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

Set-up and guidelines for monitoring

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List of acronyms and abbreviations

COP	Conference of the Parties (to the Stockholm Convention)
EtFOSA	N-ethyl-perfluoroalkane sulfonamide
EQS	Environment quality standards
FOSA	Perfluorooctane sulfonamide
FOSE	Perfluorooctane sulfonamide ethanol
GEF	Global Environment Facility
GMP	Global Monitoring Plan (for Persistent Organic Pollutants)
GMP DWH	Data Warehouse of the Global Monitoring Plan for Persistent Organic Pollutants
LC-MS/MS	Liquid chromatography/tandem mass spectrometry
MeFOSA	N-methyl-perfluoroalkane sulfonamide
PFASs	Per- and polyfluoroalkyl substances
PFOS	Perfluorooctane sulfonic acid
POSF	Perfluorooctane sulfonyl fluoride
POPs	Persistent organic pollutants
PTFE	Polytetrafluoroethylene
SOP	Standard operating procedures
TSS	Total suspended solids
UNEP	United Nations Environment Programme
WWTP	Waste water treatment plant

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1 INTRODUCTION

By its decision SC-4/31 on global monitoring plan (GMP) for effectiveness evaluation, the Conference of the Parties of the Stockholm Convention at its fourth meeting in 2009 requested, among others, updating the guidance document for the GMP with additional chapters on long-range transport, specimen banking and the impact of listing new chemicals into annexes of the Convention. At the same meeting, decision SC-4/17 listed perfluorooctane sulfonic acid (PFOS), its salts and perfluorooctane sulfonyl fluoride in the annex B of the Convention.

The addition of new chemicals to the list of persistent organic pollutants (POPs) implies the updating and development of relevant guidance, such as for POPs monitoring under the effectiveness evaluation. In order to assist in this task, the Chemicals Branch of the United Nations Environment Programme (UNEP) executed the project 'Establishing the Tools and Methods to Include the Nine New POPs into the Global Monitoring Plan (GMP)', which was implemented from 2011 to 2015 and financed by the Global Environment Facility (GEF). The objective of the project was to update the guidance for POPs GMP by recommending analytical methods for the analysis of the newly listed POPs. Further, it was recommended to include surface water as an additional matrix for PFOS. The usefulness of the matrices is as follows: air or water receive the emissions of the POPs from the source and transport them around the globe; human milk or blood characterizes human exposures at a significant stage in development.

Decision SC-6/23 of the sixth meeting of the Conference of the Parties welcomed the updated guidance on the GMP and encouraged parties to use the document for the effectiveness evaluation of the GMP work [1]. For the seventh meeting of the Conference of the Parties, an updated guidance document was endorsed [2].

The aim of this guidance is to provide an overview of challenges regarding analysis of the per- and polyfluoroalkyl substance (PFAS), focusing on PFOS in the water column and to set guidelines for international monitoring programs under GMP of the Stockholm Convention.

1.1 The Stockholm Convention and the Global Monitoring Plan

The Stockholm Convention on POPs was adopted in 2001 with twelve initial POPs that potentially damage human health and the environment. They can be divided into three categories: pesticides, industrial chemicals and unintentionally generated POPs (http://chm.pops.int/). In 2009, a set of nine POPs was added to the annexes of the Convention; in 2011 endosulfan, and in 2013 hexabromocyclododecane and their related isomers were included. Under the Convention, POPs are categorized in three annexes from the standpoint of regulation whereby annex A refers to "elimination", annex B to "restriction" and annex C to "unintentional production".

Article 16 of the Stockholm Convention indicates that the effectiveness of the Convention shall be evaluated four years after the date of entry into force of the Convention and periodically (six years based on Conference of the Parties [COP] decision SC-4/32) thereafter. The effectiveness evaluation includes the monitoring of the presence of POPs in the environment and humans as well as their regional and global transport and the preparation of regional assessment reports and one global report (for information, see [3]and SC-6/22).

The GMP focuses on the generation of high quality results in the core media of the GMP, *i.e.*, ambient air and human milk or human blood for the initial twelve POPs. As new POPs are listed in either annexes A, B or C, the guidance needs to be amended to include newly listed POPs and assigns core matrices to them.

At the fourth meeting of the Conference of the Parties to the Stockholm Convention, through decision SC-4/17, perfluorooctane sulfonic acid (PFOS), its salts and perfluorooctane sulfonyl fluoride (PFOSF) were listed in annex B of the Convention. PFOS, as well as PFOA (perfluorooctanoic acid, not included in the convention), are part of the broad class of perfluoroalkyl acids (PFAAs), which in turn belong to the family of per- and polyfluoroalkyl substances (PFASs).

In water environment, PFOS salts are dissociated into free PFOS anions and counter-cations while POSF is readily hydrolysed to the PFOS anion. Therefore, among the listed chemicals under the Convention, only PFOS is normally present and its monitoring is recommended for the core matrices, *i.e.*, ambient air and human milk or human blood. Since water is the main transport medium for PFOS in the environment, surface water was added as a core matrix for PFOS (but not for the other 22 POPs listed until 2013). This guidance document will present the rationale for including PFOS compounds into the GMP and be complementary to chapter 4.3 of the document 'Guidance on the global monitoring plan for persistent organic pollutants' [1, 2].

1.2 PFOSs in the water column

PFOS has been detected in a variety of environmental matrices, *e.g.,* biota, water, sediment and sludge. It is considered to be persistent in the environment due to its exceptional thermal and chemical stability with no known degradation. The chemical structure of PFOS enables to lower surface tension due to the hydrophobic and lipophobic properties of the perfluoroalkyl tail, and hydrophilic functional head group [4].

PFOS has been found in surface waters and concentrations have been reported both in marine and aquatic water basins worldwide [5]. PFOS is characterized by a relatively high water solubility, despite the hydrophobic tail, and water solubility is determined to 570 mg/L for PFOS [6]. Consequently, the open oceans water column has been suggested to be a final sink of PFAAs, such as PFOS and PFOA [7]. In the terrestrial environment, irrespective of the dissipation kinetics, the majority of PFOS from contaminated soils will be transported to groundwater and surface water bodies [8].

Groundwater is used for drinking water supplies and the commonly used drinking water treatment technologies do not efficiently remove these persistent compounds [9, 10]. As a consequence, drinking water has been shown to be one of the dominant exposure pathways for some PFASs to humans, together with food and dust ingestion [11]. Recently the European Commission included PFOS in the list of priority hazardous substances, which must be monitored in EU water bodies, and set environmental quality standards (EQS) for PFOS concentrations in water and biota in inland and coastal surface waters [12]. European EQS values are listed in Table 1

Table 1: European environment quality standards (EQS) of PFOS in surface waters (µg/L water) and biota (µg/kg wet weight (ww)) reported in recently adopted EU Directive (Directive 2013/39/EU [12]). Inland surface waters encompass rivers and lakes and related artificial or heavily modified water bodies, and other surface waters are transnational, coastal and territorial waters.

