FINAL

Uniform Federal Policy–Quality Assurance Project Plan Addendum for a Site Inspection for Per- and Polyfluoroalkyl Substances (PFAS) at the Current Fire Station, Iowa Army Ammunition Plant, Middletown, Iowa

Contract No. W912QR12D0019,
Delivery Order W912QR21F0421

Prepared for

U.S. Army Corps of Engineers
Louisville District

600 Dr. Martin Luther King Jr. Place
Louisville, Kentucky 40202-2232

June 2023

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Acronyms and Abbreviations

°C	degree(s) Celsius
°F	degree(s) Fahrenheit
11Cl-PF3OUdS	11-chloroeicosafluoro-3-oxaundecane-1-sulfonic acid
6:2 FTS	6:2 Fluorotelomer sulfonate
8:2 FTS	8:2 Fluorotelomer sulfonate
9Cl-PF3ONS	9-chlorohexadecafluoro-3-oxanonane-1-sulfonic acid
ADONA	4,8-dioxa-3H-perfluorononanoic acid
AEC	Army Environmental Command
AFFF	aqueous film forming foam
AO	American Ordnance
AOPI	area of potential interest
bgs	below ground surface
BS	Bachelor of Science
CCV	continuing calibration verification
CH2M	CH2M HILL, Inc.
COR	Contracting Officer's Representative
CSM	conceptual site model
DL	detection limit
DoD	United States Department of Defense
DQO	data quality objective
EIS	extracted internal standard
ELAP	Environmental Laboratory Accreditation Program
EtFOSAA	N-ethylperfluoro-1-octanesulfonamidoacetic acid
FD	field duplicate
FTP	Fire Training Pit
FTS	fluorotelomer sulfonate
HAZWOPER	Hazardous Waste Operations and Emergency Response
HCL	hydrochloric acid
HDPE	high-density polyethylene
HFPO-DA	hexafluoropropylene oxide dimer acid
HNO_3	nitric acid
IAAAP	Iowa Army Ammunition Plant
ICAL	initial calibration
ICV	initial calibration verification

IDA	Inert Disposal Area
IDNR	Iowa Department of Natural Resources
IDW-L	investigation-derived waste—liquid
IDW-S	investigation-derived waste—soil
ISC	instrument sensitivity check
ITR	independent technical review
L	liter(s)
LC/MS/MS	liquid chromatography/tandem mass spectrophotometer
LCS	laboratory control sample
LCSD	laboratory control sample duplicate
LDPE	low-density polyethylene
LOD	limit of detection
LOQ	limit of quantitation
LSOP	laboratory standard operating procedure
MB	method blank
MD	matrix duplicate
MeFOSAA	N-methylperfluoro-1-octanesulfonamidoacetic acid
mL	milliliter(s)
MS	Master of Science
MS	matrix spike
MSD	matrix spike duplicate
N/A	not applicable
NEtFOSAA	N-ethyl perfluorooctanesulfonamidoacetic acid
NMeFOSAA	N-methylperfluorooctane sulfonamidoacetic acid
oz	ounce(s)
PA	preliminary assessment
PAL	project action limit
PARCCS	precision, accuracy, representativeness, completeness, comparability, and sensitivity
PDF	portable document format
PFAS	per- and polyfluoroalkyl substances
PFBA	perfluorobutanoic acid
PFBS	perfluorobutanesulfonic acid
PFDA	perfluoro-n-decanoic acid
PFDoA	perfluoro-n-dodecanoic acid
PFHpA	perfluoro-n-heptanoic acid

PFHxA	perfluoro-n-hexanoic acid
PFHxS	perfluorohexanesulfonic acid
PFNA	perfluoro-n-nonanoic acid
PFOA	perfluorooctanoic acid
PFOS	perfluorooctanesulfonic acid
PFPA	perfluoropentanoic acid
PFPeA	perfluoro-n-pentanoic acid
PFTeDA	perfluoro-n-tetradecanoic acid
PFTrDA	perfluoro-n-tridecanoic acid
PFUdA	perfluoro-n-undecanoic acid
PM	project manager
PPE	personal protective equipment
PQO	project quality objective
PTFE	polytetrafluroethylene
PVC	polyvinyl chloride
QA	quality assurance
QAPP	Quality Assurance Project Plan
QC	quality control
QSM	Quality Systems Manual
RCRA	Resource Conservation and Recovery Act
RI	remedial investigation
RPD	relative percent difference
RSD	relative standard deviation
RSL	Regional Screening Level
RT	retention time
SI	Site Inspection
SOP	standard operating procedure
SPE	solid phase extraction
SPF	sun protection factor
SVOC	semivolatile organic compound
TBD	to be determined
TCLP	Toxicity Characteristic Leaching Procedure
UFP-QAPP	Uniform Federal Policy–Quality Assurance Project Plan
USACE	U.S. Army Corps of Engineers
USEPA	U.S. Environmental Protection Agency

VOA	volatile organic analysis
VOC	volatile organic compound

Introduction

The purpose of this Uniform Federal Policy–Quality Assurance Project Plan (UFP-QAPP) Addendum is to describe the objectives, methods, and procedures for Site Inspection (SI) activities to be completed by Jacobs at an area of potential interest (AOPI), the Current Fire Station, at the Iowa Army Ammunition Plan (IAAAP), Middletown, Iowa, as identified from a Preliminary Assessment (PA) (Arcadis 2020). This UFP-QAPP Addendum presents the requirements and procedures for conducting field investigations for Delivery Order W912QR-21-F-0421 under U.S. Army Corps of Engineers, Louisville District (USACE) Contract W912QR-21-D-0019. The focus of this UFP-QAPP Addendum is per- and polyfluoroalkyl substances (PFAS) in groundwater, specifically the PFAS with project action limits (PALs) listed in Worksheet #15: perfluorooctanesulfonic acid (PFOS), perfluorooctanoic acid (PFOA), and perfluorobutanesulfonic acid (PFBS). Data gathered during the implementation of this plan will be used to evaluate whether there is PFAS contamination at the Current Fire Station, which was not included in the original 2020 PFAS UFP-QAPP (CH2M 2020). The optimized UFP-QAPP format was used to prepare this document.

The IAAAP consists of 19,011 acres adjacent to Middletown, in Des Moines County, Iowa (Figure 10-1). The IAAAP is located approximately 8 miles west of Burlington, which has a population of approximately 25,400 and is the largest city in Des Moines County. It is an active Joint Munitions Command facility currently operated by civilian contractor American Ordnance, LLC (AO). The current mission of the IAAAP is to load, assemble, and pack ammunition items, including projectiles, mortar rounds, warheads, demolition charges; and munitions components, such as fuses, primers, and boosters (U.S. Army 2007).

Due to explosives-contaminated surface water leaving the installation boundaries, the IAAAP was placed on the National Priorities List in August 1990. In September 1990, a Federal Facility Agreement was signed by U.S. Environmental Protection Agency (USEPA) Region 7 and the U.S. Army; it became effective in December 1990. In recent years, PFAS has been identified as an emerging contaminant. In response, a PA for PFAS was conducted at the IAAAP (Arcadis 2020).

The objective of the PA was to identify the locations across the IAAAP installation where PFAS (specifically, PFOS, PFOA, and PFBS) were used and whether a suspected release occurred at each location. Efforts included document reviews, internet keyword searches, and an installation site visit comprising interviews with installation personnel and site reconnaissance to identify specific areas of suspected PFAS releases. Seven areas at IAAAP were previously identified as potential PFAS sources, but following the site research conducted during the PA, PFAS use or release was not suspected for all areas (that is, non-AOPIs). The final PA identified the Current Fire Station as an AOPI, in addition to the three areas identified and discussed in the UFP-QAPP for an SI for PFAS (CH2M 2020) (Former Fire Station 200-131-3, Former Fire Training Pit, and the Inert Disposal Area). SI activities for the Former Fire Station 200-131-3, Former Fire Training Pit, and the Inert Disposal Area were conducted in December 2020, and results were presented in the draft *Site Inspection Report: Per- and Polyfluoroalkyl Substances (PFAS) Iowa Army Ammunition Plant, Middletown, Iowa* (CH2M 2022).

This UFP-QAPP Addendum for the SI only addresses the Current Fire Station, which was not included in the original PFAS UFP-QAPP (CH2M 2020). Operations at the Former Fire Station 200-131-3 were moved in 2012 to the Current Fire Station. The Current Fire Station is located on the east side of F-Road, halfway between B-Road and D-Road. There are approximately 70 gallons of aqueous film forming foam (AFFF) currently stored at the Current Fire Station.

The SI activities described in this UFP-QAPP Addendum include groundwater investigation at the AOPI (Current Fire Station) and are being conducted in a manner consistent with USEPA (2005) guidance and additional, currently accepted guidance (e.g., ITRC 2020; USEPA 2020). This QAPP Addendum was prepared for an SI of groundwater only at the Current Fire Station; soil may be evaluated at a later time at the AOPI if deemed necessary. Following the SI, a decision will be made on whether there is PFAS

contamination at the Current Fire Station that requires further investigation or action. In accordance with Department of the Army (2018) guidance, if the SI indicates a release has occurred, either an expanded SI or Remedial Investigation (RI) will be conducted to refine the nature and extent of contamination. This UFP-QAPP Addendum has been prepared, as has the UFP-QAPP for an SI for PFAS (CH2M 2020), to ensure that data collected during the SI are of known quality, represent actual conditions, and are adequate and appropriate for making informed decisions.

Worksheets #1 and #2: Title and Approval Page

Project Name and Site Location:	SI for Per- and Polyfluoroalkyl Substances (PFAS) at Iowa Army Ammunition Plant (IAAAP), Middletown, Iowa
Document Title:	*Uniform Federal Policy–Quality Assurance Project Plan Addendum for a Site Inspection for Per- and Polyfluoroalkyl Substances (PFAS) at the Current Fire Station, Iowa Army Ammunition Plant, Middletown, Iowa* (An optimized UFP-QAPP format was selected for this UFP-QAPP Addendum.)
Contract Number:	U.S. Army Corps of Engineers (USACE) Contract W912QR-21-D-0019, Delivery Order W912QR-21-F-0421
Lead Organization:	U.S. Army Corps of Engineers (USACE) Louisville District 600 Dr. MLK Jr. Pl. Louisville, KY 40202-2232 Aaron Steele—Contracting Officer's Representative Telephone: 502-315-6372 Email: Aaron.B.Steele@usace.army.mil
Support Organization:	U.S. Environmental Protection Agency (USEPA), Region 7 11201 Renner Boulevard Lenexa, Kansas 66219 Wesley March—Remedial Project Manager Telephone: 913-551-7037 Email: March.Wesley@epa.gov
Identify Regulatory Program:	Comprehensive Environmental Response, Compensation, and Liability Act
List Organizational Partners (Stakeholders) and Connection with Lead Organization:	USACE Louisville District, lead contracting office Iowa Army Ammunition, Army stakeholder Army Environmental Command (AEC), Army stakeholder Joint Munitions Command, Army stakeholder USACE Omaha District, Army stakeholder USEPA, regulatory agency Iowa Department of Natural Resources (IDNR), regulatory agency Restoration Advisory Board

Preparation Date:	June 2022
Plans and Reports from Previous Investigations Relevant to this Project:	*Final Preliminary Assessment of Per- and Polyfluoroalkyl Substances, Iowa Army Ammunition, Plant, Middletown, Iowa* (Arcadis 2020). *Field Activity Report Related to Perfluorinated Compounds at U.S. Army Materiel Command Installations with Aqueous Fire Fighting Foam* (Tetrahedron 2017). *Final Uniform Federal Policy–Quality Assurance Project Plan for Remedial Investigation at Iowa Army Ammunition Plant, Middletown, Iowa* (CH2M 2017). *Final Uniform Federal Policy–Quality Assurance Project Plan for a Site Inspection for Per- and Polyfluoroalkyl Substances (PFAS), Iowa Army Ammunition Plant, Middletown, Iowa* (CH2M 2020)

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Jennifer Busard, IAAAP — Date
Environmental Restoration Program Manager

ERICKSON.DAVID.K.1141246026 Digitally signed by ERICKSON.DAVID.K.1141246026 Date: 2023.06.07 07:30:07 -05'00' 6/7/23

David Erickson, USACE — Date
Contracting Officer's Representative

Worksheets #3 and #5: Project Organization and QAPP Distribution

Figure 3-1. Project Organization Chart
Iowa Ammunition Plant, Middletown, Iowa

Table 3-1. Distribution List

UFP-QAPP Addendum, PFAS SI, IAAAP, Middletown, Iowa

Recipient	Title	Organization
Seth Reedy	PM	USACE
David Erickson*	Contracting Officer's Representative	USACE
Jerry Manint*	Technical Manager	USACE
Eric Fritzsch*	Technical Manager	USACE
Wesley March *	Remedial PM	USEPA
Shelley Nellesen *	PM	IDNR
Andrea Sansom	Project chemist/Alternate Technical Manager	USACE
Jennifer Busard*	Environmental Restoration Program Manager	IAAAP
Jonathan Harrington *	Environmental Support Manager	AEC
Jeffrey Morrison, PE*	PM	Jacobs
Kim-Lee Yarberry, PG	Senior technical consultant/hydrogeologist	Jacobs
Alexandra Salter-Blanc, PhD	PFAS subject matter expert/Quality Assurance Manager	Jacobs
Shane Lowe	Senior chemist	Jacobs
Catherine Dover*	Laboratory PM	Pace Analytical Services, LLC.

* This recipient will receive electronic copies of the UFP-QAPP Addendum. They will distribute within their organization as appropriate.

Lines of communication are presented in the original PFAS UFP-QAPP (CH2M 2020), Worksheet # 6.

PM = project manager

Worksheets #4, #7, and #8: Personnel Qualifications and Sign-off Sheet

Name	Project Role	Education/Experience	Specialized Training/Certifications	Location of Training Record/Certifications	Signature*/ Date
Jeff Morrison	PM	MS, Engineering, 30 years of experience; Professional Engineer	HAZWOPER 40-hour Training; 8-hour Refresher	Jacobs Human Resources Department	TBD
Kim-Lee Yarberry	Senior technical consultant/ Hydrogeologist	MS, Engineering and Science, 21 years of experience;	HAZWOPER 40-hour Training; 8-hour Refresher	Jacobs Human Resources Department	TBD
Alexandra Salter-Blanc	Subject matter expert/Quality Assurance Manager	PhD, Environmental Science and Engineering / 15 years of experience	HAZWOPER 40-hour Training; 8-hour Refresher	Jacobs Human Resources Department	TBD
Shane Lowe	Project chemist	MS, Science, 19 years of experience	None required	NA	TBD
Joe Spies	Field Manager	BS, Geologist, 4.5 years of experience	HAZWOPER 40-hour Training; 8-hour Refresher; Occupational Safety and Health Administration 30-hour Construction Awareness; Site Safety Liaison, cardiopulmonary resuscitation, and First Aid	Jacobs Human Resources Department	TBD
Catherine Dover	Laboratory PM, Pace Analytical Services, LLC.	available upon request	None required	NA	TBD

Worksheet #9: Project Scoping Session Participants Sheet

No project scoping session was conducted. This SI addendum for the Current Fire Station is following the same technical approach as that for the Former Fire Station, presented in the *Final Uniform Federal Policy–Quality Assurance Project Plan for a Site Inspection for Per- and Polyfluoroalkyl Substances (PFAS), Iowa Army Ammunition Plant, Middletown, Iowa* (CH2M 2020).

Worksheet #10: Conceptual Site Model

This worksheet describes the site background and environmental conditions in relation to the conceptual site model (CSM) for the AOPI (the Current Fire Station) identified in the PFAS PA for IAAAP (Arcadis 2020). The CSM integrates existing information and assumptions about the physical site conditions, potential chemicals of interest, and pathways/receptors of concern presented in the PA report.

Background

This background section consists of the site description, operational history, and the rationale for initiating SI activities at the AOPI (Current Fire Station).

IAAAP Installation Description

The IAAAP is located in Des Moines County, Iowa, adjacent to Middletown. The installation is approximately 8 miles west of Burlington, which has a population of approximately 25,400. The installation is bordered by U.S. Highway 34 to the north, upland agricultural farms to the east and west, and the Skunk River Valley to the south. The IAAAP is an active U.S. Army Joint Munitions Command facility installation with a mission to load, assemble, and pack ammunition items, including projectiles, mortar rounds, warheads, demolition charges, and munitions components such as fuses, primers, and boosters. The IAAAP consists of production lines, landfills, disposal areas, burn areas, a demolition area, and a fire training area. The remaining land is woodlands or property that is leased for agricultural usage. The IAAAP and the three AOPI location is shown on Figure 10-1.

Current Fire Station

Site Description

The Current Fire Station is located in the northeastern portion of the IAAAP (Figure 10-2), on the east side of F-Road, halfway between B-Road and D-Road.

Geologic and hydrogeologic data are not available for this location, since no previous investigation has been conducted at this site. This information will be collected during the SI.

Operational and Remediation History

Operations at the Former Fire Station 200-131-3 were moved in 2012 to the Current Fire Station. There are approximately 70 gallons of AFFF currently stored at the Current Fire Station. Because of this, the Current Fire Station was identified as an AOPI in addition to the Inert disposal Area (IDA), the Fire Training Pit (FTP), and the Former Fire Station 200-131-3, as presented in the UFP-QAPP for an SI for PFAS (CH2M 2020).

Current Conditions

Based on site operations, no SI was previously warranted for Current Fire Station. However, this site was reevaluated due to the emergence of PFAS as a contaminant and the storage of AFFF onsite.

Physical Setting

Climate

Des Moines County has a typical Midwestern climate of hot/humid summers and cold/wet winters. According to the National Weather Service, between 1981 and 2010, the average annual temperature in this area was 53°F. The average annual precipitation in this area is 42.2 inches. During the winter, precipitation frequently occurs as snow, and during the rest of the year it is mainly rain, and often heavy. The highest rainfall amounts tend to occur between May and July. Snowmelt during spring, combined with frozen or saturated soil conditions that reduce infiltration, can result in high runoff and substantial erosion. In addition, severe thunderstorms in summer can also result in a high volume of precipitation over a short period of time and also create high runoff volumes (H&S 2016).

Topography

IAAAP is located in the Southern Iowa Drift Plain. The highest elevation in the county, 862 feet above mean sea level (msl), is located about 13 miles north of IAAAP, near the town of Yarmouth, Iowa. The lowest elevation, about 520 feet above msl, is located where the Skunk River enters the Mississippi River at the southeastern boundary of the county. Vertical relief between lowlands and adjoining uplands generally range from 50 to 120 feet.

Where it is not dissected by drainages, the topography at IAAAP is generally flat in the uplands and slopes gently toward the south. Elevations at IAAAP range from 732 feet above msl along the northern extent of the installation to about 544 feet above msl throughout the extensive southern area of Long Creek and Skunk River.

Soil

With exception of developing soil associated with rivers and drainages, soil on IAAAP belongs to either the Mollisols or Alfilsols soil order. Mollisols are a relatively fertile soil and are characterized by a soft surface character, a high base saturation (generally indicative of fertile soil), and a dark color due to abundant humus. Alfilsols are also a relatively fertile soil with moderate to high base saturation. Agriculture plays a major role in Des Moines County, with almost 56 percent of the county designated as prime farmland.

Geology

IAAAP is located in the Dissected Till Plain section of the Central Lowland Physiographic Province of the Southern Iowa Drift Plain Landform Region. The facility is underlain by a sequence of unconsolidated glacial deposits of Pleistocene age (collectively known as overburden) overlying sedimentary bedrock units. The overburden deposits near IAAAP include alluvium, loess, and glacial drift. The bedrock underlying IAAAP consists of a sequence of limestones interbedded with varying thicknesses of shales and sandstones ranging in age from Cambrian to Mississippian.

Hydrogeology

Des Moines County has four principal aquifers: the surficial (overburden) aquifer and the bedrock aquifers of Mississippian, Devonian, and Cambro-Ordovician units. The aquifers of concern for this SI at the IAAAP are the overburden aquifer and the youngest bedrock (Mississippian) aquifer. The overburden aquifer is composed predominantly of the unconsolidated glacial drift (Kellersville Till) in the upland, northern

portion of the IAAAP and the alluvium within the lower creek and river valleys in the southern portion of the IAAAP. Groundwater flow direction in the overburden aquifer typically mimics surface topography, with flow southeasterly or southwesterly toward Brush Creek, Long Creek, Spring Creek, and the Skunk River. Groundwater flow within the bedrock aquifers primarily occurs within secondary permeability zones, including fractures, joints, or bedding planes. Overall flow direction is to the south and east toward the Skunk and Mississippi Rivers, when not intercepted by incised surface drainages.

Potential Chemicals of Interest

PFAS in groundwater are the potential chemicals of interest for this SI and exposure pathways to soil will be addressed in a future expanded SI or RI if deemed necessary. The following bullets summarize the findings from the PA report (Arcadis 2020):

- Along with the IDA, the FTP, and the Former Fire Station 200-131-3 (CH2M 2020), the Current Fire Station was identified as an area where potential PFAS impacts warrant further investigation.
- Impacted groundwater may pose an unacceptable risk to current and/or future receptors.

Receptors and Exposure Pathways

The PA identified potential exposure pathways and receptors for each of the AOPIs. Ecological receptors have a potential exposure pathway by groundwater discharge to surface water bodies, and a complete exposure pathway exists for aquatic receptors (fish, amphibians, benthic invertebrates, semiaquatic mammals, and birds).

Several ecological receptors may be present at IAAAP. According to the U.S. Fish and Wildlife Service (2022), the federally listed threatened, endangered, or proposed species listed below are known to or are believed to occur in Des Moines County, IA,

- Mammals
  - Indiana Bat *(Myotis sodalist)*—Endangered.
  - Northern Long-eared Bat *(Myotis septentrionalis)*—Threatened.
- Clams
  - Higgins Eye *(Lampsilis higginsii)*—Endangered.
  - Sheepnose Mussel *(Plethobasus cyphyus)*—Endangered.
  - Spectaclecase *(Cumberlandia monodonta)*—Endangered.
- Insects
  - Monarch Butterfly *(Danaus plexippus)*—Candidate.
- Flowering Plants
  - Eastern Prairie Fringed Orchid *(Platanthera leucophaea)*—Threatened.

Though the abovementioned endangered, threatened, or special concern species may be present at IAAAP, only potentially complete pathways exist for the aquatic receptors.

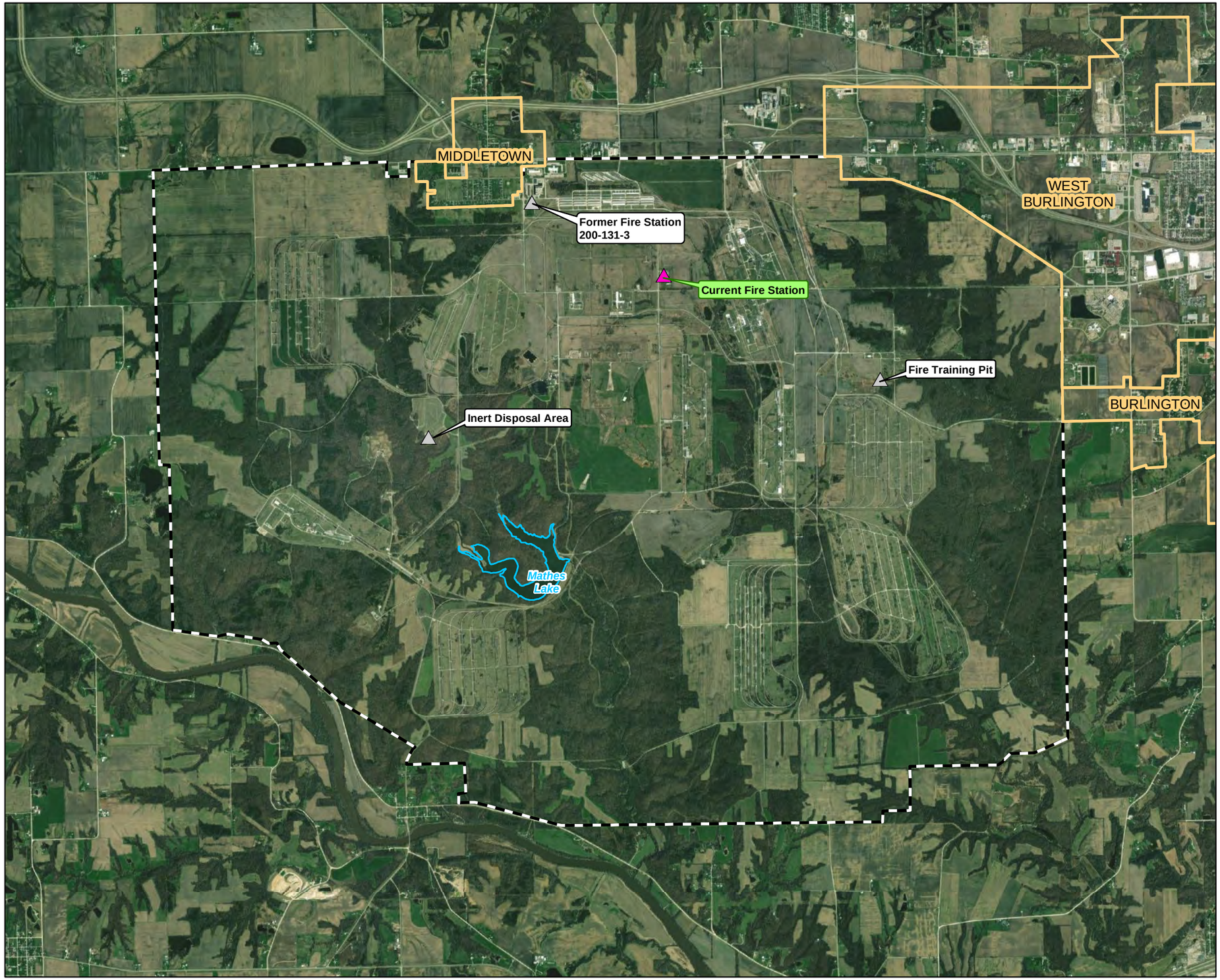
The PA identified the following routes by which PFAS compounds could migrate (Arcadis 2020):

- Soil to groundwater due to desorption or dissolution
- Groundwater to surface water through groundwater discharge

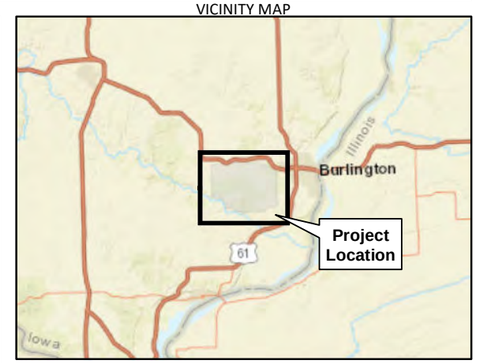
This SI will evaluate whether PFAS with project action limits (PALs) listed in Worksheet #15 are present in groundwater. The PA stated that there are no current or future potential receptors of impacted water, either groundwater or surface water, on the installation (Arcadis 2020); however, based on applicable CERCLA policy and guidance, groundwater at IAAAP is generally classified as Class IIB, a potential source of drinking water (USEPA 1989). The PA also indicated that there is a potential for exposure to groundwater through consumption of impacted groundwater off the installation. Surface runoff is channeled through ditches and culverts along the roads at the site, which direct water south and east toward an intermittent tributary and subsequently to Brush Creek, which is not known to be used as a source of drinking water. If an RI is warranted for PFAS, then current and future receptors will be reevaluated, as appropriate. A preliminary conceptual exposure model for the FTP is shown on Figure 10-3.

