# ***WSC – CAM – X A***

# Quality Control Requirements and Performance Standards for the ***Analysis of Per- and Polyfluoroalkyl Substances (PFAS) by Liquid Chromatography/Dual Mass Spectrometry (LC-MS/MS)*** in Support of Response Actions under the Massachusetts Contingency Plan (MCP)

X. Liquid Chromatography (LC) and Dual Mass Spectrometry (MS/MS) Methods

## A. Quality Control Requirements and Performance Standards for WSC-CAM-X A (Per- and Polyfluoroalkyl Substances by LC-MS/MS)

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## ACRONYM LIST

| | |
|---|---|
| **CAM** | **Compendium of Analytical Methods** |
| **CASN** | **Chemical Abstracts Service Number** |
| **DF** | **Dilution factor** |
| **EIS** | **Extracted internal standards** |
| **HDPE** | **High density polyethylene** |
| **IPR** | **Initial precision and recovery** |
| **IRAs** | **Immediate Response Actions** |
| **ISC** | **Instrument sensitivity check** |
| **LC-MS/MS** | **Liquid chromatography/dual mass spectrometry** |
| **LLOQ** | **Lower limit of quantitation** |
| **MassDEP** | **Massachusetts Department of Environmental Protection** |
| **MCP** | **Massachusetts Contingency Plan** |
| **MD** | **Matrix duplicate** |
| **MDL** | **Method detection limit** |
| **MOHML** | **Massachusetts Oil and Hazardous Materials List** |
| **MRM** | **Multiple reaction monitoring** |
| **MS** | **Matrix spike** |
| **MSD** | **Matrix spike duplicate** |
| **NA** | **Not applicable** |
| **ng/L** | **Nanograms per liter** |
| **NIS** | **Non-extracted internal standard** |
| **OPR** | **Ongoing precision and recovery** |
| **PFAS** | **Per- and polyfluoroalkyl substances** |
| **QA** | **Quality assurance** |
| **QC** | **Quality control** |
| **%R** | **Percent recovery** |
| **RCs** | **Reportable Concentrations** |
| **RL** | **Reporting limit** |
| **RPD** | **Relative percent difference** |
| **RQs** | **Reportable Quantities** |
| **%RSD** | **Percent relative standard deviation** |
| **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** |
| **µg/kg** | **micrograms per kilogram** |
| **USEPA** | **United States Environmental Protection Agency** |

**Refer to Table X A-2 for PFAS Acronym definitions.**

## 1.0 Quality Control Requirements and Performance Standards for WSC-CAM-X A

### 1.1 Overview of WSC-CAM-X A

WSC-CAM-X A, *Quality Control Requirements and Performance Standards for the Analysis of Per- and Polyfluoroalkyl Substances (PFAS) by Liquid Chromatography/Dual Mass Spectrometry (LC-MS/MS) in Support of Response Actions under the Massachusetts Contingency Plan (MCP)*, is a component of MassDEP's Compendium of Analytical Methods (CAM). Effective January 29, 2026, this revised CAM protocol, WSC-CAM-X A, replaces the previous version of the PFAS CAM document, WSC-CAM-X A (effective date, September 30, 2025). Refer to WSC-CAM-I A for an overview of the CAM process. Please note that while this protocol must be followed on and after the effective date of January 29, 2026 for the purpose of "Presumptive Certainty," the protocol may be used optionally prior to its effective date upon its publication on October 29, 2025.

This document provides Quality Control (QC) requirements and performance standards to be used in conjunction with the required analytical method United States Environmental Protection Agency (USEPA) 1633 (the most current version), analysis for PFAS in aqueous, solid, and tissue samples by LC-MS/MS preceded by sample preparation methods discussed in USEPA method 1633, and described in Section 1.3 of this protocol. The QC requirements and performance standards specified in this document in Table X A-1 together with the analytical procedures described in USEPA Method 1633, *Analysis of Per- and Polyfluoroalkyl Substances (PFAS) in Aqueous, Solid, Biosolids, and Tissue Samples by LC-MS/MS*, constitute the WSC-CAM-X A protocol. All protocols included in the CAM are considered "methods" published by the MassDEP pursuant to the provisions of 310 CMR 40.0017(2).

Sample preservation, container and analytical holding time specifications for aqueous, solid, and tissue matrices for PFAS analyzed in support of MCP decision-making are presented in Appendix X A-1 of this document and Appendix VII-A of WSC-CAM-VII A *Quality Assurance and Quality Control Guidelines for the Acquisition and Reporting of Analytical Data in Support of Response Actions Conducted Under the Massachusetts Contingency Plan (MCP)*. Data reporting requirements are also provided in WSC-CAM-VII A.

Overall usability of data produced using this CAM protocol should be evaluated for compliance with project-specific data quality objectives, regardless of "Presumptive Certainty" status. For more guidance on data usability, refer to MassDEP Policy #WSC-07-350, *MCP Representativeness Evaluations and Data Usability Assessments*.

#### 1.1.1 Reporting Limits or Lower Limits of Quantitation for WSC-CAM-X A

The reporting limit (RL) or lower limit of quantitation (LLOQ) for an individual compound using WSC-CAM-X A 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. The CAM RLs/LLOQs for WSC-CAM-X A target analytes are presented in the following table:

| Target PFAS | Aqueous CAM RL/LLOQ (ng/L)[1] | Soil/Sediment RL/LLOQ (µg/kg, wet weight, assuming 100% solids)[2] | Tissue CAM 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 |

| Target PFAS | Aqueous CAM RL/LLOQ (ng/L)[1] | Soil/Sediment RL/LLOQ (µg/kg, wet weight, assuming 100% solids)[2] | Tissue CAM RL/LLOQ (µg/kg, wet weight) |
|---|---|---|---|
| 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, 11Cl-PF3OUdS | 4 - 15 | 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] CAM 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.

[2] CAM 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).

These values are readily achievable using LC-MS/MS. For "Presumptive Certainty" purposes, if the CAM RLs/LLOQs are not achieved, respond "NO" to Question G of the "MassDEP MCP Analytical Protocol Certification Form" and address the CAM RL/LLOQ exceedance in the laboratory narrative.

