Quality Assurance Project Plan Addendum

N.W. Mauthe Superfund Site
PFAS Groundwater Sampling
Appleton, Wisconsin

November 19, 2020
Terracon Project No. 58117057
WDNR BRRTS #02-45-000127

Prepared for:
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Oshkosh, Wisconsin

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QUALITY ASSURANCE PROJECT PLAN ADDENDUM
N.W. MAUTHE SUPERFUND SITE
PFAS GROUNDWATER SAMPLING

Draft – Version 1

November 19, 2020
Terracon Project No. 58117057

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1.0 INTRODUCTION

This Quality Assurance Project Plan (QAPP) Addendum to the *Wisconsin Department of Natural Resources Site Assessment Project Assurance Project Plan* (approved by U.S. EPA on August 8, 2014) describes the sampling and analysis methods that will be implemented with the collection of water quality samples for per- and polyfluoroalkyl substances (PFAS) from the monitoring well network at the N.W. Mauthe Superfund Site (Site), Appleton, Wisconsin. The Site is a former chromium plating facility that potentially may have used PFAS in their processes. The original QAPP did not cover PFAS sampling.

2.0 PROJECT BACKGROUND

This Site is a former electroplating facility that engaged in hard chrome plating. Results of the Remedial Investigation and Feasibility Study (RI/FS) from 1991 through 1993 revealed that the site was contaminated with zinc, cadmium, chromium, and cyanide. Volatile organic compounds (VOCs) including 1,1,1-trichloroethane, 1,1,2-trichloroethane, 1,1-dichloroethene, 1,1-dichloroethane, trichloroethene and other chlorinated hydrocarbons are also present. PFAS have not been investigated at this site to date.

Remedial Design/Remedial Action (RD/RA) activities took place at the Site in a phased approach. Phase I of the RD/RA involved the excavation of contaminated soils and the installation of groundwater collection trenches in 1995. Phase II involved the construction of the existing groundwater treatment facility in 1996 which began operation in June 1997. Active treatment of collected groundwater ended on April 18, 2006, with direct discharge to the City of Appleton (COA) sanitary sewer under permit.

The monitoring well network at the site is comprised of 20 monitoring points. A Scope of Work (SOW) to sample groundwater at the Site for PFAS was sent to Terracon by the WDNR in a March 6, 2020, electronic mail. Terracon provided a proposal for PFAS groundwater sampling in a March 13, 2020, proposal, which was approved by the WDNR. The monitoring points will be sampled for PFAS analysis following approval of this QAPP Addendum. As noted earlier, the groundwater collection system is currently discharging to the COA sanitary sewer. The PFAS

groundwater monitoring results will be used to evaluate whether modifications to the groundwater collection system are warranted.

The WDNR has requested preparation of a remedial action options report to evaluate options for treating the effluent for PFAS, if detected and if the detected concentrations require pre-treatment prior to discharge to the COA sanitary sewer system. Interim measures will also be evaluated to facilitate continued operation of the groundwater collection system if PFAS is detected until the selected remedial option is implemented.

3.0 TECHNICAL APPROACH

Although the Site is a United States Environmental Protection Agency (USEPA) Superfund Site, the Wisconsin Department of Natural Resources (WDNR) is the responsible agency overseeing this project. Under this Plan, PFAS sampling and analysis method activities will be primarily focused on testing the groundwater at each monitoring well in the existing monitoring well network. The test results will provide PFAS assessment information. This information may be used to support decision-making related to treating and disposing the recovered groundwater.

The PFAS groundwater sampling program will be conducted in accordance with Wisconsin Administrative Code (WAC), Chapter NR 716 requirements. The fieldwork and data analysis will be conducted under supervision of a Chapter NR 712, WAC, hydrogeologist as required by Chapter NR 716, WAC. The project manager, Scott A. Hodgson (Wisconsin PG-1229), meets the requirements of the NR 712 hydrogeologist.

The goals and objectives to this QAPP are to collect and analyze PFAS compounds, listed later in this document, in samples from groundwater monitoring wells and groundwater recovery sumps associated with the N.W. Mauthe Superfund Site.

4.0 PROJECT ORGANIZATION

Terracon will conduct PFAS groundwater sampling activities at the N.W. Mauthe Superfund Site in Appleton, Wisconsin.

Terracon will use a laboratory to be contracted to analyze water samples for PFAS compounds as outlined later in this document (Section 9.0).

Contact information for the project team is provided in Table 1 below.

TABLE 1 - PROJECT TEAM CONTACT INFORMATION

Title / Responsibility	Name	Telephone	Email
WDNR Project Contacts	Jennifer Borski Gwen Saliares	M: 920-360-0853 M: 920-510-4343	Jennifer.Borski@wisconsin.gov Gwen.Saliares@wisconsin.gov
EPA Project Manager	Jeffrey Thomas	(312) 353-4872	Thomas.Jeffrey@epa.gov
Terracon Project Manager	Scott A. Hodgson, PG	D:414-209-7640 M:920-791-9206	sahodgson@terracon.com
Terracon Technical Support	Eduardo Gasca PE	D:630-427-8103	egasca@terracon.com
Terracon Authorized Project Reviewer	Blaine R. Schroyer, PE	D:414-423-0255 M:920-205-0011	blaine.schroyer@terracon.com
Laboratory Project Manager, Eurofins TestAmerica	Sandie Fredrick	D: 920-261-1660 M: 920-261-1660	sandie.fredrick@testamericainc.com
Laboratory Technical Director, Eurofins TestAmerica	Robert Hrabak	D: 916-374-4433 M: 916-296-1629	robert.hrabak@testamericainc.com

It is the responsibility of all personnel involved in this project to perform and document the required procedures outlined in this QAPP.

5.0 HEALTH AND SAFETY

Terracon is committed to the safety of all its employees. As such, and in accordance with our Incident and Injury Free® safety program, Terracon has developed a safety plan to be used by our personnel during field services. Prior to commencement of onsite activities, Terracon will hold a meeting to review health and safety needs for this specific project. At this time, we anticipate performing fieldwork in an OSHA Level D work uniform consisting of hard hats, safety glasses, protective gloves, and steel-toed boots in compliance with PFAS-specific PPE requirements (see Section 8.3). Prior to the PFAS sampling event, field personnel will receive in-house training on appropriate procedures, personal protective equipment, materials, and equipment to be used during PFAS sampling including potential sources of cross-contamination. The Terracon project manager, Scott Hodgson, is responsible to assure that field personnel have received the pre-task training.

It may become necessary to upgrade this level of protection, at additional cost, while sampling activities are being conducted in the event that other chemical constituents are encountered in groundwater that present an increased risk for personal exposure. Chromium is the only

compound anticipated to potentially be encountered that would result in an increased risk of personal exposure. Historically at this site, elevated chromium is apparent from bright yellow coloration in groundwater. Visual inspection of groundwater color will be conducted in the field to identify the presence of chromium. No other in field monitoring or equipment is proposed for this sampling event.

In addition, due to Covid-19, Terracon retains the right to stop work without penalty at any time Terracon believes it is in the best interests of Terracon's employees or subcontractors to do so in order to reduce the risk of exposure to the coronavirus. As such, Terracon requests WDNR to respond quickly to all requests for information made by Terracon related to Terracon's pre-task planning and risk assessment processes. WDNR acknowledges its responsibility for notifying Terracon of any circumstances that present a risk of exposure to the coronavirus or individuals who have tested positive for COVID-19 or are self-quarantining due to exhibiting symptoms associated with the coronavirus.

On the day of sampling, Terracon personnel will take their temperature before mobilizing to the site. The results will be recorded in the daily field notes. **If temperature reading is above 100.4 °F (37.8°C), staff will stay home and contact the project manager, Scott Hodgson, to discuss identifying alternative staff**. General Terracon Covid-19 procedures are included in Appendix A.

6.0 DATA QUALITY OBJECTIVES

The Data Quality Objective (DQO) process is used to establish performance or acceptance criteria for data collection activities. These criteria in turn serve as the basis for designing a plan for collecting data of sufficient quality and quantity to support goals of the groundwater monitoring project.

For the Project Action Levels, the WDNR proposes including 2 nanograms per liter (ng/L) for PFOS and PFOA, based on the Wisconsin Department of Health Services (DHS) proposed Preventive Action Limit for those two compounds (https://www.dhs.wisconsin.gov/water/gws-cycle10.htm). WDNR does not have proposed standards for any of the other compounds yet, so Project Action Levels are only proposed for those two. At this time, we are uncertain of the risks posed from some of the compounds, so if other compounds are detected, WDNR will evaluate. The Project Action Levels are included as part of the QA/QC Criteria table included in Appendix B. The Wisconsin method expectations described in the Wisconsin guidance document, *Wisconsin PFAS Aqueous (Non-Potable Water) and Non-Aqueous Matrices Method Expectations, Version 12.16.2019, Per- and Polyfluorinated Alkyl Substances (PFAS) Analysis Using Isotope Dilution by LC/MS/MS* (copy attached in Appendix B) will serve as the performance criteria.

The procedures and formulas for calculating applicable quality control (QC) statistics, for example, for precision, bias, outliers and missing data are provided in Section A.8 in the *Wisconsin Department of Natural Resources Site Assessment Project Quality Assurance Project Plan* approved by U.S. EPA on August 8, 2014.

DQO's specific to PFAS groundwater sampling at this project include:

- Reduce, with a goal to eliminate, potential cross-contamination issues through appropriate PFAS-free personal protective equipment and sampling materials (Section 8);
- Identify and assess potential procedural or site-specific sources of PFAS cross-contamination through collecting field equipment blanks and field reagent blanks (Section 8); and
- Use Wisconsin-approved laboratories that follow Wisconsin requirements. In this case there are no laboratories that are accredited through the State of Wisconsin for PFAS analysis. Instead Terracon will use a Wisconsin WDNR-approved laboratory (Eurofins TestAmerica, Sacramento, California) that is going through the accreditation process and has been audited by the State of Wisconsin (Section 9).

7.0 COMMUNICATION WITH PROGRAM STAKEHOLDERS

Communications with PFAS groundwater monitoring program stakeholders (USEPA, WDNR, , laboratory (Eurofins TestAmerica-Sacramento, California) selected for PFAS analyses) will be coordinated with the Terracon Project Manager through the use of e-mail and by phone. Terracon will coordinate with the WDNR, the laboratory (Eurofins TestAmerica-Sacramento, California) that will support the PFAS analyses, and if necessary, with other entities, as approved by and coordinated with the WDNR Project Contacts, to access sampling locations, coordinate sampling dates, and pick-up and delivery of sampling bottles from the laboratory.

8.0 FIELD PROCEDURES FOR SAMPLING

The following sections provide an overview of the planned sampling activities, including the sampling methodologies that will be implemented by Terracon. Additional precautions and procedures are required for this project due to the sensitivity of PFAS analysis and the increased risk for cross-contamination.

During the PFAS groundwater sampling event, static water levels will be measured at each monitoring well in the network prior to purging. The electronic water level indicator(s) will be decontaminated before use and between monitoring wells using certified PFAS-free water obtained from the laboratory. Field equipment blanks (two) will be collected from the final rinse

water and submitted for analysis of PFAS.

Each of the existing monitoring wells (20 total) plus two collection sump access points will be sampled as agreed in conversation with and directive from Robert Thompson of U.S. EPA on February 3, 2020. The monitoring well locations are shown on Figure 1, Appendix C.

If a sampling point becomes inaccessible, we will proceed without that data collection point. This event is being conducted as a preliminary screening. Results of this sampling event will be used to determine if implementation of an alternate plan to replace an inaccessible sampling point during future monitoring events is required.

Blind duplicates indicate the field duplicates that will be labeled in a manner that precludes the laboratory from identifying which samples were collected as duplicates.

A proposed sampling schedule Gantt Chart is included in Appendix C.

8.1 Contamination Prevention/Decontamination

Pre-task planning and discussion with Terracon field personnel about the sensitivity of PFAS analysis and increased risk of cross-contamination will take place in advance of the field sampling event. Instructions on how to prevent or reduce contamination of samples are summarized below.

8.2 Clothing and PPE

Many materials used in the course of environmental investigation can potentially contain PFAS. The following procedures are guidelines that will be followed by Terracon personnel in preparation for and during collection of groundwater samples:

- Clothing manufactured from natural fibers such as cotton is preferred (no clothing or boots containing Gore-Tex, Tyvek, or treated with aftermarket waterproofing agents or fabric softeners will be used during sampling);
- Sampling personnel will shower to remove cosmetics, moisturizers, creams, etc., on the day of sampling and cosmetics, moisturizers, creams, etc., will not be reapplied before sampling;
- Only if needed, authorized sunscreens (all organic natural sunscreens that are “free” or “natural”) and insect repellants (various natural repellents, DEET) will be used immediately before or during sampling activities; and,
- Wet weather gear such as rain jackets, pants, and muck boots will be made of polyurethane, rubber, or PVC.

8.3 Field Conditions/Sampling Equipment

Groundwater samples will be collected via low-flow methods using a peristaltic pump, dedicated high density polyethylene (HDPE) drop tubing, and a water quality meter with flow-through cell. Drop tubing used at each monitoring well will remain as dedicated tubing for future sampling events.

During sampling activities, the following sampling equipment, procedures, and restrictions shall be used/followed by Terracon and sampling personnel:

- High density polyethylene (HDPE) or polypropylene materials shall be used. No field equipment should contain Teflon, polytetrafluoroethylene (PTFE), (anything with fluoro in the name), fluorinated ethylene propylene (FEP), ethylene tetrafluoroethylene (ETFE), polyvinylidene fluoride (PVDF), or low-density polyethylene (LDPE). Safety Data Sheets (SDSs) will be obtained and reviewed before considering materials for use during sampling;
- Silicone tubing;
- Loose paper (non-water resistant; no waterproof notebooks [such as Rite in the Rain]);
- Aluminum or Masonite field clipboards, only, (no plastic clipboards or binders); and
- Food containers will not be allowed onsite other than bottled water or hydration beverages. Food and drink packaging shall be kept out of the area during sampling.

During sampling activities, the following guidelines shall also be followed by Terracon and sampling personnel:

- Store samples in coolers with regular ice only;
- Consider where all sampling equipment has been used and assess cleanliness, if there is any doubt, decontaminate thoroughly with laboratory-provided PFAS-free water or, absent PFAS-free water, distilled water;
- Be aware of field conditions such as blowing dust, which could impact equipment and sample integrity; and
- Keep detailed notes on all field activities and thoroughly document any potential contamination issues and how they were addressed.

8.4 Decontamination

The electronic water level indicator will be decontaminated before use and between monitoring wells. The decontamination water will be collected and disposed by being put into the groundwater collection system and discharged into the City of Appleton sanitary sewer.

During sampling activities, the following decontamination procedures and guidelines shall be followed by Terracon personnel:

- Decontamination final rinse water should be laboratory-provided PFAS-free water; and
- The SDSs for detergents or soaps used in decontamination procedures will be reviewed to ensure fluoro-surfactants are not listed as ingredients.

8.5 Sample Collection, Preservation, and Storage

During the PFAS groundwater sampling event, static water levels will be measured at each monitoring well in the network prior to purging. Each monitoring well will be purged and sampled using low-flow sampling techniques with a peristaltic pump, dedicated drop tubing, and a water quality meter with a flow-through cell. Purging will proceed at approximately 200 milliliters per minute with measurement of water levels, pH, temperature, specific conductance, dissolved oxygen (DO), and oxidation-reduction potential (ORP) during purging. Purging will continue until parameters are stable to within 10% for three consecutive readings taken 5 minutes apart. Once stable, groundwater samples will be collected at the same pumping rate as was used for purging. Purge water will be collected and disposed by being put into the groundwater collection system and discharged into the City of Appleton sanitary sewer.

Terracon will complete a groundwater sampling information sheet for each monitoring well. A blank groundwater sampling information sheet and a blank COC form are presented in Appendix C. A list of sampling procedures is provided below:

- Two 250-milliliter (mL) high-density polyethylene (HDPE) containers with HDPE screw caps will be used to collect the samples. No preservatives are proposed for use during this PFAS groundwater sampling event. For untreated groundwater source samples such as at Mauthe, the buffering and dechlorinating reagent Trizma® is not required to be added.
- The sample handler must thoroughly wash their hands before sampling and wear nitrile gloves while filling and sealing the sample bottles. PFAS contamination during sampling can occur from a number of common sources, such as food packaging and certain foods and beverages. Proper hand washing and wearing nitrile gloves will aid in minimizing this type of accidental contamination of the samples.
- Sample bottles must not be pre-rinsed with sample before collection.
- Fill sample bottles. Samples do not need to be collected headspace free.
- After collecting the sample, cap carefully to avoid spillage, and agitate by inverting a few times. Keep samples sealed until analysis.

- Three Field Reagent Blanks (FRB) will be collected as part of the sampling effort. One will be collected near MW-101 on the Miller Electric Property to the west, one near the railroad tracks, and one in a residential area.
  - At the laboratory, a sample bottle is filled with reagent water and preservatives, sealed, and shipped to the sampling site along with the sample bottles. For each FRB shipped, an empty sample bottle (no preservatives) must also be shipped.
  - At the sampling site, the sampler must open the shipped FRB and pour the reserved reagent water into the empty shipped bottle, seal and label this bottle as the FRB.
  - The FRB is shipped back to the laboratory along with the samples and analyzed to ensure that PFAS were not introduced into the sample during sample collection and handling.
  - If sample preservative is used for the FRB, it must be the same batch used for the samples.
- Samples must be chilled during shipment, not allowed to freeze and must not exceed 6 degrees Celsius (°C) during the first 48 hours following collection. Sample temperature must be confirmed to be at or below 6°C when samples are received at the laboratory.
- Samples stored in the laboratory must be stored below 6°C until extraction, but it should not be frozen. Do not allow samples to freeze
- Aqueous samples must be extracted within 14 days of sampling when samples are properly preserved, shipped, and stored.
- Extracts must be stored at room temperature and analyzed within 28 days after extraction.

8.6 Chain-of-Custody Procedures

The Chain-of-Custody (COC) record will be completed by the sampler and will remain with the samples. The sampler will retain responsibility for the integrity of the samples until samples are relinquished to another person or the laboratory as indicated on the COC. Prior to shipping the cooler is sealed with the COC inside. The COC will include the record of persons responsible for the samples from the time of sampling until receipt at the laboratory in conformance with standard COC protocols. A copy of the complete COC will be included as part of the laboratory report. A blank COC is included in Appendix C.

9.0 LABORATORY ANALYSIS AND CERTIFICATION

The aqueous samples will be analyzed for the WI PFAS Group (36 PFAS analytes) by LC/MS Method 537 MOD, as shown in the table below. Preparation holding time shall not exceed 14 days and the analytical holding time shall not exceed 40 days.

In addition to the groundwater samples collected, one blind duplicate will be collected for every 10 groundwater samples collected in conformance with Wisconsin Administrative Code (WAC), Chapter NR 716. For this groundwater monitoring project, three duplicate samples will be collected. Two field equipment blank samples will also be collected. The field equipment blanks will be collected from PFAS-free water obtained from the laboratory that is used to decontaminate the water level indicators (one field equipment blank for each water level indicator). Samples and completed chain-of-custody forms will be transported to the designated laboratory for analysis on a standard turnaround time as agreed between Terracon and the laboratory (normal turn-15 business days).

The laboratory, Eurofins TestAmerica, Sacramento, California, is a PFAS-certified analytical laboratory (NELAP accredited through the State of Oregon); however, it is not yet certified by the State of Wisconsin. It is one of three laboratories recommended by the WDNR that are in the process of being certified and have been audited for Wisconsin PFAS accreditation in potable water, non-potable water, and solid matrices. The certification process was delayed due to the Covid-19 pandemic, but both WDNR and Eurofins TestAmerica anticipate that certification will be completed by late summer 2020. In the interim, WDNR has accepted the data from Eurofins TestAmerica as though they were certified.

The following table summarizes the method analyses for the groundwater monitoring project:

TABLE 2 – SAMPLE QUANTITIES AND ANALYTICAL METHODS

Analysis	Number of Samples	Laboratory Method
Aqueous Matrices	20 Monitoring Wells 2 System Influent 3 QA/QC Blind Duplicates 2 Field Equipment Blanks 3 Field Reagent Blanks	WI PFAS Group by LC/MS Method 537MOD (36 analytes)

The PFAS analytes are listed below:

TABLE 3: PFAS ANALYTES

Compound Name	CAS Number
Perfluorobutanoic acid (PFBA)	375-22-4
Perfluoropentanoic acid (PFPeA)	2706-90-3
Perfluorohexanoic acid (PFHxA)	307-24-4
Perfluoroheptanoic acid (PFHpA)	375-85-9
Perfluorooctanoic acid (PFOA)	335-67-1
Perfluorononanoic acid (PFNA)	375-95-1
Perfluorodecanoic acid (PFDA)	335-76-2
Perfluoroundecanoic acid (PFUnA)	2058-94-8
Perfluorododecanoic acid (PFDoA)	307-55-1
Perfluorotridecanoic acid (PFTriA)	72629-94-8
Perfluorotetradecanoic acid (PFTeA)	376-06-7
Perfluoro-n-hexadecanoic acid (PFHxDA)	67905-19-5
Perfluoro-n-octadecanoic acid (PFODA)	16517-11-6
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
4:2 Fluorotelomer sulfonic acid (4:2 FTS)	757124-72-4
6:2 Fluorotelomer sulfonic acid (6:2 FTS)	27619-97-2
8:2 Fluorotelomer sulfonic acid (8:2 FTS)	39108-34-4
10:2 Fluorotelomer sulfonic acid (10:2 FTS)	120226-60-0
Perfluorooctane sulfonamide (FOSA)	754-91-6
N-Methyl perfluorooctane sulfonamide (NMtFOSA)	31506-32-8
N-Ethyl perfluorooctane sulfonamide (NEtFOSA)	4151-50-2
N-Methyl perfluorooctane sulfonamidoacetic acid (NMEFOSAA)	2355-31-9
N-Ethyl perfluorooctane sulfonamidoacetic acid (NEtFOSAA)	2991-50-6
N-Methyl perfluorooctane sulfonamidoethanol (NMeFOSE)	24448-09-7
N-Ethyl perfluorooctane sulfonamidoethanol (NEtFOSA)	1691-99-2
Hexafluoropropylene oxide dimer acid (HFPO-DA [GenX])	13252-13-6

Table 3 continued	
4,8-Dioxa-3H-perfluorononanoic acid (DONA)	919005-14-4
9-chlorohexadecafluoro-3-oxanonane-1-sulfonic acid (F53B-Maj)	756426-58-1
11-chloroeicosafluoro-3-oxaundecane-1-sulfonic acid (F53B-Min)	763051-92-9

10.0 MEASUREMENT PERFORMANCE CRITERIA

A central aspect of the DQO process is the documentation of the data quality indicators, which specify the performance criteria and acceptance criteria for the quality of the data collected for the plan and for existing data to be included in a project.

10.1 Precision

The laboratory objective for precision is to meet the performance for precision demonstrated for the methods on similar samples and to meet data quality objectives of the USEPA, State, and/or other regulatory programs. Precision is defined as the degree of reproducibility of measurements under a given set of analytical conditions (exclusive of field sampling variability). Precision is documented on the basis of replicate analysis, usually duplicate or matrix spike (MS) duplicate samples.

10.2 Accuracy

The laboratory objective for accuracy is to meet the performance for accuracy demonstrated for the methods on similar samples and to meet data quality objectives of the USEPA, State, and/or other regulatory programs. Accuracy is defined as the degree of bias in a measurement system. Accuracy may be documented through the use of laboratory control samples (LCS) and/or MS. A statement of accuracy is expressed as an interval of acceptance recovery about the mean recovery.

The quality assurance/quality control criteria for the analytical EPA Method 537MOD are summarized in Appendix B.

11.0 QUALITY ASSURANCE AND QUALITY CONTROL

Quality assurance is a set of operating principles that, if strictly followed during sample collection and analysis, will produce data of known and defensible quality. This will ensure that the accuracy of the data can be stated with a high level of confidence.

11.1 Field Quality Control

Approved sampling procedures will be used to ensure field procedure QC. Terracon staff performing sampling activities will receive the training necessary to ensure that approved sampling procedures are fully and properly used when completing sampling activities. Field quality control measures will include collecting three blind duplicate samples in conformance with Chapter NR 716, WAC. In addition, two field equipment blanks will also be collected. Each will be collected from laboratory-provided PFAS-free water used to rinse each of the two electronic water level indicators to be used during the monitoring event.

11.2 Data Quality Control

Three field reagent blanks will be collected during the monitoring event. One field reagent blank will be collected near monitoring well MW-101 on the Miller Electric property to the west, one near the railroad tracks, and one in a residential area.

12.0 DATA VALIDATION

The laboratory will follow the Wisconsin guidance document, *Wisconsin PFAS Aqueous (Non-Potable Water) and Non-Aqueous Matrices Method Expectations, Version 12.16.2019, Per- and Polyfluorinated Alkyl Substances (PFAS) Analysis Using Isotope Dilution by LC/MS/MS* (copy attached in Appendix B). Eurofins TestAmerica will provide a level IV analytical report within a normal turnaround time of 15 days following receipt of the samples. There are no established standards for PFAS so there is no requirement to achieve a specific level of quantitation. The Eurofins Test America lab quantitation limit is within the guidelines the WDNR established as target levels for lab certification.

Sample validation data includes any information that can be obtained about sample collection methods or onsite facility conditions that could interfere with the validity of water samples. Upon receipt of the laboratory report, the Terracon Project Manager will review the COC, laboratory report, and sampler field notes to evaluate the analytical results.

Data validation will be performed by EPA's ESAT contractor. A data validation level of 2b will be used, as discussed with Jeff Thomas of U.S. EPA on October 26, 2020. Documents related to data review and data validation can be obtained from EPA's ESAT contractor. Actions in response to data exceeding control limits are provided in Section D.3.7 in the *Wisconsin Department of Natural Resources Site Assessment Project Quality Assurance Project Plan* approved by U.S. EPA on August 8, 2014. Data validator will follow guidelines established by EPA and will report validated data to WDNR, who will respond accordingly to any issues.

13.0 PROJECT DATA AND RECORDS

WDNR will provide a report that includes a summary of the findings of the investigative sampling and the EDD will be submitted to the EPA Region 5 data portal.

Standard record-keeping and tracking practices, the document control system or other written documentation such as SOPs is included in Section B.3 of the *Wisconsin Department of Natural Resources Site Assessment Project Quality Assurance Project Plan* approved by U.S. EPA on August 8, 2014.

Investigative Derived Waste will be managed in accordance with the provisions contained in ss. NR 716.11(6) and (7), Wisconsin Administrative Code.

The data management scheme from field to final use and storage is included in Section A.9 Documentation and Records of the *Wisconsin Department of Natural Resources Site Assessment Project Quality Assurance Project Plan* approved by U.S. EPA on August 8, 2014.

14.0 PLANNED PROJECT ASSESSMENTS, CORRECTIVE RESPONSE ACTIONS, AND QUALITY ASSURANCE MANAGEMENT REPORTS

The actions to be taken when problems occur, individual(s) responsible for corrective action, and how this should be documented and reported is included in Section D Data Validation/Usability of the *Wisconsin Department of Natural Resources Site Assessment Project Quality Assurance Project Plan* approved by U.S. EPA on August 8, 2014.

APPENDIX A

Terracon Covid-19 Procedures

- Understand the Symptoms, Prevention and Treatment - Familiarize yourself with COVID-19 symptoms and guidance for prevention and treatment, as provided by the CDC or WHO.
- Wash Your Hands Frequently – Use soap and water for at least 20 seconds. When soap and water are unavailable, use an alcohol-based hand sanitizer with at least 60% alcohol.
- Stay home if you or your family members are sick - If you or your family members are sick or experiencing symptoms you should stay home. Not doing so increases the risk of spreading this as well as other illnesses. If you exhibit even mild symptoms avoid contact with others, call your healthcare provider immediately, and inform your supervisor.
  - ✓ Are you experiencing cough, congestion, shortness of breath or difficulty breathing? If yes, please do not come to work and notify your supervisor.
  - ✓ Are you experiencing any two of the following fever, chills, fatigue, muscle pain, headache, sore throat, nausea, vomiting, diarrhea, loss of taste or smell? If yes, please do not come to work and notify your supervisor.
  - ✓ Did you take your temperature and is it less than 100.4º F? If your temperature is above 100.4º F, please do not come to work and notify your supervisor.

  If you have trouble breathing, persistent pain or pressure in the chest, new confusion (unresponsive / incoherence), bluish lips or face, inability to stay awake - get medical attention immediately
- Take extra precautions if you are an at-risk group – If you are pregnant, over 60 years of age, or have underlying health conditions that weaken your immune system (heart disease, diabetes) you may be more at risk for serious illness if you contract COVID-19.
- Use social distancing when around people - The virus is spread primarily from person to person by those who are in close contact (roughly 6 feet or less) through respiratory droplets produced through coughing or sneezing that may be airborne or on an individual's skin. Social distancing is one of the most important steps you can take to prevent the disease. Avoid close contact with people – especially those who are sick. Elbow bumps and head nods should replace handshakes and hugs! During meetings, position chairs further apart (~ 6 feet) to reduce the potential spread of the virus.
- Clean your work area regularly - the COVID-19 virus can also be contracted by touching a surface or object that has the virus on it and then touching their own mouth, nose, or possibly their eyes. Cleaning of work surfaces and tools is a required proactive step.

