



# CEMP Guideline on the analysis of PFASs in seawater

(OSPAR Agreement 2010-8)<sup>1</sup>

## Contents

1. Introduction.....	2
2. Analytes .....	3
3. Sampling, transportation and storage.....	5
4. Sample preparation .....	5
4.1 Pre-treatment .....	5
4.2 Extraction .....	5
5. Instrumental analysis.....	6
5.1 Liquid chromatography.....	6
5.2 Detection methods .....	6
6. Calibration and quantification.....	8
6.1 Standards .....	8
6.2 Calibration and quantification .....	8
7. Quality Assurance and Quality Control .....	8
8. Data Reporting.....	9
9. References.....	9

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# Analysis of PFASs in seawater

## 1. Introduction

Per- and polyfluoroalkyl substances (PFASs) are man-made chemicals and ubiquitous in the environment (Giesy and Kannan, 2001). PFASs are widely used as processing additives during fluoropolymer production and as surfactants in consumer applications, including surface coatings for carpets, furniture and paper products. They are also components in breathable, waterproof fabrics, fire-fighting foams and insulators for electric wires (Kissa, 2001). From the production and use of these products, PFASs can be released into the environment (Ahrens, 2011).

In this document, the name PFASs refers to compounds with a hydrophilic functional group and a hydrophobic fully fluorinated chain which can vary in chain length. The perfluorinated acids have moderate water solubilities, low  $pK_a$  values and are therefore dissociated at environmentally relevant pH values (Kissa, 2001). Polyfluorinated sulfonamides and fluorotelomer alcohols (FTOHs) are neutral compounds with a moderate vapour pressure currently discussed as precursors to perfluorooctane sulfonic acid (PFOS) and perfluorocarboxylic acids (PFCAs) (Ellis *et al.*, 2004). Some 100–200 PFOS-precursors have been identified (KEMI 2006, Buck *et al.* 2011).

PFOS, perfluorooctanoic acid (PFOA) and other per- and polyfluoroalkyl substances (PFASs) are considered global environmental contaminants. PFOS and PFOA are chemically and biologically inert and very stable (Poulsen *et al.* 2005). PFOS meets the P (persistent) and vP (very persistent) criteria due to very long half-lifetimes. PFOS is also bioaccumulative (B) and toxic (T) (OSPAR 2005). PFOA is considered as very persistent (vP) and toxic (T), but not bioaccumulative (Van der Putte *et al.* 2010). Both have the capacity to undergo long-range transportation.

A method for the determination of PFOS and PFOA in unfiltered water is already described in the International Standard ISO 21675 (ISO 21675, 2019). The objective of this technical annex is to provide advice on the analysis of PFASs in water based on ISO 25101:2009 and ISO 21675:2019.

This guideline focusses on the sampling, extraction, instrumental analysis and quantification of PFASs from seawater and is based on previous guidelines for PFAS analysis in water (Ahrens *et al.*, 2010; ISO 21675:2019). The extraction and preconcentration of the PFASs is a crucial step in the procedure as the expected concentrations in seawater are often only in the  $pg\ L^{-1}$  range. Extraction and enrichment are usually conducted through solid phase extraction (SPE).

This guideline is not intended as a complete laboratory manual. If necessary, guidance should be sought from specialised laboratories. Laboratories should demonstrate validity of each methodological step. Moreover, use of an alternative method, carried out concurrently to the routine procedure, is recommended for validation.

Contracting parties should follow the OSPAR monitoring guideline but minor deviations from this are acceptable if the method achieves comparable results. Validation of the adopted method needs to be performed on the relevant matrix and concentration range e.g. by taking part in inter-comparison studies or proficiency testing schemes.

## 2. Analytes

Table 1 provides an overview of PFASs that are environmentally relevant in water and provides information on chemical names, acronyms, formula, and Chemical Abstracts Service (CAS) numbers, as well as suggestions for suitable isotopically labelled internal standards for use in PFAS analysis.

