Guidance for Per- and Polyfluoroalkyl Substances: Analytical

The Minnesota Pollution Control Agency (MPCA) intends to update the information within this per- and polyfluoroalkyl substances (PFAS) guidance document as new information becomes available. Users of this PFAS guidance are encouraged to visit the https://www.pca.state.mn.us/about-mpca/mpca-quality-system to access the current version of this document. See the MPCA Quality System webpage for the sampling guidance document.

PFAS are emerging contaminants composed of thousands of human-made, fluorinated organic chemicals. The actual number of compounds is continuously changing, as some PFAS are no longer produced in the United States due to regulatory and voluntary actions, while new ones are created as alternatives. Phased-out PFAS still exist in the environment, human bodies, and some products due to their extreme environmental persistence, presence in waste streams, and ongoing global production.

Purpose and objectives

This document is intended for use by laboratories, project managers and MPCA staff who generate, review or report PFAS data to the MPCA. The purpose of this document is to provide:

- MPCA data quality objectives.
- Consistency and data quality.
- Guidance to laboratories, MPCA staff, and contractors.

General PFAS analysis

Analytical methods are still evolving but the MPCA recommends that a multi-laboratory verified matrix appropriate method is used. Laboratories must incorporate the data quality objectives in this document if an approved method is unavailable or not followed. Laboratories and methods accredited by the Minnesota Department of Health Laboratory Accreditation Program can be found (MNELAP Accredited laboratories). The performance-based criteria included in this guidance document outlines specific quality processes for sample preparation, instrument calibration, and analysis when working with PFAS.

Isotope Dilution Analysis (IDA)

Isotope dilution technique involves quantitation of a compound of interest using a labeled isotope of that very compound. A variety of isotopically labeled analogs are added to each sample prior to extraction, or prior to analysis when extraction isn't required. The isotopically labeled analogs, sometimes referred to as surrogates or as extracted internal standard analytes, function from a data usability standpoint as both a surrogate standard (calculation of the recovery of the standard) and as an internal standard (used in the calculation of the target compounds). Include isotope analog recovery (IS, MS, etc.) for each sample and analyte in the data report. Analog recoveries need to be within 100 $\pm$ 30% and corrective action processes should be followed for ongoing failures. Analogs are added to samples prior to preparation and/or analysis depending on the sample matrix; for example:

- Aqueous samples: added to samples prior to extraction.
- Solid samples and biota: added after homogenization and subsampling, prior to addition of water or extraction solvent.
- Serial dilution: Aqueous film forming foam (AFFF) and other foams: added after final dilution

Instrument and analyte identification

The analytical technique of choice for PFAS is liquid chromatography - mass spectrometry - mass spectrometry (LC/MS/MS). Quantify analytes by comparing the product ion of one precursor ion and retention time in samples to calibration standards. Additional product ions and their ion ratios can be used to distinguish analytes from matrix interference. It is recommended that branched standards are used when available, PFBA and PFPeA are exceptions. Use the ion transition recommendations below when monitoring for two or more ion transitions from parent to characteristic product ions. Ion transition ratio criteria should be determined based on information obtained from standards and used to detect potential bias in sample results.

Ion Transitions:

- PFOA: 413 → 369, 413 → 319, 413 → 269
- PFOS: 499 → 80, 499 → 99, 499 → 130
- PFHxS: 399 → 80, 399 → 99, 399 → 130
- PFBS: 299 → 80, 299 → 99, 299 → 130
- 4:2FTS: 327 → 307
- 6:2FTS: 427→ 407
- 8:2FTS: 527 → 507
- N-EtFOSAA:584 → 419
- NMeFOSAA:570 → 419

Quantitate samples by integrating the total response, accounting for peaks that are identified as linear and branched isomers. Sum the different transitions. Documentation of the primary and confirmation transitions is required. If these transitions are not used, the reason must be technically justified and documented.

Interferences

Laboratories must have a process to limit and log cross-contamination as PFAS could be found in laboratory items such as polytetrafluoroethylene products (PTFE), solvent lines, aluminum foil, and methanol, which could lead to method interferences and elevated baselines in chromatograms. Laboratory equipment and supplies that contact samples should be analyzed and contain less than 1/3 the method reporting limit for each PFAS method analyte and isotope performance standards.

