State of Connecticut

Department of Energy and Environmental Protection

Recommended Reasonable Confidence Protocols

Quality Assurance and Quality Control Requirements

Per- and Polyfluoroalkyl Substances by USEPA Method 1633

Version 1.0

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Written by the Connecticut DEEP QA/QC Workgroup

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1.0	First version for publication	July 1, 2026

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Acronym List

ACRONYM	DEFINITION
%R	Percent recovery
%RSD	Percent relative standard deviation
µg/kg	Microgram per kilogram
ng/L	Nanograms per liter
CASN	Chemical Abstracts Service Number
DEEP	CT Department of Energy and Environmental Protection
DF	Dilution factor
EIS	Extracted internal standards
EP	Environmental Professional
g	grams
HDPE	High density polyethylene
IPR	Initial precision and recovery
ISC	Instrument sensitivity check
LC-MS/MS	Liquid chromatography/dual mass spectrometry
LLOQ	Lower limit of quantitation
MD	Matrix duplicate
MS	Matrix spike
MSD	Matrix spike duplicate
MRM	Multiple reaction monitoring
NA	Not applicable
NIS	Non-extracted internal standard
OHM	Oil and hazardous materials
OPR	Ongoing precision and recovery
PFAS	Per- and polyfluoroalkyl substances
QA	Quality assurance
QC	Quality control
RBCRs	Release based cleanup regulations
RCP	Reasonable confidence protocol
RL	Reporting limit
RPD	Relative percent difference
RSE	Relative standard error
RT	Retention time
S/N	Signal to noise
SPE	Solid phase extraction
TCDCA	Taurochenodeoxycholic acid
TDCA	Taurodeoxycholic acid
TSS	Total suspended solids
TUDCA	Tauroursodeoxycholic acid
USEPA	United States Environmental Protection Agency

Refer to Table 1B for PFAS acronym definitions.

1.0 Quality Assurance and Quality Control Requirements for USEPA Method 1633

1.1 Method Overview

United States Environmental Protection Agency ("USEPA") Method 1633 is a Liquid Chromatography/Dual Mass Spectrometry ("LC-MS/MS") procedure used for the analysis of per- and polyfluoroalkyl substances ("PFAS") in aqueous, solid, and tissue samples preceded by sample preparation methods discussed in USEPA method 1633 and described in Section 1.2.1 of this protocol. This procedure requires an experienced LC-MS/MS analyst familiar with Quality Assurance and Quality Control ("QA/QC") requirements of the method.

This document provides Quality Control ("QC") requirements and performance standards to be used in conjunction with the required analytical method USEPA 1633. The QC requirements and performance standards specified in this document in Table 1A together with the analytical procedures described in USEPA Method 1633, constitute the protocol.

Please note that while this protocol must be followed on and after the effective date of July 1, 2026, for the purpose of "Reasonable Confidence," the protocol may be used optionally prior to its effective date upon its publication.

All method references are to the latest version of the method published by the EPA.

1.2 Summary of USEPA Method 1633

Aqueous and solid samples are prepared using USEPA Method 1633 matrix-specific procedures and are subjected to cleanup procedures to remove interferences.

After cleanup, the extract is analyzed by injecting an aliquot into a high-performance liquid chromatograph ("LC") equipped with a C18 column, or equivalent, connected to tandem quadrupole mass spectrometers ("MS/MS") operating in the multiple reaction monitoring ("MRM") mode."

PFAS concentrations in samples are determined by isotope dilution or extracted internal standard ("EIS") quantification using isotopically labeled compounds added to the sample prior to extraction. Quantitation is accomplished by using the peak areas of quantitation ions and a response factor generated from a minimum six-point calibration curve or by using a second-order calibration model generated from a minimum seven-point calibration curve (refer to Table 1A). When linear and branched isomers are present in both the sample and qualitative or quantitative standards for a target PFAS, the target PFAS is reported as a combined response of the linear and branched isomers.

Isotope dilution and EIS quantification provide a correction for any potential losses during extraction and cleanup. Isotope dilution also provides a correction for matrix effects that could lead to signal enhancement or suppression and thus can avoid measurement bias.

Identification of target PFAS is accomplished by comparing the retention time of the target PFAS quantitation and confirmation ions in samples with the retention time of the target PFAS quantitation and confirmation ions in standards obtained under identical analytical conditions. In addition, the retention time of the target PFAS in samples is compared with the retention time of the exact corresponding isotopically labeled analog, where these exist. Quantitation/confirmation ion ratios are also used to positively identify a target PFAS.

1.2.1 Sample Extraction/Cleanup Methods for USEPA 1633

Samples for analysis by USEPA Method 1633 must be extracted using the procedures in Sections 11.0 and 12.0 of the method. Extracts must be subjected to carbon cleanup, as described in Section 12.0 of the method. In general, the following procedures are used:

- Aqueous samples are spiked with EIS, extracted using solid-phase extraction ("SPE"), and then subjected to cleanup using carbon.

- Solid and tissue samples are spiked with EIS, extracted in basic methanol, and then cleaned up using carbon followed by SPE.

1.3 Method Interferences

Refer to USEPA Method 1633 (Section 4.0, in particular) for a detailed discussion of interferences and corrective actions which may be taken to eliminate contamination. Interferences co-extracted from the samples will vary considerably from matrix to matrix and will also be dependent upon the diversity of the site being sampled. Cleanup techniques are provided as part of this method to reduce or eliminate these interferences and achieve desired degrees of discrimination and quantitation of the target PFAS.

Sources of interference in this method can be grouped into four broad categories.

- Contaminated solvents (e.g., water, methanol, and methanolic ammonium hydroxide), reagents, or sample processing hardware,
- Disposable plasticware, glass equipment, parts of the SPE manifold, filters, and equipment used to prepare samples,
- Non-target compounds simultaneously extracted from the sample matrix which cause a detector response, and
- Co-elution of target analytes.

1.3.1 Chemical Contamination

The most frequently encountered interferences in reagents and equipment are fluoropolymers. The equipment used by the laboratory must be demonstrated to be free of PFAS below the laboratory's method detection limit ("MDL") and also must not be constructed of materials which could react with or sorb target PFAS. An in-depth discussion of the causes and corrective actions for all of these interferences is beyond the scope of this guidance document.

Analysis of blanks provides information about the presence of contaminants. When potential interfering peaks or high levels of target compounds are detected in blanks, the laboratory should try and find the source of the contamination and eliminate it. **Subtracting blank concentrations from sample results is not permitted.** Any method blank exceedances should be fully documented in the laboratory report narrative.