RLs/LLOQs lower than the above-referenced CAM RLs/LLOQs for WSC-CAM-X A target analytes may be required to satisfy project requirements. The RL/LLOQ (based on a concentration at or above the lowest calibration standard) for each contaminant of concern must be less than or equal to the MCP standards or criteria that the contaminant concentrations are being compared to (e.g., Method 1 Standards, benchmark values, background, etc.). Meeting MCP standards or criteria may require method modifications, such as increasing sample mass/volume 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 the WSC-CAM-X A 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.

### 1.1.2 Initial Demonstration of Proficiency for WSC-CAM-X A

Each laboratory that uses the WSC-CAM-X A protocol is required to operate a formal quality assurance (QA) program. The minimum requirements of this program consist of an initial demonstration of laboratory proficiency, ongoing analysis of standards and blanks to confirm acceptable continuing performance, and the extraction/analysis of ongoing precision and recovery (OPR) standards to assess analytical accuracy. Matrix spikes (MS), matrix spike duplicates (MSD) or 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.

Laboratories must document and have on file an Initial Demonstration of Proficiency for each combination of sample preparation and determinative method being used. These data must meet or exceed the performance standards as presented in Table X A-1 of this protocol and USEPA Method 1633. Procedural requirements for performing the Initial Demonstration of Proficiency can be found in USEPA Method 1633 (Section 9.2). The data associated with the Initial Demonstration of Proficiency must be kept on file at the laboratory and made available to potential data users on request. The data associated with the Initial Demonstration of Proficiency for WSC-CAM-X A must include the following information:

| QC Element | Performance Criteria |
|---|---|
| Initial Calibration | WSC-CAM-X A, Table X A-1 |
| Calibration Verification | WSC-CAM-X A, Table X A-1 |
| Method Blanks | WSC-CAM-X A, Table X A-1 |
| 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 | WSC-CAM-X A, Table X A-1 |
| Non-Extracted Internal Standards Recovery (NIS) | WSC-CAM-X A, Table X A-1 |

**NOTE**: Because of the number of QC elements associated with the Initial Demonstration of Proficiency, it should be expected that one or more analytes may not meet the performance standard for one or more QC elements. Under these circumstances, the analyst should attempt to locate and correct the problem and repeat the analysis for all non-conforming analytes. All non-conforming analytes along with the laboratory- specific acceptance criteria should be noted in the Initial Demonstration of Proficiency documentation.

It is essential that 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 X A-1 to assess analytical trends (i.e., systematic bias, etc.) and improve overall method performance by preempting potential non-conformances.

It should be noted that the performance standards listed in Table X A-1 are based on USEPA Method 1633 and were derived from a multiple-laboratory validation study.

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.

## 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 ultrahigh performance liquid chromatograph (LC) equipped with a BEH 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 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 X A-1). 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.

### 1.3 Sample Extraction/Cleanup Methods for WSC-CAM-X A

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.

### 1.4 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., 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.

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.

- If a method blank contains a contaminant, data for samples associated with that blank must **not** undergo "blank correction" (i.e., if an associated sample also contains the contaminant, subtraction of the blank amount from the sample amount is not permitted).

- 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.

- 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 X A-1 for a summary of the evaluation requirements.

### 1.5 Quality Control Requirements for WSC-CAM-X A

### 1.5.1 Specific QC Requirements and Performance Standards for WSC-CAM-X A

Specific QC requirements and performance standards for the WSC-CAM-X A protocol are presented in Table X A-1. Refer to WSC-CAM-VII A for field QC requirements. Strict compliance with the QC requirements and performance standards, as well as satisfying the CAM's other analytical and reporting requirements will provide a data user with "Presumptive Certainty" in support of Response Actions under the MCP. The concept of "Presumptive Certainty" is explained in detail in Section 2.0 of WSC-CAM-VII A.

While optional, parties electing to utilize these protocols will be assured of "Presumptive Certainty" of data acceptance by agency reviewers. In order to achieve "Presumptive Certainty" for analytical data, parties must:

(a) Use the analytical method specified for the selected CAM protocol;
(b) Incorporate **all** required analytical QC elements specified for the selected CAM protocol;
(c) Implement, as necessary, required corrective actions and analytical response actions for **all** non-conforming analytical performance standards;
(d) Evaluate and narrate, as necessary, **all** identified CAM protocol non-compliances; and
(e) Comply with **all** the reporting requirements specified in WSC-CAM-VII A, including retention of reported and unreported analytical data and information for a period of ten (10) years.

In achieving "Presumptive Certainty" status, parties will be assured that analytical data sets:

- ✓ Satisfy the broad QA/QC requirements of 310 CMR 40.0017 and 40.0191 regarding the scientific defensibility, precision and accuracy, and reporting of analytical data; and

- ✓ May be used in a data usability and representativeness assessment, as required in 310 CMR 40.1056(2)(k) and 40.1057(2)(k) for Permanent and Temporary Solution submittals, consistent with the guidance described in MassDEP Policy #WSC-07-350, *MCP Representativeness Evaluations and Data Usability Assessments*.

### 1.6 Special Analytical Considerations for WSC-CAM-X A

The following bullets highlight 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. However, the initial demonstration of proficiency and all performance criteria in the method and this CAM Protocol 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 (e.g., methanolic ammonium hydroxide) 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 (e.g., methanolic ammonium hydroxide) 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 (e.g., methanolic ammonium hydroxide) 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.

  MassDEP requires that the laboratory provide details on the procedure followed 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.
  - ✓ If subsampling is unavoidable, vortexing or shaking samples prior to subsampling could mitigate this

stratification or accumulation at air/water interface.

- 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 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. Currently, the target PFAS which do not have an exact corresponding isotopically labeled analog are as follows: PFTrDA, PFPeS, PFHpS, PFNS, PFDS, PFDoS, ADONA, PFMPA, PFMBA, NFDHA, 9Cl-PF3ONS, 11Cl-PF3OUdS, PFEESA, 3:3 FTCA, 5:3 FTCA, and 7:3 FTCA.

- 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. For Presumptive Certainty purposes, if additional EIS is added to a sample extract which is diluted, respond “NO” to Question C of the “MassDEP MCP Analytical Protocol Certification Form” and address this nonconformance in the laboratory narrative.