For more information, please contact Terracon Safety
safety@terracon.com

- Practice good hygiene - cover your mouth when you cough or sneeze. Immediately dispose of tissues. If you don't have a tissue, cough or sneeze into your upper sleeve, not your hands.
- Avoid touching your face - eyes, nose or mouth especially with unwashed hands or after contact with surfaces or other workers.
- Use of Masks - Cloth face coverings may help prevent people who have COVID-19 from spreading the virus to others. CDC recommends wearing cloth face coverings in public settings where other social distancing measures are difficult to maintain (e.g., grocery stores and pharmacies) especially in areas of significant community-based transmission. The use of cloth face coverings do not replace and must be used along with other preventive measures, including social distancing, frequent handwashing, and cleaning and disinfecting frequently touched surfaces. The cloth face coverings recommended are not surgical masks or N-95 respirators. Terracon employees should wear cloth face coverings when social distancing measures are difficult to maintain, per PTP09 Cover Your Mouth or local requirements. If heat stress becomes a concern, immediately remove face coverings and stop work to rest.
- Travel
  - Reference travel guidelines on the Terracon COVID-19 resource page regarding business travel.
  - If you have personal travel planned, please be considerate of those in your office and report travel to your supervisor.
  - Consult the CDC's Considerations for Travelers page, review and follow the CDC guidance regarding self-isolation or other measures to take upon returning from travel.

COVID-19 Pre-Task Planning
Project Sites

It is the responsibility of all managers and supervisors in an office to understand, communicate, implement, and assist our employees in applying these precautionary steps as well as the General Guidelines for COVID-19 Pre-Task Planning document.

- Evaluate Job Sites and discuss with Client and or Contractor – Project managers and assigned field staff should evaluate job sites where we will be working for potential exposure. Obtain as much information as you can from the client and/or contractor on current projects and for new projects.
  - Is the site high risk for exposure – like a hospital or medical facility?
  - Have there been reported COVID-19 cases or suspected cases at the site?
  - What precautions has our client and or contractor put in place for disease transmission prevention?
  - Ask our client or contractor to immediately notify us of suspected cases at the site.
  - What requirements does our client or contractor have for Terracon personnel that will be on-site?
  - Has anything changed that will impact our services, schedule, staffing, costs? If yes, we will need to discuss with our client immediately.
- Agency shutdowns that impact our services – Be aware that some agencies may be shut down and not respond to requests. Licensing, permitting, traffic control and 811 One Call Services, and local building officials may be impacted. In no way will Terracon deviate from our Core Rules and Practices or Lifesaving Absolutes. Practice Our Rules to Live By P3 and, Step back for Safety. Stop Work if you feel it is unsafe to continue or if someone questions the safety of your behavior. Inform a supervisor of the situation and work together to identify and mitigate any hazard.
  - If any of these closings will impact our services, schedule, staffing, or costs, we will need to discuss with our client immediately.
- Review with our project team - If an existing project, our Project Manager should have a conference call with our project personnel that will be on the project site and other critical staff (e.g. dispatcher, APR, etc.) to update any changes, requirements, and raise awareness. If for a new project, incorporate this into the kick-off meeting.
  - Share details that were provided by the client / contractor about the site.
  - Discuss tasks that may place any Terracon employees in close proximity (< 6 feet) to other workers and options for maintaining social distancing in these situations, for example:
    - Exchanging / signing paperwork, handling blueprints / specifications
    - Talking to property owners, equipment operators, other site personnel
    - Riding elevators
    - Working with our subcontractors
    - Checking in/out of the site
  - Review applicable pre-task planning documents with the team to ensure everyone knows the information and that our employees are properly equipped with supplies and information outlined in these documents.
- Use of PPE - Do not share PPE (especially respirators) and clean your PPE after use. Wear gloves as frequently as possible in the field and only remove when necessary. Treat gloved hands like bare hands – avoid touching your face with gloved hands.

- Use social distancing when around people - The virus is spread primarily from person to person by those who are in close contact (~ 6 feet or less) through respiratory droplets produced through coughing or sneezing that may be airborne or on an individual's skin. Social distancing is one of the most important steps you can take to prevent the disease. Avoid close contact with people – especially those who are sick. Elbow bumps and head nods should replace handshakes and hugs! During meetings, position chairs further apart (~ 6 feet) to reduce the potential spread of the virus.
  - Take lunches and breaks alone or at least 6 feet away from others.
  - Do not share food, cigarettes, lighters, etc.
  - When accessing stairwells or using elevators and lifts maintain as much clearance as possible. Ask to be alone in the lift.
  - Because construction sites are loud, it forces you to lean in to hear conversations or talk to others. You must maintain distance from others. Take conversations away from loud areas, talk on cell phones or text.
- Wash your hands and practice good personal hygiene – The best way to prevent the spread of COVID-19 is to practice good personal hygiene. This includes:
  - Equip employees with personal hygiene kits. Do not rely on the site to provide personal hygiene supplies. Water can be carried in portable containers and labeled "non-potable water". Label containers with contents if products are transferred into portable containers.
  - Options for personal hygiene supplies include hand sanitizer or wipes with at least 60% alcohol, soap / water. Please use professional supplies and do not attempt to make 'home made' cleaning supplies. Do not use cleaning supplies on your body if the product is not designed for use on the body.
  - Wash hands immediately after using portable restrooms on the project site. Frequently wash your hands with soap and water for at least 20 seconds, before eating and after blowing your nose, coughing, or sneezing. Use an alcohol-based hand sanitizer with at least 60% alcohol if soap and water is not available. Always wash hands that are visibly soiled.
  - Cover your mouth when you cough or sneeze. Immediately dispose of tissues. If you don't have a tissue, cough or sneeze into your upper sleeve, not your hands.
  - Avoid touching your eyes, nose or mouth especially with unwashed hands or after contact with surfaces or other workers.
  - Clean and disinfect tools and equipment. At a minimum, the user must clean tools after each use. Avoid sharing tools, cell phones, tablets, PPE or any other item. If it is necessary to use shared tools, clean them before use.
    - Cleaning supplies include anti-bacterial / disinfectant spray liquid, cleaning wipes, aerosol spray, and soap/water. Please use professional supplies and do not attempt to make 'home made' cleaning supplies. Select cleaning supplies from the approved EPA list.
    - Use disposable paper towels for wipe downs not reusable rags. Dispose of paper towels in the trash immediately after use.
    - Wear safety glasses and chemical resistant gloves when cleaning equipment.
- Terracon Subcontractors – Review this Pre-Task Planning guidance document with all subcontractors used on our projects as they are required to follow all guidance outlined and project site requirements.

It is the responsibility of all managers and supervisors in an office to understand, communicate, implement, and assist our employees in applying these precautionary steps as well as the General Guidelines for COVID-19 Pre-Task Planning.

- Whenever possible assign vehicles to specific personnel and avoid pool vehicles and transport of passengers – Assign vehicles to limit multiple users and the need for passengers. If passengers must be transported in the vehicle, drive with windows down and vents blowing air to maximize ventilation. If this is not possible due to weather conditions take multiple vehicles.
    - Passenger should wear cloth face coverings or KN95 masks during travel. Drivers must not wear cloth face coverings or masks when operating a vehicle.
- Clean specific areas of the vehicle before and after use - Drivers whether assigned a vehicle or using a pool vehicle should clean frequently touched objects like door and tailgate handles, steering wheel, knobs, and seat and remove all trash from the vehicle (do not leave paperwork, food wrappers, water bottles or any other waste in the vehicle cab or bed). At a minimum, the driver must clean the vehicle areas mentioned after each use.
    - Options for cleaning supplies include wipes with at least 60% alcohol, disinfectant liquid or aerosol spray, or soap / water. Please use professional supplies and do not attempt to make 'home made' cleaning supplies. Select cleaning supplies from the approved EPA list.
    - Use disposable paper towels for wipe downs not reusable rags. Dispose of paper towels in the trash immediately after use.
    - Wear safety glasses and chemical resistant gloves when cleaning the vehicle.
    - Allow the vehicle cab to ventilate for five minutes after cleaning and before driving.
- Wash your hands and practice good personal hygiene – The best way to prevent the spread of COVID-19 is to practice good personal hygiene. This includes:
    - Wash your hands with soap and water for at least 20 seconds, before beginning your trip and immediately after arrival. Use an alcohol-based hand sanitizer with at least 60% alcohol if soap and water is not available.

APPENDIX B

QA/QC Criteria for PFAS (Group) LC/MS Technology (Method 537 MOD)

Wisconsin Method Guidance Document, (*Wisconsin PFAS Aqueous [Non-Potable Water] and Non-Aqueous Matrices Method Expectations, Version 12.16.2019, Per-and Polyfluorinated Alkyl Substances [PFAS] Analysis Using Isotope Dilution by LC/MS/MS)*

Laboratory Method Standard Operating Procedure

Limits for Project: 58117057 - Limits

Analysis Group	Method Description	Method Code	Prep Method	Analyte Description	CAS Number	RL	MDL	Project Action Limits	Units	LCS - Low	LCS - High	LCS - RPD %	MS - Low	MS - High	MS - RPD %	Surrogate Low	Surrogate High
PFAS Aq	Fluorinated Alkyl Substances	PFC_IDA	3535_PFC	Perfluorobutanoic acid (PFBA)	375-22-4	2.00	0.350		ng/L	76	136	30	76	136	30		
				Perfluoropentanoic acid (PFPeA)	2706-90-3	2.00	0.490		ng/L	71	131	30	71	131	30		
				Perfluorohexanoic acid (PFHxA)	307-24-4	2.00	0.580		ng/L	73	133	30	73	133	30		
				Perfluoroheptanoic acid (PFHpA)	375-85-9	2.00	0.250		ng/L	72	132	30	72	132	30		
				Perfluorooctanoic acid (PFOA)	335-67-1	2.00	0.850	2.000	ng/L	70	130	30	70	130	30		
				Perfluorononanoic acid (PFNA)	375-95-1	2.00	0.270		ng/L	75	135	30	75	135	30		
				Perfluorodecanoic acid (PFDA)	335-76-2	2.00	0.310		ng/L	76	136	30	76	136	30		
				Perfluoroundecanoic acid (PFUnA)	2058-94-8	2.00	1.10		ng/L	68	128	30	68	128	30		
				Perfluorododecanoic acid (PFDoA)	307-55-1	2.00	0.550		ng/L	71	131	30	71	131	30		
				Perfluorotridecanoic acid (PFTriA)	72629-94-8	2.00	1.30		ng/L	71	131	30	71	131	30		
				Perfluorotetradecanoic acid (PFTeA)	376-06-7	2.00	0.290		ng/L	70	130	30	70	130	30		
				Perfluoro-n-hexadecanoic acid (PFHxDA)	67905-19-5	2.00	0.890		ng/L	76	136	30	76	136	30		
				Perfluoro-n-octadecanoic acid (PFODA)	16517-11-6	2.00	0.460		ng/L	58	145	30	58	145	30		
				Perfluorobutanesulfonic acid (PFBS)	375-73-5	2.00	0.200		ng/L	67	127	30	67	127	30		
				Perfluoropentanesulfonic acid (PFPeS)	2706-91-4	2.00	0.300		ng/L	66	126	30	66	126	30		
				Perfluorohexanesulfonic acid (PFHxS)	355-46-4	2.00	0.170		ng/L	59	119	30	59	119	30		
				Perfluoroheptanesulfonic Acid (PFHpS)	375-92-8	2.00	0.190		ng/L	76	136	30	76	136	30		
				Perfluorooctanesulfonic acid (PFOS)	1763-23-1	2.00	0.540	2.000	ng/L	70	130	30	70	130	30		
				Perfluorononanesulfonic acid (PFNS)	68259-12-1	2.00	0.160		ng/L	75	135	30	75	135	30		
				Perfluorodecanesulfonic acid (PFDS)	335-77-3	2.00	0.320		ng/L	71	131	30	71	131	30		
				Perfluorododecanesulfonic acid (PFDoS)	79780-39-5	2.00	0.450		ng/L	67	127	30	67	127	30		
				Perfluorooctanesulfonamide (FOSA)	754-91-6	2.00	0.350		ng/L	73	133	30	73	133	30		
				NEtFOSA	4151-50-2	2.00	0.870		ng/L	78	138	30	78	138	30		
				NMeFOSA	31506-32-8	2.00	0.430		ng/L	67	154	30	67	154	30		
				N-methylperfluorooctanesulfonamidoacetic acid (NMeFOSAA)	2355-31-9	20.0	3.10		ng/L	76	136	30	76	136	30		
				N-ethylperfluorooctanesulfonamidoacetic acid (NEtFOSAA)	2991-50-6	20.0	1.90		ng/L	76	136	30	76	136	30		
				NMeFOSE	24448-09-7	4.00	1.40		ng/L	70	130	30	70	130	30		
				NEtFOSE	1691-99-2	2.00	0.850		ng/L	71	131	30	71	131	30		
				4:2 FTS	757124-72-4	20.0	5.20		ng/L	79	139	30	79	139	30		
				6:2 FTS	27619-97-2	20.0	2.00		ng/L	59	175	30	59	175	30		
				8:2 FTS	39108-34-4	20.0	2.00		ng/L	75	135	30	75	135	30		
				10:2 FTS	120226-60-0	2.00	0.190		ng/L	64	142	30	64	142	30		
				4,8-Dioxa-3H-perfluorononanoic acid (ADONA)	919005-14-4	2.00	0.180		ng/L	79	139	30	79	139	30		
				HFPO-DA (GenX)	13252-13-6	4.00	1.50		ng/L	51	173	30	51	173	30		
				9Cl-PF3ONS	756426-58-1	2.00	0.240		ng/L	75	135	30	75	135	30		
				11Cl-PF3OUdS	763051-92-9	2.00	0.320		ng/L	54	114	30	54	114	30		
				13C4 PFBA	STL00992				ng/L	25	150		25	150			
				13C5 PFPeA	STL01893				ng/L	25	150		25	150	30		
				13C2 PFHxA	STL00993				ng/L	25	150		25	150			
				13C4 PFHpA	STL01892				ng/L	25	150		25	150			
				13C4 PFOA	STL00990				ng/L	25	150		25	150			
				13C5 PFNA	STL00995				ng/L	25	150		25	150			
				13C2 PFDA	STL00996				ng/L	25	150		25	150			
				13C2 PFUnA	STL00997				ng/L	25	150		25	150			
				13C2 PFDoA	STL00998				ng/L	25	150		25	150			
				13C2 PFTeDA	STL02116				ng/L	25	150		25	150			
				13C2 PFHxDA	STL02115				ng/L	25	150		25	150			
				13C3 PFBS	STL02337				ng/L	25	150		25	150			
				18O2 PFHxS	STL00994				ng/L	25	150		25	150			
				13C4 PFOS	STL00991				ng/L	25	150		25	150			
				13C8 FOSA	STL01056				ng/L	25	150		25	150			
				d3-NMeFOSAA	STL02118				ng/L	25	150		25	150			
				d5-NEtFOSAA	STL02117				ng/L	25	150		25	150			
				d-N-MeFOSA-M	STL02275				ng/L	20	150		20	150			
				d-N-EtFOSA-M	STL02282				ng/L	20	150		20	150			
				d7-N-MeFOSE-M	STL02277				ng/L	10	120		10	120			
				d9-N-EtFOSE-M	STL02278				ng/L	10	120		10	120			
				M2-4:2 FTS	STL02395				ng/L	25	150		25	150		25	125
				M2-6:2 FTS	STL02279				ng/L	25	150		25	150			
				M2-8:2 FTS	STL02280				ng/L	25	150		25	150			
				13C3 HFPO-DA	STL02255				ng/L	25	150		25	150			

WISCONSIN DEPARTMENT OF NATURAL RESOURCES
NOTICE OF FINAL GUIDANCE & CERTIFICATION

Pursuant to ch. 227, Wis. Stats., the Wisconsin Department of Natural Resources has finalized and hereby certifies the following guidance document.

DOCUMENT ID

EA-19-0001

DOCUMENT TITLE

Wisconsin PFAS Aqueous (Non-Potable Water) and Non-Aqueous Matrices Method Expectations

PROGRAM/BUREAU

Certification Services / Environmental Analysis & Sustainability

STATUTORY AUTHORITY OR LEGAL CITATION

Wis. Stats. s. 299.11 and Wis. Admin. Code s. NR 149.41 (2)

DATE SENT TO LEGISLATIVE REFERENCE BUREAU (FOR PUBLIC COMMENTS)

9.16.19

DATE FINALIZED

12.16.19

DNR CERTIFICATION

I have reviewed this guidance document or proposed guidance document and I certify that it complies with sections 227.10 and 227.11 of the Wisconsin Statutes. I further certify that the guidance document or proposed guidance document contains no standard, requirement, or threshold that is not explicitly required or explicitly permitted by a statute or a rule that has been lawfully promulgated. I further certify that the guidance document or proposed guidance document contains no standard, requirement, or threshold that is more restrictive than a standard, requirement, or threshold contained in the Wisconsin Statutes.

Signature

Date 12/10/2019

Wisconsin PFAS Aqueous (Non-Potable Water) and Non-Aqueous Matrices Method Expectations

- Version 12.16.2019 -

Per- and Polyfluorinated Alkyl Substances (PFAS) Analysis Using Isotope Dilution by LC/MS/MS

The purpose of this document is to provide the expectations that will help the Program determine if a laboratory's method is considered suitable for analysis of PFAS in aqueous (non-potable water) and non-aqueous matrices for Wisconsin.

The Program has the legal authority under NR 149.41 (2) to determine whether the method selected by a laboratory is suitable for the matrix, type of analyte, expected level of analyte, regulatory limit, and anticipated interferences in the sample, when methods are not prescribed by covered programs under NR 149 or permits issued by the department.

Once the EPA publishes their 1600 series isotope dilution method, the Program will defer to that method for certification.

Potable water samples are analyzed utilizing EPA 537.1.

{F} = when "{F}" is listed after an expectation and the expectation is not met, then qualify the associated results on the test report. The qualifier can refer the data user to the narrative where detail is provided that indicates what the non-conformance was, and if known, the possible effects on the sample results.

Definitions are provided in Section **X, "Definitions,"** of this document.

I. Sample Handling

1. Instruct sample collectors to collect grab samples in high density polyethylene or polypropylene containers. {F} Avoid polytetrafluoroethylene (PTFE) containers and contact with PTFE surfaces.

2. Instruct sample collectors to collect an equipment blank when using equipment in the field to collect samples. {F}

3. Instruct sample collectors not to fill aqueous sample containers completely.

4. There is no chemical preservation necessary, just temperature preservation. Instruct sample collectors to ship aqueous and solid samples at above their freezing point to 6 °C. {F} Instruct sample collectors to ship tissue samples frozen. {F} Measure and document the temperature of aqueous and solid samples at sample receipt. Tissue samples received frozen can be documented as "frozen" at sample receipt.

5. Store aqueous and solid samples at above their freezing point to 6 °C at the laboratory. {F} Store tissue samples at less than or equal to -10 °C at the laboratory. {F} Store all extracts at 0 – 6 °C at the laboratory. {F}

6. Aqueous and solid sample holding times are within 28 days from collection to extraction and within 30 days from extraction to analysis. {F} Tissue sample holding times are within 1 year from collection to extraction and within 30 days from extraction to analysis. {F}

7. Rinse aqueous sample containers and all extract containers after transfers with one or more rinses of polar solvent to remove any PFAS that may have been adsorbed to container walls.

8. Thoroughly vortex or mix extracts and standards before transfer or aliquoting to remove any PFAS that may have been adsorbed to container walls.

9. Thoroughly vortex autosampler vials before loading the autosampler to remove any PFAS that may have adsorbed to container walls.

II. Initial Demonstration of Capability (IDC)

1. All analysts performing testing are expected to pass an IDC. If analysts perform only the extraction steps, then they are expected to pass the extraction portion of an IDC. If analysts perform only the analysis steps, then they are expected to pass the analysis portion of an IDC.

2. Analyze standards of all target (native) analytes and extracted internal standards (EIS) to determine retention times of the linear and branched isomers.

3. Analyze a method blank. The results are expected to be less than one-half the method reporting limit (MRL).

4. Assess precision and recovery by performing the entire procedure on four laboratory control samples (LCS) spiked at a midrange concentration of the initial calibration for each target (native) analyte. The average recovery is expected to be within 65-135%, and the RSD is expected to be less than or equal to 30%.

5. Assess recovery of the extracted internal standards (EIS) in each LCS. Except for FOSA, NMeFOSA, NEtFOSA, NMeFOSE, and NEtFOSE, EIS recoveries are expected to be within 50–150%. For FOSA, NMeFOSA, NEtFOSA, NMeFOSE, and NEtFOSE, EIS recoveries are expected to be within 20 – 150%.

III. Field Quality Control Samples

1. **Equipment blanks** (one per sampling event when equipment is used in the field to collect samples) – The results are expected to be less than the highest of the following {F}:

    a. 1/2 the MRL
    b. 1/10 the sample concentration

    It is not necessary to qualify equipment blank detections between the MDL and one-half the MRL.

2. **Field blanks** (one per sampling event for each sampling site) – The results are expected to be less than the highest of the following {F}:

    a. 1/2 the MRL
    b. 1/10 the sample concentration

    It is not necessary to qualify field blank detections between the MDL and one-half the MRL.

3. **Field duplicates** (one per sampling event for each sampling site) – The RPDs are expected to be less than or equal to 30% when analyte concentrations are greater than twice the MRL. {F} The RPDs are expected to be less than or equal to 50% when analyte concentrations are the MRL and twice the MRL. {F}

IV. Batch Quality Control Samples

1. **Method blank** (one per batch) – The results are expected to be less than the highest of the following {F}:

    a. 1/2 the MRL
    b. 1/10 the sample concentration

    It is not necessary to qualify method blank detections between the MDL and one-half the MRL.

    Method blanks are processed along with and under the same conditions, including all sample preparation steps (i.e. filtering, centrifuging), as the associated samples in the preparation batch.

2. **Laboratory control sample** (one per batch) – Spike with all target (native) analytes.

    Laboratory control samples are processed along with and under the same conditions, including all sample preparation steps (i.e. filtering, centrifuging), as the associated samples in the preparation batch.

    For aqueous and solids batches, spike the LCS at a low range (1 – 2x MRL) in each batch, or the laboratory may rotate spike concentrations between three consecutive batches alternating low range, midrange, and high range. Midrange and high range are relative to the initial calibration range. For aqueous and solid batches, the recoveries are expected to be within 60-135%, except for the low range (1 – 2x MRL) where the recoveries are expected to be within 50-150%. {F}

    For tissue batches, spike the LCS at midrange. For tissue batches the recoveries are expected to be within 60-135% with the following exceptions: for PFHxDA, PFODA, and NMeFOSA, the recoveries are expected to be within 50-135%; for PFDS, PFDoS, and 4:2 FTS, the recoveries are expected to be within 40-135%. {F}

3. **Extracted internal standards (EIS)** – Spike field samples and all quality control samples (preparation and instrument) with internal standards. The recoveries of these internal standards are used to adjust target (native) analyte concentrations. These isotopically labeled internal standards are added to the sample at the very beginning of the procedure, before extraction, centrifuging, filtering or phase separation takes place.

    In order to report quantitative results for the target (native) analytes using the EIS, a minimum signal to noise ratio of 10:1 is expected for each EIS. Do not report results with a qualifier if this minimum is not achieved.

    Except for FOSA, NMeFOSA, NEtFOSA, NMeFOSE, and NEtFOSE, the EIS recoveries are expected to be within 25-150% in samples. For FOSA, NMeFOSA, NEtFOSA, NMeFOSE, and NEtFOSE, these EIS recoveries are expected to be within 10-150% in samples. Once enough data points have been collected, the laboratory may develop their own statistical limits for these five EIS in samples. The statistical limits can be different than 10–150% as long as the expected minimum 10:1 signal to noise ratio is maintained for each EIS.

    If any EIS recoveries are outside of limits in a sample, reinject the sample. If the EIS recovery fails again, the data may be reported with a qualifier. {F}

    Use exact isotopically labeled analogs for the EIS where commercially available. As of December 2019, at least 25 of the 36 PFAS for which Wisconsin is offering certification are available as exact isotopically labeled analogs of the target (native) analytes. As of December 2019, the following 11 PFAS do not have exact isotopically labeled analogs commercially available and are therefore not currently necessary: PFTriA, PFODA, PFPeS, PFHpS, PFNS, PFDS, PFDoS, 10:2 FTSA, DONA, 9Cl-PF3ONS, and 11Cl-PF3OUdS.

For these 11 PFAS without an exact isotopically labeled analog commercially available, use an alternate EIS. The alternate EIS is expected to be isotopically labeled and is expected to be a chemically similar analyte that is close in retention time to the target (native) analyte. The alternate EIS may be from the same functional group as the target (native) analyte or have the same chain length as the target (native) analyte (whichever gives better performance). Typically, the alternate EIS comes from those EIS that are already in use. The same EIS can be used for more than one target (native) analyte.

V. Calibration (Initial and Continuing)

1. Perform initial calibration at setup and after an ICV or CCV standard failure. If an ICV or CCV standard fails, the laboratory may immediately analyze two additional consecutive ICV or CCV standards. If either of the two fails, or if immediate analysis is not possible, it is expected that a new initial calibration is performed. If both pass, then sample analysis can continue without a new initial calibration. If a CCV fails high and there are no detections in the associated samples, then analysis can proceed.

2. Initial calibration functions are expected to be as follows:

    a. Calibration factors have an RSD that is less than or equal to 20%.
    b. Linear regressions have a coefficient of determination that is greater than or equal to 0.99 and use a minimum of five non-zero concentration standards.
    c. Quadratic regressions have a coefficient of determination that is greater than or equal to 0.99 and use a minimum of six non-zero concentration standards.
    d. Do not force linear and quadratic regressions through zero.
    e. For each calibration standard, reprocess the target (native) analyte against the chosen calibration function. The reprocessed recoveries are expected to be within 70–130% of their actual concentrations, except for the lowest concentration standard, whose reprocessed recoveries are expected to be within 50–150% of their actual concentrations.

3. It is expected that sample analysis is not performed if the initial calibration fails.

4. Analyze standards of all target (native) analytes and EIS to determine retention times of the linear and branched isomers. Analyze branched isomers that have commercially available standards. As of December 2019, the following PFAS are commercially available as branched isomer analytical (quantitative) standards: PFHxS, PFOS, NMeFOSAA, and NEtFOSAA. As of December 2019, PFOA is commercially available as a branched isomer technical grade (qualitative) standard.

5. When an initial calibration is performed, it is expected that the midrange standard is used to establish absolute retention times. When an initial calibration is not performed, it is expected that the first CCV is used to establish absolute retention times.

6. Retention times of the target (native) analytes and the EIS are expected to fall within 0.4 minutes of the established absolute retention times. Comparison of the target (native) analyte and EIS retention times can help determine if analyte shifts occurred due to matrix effects.

7. **ICV (2nd source)** – It is expected that the ICV is performed with each new initial calibration before sample analysis. The ICV is analyzed after the ICB. As of December 2019, the following PFAS may be difficult to find as second sources and are therefore not currently necessary: PFHxDA, PFODA, PFDoS, NMeFOSA, NEtFOSA, NMeFOSE, and NEtFOSE. Recoveries in the ICV are expected to be within 70-130%. It is expected that sample analysis is not performed if the ICV fails.

8. **ICB** – It is expected that the ICB is analyzed immediately after the highest standard in the initial calibration and before the ICV to demonstrate the instrument is free from levels of contaminants that would bias results. The results of the ICB are expected to be less than one-half the MRL.

9. **CCV** – It is expected that CCVs are performed at the beginning and end of each analysis batch and after every 10 field samples.

    a. It is expected that the concentrations in the first CCV on non-initial calibration days are at the MRL.
    b. Target (native) analyte recoveries are expected to be within 50-150% for the CCV analyzed at the MRL.
    c. Target (native) analyte recoveries for all other CCVs are expected to be within 70-130%.
    d. It is expected that samples results are only reported when bracketed by passing CCVs unless the recovery failure is high and there are no detections of that analyte in the associated samples.

10. **CCB** – It is expected that the CCB is analyzed immediately after each CCV to demonstrate the instrument is free from levels of contaminants that would bias results. If method blanks or reagent blanks are analyzed after a CCV instead of a CCB, then it is expected that the CCB limits are used for assessment. The results of the CCBs are expected to be less than one-half the MRL.

11. It is expected that the same EIS as those used in samples are added to the initial calibration standards, ICV, CCVs, ICBs, and CCBs at the same concentration used in samples. The calibration standards (initial and continuing) are not extracted like samples. Since there is no matrix effect or extraction performed on these instrument quality control samples, the recoveries of the EIS are expected to be within 50 – 150%.

VI. Aqueous Sample Extraction

1. Extract the entire sample received in the sample container in which it was collected unless the exceptions listed below apply.

    a. Samples received at extremely high PFAS concentrations may be subsampled. {F}
    b. If more sample volume is received than what can be extracted through the solid phase extraction (SPE) cartridge, then subsampling is allowed. {F}

    Adsorption of target (native) analytes to sample collection container walls is known to occur in aqueous samples. Extract the entire aqueous sample volume. Subsampling of aqueous samples from the sample collection container is discouraged and can result in significant loss of longer-chain PFAS (e.g. carboxylic acids ≥ C9, sulfonic acids ≥ C7).

