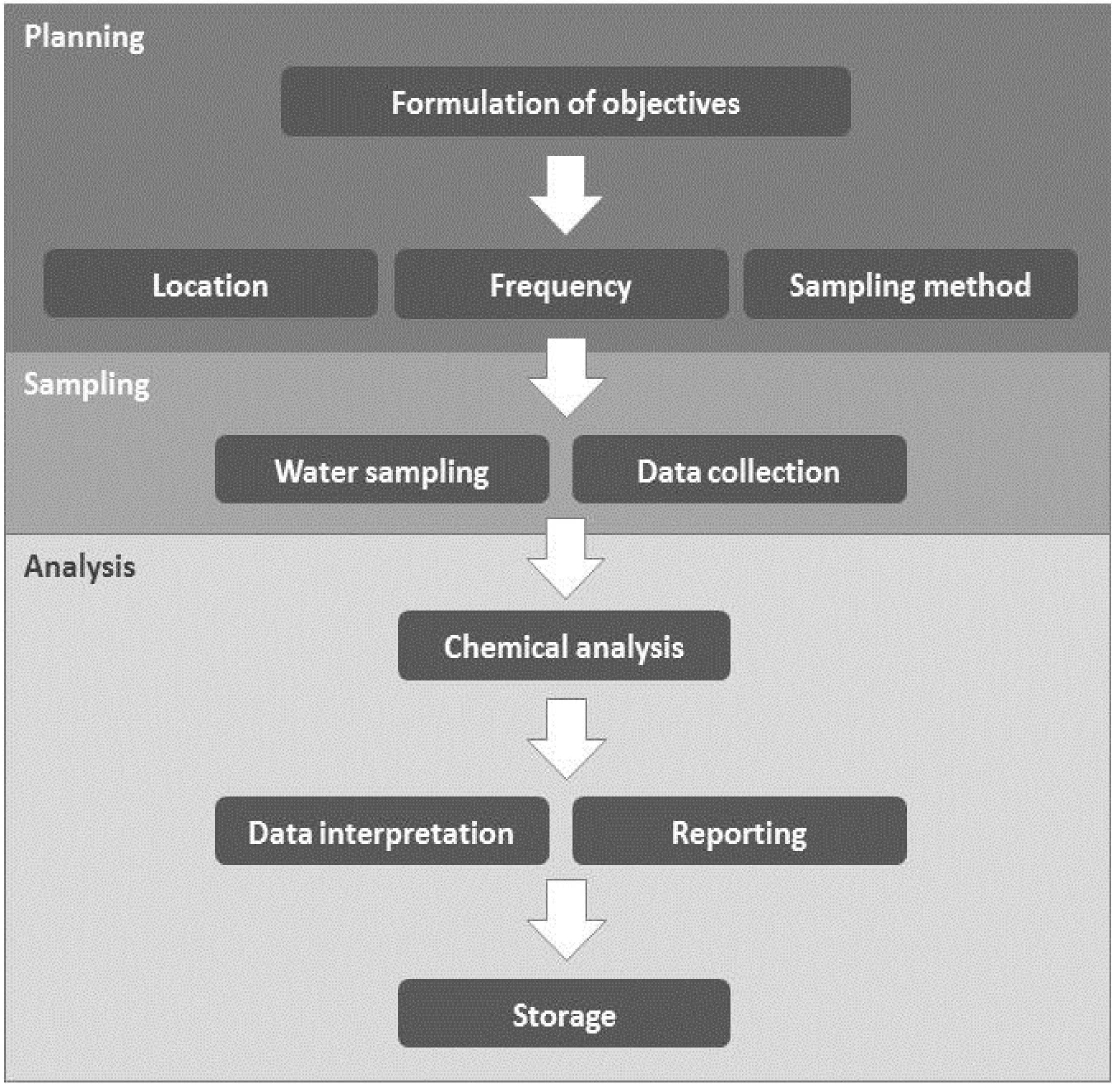
Development of the guideline for PFAS in water

Heidelore Fiedler
Örebro University
School of Science and Technology, MTM Research Centre
SE-701 82 Örebro, Sweden