Data Gaps

The PA identified the Current Fire Station, where 70 gallons of AFFF containing PFAS and constituents are stored, as an AOPI. No groundwater samples have been collected from the Current Fire Station to date. Because the groundwater at the AOPI was not evaluated for PFAS and related constituents during the 2020 SI field work, there is uncertainty associated with whether PFAS compounds are present in the groundwater at concentrations that exceed the applicable PALs (Worksheet #15).



VICINITY MAP



LEGEND

- Area of Potential Interest (AOPI) Location (Presented in the UFP-QAPP Addendum for a Site Inspection for PFAS)
- AOPI Location (Discussed in the UFP-QAPP for a Site Inspection for PFAS)
- Mathes Lake
- Plant Boundary
- City Boundary
- County Boundary

Note:
1. 2021 Esri World Imagery Basemap

N

0 0.75 1.5
Miles

FIGURE 10-1
Area of Potential Interest (AOPI) Locations
Iowa Army Ammunition Plant
Middletown, Iowa

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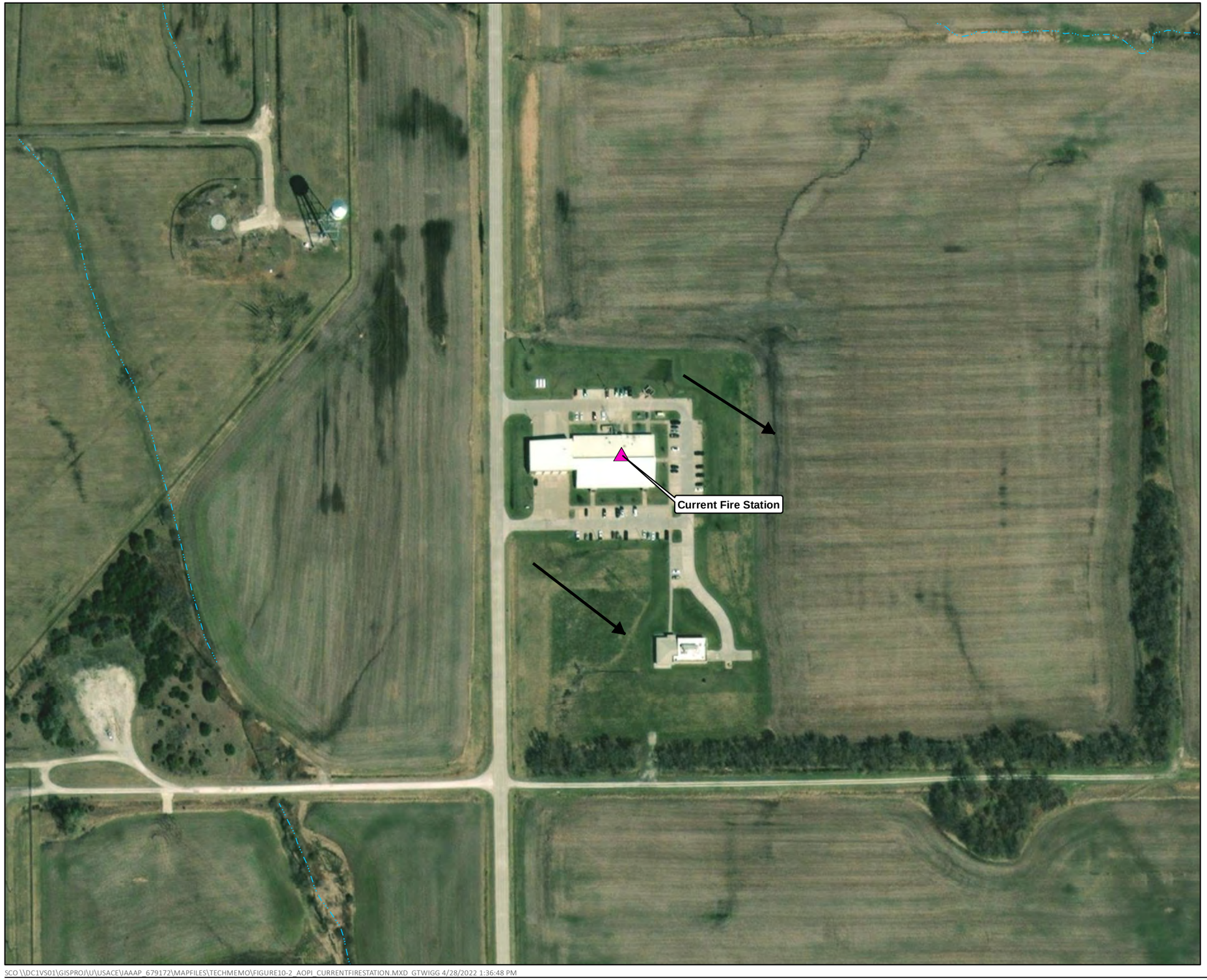
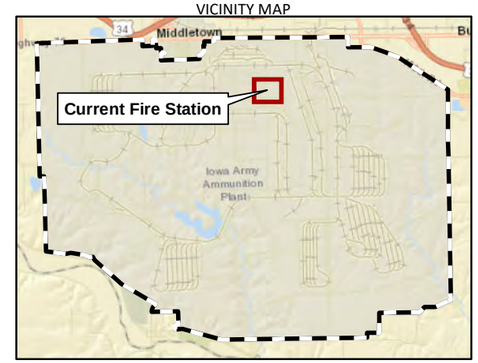
Jacobs



VICINITY MAP



LEGEND

- Area of Potential Interest (AOPI) Location
- Intermittent Stream
- Plant Boundary
- Groundwater Flow Direction (Shallow Aquifer)

Note:
1. 2021 Esri World Imagery Basemap

N

0 200 400

Feet

FIGURE 10-2
Current Fire Station
Iowa Army Ammunition Plant
Middletown, Iowa

SCO \\DC1VS01\GISPROJ\U\USACE\IAAAP_679172\MAPFILES\TECHMEMO\FIGURE10-2_AOPI_CURRENTFIRESTATION.MXD GTWIGG 4/28/2022 1:36:48 PM

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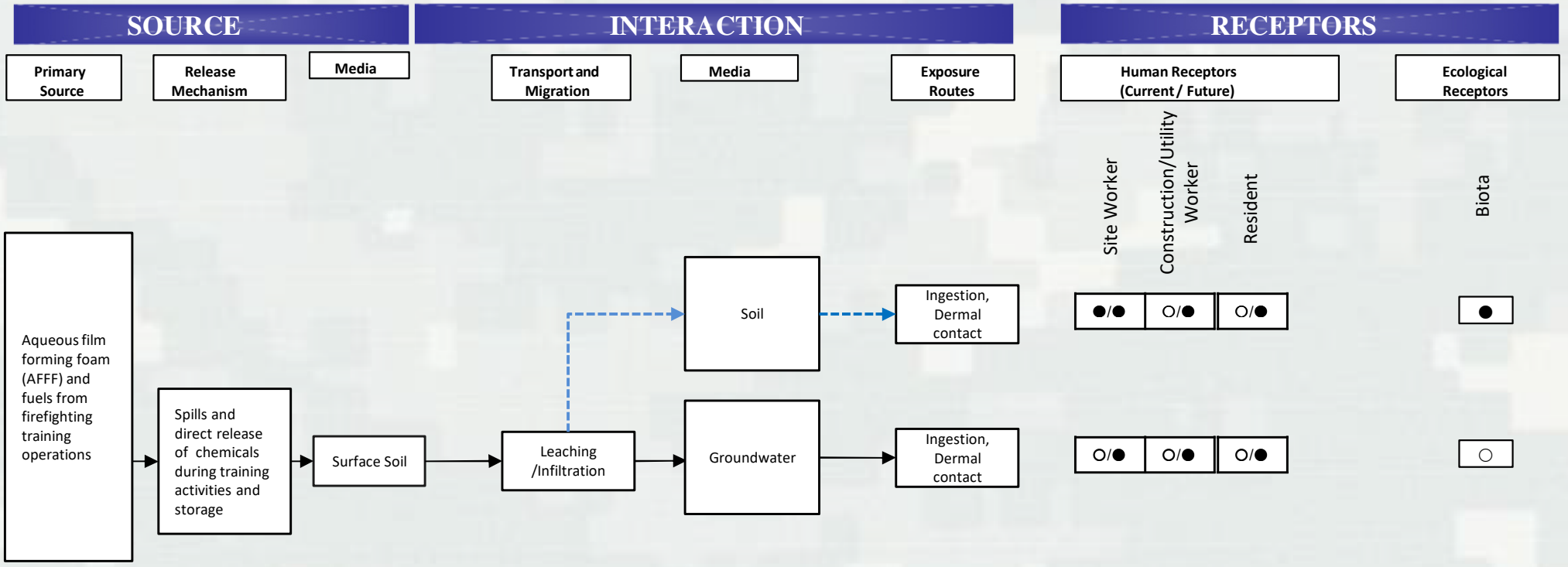


POTENTIAL GROUNDWATER EXPOSURE SCENARIOS

LEGEND

- ----▶ To be addressed in a separate RI, if deemed necessary
- ——▶ Flow-chart continues
- ● Potentially Complete Pathway
- ○ Incomplete Pathway

Receptor	Potential Exposure Activity	Exposure Media / Pathways
Site Worker (industrial)	Grounds maintenance, industrial activities	GW (Ing, Derm)
Construction/utility worker	Construction or utility activities in trenches	GW (Ing, Derm)
Resident (adult and child)	Hypothetical future residential land use	GW (Ing, Derm)

Figure 10-3
Current Fire Station *Preliminary Conceptual Exposure Model*
Iowa Army Ammunition Plant
Middletown, Iowa

Worksheet #11: Project/Data Quality Objectives

The primary project quality objective (PQO) for the SI is to gather information to support decisions regarding the need for further actions at each AOPI according to USEPA (1992) guidance. PQOs define the type, quantity, and quality of data that are needed to answer project-specific questions and the data gaps identified in Worksheet #10. The PQOs were developed during the work-planning process that included project stakeholders, as summarized in Worksheet #9 of the UFP-QAPP for an SI for PFAS (CH2M 2020).

The data quality objective (DQO) process consists of seven iterative steps. Each step defines criteria that will be used to establish the final data collection design. The project problem to be addressed and the associated developed DQOs following the seven-step process are discussed in the following sections.

Step 1: State the Problem

Due to 70 gallons of AFFF that contain PFAS being stored at the Current Fire Station, groundwater at IAAAP has been identified as an AOPI and may contain concentrations of PFAS and related constituents exceeding PALs (Worksheet #15). It is unknown whether PFAS and related constituents are present in groundwater at the AOPI since these constituents have not been analyzed for previously in this medium.

Step 2: Identify the Goals of the Study

The AOPI (Current Fire Station) has been selected for inclusion in the PFAS SI for IAAAP. The goal of the SI at the AOPI (Current Fire Station) is to perform groundwater sampling designed to determine the presence or absence of a target list of 22 PFAS chemicals. This list includes the 18 analytes defined in USEPA Method 537 version 1.1 and 4 additional analytes listed in the Army's PFAS guidance (Department of the Army 2018). In accordance with Department of Defense's (DoD's) Memorandum on Establishing a Consistent Methodology for the Analysis of Per- and Polyfluoroalkyl Substances in Media Other than Drinking Water (DoD 2019), the groundwater samples will be analyzed via the method outlined in the DoD Quality Systems Manual (QSM) version 5.4, Table B-15 (DoD 2021). If PFAS analytes are detected, concentrations will be compared to the PALs (Table 15-1) and qualitatively evaluated to assess whether additional actions may be warranted. Screening levels (referred to as PALs in this report) are risk-based, chemical-specific values based on default exposure parameters and USEPA-approved toxicity values. In general, when contaminant concentrations fall below screening levels, further action or investigation is not required.

When evaluating whether contamination is present in groundwater, the following decisions will need to be made:

1) What quantity and location of samples are required to evaluate the presence or absence of contamination?
2) Do site analytical data confirm that chemical concentrations are present above action limits for groundwater values?

Step 3: Identify Information Inputs

Elements to be considered in the project decisions for the AOPI include the following:

1) Information and data contained in the PA report.

2) Existing historical records, data, and site visual inspections.
3) Site improvements or development history that has occurred after sampling.
4) Geological site conditions and general information about the chemical properties and characteristics of the suspected chemical constituents.
5) Field observations and measurements from sampling activities.
6) Sample locations and depths.
7) Validated analytical data for PFAS in groundwater samples collected at each AOPI.
8) PALs, which for this project are the USEPA Tap Water Regional Screening Levels (RSLs) (Worksheet #15 and Table 15-1). These PALs are in accordance with the Army's 2018 PFAS guidance (Department of the Army 2018) and the DoD's 2022 *Memorandum on Investigating Per- and Polyfluoroalkyl Substances within the Department of Defense Cleanup Program* (DoD 2022), which superseded the 2019 version of this memo cited in the UFP-QAPP for an SI for PFAS (CH2M 2020). However, if toxicity values are updated or if new toxicity values are established for chemicals currently without toxicity values, then the most current action levels for PFAS at the time of the SI data evaluation will be used as PALs, given they are consistent with DoD and USEPA directives.
9) Current and Future Land Use plans and visual inspections of the site.

Step 4: Define the Boundaries of the Study

The geographical boundary of this study area is the approximate site boundary for the Current Fire Station as shown on Figure 11-1. The media for the SI activities is groundwater.

Groundwater samples will be collected from locations within the AOPI (Current Fire Station) to evaluate whether the AOPI has been impacted. (See Worksheet #17 for sample locations.)

Groundwater samples will be analyzed for a target list of 22 PFAS that includes 18 analytes defined in USEPA Method 537 version 1.1 and 4 additional PFAS identified in the Army's 2018 PFAS guidance. (See Worksheet #15, Table 15-1 for target analyte list). The locations of the proposed samples are presented on Figure 11-1.

Groundwater samples will be collected in accordance with standard operating procedure (SOP)-02. The SI data will be considered valid at least through the RI, FS, and record of decision (ROD) stages, if this SI indicates a release has occurred at the Current Fires Station and either an expanded SI or RI are required.

Step 5: Develop the Analytic Approach

The SI sample locations at AOPI (Current Fire Station) will be selected to assess potential release areas, upgradient areas, and downgradient areas, as discussed in Worksheet #17.

If analytes are detected, then the concentrations of PFAS compounds in groundwater will be compared to screening levels, provided in Worksheet #15. In accordance with Department of the Army (2018) guidance, if the SI indicates a release has occurred, either an expanded SI or RI will be conducted to refine the nature and extent of contamination.

Screening levels (referred to as PALs in this report) are risk-based, chemical-specific values based on default exposure parameters and USEPA-approved toxicity values. In general, when contaminant concentrations fall below screening levels, further action or investigation is not required. Population statistics will not be calculated since a risk assessment is not a component of the SI.

Step 6: Specify Performance or Acceptance Criteria

Decision errors will be minimized through site understanding obtained from previous site visits and adherence to SOPs during groundwater sampling.

Laboratory analyses will be conducted in accordance with this UFP-QAPP Addendum and the 2020 UFP-QAPP (CH2M 2020). A list of references from the UFP-QAPPs are provided below.

- Refer to Worksheet #28 for acceptance and performance criteria.
- Laboratory data are considered usable if data validation criteria are met (refer to Worksheets #34, #35, and #36).
- Decision errors will be minimized through site visits and refinement of the conceptual site model. Measurement errors will be minimized by following the FOPs.
- Analytical data quality will be compared to DoD Quality Systems Manual (QSM) (DoD, 2021) specification for precision, accuracy, representativeness, comparability, completeness, and sensitivity (PARCCS).
- The analytical methods will provide the lowest available DLs using standard methods that will allow the data to be screened against the PALs in Worksheet #15.

The use of these data is not restricted unless there is a quality problem, such as a recurring quality control (QC) exceedance or a gross QC exceedance that would result in rejected data as defined in Worksheet #36.

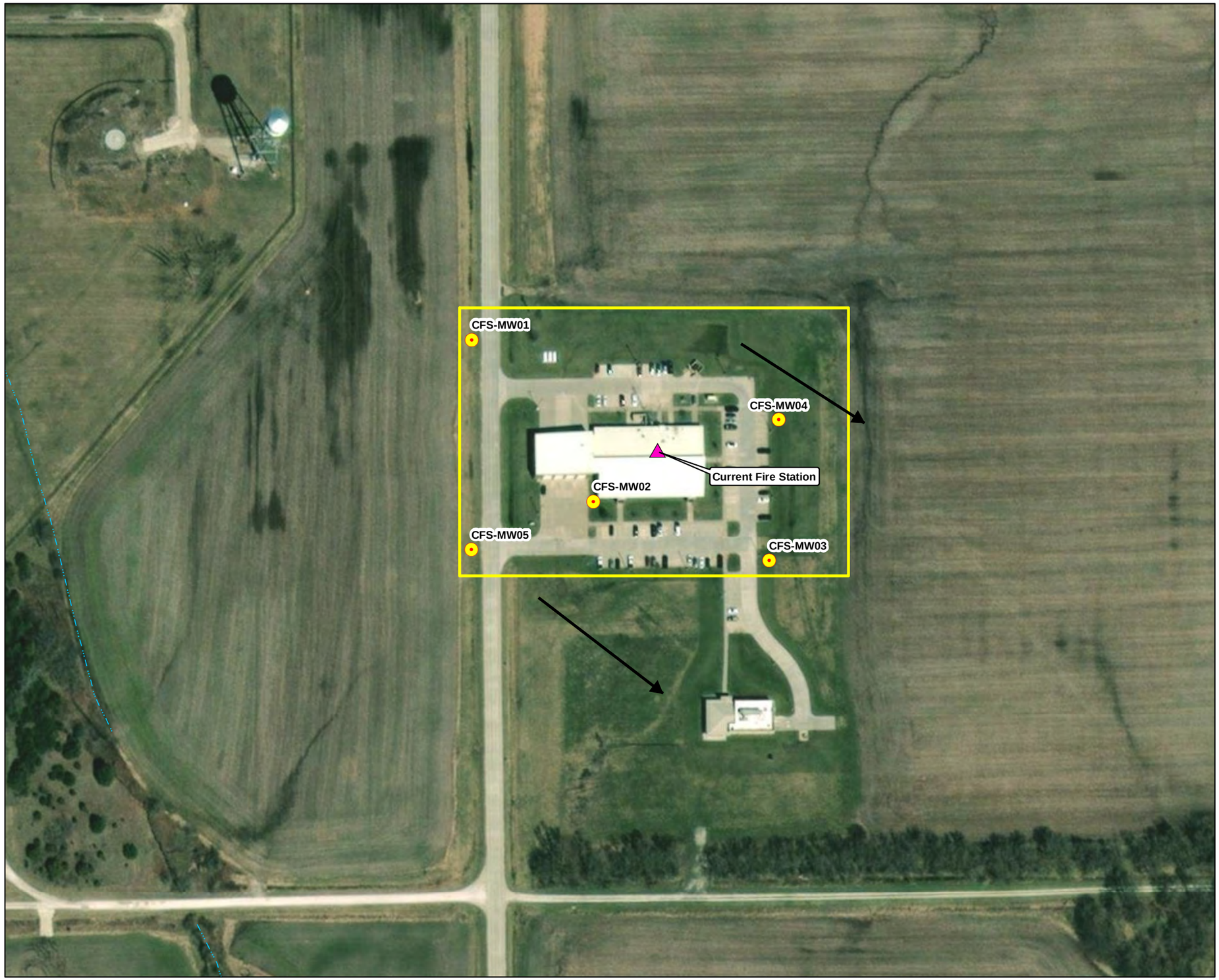
The analytical methods will provide the lowest available detection limits (DLs) that will allow for the data to be compared to action limits.

Collection and interpretation of field measurements will be conducted in accordance with standard industry practice and as specified in the SOPs provided with the 2020 UFP-QAPP and this UFP-QAPP Addendum.

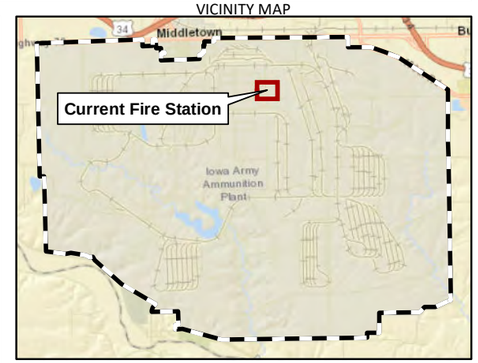
The work being performed as part of this UFP-QAPP addendum is part of a SI and therefore risk assessments will not be conducted.

Step 7: Develop the Detailed Plan for Obtaining Data

To optimize the sampling design, available data were reviewed to select the appropriate quantity and location of samples to be collected, as discussed in Worksheet #9 of the UFP-QAPP for an SI for PFAS (CH2M 2020). Five sampling locations representing potential release areas, upgradient areas, and downgradient areas at the AOPI are proposed to evaluate whether a release of PFAS compounds has occurred and evaluate whether detected chemicals require further evaluation. See Worksheet #17 for the detailed sampling design, locations, and rationale.



VICINITY MAP



LEGEND

- Area of Potential Interest (AOPI) Location
- Proposed Monitoring Well Location
- Intermittent Stream
- Approximate Site Boundary
- Plant Boundary
- Groundwater Flow Direction (Shallow Aquifer)

Note:
1. 2021 Esri World Imagery Basemap

N

0 150 300
Feet

FIGURE 11-1
Proposed Well Installation at the Current Fire Station
Iowa Army Ammunition Plant
Middletown, Iowa

Jacobs

Worksheets #14 and #16: Project Tasks and Schedule

Worksheets #14 and #16 (combined) provide an overview of project tasks and project schedule.
The primary tasks associated with this delivery order are as follows:

- Monitoring well installation
- Groundwater sampling
- Surveying
- Decontamination
- Demobilization
- Waste management
- Data management

Reporting field activities and procedures to achieve DQOs are summarized in herein. Discussions of quality assurance (QA) for the project are provided in Worksheets #27 through #37 of the UFP-QAPP for an SI for PFAS (CH2M 2020).

Mobilization

To prevent damage to the environment and injury to personnel, mobilization will include acquiring necessary permits. Work will be coordinated with USACE and appropriate installation points of contact. Work clearances and permits will be obtained for field activities. IAAAP is controlled by a locked gate. Laydown areas for equipment storage and staging will be made available and coordinated with AO, the onsite contractor at IAAAP.

Jacobs team field personnel will obtain construction identification badges with photographs from AO Security in coordination with the Plant Protection Division. Personnel will display their identification badges while working at the facility. The Field Team Leader will ensure the badges are returned to AO Security upon completion of the work.

Jacobs team personnel will display their identification badges to gain access to IAAAP general area and those limited areas specifically authorized on the face of the badge. Jacobs understands that an employee possessing a badge is bound by the Security Regulations of IAAAP. The Plant Protection Division and/or AO Security may deny issuance or revoke a badge from an individual not complying with these rules.