2. Spike the sample in the sample bottle it was received in by adding the EIS. Cap, invert and mix. It is expected that the EIS that are spiked into the sample are provided sufficient time to equilibrate in the sample before further processing. This allows the EIS time to disperse proportionally into the liquid phase and solid phase – same as the target (native) analytes and thereby providing a more accurate result. Add the EIS before any extraction, centrifuging, filtering or phase separation takes place.

    Biphasic and problematic sample matrices may have to use a different spiking procedure. It is best for the laboratory to contact the client prior to spiking and extraction to determine the best course of action to meet their data quality objectives. In these events, include detail in the narrative as to why spiking into the sample bottle was not possible, what was done instead, and if known, the possible effects on the sample results. {F}

3. If particulates in the sample have to be removed before using SPE, centrifuge the sample and take the liquid phase through the SPE. Samples should only be centrifuged when the suspended solids content visually appears to be high enough, by chemist inspection, that it would cause the SPE cartridge to clog.

   The laboratory could consider creating a "percent solids reference sample" that would include the minimum solids the laboratory has tested that would clog the SPE cartridge and use it to compare it to field samples. For reference, the Department of Defense has indicated that samples with percent solids greater than one percent may require centrifuging before performing the SPE procedure. Ideally, the entire sample is extracted, including the suspended solids.

4. If aqueous samples with a solid phase are centrifuged, the solid phase of the sample is expected to be a plug at the bottom of the container. It is expected that the solid phase remains in the container when rinsing the container walls with the polar elution solvent. Rinsing the container walls would therefore also include rinsing of the solids. If the polar elution solvent disrupts the solid phase significantly, the container can be centrifuged again before removing the solvent for use during the elution step of the SPE procedure.

5. If a total sample concentration is needed and there are significant solids in the sample, the initial spike of EIS into the sample container is sufficient for both phases. There is no need to re-spike the solid phase with EIS if it is being extracted separately.

6. Using filters to separate the solid phase from the liquid phase is discouraged unless there is data to demonstrate that the filters used do not result in contamination greater than one-half the MRL.

7. In the cases where a filter is used to separate the solid phase from the liquid phase, it is expected that the filter would also be rinsed to remove any potentially adsorbed PFAS. The filtrate is then added to the SPE cartridge during the elution step.

8. The data quality objectives from the data user should determine whether the solid phase of the sample has to be extracted or not. Not analyzing the solid phase may lead to a low bias in total sample concentration. Analyzing the liquid phase only would provide a liquid sample concentration result. It is expected that the laboratory would make it clear to the data user whether the reported concentrations are a total or liquid concentration sample result.

9. Determine sample volume by marking the sample level on the bottle or by weighing. It is expected that sample volumes would not be measured with a graduated cylinder. Sample volumes are expected to be measured and not assumed by container size.

   When the sample has significant solids, the laboratory should account for the weight or volume displaced by the solids in the initial sample volume determination and include this information in the test report.

10. Use an appropriate SPE cartridge for the target (native) analytes reported. A weak anion exchange cartridge has been shown to work with the PFAS for which Wisconsin is offering certification.

11. One or more rinses of polar solvent can be used for quantitative transfers. Rinse the sample bottle and cap with elution solvent, pour the solvent from each rinse through the SPE cartridge during the elution step, and collect the filtrate for analysis.

12. Bring to a quantitative final volume with the final injection solvent and vortex well.

VII. Non-Aqueous Sample Extraction

1. Homogenize the entire solid sample received in the sample container in which it was collected in by stirring the solids with a clean spatula or other suitable implement. This would help ensure that a representative subsample is taken.

2. For tissues (e.g. fish, wildlife), the target tissue (liver, fillet, whole fish) is isolated from the rest of the tissue sample. The target (isolated) tissue is ground and is typically provided to the analyst as a subsample. At the time of sample preparation, the analyst is to further homogenize the subsample by stirring with a clean spatula or other suitable implement. This would help ensure that a representative subsample is taken.

3. Spike a portion of the homogenized subsample by adding the EIS directly onto the sample. It is expected that the solvent used to carry the EIS spike onto the sample be allowed to evaporate prior to addition of the extraction solution.

4. Extract the PFAS from the non-aqueous samples with an appropriate solution prior to clean-up.

5. Use an appropriate clean-up cartridge (i.e. ENVI-Carb, W-AX, …) to remove the organic analytes extracted from the soil matrix. More than one type of clean-up cartridge can be used.

6. Use a clean-up cartridge on the fish tissue extract to eliminate known interferences with PFOS (e.g. bile acids such as taurodeoxycholic acid (TDCA)).

7. Ensure that all transfers are quantitative by solvent-rinsing with the elution solvent.

8. Bring to a quantitative final volume with the final injection solvent and vortex thoroughly.

VIII. Sample Analysis

1. Use an LC/MS/MS that is capable of negative ion ESI, produces unique product ions within retention time windows, and is able to provide a minimum of 10 scans across each peak.

2. Perform mass calibration such that the range of masses associated with all precursor and product ions are bracketed for both the primary and confirmation transitions. Documentation is expected to be available to demonstrate that the mass calibration covers this range. Calibrate the mass scale using the calibration analytes and procedure from the instrument manufacturer.

3. Analyte identification is performed using retention times, Signal/Noise ratio, Quantitation Parent Ion to Quantitation Daughter Ion (Quantitation Ion Transition), Confirmation Parent Ion to Confirmation Daughter Ion (Confirmation Ion Transition) and the Ion Transition Ratio.

4. Calculate sample results for the target (native) analytes that have exact isotopically labeled standards using isotope dilution (recovery correction using the EIS).

5. Calculate sample results for the target (native) analytes that do not have exact isotopically labeled standards using an alternate extracted isotopically labeled standard and internal standard quantitation recovery correction (recovery correction using the alternate EIS).

6. Use analytical (quantitative) standards containing both branched and linear isomers where commercially available. The analytical branched isomer standards are included in the initial calibration the same as the linear isomer

standards. Branched isomers in samples are quantitated against these analytical branched isomer standards. To calculate the target (native) analyte result, sum the resulting concentrations of all branched and linear isomers that have corresponding analytical standards.

7. Where analytical standards are not available for the branched isomers, use qualitative (technical grade) standards to identify the branched isomer using retention times, transitions, and ion transition ratios. Quantitate target (native) analytes that use qualitative branched isomer standards by integrating the branched and linear isomer peaks and sum the peak areas to get a total area. Calculate the target (native) analyte concentration using the linear isomer.

   Do not include branched isomer peaks in the initial calibration when qualitative standards are used, and do not use calibration functions from the qualitative branched isomer standards to quantitate branch isomer concentrations.

8. It is expected that the target (native) analytes that have exact labeled analogs would elute within 0.1 min of their analogs. {F}

9. Have a written policy on how retention time windows are established.

10. It is expected that the method reporting limit (MRL) concentration would not be below the lowest standard concentration in the initial calibration.

11. The MDL is expected to be less than the MRL.

12. Report sample results and all quality control blank results to the MDL and include the MRL with each result. Qualify results reported between the MDL and MRL as estimated concentrations.

    Example 1: MDL = 0.6, MRL = 2, sample result = 0.4. Report as:

Result	MDL	MRL
<0.6	0.6	2.0

    Example 2: MDL = 0.6, MRL = 2, sample result = 0.8. Report as:

Result	MDL	MRL
0.8 J	0.6	2.0

13. The MDL for PFOS and PFOA in non-potable waters are each expected to be no higher than 2 ng/L.

14. It is expected that high density polyethylene or polypropylene autosampler vials are single injection use only unless they are immediately recapped.

15. It is expected that all sample results are reported from a response that is no higher than the highest response in the initial calibration, except for samples that saturate the instrument. If supplemental EIS is needed to quantitate dilutions, qualify the results that used the supplemental EIS (in this case, true isotope dilution was not achieved).

16. It is expected that sample results that saturate the instrument are reported with “E” flags. {F}

17. For target (native) analytes, the Signal to Noise (S/N) ratio is expected to be greater than or equal to 3:1 for quantitation ions and confirmation ions. If the S/N is not achieved, it is expected that the peak would not be used in any way and the analyte would be reported as “not detected.”

18. All analytes that have two transitions are expected to include two transitions ions in the analysis (precursor ion to quantitation ion and precursor ion to confirmation ion). Use the confirmation ion for positive analyte identification. The department has provided a list of target (native) analytes and confirmation ions in section **XII**, "**Wisconsin Laboratory Accreditation Program PFAS Certification Offerings with Ions,"** of this document.

19. Assess primary and secondary ion transition ratios. It is expected that recoveries be within 50–150% of the value calculated from the midrange standard in the ICAL on ICAL days or from the beginning CCV on non-ICAL days. {F}

    The transition ratio = $\frac{\text{quantitation ion abundance}}{\text{confirmation ion abundance}}$ or $\frac{\text{confirmation ion abundance}}{\text{quantitation ion abundance}}$

    Either ratio protocol presented above can be used, but it is expected that the protocol is consistently used for all analytes.

    When the ion ratio fails, it is expected that the target (native) analytes would still be reported but qualify them as failing the ion ratio. {F} The ion transition ratio can help identify if bias is present. Ratios can be outside of limits due to interferences or the presence of branched isomers that are in the sample but not in the quantitation standards.

20. Document the primary and confirmation transitions and the ion transition ratio.

21. It is expected that the following transitions are used for quantitation of the following analytes [precursor – product] unless a technically justified reason is used and documented:

    a. PFOA 413-369
    b. PFOS 499-80
    c. PFHxS 399-80
    d. PFBS 299-80
    e. 4:2 FTS 327-307
    f. 6:2 FTS 427-407
    g. 8:2 FTS 527-507
    h. NEtFOSAA 584-419
    i. NMeFOSAA 570-419

22. The laboratory is expected to determine at what concentration the instrument has carryover at concentrations greater than one-half the MRL. The laboratory is expected to have a documented procedure to bring the instrument back in control after encountering a sample with carryover. PFAS have demonstrated a delayed release in the system.

23. Report results in acid form.

24. Verify standard purity and ensure that any standards with less than 98% purity are corrected for in the calculations.

25. Mass correct salt content in all calibration standards purchased as salts.

26. Perform a moisture analysis on solid samples (on a subsample different than that used for extraction) and adjust the final concentration of solid samples for the percent moisture.

27. If only the liquid phase of a biphasic sample was extracted, report the results as liquid concentration results instead of total sample concentration results. The lab should report the weight of the solid phase not prepared in this case. This can be detailed in the narrative.

28. If the data quality objective is to obtain a total sample concentration and the sample is biphasic, then extract and analyze both phases.

29. Do not subtract quality control blank values from sample result values.

30. Integrate linear and branched isomers in the samples in the same manner as the standards.

31. Include the following elements in the laboratory SOP:

    a. The extracted internal standards used to calculate the result of each target (native) analyte reported.
    b. The mass used for the precursor ion for each analyte.
    c. The mass used for the product quantitation ion for each analyte.
    d. The mass used for the product confirmation ion for each analyte.
    e. Instructions for conditioning and elution of the SPE cartridge.
    f. Indicate which branched isomers are calculated using the linear isomer standard.

32. PFOA and PFOS WP PT samples are necessary for aqueous (non-potable water) certification of PFOA and PFOS. To obtain the 36-analyte group for aqueous (non-potable water) or non-aqueous from Wisconsin, analyze a PT with a minimum of 6 PFAS that include PFOA and PFOS. It is expected that 80% of the spiked analytes pass.

33. Requirements in NR 149 still apply to this analysis unless otherwise specified in this document.

AS NEW INFORMATION IS PROVIDED BY THE EPA, THIS DOCUMENT WILL BE UPDATED.

IX. Other Considerations

1. Screen a separate aliquot of sample received prior to preparation of a quantitative analysis.
2. Prior to any quantitative analysis, at least one, if not multiple instrument blanks should be analyzed to assess the system for potential contamination. These instrument blanks should include EIS to enable quantitation of the contamination.
3. Evaluate all containers, water, reagents, solvents, materials, SPE cartridges, and equipment as sources of contamination. The lab should be able to demonstrate that these items are not introducing unacceptable positive or negative bias.
4. Supplies should be tested on a lot-by-lot basis.
5. Avoid contact with glassware.
6. Avoid any Teflon including Teflon lined caps.
7. Flush water purification system with 3 liters of reagent water before using.
8. Use LC PEEK tubing and stainless-steel frits.
9. Use polypropylene transfer lines.
10. Replace mobile phase after 48 hours of preparation.
11. Store standards in the containers they were received in and at the storage conditions recommended by the manufacturer.
12. Store solid PFSA standards in a desiccator as they can hydrate over time.
13. PFCA standards in methanol solution may undergo esterification to methyl esters. Ideally, purchase PFCA standard solutions in methanol that contain four mole equivalents of NaOH. Use basic methanol (0.3% NH_4OH v/v in methanol) rather than straight methanol for all standard dilutions to avoid this potential problem.
14. PFSA standards that are ^{18}O-labelled may exchange with water and therefore reducing purity.
15. To establish retention times, analyze individual standards of each analyte. Analyze a mixed standard of all analytes to confirm their separation and identification.
16. Validate each individual standard and labeled standard by analysis to confirm its identity and the absence of significant impurities.
17. Certified standards have been known to vary by as much as 20% between vendors. The laboratory should be able to demonstrate that the standards being used are of known and defensible quality.
18. Some certified standards are less than 90% pure and often contain impurities that are other PFAS being analyzed.
19. EIS should be 96% or greater purity. When the impurity consists of an unlabeled analyte, the EIS can result in a background artifact that is present in every sample, standard, and blank if the EIS is spiked at excessive concentrations.
20. Different certified standards can have different isomer content.
21. Calibration standards are solvent based only. Matrix matched calibration standards (such as those that include sand or fish tissue) should not be used for isotope dilution methods.
22. If the site where samples are being collected is considered a “newer” spill and source apportionment is one of the data quality objectives, ship the samples with dry ice. PFAS transformation can occur if the samples are not frozen.
23. Although matrix spikes and matrix spike duplicates (MS/MSDs) are not necessary, analyzing them would help with assessing measurement bias for those target (native) analytes that do not have exact labeled isotope analogs.
24. Solid samples should not be air dried unless required by a QAPP.
25. Perform solid and fish tissue PT samples.

X. Definitions

Confirmation Ion - one of the fragment ions (product ions) used to help qualitatively confirm presence of the analyte. The product ion chosen is typically one of the remaining ions with high sensitivity and minimum interferences, after the quantitation ion has been chosen. Not all precursor ions provide confirmation ions.

Extraction batch – a set of one to 20 environmental samples of the same certification matrix with a maximum time of 24 hours between the start of processing of the first and last samples in the batch.

Extracted Internal Standards (EIS) - isotopically labeled internal standards that undergo the same extraction and analysis as the other analytes in the sample. The EIS are added to the sample at the very beginning of the procedure before extraction, centrifugation, filtering, or phase separation. Ideally, these are exact isotopically labeled analogs of the target (native) analyte so that identical behavior can be assumed. The recoveries of these standards are used to adjust the target (native) analyte results.

Internal Standard Dilution Quantitation - measurement of native analytes using an alternate analog (surrogate) isotope (one that has the same chemical behavior and is close in retention time to the native analyte) thus providing a close approximation of matrix effects and losses that can occur during the preparatory and analytical procedures. The native analyte concentration is adjusted for the recovery of the alternate analog isotope. An alternate analog isotope is typically used when an exact analog isotope is not available.

Method Detection Limit (MDL) – the minimum measured concentration of a substance that is reported with 99% confidence that the measured concentration is distinguishable from method blank results. The MDL is generated according to the procedure specified in the latest revision of 40 CFR Part 136, Appendix B. The MDL is expected to meet S/N ratio, ion transition ratio, and both quantitation and confirmation ions.

Method Reporting Limit (MRL) – the minimum concentration reported as a quantitative value for a method analyte in a sample following analysis. This defined concentration is expected to be no lower than the concentration of the lowest calibration standard for that analyte and is only used if the recovery in the lowest standard is within 50 – 150%.

Native Analyte - the analyte being tested in the matrix of interest. It is also the analyte for which a result would be reported. It is defined as native to distinguish it from analyte standards added during the test procedure. Native analyte is also referred to as “target analyte” or “reported analyte.”

Precursor Ion – the deprotonated molecule of the analyte. The precursor ion is mass selected and fragmented to produce distinctive product ions of smaller m/z.

Product Ion – one of the fragment ions produced from the precursor ion.

Quantitation Ion – one of the fragment ions (product ions) used to quantitate analyte concentrations. The product ion chosen is typically one of high sensitivity and minimum interferences.

True Isotope Dilution Quantitation – measurement of native analytes using an exact analog (surrogate) isotope of the native analyte thus eliminating differences in chemical behavior. The native analyte concentration is adjusted for the recovery of the exact analog isotope that has been included in the preparatory and analytical procedures.

XI. Wisconsin Laboratory Accreditation Program PFAS Certification Offerings – 5.1.19

#	Acronym	Name	CAS #	# carbons	Acronyms (other)
Carboxylic Acids					
1	PFBA	Perfluorobutanoic acid	375-22-4	4	
2	PFPeA	Perfluoropentanoic acid	2706-90-3	5	
3	PFHxA	Perfluorohexanoic acid	307-24-4	6	
4	PFHpA	Perfluoroheptanoic acid	375-85-9	7	
5	PFOA	Perfluorooctanoic acid	335-67-1	8	
6	PFNA	Perfluorononanoic acid	375-95-1	9	
7	PFDA	Perfluorodecanoic acid	335-76-2	10	
8	PFUnA	Perfluoroundecanoic acid	2058-94-8	11	PFUdA, PFUnDA
9	PFDoA	Perfluorododecanoic acid	307-55-1	12	PFDoDA
10	PFTriA	Perfluorotridecanoic acid	72629-94-8	13	PFTrA, PFTrDA
11	PFTeA	Perfluorotetradecanoic acid	376-06-7	14	PFTeDA
12	PFHxDA	Perfluorohexadecanoic acid	67905-19-5	16	
13	PFODA	Perfluorooctadecanoic acid	16517-11-6	18	
Sulfonic Acids					
14	PFBS	Perfluorobutanesulfonic acid	375-73-5	4	
15	PFPeS	Perfluoropentanesulfonic acid	2706-91-4	5	
16	PFHxS	Perfluorohexanesulfonic acid	355-46-4	6	
17	PFHpS	Perfluoroheptanesulfonic acid	375-92-8	7	
18	PFOS	Perfluorooctanesulfonic acid	1763-23-1	8	
19	PFNS	Perfluorononanesulfonic acid	68259-12-1	9	
20	PFDS	Perfluorodecanesulfonic acid	335-77-3	10	
21	PFDoS	Perfluorododecanesulfonic acid	79780-39-5	12	PFDoDS
22	4:2 FTSA	4:2 Fluorotelomer sulfonic acid	757124-72-4	6	
23	6:2 FTSA	6:2 Fluorotelomer sulfonic acid	27619-97-2	8	
24	8:2 FTSA	8:2 Fluorotelomer sulfonic acid	39108-34-4	10	
25	10:2 FTSA	10:2 Fluorotelomer sulfonic acid	120226-60-0	12	
Sulfonamides, Sulfomidoacetic acids, Sulfonamidoethanols					
26	FOSA	Perfluorooctane sulfonamide	754-91-6	8	PFOSA
27	NMeFOSA	N-Methyl perfluorooctane sulfonamide	31506-32-8	9	MeFOSA
28	NEtFOSA	N-Ethyl perfluorooctane sulfonamide	4151-50-2	10	EtFOSA
29	NMeFOSAA	N-Methyl perfluorooctane sulfonamidoacetic acid	2355-31-9	11	MeFOSAA
30	NEtFOSAA	N-Ethyl perfluorooctane sulfonamidoacetic acid	2991-50-6	12	EtFOSAA

31	NMeFOSE	N-Methyl perfluorooctane sulfonamidoethanol	24448-09-7	11	MeFOSE
32	NEtFOSE	N-Ethyl perfluorooctane sulfonamidoethanol	1691-99-2	12	EtFOSE
Replacement Chemicals					
33	HFPO-DA	Hexafluoropropylene oxide dimer acid [1]	13252-13-6	6	PFPrOPrA
34	DONA	4,8-Dioxa-3H-perfluorononanoic acid [2]	919005-14-4	7	
35	9Cl-PF3ONS	9-chlorohexadecafluoro-3-oxanonane-1-sulfonic acid [3]	756426-58-1	8	F-53B Major
36	11Cl-PF3OUdS	11-chloroeicosafluoro-3-oxaundecane-1-sulfonic acid [4]	763051-92-9	10	F-53B Minor

1 - Also referred to as "GenX"

2 - Also available as the ammonium salt = ADONA (Ammonium 4,8-dioxa-3H-perfluorononanoate) # 958445-44-8

3 - Also available as the potassium salt = Potassium, 9-chlorohexadecafluoro-3-oxanone-1-sulfonate # 73606-19-6

4 - Also available as the potassium salt = Potassium, 11-chloroeicosafluoro-3-oxaundecane-1-sulfonate # 83329-89-9

XII. Wisconsin Laboratory Accreditation Program PFAS Certification Offerings with Ions – 10.27.19

The masses presented are expected to be used, although if other masses are used for the precursor or product ions, the reason is expected to be documented (such as interferences). If the confirmation ion is weak (S/N < 3), it does not have to be used but instrument optimization can increase the S/N.

#	Acronym	Name	CAS #	Precursor Ion Mass	Primary Product Ion Mass	Suggested Confirmation Product Ion Mass
Carboxylic Acids						
1	PFBA	Perfluorobutanoic acid	375-22-4	**213**	**169**	**None**
2	PFPeA	Perfluoropentanoic acid	2706-90-3	**263**	**219**	**69, None**
3	PFHxA	Perfluorohexanoic acid	307-24-4	**313**	**269**	**119**
4	PFHpA	Perfluoroheptanoic acid	375-85-9	**363**	**319**	**169**
5	PFOA	Perfluorooctanoic acid	335-67-1	**413**	**369**	**169**
6	PFNA	Perfluorononanoic acid	375-95-1	**463**	**419**	**219**
7	PFDA	Perfluorodecanoic acid	335-76-2	**513**	**469**	**219**
8	PFUnA	Perfluoroundecanoic acid	2058-94-8	**563**	**519**	**269**
9	PFDoA	Perfluorododecanoic acid	307-55-1	**613**	**569, 319**	**569, 369, 319, 269, 169**
10	PFTriA	Perfluorotridecanoic acid	72629-94-8	**663**	**619**	**369, 319, 269, 169**
11	PFTeA	Perfluorotetradecanoic acid	376-06-7	**713**	**669**	**369, 319, 269, 169**
12	PFHxDA	Perfluorohexadecanoic acid	67905-19-5	**813**	**769**	**369, 319, 269, 219, 169**
13	PFODA	Perfluorooctadecanoic acid	16517-11-6	**913**	**869**	**369, 319, 269, 219, 169**
Sulfonic Acids						
14	PFBS	Perfluorobutanesulfonic acid	375-73-5	**299**	**80**	**99**
15	PFPeS	Perfluoropentanesulfonic acid	2706-91-4	**349**	**80**	**99**
16	PFHxS	Perfluorohexanesulfonic acid	355-46-4	**399**	**80**	**99**
17	PFHpS	Perfluoroheptanesulfonic acid	375-92-8	**449**	**99, 80**	**99, 80**
18	PFOS	Perfluorooctanesulfonic acid	1763-23-1	**499**	**80**	**99**
19	PFNS	Perfluorononanesulfonic acid	68259-12-1	**549**	**80**	**99**
20	PFDS	Perfluorodecanesulfonic acid	335-77-3	**599**	**99, 80**	**99, 80**
21	PFDoS	Perfluorododecanesulfonic acid	79780-39-5	**699**	**80**	**99, 62**
22	4:2 FTSA	4:2 Fluorotelomer sulfonic acid	757124-72-4	**327**	**307**	**81, 80**
23	6:2 FTSA	6:2 Fluorotelomer sulfonic acid	27619-97-2	**427**	**407**	**81, 80**
24	8:2 FTSA	8:2 Fluorotelomer sulfonic acid	39108-34-4	**527**	**507**	**81, 80**
25	10:2 FTSA	10:2 Fluorotelomer sulfonic acid	120226-60-0	**627**	**607**	**587, 81, 80**

Sulfonamides, Sulfomidoacetic acids, Sulfonamidoethanols						
26	FOSA	Perfluorooctane sulfonamide	754-91-6	**498**	**78**	**478, 169, None**
27	NMeFOSA	N-Methyl perfluorooctane sulfonamide	31506-32-8	**512**	**169**	**219**
28	NEtFOSA	N-Ethyl perfluorooctane sulfonamide	4151-50-2	**526**	**169**	**219**
29	NMeFOSAA	N-Methyl perfluorooctane sulfonamidoacetic acid	2355-31-9	**570**	**419**	**512, 483**
30	NEtFOSAA	N-Ethyl perfluorooctane sulfonamidoacetic acid	2991-50-6	**584**	**419**	**526, 483**
31	NMeFOSE	N-Methyl perfluorooctane sulfonamidoethanol	24448-09-7	**616**	**59**	**122, None**
32	NEtFOSE	N-Ethyl perfluorooctane sulfonamidoethanol	1691-99-2	**630**	**59**	**136, None**
Replacement Chemicals						
33	HFPO-DA	Hexafluoropropylene oxide dimer acid	13252-13-6	**329**	**285, 169**	**285, 169, None**
34	DONA	4,8-Dioxa-3H-perfluorononanoic acid	919005-14-4	**377**	**251**	**85, None**
35	9Cl-PF3ONS	9-chlorohexadecafluoro-3-oxanonane-1-sulfonic acid	756426-58-1	**531**	**351**	**83, None**
36	11Cl-PF3OUdS	11-chloroeicosafluoro-3-oxaundecane-1-sulfonic acid	763051-92-9	**631**	**451**	**99, None**

NOTE: ISO 21675, SW 8327, and Wellington Laboratories provide precursor, product and confirmation ions for many of the extracted internal standards

Mass Source
EPA 537.1
DoD QSM 5.3
Janice Willey
EPA-821-R-11-007, PFAS in Sludge/Biosolids
ISO 21675
SW 8327
Wellington Laboratories
Confirmation mass have multiple sources

Title: Per- and Polyfluorinated Alkyl Substances (PFAS) in Water, Soils, Sediments and Tissue

[Method 537 (Modified), Method PFAS by LCMSMS Compliant with QSM Table B-15, Revision 5.1 and higher]

Approvals (Signature/Date):

09/19/2019	09/20/2019
Robert Hrabak Date	Joe Schairer Date
Technical Manager	Health & Safety Manager / Coordinator
09/20/2019	09/20/2019
Lisa Stafford Date	Chris Williams Date
Quality Assurance Manager	Laboratory Manager

Facility Distribution No. Uncontrolled **Distributed To:** Sacramento QA

1. SCOPE AND APPLICATION

1.1. This procedure describes the analysis of water, soil, sediment, and tissue samples for the following compounds using liquid chromatography / tandem mass spectrometry (LC/MS/MS).

Compound Name	Abbreviation	CAS #
Perfluoroalkylcarboxylic acids (PFCAs)		
Perfluoro-n-butanoic acid	PFBA	375-22-4
Perfluoro-n-pentanoic acid	PFPeA	2706-90-3
Perfluoro-n-hexanoic acid	PFHxA	307-24-4
Perfluoro-n-heptanoic acid	PFHpA	375-85-9
Perfluoro-n-octanoic acid	PFOA	335-67-1
Perfluoro-n-nonanoic acid	PFNA	375-95-1
Perfluoro-n-decanoic acid	PFDA	335-76-2
Perfluoro-n-undecanoic acid	PFUdA (PFUnA)	2058-94-8
Perfluoro-n-dodecanoic acid	PFDoA	307-55-1
Perfluoro-n-tridecanoic acid	PFTrDA	72629-94-8
Perfluoro-n-tetradecanoic acid	PFTeDA (PFTA)	376-06-7
Perfluoro-n-hexadecanoic acid (non-routine analyte)	PFHxDA	67905-19-5
Perfluoro-n-octadecanoic acid (non-routine analyte)	PFODA	16517-11-6
Perfluorinated sulfonic acids (PFSAs)		
Perfluoro-1-butanesulfonic acid	PFBS	375-73-5
Perfluoro-1-pentanesulfonic acid	PFPeS	2706-91-4
Perfluoro-1-hexanesulfonic acid	PFHxS	355-46-4
Perfluoro-1-heptanesulfonic acid	PFHpS	375-92-8
Perfluoro-1-octanesulfonic acid	PFOS	1763-23-1
Perfluoro-nonanesulfonic acid	PFNS	68259-12-1
Perfluoro-1-decanesulfonic acid	PFDS	335-77-3
Perfluoro-1-dodecansulfonic acid	PFDoS	79780-39-5
Perfluorinated sulfonamides (FOSA)		
Perfluoro-1-octanesulfonamide	FOSA	754-91-6
N-ethylperfluoro-1-octanesulfonamide	Et-FOSA	4151-50-2
N-methylperfluoro-1-octanesulfonamide	Me-FOSA	31506-32-8
Perfluorinated sulfonamide ethanols (FOSE)		
2-(N-ethylperfluoro-1-octanesulfonamido) ethanol	Et-FOSE	1691-99-2
2-(N-methylperfluoro-1-octanesulfonamido) ethanol	Me-FOSE	24448-09-7
Perfluorinated sulfonamidoacetic acids (FOSAA)		

Compound Name	Abbreviation	CAS #
N-ethylperfluoro-1-octanesulfonamidoacetic acid	EtFOSAA	2991-50-6
N-methylperfluoro-1-octanesulfonamidoacetic acid	MeFOSAA	2355-31-9
Fluorotelomer sulfonates (FTS)		
1H,1H,2H,2H-perfluorohexane sulfonate *(4:2)*	4:2 FTS	757124-72-4
1H,1H,2H,2H-perfluorooctane sulfonate *(6:2)*	6:2 FTS	27619-97-2
1H,1H,2H,2H-perfluorodecane sulfonate *(8:2)*	8:2 FTS	39108-34-4
1H,1H,2H,2H-perfluorododecane sulfonate *(10:2)*	10:2 FTS	120226-60-0

***Note**: Abbreviations in parenthesis are the abbreviations listed in Method 537/537.1, where they differ from the abbreviation used by the laboratory's LIMS.*

1.2. Additional analytes supported by this method: The following analytes can be supported by this method under special request.