Steps in setting up a monitoring plan



Planning

Formulation of objectives

Location

Frequency

Sampling method

Sampling

Water sampling

Data collection

Analysis

Chemical analysis

Data interpretation

Reporting

Storage

UNEP/GEF PFAS Expert Group

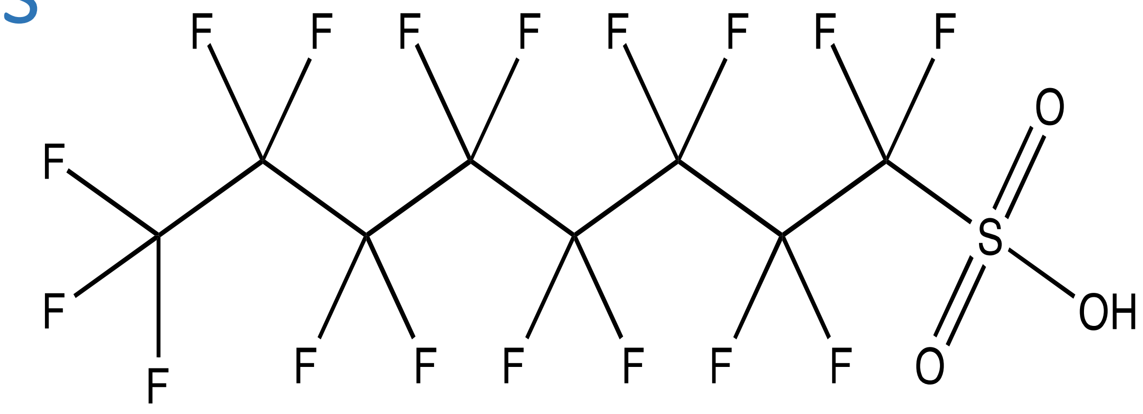
1.	Jacob de Boer/Jana Weiss	IVM, Vrije Universiteit, Amsterdam, Netherlands
2.	Derek Muir	Environment Canada, Burlington, Canada
3.	Nobuyoshi Yamashita/E. Yamazaki	AIST, Tsukuba, Ibaraki, Japan
4.	Urs Berger	UFZ, Leipzig , Germany
5.	Guibin Jiang/Ting Ruan	Chinese Academy of Sciences, Beijing, China
6.	William Aalbersberg/Shalvin Raj	University of South Pacific, Suva, Fiji
7.	Branislav Vrana/Foppe Smedes	RECETOX, Brno, Czech Republic
8.	Vincent Odongo Madadi	University of Nairobi, Kenya
9.	Alejandra Torre	LATU, Montevideo, Uruguay
10.	Yasuyuki Shibata	NIES, Tsukuba, Ibaraki, Japan
11.	Bert van Bavel	MTM Centre, Örebro University, Örebro, Sweden
12.	Esteban Abad Holgado	IDÆA-CSIC, Barcelona, Spain
13.	Christian Bogdal	ETH Zurich, Zurich, Switzerland
14.	Heidi Fiedler	UNEP Chemicals Branch, Geneva, Switzerland

Thought starter

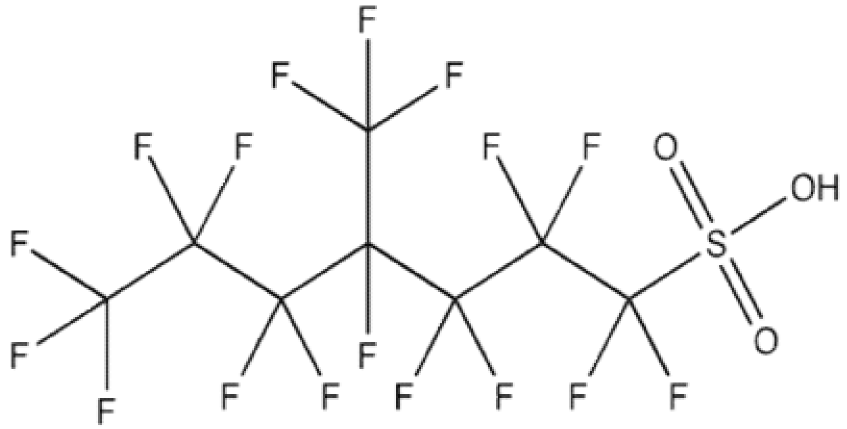
by Jana Weiss and the PFAS expert group

- PFOS and PFOA characterized by high water solubility, despite their lipophilic tail (570 mg/L for PFOS, 3400 mg/L for PFOA)
- Components of the guide
  - Sample matrices and sites
  - Guidance on storage, extraction, clean up and analysis in details
  - Sampling frequency
  - Proposal for possible sampling locations
  - Interlaboratory assessment as QA/QC tool
- Pilot testing undertaken in early 2014 (towards the end of the MSP project)
- Followed by expert consultation in fall 2014 ⇒ Prepare the guideline ⇒ present the guide to Global Coordination Group of the GMP