Jacobs team personnel will access the facility area through Gate 4. Jacobs team personnel needing to enter IAAAP with a camera will obtain a camera pass from AO prior to entering IAAAP. Photographs taken within the installation will include only project sites and operations. No photographs will be taken of production facilities.

Field Activities

Monitoring Well Installation

Five overburden monitoring wells will be installed at the Current Fire Station. Monitoring wells will be drilled and installed using combined direct-push technology and hollow-stem auger drilling methods (SOP-01 in the UFP-QAPP for an SI for PFAS [CH2M 2020]). The wells will be installed to an approximate depth of 30 feet below ground surface (bgs). Continuous soil samples will be collected from borings

advanced for new overburden monitoring wells. Photoionization detector screening of soils will be conducted using appropriate lamps for PFAS/PFOA during drilling, and results will be recorded on the boring log. Lithologic characterization and descriptions of overburden glacial deposits and bedrock will be performed by a geologist and recorded on soil boring logs. Subsurface soils will be classified according to the Unified Soil Classification System.

New monitoring wells will be constructed in accordance with EM-1110-1-4000 (USEPA 1988) and State of Iowa regulations. Monitoring wells will consist of a 2-inch-nominal-diameter Schedule 40 polyvinyl chloride (PVC) screen and riser. Well screens will be machine-slotted, 0.010 inch, and 10 feet long. Monitoring wells will be installed within the top of the overburden aquifer; the depth of the screen interval will be determined from the associated soil boring log where the first saturated soil zone is encountered. A certified-clean 20/40 silica sand or equivalent filter pack will be placed around the annular space of the well screen from the bottom of the boring extending to a depth of 2 feet above the top of the screen. A 3- to 5-foot PFAS-free bentonite layer will be placed above the top of the sand pack. After the bentonite is hydrated, a cement-bentonite grout will be placed in the remaining annular space.

Monitoring wells will be completed flush to ground surface with a watertight steel cover. A locking watertight cap will be placed on the PVC pipe, and the temporary designation will be marked on the well.

Well Development

After installation, each of the monitoring wells will be developed by a combination of bailing, surging, and pumping in accordance with SOP-01 included as Appendix A.

Newly installed monitoring wells will be developed no sooner than 24 hours following well installation as detailed in SOP-01 in the UFP-QAPP for an SI for PFAS (Appendix A). A surge-and-purge method will be used to develop the entire vertical screen interval. Development will continue until water quality parameters stabilize within the specified criteria with three consecutive readings. Groundwater purged during development will be immediately containerized in 55-gallon drums.

Groundwater Monitoring and Sampling

Water levels will be measured and recorded in each of the groundwater monitoring wells sampled for PFAS according to SOP-02 in the UFP-QAPP for an SI for PFAS (CH2M 2020).

Groundwater samples will be collected from the five newly installed monitoring wells and analyzed for PFAS, as described in Worksheet #17. Monitoring wells will be sampled in accordance with SOP-02 in the UFP-QAPP for an SI for PFAS (CH2M 2020). General groundwater quality parameters will be monitored and recorded during well purging and sampling. Groundwater samples will be collected following parameter stabilization in accordance with SOP-02 in the UFP-QAPP for an SI for PFAS (CH2M 2020).

Worksheet #18 details the number of samples and method requirements. The sample identification and labeling for each groundwater sample collected is outlined in Worksheet #26 and #27.

Special Considerations for PFAS Sampling

Protocols and prohibitions related to PFAS sampling will be implemented in field activities and are presented in SOP-02 in the UFP-QAPP for an SI for PFAS (CH2M 2020). In addition, since various clothing materials present a potential for PFAS cross-contamination in samples, field staff will adhere to the

specific personal protective equipment (PPE) requirements. Table 14-1 summarizes acceptable and prohibited items and activities during SI implementation.

Table 14-1. Prohibited and Acceptable Items During PFAS Sampling
UFP-QAPP Addendum, PFAS SI, IAAAP, Middletown, Iowa

Prohibited Items	Acceptable Items
Field Equipment	
Chemical (blue) ice packs or gel ice	Water ice
Teflon-containing materials	HDPE and silicone materials
Fluoropolymer bailers, tubing, or pump bladders; PFAS-containing bailer twine	Disposable or dedicated equipment (PFAS-free)
Non-stick aluminum foil	Thin HDPE sheeting or aluminum foil (not non-stick)
LDPE materials	HDPE and silicon materials
Storage of samples in containers made of LDPE materials	Acetate liners
Waterproof field books	Loose paper (or bound field books if non-PFAS containing) or electronic tablets
Plastic clipboards, binders, or spiral hard cover notebooks	Masonite or aluminum clipboards
Sharpies or markers	Pens
Post-It Notes	Loose paper (or bound field books if non-PFAS containing)
Field Clothing and PPE	
New clothing or water-resistant, waterproof, or stain-treated clothing, clothing containing Gore-Tex	Well-laundered clothing made of synthetic or natural fibers (preferably cotton)
Clothing laundered using fabric softener	No fabric softener
Boots containing Gore-Tex	Boots made with polyurethane and PVC or leather
Tyvek	Cotton clothing
No cosmetics, moisturizers, hand cream, or other related products as part of personal cleaning/showering routine on the morning of sampling. Many manufactured sunblock and insect repellents contain PFAS and should not be used.	Sunblock and insect repellants that do not contain PFAS. For example: **Sunscreens**: Alba Organics Natural Sunscreen, Yes To Cucumbers, Aubrey Organics, Jason Natural Sun Block, Kiss my Face, baby, or other sunscreens that are considered "free" or natural **Insect repellents**: Jason Natural Quit Bugging Me, Repel Lemon Eucalyptus Insect repellant, Herbal Armor, California Baby Natural Bug Spray, BabyGanics **Sunscreen and insect repellant:** Avon Skin So Soft Bug Guard Plus SPF 30 Lotion

Table 14-1. Prohibited and Acceptable Items During PFAS Sampling
UFP-QAPP Addendum, PFAS SI, IAAAP, Middletown, Iowa

Prohibited Items	Acceptable Items
Sample Containers	
LDPE or glass containers	HDPE or polypropylene
Teflon-lined caps	Unlined polypropylene caps
Rain Events	
Waterproof or water-resistant rain gear	Gazebo tent that is touched or moved only prior to and following sampling activities
Equipment Decontamination	
Decon 90	Alconox and/or Liquinox
Water from an onsite well	Potable water from municipal drinking water supply shown to be PFAS-free through analyses.
Decontamination water not verified to be PFAS-free	Verified laboratory-provided PFAS-free deionized water to be used for sampling equipment decontamination processes and blanks
Food Considerations	
All food and drink, with exceptions noted at right	Bottled water and hydration drinks (i.e., Gatorade and PowerAde brands) to be brought and consumed only in the staging area

Adapted from AECOM (2016) and DENIX (2017).

HDPE = high-density polyethylene

LDPE = low-density polyethylene

PFAS = per- and polyfluoroalkyl substances

PPE = personal protective equipment

PTFE= polytetrafluroethylene

PVC = polyvinyl chloride

SPF = sun protection factor

Laboratory Analysis

Laboratory analyses are described in Worksheet #17 (Sampling Design and Rational) and are summarized in the following paragraphs.

Pace Analytical Services, in West Columbia, South Carolina, is the primary laboratory and holds current DoD Environmental Laboratory Accreditation Program (ELAP) certification for the required analytical methods and will analyze the environmental and IDW samples for all parameters.

The laboratory analyses will be performed in accordance with the DoD QSM v. 5.4 (2021), this UFP-QAPP Addendum, and the laboratory SOPs (LSOPs) as defined in Worksheet #23 (Laboratory Analytical SOPs).

Surveying

Following field activities, sample locations will be surveyed in accordance with SOP-03, Geographic Land Surveying, in the UFP-QAPP for an SI for PFAS (CH2M 2020). Monitoring well installations will be surveyed by a State of Iowa–licensed professional surveyor. The survey will consist of new monitoring well location and elevation. The surveyor will provide horizontal and vertical control for the site. Accuracy of the control will be Third Order Class I as outlined in the Federal Geographic Data Committee's (2002) *Geospatial Positioning Accuracy Standards, Part 4: Standards for Architecture, Engineering, Constructions (A/E/C) and Facility Management*.

The surveyor will provide coordinates of the points *x*, *y*, and *z* to the nearest 0.01 foot. Coordinates will conform to NAD 83 (Latest Adjustment) and NAVD 88 with ties to the Iowa State Plane Coordinate System. Daily information will be recorded in field book format and the data collector information will be provided to Jacobs. Level and horizontal traverse networks will be closed to the starting point and the errors recorded. If errors exceed the standards outlined below, the survey will rerun the horizontal and vertical traverses until the errors are eliminated within the acceptable range. Field notes will include the date, names of the crew, weather conditions, barometric pressure, and collected survey data information. Benchmarks will be turned through and become part of the level loop.

Decontamination

Nondedicated and nondisposable equipment will be decontaminated in accordance with SOP-05 in the UFP-QAPP for an SI for PFAS (CH2M 2020). Table 14-2 identifies items prohibited during decontamination activities.

Demobilization

Following the completion of field activities, the site will be restored as closely as possible to original conditions.

Waste Management

Used PPE and sampling equipment will be decontaminated to the extent possible to remove gross contamination, contained, and disposed in onsite dumpsters. On the basis of the nature of the sampling activities, it is assumed that these wastes will not be hazardous.

Data Management, Review, and Usability

Data Management

Hard copy and electronic data (field and laboratory) will be tracked, stored, handled, and managed. Field activities will be recorded in project logbooks and on the applicable standard field forms as indicated in Worksheet #21 (Field SOPs) in the UFP-QAPP for an SI for PFAS (CH2M 2020). Site maps will be maintained, and sample locations will be updated on the maps as necessary. Field and analytical data will be consolidated and maintained within a proprietary electronic database management system. The database management system will be used for storage of electronic data, validation of data, querying data for analysis, and preparation of final data tables and development of Environmental Restoration Information System deliverables.

Documents and Records

Project-related data, including field logs, field forms, chain-of-custody forms, correspondence, and project reports will be maintained in hard copy and/or electronic format (PDF). These documents will be maintained by the Jacobs FTL in a field file while work is taking place and upon demobilization. The project field documents and records, electronic field data, PDF formatted laboratory data, project QAPP and reports will be maintained on a Jacobs project SharePoint site.

Data Review

A three-step data review process (verification, validation, and usability assessment) will be used to examine the collected data so that only scientifically sound data of known and documented quality are used to make environmental decisions. Worksheets #34 through #37 (Data Verification Inputs, Data Verification Procedures, Data Validation Procedures, and Data Usability Assessment) in the UFP-QAPP for an SI for PFAS (CH2M 2020) describe the process and criteria in detail.

Analytical data obtained during the project will undergo data validation by a qualified Jacobs chemist according to the specifications provided in Worksheet #36 (Data Validation Procedures) in the UFP-QAPP for an SI for PFAS (CH2M 2020). Documentation of the data validation process and the results will be provided in an appendix to the SI report.

Data Usability

The data usability assessment is an evaluation based on the results of data validation in the context of the overall project decisions and objectives. The assessment is used to determine whether the project execution and resulting data meet the project DQOs (Worksheet #11). Both the sampling and analytical activities must be considered, with the ultimate goal of assessing whether the final, qualified results support the decisions to be made with the data. Worksheet #37 (Data Usability Assessment) in the UFP-QAPP for an SI for PFAS (CH2M 2020) describes the process in detail.

As part of the data usability assessment, field data will be compiled from field logs and presented in tables listing the sampling details, field observations, and field parameter measurements. Field data will be used to refine the understanding of site conditions and to update the CSM, as appropriate. Before data presentation and evaluation, validated analytical data will be processed to identify the "best result" for a given sample based on unique location, time, medium, and depth. The best result will then be used to compare to the applicable PALs, to assess the presence of PFAS contamination. Best-result processing is needed to produce a single representative value for each sample because of multiple records that may result from the analysis of field duplicates (FDs).

A protocol has been developed that will be used to identify the best result for each sample in the project database when FDs are collected, using the following general logic:

- If all results for a given sample are qualified as detected in both the FD and parent sample and found to be usable, the maximum detected concentration will be selected as the best result.
- If some results for a given sample are qualified as detected and some qualified as nondetected in the FD pair, then the maximum detected result will be selected as best result.
- If all results for a given sample are qualified as nondetected, then the result with the lowest limit of quantitation (LOQ) will be selected as the best result.

If not rejected, flagged data will be used in the same way as the nonflagged data.

Reporting

Following completion of the investigation, the data will be reported in an SI report that will include field documentation. The specifications for reporting data collected for this project are described in Worksheet #11.

Project Schedule

Table 14-2. Project Schedule

UFP-QAPP Addendum, PFAS SI, IAAAP, Middletown, Iowa

Activity	Responsible Party	Planned Start Date	Planned Completion Date	Deliverable(s)	Deliverable Due Date
UFP-QAPP Addendum	Jacobs	April 2022	January 2023	Final UFP-QAPP	January 2023
Permitting/field mobilization/monitoring well installation	Jacobs	January 2023	February 2023	N/A	N/A
Groundwater sampling/surveying	Jacobs	February 2023	February 2023	N/A	N/A
Data management	Jacobs	February 2023	May 2023	Database submittal	May 2023
Evaluate data and prepare SI report	Jacobs	May 2023	November 2024	Final SI report	November 2024

N/A = not applicable

SI = Site Inspection

Worksheet #15: Project Action Limits and Laboratory-specific Detection/Quantitation Limits

One of the primary goals of this project-specific QAPP Addendum is to select the appropriate analytical methods to achieve DLs, limit of detections (LODs), and/or LOQs that will satisfy the overall project DQOs (as defined in Worksheet #11 [Project/Data Quality Objectives]). To determine whether the laboratory's DL, LOD, and LOQ will meet the analytical DQO's; the DLs, LODs, and LOQs are compared to the following project action limit (PAL):

- USEPA RSL for Tap Water (May 2022 [USEPA 2022]) HQ = 0.1 in accordance with the memorandum *Investigating Per- and Polyfluoroalkyl Substances within the Department of Defense Cleanup Program* (DoD 2022).

Table 15-1 presents the PALs for groundwater with respect to the current laboratory analytical DL, LOD, and LOQ for each listed target compound. Analytical methods with the lowest possible LOQs have been selected in order to meet PALs.

- If the LOQ is below the PAL, the LOD and/or the LOQ are sufficient for quantitative use in the data gap evaluation. In situations where the LOD/LOQ are not below the PAL, the target DL may be a qualitative indicator of presence or absence, although the use of the DL is a least preferred approach to screening level objective evaluations. In addition, chemical-specific factors (mobility and toxicity) may be evaluated on a more qualitative basis.
- Note that sample dilution, because of target and or nontarget compounds, concentrations or matrix interference may prevent DLs, LODs, or LOQs from being achieved. The samples must be initially analyzed undiluted when reasonable. If a dilution is necessary, then both the original and diluted result must be delivered. Samples that are not analyzed undiluted must be supported by matrix interference documentation such as sample viscosity, color, odor, or results from other analyses of the same sample to show that an undiluted sample is not possible.

Table 15-1. Groundwater Target Analytes, Methods, Action Levels, and Control Limits

UFP-QAPP Addendum, PFAS SI, IAAAP, Middletown, Iowa

Method	Chem Group	Analyte	CAS Number	Tap Water RSL (ng/L)[a]	Laboratory-specific			DoD QSM Control Limits	
					DL	LOD	LOQ	LCS and MS/MSD Recovery %	LCSD and/or MSD RPD (%)
QSM Version 5.4, Table B-15	PFAS	N-ethylperfluoro-1-octanesulfonamidoacetic acid (EtFOSAA)	2991-50-6	—	2	4	8	61-135	30
QSM Version 5.4, Table B-15	PFAS	N-methylperfluoro-1-octanesulfonamidoacetic acid (MeFOSAA)	2355-31-9	—	2	4	8	65-136	30
QSM Version 5.4, Table B-15	PFAS	Perfluoro-1-butanesulfonic acid (PFBS)	375-73-5	600	1	2	4	72-130	30
QSM Version 5.4, Table B-15	PFAS	Perfluorohexanesulfonic acid (PFHxS)	355-46-4	39	1	2	4	68-131	30
QSM Version 5.4, Table B-15	PFAS	Perfluoro-n-decanoic acid (PFDA)	335-76-2	—	1	2	4	71-129	30
QSM Version 5.4, Table B-15	PFAS	Perfluoro-n-dodecanoic acid (PFDoA)	307-55-1	—	1	2	4	72-134	30
QSM Version 5.4, Table B-15	PFAS	Perfluoro-n-heptanoic acid (PFHpA)	375-85-9	—	1	2	4	72-130	30
QSM Version 5.4, Table B-15	PFAS	Perfluoro-n-hexanoic acid (PFHxA)	307-24-4	—	1	2	4	72-129	30
QSM Version 5.4, Table B-15	PFAS	Perfluoro-n-nonanoic acid (PFNA)	375-95-1	6.0	1	2	4	69-130	30
QSM Version 5.4, Table B-15	PFAS	Perfluoro-n-octanoic acid (PFOA)	335-67-1	6.0	1	2	4	71-133	30

Table 15-1. Groundwater Target Analytes, Methods, Action Levels, and Control Limits

UFP-QAPP Addendum, PFAS SI, IAAAP, Middletown, Iowa

Method	Chem Group	Analyte	CAS Number	Tap Water RSL (ng/L)[a]	Laboratory-specific			DoD QSM Control Limits	
					DL	LOD	LOQ	LCS and MS/MSD Recovery %	LCSD and/or MSD RPD (%)
QSM Version 5.4, Table B-15	PFAS	Perfluoro-n-tetradecanoic acid (PFTeDA)	376-06-7	—	2	4	8	71-132	30
QSM Version 5.4, Table B-15	PFAS	Perfluoro-n-tridecanoic acid (PFTrDA)	72629-94-8	—	1	2	4	65-144	30
QSM Version 5.4, Table B-15	PFAS	Perfluoro-n-undecanoic acid (PFUdA)	2058-94-8	—	1	2	4	69-133	30
QSM Version 5.4, Table B-15	PFAS	Perfluorooctanesulfonic acid (PFOS)	1763-23-1	4.0	1.5	2	4	65-140	30
QSM Version 5.4, Table B-15	PFAS	11-chloroeicosafluoro-3-oxaundecane-1-sulfonicacid (11Cl-PF3OUdS)	756426-58-1	—	2	4	8	70-130	30
QSM Version 5.4, Table B-15	PFAS	9-chlorohexadecafluoro-3-oxanonane-1-sulfonic acid (9Cl-PF3ONS)	763051-92-9	—	2	4	8	70-130	30
QSM Version 5.4, Table B-15	PFAS	4,8-dioxa-3H-perfluorononanoic acid (ADONA)	919005-14-4	—	2	4	8	70-130	30
QSM Version 5.4, Table B-15	PFAS	Hexafluoropropylene oxide dimer acid (HFPO-DA)	13252-13-6	6.0	2	4	8	70-150	30
QSM Version 5.4, Table B-15	PFAS	6:2 Fluorotelomer sulfonate (6:2 FTS)	27619-97-2	—	2	4	8	64-140	30
QSM Version 5.4, Table B-15	PFAS	8:2 Fluorotelomer sulfonate (8:2 FTS)	39108-34-4	—	2	4	8	67-138	30

Table 15-1. Groundwater Target Analytes, Methods, Action Levels, and Control Limits

UFP-QAPP Addendum, PFAS SI, IAAAP, Middletown, Iowa

Method	Chem Group	Analyte	CAS Number	Tap Water RSL (ng/L)[a]	Laboratory-specific			DoD QSM Control Limits	
					DL	LOD	LOQ	LCS and MS/MSD Recovery %	LCSD and/or MSD RPD (%)
QSM Version 5.4, Table B-15	PFAS	Perfluorobutanoic acid (PFBA)	375-22-4	—	1	2	4	73-129	30
QSM Version 5.4, Table B-15	PFAS	Perfluoropentanoic acid (PFPA)	2706-90-3	—	1	2	4	72-129	30

[a] In accordance with DoD technical guidance (DoD 2022), the value shown is the residential scenario RSL for tap water based on a target cancer risk of 1×10^{-6} and target hazard quotient of 0.1 (USEPA 2022).

DL = detection limit
LCS = laboratory control sample
LCSD = laboratory control sample duplicate
LOD = limit of detection
LOQ = limit of quantitation
MS = matrix spike
MSD = matrix spike duplicate
ng/L = nanogram(s) per liter
RPD = relative percent difference
RSL = Regional Screening Level

Worksheet #17: Sampling Design and Rationale

This worksheet describes the design and rationale for the investigation activities.

Investigation Design and Rationale

The following subsections describe the proposed groundwater sample collection to evaluate whether PFAS contamination exists at the AOPI.

Numbers and Locations of Samples

Groundwater sample collection is needed at the AOPI to assess the presence or absence of PFAS contamination. Groundwater sample locations were selected upgradient of, within, cross-gradient from, and downgradient of potential release areas. The overburden aquifer will be sampled as this is the first encountered groundwater-bearing zone at IAAAP, and therefore the most likely aquifer to identify PFAS in groundwater if PFAS is present at the AOPI.

No monitoring well network exists at the Current Fire Station. Therefore, five new monitoring wells will be installed; proposed locations are shown on Figure 11-1. These new wells will be installed to a depth of up to 30 feet bgs. The soil cuttings will be continuously sampled and logged for lithologic information. No soils samples will be collected and submitted to a laboratory for analytical analysis. Because the groundwater flow direction is an uncertainty, monitoring wells are proposed to serve as cross-gradient locations. These wells will provide additional hydraulic gradient information and can support nature and extent delineation, if an RI is warranted for this AOPI in the future. Proposed well locations are summarized below:

- Upgradient well: CFS-MW01 (northwest of AFFF storage area)
- Potential release area well: CFS-MW02 (adjacent to AFFF storage area)
- Downgradient well: CFS-MW03 (southeast of AFFF storage area)
- Down-/cross-gradient well: CFS-MW04 (east of AFFF storage area)
- Cross-gradient well: CFS-MW05 (southwest of AFFF storage area)

Figure 11-1 shows the monitoring well locations of the proposed groundwater samples at the Current Fire Station.

All groundwater samples will be analyzed for a target list of 22 PFAS that includes 18 analytes defined in USEPA Method 537 version 1.1 and 4 additional PFAS identified in the Army's 2018 PFAS guidance, as referenced in Table 15-1.

Time of Sample Collection

The project schedule presented in Worksheets #14 and #16 indicates a planned start date of February 2023 for groundwater sampling activities. The proposed sampling activities will adequately identify whether PFAS is present in groundwater to meet the project DQOs.

Contingency Sampling and Decision Process

If the locations specified above cannot be sampled in accordance with the proposed project schedule (Worksheets #14 and #16), then they will be sampled at earliest possible date. Note that the new proposed monitoring well locations at the Current Fire Station (Figure 11-1) may require slight adjustments made in the field to account for underground or overhead obstructions.

Worksheet #18: Sampling Locations and Methods

Table 18-1 summarizes the sampling matrix, number of samples to be collected, and analytical parameters for the samples described in Worksheet #17 (Sampling Design and Rationale). QA/QC samples will be collected as specified in Worksheet #20 of the UFP-QAPP for an SI for PFAS (CH2M 2020). SOPs that will be used for sampling are specified in Worksheet #21 of the UFP-QAPP for an SI for PFAS (CH2M 2020). Revised SOP-01 and SOP-04 are included as Appendix A.

Table 18-1. Sample Locations and Sampling SOP Requirements

UFP-QAPP Addendum, PFAS SI, IAAAP, Middletown, Iowa

Matrix	Depth (Feet bgs)	Analytical Group	Concentration Level	Estimated Number of Samples (Identify FDs)	Sampling SOP Reference	Rationale for Sampling Location
Groundwater	Current Fire Station: CFS-MW01—Up to 30 CFS-MW02—Up to 30 CFS-MW03—Up to 30 CFS-MW04—Up to 30 CFS-MW05—Up to 30	PFAS	N/A	Up to 5 (1 FD)[a]	SOP-01 SOP-02 SOP-04 through SOP-07 and SOP-09 through SOP-11[b]	Groundwater sample locations were selected upgradient of the AFFF storage areas, near the AFFF storage area, cross-gradient of the AFFF storage areas and downgradient of AFFF storage area. See Worksheet #17 for details.

[a] QC samples will include one matrix spike, one matrix spike duplicate, two FDs, two equipment blanks, and two source blanks.

[b] SOPs are listed in Worksheet #21 of the UFP-QAPP for an SI for PFAS (CH2M 2020).

AOPI = area of potential interest

bgs = below ground surface

FD = field duplicate

N/A = not applicable

SOP = standard operating procedure

Worksheets #19 and #30: Sample Containers, Preservation, and Holding Times

Table 19-1 summarizes the analytical methods for each sampling matrix, including the required sample volume, container, preservation, and holding time requirements. Additional information about the laboratory analytical SOPs is provided in Worksheet #23 (Analytical SOPs).