Substance	**AA-EQS[1] Inland surface waters**	**AA-EQS[1] Other surface waters**	**MAC-EQS[2] Inland surface waters**	**MAC-EQS[2] Other surface waters**	**EQS Biota**
	(µg/L)	(µg/L)	(µg/L)	(µg/L)	(µg/kg ww)
PFOS and its derivatives	6.5×10^{-4}	1.3×10^{-4}	36	7.2	9.1

[1] This parameter is the EQS expressed as an annual average value (AA-EQS). The purpose of this standard is to ensure the long-term quality of the aquatic environment.
[2] This parameter is the EQS expressed as a maximum allowable concentration (MAC-EQS). The purpose of this standard is to limit short-term pollution peaks.

The concentrations of PFOS in the water column differ between regions. In Table 2 recently reported data from water studies have been summarized to reflect the widespread monitoring and range of measured data detected in different water bodies. The table is not by any means covering all reported PFOS data in the water body, but gives an idea of levels to be expected in different regions. Several reviews have been published covering different aspects of PFAS concentrations in the aquatic environment; *e.g.,* concentrations and distribution coefficients in the water environment [8], fate and effects [13], concentrations in aquatic organisms [14], concentrations and trends in the Arctic environment [15], and global distribution of the PFASs in the marine environment [16], *etc.*

Table 2: Range of PFOS concentrations (ng/L water) reported in recently performed studies around the globe.

Region	**Matrix**	**Year**	**PFOS**	**Reference**
Europe	Ground water	2008	135	[17]
North America	Lake surface water	2005-2010	0.3-5.5	[18]
China, west	Lake surface water	2011	15	[19]
China, east	Lake surface water	2011	0.35-21	[20]
Faroe Islands	Lake surface water	2012	<0.1-0.6	[21]
Europe, Danube river	River surface water	2007	8 (max 19)	[22]
Europe, River Rhine	River surface water	2008	1.1-25	[23]
China, west	River surface water	2011	4.7	[19]
China, east	River surface water	2011	<0.07-25	[20]
Europe, North Sea	Marine surface water	2008	0.42	[23]
Hong Kong	Marine surface water	2009	0.02-2.7	[24]
Adriatic Sea	Marine surface water	2011	1.3	[25]
Atlantic Ocean	Marine surface water	2002-2006	0.01-0.07	[26]

The sorption of PFASs to soils and sediment determines their fate and distribution in the environment. Sorption coefficients can differ between laboratory based experiments and compared to distributions measured in the environment [8]. The suggested log K_{oc} distribution coefficients for field situations is 4.2 for PFOS, which expresses that PFASs sorbs to some extent to soils and sediments in a partitioning process. A recent study of the distribution between the dissolved phase and particulate matter in the

River Elbe showed that PFASs were dominantly present in the dissolved phase [27]. In the suspended particulate matter perfluorooctane sulfonamide (FOSA) and PFOS showed the highest concentrations (4.0 ng/L and 2.3 ng/L, respectively).

The discharge of PFOS and other PFASs to estuaries, or from tributaries to large rivers, has been estimated in studies in Europe, China, and North America [23, 25, 27-31]. It was reported that PFOS discharge from the Rhine to the North Sea based on measured data was 420–2200 kg/yr and estimated per capita emission rates of 27 mg d^{-1}–57 mg d^{-1} [32]. Similar quantities may be entering coastal waters of China. Mass flows of PFOS in five rivers in Northern China ranged up to 28 kg/yr [33] while in the Janjiang River in Wuhan, China, which flows through a fluorochemical manufacturing region, was estimated to discharge 127 kg/yr of PFOS to the Yangtze River.

A mass balance was assembled for selected PFASs (PFHxA, PFOA, perfluorodecanoic acid (PFDA) and PFOS) in the Baltic Sea. [34]. River inflow and atmospheric deposition were the dominant inputs. Also the Great Lakes in Canada, *i.e.*, Lake Superior and Lake Siskiwit showed estimation of tributaries and precipitation to be the major contributor [31]. In contrast, Lake Ontario main inputs came from waste water treatment plants (WWTPs), through the Niagara river, due to its population density and industrial activity [31]. Moreover, the only way of discharge for both lakes and the Baltic Sea is either sedimentation or outflow of the PFASs.

A laboratory based study on the influence of salinity, pH and sediment characteristics on the sorption and desorption of PFOS in surface waters suggests that PFOS tends to exist as dissolved species in low salinity water *i.e.*, freshwater, but sorbed to sediment in high salinity water *e.g.*, in seawater [35]. This was confirmed by another study in the Tokyo Bay in Japan [36]. This together shows the relevance of the rivers as major contributors to the lakes and the marine environment. Moreover, it was found that the concentrations in the upper water layer were higher than the lower layer, suggesting that there was an incomplete vertical mixing. This is in part due to seasonal changes in the density of seawater structure. During months such as May and August, it was found that the salinity was diluted by freshwater inputs, which proceeded from rivers and heating of the water surface during warm season [36].

The Northern Hemisphere has shown to have generally higher concentrations of PFOS than the Southern, which reflects the more intense use of these compounds in the north [26]. However, recent measurements in the south Atlantic show relatively high concentrations of PFOS off the coast of Brazil and the Rio de Plata estuary [16, 37].

The guidance for the GMP on POPs recommends the analysis of PFOS and precursor compounds to be analysed in surface waters. For that purpose this guidance document (focusing on PFOS monitoring in water) has been developed to implement GMP activities to generate and compare PFOS data around the world. The analytical aspects discussed here have been added to the protocol for PFOS and FOSA determination in water, mothers' milk, human serum and air [38].

2 COMPOUNDS TO BE ANALYSED

2.1 Identity of PFOS

There is one linear PFOS (L-PFOS) and a number of branched PFOS isomers. The structures of PFOS isomers that are typically found in technical mixtures are displayed in Table 3 and molecular formula in Figure 1. Technical mixtures typically contain between 71% and 83% L-PFOS [39].

Table 3: Structural isomers of PFOS typically identified in technical mixtures

Abbreviation	Formula	Name
L-PFOS	$CF_3CF_2CF_2CF_2CF_2CF_2CF_2CF_2SO_3^-$	*n*-perfluoro-octanesulfonate
1-PFOS	$CF_3CF_2CF_2CF_2CF_2CF_2CF(\mathbf{CF_3})SO_3^-$	perfluoro-1-methyl-heptanesulfonate
2-PFOS	$CF_3CF_2CF_2CF_2CF_2CF(\mathbf{CF_3})CF_2SO_3^-$	perfluoro-2-methyl-heptanesulfonate
3-PFOS	$CF_3CF_2CF_2CF_2CF(\mathbf{CF_3})CF_2CF_2SO_3^-$	perfluoro-3-methyl-heptanesulfonate
4-PFOS	$CF_3CF_2CF_2CF(\mathbf{CF_3})CF_2CF_2CF_2SO_3^-$	perfluoro-4-methyl-heptanesulfonate
5-PFOS	$CF_3CF_2CF(\mathbf{CF_3})CF_2CF_2CF_2CF_2SO_3^-$	perfluoro-5-methyl-heptanesulfonate
6-PFOS	$CF_3CF(\mathbf{CF_3})CF_2CF_2CF_2CF_2CF_2SO_3^-$	perfluoro-6-methyl-heptanesulfonate
4,4-PFOS	$CF_3CF(\mathbf{CF_3)_2}CF_2CF_2CF_2CF_2SO_3^-$	perfluoro-4,4-dimethyl-hexanesulfonate
3,5-PFOS	$CF_3CF(\mathbf{CF_3})CF_2CF(\mathbf{CF_3})CF_2CF_2SO_3^-$	perfluoro-3,5-dimethyl-hexanesulfonate
4,5-PFOS	$CF_3CF(\mathbf{CF_3})CF(\mathbf{CF_3})CF_2CF_2CF_2SO_3^-$	perfluoro-4,5-dimethyl-hexanesulfonate
5,5-PFOS	$CF_3C(\mathbf{CF_3)_2}CF_2CF_2CF_2CF_2SO_3^-$	perfluoro-5,5-dimethyl-hexanesulfonate

