

Citation and Page Number	Current Text	Corrected Text	Date
Footnotes	None	¹ TOP Assay analysis of highly contaminated samples, such as those from an AFFF (aqueous film-forming foam) site, can result in incomplete oxidation of the samples and an underestimation of the total perfluoroalkyl substances. ² The movement of PFAS in the environment is being aggressively researched at this time; that research will eventually result in more accurate models for the behaviors of these chemicals. In the meantime, DEC has calculated the soil cleanup objective for the protection of groundwater using the same procedure used for all other chemicals, as described in Section 7.7 of the Technical Support Document (http://www.dec.ny.gov/docs/remediation_hudson_pdf/techsuppdoc.pdf).	9/15/2020
Additional Analysis, page 9	In cases... soil parameters, such as Total Organic Carbon (EPA Method 9060), soil...	In cases... soil parameters, such as Total Organic Carbon (Lloyd Kahn), soil...	1/8/2021
Appendix A, General Guidelines, fourth bullet	List the ELAP-approved lab(s) to be used for analysis of samples	List the ELAP- certified lab(s) to be used for analysis of samples	1/8/2021
Appendix E, Laboratory Analysis and Containers	Drinking water samples collected using this protocol are intended to be analyzed for PFAS by ISO Method 25101.	Drinking water samples collected using this protocol are intended to be analyzed for PFAS by EPA Method 537, 537.1, 533, or ISO Method 25101	1/8/2021
Water Sample Results Page 9	<p>“In addition, further assessment of water may be warranted if either of the following screening levels are met:</p> <p>a. any other individual PFAS (not PFOA or PFOS) is detected in water at or above 100 ng/L; or</p> <p>b. total concentration of PFAS (including PFOA and PFOS) is detected in water at or above 500 ng/L”</p>	Deleted	6/15/2021

Sampling, Analysis, and Assessment of Per- and Polyfluoroalkyl Substances (PFAS) Under NYSDEC's Part 375 Remedial Programs

Objective

New York State Department of Environmental Conservation's Division of Environmental Remediation (DER) performs or oversees sampling of environmental media and subsequent analysis of PFAS as part of remedial programs implemented under 6 NYCRR Part 375. To ensure consistency in sampling, analysis, reporting, and assessment of PFAS, DER has developed this document which summarizes currently accepted procedures and updates previous DER technical guidance pertaining to PFAS.

Applicability

All work plans submitted to DEC pursuant to one of the remedial programs under Part 375 shall include PFAS sampling and analysis procedures that conform to the guidelines provided herein.

As part of a site investigation or remedial action compliance program, whenever samples of potentially affected media are collected and analyzed for the standard Target Analyte List/Target Compound List (TAL/TCL), PFAS analysis should also be performed. Potentially affected media can include soil, groundwater, surface water, and sediment. Based upon the potential for biota to be affected, biota sampling and analysis for PFAS may also be warranted as determined pursuant to a Fish and Wildlife Impact Analysis. Soil vapor sampling for PFAS is not required.

Field Sampling Procedures

DER-10 specifies technical guidance applicable to DER's remedial programs. Given the prevalence and use of PFAS, DER has developed "best management practices" specific to sampling for PFAS. As specified in DER-10 Chapter 2, quality assurance procedures are to be submitted with investigation work plans. Typically, these procedures are incorporated into a work plan, or submitted as a stand-alone document (e.g., a Quality Assurance Project Plan). Quality assurance guidelines for PFAS are listed in Appendix A - Quality Assurance Project Plan (QAPP) Guidelines for PFAS.

Field sampling for PFAS performed under DER remedial programs should follow the appropriate procedures outlined for soils, sediments or other solids (Appendix B), non-potable groundwater (Appendix C), surface water (Appendix D), public or private water supply wells (Appendix E), and fish tissue (Appendix F).

QA/QC samples (e.g. duplicates, MS/MSD) should be collected as specified in DER-10, Section 2.3(c). For sampling equipment coming in contact with aqueous samples only, rinsate or equipment blanks should be collected. Equipment blanks should be collected at a minimum frequency of one per day per site or one per twenty samples, whichever is more frequent.