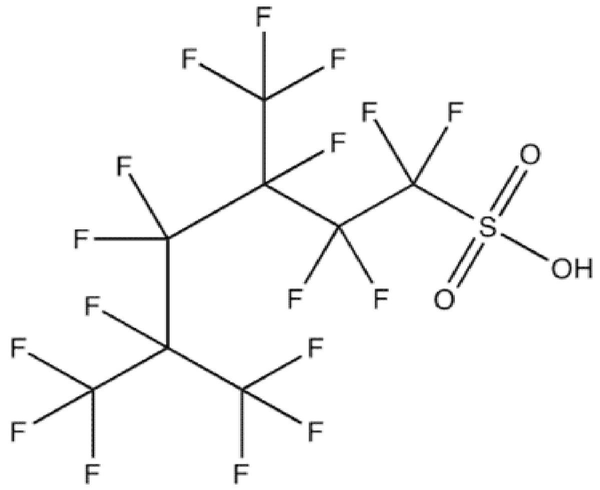
PFOS isomers



L-PFOS



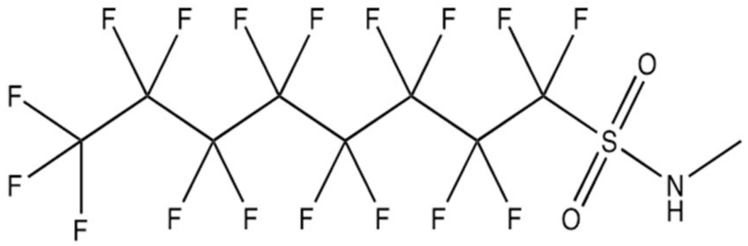
4-PFOS



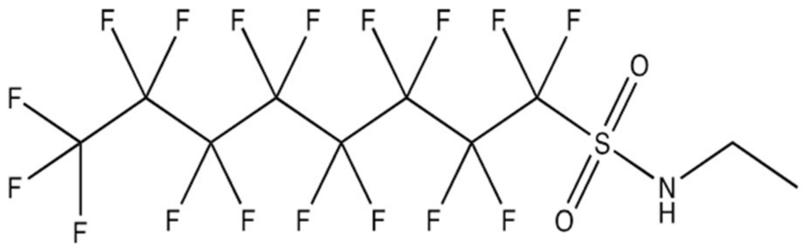
3,5-PFOS

HF, New POPs Tools, Hanoi, Jan 2016

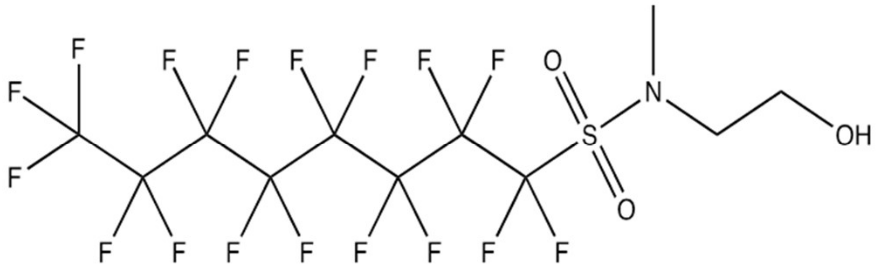
PFOS-related compounds



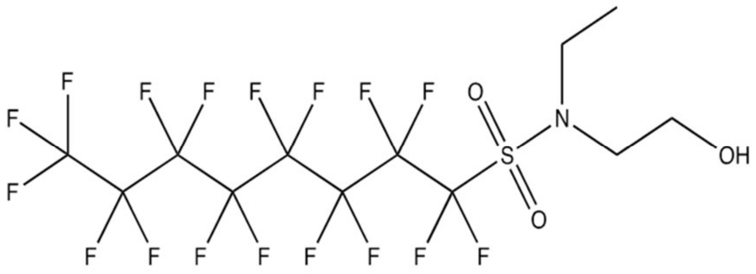
N-methyl perfluorooctane sulfonamide
MeFOSA