Table 19-1. Sample Containers, Preservation, and Hold Times

UFP-QAPP Addendum, PFAS SI, IAAAP, Middletown, Iowa

Laboratory:	Pace Analytical Services, LLC.	Certification:	DoD ELAP Certification v. 5.4
	106 Vantage Point Dr	Accreditation Expiration:	11/18/2024
	West Columbia, SC 29172	Shipment:	FedEx Overnight services
PM:	Catherine Dover	Standard Turnaround Time:	21 calendar days
	803-791-9700		

Analytical Group	Method	Matrix	Container Type	Preservation Requirements	Maximum Holding Time
PFAS by Isotope DL	QSM Version 5.4, Table B-15	Groundwater	1 × 250-mL HDPE with polyethylene screw cap	Cool, ≤ 6°C	28 days to extraction/28 days after extraction
		IDW-L	1 × 250-mL HDPE with polyethylene screw cap		
		IDW-S	1 × 4-oz HDPE with polyethylene screw cap		
VOC	SW8260D	IDW-L	3 × 40-mL VOA vial	No headspace, HCL to pH < 2, ≤ 6°C	14 days
TCLP VOC	SW1311/8260D	IDW-S	1 × 4-oz glass jar	No headspace; cool, ≤ 6°C	14 days to TCLP extraction/14 days to analysis
SVOCs	SW8270E	IDW-L	2 × 1-L amber bottle	Cool, ≤ 6°C	7 days until extraction, 40 days after extraction
TCLP SVOC	SW1311/8270E	IDW-S	1 × 4-oz glass jar[a]		14 days until TCLP extraction, 7 days to SVOC extraction, 40 days to analysis
Pesticides	SW8081B	IDW-L	2 × 1-L amber bottle	Cool, ≤ 6°C	7 days until extraction, 40 days after extraction
TCLP pesticides	SW1311/8081B	IDW-S	1 × 4-oz glass jar[a]		14 days until TCLP extraction, 7 days to Pest

Table 19-1. Sample Containers, Preservation, and Hold Times

UFP-QAPP Addendum, PFAS SI, IAAAP, Middletown, Iowa

Laboratory:	Pace Analytical Services, LLC.	Certification:	DoD ELAP Certification v. 5.4
	106 Vantage Point Dr	Accreditation Expiration:	11/18/2024
	West Columbia, SC 29172	Shipment:	FedEx Overnight services
PM:	Catherine Dover	Standard Turnaround Time:	21 calendar days
	803-791-9700		

Analytical Group	Method	Matrix	Container Type	Preservation Requirements	Maximum Holding Time
					extraction, 40 days to analysis
Herbicides	SW8151A	IDW-L	2 × 1-L amber bottle	Cool, ≤ 6°C	7 days until extraction, 40 days after extraction
TCLP herbicides	SW1311/8151A	IDW-S	1 × 4-oz glass jar[a]		14 days until TCLP extraction, 7 days to Herb extraction, 40 days to analysis
Explosives	SW8330B	IDW-L	2 × 1-L amber bottle	Cool, ≤ 6°C	7 days until extraction, 40 days after extraction
		IDW-S	1 × 8-oz glass jar		14 days until extraction, 40 days to analysis
RCRA metals	SW6010D/ 6020B/7470A	IDW-L	250-mL or 500-mL poly	HNO_3 to pH < 2; Cool, ≤ 6°C	Extraction and analysis within 180 days (except mercury within 28 days)
TCLP metals	SW1311/6010D/ 6020B/7470A	IDW-S	4-oz glass jar[a]	Cool, ≤ 6°C	180 days/28 days for mercury TCLP, 180 days/28 days for mercury analysis
pH	SW9040C	IDW-L	250-mL glass or poly	None	As soon as possible
Flashpoint (must have reporting limit of >200°F)	SW1010	IDW-L	250-mL poly	None	As soon as possible

Three times the required volume will be collected for samples designated as MS/MSD samples.

[a] Parameters may be combined into two 8-oz glass containers.

°C = degree(s) Celsius

°F = degree(s) Fahrenheit

DL = detection limit

HCL = hydrochloric acid

HDPE = high-density polyethylene

HNO_3 = nitric acid

mL = milliliter

oz = ounce(s)

RCRA = Resource Conservation and Recovery Act

SVOC = semivolatile organic compound

TCLP = Toxicity Characteristic Leaching Procedure

Table 19-1. Sample Containers, Preservation, and Hold Times

UFP-QAPP Addendum, PFAS SI, IAAAP, Middletown, Iowa

Laboratory:	Pace Analytical Services, LLC.	Certification:	DoD ELAP Certification v. 5.4
	106 Vantage Point Dr	Accreditation Expiration:	11/18/2024
	West Columbia, SC 29172	Shipment:	FedEx Overnight services
PM:	Catherine Dover	Standard Turnaround Time:	21 calendar days
	803-791-9700		

Analytical Group	Method	Matrix	Container Type	Preservation Requirements	Maximum Holding Time

IDW-L= investigation-derived waste—liquid
IDW-S = investigation-derived waste—soil
L = liter
VOA = volatile organic analysis
VOC = volatile organic compound

Worksheet #23: Analytical SOPs

The following LSOP reference was provided by Pace Analytical Services, LLC.. The LSOP is provided in Appendix B. LSOPs are supplemented by internal communication systems within the laboratory to disseminate the project requirements to technical staff.

Table 23-1. Analytical SOP Reference

UFP-QAPP Addendum, PFAS SI, IAAAP, Middletown, Iowa

SOP Number	Title and Date	Definitive or Screening Data	Matrix/ Analytical Group	Equipment Type	Laboratory	Modified for Project?
ENV-SOP-WCOL-0069 v04	Determination of Per- and Polyfluoroalkyl Substances (PFAS) by LC/MS/MS (Isotopic Dilution), QSM 5.4 Table B-15 July 2022	Definitive	Aqueous/ PFAS	LC/MS/MS	Pace Analytical Services, LLC.	No

LC/MS/MS = liquid chromatography/tandem mass spectrophotometer

QSM = quality systems manual

Worksheet #28: Analytical Quality Control and Corrective Action

Worksheet #28 presents analytical QC requirements relevant to analysis of environmental samples that the laboratories will follow to produce definitive data. The purpose of the laboratory QC activities is to produce data of known quality sufficient to meet the project-specific DQOs. Laboratory QC samples will follow method-specific requirements of the DoD QSM v. 5.4 (DoD 2021, Appendix B) and/or the analytical method and presented in Table 28-1. Tables are presented only for the methods requiring validation.

Table 28-1. Summary of Calibration and Quality Control Procedures for PFAS Using LC/MS/MS with Isotope Dilution or Internal Standard Quantification in Matrices Other Than Drinking Water

UFP-QAPP Addendum, PFAS SI, IAAAP, Middletown, Iowa

QC Check	Minimum Frequency	Acceptance Criteria	Corrective Action[a]	Flagging Criteria[b]
Aqueous Sample Preparation ▪ Samples with > 1% solids may require centrifugation prior to SPE extraction. ▪ Prescreening of separate aliquots of aqueous samples is recommended.	Each sample and associated batch QC samples.	SPE must be used unless samples are known to contain high PFAS concentrations (e.g., AFFF formulations). Inline SPE is acceptable. Entire sample plus bottle rinsate must be extracted using SPE. Known high PFAS concentration samples require serial dilution be performed in duplicate. Documented project approval is needed for samples prepared by serial dilution as opposed to SPE.	Not appropriate.	Flagging is not appropriate.
Solid Sample Preparation	Each sample and associated batch QC samples.	Entire sample received by the laboratory must be homogenized prior to subsampling.	Not appropriate.	Flagging is not appropriate.
AFFF and AFFF Mixture Samples Preparation ▪ Adsorption onto bottle is negligible compared to sample concentration so subsampling is allowed. ▪ Multiple dilutions will most likely have to be reported in order to achieve the lowest LOQ possible for each analyte.	Each sample and associated batch QC samples.	Each field sample must be prepared in duplicate (equivalent to matrix duplicate). Serial dilutions must be performed to achieve the lowest LOQ possible for each analyte.	Not appropriate.	Flagging is not appropriate.

Table 28-1. Summary of Calibration and Quality Control Procedures for PFAS Using LC/MS/MS with Isotope Dilution or Internal Standard Quantification in Matrices Other Than Drinking Water

UFP-QAPP Addendum, PFAS SI, IAAAP, Middletown, Iowa

QC Check	Minimum Frequency	Acceptance Criteria	Corrective Action[a]	Flagging Criteria[b]
Sample Cleanup Procedure	Each sample and associated batch QC samples. Not applicable to AFFF and AFFF Mixture Samples.	ENVI-Carb or equivalent must be used on each sample and batch QC sample.	Not appropriate.	Flagging is not appropriate.
Mass Calibration	Instrument must have a valid mass calibration prior to any sample analysis. Mass calibration is verified after each mass calibration, prior to ICAL.	Calibrate the mass scale of the MS with calibration compounds and procedures described by the manufacturer. Mass calibration range must bracket the ion masses of interest. The most recent mass calibration must be used for every acquisition in an analytical run. Mass calibration must be verified to be ±0.5 atomic mass unit of the true value, by acquiring a full scan continuum mass spectrum of a PFAS stock standard.	If the mass calibration fails, then recalibrate. If it fails again, consult manufacturer instructions on corrective maintenance.	Flagging is not appropriate. Problem must be corrected. No samples may be analyzed under a failing mass calibration. The mass calibration is updated on an as-needed basis (e.g., QC failures, ion masses fall outside of the ±0.5 atomic mass unit of the true value, major instrument maintenance is performed, or the instrument is moved).
Mass Spectral Acquisition Rate	Each analyte, extracted internal standard analyte.	A minimum of 10 spectra scans are acquired across each chromatographic peak.	Not appropriate.	Flagging is not appropriate.

Table 28-1. Summary of Calibration and Quality Control Procedures for PFAS Using LC/MS/MS with Isotope Dilution or Internal Standard Quantification in Matrices Other Than Drinking Water

UFP-QAPP Addendum, PFAS SI, IAAAP, Middletown, Iowa

QC Check	Minimum Frequency	Acceptance Criteria	Corrective Action[a]	Flagging Criteria[b]
Calibration, Calibration Verification, and Spiking Standards	All analytes.	Standards containing both branched and linear isomers must be used when commercially available. PFAS method analytes may consist of both branched and linear isomers, but quantitative standards that contain the linear and branched isomers do not exist for all method analytes. For PFAS that do not have a quantitative branched and linear standard, identify the branched isomers by analyzing a qualitative standard that includes both linear and branched isomers and determine retention times, transitions and transition ion ratios. Quantitate samples by integrating the total response (i.e., accounting for peaks that are identified as linear and branched isomers) and relying on the ICAL that uses the linear isomer quantitative standard.	Not appropriate.	Flagging is not appropriate. Standards containing both branched and linear isomers are to be used during method validation and when reestablishing retention times, to ensure the total response is quantitated for that analyte. Technical grade standards cannot be used for quantitative analysis.

Table 28-1. Summary of Calibration and Quality Control Procedures for PFAS Using LC/MS/MS with Isotope Dilution or Internal Standard Quantification in Matrices Other Than Drinking Water

UFP-QAPP Addendum, PFAS SI, IAAAP, Middletown, Iowa

QC Check	Minimum Frequency	Acceptance Criteria	Corrective Action[a]	Flagging Criteria[b]
Sample PFAS Identification	All analytes detected in a sample.	The chemical derivation of the ion transitions must be documented. A minimum of two ion transitions (Precursor → quant ion and precursor → confirmation ion) and the ion transitions ratio per analyte are required for confirmation. Exception is made for analytes where two transitions do not exist (PFBA and PFPeA). Documentation of the primary and confirmation transitions and the ion ratio is required. In-house acceptance criteria for evaluation of ion ratios must be used and must not exceed 50–150%. Signal-to-noise ratio must be ≥ 10 for all ions used for quantification and must be ≥ 3 for all ions used for confirmation. Quant ion and confirmation ion must be present and must maximize simultaneously (±2 seconds).	Not appropriate.	PFAS identified with ion ratios that fail acceptance criteria must be flagged. Any quantitation ion peak that does not meet the maximization criteria shall be included in the summed integration and the resulting data flagged as "estimated, biased high."

Table 28-1. Summary of Calibration and Quality Control Procedures for PFAS Using LC/MS/MS with Isotope Dilution or Internal Standard Quantification in Matrices Other Than Drinking Water

UFP-QAPP Addendum, PFAS SI, IAAAP, Middletown, Iowa

QC Check	Minimum Frequency	Acceptance Criteria	Corrective Action[a]	Flagging Criteria[b]
Ion Transitions (Precursor → Product)	Every field sample, standard, blank, and QC sample.	In order to avoid biasing results high due to known interferences for some transitions, the following transitions must be used for the quantification of the following analytes: ▪ PFOA: 413 → 369 ▪ PFOS: 499 → 80 ▪ PFHxS: 399 → 80 ▪ PFBS: 299 → 80 ▪ 4:2 FTS: 327 → 307 ▪ 6:2 FTS: 427 → 407 ▪ 8:2 FTS: 527 → 507 ▪ NEtFOSAA: 584 → 419 ▪ NMeFOSAA: 570 → 419 If these transitions are not used, the reason must be technically justified and documented (e.g., alternate transition was used due to observed interferences).	Not appropriate.	Flagging is not appropriate.

Table 28-1. Summary of Calibration and Quality Control Procedures for PFAS Using LC/MS/MS with Isotope Dilution or Internal Standard Quantification in Matrices Other Than Drinking Water

UFP-QAPP Addendum, PFAS SI, IAAAP, Middletown, Iowa

QC Check	Minimum Frequency	Acceptance Criteria	Corrective Action[a]	Flagging Criteria[b]
ICAL ▪ Calibration can be linear (minimum of 5 standards) or quadratic (minimum of 6 standards); weighting is allowed. ▪ External calibration is not allowed for any analyte.	At instrument set-up and after ICV or CCV failure, prior to sample analysis.	**ICAL** Calibration can be linear (minimum of 5 standards) or quadratic (minimum of 6 standards); weighting is allowed. The isotopically labeled analog of an analyte (EIS Analyte) must be used for quantitation if commercially available (Isotope Dilution Quantitation). Commercial PFAS standards available as salts are acceptable providing the measured mass is corrected to the neutral acid concentration. Results shall be reported as the neutral acid with appropriate CAS number If a labeled analog is not commercially available, the EIS Analyte with the closest RT or chemical similarity to the analyte must be used for quantitation. (Internal Standard Quantitation) Analytes must be within 70–130% of their true value for each calibration standard ICAL must meet one of the two options below: ▪ Option 1: The RSD of the RFs for all analytes must be ≤ 20%. ▪ Option 2: Linear or non- linear calibrations must have $r^2 \geq 0.99$ for each analyte.	Correct problem, then repeat ICAL.	Flagging is not appropriate.
RT Window Position Establishment ▪ Calculated for each analyte and EIS.	Once per ICAL and at the beginning of the analytical sequence.	Position shall be set using the midpoint standard of the ICAL curve when ICAL is performed. On days when ICAL is not performed, the initial CCV is used.	Not appropriate.	Flagging is not appropriate.

Table 28-1. Summary of Calibration and Quality Control Procedures for PFAS Using LC/MS/MS with Isotope Dilution or Internal Standard Quantification in Matrices Other Than Drinking Water

UFP-QAPP Addendum, PFAS SI, IAAAP, Middletown, Iowa

QC Check	Minimum Frequency	Acceptance Criteria	Corrective Action[a]	Flagging Criteria[b]
RT Window Width ▪ Calculated for each analyte and EIS	Every field sample, standard, blank, and QC sample.	RT of each analyte and EIS analyte must fall within 0.4 minutes of the predicted retention times from the daily calibration verification or, on days when ICAL is performed, from the midpoint standard of the ICAL. Analytes must elute within 0.1 minute of the associated EIS. This criterion applies only to analyte and labeled analog pairs.	Correct problem and reanalyze samples.	Flagging is not appropriate.
ISC	Prior to analysis and at least once every 12 hours.	Analyte concentrations must be at LOQ; concentrations must be within ±30% of their true values.	Correct problem, rerun ISC. If problem persists, repeat ICAL.	Flagging is not appropriate. No samples shall be analyzed until ISC has met acceptance criteria. ISC can serve as the initial daily CCV.
ICV	Once after each ICAL, analysis of a second source standard prior to sample analysis.	Analyte concentrations must be within ±30% of their true values.	Correct problem, rerun ICV. If problem persists, repeat ICAL.	Flagging is not appropriate. No samples shall be analyzed until calibration has been verified.

Table 28-1. Summary of Calibration and Quality Control Procedures for PFAS Using LC/MS/MS with Isotope Dilution or Internal Standard Quantification in Matrices Other Than Drinking Water

UFP-QAPP Addendum, PFAS SI, IAAAP, Middletown, Iowa

QC Check	Minimum Frequency	Acceptance Criteria	Corrective Action[a]	Flagging Criteria[b]
CCV	Prior to sample analysis, after every 10 field samples, and at the end of the analytical sequence.	Concentration of analytes must range from the LOQ to the mid-level calibration concentration. Analyte concentrations must be within ±30% of their true value.	Immediately analyze two additional consecutive CCVs. If both pass, samples may be reported without reanalysis. If either fails, or if two consecutive CCVs cannot be run, perform corrective action(s) and repeat CCV and all associated samples since last successful CCV. Alternately, recalibrate if necessary; then reanalyze all associated samples since the last acceptable CCV.	If reanalysis cannot be performed, data must be qualified and explained in the Case Narrative. Apply Q-flag to all results for the specific analyte(s) in all samples since the last acceptable calibration verification. Results may not be reported without valid CCVs. ISC can serve as a bracketing CCV.

Table 28-1. Summary of Calibration and Quality Control Procedures for PFAS Using LC/MS/MS with Isotope Dilution or Internal Standard Quantification in Matrices Other Than Drinking Water

UFP-QAPP Addendum, PFAS SI, IAAAP, Middletown, Iowa

QC Check	Minimum Frequency	Acceptance Criteria	Corrective Action[a]	Flagging Criteria[b]
Instrument Blanks	Immediately following the highest standard analyzed and daily prior to sample analysis.	Concentration of each analyte must be ≤ ½ the LOQ. Instrument blank must contain EIS to enable quantitation of contamination.	If acceptance criteria are not met after the highest calibration standard, calibration must be performed using a lower concentration for the highest standard until acceptance criteria is met. If sample concentrations exceed the highest allowed standard and the sample(s) following exceed this acceptance criteria (>½ LOQ), they must be reanalyzed.	Flagging is only appropriate in cases when the sample cannot be reanalyzed and when there is no more sample left. No samples shall be analyzed until instrument blank has met acceptance criteria. *Note:* Successful analysis following the highest standard analyzed determines the highest concentration that carryover does not occur. When the highest standard analyzed is not part of the calibration curve, it cannot be used to extend out the calibration range, it is used only to document a higher concentration at which carryover still does not occur.

Table 28-1. Summary of Calibration and Quality Control Procedures for PFAS Using LC/MS/MS with Isotope Dilution or Internal Standard Quantification in Matrices Other Than Drinking Water

UFP-QAPP Addendum, PFAS SI, IAAAP, Middletown, Iowa

QC Check	Minimum Frequency	Acceptance Criteria	Corrective Action[a]	Flagging Criteria[b]
EIS Analytes	Every field sample, standard, blank, and QC sample.	Added to solid sample prior to extraction. Added to aqueous samples, into the original container, prior to extraction. For aqueous samples prepared by serial dilution instead of SPE, added to final dilution of samples prior to analysis. EIS Analyte recoveries must be within 50% to 150% of ICAL midpoint standard area or area measured in the initial CCV on days when an ICAL is not performed.	Correct problem. If required, re-extract and reanalyze associated field and QC samples. If recoveries are acceptable for QC samples, but not field samples, the field samples must be re-extracted and analyzed (greater dilution may be needed). Samples may be re- extracted and analyzed outside of hold times, as necessary for corrective action associated with QC failure.	Apply Q-flag and discuss in the Case Narrative only if reanalysis confirms failures in exactly the same manner. Failing analytes shall be thoroughly documented in the Case Narrative. EIS should be 96% (or greater) purity. When the impurity consists of the unlabeled analyte, the EIS can result in a background artifact in every sample, standard and blank, if the EIS is fortified at excessive concentrations.

Table 28-1. Summary of Calibration and Quality Control Procedures for PFAS Using LC/MS/MS with Isotope Dilution or Internal Standard Quantification in Matrices Other Than Drinking Water

UFP-QAPP Addendum, PFAS SI, IAAAP, Middletown, Iowa

QC Check	Minimum Frequency	Acceptance Criteria	Corrective Action[a]	Flagging Criteria[b]
MB	One per preparatory batch.	No analytes detected >½ LOQ or > 1/10 the amount measured in any sample or 1/10 the regulatory limit, whichever is greater.	Correct problem. If required, re-extract and reanalyze MB and all QC samples and field samples processed with the contaminated blank. Samples may be re-extracted and analyzed outside of hold times, as necessary for corrective action associated with QC failure. Examine the project-specific requirements. Contact the client as to additional measures to be taken.	Results may not be reported without a valid MB. If reanalysis cannot be performed, data must be qualified and explained in the Case Narrative. Apply B-flag to all results for the specific analyte(s) in all samples in the associated preparatory batch. Flagging is appropriate only in cases where the samples cannot be reanalyzed.

Table 28-1. Summary of Calibration and Quality Control Procedures for PFAS Using LC/MS/MS with Isotope Dilution or Internal Standard Quantification in Matrices Other Than Drinking Water

UFP-QAPP Addendum, PFAS SI, IAAAP, Middletown, Iowa

QC Check	Minimum Frequency	Acceptance Criteria	Corrective Action[a]	Flagging Criteria[b]
LCS	One per preparatory batch.	Blank spiked with all analytes at a concentration ≥ LOQ and ≤ the mid-level calibration concentration. Acceptance limits listed in Worksheet #15	Correct problem, then re-extract and reanalyze the LCS and all samples in the associated preparatory batch for failed analytes if sufficient sample material is available. Samples may be re-extracted and analyzed outside of hold times, as necessary for corrective action associated with QC failure. Examine the project-specific requirements. Contact the client as to additional measures to be taken.	If reanalysis cannot be performed, apply Q-flag to specific analyte(s) in all samples in the associated preparatory batch and noted in the Case Narrative.

Table 28-1. Summary of Calibration and Quality Control Procedures for PFAS Using LC/MS/MS with Isotope Dilution or Internal Standard Quantification in Matrices Other Than Drinking Water

UFP-QAPP Addendum, PFAS SI, IAAAP, Middletown, Iowa

QC Check	Minimum Frequency	Acceptance Criteria	Corrective Action[a]	Flagging Criteria[b]
MS	One per preparatory batch. Not required for aqueous samples prepared by serial dilution instead of SPE.	Sample spiked with all analytes at a concentration ≥ LOQ and ≤ the mid-level calibration concentration. Acceptance limits listed in Worksheet #15.	Examine the project- specific requirements. Contact the client as to additional measures to be taken.	For the specific analyte(s) in the parent sample, apply J-flag if acceptance criteria are not met and explain in the Case Narrative.
MSD or MD	For MSD: One per preparatory batch. For MD: Each aqueous sample prepared by serial dilution instead of SPE.	For MSD: Sample spiked with all analytes at a concentration ≥ LOQ and ≤ the mid-level calibration concentration. Acceptance limits listed in Worksheet #15. RPD ≤ 30% (between MS and MSD or sample and MD).	Examine the project- specific requirements. Contact the client as to additional measures to be taken.	For the specific analyte(s) in the parent sample, apply J-flag if acceptance criteria are not met and explain in the Case Narrative. For Sample/MD: RPD criteria apply only to analytes whose concentration in the sample is ≥ LOQ.

Table 28-1. Summary of Calibration and Quality Control Procedures for PFAS Using LC/MS/MS with Isotope Dilution or Internal Standard Quantification in Matrices Other Than Drinking Water

UFP-QAPP Addendum, PFAS SI, IAAAP, Middletown, Iowa

QC Check	Minimum Frequency	Acceptance Criteria	Corrective Action[a]	Flagging Criteria[b]
Post-Spike Sample	Only applies to aqueous samples prepared by serial dilution instead of SPE that have reported value of < LOQ for analyte(s).	Spike all analytes reported as < LOQ into the dilution that the result for that analyte is reported from. The spike must be at the LOQ concentration to be reported for this sample as < LOQ. When analyte concentrations are calculated as < LOQ, the post-spike for that analyte must recover within 70–130% of its true value.	When analyte concentrations are calculated as < LOQ, and the spike recovery does not meet the acceptance criteria, the sample, sample duplicate, and post-spike sample must be reanalyzed at consecutively higher dilutions until the criteria is met.	Flagging is not appropriate. When analyte concentrations are calculated as < LOQ, results may not be reported without acceptable post-spike recoveries.

[a] Corrective action associated with project work will be documented, and records will be maintained by the laboratory. The analysis technician is responsible for corrective actions.

[b] Flagging criteria will be applied when acceptance criteria were not met (corrective action was not successful) or corrective action was not performed.

[c] DoD (2021).