Standards

Certified analytical standards when available are required. Products vary in purity and isomer profiles that can compromise accuracy, precision and reproducibility of data. Linear and branched isomers are not available for all analytes. Standards must be stored in glass ampules following manufacturer's directions on storage and shelf life for stock and working standards. Investigate stability of prepared analytical standards as some PFAS analytes form methyl esters over time in methanolic solutions.

Perfluoroalkyl carboxylic acids (PFCAs) including perfluorooctanoic acid (PFOA) have been widely recognized as persistent environmental contaminants. For accurate quantification of PFCAs, their stability in calibration solutions is important because they are criteria of quantification. Stability studies indicate that no methyl esters (perfluorooctanoate MePFOA, and methyl formate) were detected in methanol solutions immediately after preparation. MePFOA was detected in calibration solutions stored around 4 months and increased with increase in methyl formate. PFCAs including PFOA should be used immediately after preparation when methanol is used as a solvent.

Calibration

Mass calibration is done once or twice a year or as described by manufacturer. Analytical calibration curves should be run at the beginning of each day. The calibration curve should contain six, but preferably 8-10, non-zero calibration standards containing a consistent amount of stable isotope internal standards. Select the simplest curve fit possible. A linear curve fit is not likely due to the nature of PFAS. The lowest calibration point must be at or below the method reporting limit. Run appropriate blanks with the calibration curve. A calibration verification (ICV) from a source separate from the calibration standard must be analyzed after each calibration curve and before sample analyses can begin. Calibration curves should be evaluated against its regression analysis and standards equal to or less than the method reporting limit should be within ± 50% of the true value. All other calibration points should be within ± 30% of the true value.

Continuing calibration verifications (CCV) must be run prior to sample analysis, after every 10 field samples, and after the analytical sequence. The calibration acceptance criteria must be within 100 ± 30% of true known value. A standard at the method reporting limit must be analyzed prior to each analytical batch to document the instrument's ability to accurately quantitate down to the method reporting limit concentration. The acceptance criteria for the method reporting limit verification is 100 ± 30% of true known value. If these criteria are not met, the method reporting limit has been set too low and must be confirmed again at a higher concentration.

Calibration criteria for methods using isotope dilution must calibrate with the isotopically labeled analogs of the analytes. Laboratories must include the isotope analog recoveries for each sample and analyte in data reports, including the calibration curve data.

Instrument blanks

The ubiquitous nature of PFAS makes it critical to analyze instrument blanks to determine if the instrument is potentially affected by PFAS concentrations. Instrument blanks must be analyzed after highest calibration standard and daily prior to sample analysis. The concentration of each analyte must be ≤ ½ the method reporting limit. Method blanks must be PFAS-free, indicating each analyte must be ≤ 1/3 the method reporting limit.

Quality control samples

Recommended QA samples for PFAS analysis:

- Method blanks- two per batch of field samples, not to exceed 20 field samples. Same media as associated field samples and undergoes same sample prep. Each analyte must be ≤ 1/3 the method reporting limit.
- Instrument blank- minimum of 1 prior to start of daily analysis and after samples exceeding quantitation range. Must contain internal standards. Solvent
- Sample duplicate (DUP) - minimum 1 per batch of 20 field samples or fewer.
- Lab control spike (LCS) - In triplicate at 3 levels per analytical batch (low, medium, high). LCS must contain all project specific PFAS analytes in same media as associated samples. The recovery acceptance for each method analyte is 100 ± 30% and the percent relative standard deviation (RSD) of the recoveries ≤ 30%.
- Matrix spike and Matrix spike duplicate (MS/MSD) - one pair prepared with each analytical batch. The recovery acceptance for each analyte is 100 ± 30% and the RSD is ≤ 30%.

Representation sample

The following is recommended to ensure a representative sample/subsample is used for analysis:

- Use the entire sample for solid phase extraction (SPE) of aqueous samples.
- Sample filtration is not recommended with high particulate samples because retention of PFAS onto SPE filters is likely.