1.3.2 Cross-contamination/Carryover

Cross-contamination may occur when any sample is analyzed immediately after a sample containing high concentrations of PFAS. After the analysis of a sample containing high concentrations of PFAS, one or more blanks should be analyzed to check for potential cross-contamination/carryover. Concentrations of PFAS which exceed the upper limit of calibration should prompt the analyst to check for potential cross- contamination/carryover. To reduce carryover, the injector must be rinsed with solvent between sample injections.

1.3.3 Other Potential Interferences

Interferences by bile salts can be present in different matrices, including fish and wastewater, and can interfere with the chromatography of this method. Bile salts include taurodeoxycholic acid ("TDCA"), taurochenodeoxycholic acid ("TCDCA"), and tauroursodeoxycholic acid ("TUDCA"). The potential interference of these three bile salts is dependent on the solvent used as the mobile phase in the LC instrument. When acetonitrile is used as the mobile phase, the potential interference from TDCA must be evaluated. When other solvents are used as the mobile phase, the evaluation of potential interference must include TDCA, TCDCA, and TUDCA. Refer to Table 1A for a summary of the evaluation requirements.

1.4 Quality Control Requirements for USEPA Method 1633

1.4.1 Reporting Limits/Lower Limits of Quantitation for USEPA Method 1633

The reporting limit ("RL") or lower limit of quantitation ("LLOQ") for an individual compound is dependent on the concentration of the lowest non-zero standard in the initial calibration, analyzed under identical conditions as the sample, with adjustments made for the sample size, extraction concentration factor, percent solids, dilution factors, etc., as required.

Table 1.0 lists approximate RL/LLOQs for various matrices utilizing the triple mass spectrometer. These values are readily achievable using LC-MS/MS. Solid matrices in this table assume 100% solids.

Table 1.0: Typical Reporting Limits / Lower Limit of Quantitation[1,2]

Target PFAS	Aqueous RL/LLOQ (ng/L)[3]	Soil/Sediment RL/LLOQ (µg/kg, dry weight)[3,4]	Tissue RL/LLOQ (µg/kg, wet weight)
PFBA	4 - 16	0.64 - 1.6	1.6 - 4.0
PFPeA	2 - 8	0.32 - 0.8	0.8 - 1.0
PFHxA, PFHpA, PFOA	1 - 4	0.16 - 0.4	0.4 - 0.5
PFNA	1 – 4	0.16 - 1.3	0.4 - 0.5
PFDA	1 – 4	0.16 - 0.4	0.4 - 0.5
PFUnA	1 – 4	0.16 - 0.5	0.4 - 1.0
PFDoA, PFTrDA, PFTeDA	1 – 4	0.16 - 0.4	0.4 - 1.0
PFBS, PFPeS, PFHxS, PFHpS, PFOS, PFNS, PFDS, PFDoS	1 – 4	0.16 - 0.4	0.4 - 2.0
4:2 FTS, 6:2 FTS, 8:2 FTS	4 - 15	0.64 - 1.5	1.6 - 2.0
PFOSA, NMeFOSA, NEtFOSA, NMeFOSAA, NEtFOSAA	1 – 4	0.16 - 0.4	0.4 - 1.0
NMeFOSE, NEtFOSE	10 - 40	1.6 - 4.0	4.0 - 5.0
HFPO-DA, ADONA	2 – 8	0.64 - 1.6	1.6 - 2.1
PFMPA, PFMBA	4 - 16	0.32 - 0.8	0.8 - 2.0
NFDHA	2 – 7	0.32 - 0.8	0.8 - 1.0
9Cl-PF3ONS,	2	0.64 - 1.5	1.6 - 2.0
11Cl- PF3OUdS	5	0.64 - 1.5	1.6 - 2.0
PFEESA	2 – 8	0.32 - 0.7	0.8 - 1.0
3:3 FTCA	5 - 20	0.80 - 5.0	2.0 - 4.0
5:3 FTCA, 7:3 FTCA	25 - 100	4 – 10	10 – 20

[1]Note these values are intended to serve as guidance to EPs when planning analytical needs to achieve the data quality objectives to meet project-specific goals. These tables are not intended to dictate what RL/LLOQs laboratories must report.

[2]RL/LLOQ may be subject to change based on revisions to established standards regulated by the CT DPH and/or EPA. Changes to RL/LLOQs will have a compliance buffer as dictated by the CT DPH Environmental Laboratory Certification Program.

[3]RL/LLOQ for landfill leachates may be approximately 5x higher due to collection of reduced sample volumes for this matrix (e.g., 100 mL versus 500 mL for other aqueous matrices [surface water, groundwater]); this may be dependent on the laboratory's procedures.

[4]RL/LLOQ for biosolids will be approximately 10x higher due to use of a reduced sample mass for extraction for this matrix (e.g., 0.5 grams versus typical 5 grams for other soil/sediment matrices).

RLs/LLOQs lower than the above-referenced RLs/LLOQs for target analytes may be required to satisfy project requirements. It is the responsibility of the data user, in concert with the laboratory, to establish the range and

required RL/LLOQ for the target analytes to meet the project Data Quality Objectives ("DQOs"). For this class of analytes the RL/LLOQ for each contaminant of concern must be less than or equal to Release-Based Cleanup Regulations ("RBCRs") criteria.

To meet the RLs/LLOQs applicable to project DQOs, it may be necessary to modify the analytical method by using increased sample volume/mass or reducing the volume of the final extract, to improve sensitivity. All such modifications must be described in the laboratory narrative. Regardless of the modification that is used, RLs/LLOQs for target analytes will be proportionately higher for samples that require dilution, when a reduced sample size is used, or for an increased final extract volume.

1.4.2 General Quality Control Requirements

This protocol is restricted to use by, or under the supervision of, analysts experienced in the use of LC-MS/MS instrumentation and isotope dilution as a quantitative tool and skilled in the interpretation of data generated with these instruments.

Each laboratory shall maintain a formal QA program and records to document the quality of all data and be certified by the Connecticut Department of Public Health for the analysis performed. QC procedures necessary to evaluate the LC-MS/MS operation and method performance may be found in Section 9.0 in the USEPA Method 1633.

The minimum requirements for a formal QA program include Initial Demonstration of Laboratory Capability ("IDOC"), ongoing analysis of standards and blanks to confirm acceptable continuing performance, and extraction/analysis of initial precision and recovery ("IPR"), ongoing precision and recovery ("OPR"), Low-level On-going Precision and Recovery (LLOPR) standards to assess analytical accuracy. Matrix duplicates (MD) may also be used to evaluate accuracy and precision when such samples are analyzed either at the discretion of the laboratory or at the request of the data user. To assess the precision of analytical measurements for this method, matrix duplicates are required every 20 field samples. To assess accuracy/bias, equipment blanks should be collected for each piece of equipment during each sampling event and decontamination blanks should be collected if utilizing a water source that has not been provided and certified as "PFAS-free" by a certified laboratory.

Laboratories must document and have on file an IDOC for each combination of sample preparation and determinative method being used. An IDOC must be completed and documented when a method is initially started up, whenever a method is substantially modified, or new laboratory staff is trained to perform this method. These data must meet or fall within the performance standards as presented in Section 1.4 and Table 1A of this RCP and presented in USEPA Method 1633 (Section 9.2). The IDOC must include the following elements provided in Table 2.0:

Table 2.0: IDOC Requirements

QC Element	Performance Criteria
Initial Calibration	Table 1A; USEPA Method 1633
Calibration Verification	Table 1A
Method Blanks	Table 1A
Average Recovery (Initial Precision and Recovery [IPR] tests)	USEPA Method 1633, Section 9.2
% Relative Standard Deviation (IPR tests)	USEPA Method 1633, Section 9.2
Extracted Internal Standards (EIS) Recovery	Table 1A
Non-Extracted Internal Standards Recovery (NIS)	Table 1A

Because of the extensive analyte list and number of QC elements associated with the IDOC, it should be expected that one or more analytes may not meet the performance standards for one or more QC elements. The laboratory should make every effort to find and correct the problem and repeat the analysis. All non-conforming analytes along

with the laboratory acceptance criteria should be noted in the IDOC data. This information should be kept on-file at the laboratory.

Laboratories are required to generate laboratory specific performance criteria for OPR standards and EIS recoveries also be calculated and documented as described in USEPA Method 1633, Section 9.4. Laboratories are encouraged to actively monitor pertinent QC performance standards described in Table 1A to assess analytical trends (i.e., systematic bias, etc.) and improve overall method performance by preempting potential non-conformances.

1.4.3 Specific QA/QC Requirements and Performance Standards for USEPA Method 1633

Specific QA/QC requirements and performance standards for USEPA Method 1633 are presented in Table 1A. Strict compliance with the QA/QC requirements and performance standards for this method, as well as satisfying other analytical and reporting requirements will provide the EP with “Reasonable Confidence” regarding the usability of analytical data to support environmental decisions. The concept of "Reasonable Confidence" is explained on the CT Department of Energy and Environmental Protection (“DEEP”) website.

While optional, parties electing to utilize these protocols will be assured that agency reviewers will, generally, accept "Reasonable Confidence" data. To achieve “Reasonable Confidence” parties must:

1. Comply with the applicable QC analytical requirements prescribed in Table 1A for this test procedure;

2. Evaluate and narrate all protocol non-compliances and implement, as necessary, required corrective actions and analytical response actions for all non-conforming analytical performance standards; and

3. Retain reported and unreported analytical data and information for a period of 5 years or as required under applicable accreditation criteria.

Table 1A: Specific QA/QC Requirements and Performance Standards for USEPA Method 1633

Required QC Parameter	Data Quality Objective	Required Performance Standard	Required Deliverable	Required Corrective Action	Required Analytical Response Action
Initial Demonstration of Capability ("IDOC")	Laboratory Analytical Accuracy & Precision	(1) Must be performed prior to using method on samples. (2) Must be performed for each matrix. (3) Must contain all target analytes. (4) Must follow procedure in Section 9.2 of USEPA Method 1633.	No	Refer to Section 9.2 of USEPA Method 1633 and Section 1.1.2 of this protocol.	NA
Mass Calibration	Method Sensitivity and Stability	(1) Must be performed at least annually, or as recommended by manufacturer, whichever is more frequent. (2) Use mass calibration solution specified by instrument manufacturer.	No	Adjust the MS/MS if calibration masses are missing or not correctly identified.	Sample analysis cannot proceed without a valid mass calibration.
Mass Calibration Verification	Method Sensitivity and Stability	(1) After mass calibration. (2) Follow instructions for instrument software to verify mass calibration, mass resolution, and peak relative response, as per Section 10.1.7 of USEPA Method 1633.	No	Default to manufacturer guidance.	Sample analysis cannot proceed without a valid mass calibration verification.
Retention Time (RT) Windows	Laboratory Analytical Accuracy	(1) Use the midpoint of the initial calibration or the opening calibration verification to establish the RT windows. (2) Must be of sufficient width to detect earlier-eluting branched isomers.	No	NA	NA

Required QC Parameter	Data Quality Objective	Required Performance Standard	Required Deliverable	Required Corrective Action	Required Analytical Response Action
Bile Salt Interference Check	Laboratory Analytical Accuracy	(1) Performed with the initial calibration and at the beginning of each analytical sequence. (2) If using acetonitrile as LC mobile phase, perform evaluation with TDCA. If using a different solvent as the mobile phase, perform evaluation with TDCA, TCDCA, and TUDCA. (3) Ensure that there is at least a 1-minute window between the RT(s) of TDCA (or TDCA, TCDCA, and TUDCA) and linear/branched PFOS.	No	Modify the chromatographic conditions to eliminate interference from bile salts and to obtain adequate separation. Repeat initial calibration.	Sample analysis cannot proceed without demonstrating adequate separation. Report any non-conformances in laboratory narrative.
Initial Calibration	Laboratory Analytical Accuracy	(1) Must be performed at least once prior to analyzing samples, when calibration verification or instrument sensitivity check does not meet the performance standards, and when major instrument maintenance is performed. (2) Minimum of 6 standards when average response factors are used for quantitation (or 7 standards if a second-order calibration model used). Concentrations of EIS and NIS remain constant in all standards. Standards must be prepared in solvent mix described in Section 7.3.4 of USEPA Method 1633. NOTE: Second-order calibration models may include weighted linear regression or non-linear regression; regression must be weighted inversely proportional to concentration and not forced through zero. (3) Low standard must be ≤RL/LLOQ. (4) Low standard: signal/noise (S/N) ratio ≥ 3:1 for quantification and confirmation ions or ≥ 10:1 for quantification ions for target PFAS with no confirmation ions. (5) Percent relative standard deviations (%RSDs) of response factors ≤20% for each target PFAS and EIS or relative standard error (RSE) ≤20% for each target PFAS and EIS.	No	Recalibrate or prepare new calibration standards, as required by method.	Sample analysis cannot proceed without a valid initial calibration. Report non-conforming compounds (%RSD or RSE >20%) in laboratory narrative.

Required QC Parameter	Data Quality Objective	Required Performance Standard	Required Deliverable	Required Corrective Action	Required Analytical Response Action
		NOTE: correlation coefficient (“r”) and coefficient of determination (“r2”) are not appropriate for measuring linearity with this method. RSE must be used for calibration curve assessment when a weighted regression calibration is used. (6) Must contain all target PFAS, EIS, and NIS. (7) Calibration must be performed under the same conditions as the samples. (8) Laboratories may use average response factors or linear/non-linear regression curves for quantitation. (9) Quantitative standards including linear and branched isomers must be used for target PFAS if commercially available. (10) If qualitative standards exist for linear and branched isomers of a target PFAS where a quantitative standard does not exist, then the qualitative standard must be included for the identification of linear and branched isomers of the associated target PFAS.			

Required QC Parameter	Data Quality Objective	Required Performance Standard	Required Deliverable	Required Corrective Action	Required Analytical Response Action
Instrument Sensitivity Check (ISC)	Laboratory Analytical Accuracy and Method Sensitivity	(1) At beginning of each analytical sequence. (2) Concentration at level of laboratory's RL/LLOQ. (3) S/N ratio ≥ 3:1 for quantification and confirmation ions or ≥ 10:1 for quantification ions for target PFAS with no confirmation ions. (4) Must contain all target PFAS, EIS, and NIS. (5) Percent recoveries (%Rs) must be between 70-130% for each target PFAS. (6) Ion ratios for each target PFAS with confirmation ions must be within ± 50% of the ion ratio observed in the initial calibration midpoint standard. (7) The RTs of the target PFAS must fall within ±0.1 minutes of the RT of the associated EIS when there is an exact corresponding isotopically labeled analog. The RTs of the target PFAS and EIS must fall within ±0.4 minutes of the RT established in the initial calibration.	No	(1) Perform instrument maintenance, reanalyze ISC and/or recalibrate as required by method. (2) Reanalyze "associated samples" if ISC exhibited low response. (3) Reanalyze "associated samples" if ISC exhibited high response and associated target PFAS were detected in the "associated samples" within 10x the RL/LLOQ. NOTE: "Associated samples" refers to all samples analyzed since the last acceptable ISC.	If recovery is outside of 70-130% for any analyte or if the RT is outside of the acceptance window for any analyte, report non- conformances in laboratory narrative.[i]
Calibration Verification	Laboratory Analytical Accuracy	(1) Prior to samples, every 10 field samples, and at the end of the analytical sequence. (2) Concentration level near midpoint of curve. (3) Must contain all target PFAS, EIS, and NIS. (4) Recommended to be prepared using standard source different than used for initial calibration, if available (can use different lot number from same vendor). (5) %Rs must be within 70-130% for each target PFAS. (6) The RTs of the target PFAS must fall within ±0.1 minutes of the RT of the associated EIS when there is an exact corresponding isotopically labeled analog. The RTs of the target PFAS and EIS must fall within ±0.4 minutes of RT established in initial calibration.	No	(1) Perform instrument maintenance, reanalyze calibration verification and/or recalibrate as required by method. (2) Reanalyze "associated samples" if beginning or ending calibration verification exhibited low response. (3) Reanalyze "associated samples" if beginning or ending calibration verification exhibited high response and associated target	If recovery is outside of 70- 130% for any analyte or if the RT is outside of the acceptance window for any analyte, report non- conformances in laboratory narrative.

Required QC Parameter	Data Quality Objective	Required Performance Standard	Required Deliverable	Required Corrective Action	Required Analytical Response Action
		(7) Area count of NIS in calibration verification must be between 50 – 200% of the mean area count of the corresponding NIS in the most recent initial calibration. (8) Quantitative standards including linear and branched isomers must be used for target PFAS if commercially available. (9) If qualitative standards exist for linear and branched isomers of a target PFAS where a quantitative standard does not exist, then the qualitative standard must be included at the beginning of the analytical sequence for the identification of linear and branched isomers of the associated PFAS.		PFAS were detected in the "associated samples." NOTE: "Associated samples" refers to all samples analyzed since the last acceptable calibration verification.	
Instrument Blank	Laboratory Method Sensitivity (contamination evaluation)	(1) Analyzed at beginning of analytical sequence and after analysis of high concentration samples and after Calibration Verification standards. (2) Must be prepared in same solution as calibration standards and contain the EIS and NIS. (3) Must not contain target PFAS that would yield a response equivalent to the mass of the analyte that would be present in a whole-volume sample at or above the MDL.	No	(1) Analyze one or more additional instrument blanks until target PFAS not detected or locate source of contamination and correct problem. Re-analyze instrument blank and associated samples. (2) No corrective action required if concentration of contaminant in sample is >10x concentration in blank or if contaminant not detected in sample.	(1) If sample re-analysis is not possible, report non-conformance in laboratory narrative. (2) If contamination of instrument blanks is suspected or present, the laboratory, using a "B" or some other convention, should qualify the sample results. Instrument blank contamination should also be documented in the laboratory narrative.
Method Blank	Laboratory Method Sensitivity (contamination evaluation)	(1) Extracted with every batch or every 20 field samples, whichever is more frequent. (2) Matrix-specific (e.g., water, soil, tissue). (3) Aqueous method blanks must be prepared using volume typical of samples in batch. (4) Soil/sediment/biosolids and tissue method blanks must be prepared using the same nominal mass as used for samples. (5) Target PFAS must be <RL/LLOQ.	Yes	(1) If concentration of contaminant in sample is ≤10x concentration in blank, locate source of contamination; correct problem; re-extract and re- analyze method blank and associated samples.	(1) If sample re-extraction is not possible, report non-conformance in laboratory narrative. (2) If contamination of method blanks is suspected or present, the laboratory, using a "B" or some other convention, should qualify the sample results. Blank

Required QC Parameter	Data Quality Objective	Required Performance Standard	Required Deliverable	Required Corrective Action	Required Analytical Response Action
				(2) No corrective action required if concentration of contaminant in sample is >10x concentration in blank or if contaminant not detected in sample.	contamination should also be documented in the laboratory narrative. (3) If re-extraction is performed within holding time and yields acceptable method blank results, report results of the re-extraction only. (4) If re-extraction is performed outside of holding time, the laboratory must report results of both the initial extraction and re-extraction
Laboratory Equipment Blank (Tissue samples only)	Laboratory Method Sensitivity (equipment contamination evaluation)	(1) Prepared with every batch or every 20 tissue samples, whichever is more frequent by running PFAS-free water through the grinder. (2) Target PFAS must be <RL/LLOQ. Calculate concentrations in equipment blank, as per Section 11.4 of USEPA Method 1633.	Yes	Narrate.	(1) Note non-conformances in laboratory narrative.
Ongoing Precision and Recovery (OPR)	Laboratory Analytical Accuracy	(1) Mid-level OPR and low-level OPR extracted with every batch or every 20 field samples, whichever is more frequent. (2) Mid-level OPR: Concentration level near midpoint of curve. (3) Low-level OPR: Concentration at 2x RL/LLOQ. (4) Must contain all target PFAS. (5) Matrix-specific (e.g., soil, water, tissue). (6) Aqueous OPRs must be prepared using volume of water typical of samples in batch. (7) Soil/sediment/biosolids and tissue OPRs must be prepared using the same nominal mass as used for samples. (8) %Rs of target PFAS and EIS must meet acceptance limits in Tables 5 through 8 of USEPA Method 1633.	Yes	(1) Locate source of problem; re-extract and re- analyze OPR and associated samples if >10% of all analytes are outside of criteria. (2) If ≤10% of compounds are outside of the acceptance criteria, re-extraction is not required as long as recoveries are >10%. (3) If >10% of compounds are above the acceptance criteria, re-extraction is not required if affected compounds were not	(1) If sample re-extraction is not possible, report non-conformance in laboratory narrative. (2) If recovery is outside of acceptance criteria for any analyte, report non- conforming compounds in laboratory narrative. (3) If re-extraction is performed within holding time and yields acceptable OPR results, report results of the re- extraction only. (4) If re-extraction is performed outside of holding time, the laboratory must report results of both the initial extraction and re-extraction.

Required QC Parameter	Data Quality Objective	Required Performance Standard	Required Deliverable	Required Corrective Action	Required Analytical Response Action
				detected in associated samples.	
Extraction Internal Standards (EIS)	Method Accuracy in Sample Matrix	(1) EIS must consist of isotopically labeled compounds listed in Table 3 of USEPA Method 1633. As noted in method, additional isotopically labeled PFAS compounds for those target PFAS without their own EIS should be included when commercially available. In addition, deuterated EIS should be replaced with the corresponding 13C- or 18O-labeled analogues of the target PFAS, if they become commercially available. (2) %Rs must meet acceptance criteria in Table 6 of USEPA Method 1633 for aqueous samples and Table 8 of USEPA Method 1633 for soil/sediment, biosolids, and tissue samples.	Yes	(1) Perform additional cleanup of the sample extract or re-analyze the sample at a limited dilution factor. NOTE: The dilution factor must keep the EIS concentrations within the calibration curve range and recovery must be at least 5% and S/N ≥20:1 in order to be able to use the EIS for quantitation. (2) Re-extract the sample using a reduced sample volume or mass. NOTE: If EIS recoveries are high and associated target analytes are not detected in sample, corrective action is not required.	(1) Report recoveries outside of acceptance limits in laboratory narrative. (2) If re-extraction or diluted re-analysis yields similar EIS non-conformances, the laboratory must report results of both extractions/analyses. (3) If re-extraction is performed using a reduced sample volume or mass within holding time and yields acceptable EIS recoveries, the laboratory must report results of both extractions. (4) If re-extraction is performed outside of the holding time and yields acceptable EIS recoveries, the laboratory must report results of both extractions. (5) If associating EIS with compounds different than assigned in Table 10 of the method these must be noted in the laboratory narrative.

Required QC Parameter	Data Quality Objective	Required Performance Standard	Required Deliverable	Required Corrective Action	Required Analytical Response Action
Non-Extracted Internal Standards (NIS)	Laboratory Analytical Accuracy and Method Accuracy in Sample Matrix	(1) NIS must consist of isotopically labeled compounds listed in Table 3 of USEPA Method 1633. (2) Area counts of NIS in field and QC samples must be between 50 – 200% of the mean area count of the corresponding NIS in the most recent initial calibration.	No	If NIS is outside of limits, re- analyze sample. NOTE: If NIS areas are low for all field and QC samples, it may be due to a loss of instrument sensitivity. If NIS areas are low in select field and QC samples, it may be due to a bad injection or matrix suppression.	(1) Report nonconformances in laboratory narrative. Include actual recovery of NIS. (2) If re-analysis yields similar NIS non- conformances, the laboratory must report results of both analyses. (3) If re-analysis is performed within holding time and yields acceptable NIS recoveries, report results of the re-analysis only. (4) If re-analysis is performed outside of the holding time and yields acceptable NIS recoveries, the laboratory must report results of both analyses.
Matrix Spike/Matrix Spike Duplicate (MS/MSD)	Method Accuracy & Precision in Sample Matrix	(1) At the discretion of laboratory or at request of data user. (2) Matrix-specific (e.g., water, soil, tissue). (3) Concentration level near midpoint of curve. (4) Must contain all target PFAS. (5) %Rs between 40-140%. (6) Relative percent differences (RPDs) ≤20% for waters and ≤30% for solids and tissue.	Yes ONLY when requested by the data user	Check OPR; if recoveries are acceptable in OPR, narrate non-conformance.	Narrate non-conformances in laboratory narrative.
Matrix Duplicate (MD)	Method Precision in Sample Matrix	(1) Every ≤20 field samples (selected at discretion of lab or at request of data user). (2) Prepare by extracting and analyzing an additional aliquot of the field sample. NOTE: an additional bottle is required for water matrices. (3) RPDs ≤20% for waters and ≤30% for solids and tissue.	Yes	Narrate.	Narrate non-conformances in laboratory narrative.

Required QC Parameter	Data Quality Objective	Required Performance Standard	Required Deliverable	Required Corrective Action	Required Analytical Response Action
Identification and Quantitation	NA	(1) The S/N ratio for the quantitation and confirmation ions in field and QC samples must be ≥ 3:1. If a target PFAS does not have a confirmation ion, the S/N for the quantitation ion must be ≥ 10:1. (2) The RTs of target PFAS, EIS, and NIS in field and QC samples must be within ± 0.4 minutes of predicted RTs from initial calibration midpoint standard or calibration verification. (3) RTs for target PFAS with exact corresponding isotopically labeled EIS in field and QC samples must be within ± 0.1 minutes of the RT of the associated EIS. (4) Ion abundance ratios: • Ion abundance ratios must fall within 50-150% of the ion abundance ratios observed in either the mid-point initial calibration standard or the beginning calibration verification. • Note: the total response of the linear and branched isomers in the quantitative calibration standards must be used to define the ion abundance ratio. • Note: the ratio requirement does not apply for PFAS with confirmation ions that are not detectable or have inadequate signal/noise to be reliably used (PFBA, PFPeA, NMeFOSE, NEtFOSE, PFMPA, PFMBA). (5) For PFAS where quantification includes linear and branched isomers, only the branched isomers that were identified in qualitative and quantitative standards can be included in the sample quantification. (6) The laboratory must use the average response factor, linear or non-linear regression	No	If the S/N ratio is not met due to high background noise, perform instrument maintenance to correct the issue. If the S/N ratio is not met and the background is low, report the result as a non-detect.	If the ion abundance ratio is outside of the acceptance criteria, the laboratory must qualify the sample results and/or note the issue in the laboratory narrative.

Required QC Parameter	Data Quality Objective	Required Performance Standard	Required Deliverable	Required Corrective Action	Required Analytical Response Action
		curve generated from the associated initial calibration for quantitation of each target PFAS. (7) Laboratories must not report positively identified target PFAS when the confirmation ion is not present (for those target PFAS with confirmation ions).			
General Reporting Issues	NA	(1) The laboratory must report values ≥ the sample-specific RL/LLOQ. Do not report concentrations below the RL/LLOQ. If reporting estimated concentrations below the RL/LLOQ, labs must indicate that RCP was not followed. The laboratory must report results for samples and blanks in a consistent manner. (2) Dilutions: If diluted and undiluted analyses are performed, the laboratory should report results for the lowest dilution within the valid calibration range for each analyte. The associated QC (e.g., method blanks, EIS, etc.) for each analysis must be reported. (3) Results for soils/sediments must be reported on a dry-weight basis for comparison to RBCR standards. Results for tissue samples must be reported on a wet-weight basis. (4) Refer to Appendix Tables 4 and 5 for requirements regarding preservation, cooler temperature, and holding times. (5) Report all PFAS results in their acid or neutral forms. (6) The laboratory must report the procedure/option used for the preparation and analysis of aqueous samples with elevated particulates (see Section 1.5 of this RCP). (7) The laboratory must clearly document any method modifications in the laboratory narrative (see Section 1.5 of this RCP).	NA	NA	(1) Complete analytical documentation for diluted and undiluted analyses should be maintained in the laboratory records. (2) The performance of dilutions (including samples extracted at a reduced volume or mass) must be documented in the laboratory narrative. Unless due to elevated concentrations of target PFAS, reasons for dilutions (including samples extracted at a reduced volume or mass) must be explained in the laboratory narrative. (3) If samples are not preserved properly or are not received with an acceptable cooler temperature, note the non-conformances in the laboratory narrative. (4) If samples are extracted and/or analyzed outside of the holding time, note the non-conformances in the laboratory narrative.

1.5 Special Analytical Considerations for USEPA Method 1633

The following section highlights potential issues that may be encountered with the analysis of PFAS using this protocol.

USEPA Method 1633 is a performance-based method. Modifications to the method can be made to improve performance as specified by Method 1633, Section 1.5. However, the initial demonstration of proficiency capability and all performance criteria in the method and this RCP must be met after these modifications are performed. The laboratory must clearly document any method modifications in the laboratory narrative.

- All sample matrices must be allowed to equilibrate for a minimum of 30 minutes with the EIS.
- Since PFAS can adhere to the walls of the sample containers, it is important that the entire volume of the aqueous sample in the container be extracted. This will allow the laboratory to be able to rinse the sides of the container with solvent to remove any potential PFAS which may adhere. If the data user suspects the aqueous samples may contain elevated concentrations of PFAS, a smaller size container can be requested from the laboratory for collection to avoid subsampling from the container. If a smaller size container is not available, subsampling may be unavoidable.
- Aqueous samples with elevated levels of total suspended solids (TSS) may present challenges. It should be noted that filtering is **not** allowed. When elevated levels of TSS are present, there are several options for the laboratory to follow to avoid subsampling.
    - Add EIS to the entire sample, equilibrate for 30 minutes, put aqueous phase through SPE, solvent rinse the remaining particulates in the bottle, and add solvent rinse to SPE.
    - Add EIS to the entire sample, equilibrate for 30 minutes, centrifuge, put aqueous phase through SPE, solvent rinse the remaining particulates in the bottle after centrifuging, and add solvent rinse to SPE.
    - Add EIS to the entire sample, equilibrate for 30 minutes, centrifuge, separate solid and aqueous phases, extract aqueous and solid phases separately, combine extracts prior to analysis.
    - Centrifuge the entire sample, separate solid and aqueous phases, add EIS to each phase and allow to equilibrate for 30 minutes, extract each phase, perform separate analyses of each phase.

  DEEP requires that the laboratory provide details on the extraction procedure followed for samples with elevated with TSS in the laboratory narrative.
- PFAS tend to accumulate at the air/water interface and specifically in the surface layer of natural waters, In addition, PFAS may stratify in the sample container and accumulate at the air/water interface.
    - Extraction of the entire volume of sample in the container, as discussed above, will prevent any issues from stratification in the sample container.
- It is important that the laboratory bring all standards and sample extracts to room temperature followed by vortexing prior to analysis to ensure the homogeneity of the extracts.
- Although the method measures target PFAS as either anions or neutral compounds, MassDEP DEEP expects all target PFAS to be reported in their acid or neutral forms. In general, the conversion from anion to acid will cause a minimal change in the concentration. USEPA Method 1633 provides equations to perform this conversion, which should be done by the laboratory prior to reporting the data.
- Carbon cleanup can be performed using loose carbon or carbon cartridges. According to USEPA Method 1633, the loose carbon provided better adsorption of organic interferents during the single laboratory validation study. However, if the laboratory can demonstrate achievement of the method and CAM Protocol criteria using carbon cartridges, this approach can be used.

- MS/MSDs are generally not required for methods that use isotope dilution quantification since this method of quantification corrects sample results for matrix effects. However, there are several target PFAS for which an exact corresponding isotopically labeled analog is not currently available. In these instances, MS/MSDs may provide useful information. Note, there are select target PFAS which do not have exact corresponding isotopically labeled analogs.
- Potential biases of select target PFAS can occur if sample extract concentration is not performed properly.
    - Loss of the neutral compounds (N-MeFOSA, N-EtFOSA, N-MeFOSE, and N-EtFOSE) can occur if extracts are concentrated too quickly and all of the methanol is evaporated. This affects solid (i.e., soil, sediment, biosolids) and tissue matrices which have an evaporation/concentration step.
    - If the extracts contain excess methanol after concentration, the excess methanol can cause the subsequent SPE cleanup to generate poor recovery for PFTrDA, PFTeDA, PFDS, and PFDoS. This affects solid (i.e., soil, sediment, biosolids) and tissue matrices which have an evaporation/concentration step.

  Laboratories should not spike additional EIS in sample extracts when a sample requires a dilution. If the originally spiked EIS will be “diluted out” in the diluted sample, then the sample should instead be re-extracted with a reduced volume or mass.

1.6 Analyte List for USEPA Method 1633

The DEEP analyte list for USEPA Method 1633 is presented in Table 1B. The compounds listed are readily analyzable by USEPA Method 1633. Select compounds are listed in the Approved Criteria for Additional Polluting Substances. At time of publication, only five of the analytes listed in Table 1B have Additional Polluting Substances Criteria for soil and groundwater while the remaining analytes listed do not have promulgated RBCR Criteria.