N-ethyl perfluorooctane sulphonamide
EtFOSA

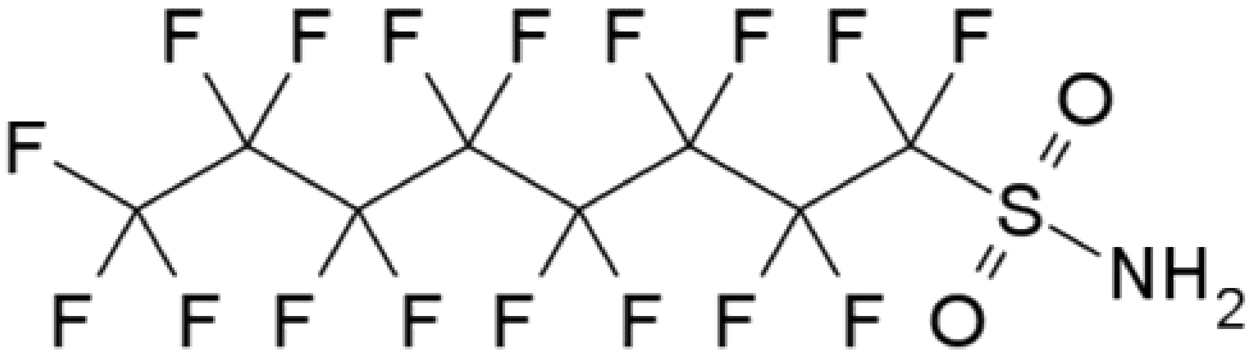


N-methyl perfluorooctane sulfonamidoethanol
MeFOSE



N-ethyl perfluorooctane sulfonamidoethanol
EtFOSE

FOSA



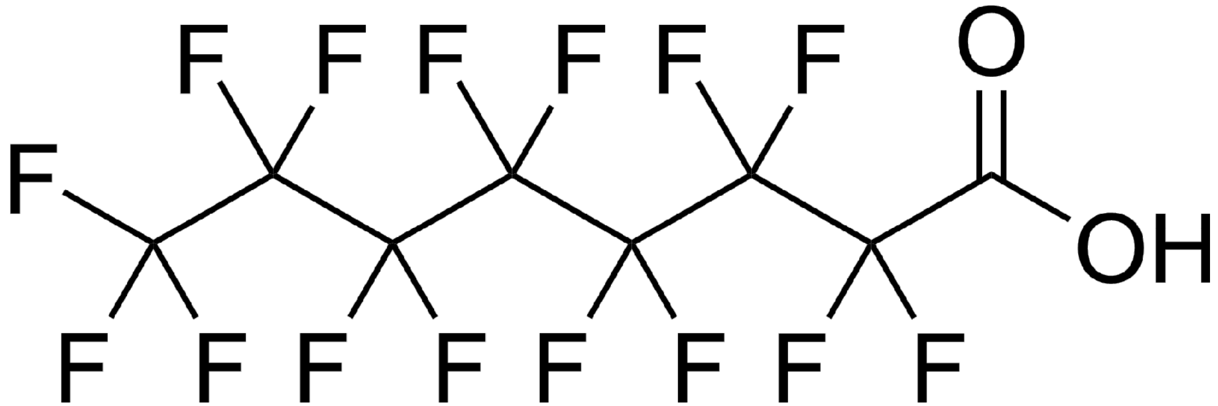
Perfluorooctanesulfonamide

FOSA was an ingredient in 3M´s Scotchgard formulation (to repel grease and water in food packaging).

FOSA is also a degradation product of N-EtFOSE or N-MeFOSE.

Given the potential complications of measuring FOSA, *i.e.*, degradation during storage, possible loss during extraction, and binding to particles in natural waters, it is **NOT recommended to analyse FOSA**.

PFOA



Perfluorooctanoic acid

- PFOA is not produced from PFOS precursors;
- Currently not listed under the Stockholm Convention (presently under discussion for listing by POPRC);
- Furthermore, analytical challenges such as much greater blank and laboratory contamination issues.

	Direct water sampling	Passive water sampling (PS)
Comparability of results WW	+	-
Achievement of a concentration (ng/L)	+	- uptake rate is a difficult parameter
Integrative sample	- highly sensitive to the water flow rate in case of a variable flow regime and to variable emissions in case of point sources	+ provide an integrative sample less sensitive to short-term variations in the water/emission regime
Costs	~	~
Required experience	- sampling itself doesn’t require much experience, but taking a representative sample requires much experience and planning	- handling and correct installation of PS requires more experience, but obtained sample is more representative of the average environmental conditions on site
Required additional data	+ Sampling site need to be specified, and weather conditions recorded	- to calculate uptake rate and state of equilibrium extra measurements need to be performed
Convenience of sampling/installation	+	- a good fixation/anchorage of PS requires planning/experience
Problems of difficult weather conditions/vandalism	+	- PS can be lost due to flooding/storms, theft. Protected spot is required.