Analysis and Reporting

As of October 2020, the United States Environmental Protection Agency (EPA) does not have a validated method for analysis of PFAS for media commonly analyzed under DER remedial programs (non-potable waters, solids). DER has developed the following guidelines to ensure consistency in analysis and reporting of PFAS.

The investigation work plan should describe analysis and reporting procedures, including laboratory analytical procedures for the methods discussed below. As specified in DER-10 Section 2.2, laboratories should provide a full Category B deliverable. In addition, a Data Usability Summary Report (DUSR) should be prepared by an independent, third party data validator. Electronic data submissions should meet the requirements provided at: <https://www.dec.ny.gov/chemical/62440.html>.

DER has developed a *PFAS Analyte List* (Appendix F) for remedial programs to understand the nature of contamination at sites. It is expected that reported results for PFAS will include, at a minimum, all the compounds listed. If lab and/or matrix specific issues are encountered for any analytes, the DER project manager, in consultation with the DER chemist, will make case-by-case decisions as to whether certain analytes may be temporarily or permanently discontinued from analysis at each site. As with other contaminants that are analyzed for at a site, the *PFAS Analyte List* may be refined for future sampling events based on investigative findings.

Routine Analysis

Currently, New York State Department of Health's Environmental Laboratory Approval Program (ELAP) does not offer certification for PFAS in matrices other than finished drinking water. However, laboratories analyzing environmental samples for PFAS (e.g., soil, sediments, and groundwater) under DER's Part 375 remedial programs need to hold ELAP certification for PFOA and PFOS in drinking water by EPA Method 537, 537.1, ISO 25101, or Method 533. Laboratories should adhere to the guidelines and criteria set forth in the DER's laboratory guidelines for PFAS in non-potable water and solids (Appendix H - Laboratory Guidelines for Analysis of PFAS in Non-Potable Water and Solids). Data review guidelines were developed by DER to ensure data comparability and usability (Appendix H - Data Review Guidelines for Analysis of PFAS in Non-Potable Water and Solids).

LC-MS/MS analysis for PFAS using methodologies based on EPA Method 537.1 is the procedure to use for environmental samples. Isotope dilution techniques should be utilized for the analysis of PFAS in all media. Reporting limits for PFOA and PFOS in aqueous samples should not exceed 2 ng/L. Reporting limits for PFOA and PFOS in solid samples should not exceed 0.5 µg/kg. Reporting limits for all other PFAS in aqueous and solid media should be as close to these limits as possible. If laboratories indicate that they are not able to achieve these reporting limits for the entire *PFAS Analyte List*, site-specific decisions regarding acceptance of elevated reporting limits for specific PFAS can be made by the DER project manager in consultation with the DER chemist.

Additional Analysis

Additional laboratory methods for analysis of PFAS may be warranted at a site, such as the Synthetic Precipitation Leaching Procedure (SPLP) and Total Oxidizable Precursor Assay (TOP Assay).

In cases where site-specific cleanup objectives for PFOA and PFOS are to be assessed, soil parameters, such as Total Organic Carbon (Lloyd Kahn), soil pH (EPA Method 9045), clay content (percent), and cation exchange capacity (EPA Method 9081), should be included in the analysis to help evaluate factors affecting the leachability of PFAS in site soils.

SPLP is a technique used to determine the mobility of chemicals in liquids, soils and wastes, and may be useful in determining the need for addressing PFAS-containing material as part of the remedy. SPLP by EPA Method 1312 should be used unless otherwise specified by the DER project manager in consultation with the DER chemist.

Impacted materials can be made up of PFAS that are not analyzable by routine analytical methodology. A TOP Assay can be utilized to conceptualize the amount and type of oxidizable PFAS which could be liberated in the environment, which approximates the maximum concentration of perfluoroalkyl substances that could be generated

if all polyfluoroalkyl substances were oxidized. For example, some polyfluoroalkyl substances may degrade or transform to form perfluoroalkyl substances (such as PFOA or PFOS), resulting in an increase in perfluoroalkyl substance concentrations as contaminated groundwater moves away from a source. The TOP Assay converts, through oxidation, polyfluoroalkyl substances (precursors) into perfluoroalkyl substances that can be detected by routine analytical methodology.¹

Commercial laboratories have adopted methods which allow for the quantification of targeted PFAS in air and biota. The EPA's Office of Research and Development (ORD) is currently developing methods which allow for air emissions characterization of PFAS, including both targeted and non-targeted analysis of PFAS. Consult with the DER project manager and the DER chemist for assistance on analyzing biota/tissue and air samples.