Compound Name	Abbreviation	CAS #
Fluorinated Replacement Chemicals		
4,8-dioxa-3H-perfluorononanoic	Dona (ADONA[(1)])	919005-14-4
Perfluoro(2-propoxypropanoic) acid or Hexafluoropropylene oxide dimer acid	HFPO-DA or GenX	13252-13-6
F53B (reported as the summation of the following)	F53B	NA
9-Chlorohexadecafluoro-3-oxanonane-1-sulfonate	F53B major (9Cl-PF3ONS)	756426-58-1
11-Chloroeicosafluoro-3-oxaundecane-1-sulfonate	F5B minor (11Cl-PF3OUdS)	83329-89-9

(1) In some literature, the acronym ADONA refers to the ammonium salt, CAS 958445-44-8, and DONA refers to the parent acid. In Method 537.1, ADONA refers to the parent acid. DONA is the acronym present on the laboratory raw data.

1.3. The working range of the method is listed below. The linear range can be extended by diluting the extracts.

Matrix	Nominal Sample Size	Reporting Limit	Working Range
Water	250 mL	2.0 ng/L – 20 ng/L	2.0 ng/L - 400 ng/L
Soil/Sediment	5 g	0.2 µg/kg – 2.0 µg/kg	0.2 µg/kg - 40 µg/kg
Tissue	1 g	1.0 µg/kg – 10 µg/kg	1.0 µg/kg – 200 µg/kg

1.4. The procedure for the analysis of water samples via in line solid phase extraction (SPE) for a subset of the list in Section 1.1 using liquid chromatography / tandem mass spectrometry (LC/MS/MS) on a [redacted] is described in Attachment 1 of this SOP.

1.5. This procedure also includes direction for preparing and analyzing samples to determine "Total Oxidizable Precursors", which may assist in improving understanding of potential PFAS environmental risk.

1.6. When undertaking projects for the Department of Defense (DoD) and/or the Department of Energy (DOE) the relevant criteria in QA Policy WS-PQA-021, "Federal Program Requirements" must be checked and incorporated.

2. SUMMARY OF METHOD

2.1. Water samples are extracted using a solid phase extraction (SPE) cartridge. PFAS are eluted from the cartridge with an [redacted] solution.

2.2. Soil/sediment/tissue samples are extracted with a KOH/methanol solution using an orbital shaker for 3 hours followed by sonication for 12 hours. The mixture is centrifuged and the solvent filtered.

2.3. The final 80:20 methanol:water extracts are analyzed by LC/MS/MS. PFAS are separated from other components on a C18 column with a solvent gradient program using [redacted]. The mass spectrometer detector is operated in the electrospray (ESI) negative ion mode for the analysis of PFAS.

2.4. An isotope dilution technique is employed with this method for the compounds of interest. The isotope dilution analytes (IDA) consist of carbon-13 labeled analogs, oxygen-18 labeled analogs, or deuterated analogs of the compounds of interest, and they are spiked into the samples at the time of extraction. This technique allows for the correction for analytical bias encountered when analyzing more chemically complex environmental samples. The isotopically labeled compounds are chemically similar to the compounds of concern and are therefore affected by sample-related interferences to the same extent as the compounds of concern. Compounds that do not have an identically labeled analog are quantitated by the IDA method using a closely related labeled analog.

2.5. Quantitation by the internal standard method is employed for the IDA analytes/recoveries. Peak response is measured as the area of the peak.

2.6. Samples for the "Total Oxidizable Precursor" assay (TOP) are analyzed in two phases – an aliquot is prepared and analyzed as a normal sample, and a second aliquot is subjected to [redacted] prior to solid phase extraction and analysis. The total perfluorocarboxylic acid value is determined for each aliquot, and the difference calculated.

3. DEFINITIONS

3.1. PFCAs: Perfluorocarboxylic acids

3.2. PFSAs: Perfluorinated sulfonic acids

3.3. FOSA: Perfluorinated sulfonamide

3.4. PFOA: Perfluorooctanoic acid

3.5. PFOS: Perfluorooctane sulfonic acid

3.6. PTFE: Polytetrafluoroethylene (e.g. Teflon®)

3.7. SPE: Solid phase extraction

3.8. PP: Polypropylene

3.9. PE: Polyethylene

3.10. HDPE: High density polyethylene

3.11. AFFF: Aqueous Film Forming Foam

3.12. IDA: Isotope dilution analyte

3.13. Further definitions of terms used in this SOP may be found in the glossary of the Laboratory Quality Assurance Manual (QAM).

4. INTERFERENCES

4.1. PFAS have been used in a wide variety of manufacturing processes, and laboratory supplies should be considered potentially contaminated until they have been tested and shown to be otherwise. The materials and supplies used during the method validation process have been tested and shown to be clean. These items are listed below in Section 6.

4.2. To avoid contamination of samples, standards are prepared in a ventilation hood in an area separate from where samples are extracted.

4.3. PTFE products can be a source of PFOA contamination. The use of PTFE in the procedure should be avoided or at least thoroughly tested before use. Polypropylene (PP) or polyethylene (PE, HDPE) products may be used in place of PTFE products to minimize PFOA contamination.

4.3.1. Standards and samples are injected from polypropylene autosampler vials with polypropylene screw caps once. Multiple injections may be performed on Primers when conditioning the instrument for analysis.

4.3.2. Random evaporation losses have been observed with the polypropylene caps causing high IDA recovery after the vial was punctured and sample re-injected. For this reason, it is best to inject standards and samples once in the analytical sequence.

4.3.3. Teflon-lined screw caps have detected PFAS at low concentrations. Repeated injection from the same teflon-lined screw cap have detected PFNA at increasing concentration as each repeated injection was performed, therefore, it is best to use polypropylene screw caps.

4.4. Volumetric glassware and syringes are difficult to clean after being used for solutions containing high levels of PFOA. These items should be labeled for use only with similarly concentrated solutions or verified clean prior to re-use. To the extent possible, disposable labware is used.

4.5. Both branched and linear PFAS isomers can potentially be found in the environment. Linear and branched isomers are known to exist for PFOS, PFOA, PFHxS, PFBS, EtFOSAA, and MeFOSAA based upon the scientific literature. If multiple isomers are present for one of these PFAS they might be adjacent peaks that completely resolve or not, but usually with a deflection point resolved during peak integration. The later of these peaks matches the retention time of its labeled linear analog. In general, earlier peaks are the branched isomers and are not the result of peak splitting.

As of this writing, only PFOS, PFOA, and PFHxS are commercially available as technical mixtures. These reference standards of the technical mixtures for these specific PFAS are used to ensure that all appropriate peaks are included during peak integration.

4.6. In an attempt to reduce PFOS bias, it is required that m/z 499>80 transition be used as the quantitation transition.

4.7. Per the Certificate of Analysis for labeled perfluorohexadecanoic acid ($13C_2$-PFHxDA) produced by Wellington Laboratories, the stock standard contains roughly 0.3% of native perfluorohexadecanoic acid. This equates to roughly 0.30 ng/L or 0.015 ug/kg of perfluorohexadecanoic acid expected in all samples and blanks.

4.8. Aluminum foil should not be used for this analysis due to the potential for PFAA.

5. SAFETY

Employees must abide by the policies and procedures in the Corporate Safety Manual, Sacramento Supplement to the CSM, and this document. All work must be stopped in the event of a known or potential compromise to the health or safety of an associate. The situation must be reported **immediately** to a supervisor, the EH&S Staff, or a senior manager.

5.1. Specific Safety Concerns

5.1.1. Preliminary toxicity studies indicate that PFAS could have significant toxic effects. In the interest of keeping exposure levels as low as reasonably achievable, PFAS and PFAS samples must be handled in the laboratory as hazardous and toxic chemicals.

5.1.2. Exercise caution when using syringes with attached filter disc assemblies. Application of excessive force has, upon occasion, caused a filter disc to burst during the process.

5.1.3. Laboratory procedures such as repetitive use of pipets, repetitive transferring of extracts and manipulation of filled separatory funnels and other glassware represent a significant potential for repetitive motion or other ergonomic injuries. Laboratory associates performing these procedures are in the best position to realize when they are at risk for these types of injuries. Whenever a situation is found in which an employee is performing the same repetitive motion, the employee shall immediately bring this to the attention of their supervisor, manager, or the EH&S staff. The task will be analyzed to determine a better means of accomplishing it.

5.1.4. Eye protection that satisfies ANSI Z87.1 (as per the TestAmerica Corporate Safety Manual), laboratory coat, and nitrile gloves must be worn while handling samples, standards, solvents, and reagents. Disposable gloves that have been contaminated will be removed and discarded; other gloves will be cleaned immediately.

5.1.5. Perfluorocarboxylic acids are acids and are not compatible with strong bases.

5.1.6. The use of vacuum systems presents the risk of imploding glassware. All glassware used during vacuum operations must be thoroughly inspected prior to each use. Glass that is chipped, scratched, cracked, rubbed, or marred in any manner must not be used under vacuum. It must be removed from service and replaced.

5.1.7. Glass containers are not to be used for “tumbling” soil samples.

5.2. Primary Materials Used

The following is a list of the materials used in this method, which have a serious or significant hazard rating. NOTE: This list does not include all materials used in the method. The table contains a summary of the primary hazards listed in the SDS for each of the materials listed in the table. A complete list of materials used in the method can be found in the reagents and materials section. Employees must review the information in the SDS for each material before using it for the first time or when there are major changes to the SDS.

Material[1]	Hazards	Exposure Limit[2]	Signs and Symptoms of Exposure
Acetic Acid (3-2-1)	Corrosive Poison Flammable	10 ppm-TWA 15 ppm-STEL	Contact with concentrated solution may cause serious damage to the skin and eyes. Inhalation of concentrated vapors may cause serious damage to the lining of the nose, throat, and lungs. Breathing difficulties may occur.
[redacted] (3-0-0)	Corrosive Poison	50 ppm-TWA	Severe irritant. Effects from inhalation of dust or mist vary from mild irritation to serious damage to the upper respiratory tract. Symptoms may include sneezing, sore throat or runny nose. Contact with skin can cause irritation or severe burns and scarring with greater exposures. Causes irritation of eyes, and with greater exposures it can cause burns that may result in permanent damage, including blindness. Brief exposure to 5000 PPM can be fatal.
Hexane (2-3-0)	Flammable Irritant	500 ppm-TWA	Inhalation of vapors irritates the respiratory tract. Overexposure may cause lightheadedness, nausea, headache, and blurred vision. Vapors may cause irritation to the skin and eyes.
Hydrochloric Acid (3-0-1)	Corrosive Poison	5 ppm (Ceiling)	Can cause pain and severe burns upon inhalation, ingestion, eye or skin contact. Exposure to concentrated solutions may cause deep ulcerations to skin, permanent eye damage, circulatory failure and swallowing may be fatal.
Methanol (2-3-0)	Flammable Poison Irritant	200 ppm (TWA)	A slight irritant to the mucous membranes. Toxic effects exerted upon nervous system, particularly the optic nerve. Symptoms of overexposure may include headache, drowsiness and dizziness. Methyl alcohol is a defatting agent and may cause skin to become dry and cracked. Skin absorption can occur; symptoms may parallel inhalation exposure. Irritant to the eyes.
Potassium Hydroxide (3-0-1)	Corrosive Poison		Severe irritant. Can cause severe burns upon inhalation, ingestion, eye or skin contact. Exposure to concentrated solutions may cause severe scarring of tissue, blindness, and may be fatal if swallowed.
[redacted] (2-0-1-OX)	Oxidizer	None	Causes irritation to the respiratory tract. Symptoms may include coughing, shortness of breath. Causes irritation to skin and eyes. Symptoms include redness, itching, and pain. May cause dermatitis, burns, and moderate skin necrosis.

Material[1]	Hazards	Exposure Limit[2]	Signs and Symptoms of Exposure
Sodium Hydroxide (3-0-1)	Corrosive Poison	2 mg/cm^3 (Ceiling)	Severe irritant. Can cause severe burns upon inhalation, ingestion, eye or skin contact. Exposure to concentrated solutions may cause severe scarring of tissue, blindness, and may be fatal if swallowed.
(1) Always add acid to water to prevent violent reactions. (2) Exposure limit refers to the OSHA regulatory exposure limit.			

6. EQUIPMENT AND SUPPLIES

6.1. 15 mL polypropylene test tubes with polypropylene screw caps.

6.2. 50 mL graduated plastic centrifuge tubes.

6.3. 125 mL HDPE bottles with HDPE screw caps.

6.4. 250 mL HDPE bottles with HDPE screw caps. The average weight of the HDPE bottles with HDPE screw caps are calibrated once per year. The calibration is performed by weighing 10 bottles with caps and dividing by 10 to get the average weight. The average weight is used in section (11.3.5.1.d).

6.5. Analytical balance capable of accurately weighing to the nearest 0.0001g, and checked for accuracy each day it is used in accordance with WS-QA-0041.

6.6. Extract concentrator or nitrogen manifold with water bath heating to 50-55°C.

6.7. Syringe filter, Millipore Millex-HV 0.45 um, or equivalent. Do not use PTFE type filters.

6.8. 300 µL autosampler vials, polypropylene, with polypropylene screw caps, Waters PN 1860004112, or equivalent.

6.9. SPE columns

6.9.1. Waters Oasis WAX 150 mg/6 cc (PN 186002493) for the cleanup of solids.

6.9.2. Waters Oasis WAX 500 mg/6 cc (PN 186004647) for extraction of PFAS from aqueous sample.

6.10. Graphitized carbon (Envi-Carb^{TM} or equivalent).

6.11. Vacuum manifold for Solid Phase Extraction (SPE).

6.12. Miscellaneous laboratory apparatus (beakers, test tubes, volumetric flasks, pipettes, etc.). These should be disposable where possible, or marked and segregated for high-level versus low-level use.

6.13. Water bath: Heated with concentric ring cover capable of temperature control (±5°C) up to 95°C. The bath must be used in a fume hood.

6.14. Plastic tub for an ice bath, AKRO-N.S.T. part No. 35-180 or equivalent.

6.15. pH indicator paper, wide range.

6.16. Bottle rotating apparatus for soil extractions.

6.17. Glass fiber filter, Whatman GF/F, catalog number 1825 090 or equivalent.

6.18. Liquid Chromatography/Tandem Mass Spectrometer (LC/MS/MS) – Either of the instruments described below, or equivalent, may be used for this method. Both HPLC are equipped with a refrigerated autosampler, an injection valve, and a pump capable of variable flow rate. The use of a column heater is required to maintain a stable temperature throughout the analytical run. Data is processed using Chrom Peak Review, version 2.1 or equivalent. The MS/MSD is capable of running in the NI-ESI mode at the recommended flow rate with a minimum of 10 scans per peak.

6.18.1. [redacted] LC/MS/MS

This system consists of a Shimadzu HPLC interfaced with a [redacted] Triple Quad MS. The instrument control and data acquisition software is SCIEX Analyst, version 1.6.3 or equivalent.

6.18.1.1. [redacted] HPLC equipped with [redacted] pumps and one DGU-20 degassing unit or equivalent.

6.18.1.2. [redacted].

6.18.1.3. PFAS Isolator column, [redacted]. This is plumbed between the UPLC pumps and autosampler valve to minimize PFAS background from the UPLC solvent lines and filters.

6.19. Preventive and routine maintenance is described in the table below

HPLC/MS/MS Preventative Maintenance	
As Needed: Change pump seals. Change in-line filters in autosampler (HPLC). Check/replace in-line frit if excessive pressure or poor performance. Replace column if no change following in-line frit change. Clean corona needle. Replace sample inlet tube in APCI (10.1 cm). Replace fused silica tube in ESI interface. Clean lenses. Clean skimmer. Ballast rough pump 30 minutes. Create all eluents in Reagent module, label eluent containers with TALS label and place 2nd label into maintenance log when put into use.	**Daily (When in use)** Check solvent reservoirs for sufficient level of solvent. Verify that pump is primed, operating pulse free. Check needle wash reservoir for sufficient solvent. Verify capillary heater temperature functioning. Verify vaporizer heater temperature. Verify rough pump oil levels. Verify turbo-pump functioning. Verify nitrogen pressure for auxiliary and sheath gasses. Verify that corona and multiplier are functioning.
Semi-Annually Replace rough-pump oil (4-6 months). Replace oil mist and odor elements. Replace activated alumina filter if applicable	**Annually** Vacuum system components including fans and fan covers. Clean/replace fan filters, if applicable.

7. REAGENTS AND STANDARDS

7.1. Reagent grade chemicals shall be used in all tests whenever available. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on the Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

7.1.1. Acetic acid, glacial

7.1.2. [redacted]. The resultant solution is filtered through a 0.22 µm filter before use. This solution has volatile components, thus it should be replaced every 7 days or sooner.

7.1.3. Ammonium hydroxide (NH4OH), 0.3% in methanol: Prepared by diluting

12 mL of ammonium hydroxide into 4L of methanol.

7.1.4. Hexane

7.1.5. Hydrochloric acid (HCl), 2.0 M solution in water

7.1.6. Hydrochloric acid (HCl), concentrated, reagent grade

7.1.7. Methanol

[redacted]

7.1.9. [redacted], reagent grade

7.1.10. Ottawa Sand

7.1.11. Sodium hydroxide (NaOH), 0.1 N, in water: Prepared by diluting 400 mL of 1N NaOH into 3.6L of water for a total volume of 4 L.

7.1.12. Sodium hydroxide (NaOH), 10 N, reagent grade

7.1.13. Water, Nanopure or Millipore, must be free of interference and target analytes.

7.2. Standards

7.2.1. PFAS are purchased as high purity solids (96% or greater) or as certified solutions. Standard materials are verified compared to a second source material at the time of initial calibration. The solid stock material is stored at room temperature or as specified by the manufacturer or vendor.

7.2.1.1. Per the Certificate of Analysis for labeled perfluorohexadecanoic acid ($13C_2$-PFHxDA) produced by Wellington Laboratories, the stock standard contains roughly 0.3% of native perfluorohexadecanoic acid. This equates to roughly 0.30 ng/L or 0.015 µg/kg of perfluorohexadecanoic acid expected in all samples and blanks.

7.2.2. As of this writing, only PFOS, PFOA, PFHxS, Et-FOSAA and Me-FOSAA are commercially available as technical mixtures. These reference standards of the technical mixtures for these specific PFAS are used to ensure that all appropriate peaks are included during peak integration.

7.2.3. If solid material is used for preparing a standard, stock standard solutions are prepared from the solids and are stored at 0 - 6°C. Stock standard solutions

should be brought to room temperature before using. Standards are monitored for signs of degradation or evaporation. Standard solutions must be replaced at least annually from the date of preparation.

7.2.4. PFBS, PFHxS, PFHpS, PFOS, PFDS, and many other PFAS are not available in the acid form, but rather as their corresponding salts, such as sodium or potassium. The standards are prepared and corrected for their salt content according to the equation below.

$Mass_{acid}$ = Measured $Mass_{salt}$ × MW_{acid} / MW_{salt}

Where: MW_{acid} is the molecular weight of PFAA

MW_{salt} is the molecular weight of the purchased salt.

7.2.5. For example, the molecular weight of PFOS is 500.1295 and the molecular weight of NaPFOS is 523.1193. Therefore, the amount of NaPFOS used must be adjusted by a factor of 0.956.

7.2.6. While PFAS standards commercially purchased are supplied in glass ampoules, all subsequent transfers or dilutions performed by the analyst must be prepared and stored in polypropylene or HDPE containers.

7.3. Calibration Standards

The calibration stock solution is prepared by diluting the appropriate amounts of stock solutions in 80% methanol/water. The calibration stock solution is diluted with methanol to produce initial calibration standards. These are the normal calibration levels used. A different range can be used if needed to achieve lower reporting limits or a higher linear range.

7.4. Initial Calibration (ICAL) Levels (ng/mL)

Compound	**CS-1**	**CS-2**	**CS-3**	**CS-4**	**CS-5**	**CS-6**	**CS-7**
Perfluoroalkylcarboxylic acids (PFCAs)							
PFBA	0.025	0.05	0.25	1	2.5	10	20
PFPeA	0.025	0.05	0.25	1	2.5	10	20
PFHxA	0.025	0.05	0.25	1	2.5	10	20
PFHpA	0.025	0.05	0.25	1	2.5	10	20
PFOA	0.025	0.05	0.25	1	2.5	10	20
PFNA	0.025	0.05	0.25	1	2.5	10	20
PFDA	0.025	0.05	0.25	1	2.5	10	20
PFUdA	0.025	0.05	0.25	1	2.5	10	20
PFDoA	0.025	0.05	0.25	1	2.5	10	20
PFTrDA	0.025	0.05	0.25	1	2.5	10	20
PFTeDA	0.025	0.05	0.25	1	2.5	10	20
PFHxDA	0.025	0.05	0.25	1	2.5	10	20

Compound	CS-1	CS-2	CS-3	CS-4	CS-5	CS-6	CS-7
PFODA	0.025	0.05	0.25	1	2.5	10	20
Perfluorinated sulfonic acids (PFSAs)							
PFBS	0.025	0.05	0.25	1	2.5	10	20
PFPeS	0.025	0.05	0.25	1	2.5	10	20
PFHxS*	0.025	0.05	0.25	1	2.5	10	20
PFHpS	0.025	0.05	0.25	1	2.5	10	20
PFOS*	0.025	0.05	0.25	1	2.5	10	20
PFNS	0.025	0.05	0.25	1	2.5	10	20
PFDS	0.025	0.05	0.25	1	2.5	10	20
PFDoS	0.025	0.05	0.25	1	2.5	10	20
Perfluorinated sulfonamides (FOSA)							
FOSA	0.025	0.05	0.25	1	2.5	10	20
Et-FOSA	0.025	0.05	0.25	1	2.5	10	20
Me-FOSA	0.025	0.05	0.25	1	2.5	10	20
Perfluorinated sulfonamide ethanols (FOSE)							
Et-FOSE	0.025	0.05	0.25	1	2.5	10	20
Me-FOSE	0.025	0.05	0.25	1	2.5	10	20
Perfluorinated sulfonamidoacetic acids (FOSAA)							
EtFOSAA*	0.025	0.05	0.25	1	2.5	10	20
MeFOSAA*	0.025	0.05	0.25	1	2.5	10	20
Fluorotelomer sulfonates (FTS)							
4:2 FTS	0.025	0.05	0.25	1	2.5	10	20
6:2 FTS	0.025	0.05	0.25	1	2.5	10	20
8:2 FTS	0.025	0.05	0.25	1	2.5	10	20
10:2 FTS	0.025	0.05	0.25	1	2.5	10	20
Labeled Isotope Dilution Analytes (IDA)							
13C4-PFBA	2.5	2.5	2.5	2.5	2.5	2.5	2.5
13C5-PFPeA	2.5	2.5	2.5	2.5	2.5	2.5	2.5
13C2-PFHxA	2.5	2.5	2.5	2.5	2.5	2.5	2.5
13C4-PFHpA	2.5	2.5	2.5	2.5	2.5	2.5	2.5
13C4-PFOA	2.5	2.5	2.5	2.5	2.5	2.5	2.5
13C5-PFNA	2.5	2.5	2.5	2.5	2.5	2.5	2.5
13C2-PFDA	2.5	2.5	2.5	2.5	2.5	2.5	2.5
13C2-PFUdA	2.5	2.5	2.5	2.5	2.5	2.5	2.5
13C2-PFDoA	2.5	2.5	2.5	2.5	2.5	2.5	2.5
18O2-PFHxS	2.5	2.5	2.5	2.5	2.5	2.5	2.5
13C4-PFOS	2.5	2.5	2.5	2.5	2.5	2.5	2.5
13C3-PFBS	2.5	2.5	2.5	2.5	2.5	2.5	2.5
13C2-PFTeDA	2.5	2.5	2.5	2.5	2.5	2.5	2.5
13C2-PFHxDA	2.5	2.5	2.5	2.5	2.5	2.5	2.5

Compound	CS-1	CS-2	CS-3	CS-4	CS-5	CS-6	CS-7
13C8-FOSA	2.5	2.5	2.5	2.5	2.5	2.5	2.5
d5-EtFOSAA	2.5	2.5	2.5	2.5	2.5	2.5	2.5
d3-MeFOSAA	2.5	2.5	2.5	2.5	2.5	2.5	2.5
M2-4:2FTS ǂ	2.5	2.5	2.5	2.5	2.5	2.5	2.5
M2-6:2FTS	2.5	2.5	2.5	2.5	2.5	2.5	2.5
M2-8:2FTS	2.5	2.5	2.5	2.5	2.5	2.5	2.5
d5-EtFOSA	2.5	2.5	2.5	2.5	2.5	2.5	2.5
d3-MeFOSA	2.5	2.5	2.5	2.5	2.5	2.5	2.5
d9-Et-FOSE	2.5	2.5	2.5	2.5	2.5	2.5	2.5
d7-Me-FOSE	2.5	2.5	2.5	2.5	2.5	2.5	2.5
Internal Standard (IS)							
13C2-PFOA	2.5	2.5	2.5	2.5	2.5	2.5	2.5

** Both branched and linear isomers are used.*

ǂ - *This compound is used as a reverse surrogate for the TOP analysis.*

***Note**: Sample extracts are in 80% MeOH/H $_2$O.*

Compound	CS-1	CS-2	CS-3	CS-4	CS-5	CS-6	CS-7
Fluorinated Replacement Chemicals							
HFPO-DA	0.025	0.05	0.25	1.0	2.5	10	20
9CI-PF3ONS (F53B major)	0.025	0.05	0.25	1.0	2.5	10	20
11CI-PF3OUdS (F53B minor)	0.025	0.05	0.25	1.0	2.5	10	20
Dona	0.025	0.05	0.25	1.0	2.5	10	20
Labeled Isotope Dilution Analytes							
13C3-HFPO-DA	0.025	0.05	0.25	1.0	2.5	10	20

***Note**: Sample extracts are in 80% MeOH/H $_2$O.*

***Note**: The above calibration limits are provided only as an example. The actual ICAL level used for each analytical batch will depend upon the LOQ requirements of the program.*

7.4.1. A technical (qualitative) grade PFOA standard which contains both linear and branched isomers is used as a retention time (RT) marker. This is used to integrate the total response for both linear and branched isomers of PFOA in environmental samples while relying on the initial calibration with the linear isomer quantitative standard This technical (qualitative) grade PFOA standard is analyzed initially, after every initial calibration or when significant changes are made to the HPLC parameters.

7.4.1.1. Attach this document to the ICV from the associated ICAL by scanning the document and associating it to the file as a

document type of High Res MS Tune in TALS. Use the following naming convention: "_TFOA_Instrument_Date." Example: _TFOA_A10_15Mar2019.

7.5. Initial Calibration Verification Standard (ICV)

A second source solution for PFAS is purchased from the same vendor; the PFC-MXB contains most of the target analytes in this mixture and is used as an ICV. A few compounds are not available in this mixture, may not be available as another lot, and are not available from another vendor. For these analytes only, a second analyst may prepare a second source standard from the same source as the ICAL to produce an ICV. The recommended concentration of the ICV standard should be in the mid-range of the calibration curve. The concentration may be adjusted if the initial calibration levels are changed or altered. The IDA and IS are added at a fixed concentration of 50 ng/mL.

7.6. LCS/Matrix PFC Spike Solution, 20 ng/mL

The PFC spike solution is prepared by diluting all PFAS to produce a solution containing each PFAS at a concentration of 20 ng/mL in methanol.

7.7. PFC Isotope Dilution Analyte Solution, 50 ng/mL

The PFC-IDA solution is prepared by diluting all labeled PFAS to produce a solution containing each compound at a concentration of 50 ng/mL in methanol. This is added to all samples prior to extraction.