## Table X A-1: Specific QC Requirements and Performance Standards for PFAS (USEPA 1633) Using WSC-CAM-X A

| Required QC Parameter | Data Quality Objective | Required Performance Standard | Required Deliverable? | Rejection Criteria per WSC-07-350[1] | Required Corrective Action | Required Analytical Response Action |
|---|---|---|---|---|---|---|
| Initial Demonstration of Proficiency | Laboratory Analytical Accuracy & Precision | (1) Must be performed prior to using method on samples.<br>(2) Must be performed for each matrix.<br>(3) Must contain all target analytes.<br>(4) Must follow procedure in Section 9.2 of USEPA Method 1633. | No | NA | 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.<br>(2) Use mass calibration solution specified by instrument manufacturer. | No | NA | 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.<br>(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 | NA | 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.<br>(2) Must be of sufficient width to detect earlier-eluting branched isomers. | No | NA | NA | NA |
| Bile Salt Interference Check | Laboratory Analytical Accuracy | (1) Performed with the initial calibration and at the beginning of each analytical sequence.<br>(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.<br>(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 | NA | 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.<br>Report any non-conformances in laboratory narrative. |

## Table X A-1: Specific QC Requirements and Performance Standards for PFAS (USEPA 1633) Using WSC-CAM-X A

| Required QC Parameter | Data Quality Objective | Required Performance Standard | Required Deliverable? | Rejection Criteria per WSC-07-350[1] | Required Corrective Action | Required Analytical Response Action |
|---|---|---|---|---|---|---|
| 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.<br>(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.<br>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.<br>(3) Low standard must be ≤RL/LLOQ.<br>(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.<br>(5) Percent relative standard deviations (%RSDs) of response factors ≤20% for each target PFAS and EIS <u>or</u> relative standard error (RSE) ≤20 for each target PFAS and EIS.<br>NOTE: correlation coefficient (“r”) and coefficient of determination (“$r^2$”) are not appropriate for measuring linearity with this method. RSE must be used for calibration curve assessment when a weighted regression calibration is used.<br>(6) Must contain all target PFAS, EIS, and NIS.<br>(7) Calibration must be performed under the same conditions as the samples.<br>(8) Laboratories may use average response factors or linear/non-linear regression curves | No | NA | Recalibrate or prepare new calibration standards, as required by method. | Sample analysis cannot proceed without a valid initial calibration.<br>Report non-conforming compounds (%RSD or RSE >20) in laboratory narrative. |

## Table X A-1: Specific QC Requirements and Performance Standards for PFAS (USEPA 1633) Using WSC-CAM-X A

| Required QC Parameter | Data Quality Objective | Required Performance Standard | Required Deliverable? | Rejection Criteria per WSC-07-350[1] | Required Corrective Action | Required Analytical Response Action |
|---|---|---|---|---|---|---|
| | | for quantitation.<br>(9) Quantitative standards including linear and branched isomers must be used for target PFAS if commercially available. Currently, these include PFOA, PFOS, PFHxS, PFOSA, PFNA, NMeFOSAA, NEtFOSAA, NMeFOSA, NEtFOSA, NMeFOSE, and NEtFOSE.<br>(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. | | | | |
| Instrument Sensitivity Check (ISC) | Laboratory Analytical Accuracy and Method Sensitivity | (1) At beginning of each analytical sequence.<br>(2) Concentration at level of laboratory's RL/LOQ.<br>(3) S/N ratio ≥ 3:1 for quantification and confirmation ions or ≥ 10:1 for quantification ions for target PFAS with no confirmation ions.<br>(4) Must contain all target PFAS, EIS, and NIS.<br>(5) Percent recoveries (%Rs) must be between 70-130% for each target PFAS.<br>(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.<br>(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 | NA | (1) Perform instrument maintenance, reanalyze ISC and/or recalibrate as required by method.<br>(2) Reanalyze "associated samples" if ISC exhibited low response.<br>(3) Reanalyze "associated samples" if ISC exhibited high response and associated target PFAS were detected in the "associated samples" within 10x the LOQ.<br>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. |

## Table X A-1: Specific QC Requirements and Performance Standards for PFAS (USEPA 1633) Using WSC-CAM-X A

| Required QC Parameter | Data Quality Objective | Required Performance Standard | Required Deliverable? | Rejection Criteria per WSC-07-350[1] | Required Corrective Action | Required Analytical Response Action |
|---|---|---|---|---|---|---|
| Calibration Verification | Laboratory Analytical Accuracy | (1) Prior to samples, every 10 samples, and at the end of the analytical sequence.<br>(2) Concentration level near midpoint of curve.<br>(3) Must contain all target PFAS, EIS, and NIS.<br>(4) Recommended to be prepared using standard source different than used for initial calibration, if available (can use different lot number from same vendor).<br>(5) %Rs must be within 70-130% for each target PFAS.<br>(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.<br>(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.<br>(8) Quantitative standards including linear and branched isomers must be used for target PFAS if commercially available. Currently, these include PFOA, PFOS, PFHxS, PFOSA, PFNA, NMeFOSAA, NEtFOSAA, NMeFOSA, NEtFOSA, NMeFOSE, and NEtFOSE.<br>(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. | No | NA | (1) Perform instrument maintenance, reanalyze calibration verification and/or recalibrate as required by method.<br>(2) Reanalyze "associated samples" if beginning or ending calibration verification exhibited low response.<br>(3) Reanalyze "associated samples" if beginning or ending calibration verification exhibited high response and associated target PFAS were detected in the "associated samples."<br><br>NOTE: "Associated samples" refers to all samples analyzed since the last acceptable calibration verification. | 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. |