Data Assessment and Application to Site Cleanup

Until such time as Ambient Water Quality Standards (AWQS) and Soil Cleanup Objectives (SCOs) for PFOA and PFOS are published, the extent of contaminated media potentially subject to remediation should be determined on a case-by-case basis using the procedures discussed below and the criteria in DER-10. Preliminary target levels for cleanup of PFOA and PFOS in other media, including biota and sediment, have not yet been established by the DEC.

Water Sample Results

PFOA and PFOS should be further assessed and considered as potential contaminants of concern in groundwater or surface water if PFOA or PFOS is detected in any water sample at or above 10 ng/L (ppt) and is determined to be attributable to the site, either by a comparison of upgradient and downgradient levels, or the presence of soil source areas, as defined below.

If PFOA and/or PFOS are identified as contaminants of concern for a site, they should be assessed as part of the remedy selection process in accordance with Part 375 and DER-10.

Soil Sample Results

Soil cleanup objectives for PFOA and PFOS will be proposed in an upcoming revision to 6 NYCRR Part 375-6. Until SCOs are in effect, the following are to be used as guidance values.

Guidance Values for Anticipated Site Use	PFOA (ppb)	PFOS (ppb)
Unrestricted	0.66	0.88
Residential	6.6	8.8
Restricted Residential	33	44
Commercial	500	440
Industrial	600	440
Protection of Groundwater ²	1.1	3.7

¹ TOP Assay analysis of highly contaminated samples, such as those from an AFFF (aqueous film-forming foam) site, can result in incomplete oxidation of the samples and an underestimation of the total perfluoroalkyl substances.

² The movement of PFAS in the environment is being aggressively researched at this time; that research will eventually result in more accurate models for the behaviors of these chemicals. In the meantime, DEC has calculated the guidance value for the protection of groundwater using the same procedure used for all other chemicals, as described in Section 7.7 of the Technical Support Document (http://www.dec.ny.gov/docs/remediation_hudson_pdf/techsupdoc.pdf).

PFOA and PFOS results for soil are to be compared against the guidance values listed above. These guidance values are to be used in determining whether PFOA and PFOS are contaminants of concern for the site and for determining remedial action objectives and cleanup requirements. Site-specific remedial objectives for protection of groundwater can also be presented for evaluation by DEC. Development of site-specific remedial objectives for protection of groundwater will require analysis of additional soil parameters relating to leachability. These additional analyses can include any or all the parameters listed above (soil pH, cation exchange capacity, etc.) and/or use of SPLP.

As the understanding of PFAS transport improves, DEC welcomes proposals for site-specific remedial objectives for protection of groundwater. DEC will expect that those may be dependent on additional factors including soil pH, aqueous pH, % organic carbon, % Sand/Silt/Clay, soil cations: K, Ca, Mg, Na, Fe, Al, cation exchange capacity, and anion exchange capacity. Site-specific remedial objectives should also consider the dilution attenuation factor (DAF). The NJDEP publication on DAF can be used as a reference:

<https://www.nj.gov/dep/srp/guidance/rs/daf.pdf>.

Testing for Imported Soil

Testing for PFAS should be included any time a full TAL/TCL analyte list is required. Results for PFOA and PFOS should be compared to the applicable guidance values. If PFOA or PFOS is detected in any sample at or above the guidance values then the source of backfill should be rejected, unless a site-specific exemption is provided by DER based on SPLP testing, for example. If the concentrations of PFOA and PFOS in leachate are at or above 10 ppt (the Maximum Contaminant Levels established for drinking water by the New York State Department of Health), then the soil is not acceptable.

PFOA, PFOS and 1,4-dioxane are all considered semi-volatile compounds, so composite samples are appropriate for these compounds when sampling in accordance with DER-10, Table 5.4(e)10. Category B deliverables should be submitted for backfill samples, though a DUSR is not required.