- Samples can be centrifuged to reduce sample particulate. This is not recommended unless target analyte absorption has been investigated.
- High PFAS concentrations can overload SPE cartridge capacity. Serial dilutions are recommended for known high concentration samples, such as AFFF.
- Homogenize soil samples prior to subsampling. SPE is not ideal for soil extraction.
- Cleanup procedures must be done on associated batch QC samples (method blank, lab control samples) if matrix interferences occur. PFAS loss may occur when extracts are evaporated to dryness or at temperatures greater than 30oC.

Dilutions

When isotope dilution samples require a dilution, the volume of the diluent contains the same concentration of labeled isotope compounds as what was originally spiked into the sample. The isotope recovery results from the initial analysis should not be used to adjust the data from the secondary dilution analysis.

When non-isotope dilution analyses require a dilution, quantitate target compounds and surrogates relative to internal standards. Note results are from a dilution on the final report. These results are not recovery-corrected.

Method reporting limits

Method reporting limits are based upon performance based method criteria and performance base instrument criteria and how they behave in each individual laboratory. Each lab has their own equipment and levels of background contamination. Below is a table of compounds broken up into different groups includes reporting limit goals the MPCA would like to work towards however, they may not be achievable for all compound or by all laboratories.

Compound	CAS number	Group	Aqueous RL goals (ng/L)	Solid RL goals (ng/L)	*Biota RL goals (ng/L)
Carboxylic Acids (C_4-C_{12} common acids)		Group 1			
Perfluorobutanoic acid (PFBA)	375-22-4	Group 1	5-10	5-10	10
Perfluoropentanoic acid (PFPeA)	2706-90-3	Group 1	5	5	10
Perfluorohexanoic acid (PFHxA)	307-24-4	Group 1	5	5	10
Perfluoroheptanoic acid (PFHpA)	375-85-9	Group 1	5	5	10
Perfluorooctanoic acid (PFOA)	335-67-1	Group 1	5	5	10
Perfluorononanoic acid (PFNA)	375-95-1	Group 1	5	5	10
Perfluorodecanoic acid (PFDA)	335-76-2	Group 1	5	5	10
Perfluoroundecanoic acid (PFUnA)	2058-94-8	Group 1	5	5	10
Perfluorododecanoic acid (PFDoA)	307-55-1	Group 1	5	5	10
Carboxylic Acids (C_{13}-C_{18} less common acids)		Group 3			
Perfluorotridecanoic Acid (PFTrA)	72629-94-8	Group 3	5	5	10
Nonafluoro-3,6-dioxaheptanoic acid (NFDHA)	151772-58-6	Group 3	5	5	10
Perfluoro-3-methoxypropanoic acid (PFMPA)	377-73-1	Group3	5	5	10
Perfluoro-4-methoxybutanoic acid (PFMBA)	863090-89-5	Group 3	5	5	10
Perfluorotetradecanoic acid (PFTeA)	376-06-7	Group 3	5	5	10