7.8. Reverse Surrogate Solution, 1000 ng/mL

The reverse surrogate solution is prepared by diluting M2-4:2 FTS to produce a solution containing this compound at a concentration of 1000 ng/mL in methanol. This is added to all samples for the TOP assay to monitor the efficiency of the oxidation process.

7.9. Internal Standard Solution, 50 ng/mL

The internal standard solution is prepared by diluting 13C2-PFOA to produce a solution containing this compound at a concentration of 50 ng/mL in methanol. This is added to all extracts prior to analysis.

8. SAMPLE COLLECTION, PRESERVATION, AND STORAGE

8.1. Water samples are collected in pre-cleaned 250 mL HDPE containers. Soil samples are collected in pre-cleaned 8 oz. HDPE containers. Other containers may also be suitable. Samples are chilled to 0 - 6°C for shipment to the laboratory.

8.1.1. Water samples collected from a known chlorinated source should be preserved with Trizma.

8.2. Samples are logged in following normal laboratory procedures and are stored under refrigeration at 0 - 6°C. Water samples must be extracted within 1±days of collection. Soil samples must also be extracted within 14 days of collection. Tissue samples must be extracted within 1 year of collection if stored at ≤-10°C. Extracts must be refrigerated at 0 - 6°C, and analyzed within 40 days from extraction.

***Note**: As of this writing, Method 537 provides for a 14 day holding time for water samples preserved with Trizma buffer. The scientific literature indicates that perfluorinated substances are highly persistent in the environment. TestAmerica Sacramento has conducted time stability studies that support a 14 day holding time for aqueous samples with and without Trizma preservation. TestAmerica Denver has conducted stability studies indicating that medium- and low-level solutions of PFOA are stable for at least three months in polystyrene and polypropylene plastics at 0-6°C. The 14/40 day holding times given above are based on the stability study and general EPA convention for the holding time of extractable organic compounds in water and soil.*

9. QUALITY CONTROL

9.1. Initial Demonstration of Capability (IDOC)

The initial demonstration and method detection limit (MDL) studies described in Section 13 must be acceptable before analysis of samples may begin.

9.2. Batches are defined at the sample preparation step. Batches should be kept together through the whole analytical process as far as possible, but it is not mandatory to analyze prepared extracts on the same instrument or in the same sequence. Refer to the QC program document (WS-PQA-003) for further details of the batch definition.

9.2.1. The quality control batch is a set of up to 20 samples of the same matrix processed using the same procedure and reagents within the same time period. The quality control batch must contain a matrix spike/matrix spike duplicate (MS/MSD), a laboratory control sample (LCS) and a method blank. Laboratory generated QC samples (Blank, LCS, MS/MSD) do not count toward the maximum 20 samples in a batch. Field QC samples are included in the batch count. In some cases, at client request, the MS/MSD may be replaced with a matrix spike and sample duplicate. If insufficient sample is available for an MS/MSD, an LCSD may be substituted if batch precision is required by the program or client. In the event that multiple MS/MSDs are run with a batch due to client requirements, the additional MS/MSDs do not count toward the maximum 20 samples in a batch.

9.3. One method blank (MB, laboratory reagent blank) must be extracted with every process batch of similar matrix, not to exceed twenty (20) samples. For aqueous samples, the method blank is an aliquot of laboratory reagent water. For solid samples, the method blank is an aliquot of Ottawa sand. The method blank is processed in the

same manner and at the same time as the associated samples. Corrective actions must be documented on a Non-Conformance memo, and then implemented when target analytes are detected in the method blank above the reporting limit or when IDA recoveries are outside of the control limits. Re-extraction of the blank, other batch QC and the affected samples are required when the method blank is deemed unacceptable. See policy WS-PQA-003 for specific acceptance criteria.

9.3.1. If the MB produces a peak within the retention time window of any of the analytes, determine the source of the contamination and eliminate the interference before processing samples.

9.3.2. The method blank must not contain any analyte at or above the reporting limit, or at or above 10% of the measured concentration of that analyte in the associated samples, whichever is higher.

9.3.3. If there is no target analyte greater than the RL in the samples associated with an unacceptable method blank, the data may be reported with qualifiers. Such action should be taken in consultation with the client.

9.3.4. Re-extraction and reanalysis of samples associated with an unacceptable method blank is required when reportable concentrations are determined in the samples.

9.3.5. Refer to WS-PQA-003 for further details of the corrective actions.

9.3.6. Projects performed under the auspices of the DOD/DOE must meet QSM specific criteria for method blanks. Results are acceptable if the blank contamination is less than ½ of the reporting limit/LOQ for each analyte, or less than 1/10 of the regulatory limit, or less than 1/10 of the sample result for the same analyte, whichever is greater. If the method blank does not meet the acceptance criteria, the source of contamination must be investigated and measures taken to correct, minimize or eliminate the problem. Reprepare and reanalyze all field and QC samples associated with the contaminated method blank.

9.4. A laboratory control sample (LCS) must be extracted with every process batch of similar matrix, not to exceed twenty (20) samples. The LCS is an aliquot of laboratory matrix (e.g. water for aqueous samples and Ottawa sand for solids) spiked with analytes of known identity and concentration. The LCS must be processed in the same manner and at the same time as the associated samples. Corrective actions must be documented on a Non-Conformance memo, then implemented when recoveries of any spiked analyte is outside of the control limits. Re-extraction of the blank, other batch QC, and all associated samples are required if the LCS is deemed unacceptable. See

WS-PQA-0003 for specific acceptance criteria. The control limits for the LCS are stored in TALS.

9.5. A matrix spike/matrix spike duplicate (MS/MSD or MS/SD) pair must be extracted with every process batch of similar matrix, not to exceed twenty (20) samples. An MS/MSD pair is aliquots of a selected field sample spiked with analytes of known identity and concentration. The MS/MSD pair must be processed in the same manner and at the same time as the associated samples. Spiked analytes with recoveries or precision outside of the control limits must be within the control limits in the LCS. Corrective actions must be documented on a nonconformance memo, and then implemented when recoveries of any spiked analyte are outside of the control limits provided by TALS or by the client.

9.6. A duplicate control sample (LCSD or DCS) may be added when insufficient sample volume is provided to process an MS/MSD pair, or is requested by the client. The LCSD is evaluated in the same manner as the LCS. See WS-PQA-003 for specific acceptance criteria.

9.7. Initial calibration verification (ICV) –A second source standard is analyzed with the initial calibration curve. The concentration should be at the mid range of the curve. Corrective actions for the ICV include:

- Rerun the ICV.
- Remake or acquire a new ICV.
- Evaluate the instrument conditions.
- Evaluate the initial calibration standards.
- Rerun the initial calibration.

9.8. Isotope Dilution Analytes

9.8.1. The IDA solution is added to each field and QC sample at the time of extraction, as described in Section 11. As described in Section 7, this solution consists of isotopically labeled analogs of the analytes of interest.

9.8.2. IDA recoveries are flagged if they are outside of the acceptance limits (25–150%). Quantitation by isotope dilution generally precludes any adverse effect on data quality due to IDA recoveries being outside of the acceptance limits as long as the signal-to-nose ratio is greater than 10:1.

9.8.2.1. Evaluate data quality for usability, flag and submit a non-conformance memo for any analytes outside of the recovery criteria, and report if data is deemed not adversely effected.

9.8.2.2. Re-extraction of samples should be performed if the signal-to-noise for any IDA is less than 10:1 or if the IDA recoveries fall below 10%.

9.8.2.2.1. Re-extraction may be necessary under other circumstances when data quality has been determined to be adversely affected.

9.8.2.3. For samples analyzed in accordance with version 5.1 of the DoD/DOE QSM, the IDA recovery criteria is 50-150%. If QC or field samples do not meet these criteria then re-extraction is required.

9.8.2.4. For samples analyzed in accordance with version 5.3 of the DOD/DOE QSM, IDA recovery are not calculated. The areas of the IDA must be within 50-150% of the areas in the ICAL, or initial CCV if an ICAL is not analyzed on the same day

9.8.2.4.1. If out, re-analyze.

9.8.2.4.2. If still out, re-extract the samples (as a greater dilution or smaller sample size may be needed).

9.9. Internal Standard

9.9.1. The Internal Standard (IS) is added to each field and QC samples prior to analysis. The CCV IS response (peak area) must not deviate by more than 50% from the average response (peak area) of the initial calibration.

9.9.2. Sample IS response (peak area) must be within ±50% of the response (peak area) in the most recent CCV.

9.9.3. If the IS does not meet criteria, re-analyze the extract. If the IS meets criteria in the second analysis, report that analysis. If the IS does not meet criteria in the second analysis, report the first analysis with narration.

9.10. TOP Oxidation Efficiency

9.10.1. If the data indicates incomplete oxidation (i.e. the Post-TOP M2-4:2 FTS recovery is greater than 10% or the Post-TOP precursor concentration is greater than 10% of the Pre-TOP concentration) then a second aliquot (10 mL or a 0.2g equivalent) should be processed.

9.10.2. A reduced sample size may be used initially if sample history or other information indicates the sample is grossly contaminated.

9.11. Ion Ratio

9.11.1. Compare the quantifier/qualifier SRM transition ratio in the sample to the SRM transition ratio in the standard.

9.11.2. The quantifier/qualifier SRM ion ratio should be within ±50% of the average of the quantifier/qualifier SRM ion ratios calculated from the midlevel ICAL point or from the CCV, if an ICAL is not run.

9.11.3. At this time the ion ratio evaluation is a quantitative identification tool. Analyst judgement should be used if the ratio does not meet criteria. Data should be qualified "I" if the ratio is not met.

9.11.4. For samples analyzed in accordance with the DoD/DOE QSM version 5.3; if the quantitation ion peak does not meet the maximization criteria the peak shall be included in the summed integration. The result should be flagged "estimated, high bias". As there not a default qualifier for this in the TALS formatter for , use the "see case narrative" flag and NCM the issue.

10. CALIBRATION

10.1. For details of the calculations used to generate the regression equations, and how to use the factors generated by these equations, refer to SOP CA-Q-P-003 "Calibration Curves and Selection of Calibration Points".

10.2. Routine instrument operating conditions are listed in the table in Section 11.16.

10.3. Instrument Tuning & Mass Calibration

10.3.1. Mass Calibration is performed by instrument manufacturer service representatives in accordance with the manufacturer's procedures during installation, and annually thereafter.

10.3.2. Instrument tuning is done initially when the method is first developed and thereafter as needed during troubleshooting. Tuning is done by infusing each individual compound (native and IDA) into the mobile phase using a tee fitting at a point just before the entrance to the electrospray probe. The responses for the parent and daughter ions for each compound are observed and optimized for sensitivity and resolution. Mass assignments are reviewed and updated as needed. The mass assignments must be within ± 0.5 amu of the values shown in the table in Section 11.16.

10.3.3. Once the optimal mass assignments (within ±0.5 amu of true) are made immediately following the initial tune, the lowest level standard from the initial calibration curve is assessed to ensure that a signal to noise ratio

greater than 10 to 1 (S/N > 10:1) is achieved for each PFAS analyte. The first level standard from the initial calibration curve is used to evaluate the tune stability on an ongoing basis. The instrument mass windows are set initially at ± 0.5 amu of the true value; therefore, continued detection of the analyte transition with S/N > 10:1 serves as verification that the assigned mass remains within ± 0.5 amu of the true value, which meets the DoD/DOE QSM 5.1 tune criterion. For QSM 5.1 work, the instrument sensitivity check (section 10.12.4) is also evaluated to ensure that the signal to noise criteria is met.

10.3.3.1. For samples run in accordance with the DoD/DOE QSM version 5.3, the instrument must have a valid mass calibration prior to sample analysis. This is verified through the acquisition of a full scan continuum mass spectrum of a PFAS stock standard. All masses must be verified to be within ± 0.5 amu of true value.

10.4. A new calibration curve must be generated after major changes to the system or when the continuing calibration criteria cannot be met. Major changes include, but are not limited to, new columns or pump seals. A new calibration is not required after minor maintenance.

10.5. With the exception of the circumstances delineated in policy CA-Q-P-003, it is not acceptable to remove points from a calibration curve. In any event, at least five points must be included in the calibration curve. Average Response Factor and linear fit calibrations require five points, whereas Quadratic (second order) calibrations require six points.

10.6. A fixed injection volume is used for quantitation purposes and is to be the same for both the sample and standards.

10.7. All units used in the calculations must be consistently uniform, such as concentration in ng/mL.

10.8. Initial Calibration

10.8.1. A number of analytical standards of different analyte concentrations are used to generate the curve. Each standard is injected once to obtain the peak response for each analyte at each concentration. These standards define the working range of the analysis.

10.8.1.1. A minimum of five analytical standards is used when using average response factor and/or linear calibration fits.

10.8.1.2. A minimum of six analytical standards is used when a quadratic fit is used to generate the curve.

10.8.2. Calibration is by average response factor, linear fit, or by quadratic fit. Quadratic fit is used for the analyte if the response is non-linear.

10.8.2.1. For average response factor (RFa), the relative standard deviation (RSD) for all compounds quantitated against an identically labeled analog must be < 35% for the curve to be valid.

10.8.2.2. For average response factor (RFa), the relative standard deviation (RSD) for all compounds quantitated against a closely related labeled analog IDA must be < 50% for the curve to be valid.

10.8.2.3. For linear fit, the intercept of the line must be less than ½ the reporting limit, and the coefficient of determination (r2) must be greater than or equal to 0.990 for the curve to be considered valid (or the correlation coefficient (r) > 0.995).

10.8.2.4. The Internal Standard (IS) response (peak area) must not deviate by more than 50% from the average response (peak area) of the initial calibration.

10.8.2.5. Criteria for samples analyzed in accordance with QSM 5.1 or higher:

- The %RSD of the RFS for all analytes must be <20%.
- Linear or non-linear calibrations must have r^2>0.99 for each analyte.
- Analytes must be within 70-130% of their true value for each calibration standard.

10.9. Calibration Curve Fits

10.9.1. Linear regression or quadratic curves may be used to fit the data to a calibration function. Detailed descriptions and formulas for each fitting type can be found in SOP CA-Q-P-003, “Calibration Curves and Selection of Calibration Points”.

10.9.2. The linear curve uses the following function:

Equation 1

$$y = bx + c$$

Where:

$$y = \frac{\text{Area (analyte)}}{\text{Area (IS)}} \times \text{Concentration (IS)}$$

$$x = \text{concentration}$$

b = slope
c = intercept

10.9.3. The quadratic curve uses the following function:

Equation 2

$$y = ax^2 + bx + c$$

Where y, x, b, and c are the same as above, and a = curvature.

10.9.4. Evaluation of Calibration Curves

The following requirements must be met for any calibration to be used:

- Response must increase with increasing concentration.
- The absolute value of the intercept of a regression line (linear or non-linear) at zero response must be less than the reporting limit.
- There should be no carryover at or above 1/2 MRL after a high CAL standard.

If these criteria are not met, instrument conditions and standards will be checked, and the ICAL successfully repeated before continuing.

10.9.5. Weighting of Calibration Points

In linear and quadratic calibration fits, the points at the lower end of the calibration curve have less absolute variance than points at the high concentration end of the curve. This can cause severe errors in quantitation at the low end of the calibration. Because accuracy at the low end of the curve is very important for this analysis, it is preferable to increase the weighting of the lower concentration points. 1/concentration or 1/x weighting is encouraged. Visual inspection of the line fitted to the data is important in selecting the best fit.

10.10. Initial Calibration Blank (ICB)

10.10.1. Immediately following the ICAL, a calibration blank is analyzed that consists of an injection of 80:20 methanol:water blank containing both IDA and IS.

10.10.2. The result for the calibration blank must be less than the reporting limit.

10.10.3. If the ICB is greater than the reporting limit then the source of contamination must be identified and any necessary cleaning completed, and then the instrument should be recalibrated.

10.10.4. Criteria for samples analyzed in accordance with QSM 5.1 or higher:

- Instrument blanks are required immediately following the highest standard analyzed and *daily prior to sample analysis*.

- The instrument blank must be < ½ the LOQ.

10.11. Initial Calibration Verification (ICV)

10.11.1. Following the ICAL and the ICB, an ICV standard obtained from a different source or vendor than the ICAL standards is analyzed. This ICV standard is a mid-range standard.

10.11.2. The recovery for the ICV must meet the appropriate following criteria:

10.11.2.1. The native analyte must be within or equal to 60-140% for all native analytes quantitated against an identically labeled analog IDA.

10.11.2.2. The native analyte must be within or equal to 50-150% for all native analytes quantitated against a closely related labeled analog IDA.

10.11.2.3. The IDA must be within or equal to 50-150%.

10.11.3. Criteria for samples analyzed in accordance with QSM 5.1 or higher: Analyte concentrations must be within ±30% of their true values for all analytes, IDA and target.

10.11.4. See Section 9.7 for corrective actions in the event that the ICV does not meet the criteria above.

10.12. Continuing Calibration Verification (CCV)

Analyze a CCV at the beginning of a run, the end of a run, and after every 10 samples to determine if the calibration is still valid. The exception is after an acceptable curve and ICV are run 10 samples can be analyzed before a CCV is required. The CCVs are usually at the mid-level range of the curve and should vary throughout the run from low level (LOQ/RL) to mid level. The curve and ICV do not need to be run every day. To start an analytical run a CCV can be analyzed and if it meets acceptance criteria a run can be started. In addition, the low standard in the curve must be analyzed and must be within ± 50% of the expected value.

10.12.1. The recovery for the CCV standards must be equal to or within 60-140% for all natives quantitated against an identically labeled analog and equal to or within 50% to 150% for all natives quantitated against a closely related labeled analog. The recovery for the IDA must be within or equal to 50-150%.

10.12.2. The Internal Standard (IS) response (peak area) must be within ± 50% from the response (peak area) from the midpoint of the initial calibration.

10.12.2.1. Sample IS response (peak area) must be within ± 50% of the response (peak area) in the most recent CCV.

10.12.3. If this is not achieved, the instrument has drifted outside the calibration limits. The instrument must be recalibrated.

10.12.4. Criteria for samples analyzed in accordance with QSM 5.1 or higher:

- All analyte concentrations must be within ± 30% of their true value.
- Additionally, prior to analysis and at least once every 12 hours an instrument sensitivity check (ISC/CCVL) must be analyzed. The analyte concentrations must be at LOQ and the concentrations must be within ± 30% of their true value. This can be used as a CCV.

11. PROCEDURE

11.1. One-time procedural variations are allowed only if deemed necessary in the professional judgment of a supervisor to accommodate variation in sample matrix, chemistry, sample size, or other parameters. Any variation in procedure shall be completely documented using an Non-Conformance Memo (NCM). The NCM process is described in more detail in SOP WS-QA-0023. The NCM shall be filed in the project file and addressed in the case narrative.

Any deviations from this procedure identified after the work has been completed must be documented in an NCM, with a cause and corrective action described.

11.2. Water Sample Preparation

11.2.1. Visually inspect samples for the presence of settled and/or suspended sediment/particulates. If present or if the sample is biphasic add IDA prior to any sample decanting or centrifugation. If the sample requires decanting or centrifugation contact the client for guidance prior to such action. Decanting or filtering of the sample can lead to a low bias.

11.2.2. If authorized by the client to filter the sample, filter the water sample through a glass fiber filter (Whatman GF/F Cat No 1825 090 or equivalent). Gravity or vacuum can be used to pass the sample through the filter. Prepare a filtration blank with any samples requiring filtration. File an NCM noting the need for filtration.

Warning: The use of a vacuum system creates the risk of glassware implosion. Inspect all glassware prior to use. Glassware with chips, scratches, rub marks or cracks must not be used.

11.2.3. Weigh the sample container prior to extraction and then weigh the sample

container after extraction to determine the initial volume. Unless otherwise directed by client, use the entire sample volume.

11.2.4. Prepare additional aliquots of a field sample for the MS/MSD, if requested.

11.2.5. Prepare two 250 mL aliquots of HPLC-grade water for the method blank and LCS.

11.2.6. Spike the LCS and MS/MSD (if requested) with 0.5 mL of the LCS/Matrix PFC Spike solution (Section 7.6). This will result in a sample concentration of 40 ng/L.

11.2.7. Add 0.5 mL of the IDA PFC solution (Section 7.7) into each sample and QC sample, for a fixed concentration of 50 ng/mL in the final sample vial.

11.3. Solid Phase Extraction (SPE) of Aqueous Samples

The automated Zymark Auto-Trace Workstation can be used as long as the program follows these conditions and passes the background check.

11.3.1. Condition the SPE cartridges (Waters WAX, 500 mg/6 cc) by passing the following without drying the column.

Note: *The cartridges should not be allowed to go dry until the final elution step with methanol. At all of the other transition steps, the solvent/sample level should be stopped at the top of the column before the next liquid is added.*

WARNING: The use of a vacuum system creates the risk of glassware implosion. Inspect all glassware prior to use. Glassware with chips, scratches, rub marks or cracks must not be used.

11.3.2. Wash with 5.0 mL [redacted].

11.3.3. Wash with 5.0 mL of 0.1N NaOH/water. Close valve when ~ 200 uL remains on top to keep column wet. After this step, the columns cannot go dry until the completion of loading and rinsing samples.

11.3.4. Appropriately label the columns and add the reservoir to the column.

11.3.5. Add samples to the columns and with vacuum, pull the entire 250 mL aliquot of the sample through the cartridge at a rate of approximately 2 to 5 drops per second.

11.3.5.1. If the SPE column should plug (flow rate <1 drop per minute) prior to the entire content of the sample container passing through the column do the following:

1. Stop adding sample to the reservoir.

2. Return any remaining sample volume back to the original container.
3. Weigh the original container and record this weight into the worksheet notes field within the TALS extraction batch.
4. Determine the full volume of sample fortified by using the "Gross Weight" – (remaining sample volume – default tare weight of a sample container (26.1 g)).
5. Enter this value into the "Initial Amount" field in the TALS extraction batch.
6. Proceed to Section 11.4, noting that additional vacuum or pressure might be needed to elute the SPE column.

11.3.6. After the entire sample has been loaded onto the column, rinse the sample bottle with two 5 mL aliquots of reagent water and pour onto the column reservoir.

11.3.7. After the final loading of the sample but before completely passed through the column, rinse the SPE column with 1 mL of water.

11.3.8. After the sample and water rinse have completely passed through the cartridge, allow the column to dry well with vacuum for 15 minutes.

11.4. SPE Column Wash of Aqueous Samples with Hexane

11.4.1. Load the first 5 mL of hexane to soak for five minutes and then elute to waste.

11.4.2. Load the second 5 mL of hexane and elute to waste (without a soaking period).

11.4.3. Allow the column to dry with vacuum for 5 to 10 minutes. Columns must be dried before continuing.

11.5. SPE Elution of Aqueous Samples – using 15 mL polypropylene test tubes as receiving tubes in the SPE manifold.

11.5.1. Rinse sample bottles with 4 mL [redacted] and transfer to the column reservoir onto the cartridge. Allow the solution to soak for 5 minutes and then elute into the 15 mL collection tube.

11.5.2. Repeat sample bottle to column reservoir rinse and cartridge elution with a second 4 mL aliquot of [redacted]. The total collection should be approximately 8 mL.

11.5.3. Proceed to Section 11.15.2 (Graphitized Carbon Cleanup) as needed. This

required for all DoD/DOE extracts.

11.5.4. Proceed to Section 11.6 for final volume.

11.6. Final volume for extract

11.6.1. Add 0.5 mL of IS 50 ng/mL concentration and 2 mL of water to the extract. This will create an extract with a final solvent composition of 80:20 methanol:water.

11.6.1.1. Seal the test tube tightly. Invert container several times and then vortex. Allow extract to settle for 10 minutes prior to moving to the next step.

11.6.2. Transfer a portion of the extract to a 300 uL polypropylene autosampler vial (7 drop-wise or approximately ½ filled is sufficient). Archive the rest of the extracts for re-injection and dilution.

11.6.3. Seal the vial with a polypropylene screw cap. Note: Teflon lined caps cannot be used due to detection of low level concentration of PFAS.

11.7. Soil, Sediment and Tissue Sample Preparation and Extraction

11.7.1. Visually inspect soil samples for homogeneity.

11.7.1.1. Projects performed in accordance with the DOD/DOE QSM, version 5.1 or higher must have the entire sample homogenized prior to subsampling (see SOP WS-QA-0018).

11.7.2. Weigh a representative 5 g aliquot of soil, sediment or 1 g of tissue sample into a 50 mL HDPE wide-mouth bottle. Weigh additional sample amounts for the matrix spike and matrix spike duplicate analyses if they are requested.

11.7.3. For the method blank and LCS matrix, use 5 g each of Ottawa sand or 0.1 g of oil.

11.7.4. Spike the LCS and MS/MSD (if requested) with 1.0 mL of the LCS/Matrix PFC Spike solution (Section 7.6). This will result in a sample concentration of 4.0 ng/g.

11.7.4.1. Spike non-concentrated samples at 0.5 mL of LCS/Matrix PFC Spike Solution.

11.7.5. Add 1.0 mL of the IDA PFC solution (Section 7.7) into each sample and QC sample, for a fixed concentration of 50 ng/mL in the final sample vial.

11.7.5.1. Spike non-concentrated samples at 0.5 mL of IDA PFC Solution.

11.7.6. Cap the bottles and allow the spike to settle into the sample matrix. Gently shake the bottles to mix the spike into the matrix.

11.7.7. Add 20 mL of [redacted] to each sample.

11.7.8. Shake each sample on an orbital shaker at room temperature for 3 hours.

11.7.9. Following the shaking, extract the samples in an ultrasonic water bath for an additional 12 hours.

11.7.10. After the completion of extraction, centrifuge each sample at 3500 rpm for 15 minutes.

11.7.11. Collect and decant the [redacted] extract to a new 50 mL centrifuge tube.

11.7.12. Add another 2 mL of [redacted] solution to the residue, briefly shake to mix and centrifuge at 3500 rpm for 15 minutes.

11.7.13. Combine the rinsate to the first corresponding tubes.

11.7.14. To the final [redacted] extract, add 2 mL of water to each.

11.7.15. Concentrate the [redacted] extract under nitrogen to less than 2 mL, and dilute with water to 15 mL final volume.

11.7.16. Acidify with 80 µL of glacial acetic acid, and mix the contents well with vortex mixer. Check the pH to ensure pH is between 6 to 8.

11.7.17. Centrifuge at 3500 rpm for 15 minutes.

11.8. Solid Extract Cleanup by SPE

Set up WAX 150 mg/6 cc SPE columns for sample cleanup using vacuum manifold.

11.8.1. Condition the SPE cartridges by passing the following without drying the column.

Note: *The cartridges should not be allowed to go dry until the final elution step with methanol. At all of the other transition steps, the solvent/sample level should be stopped at the top of the column before the next liquid is added.*

WARNING: The use of a vacuum system creates the risk of glassware implosion. Inspect all glassware prior to use. Glassware with chips, scratches, rub marks or cracks must not be used.

11.8.2. Wash with 5.0 mL of [redacted].

11.8.3. Wash with 10 mL of 0.1 N NaOH/water. Close valve when ~ 500 µL remains on top of column to keep column wet. *After this step, the columns cannot go dry until the completion of loading and rinsing samples.*

11.8.4. Add extracts to the columns and with vacuum, pull the entire extracts through the cartridge at rate of approximately 3 to 5 drops per second.

11.8.5. Rinse the sample tube with 5 mL of water and add to the SPE column.

11.8.6. Dry the columns with vacuum for 15 minutes.

11.9. SPE Column Wash of Solid Extracts with Hexane

11.9.1. Load the first 5 mL of hexane to soak for five minutes, and elute to waste.

11.9.2. Load the second 5 mL of hexane and elute to waste (without a soaking period).

11.9.3. Allow the column to dry with vacuum for 10 minutes. Columns must be dried before continuing.

11.10. SPE Elution of Solid Extracts – using 15 mL polypropylene test tube as receiving tube in the SPE manifold.

11.10.1. Rinse extraction bottles with 4 mL of [redacted] and transfer to the column reservoir onto the cartridge. Allow the solution to soak for 5 minutes and then elute into the 15 mL collection tube.

11.10.2. Repeat extract bottle to column reservoir rinse and cartridge elution with a second 4 mL aliquot of [redacted]. The total collection should be approximately 8 mL.

11.10.3. Proceed to Section 11.15.2 (Graphitized Carbon Cleanup) as needed. This is required for all DoD/DOE extracts.

11.10.4. Proceed to Section 11.6 for final volume.

11.11. Product/Dispersion Samples

11.11.1. Check the solubility of the material in both methanol and water

11.11.1.1. If the material is soluble in water, dilute 0.5 mL of sample into 250 mL of DI water and proceed to Section 11.3 (follow water

extraction procedures). Fortify sample appropriately with IDA or PFC spike solution, see Section 11.2.

11.11.1.2. If the material is soluble in methanol, dilute 1 g (if solid) or 1 mL (if liquid) of material into 10 mL of methanol (MeOH).

11.11.1.2.1. If the material does not completely dissolve, contact your immediate supervisor.

11.11.2. Take 100 µL of the 10 mL solution and dilute it to 10 mL in MeOH.

11.11.3. Take a 1 mL aliquot of this solution (effective dilution of 1000x (1 mg for solid or 0.001 mL for liquid)) and fortify with 0.5 mL of labeled IDA solution (Section 7.7).