Table 1B: Analyte List for USEPA Method 1633

Analyte	Acronym	CASN
Perfluoroalkyl Carboxylic Acids		
Perfluorobutanoic acid	PFBA	375-22-4
Perfluoropentanoic acid	PFPeA	2706-90-3
Perfluorohexanoic acid	PFHxA	307-24-4
Perfluorooctanoic acid	PFOA	335-67-1
Perfluorononanoic acid	PFNA	375-95-1
Perfluorodecanoic acid	PFDA	335-76-2
Perfluoroundecanoic acid	PFUnA	2058-94-8
Perfluorododecanoic acid	PFDoA	307-55-1
Perfluorotridecanoic acid	PFTrDA	72629-94-8
Perfluorotetradecanoic acid	PFTeDA	376-06-7

Analyte	Acronym	CASN
Perfluoroalkyl Sulfonic Acids		
Perfluorobutanesulfonic acid	PFBS	375-73-5
Perfluoropentanesulfonic acid	PFPeS	2706-91-4
Perfluorohexanesulfonic acid	PFHxS	355-46-4
Perfluoroheptanesulfonic acid	PFHpS	375-92-8
Perfluorooctanesulfonic acid	PFOS	1763-23-1
Perfluorononanesulfonic acid	PFNS	68259-12-1
Perfluorodecanesulfonic acid	PFDS	335-77-3
Perfluorododecanesulfonic acid	PFDoS	79780-39-5
Fluorotelomer Sulfonic Acids		
1H,1H,2H,2H-Perfluorohexanesulfonic acid (4:2 fluorotelomer sulfonic acid)	4:2 FTS	757124-72-4
1H,1H,2H,2H-Perfluorooctanesulfonic acid (6:2 fluorotelomer sulfonic acid)	6:2 FTS	27619-97-2
1H,1H,2H,2H-Perfluorodecanesulfonic acid (8:2 fluorotelomer sulfonic acid)	8:2 FTS	39108-34-4
Perfluorooctane Sulfonamides		
Perfluorooctanesulfonamide	PFOSA	754-91-6
N-methyl perfluorooctanesulfonamide	NMeFOSA	31506-32-8
N-ethyl perfluorooctanesulfonamide	NEtFOSA	4151-50-2
Perfluorooctane Sulfonamidoacetic Acids		
N-methyl-perfluorooctanesulfonamidoacetic acid	NMeFOSAA	2355-31-9
N-ethyl-perfluorooctanesulfonamidoacetic acid	NEtFOSAA	2991-50-6
Perfluorooctane Sulfonamide Ethanols		
N-methyl-perfluorooctanesulfonamidoethanol	NMeFOSE	24448-09-7
N-ethyl perfluorooctanesulfonamidoethanol	NEtFOSE	1691-99-2
Per- and Polyfluoroether Carboxylic Acids		
Hexafluoropropylene oxide dimer acid	HFPO-DA	13252-13-6
4,8-Dioxa-3H-perfluorononanoic acid	ADONA	919005-14-4
Perfluoro-3-methoxypropanoic acid	PFMPA	377-73-1

Analyte	Acronym	CASN
Per- and Polyfluoroether Carboxylic Acids Continued…		
Perfluoro-4-methoxybutanoic acid	PFMBA	863090-89-5
Nonafluoro-3,6-dioxaheptanoic acid	NFDHA	151772-58-6
Ether Sulfonic Acids		
9-Chlorohexadecafluoro-3-oxanonane-1-sulfonic acid	9Cl-PF3ONS	756426-58-1
11-Chloroeicosafluoro-3-oxaundecane-1-sulfonic acid	11Cl-PF3OUdS	763051-92-9
Perfluoro(2-ethoxyethane)sulfonic acid	PFEESA	113507-82-7
Fluorotelomer Carboxylic Acids		
3-Perfluoropropyl propanoic acid (3:3 Fluorotelomer carboxylic acid)	3:3 FTCA	356-02-5
2H,2H,3H,3H-Perfluorooctanoic acid (5:3 Fluorotelomer carboxylic acid)	5:3 FTCA	914637-49-3
3-Perfluoroheptyl propanoic acid (7:3 Fluorotelomer carboxylic acid)	7:3 FTCA	812-70-4

1.6.1 Additional Reporting Requirements for USEPA Method 1633

While it is not necessary to request and report all the analytes listed in Table 1B to obtain “Reasonable Confidence” status, it is necessary to document such a limitation, for site characterization and data representativeness considerations.

1.7 Routine Reporting Deliverables for USEPA Method 1633

The following table (Table 3.0) lists the routine report deliverables. Requirements listed as "YES" must always be included as part of the laboratory deliverable for this method. Note that while laboratories are not required to report certain items, they must keep the data on file and may be required to report these items in special circumstances.

Table 3.0: Report Deliverables

Parameter	Deliverable	Comments
Mass Calibration	NO	Sample analysis cannot proceed without a valid mass calibration.
Mass Calibration Verification	NO	Sample analysis cannot proceed without a valid mass calibration verification.
Retention Time Windows	NO	
Bile Salt Interference Check	NO	Sample analysis cannot proceed without demonstrating adequate separation.
Initial Calibration	NO	Sample analysis cannot proceed without a valid initial calibration.
Instrument Sensitivity Check (ISC)	NO	
Calibration Verification	NO	
Instrument Blank	NO	If contamination of instrument blanks is suspected or present, the laboratory, using a "B" or some other convention, should qualify the sample results.
Method Blank	YES	If contamination of instrument blanks is suspected or present, the laboratory, using a "B" or some other convention, should qualify the sample results.
Laboratory Equipment Blank (Tissue Samples only)	YES	See Table 1A
Ongoing Precision and Recovery (OPR): Low-level and mid- level	YES	See Table 1A
Extraction Internal Standards (EIS)	YES	See Table 1A
Non-extracted Internal Standards (NIS)	NO	See Table 1A
Matrix Spike (MS)	YES (if requested by data user)	See Table 1A
Matrix Spike Duplicate (MSD)	YES (if requested by data user)	See Table 1A
Matrix Duplicate (MD)	YES (if requested by data user)	See Table 1A
Identification and Quantitation	NO (except if ion abundance ratio outside of acceptance criteria)	See Table 1A
General Reporting Issues	YES	See Table 1A

1.7.1 Reporting and Flagging of Results

The following rules apply to reporting results:

- Non-Detects: Report all non-detects and results below the reporting limit as “ND” (Not Detected) plus the numerical value of the RL/LLOQ. The RL/LLOQ for each compound in each sample must be listed on the report, based upon the lowest calibration standard, the exact sample mass, any dilution factors, percent moisture, etc.
- Compounds detected above the RL/LLOQ in blanks and in samples shall be flagged with a “B” suffix (e.g., 25B).
- All soil/sediment results shall be reported on a dry weight basis. Tissue results must be reported on a wet-weight basis. Refer to ASTM Method D2216, Determination of Moisture Content of Soils and Sediments, for more detailed analytical and equipment specifications.