## Table X A-1: Specific QC Requirements and Performance Standards for PFAS (USEPA 1633) Using WSC-CAM-X A

| Required QC Parameter | Data Quality Objective | Required Performance Standard | Required Deliverable? | Rejection Criteria per WSC-07-350[1] | Required Corrective Action | Required Analytical Response Action |
|---|---|---|---|---|---|---|
| Instrument Blank | Laboratory Method Sensitivity (contamination evaluation) | (1) Analyzed at beginning of analytical sequence and after analysis of high concentration samples.<br>(2) Must be prepared in same solution as calibration standards and contain the EIS and NIS.<br>(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 | NA | (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.<br>(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.<br>(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 samples, whichever is more frequent.<br>(2) Matrix-specific (e.g., water, soil, tissue).<br>(3) Aqueous method blanks must be prepared using volume of water typical of samples in batch.<br>(4) Soil/sediment/biosolids and tissue method blanks must be prepared using the same nominal mass as used for samples.<br>(5) Target PFAS must be <RL/LLOQ. | Yes | NA | (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.<br>(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-extraction is not possible, report non-conformance in laboratory narrative.<br>(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 contamination should also be documented in the laboratory narrative.<br>(3) If re-extraction is performed within holding time and yields acceptable method blank results, the laboratory may report results of the re-extraction only.<br>(4) If re-extraction is performed outside of holding time, the laboratory must report results of both |

## Table X A-1: Specific QC Requirements and Performance Standards for PFAS (USEPA 1633) Using WSC-CAM-X A

| Required QC Parameter | Data Quality Objective | Required Performance Standard | Required Deliverable? | Rejection Criteria per WSC-07-350[1] | Required Corrective Action | Required Analytical Response Action |
|---|---|---|---|---|---|---|
| | | | | | | the initial extraction and re-extraction. |
| 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.<br>(2) Target PFAS must be <RL/LLOQ. Calculate concentrations in equipment blank, as per Section 11.4 of USEPA Method 1633. | Yes | NA | 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 samples, whichever is more frequent.<br>(2) Mid-level OPR: Concentration level near midpoint of curve.<br>(3) Low-level OPR: Concentration at 2x RL/LLOQ.<br>(4) Must contain all target PFAS.<br>(5) Matrix-specific (e.g., soil, water, tissue).<br>(6) Aqueous OPRs must be prepared using volume of water typical of samples in batch.<br>(7) Soil/sediment/biosolids and tissue OPRs must be prepared using the same nominal mass as used for samples.<br>(8) %Rs of target PFAS and EIS must meet acceptance limits in Tables 5 through 8 of USEPA Method 1633. | Yes | Recovery <10%; affects nondetect results for affected analyte in all samples extracted with this OPR. | (1) Locate source of problem; re-extract and re-analyze OPR and associated samples if >10% of all analytes are outside of criteria.<br>(2) If ≤10% of compounds are outside of the acceptance criteria, re-extraction is not required as long as recoveries are >10%.<br>(3) If >10% of compounds are above the acceptance criteria, re-extraction is not required if affected compounds were not detected in associated samples. | (1) If sample re-extraction is not possible, report non-conformance in laboratory narrative.<br>(2) If recovery is outside of acceptance criteria for any analyte, report non-conforming compounds in laboratory narrative.<br>(3) If re-extraction is performed within holding time and yields acceptable OPR results, the laboratory may report results of the re-extraction only.<br>(4) If re-extraction is performed outside of holding time, the laboratory must report results of both the initial extraction and re-extraction. |
| 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 $^{13}C$- or $^{18}O$-labeled analogues | Yes | Recovery <5% and S/N < 10:1; affects associated nondetect results in affected sample. | (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 | (1) Report recoveries outside of acceptance limits in laboratory narrative.<br>(2) If re-extraction or diluted re-analysis yields similar EIS non-conformances, the laboratory must report results of both |

## Table X A-1: Specific QC Requirements and Performance Standards for PFAS (USEPA 1633) Using WSC-CAM-X A

| Required QC Parameter | Data Quality Objective | Required Performance Standard | Required Deliverable? | Rejection Criteria per WSC-07-350[1] | Required Corrective Action | Required Analytical Response Action |
|---|---|---|---|---|---|---|
| | | of the target PFAS, if they become commercially available. Several PFAS do not currently have an exact isotopic standard match[2].<br>(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. | | | recovery must be at least 5% and S/N ≥20:1 in order to be able to use the EIS for quantitation.<br>(2) Re-extract the sample using a reduced sample volume or mass.<br>NOTE: If EIS recoveries are high and associated target analytes are not detected in sample, corrective action is not required. | extractions/analyses.<br>(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.<br>(4) If re-extraction is performed outside of the holding time and yields acceptable EIS recoveries, the laboratory must report results of both extractions.<br>(5) If any isotopically labeled EISs used for quantitation of target PFAS vary from Table 10 of the method, these must be noted in the laboratory narrative. |
| 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.<br>(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 | Recovery <5% and S/N < 10:1; affects associated nondetect results in affected sample.<br>Rejection of affected results will be based on professional judgement. If the %R of the associated EIS is within the acceptance criteria, rejection may not be warranted. If the NIS %R is low due to a bad injection or significant matrix suppression, | If NIS is outside of limits, re-analyze sample.<br>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.<br>(2) If re-analysis yields similar NIS non-conformances, the laboratory must report results of both analyses.<br>(3) If re-analysis is performed within holding time and yields acceptable NIS recoveries, the laboratory may report results of the re-analysis only.<br>(4) If re-analysis is |

## Table X A-1: Specific QC Requirements and Performance Standards for PFAS (USEPA 1633) Using WSC-CAM-X A

| Required QC Parameter | Data Quality Objective | Required Performance Standard | Required Deliverable? | Rejection Criteria per WSC-07-350[1] | Required Corrective Action | Required Analytical Response Action |
|---|---|---|---|---|---|---|
| | | | | rejection of the associated nondetect results may be warranted. | | performed outside of the holding time and yields acceptable NIS recoveries, the laboratory must report results of both analyses. |
| MS/MSD | Method Accuracy & Precision in Sample Matrix | (1) Every 20 samples (at discretion of laboratory or at request of data user).<br>(2) Matrix-specific (e.g., water, soil, tissue).<br>(3) Concentration level near midpoint of curve.<br>(4) Must contain all target PFAS.<br>(5) %Rs between 40-140%.<br>(6) Relative percent differences (RPDs) ≤20 for waters and ≤30 for solids and tissue. | Yes<br>ONLY when requested by the data user | Recovery <10%; affects nondetect result for affected analyte in unspiked sample only. | Check OPR; if recoveries are acceptable in OPR, narrate non-conformance. | Note non-conformances in laboratory narrative. |
| Matrix Duplicate (MD) | Method Precision in Sample Matrix | (1) At request of data user.<br>(2) Prepare by extracting and analyzing an additional aliquot of the field sample. NOTE: an additional bottle is required for water matrices.<br>(3) RPDs ≤20 for waters and ≤30 for solids and tissue. | Yes<br>ONLY when requested by the data user | NA | Narrate. | Note non-conformances in laboratory narrative. |
| 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.<br>(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.<br>(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.<br>(4) Ion abundance ratios:<br>• Ion abundance ratios must fall within ±50% of the ion abundance ratios observed in either the mid-point initial | NA | NA | If the S/N ratio is not met due to high background noise, perform instrument maintenance to correct the issue.<br>If the S/N ratio is not met and the background is low, report the result as a nondetect. | 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. |

