Development of the guideline for PFAS in water

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Steps in setting up a monitoring plan

1. Planning
   - Formulation of objectives
   - Location
   - Frequency
   - Sampling method

2. Sampling
   - Water sampling
   - Data collection

3. Analysis
   - Chemical analysis
   - Data interpretation
   - Reporting
   - Storage
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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 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;
- Furthermore, analytical challenges such as much greater blank and laboratory contamination issues.
<table>
<thead>
<tr>
<th></th>
<th>Direct water sampling</th>
<th>Passive water sampling (PS)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Comparability of results WW</td>
<td>+</td>
<td>-</td>
</tr>
<tr>
<td>Achievement of a concentration (ng/L)</td>
<td>+</td>
<td>-uptake rate is a difficult parameter</td>
</tr>
<tr>
<td>Integrative sample</td>
<td>- highly sensitive to the water flow rate in case of a variable flow regime and to variable emissions in case of point sources</td>
<td>+ provide an integrative sample less sensitive to short-term variations in the water/ emission regime</td>
</tr>
<tr>
<td>Costs</td>
<td>~</td>
<td>~</td>
</tr>
<tr>
<td>Required experience</td>
<td>- sampling itself doesn’t require much experience, but taking a representative sample requires much experience and planning</td>
<td>- handling and correct installation of PS requires more experience, but obtained sample is more representative of the average environmental conditions on site</td>
</tr>
<tr>
<td>Required additional data</td>
<td>+ Sampling site need to be specified, and weather conditions recorded</td>
<td>- to calculate uptake rate and state of equilibrium extra measurements need to be performed</td>
</tr>
<tr>
<td>Convenience of sampling/installation</td>
<td>+</td>
<td>- a good fixation/anchorage of PS requires planning/experience</td>
</tr>
<tr>
<td>Problems of difficult weather conditions/vandalism</td>
<td>+</td>
<td>- PS can be lost due to flooding/storms, theft. Protected spot is required.</td>
</tr>
</tbody>
</table>
# Sampling frequency

Recommendation from UNEP/WHO 1996)

<table>
<thead>
<tr>
<th>Baseline stations</th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Streams</strong></td>
<td>Minimum</td>
<td>4 per year, including high- and low-water stages</td>
</tr>
<tr>
<td></td>
<td>Optimum</td>
<td>24 per year (every second week); weekly for total suspended solids</td>
</tr>
<tr>
<td><strong>Headwater lakes</strong></td>
<td>Minimum</td>
<td>1 per year at turnover; sampling at lake outlet</td>
</tr>
<tr>
<td></td>
<td>Optimum</td>
<td>1 per year at turnover, plus 1 vertical profile at end of stratification</td>
</tr>
<tr>
<td><strong>Trend stations</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Rivers/estuaries</strong></td>
<td>Minimum</td>
<td>12 per year for large drainage areas, approximately 100,000 km²</td>
</tr>
<tr>
<td></td>
<td>Maximum</td>
<td>24 per year for small drainage areas, approximately 10,000 km²</td>
</tr>
<tr>
<td><strong>Lakes/reservoirs</strong></td>
<td>Minimum</td>
<td>1 per year at turnover</td>
</tr>
<tr>
<td></td>
<td>Maximum</td>
<td>2 per year at turnover, 1 at maximum thermal stratification</td>
</tr>
</tbody>
</table>
Discussion topics at expert WS

• 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.
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.
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
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.
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
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.
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
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 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.
Chemical analysis

<table>
<thead>
<tr>
<th>Compound</th>
<th>Precursor Ion (m/z)</th>
<th>Daughter ion (m/z)</th>
<th>Comment</th>
</tr>
</thead>
<tbody>
<tr>
<td>PFOS</td>
<td>499</td>
<td>80</td>
<td>Quantifier</td>
</tr>
<tr>
<td></td>
<td></td>
<td>99</td>
<td>Qualifier</td>
</tr>
<tr>
<td>$^{13}$C$_4$ PFOS</td>
<td>503</td>
<td>80</td>
<td>Quantifier</td>
</tr>
<tr>
<td></td>
<td></td>
<td>99</td>
<td>Qualifier</td>
</tr>
</tbody>
</table>

- 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'