Table 28-1. Summary of Calibration and Quality Control Procedures for PFAS Using LC/MS/MS with Isotope Dilution or Internal Standard Quantification in Matrices Other Than Drinking Water

UFP-QAPP Addendum, PFAS SI, IAAAP, Middletown, Iowa

QC Check	Minimum Frequency	Acceptance Criteria	Corrective Action[a]	Flagging Criteria[b]

AFFF = aqueous film forming foam
CCV = continuing calibration verification
EIS = extracted internal standard
FTS = fluorotelomer sulfonate
ICAL = initial calibration
ICV = initial calibration verification
ISC = instrument sensitivity check
LCS = laboratory control sample
LOQ = limit of quantitation
MB= method blank
MD = matrix duplicate
MS = matrix spike
NEtFOSAA = N-ethyl perfluorooctanesulfonamidoacetic acid
NMeFOSAA = N-methylperfluorooctane sulfonamidoacetic acid
PFBA = perfluorobutanoic acid
PFBS = perfluorobutanesulfonic acid
PFHxS = perfluorohexanesulfonic acid
PFOA = perfluorooctanoic acid
PFOS = perfluorooctanesulfonic acid
PFPeA = perfluoro-n-pentanoic acid
QC = quality control
RSD = relative standard deviation
RT = retention time
SPE = solid phase extraction

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Appendix A
Field Standard Operating Procedures

SOP-01
Monitoring Well Installation and Development

SOP-01: Monitoring Well Installation and Development

1.0 Purpose

This standard operating procedure (SOP) describes the methodology for installing and developing monitoring wells using direct-push technology (DPT), hollow stem auger (HSA), and rotary or sonic drilling methods.

2.0 Scope

This procedure applies to Jacobs, personnel and subcontractors engaged in the installation and development of monitoring wells.

This SOP focuses on the most commonly used monitoring well installation and development methods anticipated for the USACE project and should be used in conjunction with other applicable project SOPs, including the following:

- *SOP-04, Equipment Decontamination Procedures*
- *SOP-05, Organic Vapor Monitoring and Air Monitoring*
- *SOP-06, Field Water Quality Measurements and Calibration*
- *SOP-07, Note Taking and Field Logbooks*
- *SOP-08, Site Reconnaissance, Preparation, and Restoration*
- *SOP-11, Water Level Measurements*
- *SOP-12, Utility Clearance for Intrusive Operations*
- *SOP-13, Soil Boring Logging*

3.0 General

The primary function of a monitoring well is to provide a representative sample of groundwater as it exists in the formation. The wells will be installed in accordance with Iowa Department of Natural Resources, Iowa Administrative Code (IAC) 567 Chapter 49 (IDNR, 2008) and USACE EM-1110-1-4000 (USACE, 1998), as appropriate.

The overall objectives of monitoring well development are as follows:

- Restoring the aquifer properties near the well boring disturbed during drilling
- Removing the finer-grained materials from the surrounding filter pack that may otherwise interfere with water quality analyses
- Improving the hydraulic characteristics of the filter pack and hydraulic communication between the well and the hydrologic unit adjacent to the well screen
- Removing all water introduced into the borehole while drilling

Project staff are to always wear appropriate personal protective equipment (PPE) as prescribed by the health and safety plan (HSP).

4.0 Responsibilities

4.1 Project Manager

The Project Manager (PM) is responsible for providing adequate resources and ensuring that field staff have adequate experience and training to successfully comply with and execute project-specific SOPs, and implement the project health, safety, and environment (HS&E) program. The PM will solicit the appropriate technical expertise to ensure that the project has identified the best sampling methods and technology for the job given the current understanding of the site and project goals.

4.2 Health and Safety Manager

The Health and Safety Manager (HSM) is assigned to oversee the site-specific HS&E program and ensure overall compliance with project HS&E requirements. The HSM conducts PPE evaluations, selects the appropriate PPE for the project, lists the requirements in the HSP, coordinates with the Field Manager (FM) and/or Safety Coordinators (SC) to complete and certify the PPE program, and conducts project health and safety audits on the effectiveness of the HS&E program.

4.3 Safety Coordinator

The role of SC is to assist in implementing the project HSP and may either be assigned to the FM or designated to Field Team Leaders (FTL) by the FM. The SC assists the HSM and FM with the HS&E program, implements the project PPE requirements, and receives input from project staff regarding HS&E hazards, PPE requirements, and the effectiveness of ongoing HS&E procedures.

4.4 Field Team Leader

The FTL is assigned to oversee and facilitate monitoring well installation and development in the field. The FTL should ensure that monitoring wells are installed and developed in accordance with this SOP. The FTL should also be required to make rational and justifiable decisions when deviations from this SOP are necessary because of field conditions or unforeseen problems. The FTL should consult the FM if significant deviations are necessary because of field conditions. The FTL should also ensure that the applicable requirements of the HSP and the Project-specific Waste Management Plan are followed.

5.0 Procedures

- On arrival at the site, observe the site conditions and assess potential HS&E hazards or issues. Don the required PPE in accordance with the site HSP.
- Set up a staging area and organize sampling equipment near the sample location.
- Arrange sample containers, sampling equipment, and decontaminated equipment.
- Set up and calibrate instruments in accordance with manufacturer's instructions, *SOP-05, Organic Vapor Monitoring and Air Monitoring*, and *SOP-06, Field Water Quality Measurements and Calibration*.
- Decontaminate equipment/instruments in accordance with *SOP-04, Equipment Decontamination Procedures*.

5.1 Equipment and Supplies

The below equipment and supplies may be required for monitoring well installation depending on the well design and well development. Well development commonly involves using equipment to surge, pump, and/or bail a monitoring well.

Avoid using equipment containing Teflon or other forms of polytetrafluoroethylene (PTFE), "Fluoropolymer" well materials, or any materials containing per- and polyfluorinated alkyl substance (PFAS), where that material may be in contact with groundwater or soil samples.

All personnel who collect or handle soil or groundwater samples, or materials potentially in contact with samples will not wear or use the following: Gore-Tex brand or similar clothing, clothing treated with Scotch-guard brand or similar water repellent, Fluoropolymer-coated Tyvek, and Fire resistant clothing with fluorochemical treatment. Weather-proof log books with fluorochemical coatings are not acceptable.

Materials that may be required for Monitoring well installation include:

- Well casing and well screen (continuous-slot)
- Stainless-steel centralizers (if required)
- PFAS-free bentonite (pellets, powder, or chips)
- Filter pack and buffer sand
- PFAS-free potable water
- High-solids bentonite slurry for grouting (a solids content between 20 and 30 percent by weight of water)
- 4-inch, square channel, locking protective, 6-foot steel casing
- 2-inch, 6-foot long guard posts
- Deionized water and high-pressure steamer/cleaner
- Long-handled bristle brushes
- Drill rig capable of installing wells to the desired depth with the proper diameter in the expected formation materials and conditions
- Weighted tape measure with 0.1-foot increments
- Water level probe with 0.01-foot increments
- Peristaltic sampling pump or similar pump (submersible and gear pumps are not recommended because of pump damage from fine sediments)
- Disposable high density polyethylene tubing
- Water quality monitoring instrument(s) capable of measuring dissolved oxygen (DO), oxidation-reduction potential (ORP), conductivity, pH, turbidity, and temperature
- Surge block on a cable or line
- Well construction forms
- Well locks (keyed alike)
- Clean Department of Transportation (DOT)–approved 55-gallon steel drums with labels
- Clean 5-gallon buckets
- PPE (as required in the HSP)
- Field notebook (not Rite-in-the-Rain) and Well Development Datasheet

- Metal clipboard
- Pen (not Sharpie)
- Decontamination equipment and materials, as appropriate
- Paper towels or Kim wipes
- Garbage bags

5.2 Soil and Bedrock Borings

The drilling rigs (DPT, HSA, and/or sonic or rotary) will be set up and operated in accordance with standard drilling practices and in a manner consistent with the safe and efficient operation of the equipment. In addition to the general federal and state guidelines, borehole drilling, and soil sample collection (for logging purposes only) will be performed in accordance with the latest American Society for Testing and Materials (ASTM) methods D-6282-98 (Standard Guide for Direct-Push Soil Sampling for Environmental Site Characterizations), D-1452 (Soil Investigation and Sampling by Auger Borings), D-1586 (Penetration Test and Split-barrel Sampling of Soils), and D-1587, where appropriate.

Subsurface soils may be continuously logged during drilling and will follow *SOP-13, Soil Boring Logging*. The sampling and drill tools will be in good condition on the interior (i.e., free of pitting and scratches which could prevent adequate sampler decontamination.

At certain locations of the site, bedrock will be encountered at shallow depths (as little as 2 feet bgs). Bedrock varies by locality and may consist of moderately to severely weathered dolomite/limestone and shale to competent dolomite/limestone. Drilling methods into the bedrock may include roto-sonic, or air and/or mud rotary. In addition, NQ-HQ rock coring may be required at a subset of locations.

- Field equipment and supplies will be placed on clean plastic sheeting to minimize contamination of the materials.
- Set up and calibrate instruments in accordance with manufacturer's instructions and *SOP-05, Organic Vapor Monitoring and Air Monitoring*.
- Ensure that equipment and tooling used downhole or contacting soil samples at ground surface is clean. Decontaminate non-dedicated equipment and tooling in accordance with *SOP-04, Equipment Decontamination Procedures*.
- Verify that site utilities have been cleared in accordance with *SOP-12, Utility Clearance for Intrusive Operations*.
- Place clean plastic sheeting on ground surface or surface on which the soil cores will be logged and sampled. It is preferable to log the soil cores beneath a canopy or other shade implemented to minimize volatilization of compounds within the soil core.
- The augers or samplers shall be advanced to the top depth of the next successive sample interval or the desired sampling depth at a rate that allows for maximum recovery within the sampler. Samplers advanced at too quickly may result in poor recovery or sample quality.
- The drill rods and samplers shall be removed from the soil boring and will be opened by the drilling subcontractor and turned over to Jacobs field personnel for logging and/or sampling.
- The top and bottom of the sampler will be identified by the driller before logging and/or sampling commences. Jacobs field personnel should orient the sample cores the same direction when logging to minimize errors in logging the cores backwards.
- Log the soil core in accordance with *SOP-13, Soil Boring Logging*.

- Place investigation-derived waste (such as soil cores and drill cuttings) in 55-gallon drums. Label the 55-gallon drum in accordance with applicable solid waste, hazardous waste, and water quality regulations and stage in the temporary drum staging area.
- Decontaminate non-dedicated equipment and tooling in accordance with *SOP-04, Equipment Decontamination Procedures*.

5.3 Monitoring Well Construction

The permanent monitoring wells will be installed in accordance with relevant sections of IDNR, 567 IAC Private Well Rules and USACE EM 1110-1-4000.

- Monitoring wells in unconsolidated materials will be installed in at least 6-inch-diameter boreholes. In accordance with IAC 567 Chapter 49, the diameter of the borehole must be 3 inches larger than the outside diameter of the riser pipe and screen.
- In general, the monitoring wells will be constructed of 2-inch-diameter, factory manufactured, flush-jointed, Schedule 40 PVC riser and screen with a threaded bottom plug. The threaded connections will be watertight. The well screens will be 5 feet or 10 feet long, depending upon the saturated thickness and the seasonal fluctuations of the water table, and the screen slot size will be 0.010 inches.
- The annular space surrounding the well screens will be completed with a properly sized and graded, thoroughly washed, sound, durable, well-rounded siliceous sand. The primary sand filter pack will extend from the bottom of the well screen to 2 feet above the top of the well screen. Based on the depth to water encountered during drilling activities, it may not be possible to emplace the filter pack 3-5 feet above the screen. When installing a monitoring well where depth to water is less than 5 feet below ground, the filter pack must extend a minimum of 6 inches above the screen. The drilling subcontractor will use a weighted tape to monitor the depth of the sand pack during placement. The filter pack will be allowed to settle before a final measurement is taken of the top of sand.
- A bentonite seal will be installed atop the sand filter pack. The bentonite seal will consist of bentonite chips or pellets and will be placed from the top of the sand filter pack to roughly 3 feet above the sand filter pack. If the bentonite seal is located above the unsaturated zone, the bentonite chips will be hydrated using PFAS-free potable water. For bentonite seals above the saturated zone, about one gallon of PFAS-free potable water per foot of chips or pellets will be added to initiate hydration of the bentonite. After the placement of the final lift, the bentonite will be allowed to hydrate prior to placement of the grout. A weighted tape will be used to verify the top of the bentonite seal.
- The grout seal will be placed directly over the bentonite seal and will extend from the bentonite seal to the base of the surface completion. The type of grout used for the annular seal will consist of high solids sodium bentonite slurry, at least 20 to 30 percent weight by solids. The grout will be pumped into the annular space in one continual operation using a side-discharge tremie pipe. After the grout has set for 24 hours, check the seal for settlement and add grout as required.
- The monitoring wells will be completed with a flush-mount or stick-up well protector and surrounded by bollards (for stick-up wells only). The flush-mount well protector will consist of a watertight well vault equipped with a cast-iron lid and aluminum skirt. A 2-foot-square by 4-inch-thick concrete pad will be poured around the well vault. The concrete pad will be finished in such a manner that surface water drains away from the well vault. The monitoring well riser will be equipped with a watertight well cap (J-plug type) and lock keyed similar to other monitoring wells

installed as part of the investigation. The geologist or engineer providing oversight of each monitoring well installed will complete stick-up and flush-mount monitoring well completion forms.

- Soil and liquid materials generated during well installation will be containerized in steel 55-gallon drums for characterization and disposal. The drums will be labeled in accordance with the waste management plan and staged in a temporary drum staging area.
- Drilling equipment will be decontaminated between borehole locations (see *SOP-04, Equipment Decontamination Procedures*).
- A record of the constructed monitoring well will be completed by the drilling company and submitted to Iowa Department of Natural Resources.

5.4 Monitoring Well Development

The purpose of monitoring well development is to remove fine-grained material from the well screen and filter pack that may interfere with analyses and return the monitoring zone to its original hydraulic state, which was disturbed during well installation. Development also will redistribute the sand grains within the filter pack to allow for coarser sand material to congregate near the slotted screen. The well should be capable of producing clear water samples using appropriate sample methods; however, when wells are completed in a silty or clayey soil or the well screen straddles the groundwater surface, the groundwater discharged from the well may never clear up (that is, turbidity readings less than 10 nephelometric turbidity units [NTUs]).

Newly installed conventional monitoring wells will be developed no sooner than 24 hours after well installation. Use a surge and purge method to develop conventional monitoring wells whenever feasible. The entire vertical screened interval should be developed using surge blocks, bailers, pumps, or other equipment, which frequently reverse the flow of water through the well screen and prevent bridging of formation or filter pack particles.

The following procedures and guidelines will be followed during well development:

1. Measure and record the water level and total depth of the well using a water level indicator. Note any accumulated sediment thickness, and record all information in a field notebook and on the Well Development Datasheet provided as Attachment 2.
2. Remove approximately 1 to 2 pints of water from the well using a decontaminated groundwater sampling pump or disposable bailer. Measure water quality parameters (pH, temperature, conductivity, DO, ORP, and turbidity).
3. Begin well development by surging the bottom of the monitoring well and removing any sediment from the bottom of the well. To do this, slowly lower a decontaminated surge block into the well so that the surge block is within approximately 0.5 to 1 foot from the bottom of the well or measured sediment accumulation. Slowly raise and lower the surge block approximately 1 to 2 feet to create a mild surging effect at the bottom of the well; this will suspend any sediment that has settled at the bottom. Do not agitate the water violently. A general rule for well development is to start slowly and gently, and gradually increase agitation as the well is developed. After several surge strokes, remove the surge block and immediately begin to pump or bail the sediment-laden water. Repeat this process until accumulated sediment has been removed from the bottom of the monitoring well.
4. Next, develop the well from the bottom of the screened interval upward by alternately using the surge block and the bailer or pump. This will account for settlement that occurs as the filter pack is reworked through surging. Lower the surge block to the base of the well screen interval and rapidly raise and lower the surge block across a 2- to 3-foot interval above the base of the well screen for

approximately 2 to 3 minutes. However, do not overdevelop the well with overly aggressive surging. Record the surge interval and duration of surging.

5. Remove the surge block and lower the pump or bailer so that the intake is at the bottom of the surged screen interval. Turn the pump on or bail the well at the development interval until the purge water begins to clear up. Measure and record the water quality parameters every 3 to 5 minutes during pumping or bailing for each developed 2- to 3-foot screen interval, according to *SOP-06, Field Water Quality Measurements and Calibration*. Record the purge intake depth and the duration of pumping.

6. Once the water is clear, repeat Steps 4 and 5, continuing to alternate between surging and purging, until measurements stabilize for at least three consecutive water quality parameter readings, according to the following criteria:

    - ± 3 percent Celsius (°C) temperature
    - ± 0.1 pH
    - ± 3 percent conductivity
    - ± 10 millivolts (mV) ORP
    - ± 10 percent DO or 0.5 milligram per liter (mg/L)
    - ± 10 percent turbidity or ≤ 5 nephelometric turbidity units (NTUs)

7. After the parameters stabilize and the water clarity improves, move the surge block up in 2- to 3-foot intervals, and repeat Steps 4 through 6 until the entire screened interval has been developed. Afterward, continue purging at a rate intended to avoid dewatering the screened interval and record water quality parameters at regular 3- to 5-minute intervals. In total, the entire well screen interval should be developed and surging should be conducted for a minimum of 10 minutes.

    If the well is purged dry at any point during development, approximately one well casing of clean, PFAS-free potable water can be introduced into the well and surging can continue. Add water only as a last resort and only add non-formation water as necessary. After surging, purge the well dry again to complete the development process by removing at least the amount of PFAS-free potable water added to the well. If the well will recover naturally, continue development with formation water only.

8. The well will be considered adequately developed and development can stop after the water quality parameters have stabilized according to the criteria in Step 6 or a minimum of 10 well casing volumes (see Attachment 2) have been removed from the well. If none of these conditions have been achieved after 4 hours of well development, the FM will decide whether to continue development.

9. Measure and record a final depth to water and total well depth measurement after well development.

10. Record all well development data on a Well Development Datasheet and/or in a field notebook.

Notes:

- Field equipment shall be decontaminated in accordance with *SOP-04,* Equipment *Decontamination Procedures*.
- Development water will be containerized in steel 55-gallon drums. The drums will be labeled in accordance with the Project-specific Waste Management plan and transported to the temporary drum staging area.

6.0 Records

Field notes will be kept in a bound field log book following the format specified in *SOP-07, Note Taking and Field Log Books*. The following information is required:

- Verify the depths to the bottom of the borehole, top of sand filter pack, top of bentonite seal, top of grout seal; length of end cap, screen, and riser; and amounts of sand and bentonite used during installation with the subcontractor. Log this information in the field logbook and/or the monitoring well construction form. Confirm that the methods used during well installation are in accordance with this SOP.
- The quantity and composition of the grout, seals, and filter pack actually used during construction.
- Screen slot size (in inches), slot configuration, outside diameter, nominal inside diameter, schedule/thickness, composition, and manufacturer.
- Coupling/joint design and composition.
- Protective casing composition and nominal inside diameter.
- Start and completion dates.
- Discussion of procedures and any problems encountered during drilling and well construction.
- Need to add water during well installation. Note the depth that water was added and the quantity.
- Field observations and measurements (volatile screening, drilling method), volume of water removed and water quality during development
- Instrument calibration
- Weather observations (for example, precipitation, cloud cover, air temperature, water temperature, wind speed and direction).

7.0 References

Iowa Department of Natural Resources (IDNR). 2008. IAC 567 Chapter 39, Requirements for Properly Plugging Abandoned Wells. July 2.

Iowa Department of Natural Resources (IDNR). 2008. IAC 567 Chapter 49, Nonpublic Water Supply Wells. July 2.

Department of the Army, U.S. Army Corps of Engineers (USACE). 1998. CEMP-RT/CECW-EG, Engineer Manual 1110-1-4000 Monitoring Well Design, Installation, and Documentation at Hazardous, Toxic, and Radioactive Sites. November 1.

8.0 Attachments

Well construction diagram.
Well development form.

Attachment 1
Well Construction Diagram

Jacobs

PROJECT NUMBER	WELL NUMBER
	SHEET 1 OF 1

WELL CONSTRUCTION DIAGRAM

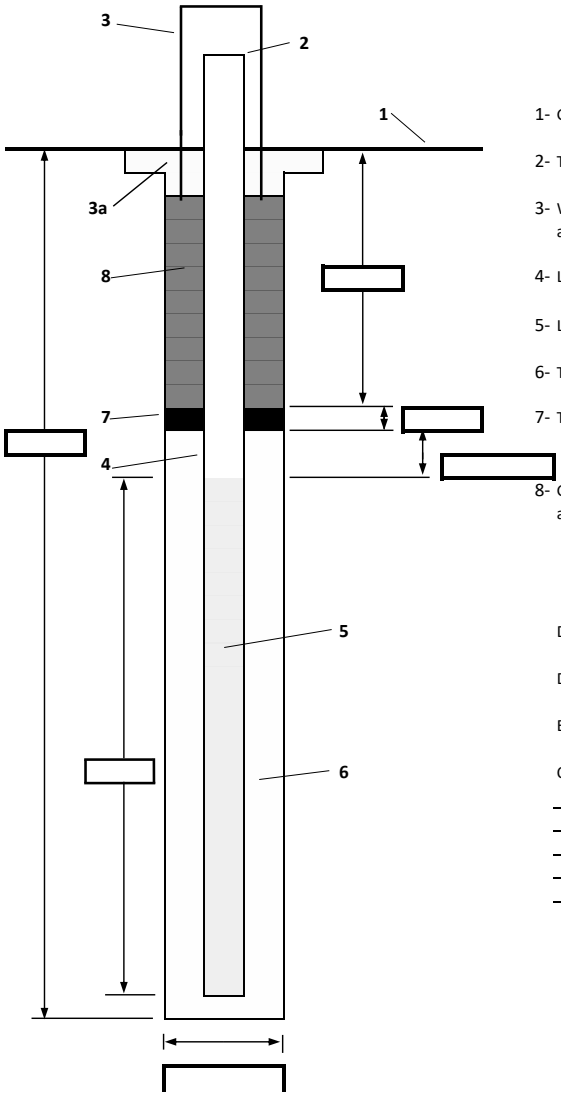
PROJECT : Location:

PROJECT MANAGER:

DRILLING CONTRACTOR :

DRILLING METHOD AND EQUIPMENT USED :

WATER LEVELS : START DATE/TIME: END DATE/TIME:



Well Construction Details

1- Ground elevation at well _____

2- Top of casing elevation _____

3- Wellhead protection cover type _____
a) concrete pad dimensions _____

4- Length (ft) & dia. (in) of well casing _____

5- Length (ft) & slot size (in) of screen _____

6- Type screen filter & quantity used _____

7- Type of seal & quantity used _____

8- Grout
a) Grout mix used _____

Well Development Details

Development method _____

Development time _____

Estimated purge volume _____

Comments _____

LOGGED BY: SIGNATURE: DATE:

DEVELOPED BY: SIGNATURE: DATE:

CHECKED BY: SIGNATURE: DATE:

Attachment 2
Well Development Form

Jacobs

PROJECT NUMBER	WELL NUMBER SHEET 1 OF 1

WELL DEVELOPMENT LOG

PROJECT : LOCATION :

DEVELOPMENT CONTRACTOR : LOGGER :

DEVELOPMENT METHOD AND EQUIPMENT USED :

START :

END :

START WATER LEVELS :

WELL DEPTH:

WELL VOLUME:

MAXIMUM DRAWDOWN DURING DEVELOPMENT:

TOTAL QUANTITY OF WATER DISCHARGED:

DISPOSITION OF DISCHARGE WATER:

Time	Water Volume Discharged (gal)	Water Level (ft BTOC)	Turbidity (NTU)	Temperature (°C)	pH	Specific Conductivity (mS/cm)	Remarks (color, odor, sheen, sediment, etc.)

SOP-04
Equipment Decontamination Procedures

SOP-04: Equipment Decontamination Procedures

1.0 Purpose

The purpose of this standard operating procedure (SOP) is to provide the step-by-step procedures for field decontamination of environmental sampling equipment and personal protective equipment (PPE). Decontamination of equipment and PPE is designed to ensure that sample cross-contamination, human-health exposure, and contamination transport are minimized.

2.0 Scope

This procedure applies to Jacobs, personnel and subcontractors engaged in collecting environmental samples or operating in environments in which hazardous or contaminating substances are expected to be present at the Iowa Army Ammunition Plant (IAAAP).

Decontamination procedures will be conducted per the following guidance documents:

- Project Health and Safety Plan (HSP)
- Project-specific Waste Management Plan

3.0 General

Decontamination consists of physically removing contaminants from the surface of sampling equipment and materials potentially exposed to those contaminants. A decontamination plan should be based on the most conservative, worst-case scenario, using all available information about the work area. The plan can be modified, if justified by supplemental information. Initially, the decontamination plan assumes that all protective clothing and equipment which leave the exclusion zone are contaminated. Based on this assumption, a system is established to wash and rinse all nondisposable equipment and dispose of all disposable equipment.

The type of decontamination procedures and solutions needed at each site should be determined after considering the following site-specific conditions:

- The type of equipment to be decontaminated
- The type of contaminant(s) present
- Extent of contamination
- Potential human and ecological risk scenarios

4.0 Responsibilities

4.1 Project Manager

The Project Manager (PM) is responsible for overall compliance with this procedure and for verifying that field staff are properly trained and meet project Health, Safety, and Environmental (HS&E) requirements.