## Table X A-1: Specific QC Requirements and Performance Standards for PFAS (USEPA 1633) Using WSC-CAM-X A

| Required QC Parameter | Data Quality Objective | Required Performance Standard | Required Deliverable? | Rejection Criteria per WSC-07-350[1] | Required Corrective Action | Required Analytical Response Action |
|---|---|---|---|---|---|---|
| | | calibration standard or the beginning calibration verification.<br>• Note: the total response of the linear and branched isomers in the quantitative calibration standards must be used to define the ion abundance ratio.<br>• 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).<br>(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.<br>(6) The laboratory must use the average response factor, linear or non-linear regression curve generated from the associated initial calibration for quantitation of each target PFAS.<br>(7) Results must be reported with 3 or more "significant figures" if ≥RL/LLOQ. If reporting values below the RL/LLOQ, report with 2 or more "significant figures".[3]<br>(8) 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. Optionally, values below the sample-specific RL/LLOQ can be reported as estimated, if requested. The laboratory must report results for samples and blanks in a consistent manner<br>(2) Dilutions: If diluted and undiluted analyses are performed, the laboratory should report | NA | NA | NA | (1) Complete analytical documentation for diluted and undiluted analyses must be made available for review during an audit.<br>(2) The performance of dilutions (including samples extracted at a reduced |

**Table X A-1: Specific QC Requirements and Performance Standards for PFAS (USEPA 1633) Using WSC-CAM-X A**

| Required QC Parameter | Data Quality Objective | Required Performance Standard | Required Deliverable? | Rejection Criteria per WSC-07-350[1] | Required Corrective Action | Required Analytical Response Action |
|---|---|---|---|---|---|---|
| | | results for the lowest dilution within the valid calibration range for <u>each</u> analyte. The associated QC (e.g., method blanks, EIS, etc.) for each analysis must be reported.<br>(3) Results for soils/sediments must be reported on a dry-weight basis for comparison to MCP regulatory standards. Results for tissue samples must be reported on a wet-weight basis.<br>(4) Refer to Appendix X A-1 for chain-of-custody requirements regarding preservation, cooler temperature, and holding times.<br>(5) Report all PFAS results in their acid or neutral forms.<br>(6) The laboratory must report the procedure/option used for the preparation and analysis of aqueous samples with elevated particulates (see Section 1.6 of this CAM Protocol).<br>(7) The laboratory must clearly document any method modifications in the laboratory narrative (see Section 1.6 of this CAM Protocol). | | | | volume or mass) must be documented in the laboratory narrative or on the report form. 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.<br>(3) If samples are not preserved properly or are not received with an acceptable cooler temperature, note the non-conformances in the laboratory narrative.<br>(4) If samples are extracted and/or analyzed outside of the holding time, note the non-conformances in the laboratory narrative.<br>(5) For Presumptive Certainty purposes, if additional EIS is added to a sample extract which is diluted, respond "NO" to Question C of the "MassDEP MCP Analytical Protocol Certification Form" and address this nonconformance in the laboratory narrative. |

[1] As per Appendix IV of MassDEP Policy #WSC-07-350, *MCP Representativeness Evaluations and Data Usability Assessments*, if these results are observed, data users should consider nondetect results as unusable and positive results as estimated with a significant low bias.

[2] Current PFAS without an exact isotopic standard match: PFTrDA, PFPeS, PFHpS, PFNS, PFDS, PFDoS, ADONA, PFMPA, PFMBA, NFDHA, 9Cl-PF3ONS, 11Cl-PF3OUdS, PFEESA, 3:3 FTCA, 5:3 FTCA, 7:3 FTCA.

[3] Reporting protocol for "significant figures" is a policy decision included for standardization and consistency for reporting of results and is not a definition of "significant" in the scientific or mathematical sense.

## 1.7 Analyte List for WSC-CAM-X A

The MCP analyte list for WSC-CAM-X A is presented in Table X A-2. The list is comprised of potential contaminants that are readily-analyzable by WSC-CAM-X A.

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. Sources of various MassDEP standards and criteria are as follows:

- Reportable Quantities (RQs) and Reportable Concentrations (RCs) as described in 310 CMR 40.1600, The Massachusetts Oil and Hazardous Materials List (MOHML), in Subpart P of the MCP may be found at the following URL: http://www.mass.gov/dep/cleanup/laws/regulati.htm#mcp
- An online searchable Oil & Hazardous Materials List of RQs and RCs values may be found at the following URL: http://eeaonline.eea.state.ma.us/DEP/MOMHL/hazmat.aspx
- An updated list of MCP Method 1 Standards may be found at the following URL: https://www.mass.gov/regulations/310-CMR-4000-massachusetts-contingency-plan

Only six of the analytes listed in Table X A-2 have a promulgated MCP Method 1 groundwater/soil standard. The remaining analytes listed are designated “consensus contaminants” and do not have promulgated MCP Method 1 Standards as of the publication date of this revision.