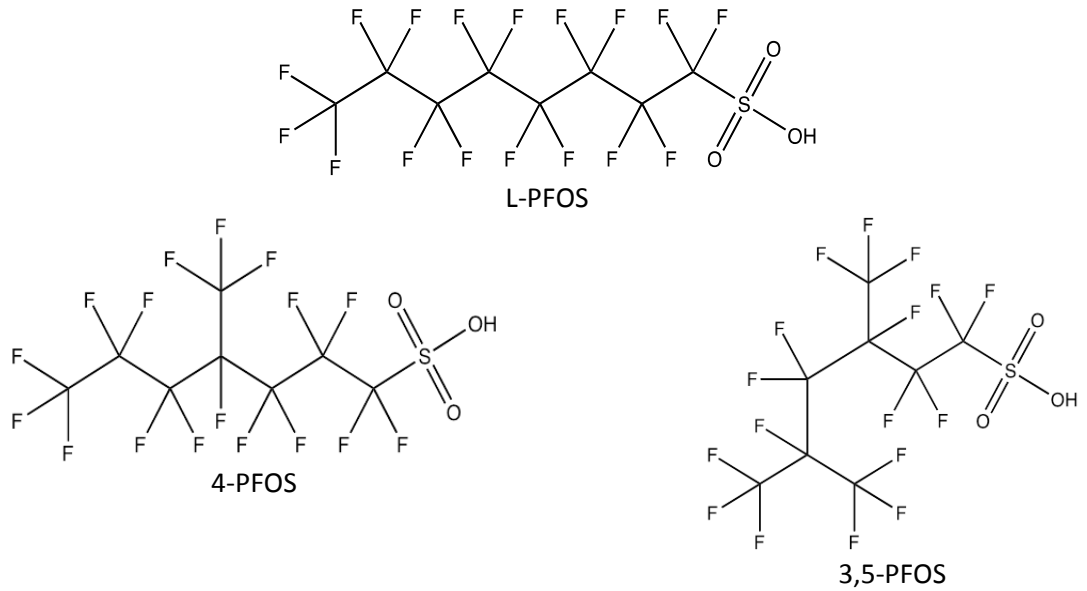


Figure 1: Molecular formula of linear and two branched PFOS isomers

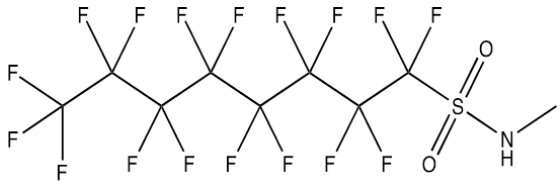
The physicochemical properties of PFOS and its salts are described in detail elsewhere [6]. Due to the surface-active properties, PFOS can form three layers in octanol/water and hence, an *n*-octanol/water

(K_{OW}) partition coefficient cannot be determined. Consequently, the various physicochemical properties (*e.g.,* bioconcentration factor, soil adsorption coefficient), which can usually be estimated for conventional organic compounds utilizing K_{OW} equations, cannot be estimated, and a calculated (estimated) log K_{OW} cannot be trusted

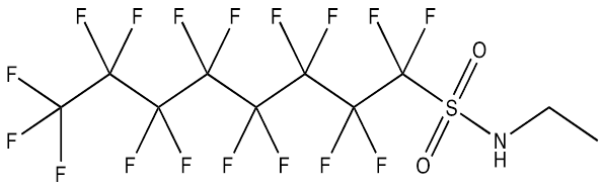
In two studies, PFOS was reported to have a mean solubility of 519 mg/L and 570 mg/L in pure water at 24 °C-25 °C. Solubility decreases significantly with increased salt content (12.4 mg/L in natural seawater at 22 °C-23 °C, and 20.0 mg/L in a 3.5% NaCl solution at 22 °C-24 °C [40]. In a related study, PFOS was reported to have a mean solubility of 56.0 mg/L in pure octanol [41]. These data suggest that any PFOS discharged to a water source would tend to remain in that medium, unless it is adsorbed onto particulate matter or assimilated by organisms. If PFOS does bind to particulate matter the material would ultimately end up in the sediment.

2.2 Other PFOS-related compounds

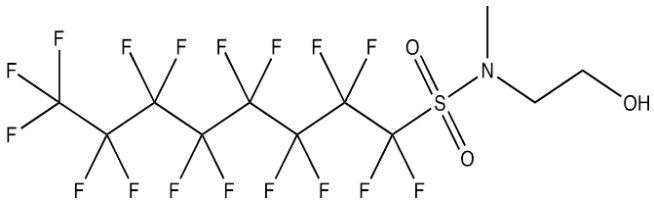
Other PFOS related compounds have been reported in water including perfluorooctanesulfonamide ethanols (FOSEs), other N-methyl and N-ethyl-perfluoroalkane sulfonamides (MeFOSA and EtFOSA), and and FOSA, the amide derivative of PFOS [42]. Their structural formula are displayed in Figure 2.



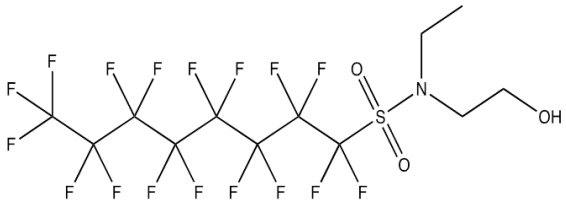
N-methyl perfluorooctane sulfonamide
MeFOSA



N-ethyl perfluorooctane sulphonamide
EtFOSA



N-methyl perfluorooctane sulfonamidoethanol
MeFOSE



N-ethyl perfluorooctane sulfonamidoethanol
EtFOSE

Figure 2: Molecular formula of PFOS related sulfonamides and sulfonamidoethanols.

The FOSEs and FOSAs have been shown to degrade abiotically [43, 44] to PFOS. FOSA has been the most widely measured PFOS precursor and shown to be important for studies with the goal of monitoring the concentrations of total PFOS precursors in the environment. It is particularly prominent in ocean waters but is generally less prominent in river and lake waters [5]. FOSA also appears to bind more strongly to particles [28]. During SPE extraction it is often separated from more polar PFASs and analysed in a separate injection to the LC-MS/MS. Given the potential complications of measuring FOSA *i.e.*, degradation during storage, possible loss during extraction, and binding to particles in natural waters,

inclusions of FOSA is not recommended for purposes of global monitoring for the Stockholm Convention.