NOTICE OF WARRANTY

By signature to the chain of custody (reverse), the signatory warrants that the information provided is truthful and accurate to the best of his/her ability. The signatory affirms that he/she is willing to testify to those facts provided and the circumstances surrounding the same. Nothing in this warranty or chain of custody negates responsibility nor liability of the signatories for the truthfulness and accuracy of the statements provided.

HANDLING INSTRUCTIONS

On day of collection, collector(s) name(s), address(es), date, geographic location of capture (attach a copy of topographic map or navigation chart), species, number kept of each species, and description of capture vicinity (proper noun, if possible) along with name of Town and County must be indicated on reverse.

Retain organisms in manila tagged plastic bags to avoid mixing capture locations. Note appropriate information on each bag tag.

Keep samples as cool as possible. Put on ice if fish cannot be frozen within 12 hours. If fish are held more than 24 hours without freezing, they will not be retained or analyzed.

Initial recipient (either DEC or designated agent) of samples from collector(s) is responsible for obtaining and recording information on the collection record forms which will accompany the chain of custody. This person will seal the container using packing tape and writing his signature, the time and the date across the tape onto the container with indelible marker. Any time a seal is broken, for whatever purpose, the incident must be recorded on the Chain of Custody (reason, time, and date) in the purpose of transfer block. Container then is resealed using new tape and rewriting signature, with time and date.

EQUIPMENT LIST

Scale or balance of appropriate capacity for the fish to be collected.

Fish measuring board.

Plastic bags of an appropriate size for the fish to be collected and for site bags.

Individually numbered metal tags for fish.

Manila tags to label bags.

Small envelopes, approximately 2" x 3.5", if fish scales are to be collected.

Knife for removing scales.

Chain of custody and fish collection forms.

Clipboard.

Pens or markers.

Paper towels.

Dish soap and brush.

Bucket.

Cooler.

Ice.

Duct tape.

Appendix G – PFAS Analyte List

Group	Chemical Name	Abbreviation	CAS Number
Perfluoroalkyl sulfonates	Perfluorobutanesulfonic acid	PFBS	375-73-5
	Perfluorohexanesulfonic acid	PFHxS	355-46-4
	Perfluoroheptanesulfonic acid	PFHpS	375-92-8
	Perfluorooctanesulfonic acid	PFOS	1763-23-1
	Perfluorodecanesulfonic acid	PFDS	335-77-3
Perfluoroalkyl carboxylates	Perfluorobutanoic acid	PFBA	375-22-4
	Perfluoropentanoic acid	PFPeA	2706-90-3
	Perfluorohexanoic acid	PFHxA	307-24-4
	Perfluoroheptanoic acid	PFHpA	375-85-9
	Perfluorooctanoic acid	PFOA	335-67-1
	Perfluorononanoic acid	PFNA	375-95-1
	Perfluorodecanoic acid	PFDA	335-76-2
	Perfluoroundecanoic acid	PFUA/PFUdA	2058-94-8
	Perfluorododecanoic acid	PFDoA	307-55-1
	Perfluorotridecanoic acid	PFTriA/PFTTrDA	72629-94-8
	Perfluorotetradecanoic acid	PFTA/PFTeDA	376-06-7
Fluorinated Telomer Sulfonates	6:2 Fluorotelomer sulfonate	6:2 FTS	27619-97-2
	8:2 Fluorotelomer sulfonate	8:2 FTS	39108-34-4
Perfluorooctane-sulfonamides	Perfluorooctanesulfonamide	FOSA	754-91-6
Perfluorooctane-sulfonamidoacetic acids	N-methyl perfluorooctanesulfonamidoacetic acid	N-MeFOSAA	2355-31-9
	N-ethyl perfluorooctanesulfonamidoacetic acid	N-EtFOSAA	2991-50-6

Appendix H - Laboratory Guidelines for Analysis of PFAS in Non-Potable Water and Solids

General

New York State Department of Environmental Conservation's Division of Environmental Remediation (DER) developed the following guidelines for laboratories analyzing environmental samples for PFAS under DER programs. If laboratories cannot adhere to the following guidelines, they should contact DER's Quality Assurance Officer, Dana Barbarossa, at dana.barbarossa@dec.ny.gov prior to analysis of samples.

Isotope Dilution

Isotope dilution techniques should be utilized for the analysis of PFAS in all media.

Extraction

For water samples, the entire sample bottle should be extracted, and the sample bottle rinsed with appropriate solvent to remove any residual PFAS.