### 1.7.1 Analyte List Reporting Requirements for WSC-CAM-X A

While it is not necessary to request and report all the WSC-CAM-X A analytes listed in Table X A-2 to obtain “Presumptive Certainty” status, it is necessary to document use and reporting of a reduced analyte list, for site characterization and data representativeness considerations. MassDEP strongly recommends use of the full analyte list during the initial stages of site investigations, and/or at sites with an unknown or complicated history of uses of oil or hazardous materials. These assessment activities may include but are not limited to:

- ✓ Immediate Response Actions (IRAs) performed in accordance with 310 CMR 40.0410;
- ✓ Initial Site Investigation Activities performed in accordance with 310 CMR 40.0405(1);
- ✓ Phase I Initial Site Investigation Activities performed in accordance with 310 CMR 40.0480 through 40.0483; and
- ✓ Phase II Comprehensive Site Investigation Activities performed in accordance with 310 CMR 40.0830

In a limited number of cases, the use of the full analyte list for a chosen analytical method may not be necessary, with respect to data representativeness concerns, including:

- ✓ Sites where substantial site/use history information is available to rule-out all but a limited number of contaminants of concern, and where use of the full analyte list would significantly increase investigative costs; or

- ✓ Well-characterized sites where initial full-analyte list testing efforts have sufficiently narrowed the list of contaminants of concern.

**Note: a data user who avoids the detection and quantitation of a contaminant that is present or likely present at a site above background levels by limiting an analyte list could be found in criminal violation of MGL c. 21E or any regulations or orders adopted or issued thereunder.**

In cases where a reduced list of analytes is requested, laboratories must still employ the specified QC requirements and performance standards in WSC-CAM-X A to obtain “Presumptive Certainty” status.

## 2.0 Data Usability Assessment

Specific guidance applicable to all Permanent and Temporary Solutions, including Permanent and Temporary Solutions on a portion of a disposal site, for preparation of Representativeness Evaluations and Data Usability Assessments pursuant to 310 CMR 40.1056(2)(k) and 40.1057(2)(k), respectively, of the MCP is provided in *MCP Representativeness Evaluations and Data Usability Assessments* (Policy #WSC-07-350). This document provides general information regarding the purpose and content of these required evaluations as a component of and in support of a Permanent or Temporary Solution submittal. The most current version of this document may be found at the following URL: http://www.mass.gov/dep/cleanup/laws/policies.htm#finpol.

Overall usability of data produced using this CAM protocol should be evaluated for compliance with project-specific data objectives using MassDEP Policy #WSC-07-350, regardless of “Presumptive Certainty” status.

## 3.0 Reporting Requirements for WSC-CAM-X A

### 3.1 General Reporting Requirements for WSC-CAM-X A

General environmental laboratory reporting requirements for analytical data used in support of assessment and evaluation decisions at MCP disposal sites are presented in WSC-CAM-VII A, Section 2.4. This guidance document provides limited recommendations for field QC, as well as the required content of the laboratory report, which includes:

- Laboratory identification information,
- Analytical results and supporting information,
- Sample- and batch-specific QC information,
- Laboratory Report Certification Statement,
- Copy of the Analytical Protocol Certification Form,
- Laboratory narrative contents, and
- Chain-of-custody form requirements.

**Table X A-2: Analyte List for WSC-CAM-X A (USEPA 1633)**

| Analyte | Acronym | CASN | Analyte | Acronym | CASN |
|---|---|---|---|---|---|
| **Perfluoroalkyl Carboxylic Acids** | | | **Perfluorooctane Sulfonamides** | | |
| Perfluorobutanoic acid | PFBA | 375-22-4 | Perfluorooctanesulfonamide | PFOSA | 754-91-6 |
| Perfluoropentanoic acid | PFPeA | 2706-90-3 | N-methyl perfluorooctanesulfonamide | NMeFOSA | 31506-32-8 |
| Perfluorohexanoic acid | PFHxA | 307-24-4 | N-ethyl perfluorooctanesulfonamide | NEtFOSA | 4151-50-2 |
| Perfluoroheptanoic acid | PFHpA | 375-85-9 | **Perfluorooctane Sulfonamidoacetic Acids** | | |
| Perfluorooctanoic acid | PFOA | 335-67-1 | N-methyl perfluorooctanesulfonamidoacetic acid | NMeFOSAA | 2355-31-9 |
| Perfluorononanoic acid | PFNA | 375-95-1 | N-ethyl perfluorooctanesulfonamidoacetic acid | NEtFOSAA | 2991-50-6 |
| Perfluorodecanoic acid | PFDA | 335-76-2 | **Perfluorooctane Sulfonamide Ethanols** | | |
| Perfluoroundecanoic acid | PFUnA | 2058-94-8 | N-methyl perfluorooctanesulfonamidoethanol | NMeFOSE | 24448-09-7 |
| Perfluorododecanoic acid | PFDoA | 307-55-1 | N-ethyl perfluorooctanesulfonamidoethanol | NEtFOSE | 1691-99-2 |
| Perfluorotridecanoic acid | PFTrDA | 72629-94-8 | **Per- and Polyfluoroether Carboxylic Acids** | | |
| Perfluorotetradecanoic acid | PFTeDA | 376-06-7 | Hexafluoropropylene oxide dimer acid | HFPO-DA | 13252-13-6 |
| **Perfluoroalkyl Sulfonic Acids** | | | 4,8-Dioxa-3H-perfluorononanoic acid | ADONA | 919005-14-4 |
| Perfluorobutanesulfonic acid | PFBS | 375-73-5 | Perfluoro-3-methoxypropanoic acid | PFMPA | 377-73-1 |
| Perfluoropentanesulfonic acid | PFPeS | 2706-91-4 | Perfluoro-4-methoxybutanoic acid | PFMBA | 863090-89-5 |
| Perfluorohexanesulfonic acid | PFHxS | 355-46-4 | Nonafluoro-3,6-dioxaheptanoic acid | NFDHA | 151772-58-6 |
| Perfluoroheptanesulfonic acid | PFHpS | 375-92-8 | **Ether Sulfonic Acids** | | |
| Perfluorooctanesulfonic acid | PFOS | 1763-23-1 | 9-Chlorohexadecafluoro-3-oxanonane-1-sulfonic acid | 9Cl-PF3ONS | 756426-58-1 |
| Perfluorononanesulfonic acid | PFNS | 68259-12-1 | 11-Chloroeicosafluoro-3-oxaundecane-1-sulfonic acid | 11Cl-PF3OUdS | 763051-92-9 |
| Perfluorodecanesulfonic acid | PFDS | 335-77-3 | Perfluoro(2-ethoxyethane)sulfonic acid | PFEESA | 113507-82-7 |
| Perfluorododecanesulfonic acid | PFDoS | 79780-39-5 | **Fluorotelomer Carboxylic Acids** | | |
| **Fluorotelomer Sulfonic Acids** | | | 3-Perfluoropropyl propanoic acid (3:3 Fluorotelomer carboxylic acid) | 3:3 FTCA | 356-02-5 |
| 1H,1H,2H,2H-Perfluorohexanesulfonic acid (4:2 fluorotelomer sulfonic acid) | 4:2 FTS | 757124-72-4 | 2H,2H,3H,3H-Perfluorooctanoic acid (5:3 Fluorotelomer carboxylic acid) | 5:3 FTCA | 914637-49-3 |
| 1H,1H,2H,2H-Perfluorooctanesulfonic acid (6:2 fluorotelomer sulfonic acid) | 6:2 FTS | 27619-97-2 | 3-Perfluoroheptyl propanoic acid (7:3 Fluorotelomer carboxylic acid) | 7:3 FTCA | 812-70-4 |
| 1H,1H,2H,2H-Perfluorodecanesulfonic acid (8:2 fluorotelomer sulfonic acid) | 8:2 FTS | 39108-34-4 | | | |

