Development of the guideline for PFAS in water

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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

HF, New POPs Tools, Hanoi, Jan 2016
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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

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PFOS-related compounds

N-methyl perfluoroctane sulfonamide
MeFOSA

N-ethyl perfluoroctane sulphonamide
EtFOSA

N-methyl perfluoroctane sulfonamidoethanol
MeFOSE

N-ethyl perfluoroctane 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 (presently under discussion for listing by POPRC);
• 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>-</td>
<td>+</td>
</tr>
<tr>
<td></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>-</td>
<td>-</td>
</tr>
<tr>
<td></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>+</td>
<td>-</td>
</tr>
<tr>
<td></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>-</td>
</tr>
<tr>
<td></td>
<td>a good fixation/anchorage of PS requires planning/experience</td>
<td></td>
</tr>
<tr>
<td>Problems of difficult weather conditions/vandalism</td>
<td>+</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>PS can be lost due to flooding/storms, theft. Protected spot is required.</td>
<td></td>
</tr>
</tbody>
</table>
# Sampling frequency

Recommendation from UNEP/WHO (1996)

<table>
<thead>
<tr>
<th>Baseline stations</th>
<th>Streams</th>
<th>Minimum</th>
<th>4 per year, including high- and low-water stages</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Optimum</td>
<td>24 per year (every second week); weekly for total suspended solids</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Headwater lakes</td>
<td>Minimum</td>
<td>1 per year at turnover; sampling at lake outlet</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Optimum</td>
<td>1 per year at turnover, plus 1 vertical profile at end of stratification</td>
</tr>
</tbody>
</table>

| Trend stations | Rivers/estuaries | Minimum | 12 per year for large drainage areas, approximately 100,000 km² |
|               |                   | Maximum | 24 per year for small drainage areas, approximately 10,000 km² |
|               | 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

<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 Target</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'

HF, New POPs Tools, Hanoi, Jan 2016