The individual compounds belong to the following compound groups: perfluoroalkyl sulfonates (PFSAs), perfluoroalkyl carboxylates (PFCAs), perfluorooctane sulfonamides (FOSAs), perfluorinated sulfinates (PFSiAs) and perfluorooctane sulfonamidoacetic acids (FOSAAs). For monitoring purposes, the chemicals PFOS, PFOA, C<sub>4</sub>-C<sub>12</sub> PFCAs, C<sub>4</sub>, C<sub>6</sub>, C<sub>8</sub> PFSAs and FOSA are considered to be the most important PFASs. Although most studies have focused on PFOS and PFOA because they are high volume chemicals, it is suggested that PFAS with shorter carbon chain lengths should also be included in the analysis, in particular perfluorobutanoate sulfonate (PFBS) and perfluorobutanoic acid (PFBA), the short-chain substitutes of PFOS and PFOA, should preferentially be monitored due to their good water solubility and their use as substitutes for PFOS in various applications.

**Table 1** Full names, acronyms, formulas and Chemical Abstract System (CAS) numbers of native and mass-labelled PFASs relevant for environmental analysis

Analyte	Acronym	Formula	CAS <sup>a</sup> -Number
Perfluorobutanoic acid	PFBA	C <sub>3</sub> F <sub>7</sub> COOH	375-22-4
Perfluoropentanoic acid	PFPA	C <sub>4</sub> F <sub>9</sub> COOH	2706-90-3
Perfluorohexanoic acid	PFHxA	C <sub>5</sub> F <sub>11</sub> COOH	307-24-4
Perfluoroheptanoic acid	PFHpA	C <sub>6</sub> F <sub>13</sub> COOH	375-85-9
Perfluorooctanoic acid	PFOA	C <sub>7</sub> F <sub>15</sub> COOH	335-67-1
Perfluorononanoic acid	PFNA	C <sub>8</sub> F <sub>17</sub> COOH	375-95-1
Perfluorodecanoic acid	PFDA	C <sub>9</sub> F <sub>19</sub> COOH	335-76-2
Perfluoroundecanoic acid	PFUnDA	C <sub>10</sub> F <sub>21</sub> COOH	4234-23-5
Perfluorododecanoic acid	PFDoDA	C <sub>11</sub> F <sub>23</sub> COOH	307-55-1
Perfluorotridecanoic acid	PFTriDA	C <sub>15</sub> F <sub>25</sub> COOH	72629-94-8
Perfluorotetradecanoic acid	PFTeDA	C <sub>13</sub> F <sub>27</sub> COOH	376-06-7
Perfluorobutanoate sulfonic acid	PFBS	C <sub>4</sub> F <sub>9</sub> SO <sub>2</sub> OH	29420-49-3 (potassium salt)
Perfluoropentane sulfonic acid	PFPeS	C <sub>5</sub> F <sub>11</sub> SO <sub>2</sub> OH	2706-91-4
Perfluorohexane sulfonic acid	PFHxS	C <sub>6</sub> F <sub>13</sub> SO <sub>2</sub> OH	3871-99-6 (potassium salt)
Perfluoroheptane sulfonic acid	PFHpS	C <sub>7</sub> F <sub>15</sub> SO <sub>2</sub> OH	375-92-8
Perfluorooctane sulfonic acid	PFOS	C <sub>8</sub> F <sub>17</sub> SO <sub>2</sub> OH	1763-23-1 (sodium salt) 2795-39-3 (potassium salt)

Analyte	Acronym	Formula	CAS <sup>a</sup> -Number
Perfluoro-1-decanesulfonic acid	PFDS	C <sub>10</sub> F <sub>21</sub> SO <sub>2</sub> OH	13419-61-9 (sodium salt)
6:2 perfluorooctane sulfonic acid	6:2 FTSA	C <sub>6</sub> F <sub>13</sub> C <sub>2</sub> H <sub>4</sub> SO <sub>3</sub> H	27619-97-2
Perfluorooctane sulfonamide	FOSA	C <sub>8</sub> F <sub>17</sub> SO <sub>2</sub> NH <sub>2</sub>	754-91-6
<b>Internal Standards</b>			
Perfluoro-n-(1,2,3,4- <sup>13</sup> C <sub>4</sub> )butanoic acid	[ <sup>13</sup> C <sub>4</sub> ]-PFBA	[2,3,4- <sup>13</sup> C <sub>3</sub> ]F <sub>7</sub> <sup>13</sup> COOH	n.a.
Perfluoro-n-(1,2- <sup>13</sup> C <sub>2</sub> )hexanoic acid	[ <sup>13</sup> C <sub>2</sub> ]-PFHxA	C <sub>4</sub> F <sub>9</sub> [2- <sup>13</sup> C]F <sub>2</sub> <sup>13</sup> COOH	n.a.
Perfluoro-n-[1,2,3,4- <sup>13</sup> C <sub>4</sub> ]octanoic acid	[ <sup>13</sup> C <sub>4</sub> ]-PFOA	C <sub>4</sub> F <sub>9</sub> [2,3,4- <sup>13</sup> C <sub>3</sub> ]F <sub>6</sub> <sup>13</sup> COOH	n.a.
Perfluoro-n-(1,2,3,4,5,6,7,8- <sup>13</sup> C <sub>8</sub> )octanoic acid	[ <sup>13</sup> C <sub>8</sub> ]-PFOA	(2,3,4,5,6,7,8- <sup>13</sup> C <sub>7</sub> )F <sub>15</sub> <sup>13</sup> COOH	n.a.
Perfluoro-n-[1,2,3,4,5- <sup>13</sup> C <sub>5</sub> ]nonanoic acid	[ <sup>13</sup> C <sub>5</sub> ]-PFNA	C <sub>4</sub> F <sub>9</sub> [2,3,4,5- <sup>13</sup> C <sub>4</sub> ]F <sub>8</sub> <sup>13</sup> COOH	n.a.
Perfluoro-n-[1,2- <sup>13</sup> C <sub>2</sub> ]decanoic acid	[ <sup>13</sup> C <sub>2</sub> ]-PFDA	C <sub>8</sub> F <sub>17</sub> <sup>13</sup> CF <sub>2</sub> <sup>13</sup> COOH	n.a.
Perfluoro-n-[1,2- <sup>13</sup> C <sub>2</sub> ]undecanoic acid	[ <sup>13</sup> C <sub>2</sub> ]-PFUnDA	C <sub>9</sub> F <sub>19</sub> <sup>13</sup> CF <sub>2</sub> <sup>13</sup> COOH	n.a.
Perfluoro-n-[1,2- <sup>13</sup> C <sub>2</sub> ]dodecanoic acid	[ <sup>13</sup> C <sub>2</sub> ]-PFDoDA	C <sub>10</sub> F <sub>21</sub> <sup>13</sup> CF <sub>2</sub> <sup>13</sup> COOH	n.a.
Perfluoro-n-[1,2- <sup>13</sup> C <sub>2</sub> ]tetradecanoic acid	[ <sup>13</sup> C <sub>2</sub> ]-PFTeDA	C <sub>12</sub> F <sub>25</sub> <sup>13</sup> CF <sub>2</sub> <sup>13</sup> COOH	n.a.
Perfluoro-1-hexane[ <sup>18</sup> O <sub>2</sub> ]sulfonate	[ <sup>18</sup> O <sub>2</sub> ]-PFHxS	C <sub>6</sub> F <sub>13</sub> S[ <sup>18</sup> O <sub>2</sub> ]O <sup>-</sup>	n.a.
Perfluoro-1-[1,2,3,4- <sup>13</sup> C <sub>4</sub> ]octanesulfonate	[ <sup>13</sup> C <sub>4</sub> ]-PFOS	C <sub>4</sub> F <sub>9</sub> [1,2,3,4- <sup>13</sup> C <sub>4</sub> ]F <sub>8</sub> SO <sub>2</sub> O <sup>-</sup>	n.a.
Perfluoro-1-(1,2,3,4,5,6,7,8- <sup>13</sup> C <sub>8</sub> )octanesulfonate	[ <sup>13</sup> C <sub>8</sub> ]-PFOS	(1,2,3,4,5,6,7,8- <sup>13</sup> C <sub>8</sub> )F <sub>17</sub> SO <sub>2</sub> O	n.a.
6:2 fluorotelomer sulfonate (1,2- <sup>13</sup> C <sub>2</sub> )	[ <sup>13</sup> C <sub>2</sub> ]-6:2 FTSA	(1,2- <sup>13</sup> C <sub>2</sub> )C <sub>6</sub> H <sub>4</sub> F <sub>13</sub> SO <sub>3</sub> <sup>-</sup>	n.a.
Perfluoro-1-(1,2,3,4,5,6,7,8- <sup>13</sup> C <sub>8</sub> )octanesulfonamide	[ <sup>13</sup> C <sub>8</sub> ]-FOSA	(1,2,3,4,5,6,7,8- <sup>13</sup> C <sub>8</sub> )F <sub>17</sub> SO <sub>2</sub> NH <sub>2</sub>	n.a.
<sup>a</sup> , Chemical Abstract System; n.a., not available			

### 3 Sampling, transportation and storage

The sampling should be carried out by trained personnel being aware of the risk of contamination of samples if incorrectly handled. It is recommended to take, preserve and handle samples as specified in ISO 5667-1. Materials and clothes that contain, or may adsorb, fluorinated compounds, such as polytetrafluoroethylene (PTFE), must be avoided during sampling and sample processing. In particular, the containers that come into direct contact with the sample must not contain any fluorinated polymers (e.g. PTFE). Containers and equipment made of polypropylene (according to ISO 25101:2009), polyethylene, glass, or stainless steel shall be checked for possible background contamination before use. Especially glass and polypropylene sampling and storage containers should be carefully checked for PFASs, as longer chained PFASs tend to sorb to glass walls, and cleaned before use (e.g. the sample container or filtration equipment must be rinsed with a polar solvent, such as methanol and dried before use) in order to minimise contamination. Every material that may come into contact with the sample must be free of fluorinated compounds. The highest contamination risk was observed for PFOA and perfluorononanoic acid (PFNA; Theobald *et al.*, 2007).

The use of intermediate sample tubes and vials should be limited in the overall process to avoid contamination or loss by sorption (ISO 21675, 2019).

### 4. Sample preparation

#### 4.1 Pre-treatment

In general, samples can be analysed without pre-treatment (ISO 21675, 2019). In case that the samples are filtered prior to extraction to remove suspended particulate matter (SPM), the possible risk of sorption to the filter material (e.g. glass fibre filter (GFFs) must be taken into account and checked for by quality control measures. It is important to sonicate the sample for approximately 5 min before filtration, to minimise the sorption of PFASs to the sample container wall. As flat-bed filters have a very limited capacity, the use of coiled glass fibre filter is recommended for filtration of volumes larger than 10 L and water samples with high amounts of suspended matter. A pump is necessary to force the water through the filter. Due to the additional steps, this operation affords a number of additional quality control measures (adsorption losses, contamination problems) as the filtration equipment may be a source of contamination (Ahrens *et al.*, 2009b; Arp and Goss, 2009). After filtration, the equipment should be rinsed with a polar solvent and the sample should be spiked with a mass-labelled internal standard (IS) mixture at concentrations close to the environmental level in order to correct for losses during extraction and concentration, and for matrix effects during analysis.

#### 4.2 Extraction

Large-volume injection can be used to analyse PFAS directly without sample pre-treatment (Schultz *et al.*, 2006) if concentrations in the samples are high enough with the advantage that no further clean-up is required and eluates may be analysed directly or after being concentrated to ~ 1 mL.

The extraction of PFAS from seawater samples with low concentration is carried out using solid phase extraction (SPE) according to the ISO 21675 method.

## 5. Instrumental analysis

An injection standard (InjS) can be added to the final extract for correction of the injection volumes and calculation of the recoveries of the mass-labelled IS. The InjS should not occur in environmental samples, hence, the use of a mass-labelled InjS is suggested.

The solvent composition of the final extract should correspond to the mobile phase of the liquid-chromatography (LC) method in order to obtain a satisfactory peak shape of the compounds, in particular of early eluting short-chain PFASs. Unless the samples are analysed immediately, the vials should be kept at < 4°C in the dark and analysed within one week. It is important to sonicate and vortex the vials before analysis to minimise the sorption of PFASs to the vial wall.

Instrumental analysis of PFAS in aquatic matrices has not changed substantially in the past decade. HPLC-MS/MS is still most widely used, although some studies used HRMS such as Orbitrap- or time-of-flight (TOF)-MS for quantitative and qualitative analyses (Nakayama et al., 2019). Since most target PFAS are anionic, MS is generally operated in ESI-negative mode (Hansen et al., 2001; Berger and Haukas, 2005). For neutral PFAS, atmospheric pressure chemical ionisation (APCI) and atmospheric pressure photo ionisation (APPI) have also been tested (Ayala-Cabrera et al. 2018).

Alternatively, gas chromatography coupled with mass spectrometry (GC/MS), with derivatisation of the ionic PFCs, can be used, which has the advantage of resolving isomers (Chu & Letcher, 2009).

### 5.1 Liquid chromatography

Modifications of the instrument might be necessary to minimise contact with fluorine-containing materials (Yamashita *et al.*, 2004). A scavenger cartridge can be installed between the pump and injector to trap contaminants originating from the degasser, connecting tubes and the mobile phase.