11.11.4. DO NOT PASS EXTRACT THROUGH SPE CARTIRIDGE (omit steps 11.9 – 11.11).

11.11.5. Proceed to Section 11.6 of this SOP for extract concentration.

11.12. TOP (Total Oxidizable Precursor) Assay for Aqueous Samples

11.12.1. Prepare 3-250 mL HDPE containers with HPLC grade water to create the needed QC Samples (MB, LCS/LCSD).

11.12.2. Prepare enough 125 mL HDPE containers as needed for all “Pre” and “Post” samples, including QC. Label each appropriately.

11.12.3. Spike the “Pre” and “Post” MB 125 mL containers with 25 µL of the reverse surrogate solution of M2-4:2 FTS (Section 7.8).

11.12.4. Spike the “Pre” and “Post” LCS/LCSD 125 mL containers with 0.5 mL of the LCS Spike solution (Section 7.6), both regular and “add-on”, and 25 uL of the reverse surrogate solution (Section 7.8).

11.12.5. Remove the methanol solvent from all Post QC sample 125 mL containers (MB and LCS/LCSD) by using N2 evaporation.

11.12.6. Add 2g of [redacted] and 1.9 mL of [redacted] to each “Post” sample container.

11.12.7. Subsample 100 mL aliquots of water from each field sample and QC from the 250 mL containers into each of the corresponding 125 mL containers for both the “Pre” and “Post” samples. Spike all “Pre” and “Post” samples with 25uL of the reverse surrogate solution (Section 7.8).

11.12.8. Set aside all "Pre" sample containers.

11.12.9. Cap each "Post" sample container, invert 2-3 times prior to placing container into water bath.

11.12.10. Add 2 g of [redacted] and 1.9 mL of [redacted] to each "Post" sample container.

11.12.11. Heat each "Post" sample container in a water bath (KD) at 85°C for 6 hours.

11.12.12. After digestion for 6 hours, place the "Post" sample containers in an ice bath for 30 minutes.

11.12.13. Adjust the pH of "Post" samples and associated QC aliquots to 7 with concentrated HCl. Use pH paper to determine the pH.

11.12.14. Spike both "Pre" and "Post" samples and their associated QC samples with 0.5 mL of PFC IDA solution (Section 7.7), both regular and add-on.

11.12.15. Use the following SPE procedure for both "Pre" and "Post" samples:

11.12.15.1. Set up WAX 150 mg/6 cc SPE columns for sample extraction using a vacuum manifold.

11.12.15.2. Establish a sample loading flow rate of 3-5 drops per second for each port of the vacuum manifold, for as many ports as will be used simultaneously during sample loading.

11.12.15.3. Wash/condition the SPE column with 5 mL of [redacted], then 5 mL water.

11.12.15.4. Load 100 mL of sample onto the SPE cartridge at a flow rate of 3-5 drops per second.

11.12.15.5. Add 5 mL rinse water

11.12.15.6. After the sample and water rinse have completely passed through the column, allow it to dry well using vacuum with a flow rate of 1 mL/minute for 15 minutes.

11.12.15.7. Wash the SPE column with 10 mL hexane rinse eluting all to waste.

11.12.15.8. Allow the column to dry well using vacuum for 5 minutes. Columns must be dry before continuing.

11.12.15.9. Elute the samples into 15 mL polypropylene test tubes in the SPE manifold by rinsing each 125 mL sample container with 5

mL of [redacted], and add to the SPE cartridge as eluent.

11.12.15.10. Repeat with another 5 mL of [redacted].

11.12.15.11. Collect the 10 mL of eluent and concentrate per Section 11.6.

11.13. TOP (Total Oxidizable Precursor) Assay for Soil Samples

11.13.1. Weigh representative 2 g aliquots of soil for each “Pre” and “Post” sample into a 50 mL centrifuge tube.

11.13.2. For the method blank and LCS matrix, use 2 g each of Ottawa sand for each “Pre” and “Post” QC sample.

11.13.3. Add 20 mL of [redacted] to each sample.

11.13.4. Shake each sample on an orbital shaker at room temperature for 3 hours.

11.13.5. Following the shaking, extract the samples in an ultrasonic water bath for an additional 12 hours.

11.13.6. After the completion of extraction, centrifuge each sample at 3500 rpm for 15 minutes.

11.13.7. Collect and decant the [redacted] extract to a new 50 mL centrifuge tube.

11.13.8. Add another 2 mL of [redacted] solution to the residue, briefly shake to mix and centrifuge at 3500 rpm for 15 minutes.

11.13.9. Combine the rinsate to the first corresponding tubes.

11.13.10. Proceed to Section 11.16.2 (Envi-carb clean up)

11.13.11. To the final [redacted] extract, add 0.5 mL of water to each.

11.13.12. Concentrate the [redacted] extract under nitrogen to less than 0.25 mL.

11.13.13. Dilute extract up to 50 mL with water in the centrifuge tube and vortex.

11.13.14. Prepare enough 125 mL HDPE containers as needed for all “Pre” and “Post” samples, including QC. Label each appropriately.

11.13.15. Spike the “Pre” and “Post” MB 125 mL containers with 25 µL of the reverse

surrogate solution of M2-4:2 FTS (Section 7.8).

11.13.16. Spike the "Pre" and "Post" LCS/LCSD 125 mL containers with 0.5 mL of the LCS Spike solution and 25 µL of the reverse surrogate solution (Section 7.8).

11.13.17. Remove the methanol solvent from all "Post" QC sample 125 mL containers (MB and LCS/LCSD) by using N2 evaporation.

11.13.18. Add 2 g of [redacted] and 1.9 mL of [redacted] to each "Post" sample container.

11.13.19. Transfer extract from the centrifuge tube to the appropriate 125 mL container.

11.13.20. Rinse the centrifuge container with an additional 50 mL of water and transfer to the appropriate 125 mL container.

11.13.21. Set aside all "Pre" sample containers.

11.13.22. Cap each "Post" sample container, invert 2-3 times prior to placing container into water bath.

11.13.23. Heat each "Post" sample container in a water bath (KD) at 85°C for 6 hours.

11.13.24. After digestion for 6 hours, place the "Post" sample containers in an ice bath for 30 minutes.

11.13.25. Adjust the pH of "Post" samples and associated QC aliquots to 7 with concentrated HCl. Use pH paper to determine the pH.

11.13.26. Spike both "Pre" and "Post" samples and their associated QC samples with 0.5 mL of PFC IDA solution (Section 7.7).

11.13.27. Use the following SPE procedure for both "Pre" and "Post" samples:

11.13.27.1. Set up WAX 150 mg/6 cc SPE columns for sample extraction using a vacuum manifold.

11.13.27.2. Establish a sample loading flow rate of 3-5 drops per second for each port of the vacuum manifold, for as many ports as will be used simultaneously during sample loading.

11.13.27.3. Wash/condition the SPE column with 5 mL of [redacted], then 5 mL water.

11.13.27.4. Load 100 mL of sample onto the SPE cartridge at a flow rate of 3-5 drops per second.

11.13.27.5. Add 5 mL rinse water

11.13.27.6. After the sample and water rinse have completely passed through the column, allow it to dry well using vacuum with a flow rate of 1 mL/minute for 15 minutes.

11.13.27.7. Wash the SPE column with 10 mL hexane rinse eluting all to waste.

11.13.27.8. Allow the column to dry well using vacuum for 5 minutes. Columns must be dry before continuing.

11.13.27.9. Elute the samples into 15 mL polypropylene test tubes in the SPE manifold by rinsing each 125 mL sample container with 4 mL of [redacted], and add to the SPE cartridge as eluent.

11.13.27.10. Repeat with another 4 mL of [redacted].

11.13.27.11. Collect the 8 mL of eluent and bring to final volume per Section 11.6.

11.14. Other Types of Sample Cleanup

11.14.1. Freezing technique to remove lipids.

If samples contain lipids then freeze the methanolic extract and QC extracts at -20^{o}C for at least 1 hour. Collect the solvent layer.

11.14.2. Cleanup with graphitized carbon will be applied to all samples as needed but is required for all DoD/DOE extracts.

11.14.2.1. Add 100 mg of graphitized carbon to each sample extract and QC extracts.

11.14.2.2. Shake vigorously and then let sit for 10 minutes.

11.14.2.3. Centrifuge each sample for 2 minutes at 1000 rpm.

11.14.2.4. Decant the solvent layer.

11.14.2.5. Proceed to Section 11.6.

11.15. AFFF Sample Preparation

11.15.1. QC for AFFF samples consists of a method blank, a laboratory control

sample and a sample or matrix duplicate only. No matrix spike or matrix spike duplicate is needed.

11.15.2. Perform a 1,000,000 X serial dilution of the AFFF sample. Dilute 1 mL of AFFF sample to 1 L with laboratory supplied water. Then dilute 1mL of this dilution to 1 L with laboratory supplied water.

11.15.2.1. Be sure to retain all dilutions should the initial analysis warrant re-analysis at higher concentration.

11.15.3. Subsample 2.0 mL of this dilution and fortify with 0.5 mL IDA solution and 0.5 mL of IS (50 ng/mL) solution: then add 7.0 mL of methanol.

11.15.4. Transfer a portion of the sample to a 300 µL polypropylene autosampler vial (7 drop-wise or approximately ½ filled is sufficient). Archive the rest of the sample for re-injection or dilution.

11.16. Instrument Analysis

Suggested operating conditions are listed in Tables 1-4 for the SCIEX LCMS systems:

Table 1 - Recommended Instrument Operating Conditions

HPLC Conditions ([redacted])				
Column (Column temp = [redacted]°C)	[redacted]			
Mobile Phase Composition	A = [redacted]		B = [redacted]	
Gradient Program	**Time**	**%A**	**%B**	**Flow Rate - mL/min**
	[redacted]	[redacted]	[redacted]	[redacted]
	[redacted]	[redacted]	[redacted]	[redacted]
	[redacted]	[redacted]	[redacted]	[redacted]
	[redacted]	[redacted]	[redacted]	[redacted]
	[redacted]	[redacted]	[redacted]	[redacted]
	Maximum pressure limit = 5,000 psi			
Injection Size	[redacted] (fixed amount throughout the sequence).			
Run Time	~[redacted]			
Mass Spectrometer Interface Settings ([redacted])				
MS Interface Mode	ESI Negative Ion. Minimum of 10 scans/peak.			
Ion Spray Voltage (kV)	[redacted]			
Entrance Potential (V)	[redacted]			
Declustering Potential (V)	[redacted]			
Desolvation Temp	[redacted]			
Curtain Gas	[redacted]			
Collision Gas	[redacted]			

Table 2 - Recommended Instrument Operating Conditions								
Mass Spectrometer Scan Settings ([redacted])								
Compound	Comments	Reaction (MRM)	Dwell (sec)	Ent. Pot. (V)	Col. Energy (V)	Declu. Pot. (V)	Cell Exit Pot. (V)	Typ RT (Min)
PFBA	Native analyte	212.9 > 169	0.011	[redacted]				
13C4-PFBA	IDA	217 > 172	0.011					
PFBS	Native analyte	298.9 > 80	0.011					
PFBS_2	Native analyte	298.9 > 99	0.011					
13C3-PFBS	IDA	301.9 > 83	0.011					
PFPeA	Native analyte	262.9 > 219	0.011					
13C5-PFPeA	IDA	267.9 > 223	0.011					
4:2 FTS	Native analyte	327 > 307	0.011					
M2-4:2FTS	IDA or Reverse Surrogate for TOP	329 > 81	0.011					
PFHxA	Native analyte	313 > 269	0.011					
PFHxA_2	Native analyte	313 > 119	0.011					
13C2-PFHxA	IDA	315 > 270	0.011					
PFHpA	Native analyte	363 > 319	0.011					
PFHpA_2	Native analyte	363 > 169	0.011					
13C4-PFHpA	IDA	367 > 322	0.011					
PFPeS	Native analyte	349 > 80	0.011					
PFPeS_2	Native analyte	349 > 99	0.011					
PFHxS	Native analyte	399 > 80	0.011					
PFHxS_2	Native analyte	399 > 99	0.011					
18O2-PFHxS	IDA	403 > 84	0.011					
6:2 FTS	Native analyte	427 > 407	0.011					
M2-6:2FTS	IDA	429 > 81	0.011					
PFOA	Native analyte	413 > 369	0.011					
PFOA_2	Native analyte	413 > 169	0.011					
13C4-PFOA	IDA	417 > 372	0.011					
13C2-PFOA	IS	415 > 370	0.011					
PFHpS	Native analyte	449 > 80	0.011					
PFHpS_2	Native analyte	449 > 99	0.011					
PFNA	Native analyte	463 > 419	0.011					
PFNA_2	Native analyte	463 > 169	0.011					
13C5-PFNA	IDA	468 > 423	0.011					
PFOS	Native analyte	499 > 80	0.011					
PFOS_2	Native analyte	499 > 99	0.011					
PFNS	Native analyte	549 > 80	0.011					
PFNS_2	Native analyte	549 > 99	0.011					
PFDoS	Native analyte	699 > 80	0.011					
PFDoS_2	Native analyte	699 >99	0.011					
13C4-PFOS	IDA	503 > 80	0.011					

Table 2 - Recommended Instrument Operating Conditions								
Mass Spectrometer Scan Settings ( )								
Compound	Comments	Reaction (MRM)	Dwell (sec)	Ent. Pot. (V)	Col. Energy (V)	Declu. Pot. (V)	Cell Exit Pot. (V)	Typ RT (Min)
PFDA	Native analyte	513 > 469	0.011					
PFDA_2	Native analyte	513 > 169	0.011					
13C2-PFDA	IDA	515 > 470	0.011					
8:2 FTS	Native analyte	527 > 507	0.011					
10:2 FTS	Native analyte	627 > 607	0.011					
M2-8:2FTS	IDA	529 > 81	0.011					
PFOSA	Native analyte	498 > 78	0.011					
13C8-PFOSA	IDA	506 > 78	0.011					
N-MeFOSAA	Native analyte	570 > 419	0.011					
d3-MeFOSAA	IDA	573 > 419	0.011					
PFDS	Native analyte	599 > 80	0.011					
PFDS_2	Native analyte	599 > 99	0.011					
PFUdA	Native analyte	563 > 519	0.011					
PFUdA_2	Native analyte	563 > 169	0.011					
13C2-PFUdA	IDA	565 > 520	0.011					
N-EtFOSAA	Native analyte	584 > 419	0.011					
d5-EtFOSAA	IDA	589 > 419	0.011					
PFDoA	Native analyte	613 > 569	0.011					
PFDoA_2	Native analyte	613 > 169	0.011					
13C2-PFDoA	IDA	615 > 570	0.011					
PFTrDA	Native analyte	663 > 619	0.011					
PFTrDA_2	Native analyte	663 > 169	0.011					
PFTeDA	Native analyte	713 > 169	0.011					
PFTeDA_2	Native analyte	713 > 219	0.011					
13C2-PFTeDA	IDA	715 > 670	0.011					
Et-FOSA	Native analyte	526 > 169	0.011					
d5-EtFOSA	IDA	531 > 169	0.011					
Me-FOSA	Native analyte	512 > 169	0.011					
d3-MeFOSA	IDA	515 > 169	0.011					
Et-FOSE	Native analyte	630 > 59	0.011					
d9-EtFOSE	IDA	639 > 59	0.011					
Me-FOSE	Native analyte	616 > 59	0.011					
d7-MeFOSE	IDA	623 > 59	0.011					
PFHxDA	Native analyte	813 > 769	0.011					
PFHxDA_2	Native analyte	813 > 169	0.011					
13C2-PFHxDA	IDA	815 > 770	0.011					
PFODA	Native analyte	913 > 869	0.011					
PFODA_2	Native analyte	913 > 169	0.011					

Table 3 - Recommended Instrument Operating Conditions Mass Spectrometer Scan Settings (SCIEX 5500) for Fluorinated Replacement Chemicals								
Compound	Comments	Reaction (MRM)	Dwell (sec)	Ent. Pot. (V)	Col. Energy (V)	Declu. Pot. (V)	Cell Exit Pot. (V)	Typ RT (Min)
HFPO-DA	Native analyte	329.1 > 285	0.011	[redacted]	[redacted]	[redacted]	[redacted]	[redacted]
13C3-HFPO-DA	IDA	332.1 > 287	0.011	[redacted]	[redacted]	[redacted]	[redacted]	[redacted]
9Cl-PF3ONS (F53B major)	Native analyte	531 > 351	0.011	[redacted]	[redacted]	[redacted]	[redacted]	[redacted]
11Cl-PF3OUdS (F53B minor)	Native analyte	631 > 451	0.011	[redacted]	[redacted]	[redacted]	[redacted]	[redacted]
Dona	Native analyte	377 > 251	0.011	[redacted]	[redacted]	[redacted]	[redacted]	[redacted]
Dona_2	Native analyte	377 > 85	0.011	[redacted]	[redacted]	[redacted]	[redacted]	[redacted]

Table 4 - Retention Times & Quantitation (SCIEX 5500)				
Native Compounds	**Typical Native RT (minutes)**	**IDA analog**	**Typical IDA RT (minutes)**	**Quantitation Method**
PFBA	[redacted]	13C4-PFBA	[redacted]	Isotope Dilution
PFPeA	[redacted]	13C5-PFPeA	[redacted]	Isotope Dilution
PFBS	[redacted]	13C3-PFBS	[redacted]	Isotope Dilution
PFHxA	[redacted]	13C2-PFHxA	[redacted]	Isotope Dilution
PFPeS	[redacted]	13C3-PFBS	[redacted]	Isotope Dilution
PFHpA	[redacted]	13C4-PFHpA	[redacted]	Isotope Dilution
PFHxS	[redacted]	18O2-PFHxS	[redacted]	Isotope Dilution
PFOA	[redacted]	13C4-PFOA	[redacted]	Isotope Dilution
PFHpS	[redacted]	13C4-PFOS	[redacted]	Isotope Dilution
PFNA	[redacted]	13C5-PFNA	[redacted]	Isotope Dilution
PFOS	[redacted]	13C4-PFOS	[redacted]	Isotope Dilution
PFNS	[redacted]	13C4-PFOS	[redacted]	Isotope Dilution
PFDA	[redacted]	13C2-PFDA	[redacted]	Isotope Dilution
FOSA	[redacted]	13C8-FOSA	[redacted]	Isotope Dilution
PFDS	[redacted]	13C4-PFOS	[redacted]	Isotope Dilution
PFUdA	[redacted]	13C2-PFUdA	[redacted]	Isotope Dilution
PFDoA	[redacted]	13C2-PFDoA	[redacted]	Isotope Dilution
PFTrDA	[redacted]	13C2-PFDoA	[redacted]	Isotope Dilution
PFDoS	[redacted]	13C4-PFOS	[redacted]	Isotope Dilution
PFTeDA	[redacted]	13C2-PFTeDA	[redacted]	Isotope Dilution
EtFOSA	[redacted]	d5-EtFOSA	[redacted]	Isotope Dilution
MeFOSA	[redacted]	d3-MeFOSA	[redacted]	Isotope Dilution
EtFOSE	[redacted]	d9-EtFOSE	[redacted]	Isotope Dilution
MeFOSE	[redacted]	d7-MeFOSE	[redacted]	Isotope Dilution
PFHxDA	[redacted]	13C2-PFHxDA	[redacted]	Isotope Dilution

Table 4 - Retention Times & Quantitation (SCIEX 5500)				
Native Compounds	**Typical Native RT (minutes)**	**IDA analog**	**Typical IDA RT (minutes)**	**Quantitation Method**
PFODA	[redacted]	13C2-PFHxDA	[redacted]	Isotope Dilution
EtFOSAA	[redacted]	d5-EtFOSAA	[redacted]	Isotope Dilution
MeFOSAA	[redacted]	d3-MeFOSAA	[redacted]	Isotope Dilution
4:2 FTS	[redacted]	M2-4:2 FTS (If TOP then 13C-PFBS)	[redacted]	Isotope Dilution
6:2FTS	[redacted]	M2-6:2FTS	[redacted]	Isotope Dilution
8:2FTS	[redacted]	M2-8:2FTS	[redacted]	Isotope Dilution
HFPO-DA	[redacted]	13C3-HFPO-DA	[redacted]	Isotope Dilution
9Cl-PF3ONS (F53B major)	[redacted]	13C4-PFOS	[redacted]	Isotope Dilution
11Cl-PF3OUdS (F53B minor)	[redacted]	13C4-PFOS	[redacted]	Isotope Dilution
Dona	[redacted]	13C4-PFOS	[redacted]	Isotope Dilution
10:2 FTS	[redacted]	M2-8:2 FTS	[redacted]	Isotope Dilution

11.16.1. Post Spike Sample Analysis for AFFF samples

11.16.1.1. This section only applies to aqueous samples prepared by serial dilution instead of SPE that have reported value of <LOQ (RL) for any analyte.

11.16.1.2. Spike aliquots of the sample at the final dilution reported for the sample with all analytes that have reported of <LOQ in the final dilution. The spike must be at the LOQ concentration to be reported with the sample (the < LOQ value).

11.16.1.3. When analyte concentrations are calculated as <LOQ, the spike must recover within 70-130% of its true value.

11.16.1.4. It the recovery does not meet this criteria, the sample, sample duplicate and post spike sample must be reanalyzed at consecutively higher dilutions until the criteria is met.

11.16.2. Tune and calibrate the instrument as described in Section 10.

11.16.3. A typical run sequence is as follows:

- Rinse Blank (RB, not linked to anything)
- Start ICAL with CCVL but called IC in TALS (starts the 12 hour clock or time 0:00)
- Rest of ICAL

- ICB: link to midpoint of ICAL and samples
- ICV: link to midpoint of ICAL and samples (If ICAL good)
- CCB: link to midpoint of ICAL and samples
- PFOA RT marker
- Rinse Blank (RB, not linked to anything)
- 10 samples: link to midpoint of ICAL
- CCV: link to midpoint of ICAL
- 10 more samples: link to midpoint of ICAL
- CCV: link to midpoint of ICAL
- Etc.
- CCVL (within 12 hours from CCVL in ICAL, can be the ending CCV and starts 12 hours all over again): if this occurs link to the midpoint of the ICAL/toggle it as opening/closing CCV.
- CCV: link to midpoint of ICAL
- 10 samples: link to midpoint of ICAL
- CCV: link to midpoint of ICAL
- If no ICAL run that day
- CCB: link to CCVIS
- CCVL (starts 12 hour clock): link to CCVIS
- CCVIS: link to midpoint of ICAL
- 10 samples: link to CCVIS
- CCV: link to CCVIS
- 10 samples: link to CCVIS
- CCV: link to CCVIS
- Etc.
- If going over 12 hours in the sequence: CCVL (within 12 hours from CCVL at item 2 above, can be the ending CCV and starts 12 hours all over again): if this occurs link to the CCVIS /toggle as opening and closing CCV.
- CCV: link to CCVIS
- 10 samples: link to CCVIS
- CCV: link to CCVIS

12. CALCULATIONS

12.1. If the concentration of the analyte ions exceeds the working range as defined by the

calibration standards, then the sample must be diluted and reanalyzed. It may be necessary to dilute samples due to matrix.

12.2. Extracts can be diluted up to 100X without diluting out the IDA and thus preserving quantitation via isotope dilution. Dilutions greater than 100X can be performed but additional IDA must be added. The quantitation will now be via internal standard as a result. Consult the client for authorization of such a dilution.

12.3. Results less than the reporting limit are flagged in the client report as estimated. Generally, the "J" flag is used to denote ≥ MDL and ≤ RL, but the specific flag may change based on client requirements.

12.4. Qualitative Identification

12.4.1. The retention times of PFAS with labeled standards should be the same as that of the labeled IDA's to within 0.05 min. For PFAS with no labeled standards, the RT must be within ± 0.3 minutes of the ICV and CCV standards.

***Note**: The IDA RT and native RT may be offset by 0.02 to 0.04 minutes.*

12.4.1.1. Criteria for samples analyzed in accordance with QSM 5.3: The peak RT must be within 0.4 mins of the CCV or midpoint of the ICAL. The target analyte must elute within 0.1 mins of the IDA for those analytes with their own IDA.

12.5. The ICAL established in Section 10 is used to calculate concentrations for the extracts.

12.6. Extract concentrations are calculated as below. The first equation applies to the linear fit, the second to the quadratic line fit.

Equation 3

$$\text{Concentration, ng/mL} = \frac{y - c}{b}$$

Equation 4

$$\text{Concentration, ng/mL} = \frac{-b + \sqrt{b^2 - 4a(c - y)}}{2a}$$

Where:

y = $\frac{\text{Area (analyte)}}{\text{Area (IS)}} \times \text{Concentration (IS)}$

x = concentration

a = curvature

b = slope

c = intercept

12.7. Water Sample Result Calculation:

Equation 5

$$\text{Concentration, ng/L} = \frac{C_{ex} V_t}{V_o}$$

Where:

C_{ex} = Concentration measured in sample extract (ng/mL)
V_t = Volume of total extract (mL)
V_o = Volume of water extracted (L)

12.8. Soil Sample Result Calculation:

Equation 6

$$\text{Concentration, } ng/g = \frac{C_{ex} V_t}{W_s D}$$

Where ng/g = µg/kg and:

C_{ex} = Concentration measured in sample extract (ng/mL)
V_t = Volume of total extract (mL)
W_s = Weight of sample extracted (g)
D = Fraction of dry solids, which is calculated as follows:

$$\frac{100 - \%\,\text{moisture in sample}}{100}$$ (for dry weight result)

12.9. IDA Recovery Calculation:

Equation 7

$$\%\,\text{Recovery} = \frac{A_t Q_{is}}{A_{is} Q_t RRF_{IDA}} X 100$$

Where ng/g = µg/kg and:

RF_{IDA} = Response Factor for IDA compound
A_t = Area response for IDA compound
A_{IS} = Area Response for IS compound
Q_{IS} = Amount of IS added
Q_t = Amount of IDA added

12.10. Raw data, calibration summaries, QC data, and sample results are reviewed by the analyst. These must also be reviewed thoroughly by a second qualified person. See the Data Review Policy (WS-PQA-0012). These reviews are documented on the Data Review Checklist.

13. METHOD PERFORMANCE

13.1. The group/team leader has the responsibility to ensure that this procedure is performed by an associate who has been properly trained in its use and has the required expertise.

13.2. Method Detection Limit

The laboratory must generate a valid method detection limit for each analyte of interest. The MDL must be below the reporting limit for each analyte. The procedure for determination of the method detection limit is given in 40 CFR Part 136, Appendix B, and further defined in SOP WS-QA-0006 and policy WS-PQA-003. MDLs are available in the Quality Assurance Department.

13.3. Initial Demonstration of Capability (IDOC)

Each analyst performing this procedure must successfully analyze four LCS QC samples using current laboratory LCS control limits. IDOCs are approved by the Quality Assurance Manager and the Technical Director. IDOC records are maintained by the QA staff in the central training files.

13.4. The laboratory must generate a valid method detection limit for each analyte of interest. The MDL must be below the reporting limit for each analyte. The procedure for determination of the method detection limit is given in 40 CFR Part 136, Appendix B, and further defined in WS-QA-0006 and policy WS-PQA-003.

14. POLLUTION PREVENTION

14.1. All waste will be disposed of in accordance with Federal, State and Local regulations.

14.2. Solid phase extraction used for water samples greatly reduces the amount of solvent used compared to liquid-liquid extraction.

14.3. Standards and reagents are purchased and prepared in volumes consistent with laboratory use to minimize the volume of expired standards and reagents requiring disposal.

14.4. Where reasonably feasible, technological changes have been implemented to minimize the potential for pollution of the environment. Employees will abide by this method and the policies in Section 13 of the Corporate Safety Manual for “Waste Management and Pollution Prevention.”

14.5. Do not allow waste solvent to vent into the hoods. All solvent waste is stored in capped containers unless waste is being transferred.

14.6. Transfer waste solvent from collection cups (tri-pour and similar containers) to jugs and/or carboys as quickly as possible to minimize evaporation.

15. WASTE MANAGEMENT

The following waste streams are produced when this method is carried out:

15.1. Assorted test tubes, autovials, syringes, filter discs and cartridges. Dump the solid waste into a yellow contaminated lab trash bucket. When the bucket is full or after no more than one year, tie the plastic bag liner shut and put the lab trash into the hazardous waste – landfill steel collection drum in the H3 closet. When the drum is full or after no more than 75 days, move it to the waste collection area for shipment.

15.2. Extracted soil samples, used sodium sulfate, paper funnel filters, glass wool, thimbles, and extracted solids saturated with solvents. Dump these materials into an orange contaminated lab trash bucket. When the bucket is full or after no more than one year, tie the plastic bag liner shut and put the lab trash into the incineration steel collection drum in the H3 closet. When the drum is full or after no more than 75 days, move it to the waste collection area for shipment.

15.3. Waste Methanol. Collect the waste solvents in tripours during use. Empty the tripours into a 1-liter to 4-liter carboy at the fume hood. When the carboy is full, or at the end of your shift, whichever comes first, empty the carboy into the steel flammable solvent drum in the H3 closet. When the drum is full to between four and six inches of the top, or after no more than 75 days, move the steel flammable solvent drum to the waste collection area for shipment.