**CASN – Chemical Abstracts Service Numbers**

### 3.2 Specific Reporting Requirements for WSC-CAM-X A

Specific QC requirements and performance standards for WSC-CAM-X A are presented in Table X A-1. Specific reporting requirements for WSC-CAM-X A are summarized below in Table X A-3 as "Required Analytical Deliverables (**YES**)". Requirements listed as "YES" must always be included as part of the laboratory deliverable for this method. It should be noted that data for those items listed as "NO" under "Required Analytical Deliverables" must be available for review during an audit and may also be requested for inclusion in the analytical deliverable on a client-specific basis.

Soil and sediment results must 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.

### 3.2.2 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, $\text{RL/LLOQ}_d$:

$$\text{RL/LLOQ}_d = \text{DF X Lowest Calibration Standard for Target Analyte}$$

It should be understood that samples with elevated RLs/LLOQs as a result of a dilution may not be able to satisfy MCP standards/criteria in some cases if the $\text{RL/LLOQ}_d$ is greater than the applicable MCP standard or criterion 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.

<u>**NOTE**</u>: **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.

**Table X A-3 Routine Reporting Requirements for WSC-CAM-X A (USEPA 1633)**

| Parameter | Required Analytical Deliverable |
|---|---|
| Mass Calibration | ***NO*** |
| Mass Calibration Verification | ***NO*** |
| Retention Time Windows | ***NO*** |
| Bile Salt Interference Check | ***NO*** |
| Initial Calibration | ***NO*** |
| Instrument Sensitivity Check (ISC) | ***NO*** |
| Calibration Verification | ***NO*** |
| Instrument Blank | ***NO*** |
| Method Blank | ***YES*** |
| Equipment Blank (Tissue Samples only) | ***YES*** |
| Ongoing Precision and Recovery (OPR): Low-level and mid-level | ***YES*** |
| Extraction Internal Standards (EIS) | ***YES*** |
| Non-extracted Internal Standards (NIS) | ***NO*** |
| Matrix Spike (MS) | ***YES (if requested by data user)*** |
| Matrix Spike Duplicate (MSD) | ***YES (if requested by data user)*** |
| Matrix Duplicate (MD) | ***YES (if requested by data user)*** |
| Identification and Quantitation | ***NO (except if ion abundance ratio outside of acceptance criteria)*** |
| General Reporting Issues | ***YES*** |

# Appendix X A-1

## Sample Collection, Preservation, and Handling Procedures for PFAS Analyses

Sample preservation, container and analytical holding time specifications for aqueous, solid, and tissue matrices for PFAS analyzed in support of MCP decision-making are summarized below and presented in Appendix VII A-1 of WSC-CAM-VII A, *Quality Assurance and Quality Control Guidelines for the Acquisition and Reporting of Analytical Data Conducted in Support of Response Actions Conducted Under the Massachusetts Contingency Plan (MCP)*.

| Matrix | Container[1] | Preservation[2] | Holding Time |
|---|---|---|---|
| Aqueous Samples (with exception of landfill leachates) | (2) 500-mL* high density polyethylene (HDPE) container w/ linerless HDPE or polypropylene caps<br>(1) 125-mL* HDPE container w/ linerless HDPE or polypropylene cap[3] | Cool to ≤6ºC or ≤-20ºC | See next page |
| Landfill Leachates | (3) 125-mL* HDPE container w/ linerless HDPE or polypropylene caps[4] | Cool to ≤6ºC or ≤-20ºC | |
| Soil/Sediment/ Biosolids Samples | (1) 500-mL* HDPE container w/ linerless HDPE or polypropylene cap, no more than ¾ full | Cool to ≤6ºC or ≤-20ºC | |
| Tissue Samples | Tissue: wrap in aluminum foil or insert into resealable plastic bag or food-grade polyethylene tubing<br>Homogenized fish: (1) 100-mL HDPE container w/ linerless HDPE or polypropylene cap | Cool to ≤6ºC; must be received by laboratory within 24 hours.<br>Freeze sample (≤-20ºC) 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.**

| **Holding Times*** | | | |
|---|---|---|---|
| **Aqueous** | | **Soil/Sediment/Biosolids** | **Tissue** |
| **Samples stored at 0-6°C and protected from light** | **Samples stored at ≤-20°C and protected from light** | **Samples stored at either 0-6°C or ≤-20°C and protected from light** | **Samples stored at ≤-20°C and protected from light** |
| 28 days from collection to extraction[1,2] | 90 days from collection to extraction[1] | 90 days from collection to extraction[1,3]<br>**<u>Soils and Sediments</u>**: Some soils and sediments may exhibit microbial growth when stored at 0-6◦C.<br>**<u>Biosolids</u>**: Microbial activity in biosolids samples at 0-6°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. | 90 days from collection to extraction[1,3] |
| **Extracts stored at 0-6°C or ≤-20°C and protected from light and stored in sealed polypropylene vials.** | | | |
| 90 days from extraction to analysis[4] | | | |

***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.**

**Note: According to Appendix IV of MassDEP Policy #WSC-07-350, *MCP Representativeness Evaluations and Data Usability Assessments*, if the holding time is exceeded by >2x the allowable holding time, data users should consider nondetect results as unusable and positive results as estimated with a significantly low bias. However, for PFAS, this rule does not apply as the target PFAS negatively affected by a holding time exceedance (polyfluoroalkyl PFAS) can transform and cause a potential high bias for the regulated PFAS.**

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

[2] 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). MassDEP expects the 28-day holding time to be followed in this instance. However, data users should note that extractions performed greater than 7 days from collection may result in potential low bias for NMeFOSE and NEtFOSE and potential high bias for the transformation products, NMeFOSAA, and NEtFOSAA. If NMeFOSE, NEtFOSE, NMeFOSAA, and NEtFOSAA are contaminants of concern, data users may want to use the freezing option to extend the holding time.