The C8 or C18 reversed-phase columns may be used for the LC separation of PFAS. The use of a guard column is recommended in order to maintain chromatographic performance and extend the lifetime of the chromatographic column. To reduce interference derived from the aqueous solvent, the use of a PFAS trapping column is highly recommended (Stone et al. 2010).

To overcome separation problems (e.g. co-eluting matrix compounds), it may be helpful to use reversed-phase columns with polar groups instead of C8 or C18 columns. Mixtures of water and either methanol or acetonitrile can be used as the mobile phase, in each case with 2 – 10 mM ammonium acetate as an ionisation aid. Gradients ranging from 10 % to 100 % methanol or acetonitrile are required for the separation of the compounds listed in Table 1. To ensure stability of retention times, the use of a temperature-controlled column oven is recommended.

### 5.2 Detection methods

The most widely used technique for detection of PFASs is tandem MS (MS/MS) operated in the MRM mode. Mass spectrometry parameters, such as collision energy, clustering potential, and cone voltage, must be optimised for each individual compound and each instrument. Typical precursor and product ions are given in Table 2 and in ISO 21675.

**Table 2** Selected diagnostic ions used in the determination of PFASs

Analyte	Precursor ion (m/z)	Product ion (m/z)	Product ion (m/z)
PFBA	213	169	
PFPA	263	219	69
PFHxA	313	269	119
PFHpA	363	319	169
PFOA	413	369	169
PFNA	463	419	219
PFDA	513	469	219
PFUnDA	563	519	269
PFDoDA	613	569	269
PFTriDA	663	619	269
PFTeDA	713	669	369
PFBS	299	80	99
PFPeS	350	80	99
PFHxS	399	80	99
PFHpS	449	80	99
PFOS	499	80	99
PFDS	599	80	99
6:2 FTSA	427	407	81
FOSA	498	78	169
[ <sup>13</sup> C <sub>4</sub> ]-PFBA	217	172	
[ <sup>13</sup> C <sub>2</sub> ]-PFHxA	315	270	119
[ <sup>13</sup> C <sub>4</sub> ]-PFOA	417	372	169
[ <sup>13</sup> C <sub>5</sub> ]-PFNA	468	423	219
[ <sup>13</sup> C <sub>2</sub> ]-PFDA	515	470	219
[ <sup>13</sup> C <sub>2</sub> ]-PFUnDA	565	520	269
[ <sup>13</sup> C <sub>2</sub> ]-PFDoDA	615	570	269
[ <sup>13</sup> C <sub>2</sub> ]-PFTeDA	715	670	369
[ <sup>18</sup> O <sub>2</sub> ]-PFHxS	403	84	103
[ <sup>13</sup> C <sub>4</sub> ]-PFOS	503	80	99
[ <sup>13</sup> C <sub>8</sub> ]-PFOS	507	80	99
[ <sup>13</sup> C <sub>2</sub> ]-6:2 FTSA	429	409	81
[ <sup>13</sup> C <sub>8</sub> ]-FOSA	506	78	172

Analyte	Precursor ion (m/z)	Product ion (m/z)	Product ion (m/z)
[ <sup>13</sup> C <sub>8</sub> ]-PFOA	421	376	172

## 6. Calibration and quantification

### 6.1 Standards

The use of commercially available standards with a purity of > 99% is recommended. Suggestions for mass-labelled IS are given in Table 1. It is strongly recommended to use IS for PFAS-analysis, to compensate for signal enhancement/suppression or losses during sample preparation. If possible, the corresponding mass-labelled IS should be used for each target analyte. In case a mass-labelled standard is not available, an IS with physicochemical characteristics and recovery rates similar to that of the target compound can be used but matrix suppression/enhancement effects must first be checked in LC-ESI-MS/MS (for further details see ISO 25101). When using a PFAS standard solution of mixed isomers, it should be determined whether the nominal concentration corresponds to the linear PFAS or to the total amount of isomers (Kaupmees & Rebane, 2017; see also section 6.2).

### 6.2 Calibration and quantification

The calibration and quantification should be carried out using the method of internal standard according to the ISO 21675 method. In case of matrix effects, standard addition may be an alternative calibration option.