1.7.2 Sample Dilution

Under circumstances that sample dilution is required because either the concentration of one or more of the target analytes exceed the concentration of their respective highest calibration standard or any non-target peak exceeds the dynamic range of the detector (i.e., “off scale”), the RL/LLOQ for each target PFAS must be adjusted (increased) in direct proportion to the Dilution Factor (DF).

Two options are available for dilutions:

- **Option #1:** A dilution may be performed on the sample extract. If this is performed, the dilution must be performed with the same solvent/solution as used for sample extracts. The dilution factor must keep the EIS concentrations within the calibration curve range and recovery must be at least 5% and S/N ≥20:1 in order to be able to use the EIS for quantitation If the %R of the EIS is <5% and S/N <20:1, option #2 must be performed for the target PFAS associated with the EIS non-conformance.
- **Option #2:** A reduced volume or mass of sample can be extracted.

The revised RL/LLOQ for the diluted sample ($RL/LLOQ_d$):

$$RL/LLOQ_d = DF \times Lowest\ Calibration\ Standard\ for\ Target\ Analyte$$

It should be understood that samples with elevated RLs/LLOQs as a result of a dilution may not be able to satisfy project DQOs in some cases if the $RL/LLOQ_d$ is greater than applicable RBCR criteria to which the concentration is being compared. Such increases in RLs/LLOQs are the unavoidable but acceptable consequence of sample dilution that enable quantification of target analytes which exceed the calibration range. All dilutions must be fully documented in the laboratory narrative.

NOTE: Over dilution is an unacceptable laboratory practice. The post-dilution concentration of the target analyte with the highest concentration must be within the calibration range and 10 times higher than the RL/LLOQ. This will avoid unnecessarily high RLs/LLOQs for other target analytes which did not require dilution.

1.8 Sample Containers, Preservations, and Holding Times

Table 4.0 identifies the type of containers, preservation requirements, and Table 5.0 provides holding times for aqueous, solid, and tissue matrices for PFAS analysis.

Table 4.0: Sample Containers, Preservations and Holding Times

Matrix	Container[1]	Preservative[2]	Holding Time
Aqueous Samples (with exception of landfill leachates)	(2) 500-mL* high density polyethylene (HDPE) container w/ liner-less HDPE or polypropylene caps (1) 125-mL* HDPE container w/ liner-less HDPE or polypropylene cap[3]	Cool to 4 ± 2°C or Freeze ≤20°C	See Table 5.0
Landfill Leachates	(3) 125-mL* HDPE container w/ liner-less HDPE or polypropylene caps[4]	Cool to 4 ± 2°C or Freeze ≤20°C	
Soil/Sediment/ Biosolids Samples	(1) 500-mL* HDPE container w/ liner-less HDPE or polypropylene cap, no more than ¾ full	Cool to 4 ± 2°C or Freeze ≤20°C	
Tissue Samples	Tissue: wrap in aluminum foil or insert into resealable plastic bag or food-grade polyethylene tubing Homogenized fish: (1) 100-mL HDPE container w/ liner-less HDPE or polypropylene cap	Cool to 4 ± 2°C; must be received by laboratory within 24 hours. Freeze sample (≤-20°C) before shipping if longer transport time is necessary.	

*Smaller size sample containers can be used, as long as performance and regulatory criteria will still be achieved.

[1]The number of sampling containers specified is not a requirement. For specific analyses, the collection of multiple sample containers is encouraged to avoid resampling if sample is consumed or compromised during shipping and/or analysis.

[2]If samples were received by the laboratory on the same day of collection and were stored and transported to the laboratory on ice, cooler temperatures above 6ºC are acceptable.

[3]This container is used for determination of TSS and pre-screening analyses, if warranted.

[4]One of the three containers is used for determination of TSS and pre-screening analyses, if warranted.

Table 5.0: Detailed Holding Times* Based on Sample Matrix

	When Stored at 4 ± 2°C[1]		When Stored at ≤ -20˚C[1]	
Field Samples by Matrix Type	**Holding Time[2,3]**	**Exceptions**	**Holding Time[2,3]**	**Exceptions**
Aqueous, including leachates	28 days	7 days, if NMeFOSE, NEtFOSE, NMeFOSAA, and/or NEtFOSAA are analytes of interest[4]	90 days	None
Soils and sediments[5]	90 days	3 days, if NFDHA is an analyte of interest[6]	90 days	3 days, if NFDHA is an analyte of interest[6]
Biosolids[7]	90 days	None	90 days	None
Tissues	90 days	3 days, if NFDHA is an analyte of interest[6]	90 days	None
	When Stored at either 4 ± 2°C or at ≤ -20˚C[1]			
Sample Extracts	**Holding Time**	**Exceptions**		
All Matrix Types	90 days	28 days, if 11Cl-PF3OUdS and/or 9Cl-PF3ONS are analytes of interest[8]		

[1]All samples should be protected from light in addition to being maintained at the prescribed temperatures.

[2]Holding time begins from time of sample collection except for fish samples. If whole fish samples are frozen within 48 hours of collection, the holding time begins when the whole fish is processed (e.g., filleted) for analysis.

[3]Greater than 28 days (or 90 days, as applicable) results in potential low bias for polyfluoroalkyl PFAS and potential high bias for perfluoroalkyl PFAS.

[4]This is noted in Sections 8.5.1 and 8.5.6 of USEPA Method 1633 and was derived from the single-laboratory validation study performed for this method (https://www.epa.gov/system/files/documents/2022-01/pfas-slvs-report-final-with-appendices.pdf; Appendix K, Section 5.0). DEEP expects the 28-day holding time to be followed in this instance. Data users may want to use the freezing option to extend the holding time.

[5]Some soils and sediments may exhibit microbial growth when stored at 4 ± 2°C.

[6]This exception is noted in Sections 8.5.2, 8.5.3, and 8.5.6 of USEPA Method 1633. DEEP expects the 90-day holding time to be followed in this instance.

[7]Microbial activity in biosolids samples at 4 ± 2°C may cause production of gases which can result in sample being expelled from container when opened as well as noxious odors. Therefore, USEPA Method 1633 recommends samples be stored at ≤-20°C if extraction will be delayed for a few days.

[8]This exception is noted in Sections 8.5.5 and 8.5.6 of USEPA Method 1633. DEEP expects the 90-day holding time to be followed in this instance.

*Additional guidance related to the shorter holding times for certain analytes is available on the DEEP Quality Assurance Webpage in the 2025 Department of Defense (DoD) Environmental Data Quality Workgroup memorandum.