For samples with high particulates, the samples should be handled in one of the following ways:

1. Spike the entire sample bottle with isotope dilution analytes (IDAs) prior to any sample manipulation. The sample can be passed through the SPE and if it clogs, record the volume that passed through.
2. If the sample contains too much sediment to attempt passing it through the SPE cartridge, the sample should be spiked with isotope dilution analytes, centrifuged and decanted.
3. If higher reporting limits are acceptable for the project, the sample can be diluted by taking a representative aliquot of the sample. If isotope dilution analytes will be diluted out of the sample, they can be added after the dilution. The sample should be homogenized prior to taking an aliquot.

If alternate sample extraction procedures are used, please contact the DER remedial program chemist prior to employing. Any deviations in sample preparation procedures should be clearly noted in the case narrative.

Signal to Noise Ratio

For all target analyte ions used for quantification, signal to noise ratio should be 3:1 or greater.

Blanks

There should be no detections in the method blanks above the reporting limits.

Ion Transitions

The ion transitions listed below should be used for the following PFAS:

PFOA	413 > 369
PFOS	499 > 80
PFH _x S	399 > 80
PFBS	299 > 80
6:2 FTS	427 > 407
8:2 FTS	527 > 507
N-EtFOSAA	584 > 419
N-MeFOSAA	570 > 419

Branched and Linear Isomers

Standards containing both branched and linear isomers should be used when standards are commercially available. Currently, quantitative standards are available for PFHxS, PFOS, NMeFOSAA, and NEtFOSAA. As more standards become available, they should be incorporated in to the method. All isomer peaks present in the standard should be integrated and the areas summed. Samples should be integrated in the same manner as the standards.

Since a quantitative standard does not exist for branched isomers of PFOA, the instrument should be calibrated using just the linear isomer and a technical (qualitative) PFOA standard should be used to identify the retention time of the branched PFOA isomers in the sample. The total response of PFOA branched and linear isomers should be integrated in the samples and quantitated using the calibration curve of the linear standard.

Secondary Ion Transition Monitoring

Quantifier and qualifier ions should be monitored for all target analytes (PFBA and PFPeA are exceptions). The ratio of quantifier ion response to qualifier ion response should be calculated for each target analyte and the ratio compared to standards. Lab derived criteria should be used to determine if the ratios are acceptable.

Reporting

Detections below the reporting limit should be reported and qualified with a J qualifier.

The acid form of PFAS analytes should be reported. If the salt form of the PFAS was used as a stock standard, the measured mass should be corrected to report the acid form of the analyte.

Appendix I - Data Review Guidelines for Analysis of PFAS in Non-Potable Water and Solids

General

These guidelines are intended to be used for the validation of PFAS analytical results for projects within the Division of Environmental Remediation (DER) as well as aid in the preparation of a data usability summary report. Data reviewers should understand the methodology and techniques utilized in the analysis. Consultation with the end user of the data may be necessary to assist in determining data usability based on the data quality objectives in the Quality Assurance Project Plan. A familiarity with the laboratory's Standard Operating Procedure may also be needed to fully evaluate the data. If you have any questions, please contact DER's Quality Assurance Officer, Dana Barbarossa, at dana.barbarossa@dec.ny.gov.

Preservation and Holding Time

Samples should be preserved with ice to a temperature of less than 6°C upon arrival at the lab. The holding time is 14 days to extraction for aqueous and solid samples. The time from extraction to analysis for aqueous samples is 28 days and 40 days for solids.

Temperature greatly exceeds 6°C upon arrival at the lab*	Use professional judgement to qualify detects and non-detects as estimated or rejected
Holding time exceeding 28 days to extraction	Use professional judgement to qualify detects and non-detects as estimated or rejected if holding time is grossly exceeded

*Samples that are delivered to the lab immediately after sampling may not meet the thermal preservation guidelines. Samples are considered acceptable if they arrive on ice or an attempt to chill the samples is observed.

Initial Calibration

The initial calibration should contain a minimum of five standards for linear fit and six standards for a quadratic fit. The relative standard deviation (RSD) for a quadratic fit calibration should be less than 20%. Linear fit calibration curves should have an R^2 value greater than 0.990.