4.2 Field Team Leader

The Field Team Leader (FTL) is responsible for following these procedures or delegating tasks to technicians to perform decontamination tasks. The FTL should verify that subcontractors are taking necessary precautions to decontaminate field equipment before and throughout field activities. The FTL should also verify that decontamination waste and PPE are disposed of appropriately according to the Project-specific Waste Management Plan.

4.3 Health and Safety Manager

The Health and Safety Manager (HSM) is assigned to oversee site-specific HS&E and overall compliance with project HS&E requirements. The HSM conducts PPE evaluations, selects the appropriate PPE for the project, lists the requirements in the Project HSP, coordinates with the Field Manager (FM) and/or Safety Coordinators (SCs) to complete and certify the PPE program, and conducts project health and safety audits on the effectiveness of the HS&E program.

4.4 Safety Coordinator

The role of SC is either taken by the FM or is designated to FTLs by the FM, to assist in implementing the project HSP. The SC assists the FM and HSM with the health and safety program, implements the PPE requirements described in the project HSP, and receives input from project staff that the assigned PPE requirements and on-going HS&E procedures are effective.

5.0 Procedure

Decontaminate nondisposable sampling equipment used at the site both before activities begin and after each sample is collected. Decontaminate drilling and excavation equipment both before activities begin and between each investigation location. Take care that materials and solutions used for decontamination procedures are themselves not hazardous or could potentially contaminate samples (that is, are acids and solvents).

5.1 Decontamination Area

Identify a localized decontamination area or drill rigs and other sampling equipment. Select the decontamination area so that decontamination fluids and soil wastes can be managed in a controlled area with minimal risk to the surrounding environment. The decontamination area should be large enough to allow temporary storage of cleaned equipment and materials before use, as well as to stage drums of decontamination investigation-derived waste (IDW). In the case of large decontamination areas (for example, for hollow-stem-auger decontamination), line each area with a heavy-gauge plastic sheeting and include a collection system designed to capture potential decontamination IDW. Decontamination areas will, in all cases, be laid out in such a way as to prevent overspray while performing equipment and personnel decontamination.

Smaller decontamination tasks, such as surface water and sediment equipment decontamination, may take place at the sampling locations. In this case, all required decontamination supplies and equipment must be mobilized to the site and smaller decontamination areas for personnel and portable equipment will be provided as necessary. These locations will include basins or tubs to capture decontamination IDW, which will be transferred to larger containers as necessary.

5.2 Decontamination Equipment

All personnel who collect or handle soil or groundwater samples, or materials potentially in contact with samples will not wear or use the following: Gore-Tex brand or similar clothing, clothing treated with Scotch-guard brand or similar water repellent, Fluoropolymer-coated Tyvek, and Fire resistant clothing

with fluorochemical treatment. Weather-proof log books with fluorochemical coatings are not acceptable. Avoid using equipment containing Teflon or other forms of polytetrafluoroethylene (PTFE), "Fluoropolymer" well materials, or any materials containing per- and polyfluorinated alkyl substance (PFAS), where that material may be in contact with groundwater or soil samples.

The following is a list of equipment and materials that may be needed to perform decontamination:

- Concrete or synthetic material-lined decontamination pad
- Plastic sheeting/membrane to serve as secondary containment for liquids
- Brushes and flat-bladed scrapers
- Garden-type water sprayers (without oil-lubricated, moving parts)
- High-pressure washer
- Portable steam cleaner
- Sump or collection system for contaminated liquid
- Wash basins and buckets
- Spray and rinse bottles
- Any water used for cleaning/decontamination must be certified PFAS-free by a laboratory and laboratory-grade detergent (Liquinox or Alconox)
- Plastic waste bags
- Leak-tight liquid waste containers (55-gallon drums or similar)
- Bulk solid waste containers (super-sacks, 55-gallon drums, or similar)
- Polyvinyl chloride piping without glued end-cap

5.3 Decontamination Procedures

5.3.1 Personnel and Personal Protective Equipment

Decontamination of personnel and PPE prevents undesired human-health exposure to contaminants via ingestion, absorption, and inhalation. All personnel and PPE will be decontaminated as outlined in the HSP. Any further concerns regarding personnel and PPE decontamination procedures may be addressed directly with the FM, PM, or HSM.

5.3.2 Sampling Equipment

Conduct consistent decontamination of sampling equipment to ensure the quality of the samples collected. Decontaminate all equipment that comes into contact with potentially contaminated samples. Disposable equipment intended for one-time use that is factory wrapped generally does not need to be decontaminated before use, unless evidence of contamination is present. Disposable equipment, such as disposable bailers, spoons, TerraCore® or Encore® volatile organic compound samplers, is preferred over reusable equipment; use wherever appropriate. Decontaminate sampling equipment, including split-barrel samplers, hand-augers, reusable bailers, spoons, trowels, shovels, and pumps used to collect samples for chemical analyses before each use and before sampling at a new sampling location.

Take the following steps to decontaminate non-dedicated sampling equipment:

- Decontamination personnel will wear the appropriate PPE as required by the HSP.

- The sequence of actual decontamination will be as follows:

    1. Remove as much gross contamination (such as pieces of soil) as possible off equipment at the sampling site.

    2. If heavy petroleum residuals are encountered during sampling, an appropriate solvent such as methanol will be used to remove any petroleum residues from sampling equipment. If a solvent is used, it must be properly used, collected, stored, and disposed of according to the HSP and the Project Waste Management Plan. If heavy petroleum residuals are not encountered, this step should be omitted.

    3. Wash water-resistant equipment thoroughly and vigorously with PFAS-free potable water containing non-phosphate laboratory-grade detergent such as Liquinox or Alconox, and using a bristle brush or similar utensil to remove any remaining residual contamination.

    4. Rinse equipment thoroughly with PFAS-free potable water (1st rinse).

    5. Rinse equipment thoroughly with PFAS-free distilled or deionized water (2nd rinse).

    6. For sensitive field instruments, rinse equipment with PFAS-free distilled, deionized, or American Society for Testing and Materials (ASTM) reagent grade water (3rd rinse).

    7. Air dry at a location where dust or other fugitive contaminants may not contact the sample equipment. Alternatively, wet equipment maybe dried with a clean, disposable paper towel to assist the drying process. All equipment should be dry before reuse.

- If the equipment is not used soon after decontamination, it should be covered or wrapped in new, oil-free aluminum foil or new, unused plastic bags to protect the decontaminated equipment from fugitive contaminates before reuse.

- Store decontaminated equipment at a secure, unexposed location out of the weather and any potential contaminant exposure.

- Depending on site conditions and the number of samples collected at each location, rinse and detergent water will normally be replaced with new solutions between borings or sample locations.

NOTE: See Section 5.3.3 for information on groundwater sampling pumps.

5.3.3 Groundwater Sampling

Proper decontamination between wells is essential to avoid introducing contaminants from the sampling equipment. For sampling with decontamination of peristaltic pumps, all that is necessary is to replace the pump head tubing after sampling each well. If sampling with pumps such a submersible or similar pump in which mechanisms of the pump come in direct contact with contaminated water, or sampling with a reusable stainless steel bailer, decontaminate the pump or bailer. The following steps will be used for pumps and bailers contaminated with dissolved phase contamination only:

- Wash the exterior of the pump or bailer and any associated cable thoroughly and vigorously with PFAS-free potable water containing non-phosphate laboratory-grade detergent (Liquinox or Alconox) and using a dedicated wash bristle brush or similar brush.

- Place the pump into a PFAS-free potable water wash basin/reservoir containing non-phosphate laboratory-grade detergent making sure that the pump intake is fully submerged and the pump outlet is allowed to flow directly back into the wash reservoir. Set the pump to a very low flow rate and turn the pump on, allowing the wash water to recirculate through the pump mechanism for a minimum of 5 minutes. Disregard this step for reusable bailers.

- Initially, rinse the pump or bailer by repeating Steps 1 and 2 using PFAS-free potable water, a dedicated rinse bristle brush, and a rinse basin/reservoir containing only PFAS-free potable water (1st rinse).
- Final rinse the pump or bailer by duplicating Step 3 using distilled, deionized, or ASTM reagent grade water (2nd rinse).
- Dry off any excess water with a clean, disposable paper towel and allow to air dry at a location where dust or other fugitive contaminants may not contact the sample pump or bailer.

NOTE: Replace detergent water and initial rinse water with new solutions between borings. Dismantle the pump for decontamination at all sampling locations.

At all sampling locations, field-dismantle (field-strip) the equipment per the manufacturer's guidelines and decontaminate the interior and exteriors surfaces of the pump or bailer using the wash, double rinse, and dry steps outlined in the previous Steps 1, 3, 4, and 5.

If significant heavy petroleum residue is encountered during decontamination, use an appropriate solvent such as methanol to remove any petroleum residues from pump or bailer surfaces. If a solvent is used, it must be properly used, collected, stored, and disposed of according to the HSP and the Project Waste Management Plan. If heavy petroleum residuals are not encountered, omit this step.

5.3.4 Measurement Devices and Monitoring Equipment

For water quality instruments, oil-water interface indicators, water level indicators, continuous water level dataloggers, and other field instruments that have the potential to come into contact with site media, at a minimum, wash with dilute laboratory-grade detergent (Liquinox or Alconox) and double rinse with PFAS-free potable and distilled/deionized water before and after each use using a similar procedure as discussed in Section 5.3.2. If heavy petroleum residuals are encountered during sampling, use an appropriate solvent such as methanol to remove petroleum residues per the manufacturer's maintenance guidelines.

5.3.5 Drilling and Subsurface Soil Sampling Equipment

Drilling equipment and associated materials will be decontaminated by the drilling contractor prior to any drilling operations and between borings. Decontaminate tools used for soil sampling (for example, split spoon samplers) before and between collecting any analytical samples, as outlined in Section 5.3.2. Thoroughly clean external and internal surfaces of drilling equipment (that is, drill bits, auger, drilling stem, and hand tools) before beginning any drilling operations and between borings using the following basic sequence:

- Remove as much gross contamination as possible off equipment at the sampling site.
- Wash equipment thoroughly and vigorously with high-temperature PFAS-free potable water using a high-pressure washer and/or steam cleaner. A bristle brush is also suggested to remove any persistent gross contamination.
- Rinse equipment twice thoroughly with PFAS-free potable water (1st and 2nd rinse).
- Air dry at a location where dust or other fugitive contaminants may not contact the sample equipment. All equipment should be dry before reuse.
- Store decontaminated equipment at a location away from any potential exposure from fugitive contamination.

5.3.6 Decontamination of Earthwork Equipment

Wash earthwork equipment (such as excavators, back-hoes, and trucks) with high-pressure PFAS-free potable water, if possible, before leaving a contaminated area, using similar steps as outlined in Section 5.3.5. Portable steam-cleaners and hand washing with a brush and detergent, followed by a PFAS-free potable water rinse, can also be used. In some instances, tires and tracks of equipment maybe only need to be thoroughly brushed with a dry brush. Take particular care with the components in direct contact with contaminants, such as tires and backhoe buckets. Any part of earthwork equipment that may come in direct contact with analytical samples (that is, sampling from the excavator bucket) must be thoroughly decontaminated before excavation activities and between sample locations.

5.4 Investigation-derived Wastes

Depending on the contaminant, potentially hazardous IDW (such as wash water or rinsate solutions) will be accumulated in 55-gallon drums and subsequently transported to a waste storage area designated by the client, according to project-specific and installation-wide procedures for management of IDW as described in the Project-specific Waste Management Plan and in accordance with federal, state, and local waste regulations.

6.0 Records

Sampling personnel will be responsible for documenting decontamination of sampling and drilling equipment. Record documentation in the Field Log Book or on a Field Datasheet as discussed in *SOP-07, Note Taking and Field Log Books*. The information entered in the Field Log Book concerning decontamination should include the following:

- Decontamination personnel
- Decontamination solutions used (such as Alconox or distilled water)
- Date and time (start and end)
  - Location of decontamination
- General decontamination methods, tools used, and observations
  - Any deviations from the decontamination methods outlined in SOP-14
- Equipment identification numbers
- Manufacturer names and lot numbers of decontamination solutions
  - Location and amount of decontamination IDW collected, stored, and/or disposed
  - Identification number, date, sampling area, and information of stored decontamination IDW
  - Any decontamination IDW spills or releases and associated corrective actions

7.0 References

American Society for Testing and Materials (ASTM) International. 2008. Standard D5088-02: Standard Practice for Decontamination of Field Equipment Used at Nonradioactive Waste Sites.

Nielsen, D.M. 1991. *Practical Handbook of Ground-Water Monitoring*. Lewis Publishers. Pages 625-636.

U.S. Environmental Protection Agency (EPA). 1999. *Procedures to Schedule and Complete Sampling Activities in Cooperation with EPA Region VII Environmental Services Division*. February.

U.S. Environmental Protection Agency (EPA), Region VII. 1991. *Environmental Services Division Operations and Quality Assurance Manual.* February 1.

U.S. Environmental Protection Agency (EPA). 1987. *A Compendium of Superfund Field Operations Methods.* Volumes I and II. EPA/540/P 87/001a & b. August.

8.0 Definitions

Decontamination area: An area that is not expected to be contaminated and is upwind of suspected contaminants.

Decontamination equipment: Equipment used during the process of decontamination of personnel or sampling equipment.

Drilling and subsurface soil sampling equipment: Equipment and tools used during the process of drilling or subsurface soil sampling.

Health and Safety Plan: A plan developed to ensure that hazards associated with a site are evaluated prior to site entry.

Measurement\monitoring equipment: Equipment used to check or evaluate site conditions.

Personal protective equipment (PPE): Personal health and safety equipment used to protect the individual from contaminant exposure, physical injury, or death.

Potable: Water acceptable for drinking and washing.

Sampling equipment: Equipment used during the process of sample collection.

Earthwork equipment: Heavy earthmoving equipment typically used for excavation and test pit investigations.

9.0 Attachments

None.

Appendix B
Laboratory Standard Operating Procedures

1.0 Scope And Application

This standard operating procedure (SOP) describes the laboratory procedure for the determination of Per- and Polyfluoroalkyl Substances (PFAS) by Liquid Chromatography Tandem Mass Spectrometry (LC/MS/MS) with Isotope Dilution Quantification in aqueous and solid matrices.

The requirements outlined in this SOP conform to those presented in Table B-15 of the Department of Defense (DoD)/Department of Energy (DOE) Consolidated Quality Systems Manual (QSM) for Environmental Laboratories. Table B-15 requirements are included in Appendix H for reference. Additional appendices are included for state and/or program specific method criteria, which supersede and/or supplement the method criteria prescribed in this SOP

1.1 Target Analyte List and Limits of Quantitation (LOQ)

The target analytes and the normal LOQ that can be achieved with this procedure are provided in Appendix A.

LOQ are established in accordance with Pace policy and SOPs for method validation and for the determination of detection limits (DL) and quantitation limits (LOQ). DL and LOQ are routinely verified and updated when needed. The current LOQ for each target analyte that can be determined by this SOP as of the effective date of this SOP is provided in Appendix A.

The reporting limit (RL) is the value to which analytes are reported as detected or not detected in the final report. When the RL is less than the lower limit of quantitation (LLOQ), all detects and non-detects at the RL are qualitative. The LLOQ is the lowest point of the calibration curve used for each target analyte.

DL, LOQ, and RL are always adjusted to account for actual amounts used and for dilution.

2.0 Summary of Method

NOTE: Refer to appendices for state and/or program specific method criteria, which supersede and/or supplement the method criteria prescribed in this SOP.

2.1 **PFAS Isotope Dilution method (aqueous; ID-AQ)** - A 250-mL water sample is fortified with surrogates (SUR; also referred to as extracted internal standards [EIS] or isotope dilution standards [IDS]) and passed through a stacked Polymeric Weak Anion Exchange (WAX)/Graphitized Carbon (GCB) SPE/filtration cartridge (Phenomenex Strata-PFAS (WAX/GCB), or equivalent) to extract the method analytes and SUR. The compounds are eluted from the SPE cartridge with 4-mL of methanol and 4-mL of ammonia-methanol (0.6%), with a separate final cartridge rinse of 2-mL of clean MeOH. With the final cartridge rinse, the extract volume is approximately 10 mL. Sample extracts are concentrated in a heated water bath under nitrogen to final volume of either 5mL or 2mL, depending on project objectives. A 10 µL aliquot of the concentrated extract is injected on an LC equipped with a C18 column that is coupled to an MS/MS detector. The analytes are separated and identified by comparing the acquired mass spectra and retention times to the reference spectra and retention times for calibration standards acquired under identical LC/MS/MS conditions. The concentration of each analyte is determined by using the internal standard isotope dilution technique.

2.2 **PFAS Isotope Dilution method (solid; ID-Solid)** - Approximately 1g of solid sample is spiked with SUR/EIS/IDS and mixed with 4mL of methanol and 4mL of ammonia-methanol (0.6%). The spiked sample with extraction solvent is then shaken on an orbital shaker, followed by sonication and centrifugation. The extract is filtered by SPE (Strata-GCB or equivalent), with a tube rinse of 2-mL of clean MeOH. The extract volume following the filtration step is approximately 10 mL. Sample extracts are concentrated in a heated water bath under nitrogen to final volume of either 5mL or 2mL, depending on project objectives. A 10 µL aliquot of the concentrated extract is injected on an LC equipped with a C18 column that is coupled to an MS/MS detector. The analytes are separated and identified by comparing the acquired mass spectra and retention times to the reference spectra and retention times for calibration standards acquired under identical LC/MS/MS conditions. The concentration of each analyte is determined by using the internal standard isotope dilution technique. See Appendix B for specific procedures for preparing and analyzing solid samples by ID-Solid.

2.3 **PFAS Isotope Dilution method (Aqueous Serial Dilution; ID-SD)** - Samples of known high PFAS concentrations, such as AFFF pure product formulations, can be prepared by serial dilution instead of SPE, with documented project approval. The sample serial dilutions will be prepared in 96% MeOH: 4% water. SUR will be spiked into the diluted sample (not the original sample collected) in the preparation vial. Any target analytes found to be ND in any samples shall be spiked at the LOQ level (post-spike) in those samples at the dilution reported and analyzed again. Recovery for the post-spiked analytes must fall within 70-130% of the expected value; if these criteria are not met, the post-spike analysis will be repeated at successively higher dilutions until recovery is acceptable. The spiking concentration will be used to calculate the project specific LOQ for each analyte. 10-µL of the prepared dilution aliquot is injected on an LC equipped with a C18 column that is coupled to an MS/MS detector. The analytes are separated and identified by comparing the acquired mass spectra and retention times to the reference spectra and retention times for calibration standards acquired under identical LC/MS/MS conditions. The concentration of each analyte is determined by using the internal standard isotope dilution technique. See Appendix E for specific procedures for preparing and analyzing serial dilution samples by ID-SD.

3.0 Interferences

3.1 Non-volumetric glassware can be solvent rinsed or heated in a muffle furnace at 400°C for 2-hours. Volumetric glassware should be solvent rinsed and can be heated in an oven at a temperature below 120°C. Store clean glassware inverted or capped. Do not cover with aluminum foil since PFAS may potentially be transferred from the aluminum foil to the glassware.

NOTE: PFAS standards, extracts and samples should not come into contact with any glass containers or pipettes as these analytes can potentially adsorb to glass surfaces. PFAS analyte, internal standards (IS) and surrogate standards (SUR) commercially purchased in glass ampoules are acceptable; however, all subsequent transfers or dilutions performed by the analyst must be prepared and stored in HDPE or polypropylene containers.

3.2 Method interferences may be caused by contaminants in solvents, reagents (including reagent water), sample containers and caps, and other sample processing equipment that lead to discrete artifacts and/or elevated baselines in the chromatograms. Method analytes may also be found in many common laboratory supplies and equipment, such as PTFE (polytetrafluoroethylene) products, LC solvent lines, methanol, aluminum foil, SPE sample transfer lines, etc. Supplies and equipment are demonstrated to be free from interference (no analyte detected > ½ LOQ) by evaluation of routine method blanks (MB). Subtracting blank values from sample results is not permitted.

3.3 Matrix interferences may be caused by contaminants that are co-extracted from the sample. The extent of matrix interferences will vary considerably from source to source, depending upon the nature of the water. Humic and/or fulvic material can be co-extracted during SPE and high levels can cause

enhancement and/or suppression in the electrospray ionization source or low recoveries on the SPE sorbent.

3.4 SPE cartridges/tubes can be a source of interferences. The analysis of field and laboratory reagent blanks can provide important information regarding the presence or absence of such interferences. Brands and sorbent lots of SPE devices should be tested to ensure that contamination does not prevent analyte identification and quantitation.

4.0 Definitions

Refer to the Laboratory Quality Manual [QAMP ME0012K] for a glossary of common lab terms and definitions.

4.1 **Collisionally Activated Dissociation (CAD)** – The process of converting the precursor ion's translational energy into internal energy by collisions with neutral gas molecules to bring about dissociation into product ions.

4.2 **Surrogate/Extracted Internal Standard/Isotope Dilution Standard (SUR/EIS/IDS)** – A pure chemical which chemically resembles method analytes and is extremely unlikely to be found in any sample. This chemical is added to a sample aliquot (field and QC) in known amount(s) before the extraction and analysis processes. The purpose of the SUR is to monitor method performance from extraction to final chromatographic measurement. For the ID methods, the SUR is used as an isotope dilution standard for measuring the relative response and quantification of other method analytes.

4.3 **Field Duplicates (FD1 and FD2)** – Two separate samples collected at the same time and place under identical circumstances and treated exactly the same throughout field and laboratory procedures. Analyses of FD1 and FD2 give a measure of the precision associated with sample collection, preservation, and storage, as well as laboratory procedures.

4.4 **Precursor Ion** – The precursor ion is typically the deprotonated molecule ([M-H]-) of the method analyte. In MS/MS, the precursor ion is the mass selected and fragmented by collisionally activated dissociation to produce distinctive product ions of smaller m/z.

4.5 **Product Ion** – A product ion is one of the fragment ions produced in MS/MS by collisionally activated dissociation of the precursor ion.

4.6 **Non-conformance Memo (NCM)** - A form used to document a non-conforming event. An analyst must document a non-conformance memo when a non-conforming event occurs. A non-conforming event may include the reporting of analytical data outside of method or SOP criteria, or when there is a deviation from a written policy or procedure. Information in an NCM may be used by project managers to flag data in the report narrative, or by the quality department to track trends and initiate corrective actions, where applicable. Additional information on the NCM policy and procedure is located in the Nonconformance and Corrective Action SOP [QA SOP ME0012BO].

4.7 **Minimum Reporting Level (MRL) [WI DNR Compliance]** - The minimum concentration that can be reported as a quantitated value for a method analyte in a sample following analysis. This defined concentration can be no lower than the concentration of the lowest calibration standard for that analyte and can only be used if acceptable QC criteria for this standard are met. Synonymous with Limit of Quantitation (LOQ).

5.0 Health And Safety

The toxicity or carcinogenicity of each chemical material used in the laboratory has not been fully established. Each chemical should be regarded as a potential health hazard and exposure to these compounds should be as low as reasonably achievable.

The laboratory maintains documentation of hazard assessments and OSHA regulations regarding the safe handling of the chemicals specified in each method. Safety data sheets for all hazardous chemicals are available to all personnel. Employees must abide by the health, safety and environmental (HSE) policies and procedures specified in this SOP and in the Pace Chemical Hygiene / Safety Manual.

Personal protective equipment (PPE) such as safety glasses, gloves, and a laboratory coat must be worn in designated areas and while handling samples and chemical materials to protect against physical contact with samples that contain potentially hazardous chemicals and exposure to chemical materials used in the procedure.

Concentrated corrosives present additional hazards and are damaging to skin and mucus membranes. Use these acids in a fume hood whenever possible with additional PPE designed for handing these materials. If eye or skin contact occurs, flush with large volumes of water. When working with acids, always add acid to water to prevent violent reactions. Any processes that emit large volumes of solvents (evaporation/concentration processes) must be in a hood or apparatus that prevents employee exposure.

Contact your supervisor or local HSE coordinator with questions or concerns regarding safety protocol or safe handling procedures for this procedure.

6.0 Sample Collection, Preservation, Holding Time, And Storage

Samples should be collected in accordance with a sampling plan and procedures appropriate to achieve the regulatory, scientific, and data quality objectives for the project.

The laboratory performs samples collection for samples to be analyzed by this SOP in accordance with the *Field Services* SOP [FS SOP ME001BS]. Refer to this SOP for these instructions.

The laboratory will provide containers for the collection of samples upon client request for analytical services. Bottle kits are prepared in accordance with the *Sample Container Shipping* SOP [AD SOP ME001DS].

Requirements for container type, preservation, and field quality control (QC) for the common list of test methods offered by Pace are listed in the *Pace-WCOL Analytical Methods List* [ME002BS].