Some PFASs show more than one peak in the chromatogram, which is due to the presence of branched isomers. The ratio of linear to branched isomers can differ between the calibration standard and environmental samples. If the peak area of the branched isomer exceeds 10 % of that of the linear isomer, it is recommended to estimate its concentration based on the response factor of the linear standard.

The PFCAs and PFSAAs are almost completely dissociated in environmental matrices. If salts are used for the preparation of calibration standards, quantification results should be calculated for the corresponding acids.

## 7. Quality Assurance and Quality Control

Prior to the analysis of environmental samples, the method should be subject to a full in-house validation according to the requirements of the monitoring programme. This should include the determination of limits of detection, limits of quantification, trueness, precision, linearity of calibration, measurement uncertainty and robustness (for further details see ISO 21675).

Within each sample batch, at least one sample should be extracted in duplicate and a laboratory control sample should be included, and the results recorded in control charts.

Laboratories should demonstrate their competence by participation in laboratory proficiency testing schemes relevant for the monitoring programme. Such exercises for seawater are still rarely offered by proficiency testing providers, but two interlaboratory studies aiming at method validation



demonstrated acceptable performance of laboratories in analysing PFASs in water/seawater (van Leeuwen *et al.*, 2009; ISO 21675, 2019).

## 8. Data Reporting

For routine analysis, the data report should be in accordance with the relevant monitoring program; it should e.g. include information about sampling, sample processing, storage and analysis, and results reported along with the associated measurement uncertainty (estimated using ISO 11352:2012). Estimation should be based on within-laboratory reproducibility, data from proficiency tests, industry reference material (IRM), and, when available, certified reference material (CRM).

## 9. References

- Ahrens, L., Vorkamp, K., Lepom, P., Bersuder, P., Theobald, N., Ebinghaus, R., Bossi, R., Barber, J. L., McGovern, E. 2010. Determination of perfluoroalkyl compounds in water, sediment, and biota. ICES Techniques in Marine Environmental Sciences No. 48. 16 pp.
- Ahrens, L. 2011. Polyfluoroalkyl compounds in the aquatic environment: A review of their occurrence and fate. *J Environ Monitor.* 13, 20–31.
- Ahrens, L., Plassmann, M., Xie, Z., and Ebinghaus, R. 2009. Determination of polyfluoroalkyl compounds in water and suspended particulate matter in the River Elbe and North Sea, Germany. *Frontiers of Environmental Science and Engineering in China*, 3: 152 – 170.
- Arp, H. P. H., and Goss, K-U. 2009. Gas/particle partitioning behavior of perfluorocarboxylic acids with terrestrial aerosols. *Environmental Science and Technology*, 43: 8542 – 8547.
- Ayala-Cabrera, J.F., Javier Santos F. and Moyano E. (2018). Negative-ion atmospheric pressure ionisation of semi-volatile fluorinated compounds for ultra-high-performance liquid chromatography tandem mass spectrometry analysis. *Anal. Bioanal. Chem.*, 410 (2018), pp. 4913-4924, 10.1007/s00216-018-1138-z
- Berger, U.; Langlois, I.; Oehme, M.; Kallenborn, R. Comparison of three types of mass spectrometer for high-performance liquid chromatography/ mass spectrometry analysis of perfluoroalkylated substances and fluorotelomer alcohols. *Eur. J. Mass. Spectrom.* 2004, 10, 579-588.
- Berger, U.; Haukas, M. Validation of a screening method based on liquid chromatography coupled to high-resolution mass spectrometry for analysis of perfluoroalkylated substances in biota. *J. Chromatogr. A* 2005, 1081, 210-217.
- Buck, R.C., Franklin, J., Berger, U., Conder, J.M., Cousins, I.T., de Voogt, P., Jensen, A.A., Kannan, K., Mabury, S.A., van Leeuwen, S.P.J 2011. Perfluoroalkyl and Polyfluoroalkyl Substances in the Environment: Terminology, Classification, and Origins. *Integr Environ Assess Manag.* 2011 Oct; 7(4): 513–541.
- Chu, S., and Letcher, R. J. 2009. Linear and branched perfluorooctane sulfonate isomers in technical product and environmental samples by in-port derivatization – gas chromatography – mass spectrometry. *Analytical Chemistry*, 81: 4256 – 4262.