PFOA is usually reported along with PFOS in monitoring of PFASs in water. However, PFOA is not produced from PFOS precursors and is not currently listed under the Stockholm Convention. Therefore it should not be reported for purposes of global monitoring. Furthermore there are analytical challenges associated with determination of PFOA such as much greater blank and laboratory contamination issues due to its presence in polytetrafluoroethylene (PTFE) containing products. Therefore side costs are associated with reporting PFOA as an additional analyte may be higher.

3 SETTING UP A MONITORING PLAN

3.1 General considerations

PFAS analysis in environmental samples has been ongoing for the last few decades with a wide range of quality. Recent developments, improvements, and trends in the ultra-trace determination of PFASs in environmental and human samples were recently reviewed and the remaining challenges and uncertainties were outlined and discussed [45]. Understanding the analytical implications of factor such as adsorption of PFASs to surfaces, effects of differing matrices, varying PFAS isomer response factors, potential bias effects of sampling, sample preparation, and analysis is critical to measuring highly fluorinated compounds at trace levels. These intricate analytical issues and the potential consequences of ignoring to deal with them correctly can significantly affect the results reported in this guidance. Important sampling and analytical aspects are highlighted to successfully set up a monitoring of PFOS in water and results experienced from interlaboratory comparisons are discussed.

In principle, the setup of a monitoring plan consists of three major parts; the planning, sampling and analysis (Figure 3). The different steps will be addressed separately with a discussion of the different aspects to consider before decisions are made.

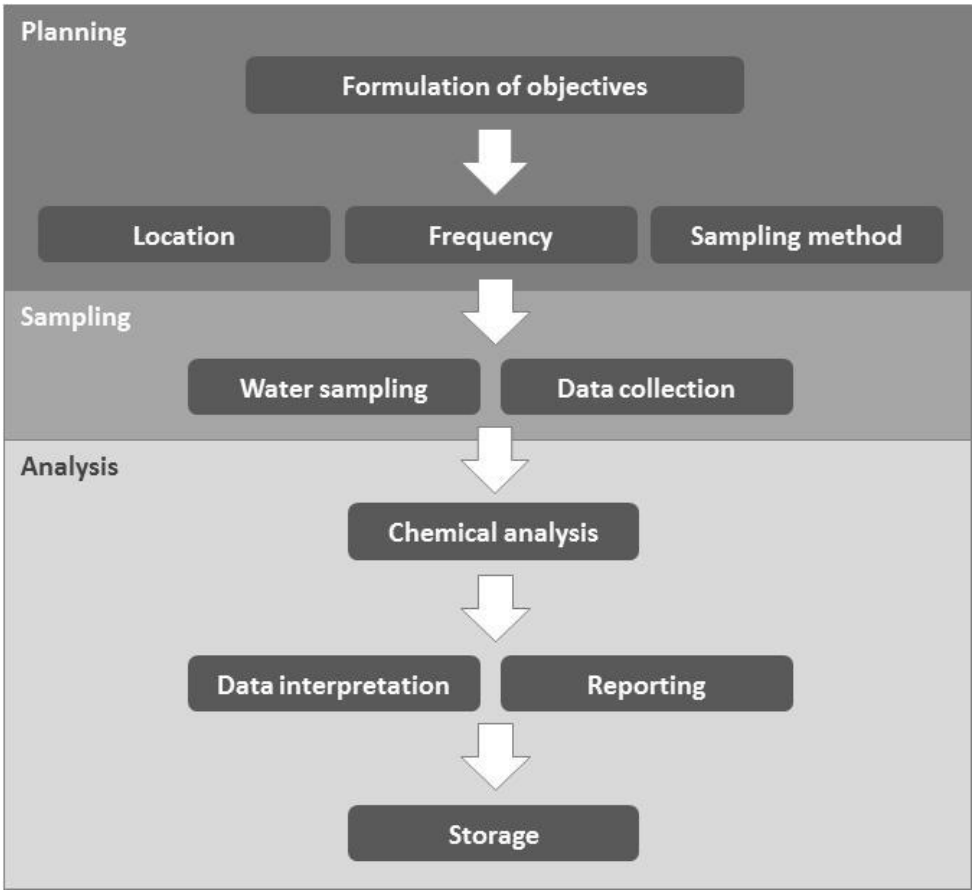


Figure 3: Steps included in the setup of a monitoring plan

3.2 Monitoring objectives

There are certain decisions to be made before a monitoring plan is set and those decisions should be formulated in a set of objectives. The basic aim of the monitoring for the Convention is to have a tool to measure the current state of the PFOS concentration in water globally, and to monitor temporal changes. The recommendations made here are based on those objectives. The monitoring can be used for internal purposes as well, and for that other objective may be added to the plan before execution.

GMP objectives:

- To determine the baseline levels of PFOS in water, caused by global dispersion/diffusion
- To monitor the temporal trends of PFOS concentrations as a result of actions following implementation of the Stockholm Convention provisions.

A range of objectives are discussed in the following text, addressing each issue that should be considered in order to optimise the monitoring plan for the executing member state.

4 SAMPLING CONSIDERATIONS AND GUIDELINES

4.1 Sampling location and matrices

Processes affecting water quality and their influence should be taken into account when sampling sites are selected. Selection of sampling sites requires consideration of the monitoring objectives and some knowledge of the geography of the water-course system, as well as of the uses of the water and of any discharges of wastes into it. Sampling sites can be marked on a map or an aerial photograph, but a final decision on the precise location of a sampling station can be made only after a field investigation.

It is strongly recommended to collaborate with local hydrologists, limnologists and geologists to optimally select the sampling sites. As much data as possible should be gathered, also considering the long term feasibility of the site; are alterations on the site planned (dams, drainage); will the surrounding of the site change (agricultural or city planning)?

For a global monitoring purpose different sampling characteristics could be selected with different aims;

a) Surface waters from remote lakes and upstream rivers which reflects ambient levels due to atmospheric depositions. Mountain snow would also meet that aim;
b) Surface waters from more populated areas (lakes, estuarine and marine waters) to measure ongoing spatial distribution and trends due to a combination of effluent discharge and atmospheric deposition;
c) Riverine surface waters downstream of populated areas and in tributaries to find point sources to which measurements could be taken;
d) Sediments in selected lakes and depositional areas of rivers and estuaries to follow time trends. Sediments may have the advantage of being less susceptible to environmental changes (*e.g.*, temperature, salinity, and mixings);
e) Biota (*e.g.*, fish) is an alternative matrix to reflect the contamination level of the surrounding water. Although, this matrix is not recommended for the global monitoring purpose as variations can be due to many aspects complicating the interpretation of the results. Levels can depend on for example organism size, age, seasonal variations and above all species selected for analysis. It is a challenge to find a representative species living at all sites of the monitoring program. Biota is measured for food safety reasons and food safety data can be included in the final interpretation for comparison.

Measuring PFOS in water sources present in remote areas results in baseline levels and reflects atmospheric concentrations, *i.e.*, inputs from precipitation and on airborne particles. Air measurements of PFOS and its precursors are covered in air monitoring programmes. It is therefore not recommended for a water monitoring purpose to select remote areas for the water monitoring programme. However, if the objectives of the water sampling project is to profile riverine concentrations it is wise to establish the prevailing baseline level upstream of populated areas.