15.4. Mixed water/methanol waste from soil extraction. Collect the waste in the HPLC waste carboy. When full, or after no more than one year, dump into the blue plastic HPLC collection drum in the H3 closet. When the drum is full to between four and six inches of the top or after no more than 75 days, move it to the waste collection area for shipment.

15.5. Aqueous acidic waste from the LCMS instrument contaminated with methanol. This is collected in a 1-gallon carboy at the instrument. When the carboy is full, or after no more than one year, it is emptied into the blue plastic HPLC collection drum in the H3 closet. When the drum is full to between four and six inches of the top or after no more than 75 days, move it to the waste collection area for shipment.

15.6. Autovials contaminated with methanol. As the autovials are removed from the instrument after analysis, they are collected in open containers at the instrument. After all autovials are removed, the open container must be dumped into a closed satellite collection container in a fume hood, as the punctured septa in the autovial can allow methanol and other contaminants to evaporate into the atmosphere. The satellite collection containers are transferred to the waste disposal area when full or after no more than one year, where they are disposed through the vial eater.

16. REFERENCES

16.1. Cheryl Moody, Wai Chi Kwan, Johnathan W. Martin, Derek C. G. Muir, Scott A. Mabury, “Determination of Perfluorinated Surfactants in Surface Water Samples by

Two Independent Analytical Techniques: Liquid Chromatography/Tandem Mass Spectrometry and 19FNMR," Analytical Chemistry 2001, 73, 2200-2206.

16.2. John Giesy et al., "Accumulation of Perfluorooctane Sulfonate in Marine Mammals", Environmental Science & Technology, 2001 Vol. 35, No. 8, pages 1593-1598.

16.3. U.S. EPA, "Residue Chemistry Test Guidelines, OPPTS 860.1340, Residue Analytical Method", EPA 712-C-95-174, August 1995.

16.4. STL Denver White Paper DEN-W-LC-002, "Method Validation Study for Analysis of Ammonium Perfluorooctanate in Soil Matrices by High Performance Liquid Chromatography/Mass Spectrometry (HPLC/MS/MS)", Mark Dymerski, September 5, 2003.

16.5. STL Denver White Paper DEN-W-LC-003, "Addendum A to Method Validation Study for Analysis of Ammonium Perfluorooctanate in Soil Matrices by High Performance Liquid Chromatography/Mass Spectrometry (HPLC/MS/MS)", Mark Dymerski, August 6, 2003.

16.6. STL Denver White Paper DEN-W-LC-004, "Method Validation Study for Analysis of Perfluorooctanoic Acid in Waters by High Performance Liquid Chromatography/Tandem Mass Spectrometry (HPLC/MS/MS)", Mark Dymerski, January 26, 2005.

16.7. Waters application note; "Acquity UPLC System for Quantifying Trace Levels of Perfluorinated Compounds with an Acquity PFC Analysis Kit", Peter J. Lee, Evan T. Bernier, Gordon T. Fujimoto, Jeremy Shia, Michael S. Young, and Alice J. Di Gloia, Waters Corporation, Milford, MA. USA.

16.8. US EPA, "Method 537 - Determination of Selected Perfluorinated alkyl acids in Drinking Water by Solid Phase Extraction and Liquid Chromatography/Tandem Mass Spectrometery (LC/MS/MS)", Version 1.1, September 2009, J.A. Shoemaker, P.E. Grimmett, B.K. Boutin, EPA Document #: EPA/600/R-08/092

16.9. Erika F. Houtz and David L. Sedlak, "Oxidative Conversion as a Means of Detecting Precursors to Perfluoroalkyl Acids in Urban Runoff," Environmental Science and Technology 46, no. 17 (2012): 9342-49.

16.10. U.S. Department of Denfense (DoD)/Department of Energy (DOE) Consolidated Quality Systems Manual (QSM) for Environmental Laboratories, Version 5.1.1, dated 2017.

16.11. U.S. Department of Denfense (DoD)/Department of Energy (DOE) Consolidated Quality Systems Manual (QSM) for Environmental Laboratories, Version 5.3 dated 2019.

17. METHOD MODIFICATIONS

17.1. Modifications from Method 537 are detailed below:

17.1.1. Target analyte results are quantitated via isotope dilution.

17.1.2. Two ion transitions (precursor to quant ion and precursor to confirmation ion) are monitored for those analytes that have two transitions. Ion ratios are monitored as well for these analytes.

17.1.3. Water sample containers are not preserved with Trizma.

17.1.4. The method has been modified to address soil/solid matrices. The extraction holding time is set at 14 days.

17.1.5. The analyte list has been expanded. The number of labeled analytes has been expanded as well to improve quantitation.

17.1.6. The reporting limits differ as they are all set at one consistent value.

17.1.7. Calibration levels differ from the referenced method.

17.1.8. More labeled analytes are fortified into the samples prior to the extraction process. Most target analytes are quantitated against a labeled analyte.

17.1.9. There is no symmetry requirement.

17.1.10. Calibration, both initial and continuing, has different acceptance criteria due to the longer list of analytes, and the use of isotope dilution quantitation.

17.1.11. The eluents and HPLC configuration differs. As a result the final extract is in 80:20 methanol:water.

17.1.12. The LCS and MS/MSD are spiked at one concentration and do not rotate between a low to high levels.

17.1.13. Samples are not checked for residual chlorine or pH.

17.1.14. A different SPE cartridge (Waters OASIS WAX) is used for the extraction process. As a result solvents and elution procedures are different.

18. ATTACHMENTS

18.1. Attachment 1 – Analysis of Perfluorinated Compounds (PFAS) in Water via In Line Solid Phase Extraction (SPE).

19. REVISION HISTORY

Revisions to Attachment 1 are documented in the attachment.

Revisions prior to 05/01/2017 have been removed and are available in previous versions of this SOP.

19.1. WS-LC-0025 Revision 3.8, Effective 09/23/2019

19.1.1. Removed Section 6.9.1, "[redacted]"

19.1.2. Removed Section 6.9.4, "[redacted]"

19.1.3. Removed Section 6.9.5, "[redacted]"

19.1.4. Removed Section 6.9.6, "[redacted]"

19.1.5. Revised Section 9.8.2.3, "For samples analyzed in in accordance with version 5.1 of the DOD/DOE QSM, the IDA recovery criteria is 50-150%. If QC or field samples do not meet these criteria then re-extraction is required"

19.1.6. Added Section 9.8.2.4, "For samples analyzed in accordance with version 5.3 of the DOD/DOE QSM, IDA recovery are not calculated. The areas of the IDA must be within 50-150% of the areas in the ICAL, or initial CCV if an ICAL is not analyzed on the same day"

19.1.7. Added Section 9.11.4, "For samples analyzed in accordance with the DoD/DOE QSM version 5.3; if the quantitation ion peak does not meet the maximization criteria the peak shall be included in the summed integration. The result should be flagged "estimated, high bias". As there not a default qualifier for this in the TALS formatter for , use the "see case narrative" flag and NCM the issue."

19.1.8. Added Section 10.3.1, "Mass Calibration is performed by instrument manufacturer service representatives in accordance with the manufacturer's procedures during installation, and annually thereafter."

19.1.9. Section 10.3.2 revised, "to maintain the sensitivity and selectivity f the method" to "during troubleshooting" and "calibrated if necessary" to "updated as needed".

19.1.10. Added Section 10.3.3.1, "For samples run in accordance with the DoD/DOE

QSM version 5.3, the instrument must have a valid mass calibration prior to sample analysis. This is verified through the acquisition of a full scan continuum mass spectrum of a PFAS stock standard. All masses must be verified to be within ± 0.5 amu of true value."

19.1.11. Revised Section 10.8.2.5 to, "Criteria for samples analyzed in accordance with QSM 5.1 or higher:"

19.1.12. Revised Section 10.10.4 to, "Criteria for samples analyzed in accordance with QSM 5.1 or higher:"

19.1.13. Section 10.11.3 revised, "Criteria for samples analyzed in accordance with QSM 5.1 or higher:"

19.1.14. Section 10.12.4 revised to, "Criteria for samples analyzed in accordance with QSM 5.1 or higher:"

19.1.15. Section 11.7.1.1 revised to, "Projects performed in accordance with the DOD/DOE QSM, version 5.1 or higher must have the entire sample homogenized prior to subsampling (see SOP WS-QA-0018)."

19.1.16. Added Section 12.4.1.1, "Criteria for samples analyzed in accordance with QSM 5.3: The peak RT must be within 0.4 mins of the CCV or midpoint of the ICAL. The target analyte must elute within 0.1 mins of the IDA for those analytes with their own IDA."

19.1.17. Added Section 6.10, "U.S. Department of Denfense (DoD)/Department of Energy (DOE) Consolidated Quality Systems Manual (QSM) for Environmental Laboratories, Version 5.1.1, dated 2017."

19.1.18. Added Section 6.11, "U.S. Department of Denfense (DoD)/Department of Energy (DOE) Consolidated Quality Systems Manual (QSM) for Environmental Laboratories, Version 5.3 dated 2019."

19.1.19. Editorial changes

19.2. WS-LC-0025 Revision 3.7, Effective 08/13/2019

19.2.1. Added Et/Me FOSA and Et/Me-FOSE and related labeled analogs to all calibration and instrument specification tables.

19.2.2. Removed all references to Waters LCMS systems.

19.2.3. Removed all references and procedures for concentrating extracts.

19.2.4. Removed all references and requirements for the state of New Jersey as there is now a separate SOP.

19.2.5. Added Sections 12.2, "Extracts can be diluted up to 100X without diluting out the IDA and thus preserving quantitation via isotope dilution. Dilutions greater than 100X can be performed but additional IDA must be added. The quantitation will now be via internal standard as a result. Consult the client for authorization of such a dilution."

19.2.6. Added Section 12.3, "Results less than the reporting limit are flagged in the client report as estimated. Generally, the "J" flag is used to denote ≥ MDL and ≤ RL, but the specific flag may change based on client requirements."

19.2.7. Added Section 17.1.1, "Target analyte results are quantitated via isotope dilution."

19.2.8. Added Section 17.1.2, "Two ion transitions (precursor to quant ion and precursor to confirmation ion) are monitored for those analytes that have two transitions. Ion ratios are monitored as well for these analytes."

19.2.9. Editorial changes.

19.3. WS-LC-0025 Revision 3.6, Effective 05/14/2019

19.3.1. Section 1.1 updated CAS numbers for "Perfluoro-1-pentanesulfonic acid" and "Perfluoro-nonanesulfonic acid".

19.3.2. Section 1.2 updated table with correct compound names, abbreviations, and CAS numbers.

19.3.3. Section 1.2 added note, "[(1)] In some literature, the acronym ADONA refers to the ammonium salt, CAS 958445-44-8, and DONA refers to the parent acid. In Method 537.1, ADONA refers to the parent acid. DONA is the acronym present on the laboratory raw data."

19.3.4. Section 7.4 added "*" to "EtFOSAA" and "MeFOSAA" to indicate that both linear and branched isomers are used.

19.3.5. Section 7.4.1.1 revised last sentence to, "Use the following naming convention: "_TFOA_Instrument_Date." Example: _TFOA_A10_15Mar2019."

19.3.6. Sections 15.3, 15.4, and 15.5 revised, "When full to no less than six inches of the top" to "When the drum is full to between four and six inches of the top".

19.3.7. Editorial changes.

19.4. WS-LC-0025, Revision 3.5, Effective 02/27/2019

19.4.1. Added Section 11.3.6, “After the entire sample has been loaded onto the column, rinse the sample bottle with two 5 mL aliquots of reagent water and pour onto the column reservoir.”

19.4.2. Editorial changes.

19.5. WS-LC-0025, Revision 3.4, Effective 02/13/2019

19.5.1. Section 6.4 added, “The average weight of the HDPE bottles with HDPE screw caps are calibrated once a year. The calibration is performed by weighing 10 bottles with caps and dividing by 10 to get the average weight. The average weight is used in section (11.3.5.1.d).”

19.5.2. Section 7.4.1 revised, “an” to “every” and removed “or when a new column is installed”.

19.5.3. Add Section 7.4.1.1, “Attach this document to the ICV from the associated ICAL by scanning the document and associating it to the file as a document type of High Res MS Tune in TALS. Use the following naming convention: “_ZbatchnumberTPFOA”.”

19.5.4. Added Section 8.2.1, “Projects performed for the state of New Jersey have an analytical holding time 28 days from the extraction date.”

19.5.5. Added Section 8.2.2, “For projects performed for the state of New Jersey a field reagent blank (FRB) must be collected with each sample set. Acceptance limits are <RL for each analyte.”

19.5.6. Added Section 9.4.1, “Projects performed for the state of New Jersey: LCS (mid and high spike) recovery limits are 70-130%. Low level LCS recovery limits are 50-150%. The spike level must rotate between low, medium and high.”

19.5.7. Added Section 9.5.1, “Projects performed for the state of New Jersey: MS/MSD (mid and high spike) recovery limits are 70-130%. Low level MS/MSD recovery limits are 50-150%. The spike level must rotate between low, medium and high.”

19.5.8. Added Section 9.10, “TOP Oxidation Efficiency” and its associated subsections.

19.5.9. Added Section 9.11, “Ion Ratio” and associated subsections.

19.5.10. Added Section 10.8.2.6, “Projects performed for the state of New Jersey: MS/MSD (mid and high spike) recovery limits are 70-130%. Low level MS/MSD recovery limits are 50-150%. The spike level must rotate between low, medium and high.”

19.5.11. Section 10.11.3 added, “and the state of New Jersey”.

19.5.12. Added Section 10.12.5, “Projects performed for the state of New Jersey: All analyte concentrations in the CCV must be within + 30% of their true value. All analyte concentrations in the low level CCV must be within + 50% of their true value.”

19.5.13. Added Section 11.3.5.1, “If the SPE column should plug (flow rate <1 drop per minute) prior to the entire content of the sample container passing through the column do the following:” and its associated subsections.

19.5.14. Sections 11.14.15.8 and 11.15.27.8 removed, “with a flow rate of 1 mL/minute”.

19.5.15. Section 11.18.3 removed, “(as needed)” from the PFOA RT marker.

19.5.16. Throughout SOP revised, “1 mL/minute” to “3-5 drops per second”.

19.5.17. Editorial changes.

19.6. WS-LC-0025, Revision 3.3, Effective 12/03/2018

19.6.1. Added Section 6.9, “[redacted]”

19.6.2. Tables 2 and 6 revised comment for M2-4:2 FTS to, “IDA or Reverse Surrogate for TOP”.

19.6.3. Tables 4 and 7 revised header from “IS Analog” to “IDA Analog”, and revised “4:2 FTS” entry to “M2-4:2 FTS (If TOP then 13C-PFBS)”.

19.6.4. Editorial changes.

19.7. WS-LC-0025, Revision 3.2, Effective 08/20/2018

19.7.1. Section 1 added, “1H,1H,2H,2H-perfluorododecane sulfonate” and “Perfluoro-1-dodecansulfonic acid” entries to table.

19.7.2. Section 1.2 revised table entry for “Adona” to “Dona”.

19.7.3. Section 7.4 added, “PFDoS” and “10:2 FTS” entries to table.

19.7.4. Section 7.4 revised, “Adona” entry to “Dona”.

19.7.5. Table 2 added, “PFDoS”, “PFDoS_2”, and “10:2 FTS” entries to table.

19.7.6. Table 3 revised, “Adona” and “Adona_2” entries to “Dona” and “Dona_2”.

19.7.7. Table 4 added, “PFDoS” and “10:2 FTS” entries to table.

19.7.8. Table 4 revised, “Adona entry to “Dona”.

19.7.9. Editorial changes.

19.8. WS-LC-0025, Revision 3.1, Effective 06/21/2018

19.8.1. Section 11.2.1 revised to, “Visually inspect samples for the presence of settled and/or suspended sediment/particulates. If present or if the sample is biphasic add IDA prior to any sample decanting or centrifugation. If the sample requires decanting or centrifugation contact the client for guidance prior to such action. Decanting or filtering of the sample can lead to a low bias.”

19.8.2. Editorial changes.

19.9. WS-LC-0025, Revision 3.0, Effective 04/13/2018

19.9.1. Section 1.1 updated table with PFPeS and PFNS analytes.

19.9.2. Added Section 2.2, which details the analytes that can be covered by the method under special request.

19.9.3. Added Section 3.13, “AFFF: Aqueous Film Forming Foam”.

19.9.4. Section 6.19 added, “Create all eluents in Reagent module, label eluent containers with TALS label and place 2nd label into maintenance log when put into use” to table.

19.9.5. Section 7.1.2 added, “[redacted] The resultant solution is filtered through a 0.22um filter before use. This solution has volatile components, thus it should be replaced every 7 days or sooner.”

19.9.6. Section 7.1.3 added, “[redacted]”

19.9.7. Section 7.1.8 added, "[redacted]."

19.9.8. Section 7.1.11 added, "Prepared by diluting 400mL of 1N NaOH into 3.6L of water for a total volume of 4L."

19.9.9. Section 7.4 updated table with PFPeS and PFNS analytes.

19.9.10. Section 7.4, added table to detail ICAL for Fluorinated Replacement Compounds.

19.9.11. Added Section 8.1.1, "Water samples collected from a known chlorinated source should be preserved with Trizma."

19.9.12. Added Section 9.9.3, "If the IS does not meet criteria, re-analyze the extract. If the IS meets criteria in the second analysis, report that analysis. If the IS does not meet criteria in the second analysis, report the first analysis with narration."

19.9.13. Added Section 11.14.6, "Add 2g of [redacted] and 1.9 mL of [redacted] to each "Post" sample container."

19.9.14. Removed Section 11.14.8, "Add 2g of [redacted] and 1.9 mL of [redacted] to each "Post" sample container."

19.9.15. Added Section 11.14.9, "Cap each "Post" sample container, invert 2-3 times prior to placing container into water bath."

19.9.16. Added Section 11.5 and associated subsections, which detail the "TOPS (Total Oxidizable Precursor) Assay for Soil Sample".

19.9.17. Section 11.8 updated Table labeling, added PFPeS and PFNS analytes throughout Tables where applicable, and updated Table 7 to reflect current retention times and quantitation.

19.9.18. Section 11.8 added Table 6, "Recommended Instrument Operating Conditions Mass Spectrometer Scan Settings ([redacted]) for Fluorinated Replacement Chemicals"

19.9.19. Section 11.18.3 removed outdated run sequence and replaced with current run sequence.

19.9.20. Editorial changes.

19.10. WS-LC-0025, Revision 2.9, Effective 11/22/2017

19.10.1. Section 1.2, table updated to reflect ranges after removing MeFOSA and EtFOSA from the SOP in the previous revision.

19.10.2. Section 9.3.6, last sentence changed to read, "Reprepare and reanalyze all field and QC samples associated with the contaminated method blank."

19.10.3. Section 9.7, first sentence changed to read, "Initial calibration verification (ICV) – A second source standard is analyzed with the initial calibration curve.

19.10.4. Section 1.3.1 revised to read, "Once the optimal mass assignments (within ±0.5 amu of true) are made immediately following the initial tune, the lowest level standard from the initial calibration curve is assessed to ensure that a signal to noise ratio greater than 10 to 1 (S/N > 10:1) is achieved for each PFAS analyte. The first level standard from the initial calibration curve is used to evaluate the tune stability on an ongoing basis. The instrument mass windows are set initially at ± 0.5 amu of the true value; therefore, continued detection of the analyte transition with S/N > 10:1 serves as verification that the assigned mass remains within ± 0.5 amu of the true value, which meets the DoD/DOE QSM tune criterion. For QSM work, the instrument sensitivity check (section 10.12.4) is also evaluated to ensure that the signal to noise criteria is met."

19.10.5. Editorial changes.

19.11. WS-LC-0025, Revision 2.8, Effective 11/06/2017

19.11.1. Revised Section 4.5 to "Both branched and linear PFAS isomers can potentially be found in the environment. Linear and branched isomers are known to exist for PFOS, PFOA, PFHxS, PFBS, EtFOSAA, and MeFOSAA based upon the literature. If multiple isomers are present for one of these PFAS they might be adjacent peaks that completely resolved or not, but usually with a deflection point resolved during peak integration. The later of these peaks match the retention time of its labeled linear analog. In general, earlier peaks are the branched isomers and are not the result of peak splitting.

At this time only PFOS, PFOA and PFHxS are commercially available as technical mixtures. These reference standards of the technical mixtures for these specific PFAS are used to ensure that all appropriate peaks are included during peak integration."

19.11.2. Sections 4.8 and 7.2.1.1, corrected the in-sample contributions to 0.30 ng/L

and 0.015 ug/kg.

19.11.3. Removed Section 7.1.14, "Methanol-Water, 78:22 vol./vol., prepared by mixing 780 mL methanol and 220 mL reagent water. Stored in polypropylene bottle and sealed with polypropylene screw cap." Reagent was added incorrectly.

19.11.4. Section 7.2.4, corrected the factor to 0.956 from 1.046.

19.11.5. Added Section 7.4.1, "A technical (qualitative) grade PFOA standard which contains both linear and branched isomers is used as a retention time (RT) marker. This is used to integrate the total response for both linear and branched isomers of PFOA in environmental samples while relying on the initial calibration with the linear isomer quantitative standard This technical (qualitative) grade PFOA standard is analyzed initially, after an initial calibration when a new column is installed or when significant changes are made to the HPLC parameters."

19.11.6. Section 9.7, added "Rerun the initial calibration" as the last bullet item.

19.11.7. Added Section 10.3.1, "The first level standard from the initial calibration curve is used to evaluate the tune criteria. The instrument mass windows are set at ±0.5 amu; therefore, detection of the analyte serves as verification that the assigned mass is within ±0.5 amu of the true value, which meets the DoD/DOE QSM tune criterion.

19.11.8. Section 10.10.1, appended "containing both IDA and IS" to the end of the paragraph.

19.11.9. Sections 11.6.3 and 11.12.2.3, changed "78:22 methanol:water" to "methanol".

19.11.10. Sections 1.1 and 7.4, removed EtFOSA and MeFOSA from tables due to low volume of requests for those analytes.

19.11.11. Removed Section 2.2.1, "Optional cleanups may include sample freezing and/or cleanup by SPE cartridge, unless EtFOSA and MeFOSA are requested."

19.11.12. Removed EtFOSA/MeFOSA specific comments in various sections throughout the document.

19.11.13. Section 7.4 Note added, "The concentration of the calibration solutions for non-concentrated extracts is 1/20th the levels indicated above."

19.11.14. Section 7.9, changed 1000 ng/mL to 250 ng/mL and replaced final sentence with “The internal standard solution used for the non-concentrated extracts is at a concentration of 50 ng/mL.”

19.11.15. Removed Section 11.2.8, “If EtFOSA and/or MeFOSA are requested, add 100uL of IS and then adjust the final volume (FV) of these aliquots to 5.0 mL with MeOH. QC samples, LCS, MS, and MSD will require concentration via nitrogen to adjust the FV to 5.0 mL. Vortex each sample. Then, transfer a portion of the extract to a 300 uL polypropylene autosampler vial (7 drop-wise or approximately ½ filled is sufficient). Archive the rest of the extracts for re-injection and dilution.”

19.11.16. Added Section 11.5.4, “Proceed to Section 11.15.2 (Graphitized Carbon Cleanup) as needed. This is required for all DoD/DOE extracts.”

19.11.17. Added Section 11.7.1.1, “Seal the test tube tightly. Invert container several times and then vortex. Allow extract to settle for 10 minutes prior to moving to the next step.”

19.11.18. Inserted Section 11.8.1.1, “Projects performed under the auspices of the DoD/DOE must have the entire sample homogenized prior to subsampling in accordance with QSM 5.1 criteria.”

19.11.19. Section 11.11.4, added “(Graphitized Carbon Cleanup) as needed. This is required for all DoD/DOE extracts.”

19.11.20. Section 11.14.6, added “Spike all “Pre” and “Post” samples with 25uL of the reverse surrogate solution (Section 7.8).”

19.11.21. Section 11.15.2, revised to read, “Cleanup with graphitized carbon will be applied to all samples as needed but is required for all DoD/DOE extracts.”

19.11.22. Added Section 11.15.2.5, “Proceed to Section 11.6, 11.7, or 11.12 as applicable.”

19.11.23. Removed Sections 11.15.3 through 11.15.6.

19.11.24. Added Section 11.16, “AFFF Sample Preparation”.

19.11.25. Section 11.17, removed EtFOSA, MeFOSA, d5-EtFOSA, and d3MeFOSA from all tables.

19.11.26. Section 11.17, changed masses for M2-4:2FTS, M2-6:2FTS, and M2-8:2FTS. Initially assigned daughter masses were bleeding through from the native analog.

19.11.27. Section 11.17, all tables on MS Interface Mode Line, added "Minimum of 10 scans/peak."

19.11.28. Added Section 11.17.1, "Post Spike Sample Analysis for AFFF Samples".

19.11.29. Added Section 11.8.4.1 "Spike non-concentrated samples at 0.5 mL of LCS/Matrix Spike Solution."

19.11.30. Added Section 11.8.5.1, "Spike non-concentrated samples at 0.5 mL of IDA PFC Solution."

19.11.31. Editorial changes.

19.12. WS-LC-0025, Revision 2.7, Effective 09/20/2017

19.12.1. Section 1.1 table, added 1H,1H,2H,2H-perfluorohexane sulfonate *(4:2)*.

19.12.2. Section 1.1, removed "Sample results for PFOA may also be reported as APFO, at the request of the client. (See Section 12.7)."

19.12.3. Section 1.2 and 11.8.2, updated tissue extracted mass and RL.

19.12.4. Section 2.5, removed "and assumes a proportional relationship between the initial calibration and the analyte in the extract. The ratio of the peak response to mass or concentration injected is used to prepare a calibration curve."

19.12.5. Added Section 6.6, "Extract concentrator or nitrogen manifold with water bath heating to 50-55°C".

19.12.6. Added Section 7.1.14, "Methanol-Water, 78:22 vol./vol., prepared by mixing 780 mL methanol and 220 mL reagent water. Stored in polypropylene bottle and sealed with polypropylene screw cap."

19.12.7. Section 7.2.1.1, revised "roughly 0.15 pg/L" to "roughly 0.15 ng/L".

19.12.8. Section 7.4 table, added:

4:2 FTS	0.5	1.0	2.0	20	50	200	400

19.12.9. Section 7.4 table, revised Labeled Isotope Dilution Analytes (IDA) Section.

19.12.10. Section 7.4 table, added:

Internal Standard (IS)							
13C2-PFOA	50	50	50	50	50	50	50

19.12.11. Section 7.4, removed “FOSAA may be added to the mix and are added at the same concentration as FOSA.”

19.12.12. Added Section 7.9, “Internal Standard Solution, 1000 ng/mL. The internal standard solution is prepared by diluting 13C2-PFOA to produce a solution containing this compound at a concentration of 1000 ng/mL in methanol. This is added to all extracts prior to analysis. Non-concentrated extracts are fortified with a 5X dilution of this solution.”

19.12.13. Section 8.1, changed “250 mL” to “8 oz.”

19.12.14. Added Sections 9.3.6, 9.8.2.3, 10.10.4, 10.8.2.5, 10.11.3, and 10.12.4 to address DOD QSM 5.1 Table B-15 criteria.

19.12.15. Added Section 9.9, “Internal Standard.”

19.12.16. Updated all tables to indicate target analyte quantitation via isotope dilution. Internal standard quantitation is only used to quantitate the IDA recoveries.

19.12.17. Added Section 10.8.2.4, 10.12.2, and 10.12.2.1 to incorporate IS criteria into calibrations.

19.12.18. Section 11.2.1, “Evaluate if the sample can be decanted or centrifuged; if not, contact the client for guidance. Filtering the sample can lead to a low bias.”

19.12.19. Added Section 11.2.3.1, “Alternatively, weigh the sample container prior to extraction and then weigh the sample container after extraction to determine the initial volume.”

19.12.20. Added Section 11.5.3, “Note: If the extracts will not be concentrated elute extract with a total of 8 mL of [redacted].”

19.12.21. Added Section 11.6.2.3, “Add 300 uL of the 78:22 methanol:water solution and mix the contents well using a vortex mixer.”

19.12.22. Added Section 11.6.2.4, “Add 100 uL of Internal Standard (IS) solution to each extract and vortex to mix.”

19.12.23. Added Section 11.7, “Final volume for non-concentrated extract”.

19.12.24. Revised Section 11.11, “SPE Elution of Solid Extracts”.

19.12.25. Revised Section 11.12, “Extract Concentration for Solid Samples”.

19.12.26. Removed Section 12.8, “If results are to be reported as ammonium

perfluorooctanoate (APFO), instead of PFOA, apply a multiplier of 1.0406 to the sample results to correct for the molecular weight differences between PFOA and APFO or this adjustment can be made during the preparation of the standards used for calibration. (Use one, not both.)"

19.12.27. Removed Section 13.4 – it was a copy of Section 13.2.

19.12.28. Various revisions to fulfill requirements based on DOD/DOE QSM 5.1.

19.12.29. Editorial changes.

19.13. WS-LC-0025, Revision 2.6, Effective 08/15/2017

19.13.1. Section 7.4, added MPFBS, MPFTeDA, and MPFHxDA to the table.

19.13.2. Section 11.15, added 13C-PFBS to the Recommended Instrument Operating Conditions table for [redacted].

19.13.3. Section 11.15 Recommended Instrument Operating Conditions table, changed the mass transitions for native PFTeDA from 713 > 669 (quant) and 713 > 169 (qualifier) to 713 > 169 (quant) and 713 > 219 (qualifier).