General Requirements

Matrix	Routine Container	Min. Sample Amount[1]	Preservation	Holding Time
Aqueous	250 mL HDPE bottle fitted with polyethylene screw-cap lid	250 mL	**Thermal:** ≤ 10°C[2] **Chemical:** None	**Collection to Prep:** 28 days **Prep to Analysis:** 28 days
Solid	4 oz. HDPE bottle fitted with polyethylene screw-cap lid	10 g	**Thermal:** ≤ 10°C **Chemical:** None	**Collection to Prep:** 28 days **Prep to Analysis:** 28 days

[1]*Minimum amount needed for each discrete analysis.*
[2]*For Wisconsin compliance, samples must be received at above their freezing point to 6°C*

Field / Matrix QC

Trip Blank	MS/MSD	Field Duplicate

Analysis of TB required only if sample contains analyte concentrations at or above the LoQ.[1]	Analysis of an MS is required in each extraction batch. Assessment of method precision can be accomplished by analysis of a FD; however, infrequent occurrence of method analytes might hinder this assessment. If the occurrence of method analytes in the samples is infrequent, or if historical trends are unavailable, an MSD must be analyzed. Extraction batches that contain MSD will not require the extraction of an FD.	Within each extraction batch a minimum of one FD or MSD must be analyzed. If method analytes are not routinely observed in field samples, an MSD should be analyzed rather than an FD.

[1] Lab analyzes all TB, regardless of sample concentration.

Thermal preservation is checked and recorded on receipt in the laboratory in accordance with the *Sample Receiving* SOP [AD SOP ME0013H]. Chemical preservation is checked and recorded at time of receipt or prior to sample preparation.

After receipt, samples are stored at 4±2°C until sample preparation. Prepared samples (extracts, digestates, distillates, other) are stored at room temperature until sample analysis.

NOTE: Wisconsin compliance sample extracts will be stored at 0-6°C until sample analysis.

After analysis, unless otherwise specified in the analytical services contract, samples are retained for 30 days from date of final report and then disposed of in accordance with Federal, State, and Local regulations.

7.0 Equipment And Supplies

7.1 Equipment

NOTE: Refer to the Major Operational Equipment List [QA Control Log ME001PM] for specific details regarding the equipment and data processing software utilized during this procedure.

NOTE: Due to the possibility of adsorption of analytes onto glass, HDPE containers are used for all standard, sample and extraction preparations. Any time a new lot of SPE cartridges/tubes, solvents, cryovials, or autosampler vials are used, it must be demonstrated that a MB is reasonably free of contamination and that the criteria in Section 11.4.1 are met.

7.1.1 **Analytical Balance** – Capable of weighing to the nearest 0.0001 g

7.1.2 **Point of Use water preparation system –** Millipore Direct-Q 8 UV

7.1.3 **Solid Phase Extraction (SPE) Apparatus**

7.1.3.1 Stacked SPE/filtration cartridges: Strata PFAS(WAX/GCB), 500mg/50mg/6mL, Phenomenex part# CS0-9208, or equivalent

7.1.3.2 25mg GCB pass-through filtration cartridges (for solid extract clean-up): Strata GCB 25mg/1mL Cartridge, Phenomenex part# 8B-S528-CAJ

7.1.3.3 Vacuum Extraction Manifold – VisiPrep 24-port SPE manifold, Millipore-Sigma part# 57265, or equivalent. Care must be taken with automated SPE systems to ensure the PTFE commonly used in these systems does not contribute to unacceptable analyte concentrations in the MB.

7.1.3.4 Disposable liners for Visiprep Manifold – Millipor-Sigma part# 57059 / Restek part# 28310-VM, or equivalent.

7.1.3.5 SPE reservoirs – 60 mL and 12 mL polypropylene, Phenomenex part# AH0-7189 and AH0-7003, or equivalent.

7.1.3.6 SPE adapter caps – Phenomenex Part# AH0-7191 (Adapter cap for 1, 3, 6mL SPE tubes)

7.1.3.7 Vacuum tubing – 1/4" ID, 5/8" OD, 3/16" wall; Fisher Scientific part# 14-176-6B or equivalent

7.1.4 **Vacuum Pump** – Sufficient capacity to maintain a vacuum of approximately 10 to 15 inches of mercury for extraction cartridges. Millipore model# WP6111560, 115V, 60Hz, 3.5A.

7.1.5 **Liquid Chromatography (LC)/Tandem Mass Spectrometer (MS/MS) with Data System**

7.1.5.1 LC System – Agilent Model 1260, with Degasser (G4225A), Binary Pump (G1312B), Autosampler (G1329B), Thermostat (G1330B), Column Compartment (G1316A).
Shimadzu Model LC-30AD, with Communication Bus Module (CBM-20A), Column Oven (CTO-30A), Degassing Unit (DGU-20A5R), Autosampler (SIL-20AC XR).

NOTE: PFAS can build up in the PTFE solvent transfer lines and PTFE solvent frits. To prevent long delays in purging high levels of PFAS from the LC solvent lines, PEEK tubing and stainless-steel frits are used.

7.1.5.2 Tandem Mass Spectrometer (MS/MS) – Sciex 4500 or 5500 MS/MS, in negative ion electrospray ionization (ESI) mode. A minimum of 10 scans across the chromatographic peak is required to ensure adequate precision.

7.1.5.3 Analytical Column – Phenomenex Gemini® 3µm C18 110Å LC column 50 x3mm, (part# 00B-4439-Y0). Any column that provides adequate resolution, peak shape, capacity, accuracy, and precision may be used.

7.1.5.4 Mixing/Delay Column – Phenomenex Luna 5µm C18 100Å LC column 30 x 3mm (part# 00A-4252-Y0) or equivalent.

7.1.5.5 Guard cartridge – SecurityGuard Cartridges: Gemini C18, 2-3mm ID, 10/pk; Part# AJ0-7596/AJ0-7597; Phenomenex Part# KJ0-4282 (SecurityGuard Guard Cartridge Kit)

7.1.6 **Extract Concentration System** – Extracts are concentrated by evaporation with nitrogen using a water bath set to 55-60 °C (TurboVap LV, Biotage Inc, or equivalent).

7.1.7 **Vortex Mixer** - Bibby Scientific/Stuart Vortex Mixer, Model SA8, or equivalent.

7.1.8 **Orbital shaker table** - VWR Model 3500 Standard Shaker, 120V, or equivalent

7.1.9 **Centrifuge** - VWR Clinical 200, Hettich Rotanta 460, or equivalent

7.1.10 **Sonicator** - VWR Model 97043-976, or equivalent

7.1.11 **Kimwipes –** Fisher Scientific part # 06-666A, or equivalent

7.2 Supplies

7.2.1 **Extract/Standard storage containers** – 15-mL, 8-mL, or 4-mL narrow-mouth HDPE container - Thermo Scientific item# 2002-9050, 2002-9025, 2002-9125; 2.0-mL screw-top polypropylene

cryogenic vials – Grainger item# 6EMV1;1.5-mL snap-cap polypropylene microcentrifuge tubes - Fisher item# 05-408-129; or equivalent.

7.2.2 **Centrifuge Tubes** – 15-mL conical polypropylene tubes with or without (MoldPro) polypropylene screw caps for preparing and storing extract solutions and for collection of eluents (VWR catalogue# 10026-076 or equivalent; MoldPro, Inc. item# MP-100, 17x100mm sample tubes or equivalent - alternate extract collection tubes). 500-mL conical polypropylene bottles with polypropylene screw caps for centrifuging aqueous samples containing high solids content (Fisher catalogue# 07-200-621 or equivalent).

7.2.3 **Autosampler Vials** – Polypropylene vials (Agilent part# 5188-2788) with polypropylene caps (Agilent part# 5182-0542), or equivalent.

NOTE: Polypropylene vials and caps are necessary to prevent contamination of the sample from PTFE coated septa. However, polypropylene caps do not reseal, so evaporation occurs after injection. Thus, multiple injections from the same vial are not advisable.

7.2.4 **Micropipettes** – Range of volumes (see section 8 for volumes needed)

7.2.5 **Plastic Pipettes** – Polypropylene or polyethylene disposable pipettes, Fisher Cat# 13-711-7M or equivalent.

7.2.6 **Ottawa Sand** - for solid QC preparation (VWR catalog #: EM-SX0075-3 or equivalent)

8.0 Reagents And Standards

NOTE: Reagent grade or better chemicals should be used. Unless otherwise indicated, it is intended that ACS reagents be used, where such specifications are available. Other grades may be used, provided it is first determined that the reagent is of sufficiently high purity to permit its use without lessening the quality of the analysis.

8.1 Reagents

8.1.1 **Reagent Water** – Optima LC/MS water, Fisher part# W6-4 or equivalent.

8.1.1.1 The reagent water should not contain any measurable quantities of any method analytes or interfering compounds greater than 1/2 the LOQ for each analyte of interest.

8.1.2 **Methanol (MeOH, CH3OH, CAS#: 67-56-1)** – HPLC grade, demonstrated to be free of analytes and interferences (Fisher part# A452-4 or equivalent).

8.1.3 **Ammonium Acetate (NH4C2H3O2, CAS#: 631-61-8)** – LC/MS grade (Fisher part# A114-50 or equivalent).

8.1.4 **20 mM Ammonium Acetate** – To prepare 1 L, add 1.54 g ammonium acetate to 1L of reagent water (0.77g into 0.5L reagent water). This solution is prone to volatility losses and should be replaced at least every 96 hours.

8.1.5 **Ammonium Hydroxide (NH4OH, CAS#: 1336-21-6)** – ACS Plus grade (Fisher part# A669C-212 or equivalent)

8.1.6 **Ammonia-Methanol (Amm-MeOH, 0.6%)** – In a 1000 mL graduated cylinder, add 20 mL NH4OH (Ammonium Hydroxide) and fill to volume with methanol (980 mL reagent MeOH). Invert to mix.

8.1.7 **Ammonium Acetate/Acetic Acid buffer (25mM, pH 4)** – In a 2000 mL volumetric flask, add 2.32 mL acetic acid and 0.80 g ammonium acetate then fill to volume with reagent water (1997.68 mL reagent water). Invert to mix.

8.1.8 **Nitrogen** – Nitrogen aids in aerosol generation of the ESI liquid spray and is used as collision gas in some MS/MS instruments. The nitrogen used should meet or exceed instrument manufacturer's specifications.

8.2 Standards

NOTE: When a compound purity is assayed to be 96% or greater (standards purchased from Wellington are >98%), the weight can be used without correction to calculate the concentration of the stock standard. PFAS analyte, IS, and SUR standards commercially purchased in glass ampoules are acceptable; however, all subsequent transfers or dilutions performed by the analyst must be prepared and stored in HDPE containers. Solution concentrations listed in this section were used to develop this method and are included as an example. Alternate concentrations may be used as necessary depending on instrument sensitivity and the calibration range used. Standards for sample fortification generally should be prepared in the smallest volume that can be accurately measured to minimize the addition of excess organic solvent to aqueous samples.

NOTE: The final compositions for all standards in section 8.2 contain 96:4% (v/v) methanol/water. The solutions are stored at 2-6°C in HDPE containers, except for the solutions in 8.2.8, 8.2.11, and 8.2.16.2, which are routinely stored at room temperature.

8.2.1 **Surrogate (SUR) Stock Standard Solutions –** The SUR standard stocks are obtained from Wellington Labs (catalog #s: M2PFHxDA, M2-4:2FTS, M2-6:2FTS, M2-8:2FTS, M8FOSA-I, d-N-EtFOSA-M, d-N-MeFOSA-M, d5-N-EtFOSAA-M, d3-N-MeFOSAA-M and MPFAC-C-ES). SUR stock standard solutions are stable for at least 12 months when stored at 2-6°C.

8.2.2 **SUR 50X Mix** - Dilute the stock standards with methanol/water in accordance with the table below:

SUR 50X Mix Preparation (Aqueous)				
Standard Name	**Conc. of Stock Std. (µg/mL)**	**Aliquoted Volume (µL)**	**Dilution Volume (mL)**	**Final Conc. (µg/mL)**
Sodium 1H, 1H, 2H, 2H-perfluoro-[1,2-$^{13}C_2$] hexane sulfonate (13C2-4:2FTS)	50	1000	10	5.0
Sodium 1H, 1H, 2H, 2H-perfluoro-[1,2-$^{13}C_2$] octane sulfonate (13C2-6:2FTS)	50	1000	10	5.0
Sodium 1H, 1H, 2H, 2H-perfluoro-[1,2-$^{13}C_2$] decane sulfonate (13C2-8:2FTS)	50	1000	10	5.0
Perfluoro-1-[$^{13}C_8$] octanesulfonamide (13C8-PFOSA)	50	200	10	1.0

N-ethyl-d5-perfluoro-1-octanesulfonamide (d5-EtFOSA)	50	200	10	1.0
N-methyl-d3-perfluoro-1-octanesulfonamide (d3-MeFOSA)	50	200	10	1.0
N-ethyl-d5-perfluoro-1-octanesulfonamidoacetic acid (d5-EtFOSAA)	50	1000	10	5.0
N-methyl-d3-perfluoro-1-octanesulfonamidoacetic acid (d3-MeFOSAA)	50	1000	10	5.0
2,3,3,3-Tetrafluoro-2-(1,1,2,2,3,3,3-heptafluoropropoxy)-$^{13}C_3$-propanoic acid (13C3-GenX)	50	1000	10	5.0
2-(N-methyl-d3-perfluoro-1-octanesulfonamido) ethan-4-ol (d7-MeFOSE)	50	200	10	1.0
2-(N-ethyl-d5-perfluoro-1-octanesulfonamido) ethan-4-ol (d9-EtFOSE)	50	200	10	1.0
Perfluoro-n-[1,2-$^{13}C_2$] hexadecanoic acid (13C2-PFHxDA)	50	200	10	1.0

8.2.3 **100 ppb SUR Mix** - Combine the SUR 50X mix and Wellington Labs standard part# MPFAC-C-ES and dilute with methanol/water in accordance with the table below:

100 ppb SUR Mix Preparation (Aqueous)				
Standard Name	**Conc. of Stock Std. (µg/mL)**	**Aliquoted Volume (µL)**	**Dilution Volume (mL)**	**Final Conc. (µg/mL)**
SUR 50X Mix	1	2200	22	0.10
MPFAC-C-ES Stock	2	1100	22	0.10

NOTE: The complete list of compounds included in the ID (Aqueous and Solid) 100 ppb SUR Mix is found under Table 5.

8.2.4 **Analyte Primary Dilution Standards (PDS)** – Analyte standards are purchased from Wellington Labs as ampoulized solutions. The PDS standards are stable for at least 12 months when stored at 2-6°C.

8.2.4.1 PFHxS, PFOS and other sulfonic acids are not available as the acid form, but rather as their corresponding salts, such as Na+ and K+. These salts are acceptable for use as stock standards as long as the weight is corrected for the salt content according to the equation below.

$$Mass_{acid} = Measured\ Mass_{salt} \times \frac{MW_{acid}}{MW_{salt}}$$

Where:
MW_{acid} = the molecular weight of PFAA
MW_{salt} = the molecular weight of purchased salt

8.2.5 **10X Stock Analyte PDS** – Contains all target analytes at 0.2 ug/mL, except GenX which is present at 0.4 ug/mL (GenX is present in PFAC-30PAR; additional spike of individual stock standard is added to give double concentration). Prepare as outlined below:

8.2.5.1 2 mL of the primary lot of PFAC-30PAR standard mix, 40 uL of MeFOSA, EtFOSA, 10:2 FTS, MeFOSE, EtFOSE, GenX, PFDOS, PFHxDA, and PFODA primary standards, are diluted to 10 mL with methanol and reagent water, for a final composition of 96%MeOH.

8.2.6 **100X Analyte PDS** - Contains all target analytes at 20 ng/mL, except GenX which is present at 40 ng/mL. Prepare as outlined below:

8.2.6.1 1 mL of Stock (10X) Analyte PDS is diluted to 10 mL with 9 mL of 96% MeOH

8.2.7 **1000X Analyte PDS** - Contains all target analytes at 2.0 ng/mL, except GenX which is present at at 4.0 ng/mL. Prepare as outlined below:

8.2.7.1 1 mL of 100X Analyte PDS is diluted to 10 mL with 9 mL of 96% MeOH

8.2.8 **Initial Calibration Standards (ICAL)** – According to the table below, prepare calibration standards at the following nominal concentrations in pg/mL (ng/L): 50, 100, 200, 500, 1000, 2000, 5000, 10000, 15000 and 20000, except for GenX which will be at double these concentrations. The ICAL standards are stable for at least three months when stored at room temperature, or 12 months when stored at 2-6°C. See Table 5 for a list of analytes and exact concentrations.

ICAL Preparation (Aqueous)							
ICAL Level	**PFAS Conc. (pg/mL)**	**SUR Conc. (pg/mL)**	**PFAS PDS 10X (mL)**	**PFAS PDS 100X (mL)**	**PFAS PDS 1000X (mL)**	**100 ppb SUR (mL)**	**Final Volume (mL)**
1	50	2000	-	-	0.125	0.1	5
2	100	2000	-	-	0.250	0.1	5
3	200	2000	-	-	0.500	0.1	5
4	500	2000	-	0.125	-	0.1	5
5	1000	2000	-	0.250	-	0.1	5
6	2000	2000	-	0.500	-	0.1	5
7	5000	2000	0.125	-	-	0.1	5
8	10000	2000	0.25	-	-	0.1	5
9	15000	2000	0.375	-	-	0.1	5
10	20000	2000	0.50	-	-	0.1	5

NOTE: ICAL preparation procedures are subject to change without notice

8.2.9 **10X ICV PDS mix** – Second source standard containing required target analytes at 0.2 ug/mL or 200ppb, except those compounds not contained in the PFAC-24PAR stock mix, which are present at a nominal concentration of 1.0 ug/mL or 1000ppb. Prepare as outlined below:

8.2.9.1 Dilute PFAC-24PAR standard mix (secondary source/preparation) and 40uL each of GenX, ADONA, 9Cl-PF3ONS, and 11Cl-PF3OUDS secondary standards are diluted to 2mL with methanol and water, for a final solvent composition of 96:4% MeOH:water. The PFAC-24PAR standard includes all analytes listed in Table 5 except the following: GenX, ADONA, 9Cl-PF3ONS, 11Cl-PF3OUDS, 10:2FTS, MeFOSA, EtFOSA, MeFOSE, EtFOSE, PFDOS, PFHxDA, and PFODA.

8.2.10 **100X ICV Mix** - Second source standard containing required target analytes at 0.02 ug/mL or 20ppb. Prepare as outlined below:

8.2.10.1 Dilute 0.5 mL of the 10X ICV PDS mix to 5mL using 96:4% MeOH:water.

8.2.11 **ICV Sample Solution (500ppt)** – Prepare according to the table below. Note: secondary standards for the following compounds are not included in the ICV sample: 10:2 FTS, MeFOSA, EtFOSA, MeFOSE, EtFOSE, PFDOS, PFHxDA, PFODA

ICV Preparation (Aqueous)				
Standard Name	**Conc. of Stock Std. (pg/mL)**	**Aliquoted Volume (µL)**	**Dilution Volume (mL)**	**Final Conc. (pg/mL)**
PFAS ICV 100X Mix	20000	25	1.0	500
Full List SUR mix, 100ppb	100000	20	1.0	2000

8.2.12 **Isomer check** – For target compounds which have multiple chromatographic peaks due to branched and linear isomers, but for which quantitative standards are not available, a qualitative check is analyzed with each calibration event to demonstrate the peak shape and retention time of the branched isomers. See sections 10.5, 10.6 for integration information.

8.2.12.1 **Isomer Check 50X Mix** – 20 µL each of TPFOA, br-MeFOSAA, and br-EtFOSAA standards (Wellington Laboratories item #s T-PFOA, br-MeFOSAA, and br-EtFOSAA) are diluted to 1 mL with 900 µL of MeOH and 40 µL of reagent water. Final solvent composition is 96:4% MeOH:water. This solution is used to create the actual isomer check standard to be analyzed with each ICAL. Note: branched/linear isomer mixes of MeFOSAA and EtFOSAA are now present in the analyte PDS solutions, so these compounds will be calibrated with branched and linear isomers summed, but will also continue to be present in the Isomer Check mix.

8.2.12.2 **Isomer Check Standard** - 10 µL of the Isomer Check 50X Mix plus 20 µL of the 100 ppb SUR are diluted to 1 mL with 96% MeOH. The concentrations of the isomer components should be approximately 10000 ppt. This sample will be analyzed with each calibration event to demonstrate peak shape and retention time of the additional branched isomers of the included compounds.

8.2.12.3 As more qualitative standards containing mixes of branched and linear isomers become commercially available, the lab will add those newly available compounds/standards to the isomer check mix and analyze them in the manner described in Sec. 8.2.12.

8.3 Instrument Blank (IBLK) – The instrument blank is prepared by spiking 942 µL of MeOH and 38 µL of Water with 20 µL of SUR 100ppb; cap and vortex to mix, then aliquot into auto-sampler vial.

8.4 Method Blank (MB) – For 5mL FV extracts, spike 250 mL reagent water with 100 µL of the 100ppb SUR Mix. Mix well, extract as normal alongside client samples. For 2mL FV extracts, spike 250 mL reagent water with 40 µL of the 100ppb SUR Mix. Mix well, extract as normal alongside client samples.

9.0 Procedure

9.1. Equipment Preparation

9.1.1 Support Equipment

9.1.1.1 Refrigerator units are maintained and verified as required by the Quality Assurance Management Plan [QAMP ME0012K].

9.1.1.2 The balance is verified at the beginning of each analytical day using a certified weight set. Refer to the Equipment and Instrumentation SOP [QA SOP ME002JT] for balance verification procedures and acceptance criteria.

9.1.1.3 Bottletop dispensers, pipettes, and thermometers are maintained and verified as required by the Equipment and Instrumentation SOP [QA SOP ME002JT].

9.1.2 Instrument

9.1.2.1 Example Chromatographic Conditions

Step	Total Time (min)	Flow Rate (uL/min)	A: 20mM Ammonium Acetate (%)	B: Methanol (%)
0	0.00	1200	95.0	5.0
1	0.10	1200	45.0	55.0
2	4.50	1200	1.0	99.0
3	6.00	1200	1.0	99.0
4	6.10	1200	95.0	5.0
5	8.10	1200	95.0	5.0

9.1.2.2 Example Mass Spectrometric Conditions

Parameter	Setting or Value
Syringe Size	100 µL
Injection Volume	10 µL
Draw Speed	50.0 µL/min
Eject Speed	50.0 µL/min
Needle Level	3.0 mm
Column Oven Temperature	40°C
MRM Scan Window	60 sec
Curtain Gas (CUR)	30.0
Collision Gas (CAD)	9
Ion Spray Voltage (IS)	-4500.0 V
Temperature (TEM)	450.0°C
Ion Source Gas 1 (GS1)	40.0

Ion Source Gas 2 (GS2)	60.0

9.2. Initial Calibration

9.2.1 Mass Calibration – calibrate the mass scale of the MS with the calibration compounds and procedures prescribed by the manufacturer. Mass calibration/mass tune will be performed any time major maintenance is performed on the MS, or following any catastrophic instrument failure (power loss, etc.)

9.2.2 Mass Calibration verification – a mass calibration verification will be analyzed following mass calibration/mass tune, prior to initial calibration (ICAL). A prepared standard containing PFAS targets will be injected using the normal LC parameters for analysis but set up to perform a product ion (MS2) scan for the quantitation product ions of PFOA (m/z 369) and PFOS (m/z 80). If these target product ions are detected at the expected RT, the mass calibration has been verified.

9.2.3 Prepare a set of at least five ICAL standards (six ICAL standards for quadratic regressions) as described in Section 8. The lowest concentration ICAL standard must be at or below the LOQ, which may depend on system sensitivity. It is recommended that at least four of the ICAL standards are at a concentration greater than or equal to the LOQ.

9.2.4 The LC/MS/MS system is calibrated using the IS technique. A calibration curve for each of the analytes is generated by average response factor (AVG RF) or linear regression. Linear regression curves may be concentration weighted, if necessary. Linear or quadratic calibration regressions are not expected to be set through zero.

9.2.4.1 The linear regression curve is expressed as below:

$y = ax + b$

Where a is the slope and b is the y-intercept. When forced through 0, b=0.

$y = AS/ASUR$ $x = CS/CSUR$

AS is peak response of target analyte in calibration standards
ASUR is peak response of surrogate standard (SUR) in calibration standards
CS is concentration of target analyte in calibration standards
CSUR is concentration of surrogate standard (SUR) in calibration standards

9.2.5 Calibration Sequence

9.2.5.1 Calibration standards must be analyzed in sequence from lowest to highest concentration to minimize the chance that carryover from a higher concentration standard will boost the area of a lower concentration standard.

9.2.6 ICAL Evaluation

9.2.6.1 Acceptance Criteria – When quantitated using the ICAL curve, each calibration level for each analyte must calculate to be within 70-130% of its true value (±30% RE). For calibration curves produced using average response factors, the percent relative standard deviation (%RSD) of the RFs for all analytes must be <20%. Linear or non-linear regressions must have $r^2 \geq 0.99$ ($r \geq 0.995$) for each analyte. Weighting (typically 1/x or 1/x2) is allowed for linear and non-linear regressions. If these criteria cannot be met, the analyst will have difficulty

meeting ongoing QC criteria. It is recommended that corrective action is taken to reanalyze the ICAL standards, restrict the range of calibration, or select an alternate method of calibration.