Compound	CAS number	Group	Aqueous RL goals (ng/L)	Solid RL goals (ng/L)	*Biota RL goals (ng/L)
Perfluorohexadecanoic acid (PFHxDA)	67905-19-5	Group 3	5	5	10
Perfluorooctadecanoic acid (PFODA)	16517-11-6	Group 3	5	5	10
Sulfonates (C_4-C_{12} common sulfonates)		Group 2			
Perfluorobutanesulfonic acid (PFBS)	375-73-5	Group 2	5	5	10
Perfluoropentanesulfonic acid (PFPeS)	2706-91-4	Group 2	5	5	10
Perfluorohexanesulfonic acid (PFHxS)	355-46-4	Group 2	5	5	10
Perfluoroheptanesulfonic Acid (PFHpS)	375-92-8	Group 2	5	5	10
Perfluorooctanesulfonic acid (PFOS)	1763-23-1	Group 2	5	5	10
Perfluorononanesulfonic acid (PFNS)	474511-07-4	Group 2	5	5	10
Perfluorodecanesulfonic acid (PFDS)	335-77-3	Group 2	5	5	10
Perfluorododecanesulfonic acid (PFDoS)	79780-39-5	Group 2	5	5	10
Perfluoro(2-ethoxyethane)sulfonic acid (PFEESA)	113507-82-7		5	5	10
Amides		Group 4			
Perfluorooctane Sulfonamide (FOSA)	754-91-6	Group 4	10	10	20
N-methyl perfluorooctane sulfonamidoacetic acid (NMeFOSAA)	2355-31-9	Group 4	10	10	20
N-ethyl perfluorooctane sulfonamidoacetic acid (NEtFOSAA)	2991-50-6	Group 4	10	10	20
Telomer Sulfonic Acids		Group 5			
4:2 Fluorotelomer sulfonic acid (4:2 FTSA)	757124-72-4	Group 5	10	10	20
6:2 Fluorotelomer sulfonic acid (6:2 FTSA)	27619-97-2	Group 5	10	10	20
8:2 Fluorotelomer sulfonic acid (8:2 FTSA)	39108-34-4	Group 5	10	10	20
8:2 Fluorotelomer alcohol (8:2 FTOH)	678-39-7	Group 5	10	10	20
8:2 Fluorotelomer unsaturated carboxylic acid (8:2 FTUCA)	70887-84-2	Group 5	10	10	20
8:2 Polyfluoroalkyl phosphate diester (8:2 diPAP)	678-41-1	Group 5	10	10	20
4:2 Fluorotelomer sulfonic acid (4:2 FTSA)	757124-72-4	Group 5	10	10	20
10:2 Fluorotelomer sulfonic acid (10:2 FTSA)	120226-60-0	Group 5	10	10	20
N-Methyl perfluorooctane sulfonamidoethanol (N-MeFOSE)	24448-09-7				
N-Ethyl perfluorooctane sulfonamidoethanol (N-EtFOSE)	1691-99-2				
N-Methyl perfluorooctane sulfonamide (MeFOSA)	31506-32-8				

Compound	CAS number	Group	Aqueous RL goals (ng/L)	Solid RL goals (ng/L)	*Biota RL goals (ng/L)
N-Ethyl perfluorooctane sulfonamide (EtFOSA)	4151-50-2				
N-methyl perfluorooctanesulfonamidoacetic acid (NMeFOSAA)	2355-31-9				
N-ethyl perfluorooctanesulfonamidoacetic acid (NEtFOSAA)	2991-50-6				
Decafluoro-4-(pentafluoroethyl) cyclcohexanesulfonic acid (PFecHS)					
2-perfluorohexyl ethanoic acid (FHEA)					
2-perfluorooctyl ethanoic acid (FOEA)					
2-perfluorodecyl ethanoic acid (FDEA)					
2H-perfluoro-2-decenoic acid (FOUEA)					
3-perfluoroheptyl propanoic acid (FHpA)	812-70-4				
2H-perfluoro-2-octenoic acid (FHUEA)					
2,3,3,3-tetrafluoro-2-(heptafluoropropoxy) propanoate ($CF_3CF_2CF_2OCF(CF_3)COO^-NH_4^+$ (Gen-X)	62037-80-3				
11-chloroeicosafluoro-3-oxaundecane-1-sulfonic acid (11CL-PF3OUdS)	763051-92-9				
2-(6-Chloro-1,1,2,2,3,3,4,4,5,5,6,6-dodecafluorohexoxy)-1,1,2,2-tetrafluoroethanesulfonate (9Cl-PF3ONS)	73606-19-6				
3H-Perfluoro-3-[(3-methoxy-propoxy) propanoic acid] (ADONA)	919005-14-4				
Hexafluoropropylene oxide dimer acid (HFPO-DA)	13252-13-6				
9-Chlorohexadecafluoro-3-oxane-1-sulfonic acid (9Cl-PF3ONS)	756426-58-1				
3- Perfluoropropyl propanoic acid (3:3FTCA)	356-02-5				
2H,2H,3H,3H-Perfluorooctanoic acid (5:3FTCA)	914637-49-3				

*Biota reporting limits will depend on the biota sampled. Biota can cause matrix enhancement and greatly increase the method reporting limits.