Sampling frequency

Recommendation from UNEP/WHO (1996)

Baseline stations		
Streams	Minimum	4 per year, including high- and low-water stages
	Optimum	24 per year (every second week); weekly for total suspended solids
Headwater lakes	Minimum	1 per year at turnover; sampling at lake outlet
	Optimum	1 per year at turnover, plus 1 vertical profile at end of stratification
Trend stations		
Rivers/ estuaries	Minimum	12 per year for large drainage areas, approximately 100,000 km^2
	Maximum	24 per year for small drainage areas, approximately 10,000 km^2
Lakes/ reservoirs	Minimum	1 per year at turnover
	Maximum	2 per year at turnover, 1 at maximum thermal stratification

Discussion topics at expert WS (fall 2014)

- Sampling methods
  - passive, active,
  - volume, equipment,
  - additional data acquisition
- Sampling frequency
  - baseline, trends
- Sampling locations and how to take representative samples
- Logistics, networks, data storage…
- Chemical analysis
  - method, training, Interlaboratory assessments, *etc.*

1. Recommendation for location

- Define objectives of the project and selected monitoring site.
- Gather hydrological and other relevant data (presence of industry and WWTP, population density, *etc.*).
- **Estuaries are recommended as sampling sites**, but data from other sites are welcome and should have one of the following characteristics:
  - Estuary and larger tidal rivers and bays
  - River downstream populated area (sufficient mixture distance from any influent)
  - Lake with a defined surrounding population
  - Tributary (before entering the main stream)
- Adapt the distance to shore to existing circumstances at the site. Make sure the water sampled is from a zone where it is mixed.
- Ease of access by limnological or oceanographic vessels with capacity to deploy water sampling equipment or from land based sites such as bridges.

2. Recommendation for frequency

- Sample at a selected site 4 times a year (same site and with the same method);
- Carefully determine the sampling occasions depending on optimal conditions, preferably consistent between years, *e.g.*,:
  - 2 times high-water stage and
  - 2-timed low-water stage,
  - Although avoiding drought conditions or freezing conditions

3. Recommendation for sampling method

- Active/grab sampling is the recommended method;
- Use, remotely activated water samplers (*e.g.*, Niskin^{TM}), or hand-dipping;
- Avoid sampling the surface;
- For sampling use a 500 mL wide mouth HDPE bottle;
- Use HDPE sampling and storage containers (bottles, test tubes, vials, *etc.);*
- All material should be rinsed with methanol before usage;
- Analysis volume is typically 50 mL-500 mL; be determined by the analytical laboratory;
- To avoid cross contamination, the sample bottles should only be used once;
- Take 2 samples, one for analysis and one for later confirmation if needed;
- Store the samples in the fridge until analysis;
- It is recommended to perform a pilot sampling to establish the levels and practice the sampling.

4. Minimum data to report

- Site ID code
- Location name
- Date
- Names of personnel conducting the sampling
- GPS coordinates of sampling site
- Marine/fresh water
- Distance to shore
- Water depth
- Sampling depth
- Total suspended solid (TSS)
- Conductivity

5. Recommendation for reporting

- Investigate existing monitoring programs and collaborate for data collection and at sampling occasions;
- Provide the Convention with the minimum data set asked for.

6. Recommendation sample pre-treatment

- The sample shall not be filtered before analysis, unless it is necessary to avoid blocking of the solid phase extraction cartridges.
- The analysed phase should be properly reported with the data.
- Add recovery internal standards as soon as the samples arrive at the analytical laboratory.
- Let the sample equilibrate with the recovery internal standard added before analysis (~month).
- It is recommended to use the whole sample from one bottle for analysis.
- **Recommendation for PFOS extraction of water:**
  Use WAX SPE column for extraction and clean up

7. Recommendation for analysis and reporting

- Recommended instrument is LC-MS/MS;
- Minimum demand is that the analytical instrument has multiple MS capacity to produce quantifier and qualifier ions for quantification;
- Determine the linear range of the calibration curve;
- The linear- and the total PFOS concentrations should be reported;
- A procedural blank shall be determined in parallel;
- The blank levels should be less than 10% and the reported concentrations corrected for blank levels.

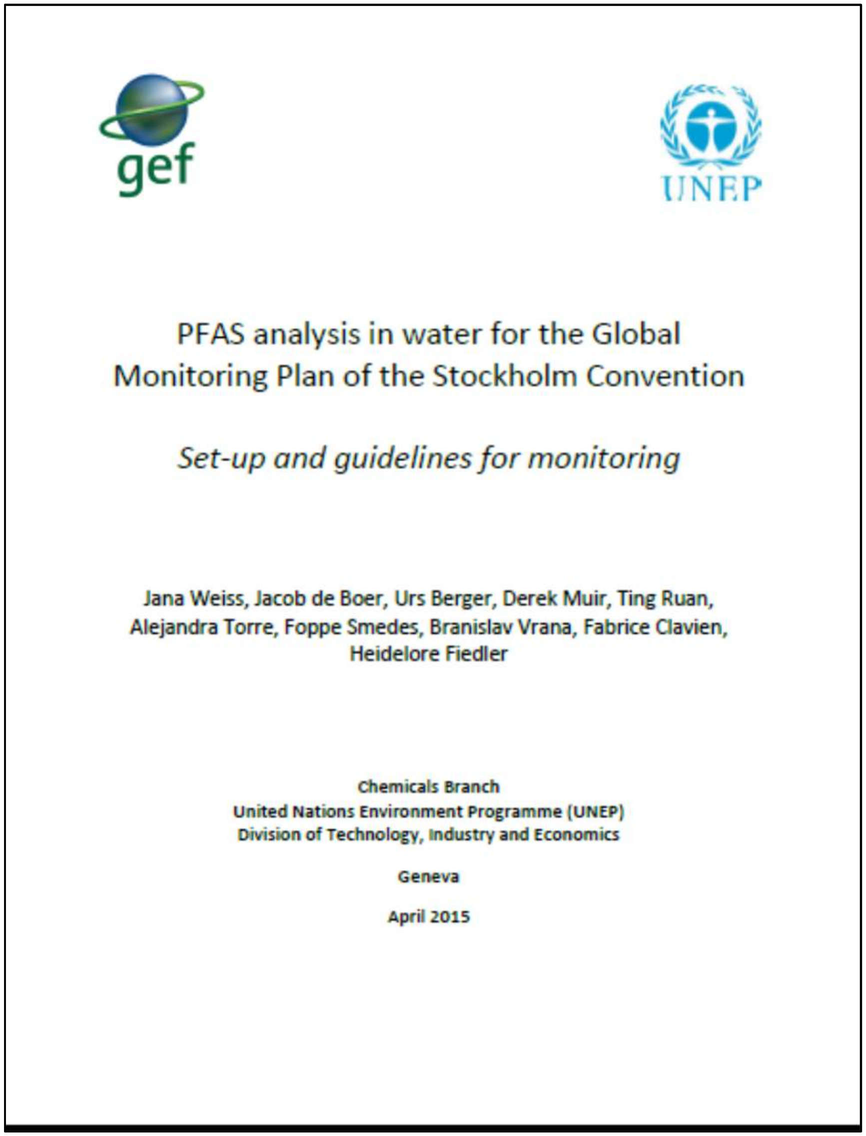
8. Chemical analysis

Compound		**Precursor Ion (m/z)**	**Daughter ion (m/z)**	**Comment**
PFOS	Target compound	499	80	Quantifier
			99	Qualifier
$^{13}C_4$ PFOS	Internal standard	503	80	Quantifier
			99	Qualifier

- The results should be reported on sulfonate anion basis, *i.e.*, corrected for the molecular weight of the PFOS salt
- In general, a five point calibration curve (5 different concentrations) needs to be constructed to demonstrate there is a linear dependence between signal and concentration;
- The sample preparation should be adapted to fit the final concentration to be inside the concentration range;
- Report concentration of L-PFOS and total PFOS (linear and branched as a sum)

Tools for new POPs sampling network

- UNEP/GEF project 'Establishing the Tools and Methods to Include the Nine New POPs into the Global Monitoring Plan', GEF 4B97
- Method development 'PFAS guide' http://www.unep.org/chemicalsandwaste/Portals/9/POPs/Guide%20PFAS%20water_UNEP%202015.pdf



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