- Ellis, D. A.; Martin, J. W.; Mabury, S. A.; De Silva, A. O.; Hurley, M. D.; Sulbaek Anderson, M. D.; Wallington, T. J. Degradation of fluorotelomer alcohols: A likely atmospheric source of perfluorinated carboxylic acids. *Environ. Sci. Technol.* 2004, 38, 3316-3321.
- Giesy, J. P.; Kannan, K. Global distribution of perfluorooctane sulfonate in wildlife. *Environ. Sci. Technol.* 2001, 35, 1339-1342.
- Hansen, K. J.; Clemen, L. A.; Ellefson, M. E.; Johnson, H. O. Compound-specific, quantitative characterisation of organic fluorochemicals in biological matrices. *Environ. Sci. Technol.* 2001, 35, 766-770.
- International Standards Organisation, Water quality - Determination of perfluorooctanesulfonate (PFOS) and perfluorooctanate (PFOA) - Method for unfiltered samples using solid phase extraction and liquid chromatography/mass spectrometry, ISO 25101, 2009.
- International Standards Organisation, Water quality - Determination of perfluoroalkyl and polyfluoroalkyl (PFAS) in water - Method using solid phase extraction and liquid chromatography/mass spectrometry (LC-MS/MS), ISO 21675, 2019.
- International Standards Organisation, Water quality - Estimation of measurement uncertainty based on validation and quality control data, ISO 11352:2012
- Kaupmees, S., Rebane, R. 2017. Analysis and validation of perfluorinated compounds in water, sediment and fish with LCESI-MS/MS. *International Journal of Environmental Analytical Chemistry*, Vol. 97, No. 8, 695–709. <https://doi.org/10.1080/03067319.2017.1356922>.
- KEMI 2006. Perfluorinated substances and their uses in Sweden. Swedish Chemical Agency (KEMI) Report 7/06. 58 pp.
- Kissa, E. *Fluorinated Surfactants and Repellents*. Marcel Dekker 2001, 97.
- Nakayama, S. F., Yoshikane, M., Onoda, Y., Nishihama, Y., Iwai-Shimada, M., Takagi, M., Kobayashi, Y., Isobe, T. 2019. Worldwide trends in tracing poly- and perfluoroalkyl substances (PFAS) in the environment. *Trends in Analytical Chemistry*, Vol. 121, 115410 <https://doi.org/10.1016/j.trac.2019.02.011>.
- Powley, C. R.; George, S. W.; Ryan, T. W.; Buck, R. C. Matrix effect-free analytical methods for determination of perfluorinated carboxylic acids in environmental matrixes. *Anal. Chem.* 2005, 77, 6353-6358.
- Schultz, M. M., Barofsky, D. F., and Field, J. A. 2006. Quantitative determination of fluorinated alkyl substances by large-volume-injection liquid chromatography tandem mass spectrometry-characterisation of municipal wastewaters. *Environmental Science and Technology*, 40: 289 – 295.
- Stone, P.K.W., Cote, L., Gushue, J., Letcher, R.J., Chu S. 2010. Agilent App. Note, 5990
- Theobald, N., Gerwinski, W., Caliebe, C., and Haarich, M. 2007. Development and validation of a method for the determination of polyfluorinated organic substances in sea water, sediments and biota. Occurrence of these compounds in the North and Baltic Seas. *Umweltforschungsplan des Bundesministeriums für Umwelt, Naturschutz, und Reaktorsicherheit, Forschungsbericht 202 22 213, UBA-FB 00 001409*. 133 pp. (in German, with English abstract)

van Leeuwen, S. P. J.; Swart, C.P.; de Boer, J. Significant improvements in the analysis of perfluorinated compounds in water and fish: results from an interlaboratory method evaluation study. *J. Chromatogr. A*, 2009, 1216, 401-409.

Van der Putte, I., Murin, M., Van Velthoven, M., Affourtit, F. 2010. Analysis of the risks arising from the industrial use of Perfluorooctanoic acid (PFOA) and Ammonium Perfluorooctanoate (APFO) and from their use in consumer articles. Evaluation of the risk reduction measures for potential restrictions on the manufacture, placing on the market and use of PFOA and APFO. RPS Advies B.V. 82 pp. + annexes.

Yamashita, N.; Kannan, K.; Taniyasu, S.; Horii, Y.; Okazawa, T.; Petrick, G.; Gamo, T. Analysis of perfluorinated acids at parts-per-quadrillion levels in seawater using liquid chromatography-tandem mass spectrometry. *Environ. Sci. Technol.* 2004, 38, 5522-5528.