19.13.4. Editorial changes.

19.14. WS-LC-0025, Revision 2.5, Effective 07/10/2017

19.14.1. Revised Section 11.6.1 to read "Prior to concentrating each sample, add 100 uL of water."

19.14.2. Revised Section 11.6.2 to read "Concentrate each sample under a gentle stream of nitrogen until the methanol is evaporated and the 100 uL of water remains.

11.6.2.1 This blow down must take a minimum of 3.5 hours.

11.6.2.2 Extracts can not remain in the water bath longer than 5 minutes once concentrated."

19.14.3. Revised Section 11.6.3 to read "Add 400 uL of methanol to each extract, soak, and vortex to mix well. This will create an extract with a final solvent composition of 80:20 methanol:water."

19.14.4. Revised Section 11.11.1 to read "Prior to concentrating each sample, add 200 uL of water."

19.14.5. Revised Section 11.11.2 to read "Concentrate each sample under a gentle

stream of nitrogen until the methanol is evaporated and the 200 uL of water remains."

11.11.2.1 This blow down must take a minimum of 3.5 hours.

11.11.2.2 Extracts can not remain in the water bath longer than 5 minutes once concentrated."

19.14.6. Revised Section 11.11.3 to read "Add 800 uL of methanol to each extract, soak, and vortex to mix well. This will create an extract with a final solvent composition of 80:20 methanol:water."

1. SCOPE AND APPLICATION

1.1. This procedure describes the analysis of water samples via in line solid phase extraction (SPE) for the following compounds using liquid chromatography / tandem mass spectrometry (LC/MS/MS) on a [redacted].

Compound Name	Abbreviation	CAS #
Perfluoroalkylcarboxylic acids (PFCAs)		
Perfluoro-n-heptanoic acid	PFHpA	375-85-9
Perfluoro-n-octanoic acid	PFOA	335-67-1
Perfluoro-n-nonanoic acid	PFNA	375-95-1
Perfluorinated sulfonic acids (PFSAs)		
Perfluoro-1-butanesulfonic acid	PFBS	375-73-5
Perfluoro-1-hexanesulfonic acid	PFHxS	355-46-4
Perfluoro-1-octanesulfonic acid	PFOS	1763-23-1

1.2. The working range of the method is listed below. The linear range can be extended by diluting the extracts.

Matrix	Nominal Sample Size	Reporting Limit	Working Range
Water	1.0 mL	2.0 ng/L	2 to 200 ng/L

2. SUMMARY OF METHOD

2.1. A 1 mL aliquot of sample is diluted to a 40:60 methanol:water extract and analyzed by LC/MS/MS. PFAS are separated from other components on a C18 column with a solvent gradient program using [redacted].

3. DEFINITIONS

Refer to Section 3 of the main body of this SOP for a summary of definitions.

4. INTERFERENCES

Refer to Section 4 of the main body of this SOP for interferences.

5. SAFETY

Refer to Section 5 of the main body of this SOP for safety information.

6. EQUIPMENT AND SUPPLIES

Refer to Section 6 of the main body of this SOP for supplies, other than those listed below specific to the in line SPE analysis.

6.1. 2 mL auto sampler vials, clear glass, Thermo Scientific Nation surestop vial, part no. C5000-1, or equivalent.

6.2. Vial caps, Thermo Scientific National AVCS blue cap, pre slit TEF/STL septa, part no. C5000-55B or equivalent.

6.3. Eppendorf 1000 uL epTIPS, part no. 022491954 or equivalent.

6.4. Eppendorf 200 uL epTIPS, part no. 022491938 or equivalent.

6.5. 50 mL graduated plastic centrifuge tubes, SCP Science DigiTUBES part no. 010-500-263 or equivalent.

6.6. 1000 uL Pipette: Eppendorf Research Plus.

6.7. 100 uL Pipette: Rainin EDP3-Plus.

6.8. 250 mL HDPE bottles with PPE screw caps, ESS part no. 0250-1902-QC or equivalent.

6.9. Analytical columns

6.9.1. [redacted] or equivalent.

6.9.2. PFAS Isolator column, [redacted] or equivalent.

6.10. [redacted]. The system utilizes Chrom Peak Review, version 2.1 or equivalent.

6.11. [redacted] HPLC equipped with [redacted] pumps and one [redacted] degassing unit or equivalent.

7. REAGENTS AND STANDARDS

Refer to Section 7 of the main body of this SOP for reagents and standards, other than those listed below specific to the in line SPE analysis.

7.1. Reagent grade chemicals shall be used in all tests whenever available. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on the Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

7.1.1. Ammonium acetate, Fisher Optima LCMS grade (20 mM in water), part no. A114-50, or equivalent.

7.1.2. Methanol, Baker HPLC grade, part no. 9093-03.

7.1.3. Water, Nanopure or Millipore or Fisher Optima LCMS grade, part no. W6-4, must be free of interference and target analytes.

7.2. Calibration Standards

The calibration stock solution is prepared by diluting the appropriate amounts of the stock solutions (Section 7.2 of the main body of this SOP) in 40:60 methanol:water. The calibration stock solution is diluted with methanol to produce initial calibration standards. These are the normal calibration levels used. A different range can be used if needed to achieve lower reporting limits or a higher linear range.

7.3. Initial Calibration (ICAL) Levels (ng/L)

Compound	**CS-1**	**CS-2**	**CS-3**	**CS-4**	**CS-5**	**CS-6**	**CS-7**	**CS-8**
Perfluoroalkylcarboxylic acids (PFCAs)								
PFHpA	1.0	2.0	5.0	10	20	50	100	200
PFOA	1.0	2.0	5.0	10	20	50	100	200
PFNA	1.0	2.0	5.0	10	20	50	100	200
Perfluorinated sulfonic acids (PFSAs)								
PFBS	1.0	2.0	5.0	10	20	50	100	200
PFHxS	1.0	2.0	5.0	10	20	50	100	200
PFOS	1.0	2.0	5.0	10	20	50	100	200
Labeled Isotope Dilution Analytes (IDA)								
13C4-PFHpA	50	50	50	50	50	50	50	50
13C4-PFOA	50	50	50	50	50	50	50	50
13C5-PFNA	50	50	50	50	50	50	50	50
18O2-PFHxS	50	50	50	50	50	50	50	50
13C4-PFOS	50	50	50	50	50	50	50	50
13C3-PFBS	50	50	50	50	50	50	50	50

Note: *The above calibration levels are provided only as an example. The actual ICAL level used for each analytical batch will depend upon the LOQ requirements of the program.*

7.4. LCS/Matrix PFC Spike Solution, 100 ng/mL.

The PFC spike solution is prepared by diluting all PFAS to produce a solution containing each PFAS at 100 ng/mL in methanol.

7.5. PFC Isotope Dilution Analyte (IDA) Spike Solution, 1 ng/mL.

The PFC-IDA solution is prepared by diluting all labeled PFAS to produce a solution containing each at 1 ng/mL in methanol.

8. SAMPLE COLLECTION, PRESERVATION, AND STORAGE

8.1. Water samples are collected in pre-cleaned 250 mL HDPE containers. Other containers may also be suitable. Samples are chilled to 0 - 6 °C for shipment to the laboratory.

8.2. Samples are logged in following normal laboratory procedures and are stored under refrigeration at 0 - 6 °C. Water samples must be analyzed within 28 days of collection.

9. QUALITY CONTROL

Refer to Section 9 of the main body of this SOP for Quality Control information.

9.1. If potable water samples from the state of New York (NY) are analyzed via this method the control limits for LCS and IDA for PFOS and PFOA recoveries are 70-130%. If these limits are not met, refer to Section 9 of the main body of this SOP for corrective action.

9.2. If POST (treatment) samples have positive detections, review the associated PRE and MID (treatment) samples for similar detections. Re-preparation and re-analysis may be needed.

9.3. If PFBS is detected in the method blank greater than the RL, evaluate data for impact. PFBS is a known laboratory artifact. Re-preparation and re-analysis may be needed.

10. CALIBRATION

Refer to Section 10 of the main body of the SOP for calibration information.

11. PROCEDURE

Refer to Section 11 of the main body of this SOP for procedures, other than those listed below specific to the in line SPE analysis.

11.1. Water Sample Preparation

11.1.1. Visually inspect samples for the presence of settled and or suspended sediment/particulate. Evaluate if the sample can be decanted or centrifuged; if not, contact the client for guidance. Filtering the sample can lead to a low bias.

If authorized by the client to filter the sample, filter the water sample through a glass fiber filter (Whatman GF/F Cat No 1825 090 or equivalent).

Gravity of vacuum can be used to pass the sample through the filter. Prepare a filtration blank with any samples requiring filtration. File an NCM noting the need for filtration.

Warning: The use of a vacuum system creates the risk of glassware implosion. Inspect all glassware prior to use. Glassware with chips, scratches, rub marks or cracks must not be used.

11.1.2. Prepare an LCS and method blank by adding 250 mL of HPLC grade water into a 250 mL HDPE bottle.

11.1.3. If requested, find the client assigned sample for MS/MSD.

11.1.4. Spike directly into the sample bottles for the LCS and MS/MSD (if requested) with 0.050 mL (50 uL) of the LCS/Matrix PFC Spike solution (Section 7.4). This will result in a sample concentration of 20 ng/L. Shake well to disperse spike.

11.1.5. Measure 1 mL of each sample using an Eppendorf pipette and pour into a labeled 2.0 mL injection vial. This includes the LCS and method blank samples as well.

11.1.6. Be sure to "prepare" the pipette by collecting two 1 mL aliquots and disposing of them, and then collect the aliquot for testing.

11.1.7. Add 83 uL of surrogate solution (PFC IDA Spike Solution, Section 7.5) into each vial for each sample and QC sample. This will result in an extract concentration of 50 ng/L for the surrogate.

11.1.8. Add 577 uL of methanol to each sample for a final solvent composition of 40:60 methanol:water.

11.1.9. Seal the vial with a polypropylene screw cap. Note: Teflon lined caps can not be used due to detection of low level concentration of PFAS.

11.1.10. Vortex to mix the mixture well.

11.2. Instrument Analysis

11.2.1. Suggested operation conditions are listed in Tables 1A-1C below:

Table 1A - Routine Instrument Operating Conditions	
HPLC Conditions (***)***	
Column (Column temp = °C)	
Mobile Phase Composition	A = B =

Table 1A - Routine Instrument Operating Conditions					
HPLC Conditions (***)***					
Gradient Program	**Time (min)**	**%A**	**%B**	**Curve**	**Flow Rate (mL/min)**
	Maximum Pressure limit = 5,000 psi				
Injection Size	(fixed amount throughout the sequence)				
Run Time					
MS Interface Mode	ESI Negative Ion. Minimum of 10 scans/peak.				
Ion Spray Voltage (kV)					
Entrance Potential (V)					
Declustering Potential (V)					
Desolvation Temp					
Curtain Gas (nitrogen) Flow					
Collision Gas (nitrogen) Flow					

Table 1B - Routine Instrument Operating Conditions						
Mass Spectrometer Scan Settings (***)***						
Compound	**Comments**	**Reaction (MRM)**	**Dwell (sec)**	**Ent. Pot. (V)**	**Col. Energy (V)**	**Declu. Pot. (V)**
PFBS	Perfluorobutanesulfonate	299 > 80				
13C3-PFBS	IDA	302 > 83				
PFHpA	Perfluoroheptanoic acid	363 > 319				
13C4-PFHpA	IDA	367 > 322				
PFHxS	Perfluorohexanesulfonate	399 > 80				
18O2-PFHxS	IDA	403 > 84				
PFOA	Perfluorooctanoic acid	413 > 369				
13C4PFOA	IDA	417 > 372				
PFNA	Perfluorononanoic acid	463 > 419				
13C5-PFNA	IDA	468 > 423				
PFOS	Perfluorooctanesulfonate	499 > 80				
13C4-PFOS	IDA	503 > 80				

Table 1C					
Native Compounds	**Typical Native RT (minutes)**	**IDA analog**	**Typical IDA RT (minutes)**	**Quantitation Method**
PFBS	[redacted]	13C3-PFBS	[redacted]	Isotope Dilution
PFHpA	[redacted]	13C4-PFHpA	[redacted]	Isotope Dilution
PFHxS	[redacted]	18O2-PFHxS	[redacted]	Isotope Dilution
PFOA	[redacted]	13C4-PFOA	[redacted]	Isotope Dilution
PFNA	[redacted]	13C5-PFNA	[redacted]	Isotope Dilution
PFOS	[redacted]	13C4-PFOS	[redacted]	Isotope Dilution

11.2.2. Tune and calibrate the instrument as described in Section 10.

11.2.3. A typical run sequence is as follows:

- Primer (A number of primers are injected for conditioning of the instrument before analysis, especially when the instrument was idled or changed from a different analysis).
- Blank
- Calibration Curve
- ICB
- ICV
- PFOA RT marker (as needed)
- Rinse Blank (RB, not linked to anything)
- MB
- LCS
- LCSD (if applicable)
- Sample 1
- Sample 1 MS (if applicable)
- Sample 1 MSD (if applicable)
- Sample 2 (up to sample 10 before next CCV)
- CCV
- Up to 10 samples.
- End sequence with CCV

12. CALCULATIONS

Refer to Section 12 of the main body of this SOP for calculation information.

13. METHOD PERFORMANCE

Refer to Section 13 of the main body of this SOP for method performance information.

14. POLLUTION PREVENTION

Refer to Section 14 of the main body of this SOP for pollution prevention information.

15. WASTE MANAGEMENT

Refer to Section 15 of the main body of this SOP for waste management information.

16. REFERENCES

Refer to Section 16 of the main body of this SOP for reference information.

17. METHOD MODIFICATIONS

17.1. Refer to Section 17 of the main body of this SOP for modifications from Method 537, except as detailed below:

17.1.1. Water samples are prepared at 1.0 mL, not 250 mL.

17.1.2. Water sample containers are not preserved with Trizma. Holding time has been changed to 28 days for analysis.

17.1.3. The eluents and HPLC configuration differs. As a result the final extract is in 40:60 methanol:water.

18. ATTACHMENTS

There are no attachments to this Appendix.

19. REVISION HISTORY

Revisions prior to 04/10/2017 have been removed and are available in previous versions of this SOP.

19.1. WS-LC-0025, Attachment 1, Revision 3.8, Effective 09/23/2019

19.1.1. No changes to the attachment with this revision.

19.2. WS-LC-0025, Attachment 1, Revision 3.7, Effective 08/05/2019

19.2.1. No changes to the attachment with this revision.

19.3. WS-LC-0025, Attachment 1, Revision 3.6, Effective 05/14/2019

19.3.1. No changes to the attachment with this revision.

19.4. WS-LC-0025, Attachment 1, Revision 3.5, Effective 02/27/2019

19.4.1. No changes to the attachment with this revision.

19.5. WS-LC-0025, Attachment 1, Revision 3.4, Effective 02/13/2019

19.5.1. Removed Section 3.6, "MPFOA: Perfluoro-n-[1,2,3,4-13C4]octanoic acid. Carbon-13 labeled PFOA".

19.5.2. Removed Section 3.7, "MPFOS: Perfluoro-1-[1,2,3,4-13C4]octanesulfonic acid. Carbon-13 labeled PFOS".

19.5.3. Section 7.2.3 removed, "MPFOS".

19.5.4. Section 7.3 removed, "PFCA and PFSA".

19.5.5. Section 7.3 added "13C3-PFBS" entry to table.

19.5.6. Section 10.11.3 revised to, "Projects performed under the auspices of the DoD/DOE QSM (Version 5.1) and the state of New Jersey must meet these criteria for the ICV: Analyte concentrations must be within ±30% of their true values for all analytes, IDA and target."

19.5.7. Table 1B, revised PFBS IDA from "18O2-PFHxS" to "13C3-PFBS" and updated entry values.

19.5.8. Table 1C, revised "IS Analog" to "IDA Analog", revised the PFBS IDA from "18O2-PFHxS" to "13C3-PFBS", and updated entry values.

19.5.9. Editorial changes.

19.6. WS-LC-0025, Attachment 1, Revision 3.3, Effective 12/03/2018

19.6.1. No changes to the attachment with this revision.

19.7. WS-LC-0025, Attachment 1, Revision 3.2, Effective 08/20/2018

19.7.1. No changes to the attachment with this revision.

19.8. WS-LC-0025, Attachment 1, Revision 3.1, Effective 06/21/2018

19.8.1. No changes to the attachment with this revision.

19.9. WS-LC-0025, Attachment 1, Revision 3.0, Effective 04/13/2018

19.9.1. Updated labeling and formatting of Tables 1A-1C.

19.9.2. Added section 11.2.3, detailing a typical run sequence.

19.10. WS-LC-0025, Attachment 1, Revision 2.9, Effective 11/27/2017

19.10.1. No changes to the attachment with this revision.

19.11. WS-LC-0025, Attachment 1, Revision 2.8, Effective 11/06/2017

19.11.1. Section 11.2.1, Routine Instrument Operating Conditions table ([redacted]), added "Minimum of 10 scans/peak".

19.12. WS-LC-0025, Attachment 1, Revision 2.7, Effective 09/22/2017

19.12.1. Section 6.5, removed "The 5 items above are to be maintained in the drawer labeled "Segregated Supplies for in line SPE Analysis" in the LC/MS instrument room."

19.12.2. Added Sections 9.1 – 9.3.

19.12.3. Updated Section 11.1.

19.12.4. Editorial changes.

19.13. WS-LC-0025 Attachment 1, Revision 2.6, Effective 08/11/2017

19.13.1. No revisions to this attachment.

19.14. WS-LC-0025 Attachment 1, Revision 2.5, Effective 07/10/2017

19.14.1. No revisions to this attachment.

19.15. WS-LC-0025 Attachment 1, Revision 2.4, Effective 04/25/2017

19.15.1. No revisions to this attachment.

19.16. WS-LC-0025 Attachment 1, Revision 2.3, Effective 04/10/2017

19.16.1. Changed all mentions of "direct aqueous injection (DAI)" to "in line solid phase extraction (SPE)."

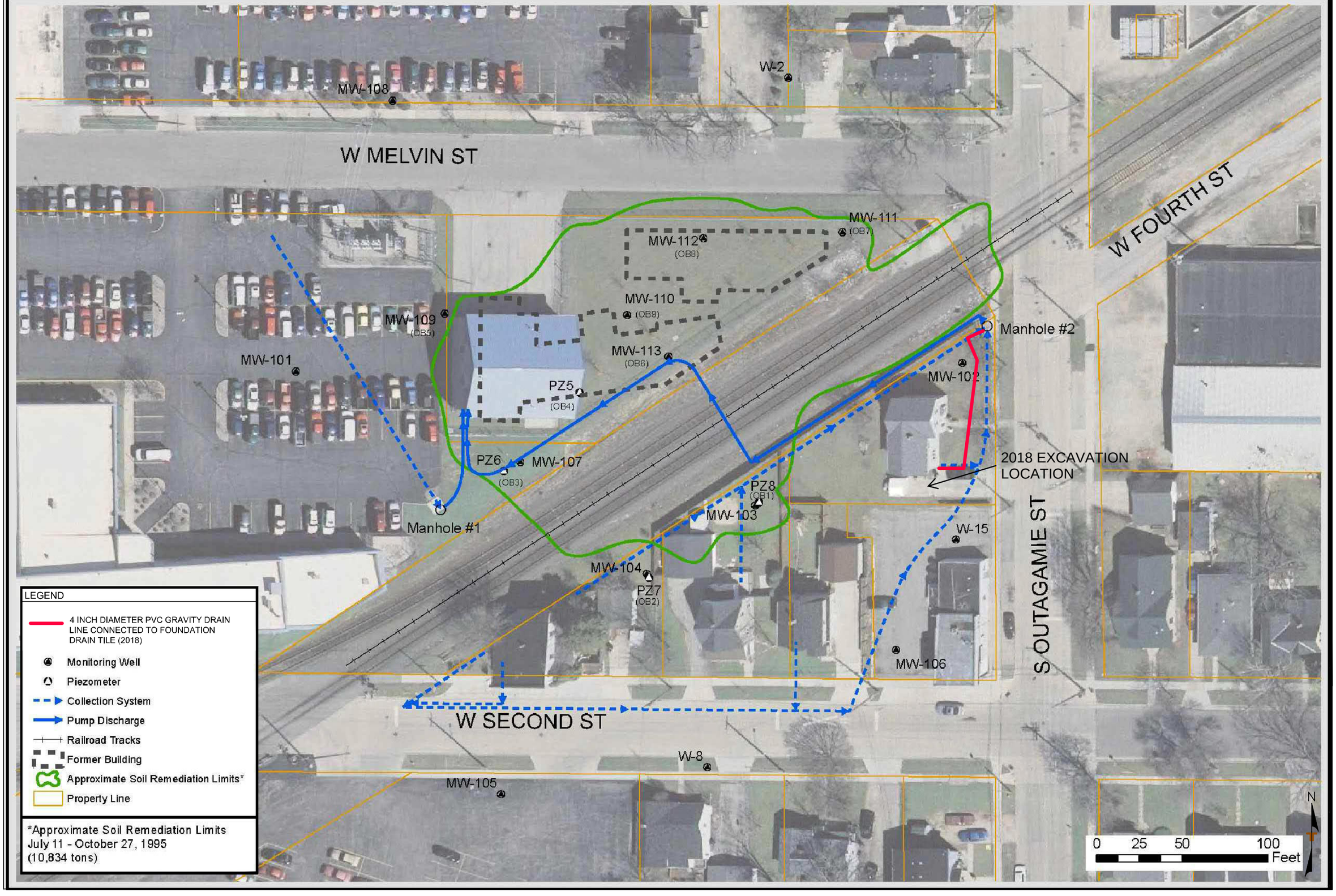
19.16.2. Inserted Section 17.1, and changed formatting of the modifications to Method 537 to Section 17.2 and subheadings.

APPENDIX C

Figure 1: Site Map

Sampling Schedule Gantt Chart

PFAS Sampling Field Forms



Note: Figure taken from Omni Site Detail Map, January 2011

FIGURE 1 (FIG2)

SITE DETAIL MAP

N.W. MAUTHE SITE
725 SOUTH OUTAGAMIE STREET
APPLETON, WISCONSIN

Terracon
Consulting Engineers and Scientists
9856 South 57th Street Franklin, WI 53132
PH: (414) 423-0256 FAX: (414) 423-0686

Project No.	58117057		
Scale:	As Shown		
File No.	58117057C2R2		
Date:	10/2020		
Project Mngr:	SAH	Checked By:	SAH
Drawn By:	JMN	Approved By:	SAH

Mauthe PFAS Sampling

Terracon
MKE

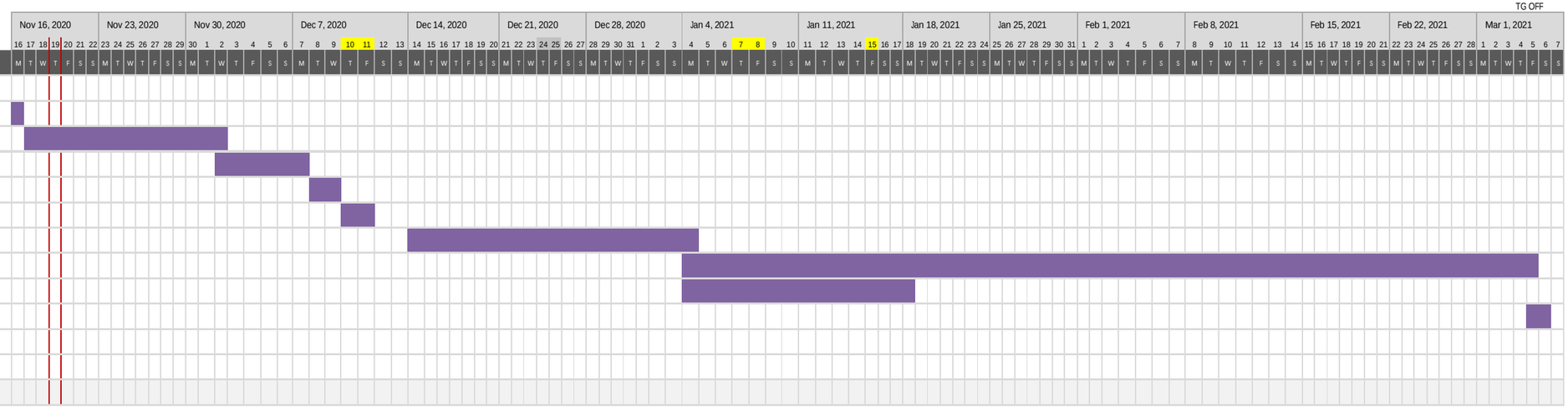
SIMPLE GANTT CHART by Vertex42.com
https://www.vertex42.com/ExcelTemplates/simple-gantt-chart.html

Project Start: Mon, 11/16/2020

Display Week: 1

TG OFF

TASK	ASSIGNED TO	PROGRESS	START	END
PFAS Coordination/Sampling/Reporting				
QAPP Approval (Conditional)	EPA	0%	11/16/20	11/16/20
Lab/Field Coordination	PM / FIELD	0%	11/17/20	12/2/20
Training	PM	0%	12/2/20	12/7/20
Fieldwork	CREW	0%	12/8/20	12/9/20
Shipping to Lab	FIELD	0%	12/10/20	12/11/20
Lab Analysis	EUROFINS, CA	0%	12/14/20	1/4/21
Third Party Data Validation	EPA	0%	1/4/21	3/5/21
Draft Report	PM	0%	1/4/21	1/18/21
Final Report	PM	0%	3/5/21	3/12/21
Insert new rows ABOVE this one				



TERRACON GROUND WATER SAMPLING INFORMATION SHEET

PROJECT NAME:		**PROJECT NO.**
PROJECT LOCATION:		
SAMPLE POINT:	**SAMPLE POINT DESCRIPTION:**	
CASING DIAMETER:		
WELL DEPTH:		
DATE:	**TIME** AM /PM	**DEPTH TO GROUND WATER (FT):**
SAMPLING METHOD:		**FLOW RATE:**
SAMPLE TIME:		**TOTAL PURGED:**

TIME	WATER LEVEL	TEMP.(º)	pH	COND. ( )	ORP ( )	DO ( )

SAMPLE APPEARANCE: VERY TURBID TURBID SLIGHTLY TURBID CLEAR	**ODOR:** YES NO NOT NOTED	**ANALYSES:**

CLEANING PERFORMED IN FIELD: ***Alconox and Distilled Water AND Disposable gloves*** *INITIAL TO VERIFY OR NOTE OTHER CLEANING METHOD PERFORMED

COMMENTS:

SAMPLED BY:	**DATE:**
REVIEWED BY:	**DATE:**

Eurofins TestAmerica, Sacramento
880 Riverside Parkway

West Sacramento, CA 95605-1500
phone 916.373.5600 fax 303.467.7248

Chain of Custody Record

eurofins | Environment Testing TestAmerica

Regulatory Program: ☐DW ☐NPDES ☐RCRA ☐Other:

TestAmerica Laboratories, Inc. d/b/a Eurofins TestAmerica

Client Contact	**Project Manager:**		COC No:
Your Company Name here	**Email:**	**Site Contact:**	**Date:**	_____ of _____ COCs
Address	**Tel/Fax:**	**Lab Contact:**	**Carrier:**	TALS Project #:
City/State/Zip	**Analysis Turnaround Time**			Sampler:
(xxx) xxx-xxxx Phone	☐ CALENDAR DAYS ☐ WORKING DAYS			**For Lab Use Only:**
(xxx) xxx-xxxx FAX	TAT if different from Below _____			Walk-in Client:
Project Name:	☐ 2 weeks			Lab Sampling:
Site:	☐ 1 week			
P O #	☐ 2 days			Job / SDG No.:
	☐ 1 day			

Sample Identification	Sample Date	Sample Time	Sample Type (C=Comp, G=Grab)	Matrix	# of Cont.	Filtered Sample (Y / N)	Perform MS / MSD (Y / N)															Sample Specific Notes:

Preservation Used: 1= Ice, 2= HCl; 3= H2SO4; 4=HNO3; 5=NaOH; 6= Other _____

Possible Hazard Identification:
Are any samples from a listed EPA Hazardous Waste? Please List any EPA Waste Codes for the sample in the Comments Section if the lab is to dispose of the sample.

☐ Non-Hazard ☐ Flammable ☐ Skin Irritant ☐ Poison B ☐ Unknown

Sample Disposal (A fee may be assessed if samples are retained longer than 1 month)

☐ Return to Client ☐ Disposal by Lab ☐ Archive for_____ Months

Special Instructions/QC Requirements & Comments:

Custody Seals Intact: ☐ Yes ☐ No | Custody Seal No.: | Cooler Temp. (°C): Obs'd:_____ Corr'd:_____ Therm ID No.:_____

Relinquished by:	Company:	Date/Time:	Received by:	Company:	Date/Time:
Relinquished by:	Company:	Date/Time:	Received by:	Company:	Date/Time:
Relinquished by:	Company:	Date/Time:	Received in Laboratory by:	Company:	Date/Time: