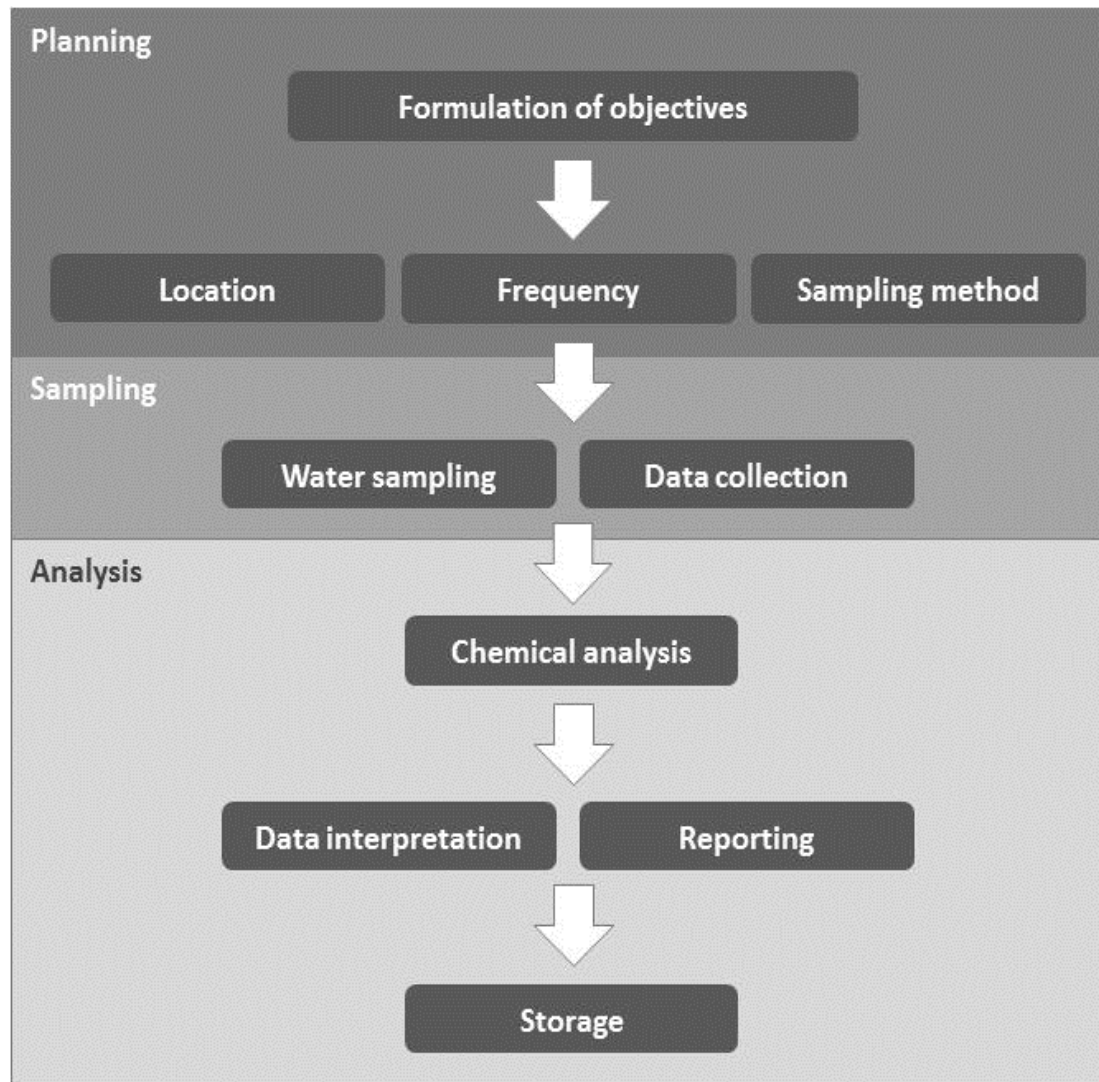




# Development of the guideline for PFAS in water

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# Steps in setting up a monitoring plan



# UNEP/GEF PFAS Expert Group

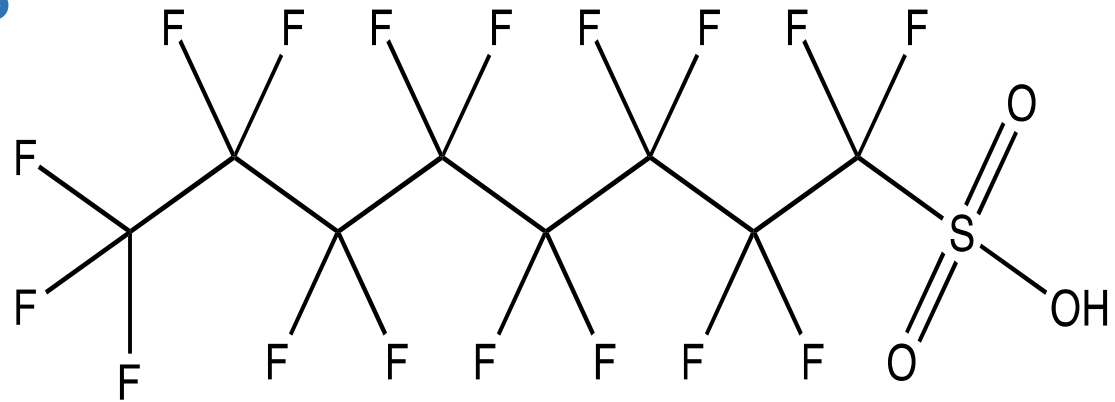
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# Thought starter

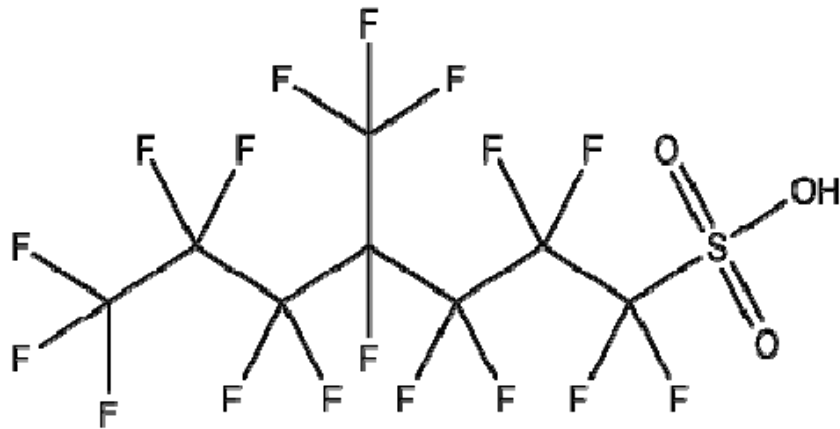
## by Jana Weiss and the PFAS expert group

- 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

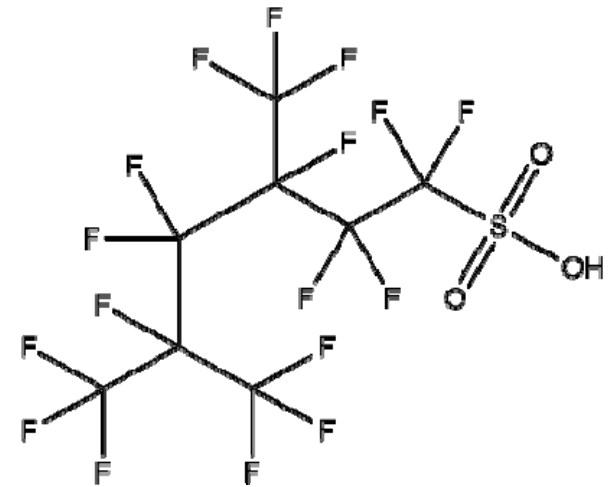
# PFOS isomers



L-PFOS

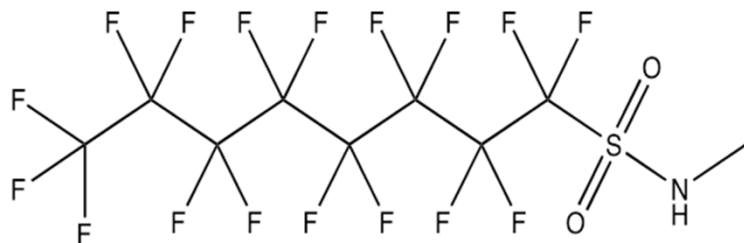


4-PFOS

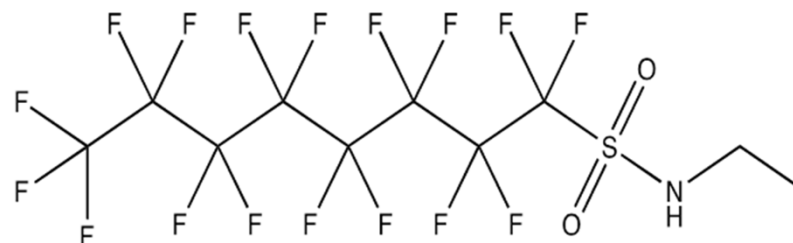


3,5-PFOS

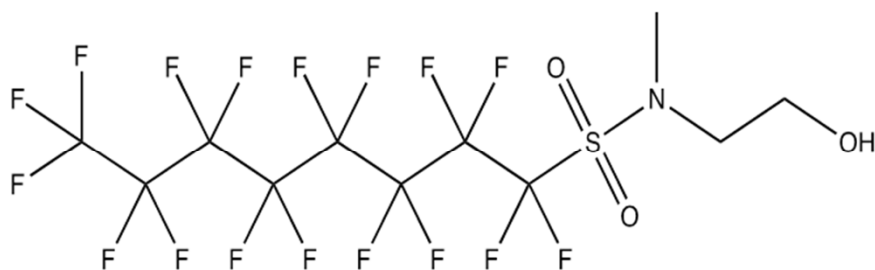
# PFOS-related compounds



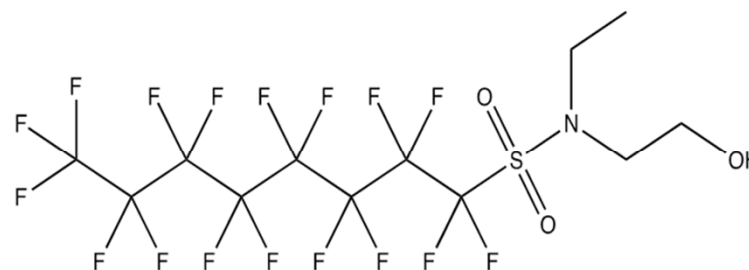
N-methyl perfluorooctane sulfonamide  
MeFOSA



N-ethyl perfluorooctane sulphonamide  
EtFOSA

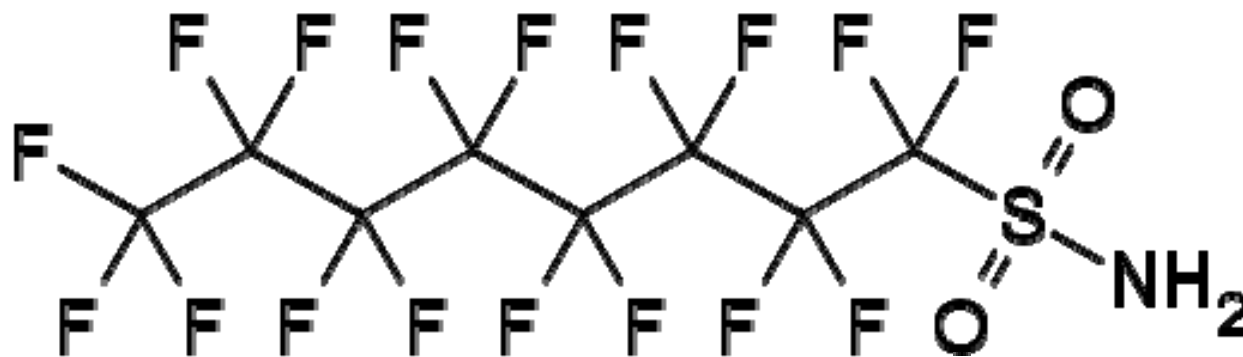


N-methyl perfluorooctane sulfonamidoethanol  
MeFOSE



N-ethyl perfluorooctane sulfonamidoethanol  
EtFOSE

# FOSA



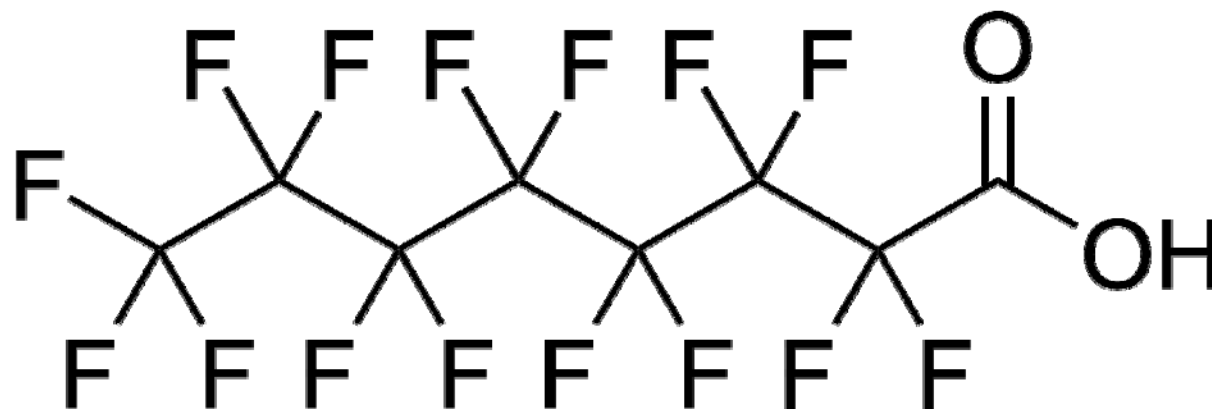
Perfluorooctanesulfonamide

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 <sup>2</sup>
	Maximum	24 per year for small drainage areas, approximately 10,000 km <sup>2</sup>
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™), 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
<sup>13</sup> C <sub>4</sub> 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%20UNEP%202015.pdf>

HF, New POPs Tools, Accra, July 2016



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

*Set-up and guidelines for monitoring*

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Alejandra Torre, Foppe Smedes, Branislav Vrana, Fabrice Clavien,  
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April 2015