The low-level calibration standard should be within 50% - 150% of the true value, and the mid-level calibration standard within 70% - 130% of the true value.

%RSD >20%	J flag detects and UJ non detects
$R^2 >0.990$	J flag detects and UJ non detects
Low-level calibration check <50% or >150%	J flag detects and UJ non detects
Mid-level calibration check <70% or >130%	J flag detects and UJ non detects

Initial Calibration Verification

An initial calibration verification (ICV) standard should be from a second source (if available). The ICV should be at the same concentration as the mid-level standard of the calibration curve.

ICV recovery <70% or >130%	J flag detects and non-detects
----------------------------	--------------------------------

Continuing Calibration Verification

Continuing calibration verification (CCV) checks should be analyzed at a frequency of one per ten field samples. If CCV recovery is very low, where detection of the analyte could be in question, ensure a low level CCV was analyzed and use to determine data quality.

CCV recovery <70 or >130%	J flag results
---------------------------	----------------

Blanks

There should be no detections in the method blanks above the reporting limits. Equipment blanks, field blanks, rinse blanks etc. should be evaluated in the same manner as method blanks. Use the most contaminated blank to evaluate the sample results.

Blank Result	Sample Result	Qualification
Any detection	<Reporting limit	Qualify as ND at reporting limit
Any detection	>Reporting Limit and >10x the blank result	No qualification
>Reporting limit	>Reporting limit and <10x blank result	J+ biased high

Field Duplicates

A blind field duplicate should be collected at rate of one per twenty samples. The relative percent difference (RPD) should be less than 30% for analyte concentrations greater than two times the reporting limit. Use the higher result for final reporting.

RPD >30%	Apply J qualifier to parent sample
----------	------------------------------------

Lab Control Spike

Lab control spikes should be analyzed with each extraction batch or one for every twenty samples. In the absence of lab derived criteria, use 70% - 130% recovery criteria to evaluate the data.

Recovery <70% or >130% (lab derived criteria can also be used)	Apply J qualifier to detects and UJ qualifier to non detects
--	--

Matrix Spike/Matrix Spike Duplicate

One matrix spike and matrix spike duplicate should be collected at a rate of one per twenty samples. Use professional judgement to reject results based on out of control MS/MSD recoveries.

Recovery <70% or >130% (lab derived criteria can also be used)	Apply J qualifier to detects and UJ qualifier to non detects of parent sample only
RPD >30%	Apply J qualifier to detects and UJ qualifier to non detects of parent sample only

Extracted Internal Standards (Isotope Dilution Analytes)

Problematic analytes (e.g. PFBA, PFPeA, fluorotelomer sulfonates) can have wider recoveries without qualification. Qualify corresponding native compounds with a J flag if outside of the range.

Recovery <50% or >150%	Apply J qualifier
Recovery <25% or >150% for poor responding analytes	Apply J qualifier
Isotope Dilution Analyte (IDA) Recovery <10%	Reject results

Secondary Ion Transition Monitoring

Quantifier and qualifier ions should be monitored for all target analytes (PFBA and PFPeA are exceptions). The ratio of quantifier ion response to qualifier ion response should be calculated from the standards for each target analyte. Lab derived criteria should be used to determine if the ratios are acceptable. If the ratios fall outside of the laboratory criteria, qualify results as an estimated maximum concentration.

Signal to Noise Ratio

The signal to noise ratio for the quantifier ion should be at least 3:1. If the ratio is less than 3:1, the peak is discernable from the baseline noise and symmetrical, the result can be reported. If the peak appears to be baseline noise and/or the shape is irregular, qualify the result as tentatively identified.

Branched and Linear Isomers

Observed branched isomers in the sample that do not have a qualitative or quantitative standard should be noted and the analyte should be qualified as biased low in the final data review summary report. Note: The branched isomer peak should also be present in the secondary ion transition.

Reporting Limits

If project-specific reporting limits were not met, please indicate that in the report along with the reason (e.g. over dilution, dilution for non-target analytes, high sediment in aqueous samples).

Peak Integrations

Target analyte peaks should be integrated properly and consistently when compared to standards. Ensure branched isomer peaks are included for PFAS where standards are available. Inconsistencies should be brought to the attention of the laboratory or identified in the data review summary report.