Sampling of rivers can answer a wide range of objectives, ambient levels upstream, the influence of point sources such WWTP or industrial discharges, correlation to population density and contribution to lake and marine waters. It is therefore of great importance to establish the objectives before designing the monitoring and selecting the sites. Despite the potential value of data gathered from sediment samples the matrix is not recommended for national or global monitoring program as the sediment composition (particle size, organic matter, sedimentation rate) will vary significantly between different

environments and reduce the comparability of the data. The variety of the calculated log Koc in several different studies was reported to be large, from 2 to 6. Therefore, only monitoring the water phase will be further discussed.

Estuaries are interesting to select as monitoring site as they can represent what's entering along the whole river system. Changes over time could be used to evaluate measurements taken upstream, *e.g.*, improved WWTP cleaning processes, regulatory actions towards industry, *etc*. In addition, they represent the contribution to global marine levels of these persistent compounds. Sampling should be done during low tide to reduce the influence of marine waters. In some studies salinity has been shown to be an important parameter in controlling the sediment–water interactions and the fate of PFOS in estuarine waters, therefore parallel measurement of salinity is a prerequisite [46]. Sampling of estuaries can be logistically challenging and often upstream sites, located downstream of most sources are used [22, 31].

Sampling stations on rivers should, as a general rule, be established at places where the water is sufficiently well mixed for that only a single sample will be required (however a backup sample should be collected for confirmatory analysis when necessary). The lateral and vertical mixing of a wastewater effluent or a tributary stream with the main river can be rather slow, particularly if the flow in the river is laminar and the waters are at different temperatures. Complete mixing of tributary and main stream waters may not take place for a considerable distance, sometimes many kilometres, downstream of the confluence. However, if there is any doubt, the extent of mixing should be checked by measurements of temperature or some other characteristic variable at several points across the width of the river. There are standard operating procedures (SOP) for cross sectional sampling of rivers which should be followed [47] and European Commission developed a technical guidance document for the identification of mixing zones under Article 4 of the EQS Directive2008/105/EC under the Water Framework Directive 2000/60/EC [48].

Just as with rivers, lakes and reservoirs can be subject to several influences that cause water quality to vary from place to place and from time to time. It is, therefore, prudent to investigate that sampling stations are truly representative of the water body. Where feeder streams or effluents enter lakes or reservoirs there may be local areas where the incoming water has not yet mixed with the main water body. Isolated bays and narrow inlets of lakes are frequently poorly mixed and may contain water of a different quality from that of the rest of the lake. Wind action and the shape of a lake may lead to a lack of homogeneity; for example when wind along a long, narrow lake causes a concentration of algae at one end. The most important feature of water in lakes and reservoirs, especially in temperate zones, is vertical stratification, which results in differences in water quality at different depths. Temperature reading at different depths could hence be necessary.

There are detailed guidelines available describing all aspects regarding water sampling strategies [47]. After selection of objectives, sites and matrixes a sampling strategy should be formed in detail, advised by such documents. Parameters such as sampling depth, stratification layers, water flow and particulate matter *etc.* should be considered and excluded/included where appropriate. The US EPA also provides guidance for design of water quality monitoring programs in estuaries [49].

Recommendation for location of water sampling for PFOS analysis:

- Define the objectives of the project and the selected monitoring site.
- Gather hydrological and other relevant data (presence of industry and WWTP, population density, *etc.*).

- For monitoring purpose estuaries are recommended as sampling sites, but data from other sites are welcome and should have one of the following characteristics:
    - Estuary (see for US EPA for guidance on both small, discrete site (<10 km^2) and larger tidal rivers and bays [49])
    - 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.

4.2 Frequency

The sampling frequency has to be realistic in terms of number of samples (costs and logistics), but still represent a statistical validated set of samples for the monitoring purpose. Both the temporal and spatial sampling design need to have sufficient resolution. Grab samples of surface water samples could be used to see temporal and regional variations and the sampling frequency should be high enough to filter out short term variability (*e.g.*, precipitation events). In Table 4 recommended minimum and optimum frequencies are listed according to the "Water Quality Monitoring - A Practical Guide to the Design and Implementation of Freshwater Quality Studies and Monitoring Programmes" [47].

Sampling frequency at stations where water quality varies considerably should be higher than at stations where quality remains relatively constant. A new monitoring, however, with no advance information on quality variation, should be preceded by a preliminary survey and then begin with a fixed sampling schedule that can be revised when the need becomes apparent.

Table 4: Sampling frequency recommendations from WHO [47]

Baseline stations	**Goal**	**Frequency**
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

Recommendation for the frequency of the sampling of PFOS in water:

- 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- and 2 low-water stage, although avoiding drought conditions or freezing conditions)

4.3 Sampling equipment and method

Containers (sampling bottles, test tubes, vials, *etc.*) should be of high density polyethylene (HDPE) material to avoid sorption of PFOS to the material [45, 50]. If the goal is to include analyses of other PFAS compounds, PTFE material should be avoided (*e.g.*, it is often used to line the interior of samplers such as Niskin™, GoFlo™ bottles and tubing, as that is a source of PFOA and PFNA [51, 52]. To minimize contamination sources use the strategy of clean-hands/dirty hands while sampling, *i.e.*, be two persons taking the sample, one is holding the sample equipment (clean-hands) and one person does the sampling (dirty hands). Sample caps should also be checked to confirm that they have HDPE liners.

Sampling volume is determined by the analytical laboratory and should be adapted to expected PFOS levels and analytical capacities. The instrumental limit of detection is the main factor limiting the sensitivity and the volume should be enough to reach quantification levels.

A difference in the density of seawater between the upper and the lower layers can cause a significant difference in PFOS concentration depending on the sampling depth. This stratification of the water column changes with ambient temperature. In Tokyo bay, *e.g.*, was the lower density of the upper layer most pronounced in August, reflecting greater dilution of the salinity by freshwater from inflowing rivers and heating of the water's surface in warmer seasons [36]. The concentration of PFOS in the upper layer in Tokyo Bay was statistically significantly higher than in the lower layer. The main reason is that PFOS is enriched (possibly by orders of magnitude) in the surface layer compared to the bulk water due to its surfactant properties. Therefore it is important to always avoid sampling of the surface layer. Hence, use hand-dipping sampling at >10 cm below surface, and the sampling bottle should be opened below the surface to avoid the surface layer.

Direct sampling of 50 mL-500 mL of water is the most commonly used approach for PFAS analysis in water. Recently passive sampling has been investigated for polar compounds and the results have been satisfactory [53]. Passive samplers have an advantage of collecting time integrated samples which may be more representative of prevailing water concentrations. The major disadvantage is the complexity to determine the kinetics of the passive sampler material and design. In Table 5 some advantages and disadvantages are highlighted.