[3] This exception is noted in Sections 8.5.2, 8.5.3, and 8.5.6 of USEPA Method 1633. MassDEP expects the 90-day holding time to be followed in this instance. Data users should note that extractions performed greater than 3 days from collection may result in potential low bias for NFDHA in soil, sediment, and tissue samples, regardless of storage temperature for soil/sediment and tissue. No issues are noted in the method for NFDHA in biosolids samples.

[4] This exception is noted in Sections 8.5.5 and 8.5.6 of USEPA Method 1633. MassDEP expects the 90-day holding time to be followed in this instance. Data users should note that analyses performed greater than 28 days from extraction may result in potential high bias for 9Cl-PF3ONS and 11Cl-PF3OUdS.

# Appendix X A-2

# Data Deliverable Requirements for Data Audits

If requested by MassDEP, submission of the information listed below may be required to perform a data audit to verify compliance with the analytical methods and to evaluate accuracy and reliability of the reported results. These deliverables represent a "full data package" including all sample documentation from receipt through preparation, analysis, and data reporting. The laboratory must ensure that these deliverables are available, in the event a data audit is performed. The laboratory is required to retain these deliverables for a period of 10 years from the date generated.

| **DELIVERABLE REQUIREMENTS FOR DATA AUDITS<br>WSC-CAM-X A (PFAS by LC-MS/MS: USEPA 1633)** | |
|---|---|
| **Laboratory Narrative** | Must comply with the required laboratory narrative contents as described in WSC-CAM-VII A |
| **Sample Handling Information** | Chains-of-custody (external and internal), sample receipt logs (cooler temperatures), correspondences |
| **Miscellaneous Logs** | Dry weight logs Injection logs<br>Soil/sediment/tissue sample weight logs<br>Freezer logs<br>Sample preparation/cleanup logs[1] |
| **Mass Calibration Data** | Documentation that initial mass calibration and mass calibration verification performed annually, at a minimum |
| **Bile Salt Interference Check Data** | Extracted ion chromatograms for PFOS, TDCA, TCDCA, and/or TUDCA, as applicable for each interference check<br>Quantitation reports for each interference check |
| **Initial Calibration Data** | Summary of response factors for all standards in initial calibration; average response factors, %RSDs or RSEs for all target PFAS and EIS<br>Extracted ion chromatograms for all target PFAS, EIS, and NIS included in initial calibration<br>Quantitation reports for all standards used in initial calibration<br>S/N ratios for target PFAS<br>Concentrations of target PFAS, EIS, and NIS used must be clearly presented<br>Raw data for qualitative standards used for linear and branched PFAS isomers, if included |
| **Instrument Sensitivity Check (ISC) Data** | Summary of %Rs for all target PFAS and EIS<br>Extracted ion chromatograms for all ISCs<br>S/N ratios for target PFAS<br>Quantitation reports for all ISCs |
| **Calibration Verification Data** | Summary of %Rs for all target PFAS and EIS<br>Extracted ion chromatograms for all calibration verification standards<br>Quantitation reports for all calibration verification standards<br>S/N ratios for target PFAS<br>Concentrations of target PFAS, EIS, and NIS used must be clearly presented |

**DELIVERABLE REQUIREMENTS FOR DATA AUDITS**
**WSC-CAM-X A (PFAS by LC-MS/MS: USEPA 1633)**

| | |
|---|---|
| | Raw data for qualitative standards used for linear and branched PFAS isomers, if included |
| **Sample Results** | Extracted ion chromatograms for all sample analyses, re-analyses, re-extractions, and dilutions<br>Quantitation reports for all sample analyses, re-analyses, re-extractions, and dilutions<br>S/N ratios for detected target PFAS<br>Percent solids results<br>Summary of results, including RLs/LLOQs for each target PFAS<br>Dates of extraction and analysis |
| **Method Blank, Instrument Blank, and Equipment Blank Results** | Extracted ion chromatograms for all blanks<br>Quantitation reports for all blanks<br>Summary of results, including RLs/LLOQs<br>Summary of how method blank was prepared in solid, aqueous, and tissue matrices, as appropriate |
| **OPR Results** | Extracted ion chromatograms for all low-level and mid-level OPRs<br>Quantitation reports for all low-level and mid-level OPRs<br>Summary of results, including concentrations detected, concentrations spiked, and %Rs<br>Summary of how low-level and mid-level OPRs were prepared in solid, aqueous, and tissue matrices, as appropriate |
| **MS/MSD Results (if performed)** | Extracted ion chromatograms for all MS/MSDs<br>Quantitation reports for all MS/MSDs<br>Summary of results, including unspiked sample concentrations, concentrations detected, concentrations spiked, %Rs, and RPDs<br>Summary of how MS/MSDs were prepared in solid, aqueous, and tissue matrices, as appropriate |
| **Matrix Duplicate Results (if performed)** | Extracted ion chromatograms for all MDs<br>Quantitation reports for all MDs<br>Summary of results, including concentrations detected in the original and duplicate analyses and RPDs |
| **QC Summaries** | EIS recoveries<br>Summary of NIS area counts |
| **Other Information** | Ion ratios for detected PFAS in samples and QC samples |

Quantitation reports must exhibit quantitation ion and confirmation ion (as appropriate) area counts of target PFAS, EIS, and NIS.

[1] Must clearly indicate sample weights or volumes, solvents used, final extract volumes, extraction method used, SPE cartridge, elution solvents, procedures used for aqueous samples with elevated particulates, where appropriate for the matrix