Table 5: Advantages (+) and disadvantages (-) of direct and passive sampling for PFASs in water (~ = no difference)

	Direct water sampling	**Passive water sampling**
Comparability of results worldwide	+	-
Achievement of a concentration (ng/L)	+	- (unless an equilibrium sampler can be developed, uptake rate is a difficult parameter)
Integrative sample	- (Direct sampling is highly sensitive to the water flow rate in case of a variable flow regime and to variable emissions in case of point sources)	+ (passive samplers 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 passive samplers requires more experience, but the 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 passive samplers requires planning/experience)
Problems of difficult weather conditions/vandalism	+ (Sampling site cannot be approached due to flooding/storms)	- (passive samplers can be lost due to flooding/storms or theft. A protected spot is required.)

It has been demonstrated that a modified POCIS (Polar Organic Chemical Integrative Sampler) with a weak anion exchange sorbent as a receiving phase could be used to determined PFOS and other PFASs in water [53]. They found linear uptake of PFOS over a 3-day period and were able to calculate PFOS concentrations in water from the sorbent−water sorption coefficient estimated from calibration experiments and the sampling rate. However the authors noted that the influence of temperature, pH, and salinity and the magnitude of K_{SW} also requires further study.

Development of passive sampling for PFAS are just starting and the advantages of passive sampling are presently "potential". Consequently direct water sampling is currently recommended for PFOS monitoring. This recommendation can be reviewed when methods for passive sampling become further mature.

Further, it is recommended to perform a pilot study at the sampling site to establish the expected PFOS levels. This will aid the analytical laboratory to determine the minimum sample intake needed for quantifiable results. In addition, a pilot study will help the executing personnel to test their sampling skills and identify possible sources of errors.

Recommendation for PFOS sampling method in water:

- Active/grab sampling is the recommended method.
- Use, *e.g.*, Niskin™ or other remotely activated water samplers, or simply hand-dipping.
- Avoid sampling the surface.
- For sampling use a 500 mL wide mouth HDPE bottle.
- Use HDPE sampling and storage containers (sampling bottles, test tubes, vials *etc.*).
- All material should be rinsed with methanol before usage.
- Analysis volume is typically 50 mL-500 mL and should 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.

4.4 Logistics and reporting

Use existing networks and data collected. For example the Pan-European study of emerging contaminants in river water which included measurements of PFOS [29] utilized existing monitoring networks and agencies in each member state [29].

There should be three to five countries within each region (to be selected by countries). Selection should be sensitive of geopolitical, as well as (socio-)economic aspects within region. UNEP should discuss with countries for sites' selection (*e.g.*, within UNEP/GEF GMP2 projects). However, the final sampling design will be left to scientists in the participating countries to decide about details on sites and depth, because we cannot anticipate all the different scenarios. Developing countries with no previous measurements of PFAS may need relatively remote baseline, yet representative and integrative data (although sometimes UNEP may also want to know what is happening next to contaminated sites, and sometimes want to capture local contributions or deposition).

When all planning is set the sampling can start. The logistics of a sampling exercise need to be well prepared. It is recommended to use existing networks and data collected to avoid double work. Investigate if existing programs (*e.g.*, air sampling programs) are collecting the data needed, and synchronize the sampling occasions to take advantage of personnel and expensive sampling equipment (*e.g.*, boats). The analysing laboratory shall supply the sampling personnel with pre-cleaned sampling equipment, detailed sampling instructions depending on their objectives, and the package to return the samples in a safe way.

Collected data shall be submitted, together with the analytical results to the GMP data warehouse (GMP DWH) according to instructions available on the web site (http://www.pops-gmp.org/index.php?pg=gmp1).

Salinity is good to measure in tributaries to see the influence of marine water. Since conductivity also expresses the ion (salt) content and is easily analysed this could be performed routinely at several water bodies. Therefore, conductivity should always be reported, whereas measurement of salinity is encouraged to be reported when available. Knowing the total suspended solid (TSS) measurements will allow to identify if elevated levels could be caused by a large TSS bound fraction or not. Hence, TSS should always be reported.

Minimum data to report is:

- Site ID code (generated by the GMP DWH once the site is added to the Site dictionary)
- 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

The above is the data asked for from the Convention is sufficient to be able to set the baseline PFOS concentration in the water bodies. However, it is possible to use other markers to indicate influences of other anthropogenic activities *e.g.*, waste water. Sucralose or caffeine have been measured for that purpose [54-57]. This information is not influencing the PFOS data but can be useful to identify sources, and to determine mixture zones *etc*. It is common to try to gather as much data as possible to explain eventual extreme data. This collection need to be put into relation to costs and effectiveness.

Recommendation for reporting of PFOS analysis in water:

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

5 ANALYSIS

The SOP for water analysis of PFOS is in detail described in the guidance document compiled by UNEP GEF [38].

5.1 Pre-treatment

Filtration before extraction is not recommended since the filter may absorb PFASs or be a source of contamination. In addition, PFOS can be associated with the suspended particulate matter as well as in the dissolved phase [27]. For research purposes the separation and analysis of the dissolved and particulate phase can be relevant to understand the distribution of the compound, transport mechanisms and the risk level of the available fraction. For monitoring purpose it is recommended to avoid filtration to analyse the total PFOS concentration in the water column. Although for spatial as well as temporal changes it is necessary to have the same sample all the time, and as the TSS content will vary causing variability it is important to always report the TSS content with the monitoring data.

In addition, filtration adds a step to the procedure and could both contaminate as also alter the result due to partial absorbance to the filter material.

However, to prevent clogging of the SPE column it might be necessary to perform a filtration for samples with high suspended solid content. In such case, it should be noted that only the dissolved fraction of PFASs has been determined. In addition, the filter could also be extracted and analyzed separately.

It is very important to fortify the samples with the Internal Standard (IS) directly after being sampled, to cover for any losses due to sample handling (bottle material sorption, handling, transport and other treatments). Let the sample and IS equilibrate for about a month before analysis, to make sure the IS has properly partitioned to the particle or dissolved phase. General rules for QA/QC during sampling and sample transport are given in the document ISO 5667-14:2014 [58].

As the PFOS can be unevenly distributed in the sample it is recommended to use the whole sample from one bottle for analysis. The solvent used for elution of PFOS from the SPE should be used to rinse the bottle, and then added to the SPE. If not the whole sample is being used for analysis it is important to

rigorously shake the sample container before subsamples are taken out, to avoid non-homogenous sample solution.

See UNEP protocol for further details on the PFOS analysis procedure [38].

Recommendation for PFOS 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.

5.2 Extraction

The most common extraction method used is solid phase extraction (SPE). The suspended solids will be collected on the column and large amount of suspended solids could be clogging the column, preventing further sample extraction and cause problems with elution of the column. This problem is not expected to be major and if possible, sample sites or sample occasions should be avoided where TSS concentration is very high. The SPE combines extraction and clean-up of the water sample. The two major types of SPE columns used are the WAX column and the HLB columns which are both mixed-mode columns including ion-exchange functionalities.

HLB is an all-purpose, strongly hydrophilic column, and the divinyl benzene based sorbent is ideal for acidic, basic and neutral analytes. HLB SPE columns are appropriate for the determination of all PFAAs and neutral PFASs. WAX is a mixed-mode, reversed-phase/weak anion-exchange column and used to retain and release strong acids and is the recommended column for PFOS analysis.

Recommendation for PFOS extraction of water:

- Use WAX SPE column for extraction and clean up

5.3 Chemical analysis

For PFAS determination it is strongly recommended to use liquid chromatography-tandem mass spectrometry (LC-MS/MS) instrumentation with the capacity to determine qualifying and quantifying ions. Instruments such as a LC with quadrupole Time-of-Flight (Q-TOF) or quadrupole ion trap (Q-Trap) detectors are also suitable. A Fourier Transform Ion Cyclotron Resonance (FTICR) MS instrument (*e.g.,* orbitrap) can be interfaced to a linear ion trap to produce daughter ions. Liquid chromatography with single stage low-resolution MS instrumentation should not be used.

For LC-MS/MS identification 1 precursor ion and 2 daughter ions are requested [59]. One daughter ion is *m/z* 80, which is the sulfonate group leaving the fluorinated carbon chain and the sulfite ion is used for quantification. The Qualifier is the $F\text{-}SO_3^-$ anion *m/z* 99 and both the quantifier and qualifier (Table 6) are the same for the linear and the branched PFOS isomers. To quantify the branched PFOS it is recommended to use both m/z 80 and 99 as quantifiers take the average concentration for the two values, as one is commonly overestimating and the other underestimating the concentration when using MS/MS and the linear isomer as external calibration standard.

Table 6. The mass over charge (m/z) of the precursor and product ions of PFOS and the labelled internal standard.

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. For example, the sodium salt (PFOS-Na) molecular weight is 522.11 g/mol and the M-Salt is 499.12. Hence, a correction factor of 0.96 should be applied when standard solutions are weighted and diluted.

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.

5.3.1 Linear and branched isomers

The linear and branched PFOS isomers should be separated for individual quantification (Figure 4). It is recommended to report both types of isomers, *i.e.*, linear PFOS (L-PFOS) and total PFOS (linear and branched). L-PFOS is generally well separated from branched isomers and quantifying in separately more reliable data. However total PFOS should also be reported because much of the published literature for PFOS in water includes just the single value. Analytical standards are available for L-PFOS but not for all branched isomers. Furthermore branched isomers are difficult to separate and have different response factors which leads to higher uncertainties of analysis. The ratio of linear vs branched isomers differs significantly between samples. Monitoring the linear isomer offers a good basis to predict branched isomers as well, as they have the same source.

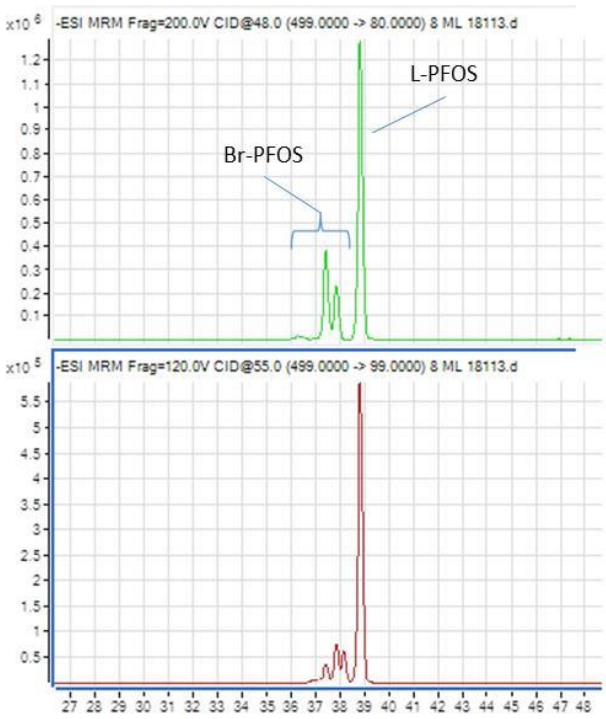


Figure 4: The chromatogram of linear and branched PFOS

5.3.2 Quality control

For quality control purposes, include a blank consisting of all materials and reagents used. Purified laboratory water, *e.g.*, MilliQ™ or distilled water can be used but should be confirmed to be free of PFASs. Typically lab purified waters are not good blanks due to presence of low level PFAS contamination. There are no certified reference materials yet available for PFOS in water. If possible use an internal reference water obtained via an interlaboratory study. Note that these settings apply to both linear and branched isomers. Contamination, usually from PFOA is also encountered LC instruments due to presence of PTFE tubing or fittings. It can be minimized with a pre-column installed prior to the injection port.

The gradient and mass spectrometer settings are dependent of the LC-MS/MS system and on the type of columns used. Those settings should be optimized for the in-house instruments and columns. Final results (using in ng/mL) should be corrected for the blank levels (ng/mL) prior to calculating concentrations (ng/L). Instrumental and procedural blank concentrations should be less than 10% of the concentrations found in environmental samples for reliable quantification [60].

Recommendation for PFOS 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.

6 INTERLABORATORY ASSESSMENTS

As a consequence of the increasing number of reports confirming the world-wide distribution of PFASs the demand for qualitative and quantitative environmental occurrence data is requested for accurate risk assessments. For several years, the quality of data obtained was a major issue of concern [61]. Problems identified in the quantification were the limited availability of high quality and mass labelled standards, severe matrix effects and interferences, the occurrence of branched PFAS isomers in industrial materials and samples, and blank problems due to contamination from laboratory ware and instrumentation. To improve the analytical quality of the PFAS determination in food and environmental samples several international interlaboratory assessments have been organized. This is an efficient way to establish the laboratories' credibility and to support improvement of the quality of data reported.

This was reflected in the unsatisfactory results obtained in the 1st interlaboratory study conducted in 2004/2005 on human and environmental matrices [62]. Meanwhile, a large number of high quality standards became commercially available, as well as a wide range of mass labelled internal standards. A follow-up study on water and fish showed that accurate and precise analysis of PFASs in water and fish is feasible if several critical steps in the analysis are properly addressed, *e.g.*, the use of high quality native standards and multiple mass labelled internal standards [63]. Precise and accurate results were obtained because all participants used the mass labelled internal standards that were provided in that study. The 3rd interlaboratory study on PFASs was organized to assess if the level of performance could be maintained [64]. Despite recommendations, many laboratories used only a limited number of mass-labeled standards. For PFOS, specifically, significant amounts of branched isomers present in the water samples appeared to be a significant source of variation, due to calibration procedures being based on only the linear isomer. Also, some results reported might have been based on the concentration of the PFOS salts rather than on the anion.

A 5th interlaboratory study conducted in 2011 focused on clear instructions regarding sources of errors and reporting demands, although participating laboratories were free to use their own in-house methods, *i.e.*, extraction, clean-up and analysis methods. The results showed that the built-up experience of the participants has improved the analytical quality over the last decades [65]. The majority of the laboratories obtained satisfactory z-scores for drinking water (50%-71%). The analyte levels in the matrix were low in that study, often close to LOQ, which reflected real-life scenarios but also increased the difficulty to perform accurate analysis. Several sources of errors were identified and methods to avoid them were suggested. The 6th interlaboratory study organized in 2013 showed similar results as the 5th ILS regarding the water analysis [66]. Again, the PFOS concentration was low which challenged the analytical performance. Throughout all interlaboratory studies on PFAS around 30 laboratories world-wide have participated, with a dominant representation of Europe. The analytical performance needs to be established in a larger number of laboratories covering all continents.

The latest interlaboratory study demonstrates the most commonly applied extraction and analytical method for PFOS analysis in water today [66]. Solid phase extraction (SPE), which combines extraction and a clean-up step for the water samples was used by 90% of the participants. The two major types of SPE columns used are the WAX column and the HLB column. The remaining laboratories used no or minor pre-treatment of the sample before analysis. The majority of the laboratories used LC-QQQ- MS

(LC-MS/MS). The instructions to report the perfluoroalkane sulfonic acids (PFSAs) on anion base and not on a salt basis helped to improve the accuracy of the reported results, and guidelines should contain clear instructions regarding this. Moreover, typically participants quantify against a standard consisting of only the linear alkane isomer. The branched alkane isomers have different response factors when using MS/MS detection than the linear isomers [67], which could bias the results observed. This problem is limited when the isomer profile in a sample is dominated by the linear PFOS, but in the drinking water used in this ILS the branched isomers constituted ca 40% of the total PFOS.

The Japanese Industrial Standards (JIS) committee plays a central role in the standardization activities in Japan, and as a part of that a protocol for the analysis of PFOS and PFOA in water was formed. Three ILS have been conducted (2006, 2008 and 2009) following that protocol (ISO 25101) and the results reported were satisfactory [60]. The ILS 2011 and the JIS methods are compared in Annex 2, together with the UNEP suggested PFOS analysis in water approach.

Meanwhile the 2nd UNEP interlaboratory assessment, performed in 2012/2013, has included PFOS and other PFASs for the first time [68]. The results are summarized as follows

- More than 30 laboratories submitted results for the PFAS compounds but these were only from Asia and WEOG indicating that still very little or no capacity is available in Africa, CEE and GRULAC.
- The results for the standard solution were excellent, showing a CV of less than 10% for PFOS in these two regions. Results for the sediment were also good, with CV values of 15% and 17% for Asia and WEOG, respectively. The results for the fish samples for PFOS were also promising for both regions (WEOG, CV = 10%, n = 10; Asia, CV = 19%, n = 9).
- The limited results for the mothers' milk sample were good for Asia (CV = 13%, n = 3), but not satisfactory for WEOG (CV = 72%, n = 5) due to one outlier.
- The results for the fortified air extract were good for WEOG (CV = 13%, n = 5), and although only three results were submitted for PFOS for Asia, the variation was relatively large (CV = 81%). In both regions, less than two results for the precursor compounds were submitted and no further regional evaluation was performed for these compounds.
- For the PFAS compounds, water and human blood serum samples were sent for testing. In total, 13 laboratories reported for the human blood serum sample and 25 for the water sample. For the human blood serum, the results were somewhat disappointing in both regions, with a relatively large variation in both Asia (CV = 37%, n = 4) and WEOG (CV = 25%, n = 4) for PFOS. The results for the water sample were excellent for Asia for PFOS (CV = 7%, n = 10) but not satisfactory for WEOG (CV = 38%, n = 10).
- Most laboratories did not report all PFAS compounds and no sum of PFAS compounds was included in the reporting file. When using the sum of PFASs the results are clearly not as good for individual compounds as, for example, for PFOS.

7 FURTHER CONSIDERATIONS

This guide has not included step by step procedures for the extraction and quantification analysis of PFOS in water. Additional information is provided in the guidance document on the GMP for persistent organic pollutants [1]. Step by step procedure for the determination of PFOS in water is found in the protocol from the PFOS in water working group [38] and ISO 25101 (2009). It should be noted that the ISO method has a limit of quantification of 10 ng L^{-1} for PFOS, whereas many environmental samples especially for marine waters typically contain concentrations at pg L^{-1} range. Nevertheless, sample size and analytical standard calibrations can be adjusted to achieve lower detection limits.

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ANNEX 1 – RECOMMENDATION FOR PFOS MONITORING IN WATER

- Define the objectives of the project and the selected monitoring site.
- Gather hydrological and other relevant data (presence of industry and WWTP, population density, *etc.*).
- For monitoring purpose estuaries are recommended as sampling sites, but data from other sites are welcome and should have one of the following characteristics:
    - Estuary (see for US EPA for guidance on both small, discrete site (<10 km^2) and larger tidal rivers and bays [49])
    - 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.
- 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- and 2 low-water stage, although avoiding drought conditions or freezing conditions)
- Active/grab sampling is the recommended method.
- Use *e.g.*, Niskin™ or other remotely activated water samplers, or simply hand-dipping.
- Avoid sampling the surface.
- For sampling use a 500 mL wide mouth HDPE bottle.
- Use HDPE sampling and storage containers (sampling bottles, test tubes, vials *etc.*).
- All material should be rinsed with methanol before usage.
- Analysis volume is typically 50-500 mL and should 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 to be reported:
    - Site ID code (generated by the GMP DWH once the site is added to the Site dictionary)
    - 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
- Investigate existing monitoring programs and collaborate for data collection and at sampling occasions.
- Provide the Convention with the minimum data set asked for

- 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.
- Use WAX SPE column for extraction and clean up
- 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.

ANNEX 2 – TWO INTERLABORATORY STUDY RESULTS AND THE RECOMMENDED ANALYTICAL METHODOLOGY FOR PFOS DETERMINATION IN WATER SAMPLES

	JIS 2009 [60]	4th ILS 2011 [65]	Recommended method
Method	ISO 25101 acc. JIS	In-house methods	UNEP/GMP Monitoring guidance
Sample volume	500 mL surface water	<500 mL drinking water	100 mL-500 mL
Sample pre-treatment	Filtration	Homogenization	Homogenization
Extraction technique	SPE (OASIS WAX Waters), pre-conditioned with 4 mL of 0.1% ammonia/ methanol, 4 mL methanol and 4 mL water.	SPE (WAX 32%, HLB 23% and 32% unspecified SPE)	SPE (OASIS WAX Waters), pre-conditioned with 4 mL of 0.1% ammonia/methanol, 4 mL methanol and 4 mL water.
Extraction and clean-up	After sample is added to the SPE column, rinse with 4 mL acetate buffer (pH 4). Discard the eluate and centrifuge the column to absolute dryness. Extract was eluted with 4 mL methanol and 4 mL 0.1% ammonia/methanol.	Different between participants	After sample is added to the SPE column, rinse with 4 mL acetate buffer (pH 4) and 8 mL THF:MeOH (75:25). Discard the eluate and let the column dry. Extract was eluted with 4 mL methanol with 0.1% ammonia.
LC-Column	Different between participants	Almost everyone used C_{18} column of different origins.	C_{18} column
LC/MS(MS)	Different between participants	The majority of the laboratories used LC - QQQ- MS (LC-MS/MS) (53%), and a few laboratories used Q-trap (13%), Orbitrap (7%) or a different LC-MS method.	Multiple MS acquisition Two transitions per analyte
Mass labeled standards	Yes (Wellington commercial)	All participants used mass labeled internal standards but not for all target compounds	Yes
Target compounds	PFCA (C_4-C_{18}) and PFSA (C_4-C_{10}) and FOSA	PFCA (C_4-C_{14}) and PFSA (C_4-C_{10}), FOSA and 6:2 FTS	Linear-PFOS and total-PFOS