9.2.6.1.1 Calibration Point Dropping – If more than the minimum number of standards are analyzed and levels are excluded from the calibration, only the lowest or highest standards may be excluded, except as noted here. The removal of calibration levels from the interior of the curve is allowed only when there is sound technical reason for doing so and when the level is removed for all analytes; for example, when it can be proven that the wrong standard was analyzed for the calibration level or there is obvious evidence that the instrument malfunctioned during injection of the standard. **The removal of any calibration level from the interior of the curve must be approved by the department supervisor/manager. Management approval and the rationale for the level removal must be documented and kept with the technical record.**

9.2.6.1.2 Calibration Point Replacement – replacing a calibration standard may sometimes be needed to correct for a technical problem that occurred during analysis such as power failure, incomplete injection of the standard or similar situation. Replacement of one standard, when analyzed within 24 hours of original analysis time and replacing all analytes in the original standard, is permitted. **The replacement of the standard must be approved by the department supervisor/manager; approval and the reason for replacement must be documented and kept with the technical record.**

9.2.6.1.3 For Wisconsin compliance analysis, re-quantitated concentrations for all target compounds at all concentration levels must be within the range 70-130% of their actual concentrations, except for the lowest calibration concentration level, which must be within the range of 50-150% of actual concentrations.

9.2.6.1.4 Calibration results for labeled Surrogate and Internal Standard compounds will be evaluated by comparing the area response of each level to the ICAL midpoint level (L5 – 1000ppt). Any ICAL points for which SUR or IS responses fall outside of 50-200% of the midpoint ICAL shall be removed. If any more than two ICAL points fail these criteria, the system should be inspected, and maintenance should be performed if needed. A new ICAL will then be analyzed following any maintenance.

NOTE: When acquiring MS/MS data, LC operating conditions must be carefully reproduced for each analysis to provide reproducible retention times. If this is not done, the correct ions will not be monitored at the appropriate times. As a precautionary measure, the chromatographic peaks in each window must not elute too close to the edge of the segment time window.

9.2.7 Calibration Locking – After all ICAL and ICV acceptance criteria are met, the calibration is considered “locked” and no further changes may be made until the next calibration event. In the AIM2 data processing software, the primary review (L1) analyst will set the “Sample State” for all files of the calibration event to “Locked” state. When files are in “Locked” state, no permanent changes can be made to the samples. The calibration design or fit must never be changed during routine data processing of any analytical sequence associated with the calibration; the only exception is when a problem with the original calibration curve is found. In that case, the problem must be handled as a quality incident. If the investigation of the incident indicates that the calibration is invalid, then all data associated with the calibration must be reprocessed under the corrected calibration.

9.2.8 Relative Error

9.2.8.1 Each calibration level for each analyte must calculate to be within 70-130% of its true value (±30% RE); except for Wisconsin compliance – see section 9.2.6.1.3.

9.2.9 Initial Calibration Verification (ICV)

9.2.9.1 As part of the IDOC, each time a new Analyte PDS is prepared, and once after each ICAL, analyze an ICV sample from a second source (different from the source of the ICAL standards). If a second vendor is not available, then a different lot of the standard from the same vendor should be used. The ICV should be prepared and analyzed just like a CCV. Acceptance criteria for the ICV are identical to the CCVs; the calculated amount for each analyte must be ± 30% of the expected value. If measured analyte concentrations are not of acceptable accuracy, correct the problem and rerun the ICV. If the problem persists, repeat the ICAL. Samples are not to be analyzed until the ICAL has been verified by acceptable ICV accuracy. The lab will add additional target analytes to the ICV mix as second source standards become commercially available.

9.2.10 Continuing Calibration Verification/Instrument Sensitivity Check (CCV/ISC)

9.2.10.1 CCV Standards are analyzed at the beginning of each analysis batch, after every 10 samples, and at the end of the analysis batch. In this context, a “sample” is considered to be a field sample. MBs, CCVs, LCSs, MSs, FDs, TBs and MSDs are not counted as samples. In the event that 10 field samples and various non-field sample QC (BLKs, MBs, CCVs, LCSs, MSs, FDs, TBs and MSDs) are injected between a set of CCVs, the maximum injections between CCVs is limited to 20. Inject an aliquot of the appropriate concentration ICAL standard and analyze with the same conditions used during the initial calibration.

9.2.10.1.1 The daily Instrument Sensitivity Check (ISC; DOD required) will be used as the daily opening CCV and will be analyzed at a concentration at or below the LoQ using prepared ICAL standards.

9.2.10.1.2 The prepared mid-level ICAL solution will be analyzed for subsequent bracketing and closing CCVs.

9.2.10.1.3 Calculate the concentration of each analyte and surrogate in the CCV. The calculated amount for each analyte must be within ± 30% of the true value. The area response for each surrogate compound must be within ±50% of the area of the corresponding compound in the ICAL midpoint, or the ISC on days that an ICAL is not analyzed. If these conditions do not exist, then all data for the problem analyte must be considered invalid, and remedial action should be taken which may require recalibration. Any field or QC samples that have been analyzed since the last acceptable calibration verification should be reanalyzed after adequate calibration has been restored, with the following exception: if the CCV fails because the calculated concentration is greater than 130% for a particular method analyte, and the associated field sample extracts show no detection for that method analyte, non-detects may be reported with appropriate narrative, without the need for re-analysis.

9.2.10.1.3.1 For Wisconsin and other non-DoD compliance samples, the calculated amount for each analyte must be within ± 30% of the true value except for the ISC, for which the calculated amount of each analyte must be within ± 50% of the true value.

9.2.10.1.4 Remedial Action – Failure to meet CCV QC performance criteria may require remedial action. Major maintenance, such as cleaning the electrospray probe, cleaning the mass analyzer, replacing the LC column, etc., requires recalibration and verification of sensitivity by analyzing a CCV at or below the LOQ.

9.2.10.1.4.1 Remedial Actions taken to correct for ICAL, ICV, and CCV acceptance criteria exceptions must be documented and must be traceable to the ICAL/ICV/CCV for which the corrective action was performed. The instrument maintenance log entry for the remedial action must include some reference to the failing result (batch, ID, file number, etc) for which the remedial action is being taken.

9.2.10.1.5 If reanalysis cannot be performed, the data must be qualified. An NCM must be generated which describes the reason that reanalysis is not being performed.

9.3. Sample Preparation (Aqueous)

Some of the PFAS adsorb to surfaces, including polypropylene and HDPE. Therefore, aqueous sample containers must be rinsed with the elution solvent. The container rinse is passed through the cartridge to elute the method analytes and is then collected.

NOTE: The SPE cartridges, reservoirs, and sample containers described in this section are designed as single use items and should be discarded after use. They may not be refurbished for reuse in subsequent analyses.

9.3.1 Inspect samples; determine if sample centrifugation is warranted for each sample. Samples containing settled or suspended solids may require centrifugation in order to be fully loaded through the SPE sorbent; see Appendix C for more guidance in the Aqueous Sample Centrifugation Protocol. If centrifugation is warranted, follow the PFAS centrifuge procedure in Appendix C of this SOP.

9.3.1.1 Leachate samples and most samples from landfill-impacted sites will be prepared at an up-front (pre-extraction) dilution of 10X (25mL aliquot of sample into final volume of 250mL, using verified pipette).

9.3.2 Weigh the full sample container and document in LIMS3 prep batch. Initial volume for samples requiring centrifugation should be recorded after the centrifugation procedure has been completed.

9.3.3 Spike the sample containers with 100 µL of the 100 ppb SUR Mix. Invert the sample to mix.

9.3.4 Spike the LCS/LCSD, MS, and either FD or MSD appropriately according to the corresponding section under Quality Control and Method Performance (Section 11)

9.3.5 Clean SPE adapter caps by thoroughly rinsing with MeOH and allow to dry before using them to connect the cartridges/reservoirs.

9.3.6 Insert a disposable liner gently into the center of the flow valve. NOTE: tip of liner may catch and bend/break the liner. If that happens, try again with a new liner.

9.3.7 Attach the SPE extraction cartridges (Strata PFAS [WAX/GCB]) to the converter caps and the reservoirs. Place the cartridge setups in the active SPE manifold ports.

9.3.8 Wet the rim of the manifold body with DI water to form a proper seal with the manifold top.

9.3.9 Place the top on the SPE manifold, start the vacuum pump, and ensure the vacuum is approximately 5-10in. Hg.

9.3.10 Condition each SPE cartridge in individual steps with the following solvents. Solvent volumes used for conditioning step 1 should be used to rinse down the inside of the SPE reservoirs, to remove any potential contamination from the inside of the reservoirs. After adding the conditioning solvent to the reservoir/cartridge setup and before passing the solvent through the SPE sorbent for each conditioning step: in a *dropwise fashion*, the analyst must allow the conditioning solvent to soak the sorbent for 2 minutes, ensuring both sorbent beds (WAX and GCB) are fully soaked **(do not allow sorbent to go dry during conditioning).**

9.3.10.1 Conditioning step 1: 4mL Ammonia-MeOH (0.6%) + 4mL MeOH

9.3.10.2 Conditioning step 2: 4mL Ammonium acetate/acetic acid buffer

If the SPE cartridge goes dry during any step of the conditioning process, restart conditioning with first step (Amm-MeOH+MeOH).

9.3.11 Add the entire water sample to the SPE tube/reservoir **(do not allow sorbent to go dry during sample loading).**

9.3.11.1 Samples containing settled or suspended solids may require centrifugation in order to be fully loaded through the SPE sorbent; see Appendix C for the Aqueous Sample Centrifugation Protocol.

9.3.12 Adjust the pressure/SPE flow control valves to load the sample at approximately 10-15mL/min; this rate equates to loading time of 17-25 mins for a 250mL sample.

9.3.12.1 If the sample takes longer than 30 minutes to load through the SPE sorbent due to clogging, even after centrifugation, stop and continue with 9.3.13. A nonconformance memo must be used to document this.

9.3.13 Once the entire sample has passed through the SPE cartridge, wash the cartridge by passing 4 mL of the Ammonium Acetate/Acetic Acid buffer through the sorbent at a rate similar to the sample loading rate in 9.3.11

9.3.14 Use the vacuum to dry cartridges under high vacuum (≤20in. Hg) for ~5mins. Record drying start and end times.

9.3.15 Release the vacuum, remove the top from the SPE manifold and wet the rim of the manifold. Place the rack with the eluent collection tubes in the manifold and replace the top, ensuring that the active SPE ports are set in the corresponding collection tubes and a proper seal is formed. Turn the pump back on and ensure the pressure is approximately 5-10in. Hg.

9.3.16 Add 4mL MeOH to each empty sample container, then cap and shake each bottle to ensure all interior surfaces get rinsed. Transfer rinsate to the SPE, using a pipette to swirl MeOH along the insides of the reservoir to rinse.

9.3.17 Rinse each empty sample container a second time with 4mL Ammonia-MeOH (0.6 %). Transfer to the SPE, again using a pipette to swirl the Ammonia-MeOH solution along the inside of the reservoir to rinse.

9.3.18 Allow the eluent to soak the sorbent bed for 2 minutes before elution, as in 9.3.10. Collect the total eluent in the previously positioned collection tubes. Adjust the pressure/SPE flow control valves to elute in a ***slow*** dropwise fashion. Close each flow control valve just after the eluent level drops below the top frit of the cartridge – do not fully dry cartridges at this step.

9.3.19 Add 2mL MeOH to each cartridge, allowing the rinse solvent to soak the sorbent bed for 2 mins before eluting from the cartridge, as in 9.3.10.

NOTE: This soak may be visually different than previous soak steps in this protocol, as the entire volume of MeOH may fit in the body of the sorbent beds – there may not be any visible MeOH volume sitting on top of the sorbent bed.

9.3.20 Collect the entirety of the MeOH rinsate into the eluent collection tubes in a slow dropwise fashion, allowing the cartridges to fully dry. Release vacuum and remove collection tubes to a rack when elution is complete.

9.3.21 Weigh the empty container and document the weight in LIMS3 prep batch.

9.3.22 The difference between the weights from 9.3.2 and 9.3.21 is the sample volume (assuming 1g/mL density). Sample volumes will be rounded to the nearest 1.0 mL for use in calculations.

9.3.23 Using clean MeOH and individual Kimwipes, clean enough nozzles on the TurboVap LV concentrator to accommodate the number of sample extracts being concentrated. Make sure any nozzles not in use are firmly capped.

9.3.24 Concentrate extracts to an approximate volume of 4.0 mL (1.5mL if targeted final volume is 2 mL) using the TurboVap LV under a gentle stream of nitrogen in a heated water bath (55–60 °C). Set Nitrogen flow at a level which creates a vortex in the extract tube but does not cause splash-out; suggested starting flow rate is 1.5L/min.

9.3.25 Create a final volume (FV) reference tube: using a verified pipette, place a 5 mL or 2 mL aliquot of 96% MeOH into a clean extract tube – reference aliquot volume will depend on the targeted FV for the particular analysis selected

9.3.26 Once the sample extract has been concentrated to approximately 4.0 mL (1.5 mL if targeted final volume is 2 mL), remove elution tube from the TurboVap and allow to cool to room temperature.

9.3.27 Once cooled, reconstitute the extract following the appropriate row in the table below. After adding the water aliquot, use a transfer pipet and the reference tube created in 9.3.25 to bring the extract to the appropriate FV with clean reagent MeOH. Mix reconstituted extract to ensure homogeneity. Final reconstituted extract solvent composition is 96% MeOH: 4% water.

Extract targeted FV (mL)	Water (µL)
5	200
2	80

9.3.28 Transfer the reconstituted extracts to either 8mL HDPE Nalgene bottles or 2 mL cryovials, depending on extract FV, for storage at room temperature until instrumental analysis. Ensure caps are fully sealed on all extract storage bottles.

NOTE: For Wisconsin compliance samples, sample extracts must be stored at 0-6°C

9.3.29 Manifold cleanup – open flow control valves all the way and use the methanol squirt bottle to thoroughly rinse all flow control valves on the vacuum manifold top. Turn the manifold top on the side and rinse lures with methanol and flip the side and rinse the other side with methanol as well. Repeat the aforementioned steps with 0.6% ammonium methanol followed by methanol. If samples with high levels of contamination are processed, or if there is a concern that carryover contamination could impact samples yet to be prepared, Isopropyl Alcohol may be used to clean the manifold and flow control valves before the first methanol rinse.

9.3.30 For samples that show analyte detections above the range of the ICAL, sample dilutions will need to be prepared. See Appendix F for dilution preparation scheme.

9.3.30.1 Samples requiring analyses prepared at post-extraction dilutions of 50X or greater will be refortified with EIS to enable proper quantitation. Samples diluted in this manner are no longer technically quantitated using isotope dilution quantitation. All analyses prepared at post-extraction dilutions of 20X, 10X, or 5X will not be refortified with EIS and will thus maintain isotope dilution quantitation.

9.4. Analysis

9.4.1 Column Flush – Each day of analysis, the column must be thoroughly flushed with 100% MeOH for at least 30 minutes to clear any accumulated impurities and interferents from the sample pathway and equilibrate the system. It is also good practice to open the purge valve on the pumps for the first ~1min of flush time. The column should then be equilibrated to the analysis starting conditions by flushing for approximately 15 mins with 50:50 Ammonium Acetate: MeOH and finally approximately 15 mins with 95:5 Ammonium acetate: MeOH. Ensure that pressure is stable.

9.4.2 Analytical Sequence – Following the daily column flush, two to three (2-3) high ICAL standard (L9 or L10) injections and one blank injection will be made in order to prime the system before analyzing opening QC and client samples. Following these opening injections, Instrument Sensitivity Check (ISC) samples will be analyzed as the opening CCV (9.2.10). When a passing ISC sample(s) has been evaluated, an instrument blank will be analyzed to demonstrate the absence of system contamination. After system contamination is determined to be acceptable (no target analyte concentrations >1/2 LOQ), samples may be analyzed. After every tenth field sample analyzed in a sequence, a CCV will be analyzed (9.2.10), as well as at the end of the sequence. Each bracketing CCV should be followed by a CCB/IBLK sample injection. If system contamination is detected (any target analyte concentration >1/2 LOQ) in a CCB/IBLK following a bracketing CCV, and a Wisconsin compliance sample in the associated analysis window (prior to next CCV) shows a concurrent target analyte detection, that sample will be reanalyzed with an acceptable CCB. If the sample cannot be reanalyzed for some reason, the data for the CCB-detected compound(s) in the affected sample will be qualified with an NCM.

10.0 Data Analysis And Calculations

10.1 Qualitative Identification

10.1.1 Manual Integration

10.1.2.1 Manual changes to automated integration is called manual integration. Manual integration is sometimes necessary to correct inaccurate automated integrations but must never be used to meet QC criteria or to substitute for proper instrument maintenance and/or method set-up. To assure that all manual integrations are performed consistently and are ethically justified,

all manual integrations must be performed, reviewed, and recorded in accordance with corporate SOP ENV-SOP-CORQ-0006, Manual Integration.

10.2 Calculations

See the Laboratory Quality Assurance Manual [QAMP ME0012K] for equations for common calculations.

NOTE: The surrogate standard/Extracted Internal Standard (SUR/EIS) is used for quantitation in the PFAS ID methods.

10.2.1 Complete chromatographic resolution is not necessary for accurate and precise measurements of analyte concentrations using MS/MS. Concentrations are calculated by measuring the product ions (Q3 Mass) listed in Table 4. Other ions may be selected at the discretion of the analyst.

10.2.2 Calculate analyte and surrogate concentrations using the multipoint calibration established in Section 9.2. Do not use daily calibration verification data to quantitate analytes in samples. Final analyte concentrations are adjusted to reflect the actual sample volume determined in Section 9.

Sample concentration for aqueous samples:

$$\text{Concentration (ng/L)} = (\text{Cs})(\text{DF})$$

Where:

DF = dilution factor
Cs – see below

From the equation in section 10.3.2, Cs is calculated as follows:

$$\text{Cs} = \left(\frac{As}{Asur} - b\right) \cdot \left(\frac{Csur}{a}\right)$$

Where:

As is peak response of target analyte in the sample
Asur is peak response of internal standard in the sample (SUR for isotope dilution methods)
Cs is concentration of target analyte in the sample
Csur is concentration of internal standard in the sample (SUR for isotope dilution methods)
a is the slope from the ICAL linear regression
b is the y-intercept from the ICAL linear regression

10.2.3 Results for target analytes must be quantified from the most recent ICAL analyzed on the same instrument. During both primary (L1) and secondary (L2) review, analysts must review the ICAL Form 6 RF report (ICAL summary) to ensure that the most recent ICAL analyzed on the same instrument was utilized for the quantitation of all samples.

10.3 Prior to reporting the data, the chromatogram must be reviewed by a trained analyst for any incorrect peak identification or poor integration.

10.4 Dilution - When the concentrations of target analytes on-column exceed the highest concentration of initial calibration standard, dilution analyses are required. An appropriate dilution should be in the upper half of the calibration range, or close to the CCV. The diluted extract must maintain the same methanol/water ratio as the original extract. If a dilution greater than 20X of the extract is required,

fortification of the SUR/EIS in the diluted extract is necessary. Samples requiring >20-fold diluted analyses post-extraction will be refortified with SUR/EIS to enable proper quantitation. Samples diluted in this manner are no longer technically quantitated using isotope dilution quantitation. Refer to Appendix F for dilution preparation information.

10.5 PFHxS, PFOS, MeFOSAA and EtFOSAA have multiple chromatographic peaks using the LC conditions in Table 4 due to the linear and branched isomers of these compounds. The areas of all the linear and branched isomer peaks observed in the ICAL standards for each of these analytes must be integrated together and summed. The concentrations are reported as a total for each of these analytes. Purchased standards contain both linear and branched isomers; therefore, individual ICALs for the linear and branched isomers will not be possible. PFOA also has multiple chromatographic peaks using the LC conditions in Table 4 due to linear and branched isomers of this compound. However, a quantitative standard containing both linear and branched isomers is not currently available, so ICAL standards will not show multiple peaks for PFOA. A technical (qualitative) standard is analyzed with each calibration event to identify where the branched isomer peak elutes, relative to the linear isomer peak. In client samples, the areas of the linear and branched isomer peaks observed must be integrated together and summed. The concentration of PFOA in client samples will be reported as a sum total of branched and linear isomers. As more standards (quantitative or qualitative) containing both branched and linear isomers for other target analytes become available, these will be used in the same way as for PFHxS/PFOS/MeFOSAA/EtFOSAA or PFOA. Following the same procedure, any target analyte for which a standard has been purchased and analyzed will be integrated and reported as a sum total of branched and linear isomers.

10.5.1 MeFOSAA and EtFOSAA standards containing branched and linear isomers are also present in the Isomer Check solutions.

10.6 Integration - Sample integration is performed automatically by quantitation software and reviewed by the analyst for any incorrect analyte identification or poor integration. A peak is considered a positive detection if the primary (quantitation) ion transition peak shows a signal-to-noise ratio (S/N) of at least 10.0:1 and is defined by at least 10 MS scans (data points) across the baseline of the peak. For analytes with a secondary (confirmation) ion transition, the primary and secondary ion transitions must elute at nominally the same retention time (±2 seconds). Further, the secondary transition must show S/N of at least 3.0:1.

10.6.1 For Wisconsin compliance and other analyses not regulated by the DoD, quantitation ion transition peaks are considered positive detections if the S/N is at least 3.0:1

10.6.2 Retention Time (RT) acceptance – RT of each analyte, SUR, and IS must fall within 0.4 minutes (±0.2 mins) of the corresponding RTs from the ICAL midpoint, or the daily ISC on days when ICAL is not performed. Analytes with matched (labeled analogue) SUR compounds must elute within 0.1 mins of the associated SUR.

10.7 Calculations must utilize all available digits of precision, but final reported concentrations should be rounded to an appropriate number of significant figures (one digit of uncertainty), typically two, and not more than three significant figures.

10.8 Calculate the % recovery for the LCS using the following equation:

$$\%\ \text{Recovery} = \frac{\text{Concentration (or amount)found}}{\text{Concentration (or amount) spiked}} \times 100$$

10.9 Calculate the MS % recovery for each analyte using the equation:

$$\%\ \text{Recovery} = \frac{Xs - X}{t} \times 100$$

Where:
Xs = measured concentration in the spiked sample
X = measured concentration in the unspiked sample
t = spike concentration

10.10 Calculate the relative percent difference (RPD) for duplicate measurements (FD1 and FD2 or MS and MSD) using the equation:

$$\text{RPD} = \frac{|X2 - X1|}{\frac{X2 + X1}{2}} \times 100$$

Where:
X1 = FD1 or MS result
X2 = FD2 or MSD result

10.11 Calculate the percent relative standard deviation (%RSD) for calibration curves produced using average response factor using the equation:

$$\%\ \text{RSD} = \frac{SD}{AVG} \times 100$$

Where:
SD = the standard deviation of the curve
AVG = the average response factor for the curve (y = AVG*x)

10.12 Calculate the relative error (RE) using the equation:

$$\%RE = \frac{x_2 - x_1}{x_1} \text{ x } 100$$

Where:
X1 = true value of the calibration standard
X2 = measured concentration of the calibration standard

11.0 Quality Control And Method Performance

11.1 Quality Control

The following QC samples are prepared and analyzed with each batch of samples.

QC Item	Frequency
Method Blank (MB)	1 per batch
Laboratory Control Sample (LCS)	1 per batch
Laboratory Control Sample Duplicate (LCSD)	As needed
Matrix Spike (MS)	1 per batch
Matrix Spike Duplicate (MSD)	1 per batch or as needed
Sample Duplicate	1 per batch or as needed

11.2 Instrument QC

The following Instrument QC checks are performed.

QC Item	Frequency
Initial Calibration (ICAL)	Following major instrument maintenance, when new ICAL standards are prepared, and as needed to account for instrumental drift
Instrument Blank (IBLK)	After calibration, daily prior to sample analysis, after each CCV
Initial Calibration Verification (ICV)	After calibration.
Continuing Calibration Verification (CCV)	At the beginning of each batch, after every 10 samples, and at end of each batch
Instrument Sensitivity Check (ISC)	Daily opening CCV(s)

11.3 Instrument Blank (IBLK) – One instrument blank (IBLK) is analyzed immediately following the highest ICAL standard analyzed, on a daily basis prior to sample analysis, and following each bracketing CCV in a sequence, to check for carryover and instrument contamination. The concentration of each analyte must be ≤ 1/2 the LOQ. If the instrument blank does not pass this requirement after the highest ICAL standard, the calibration must be performed using a lower concentration for the highest standard until the acceptance criteria is met.

11.3.1 If any target analyte is detected in both a Wisconsin compliance sample and the IBLK/CCB immediately preceding (following bracketing CCV), an NCM will be generated to document the potential bias. See 9.4.2.

11.4 Method Blank (MB) – One method blank (MB) must be processed with each extraction batch. If more than 20 samples are included in a batch, analyze an MB for every 20 samples. The MB is to contain all reagents specific to the method that is carried through the entire analytical procedure, including preparation and analysis.

11.4.1 The MB must not contain any analyte of interest at or above 1/2 of the LOQ or project specific-requirements. (Note: see appendices for state or program specific requirements). If the MB contains an analyte of interest at or above 1/2 of the LOQ, then the MB and associated samples must be reanalyzed. If the MB contamination is confirmed, the entire batch must be re-prepared and reanalyzed. Reanalysis or re-extraction is not required if the samples are not impacted. Samples are not impacted when:

11.4.1.1 The MB detection is not present in the sample.

11.4.1.2 The sample concentration is ≥10x the concentration of the detection in the MB.

11.4.1.3 For any MB not associated with DOD-compliance samples OR Wisconsin-compliance samples, contamination must only be **≤LOQ** for each analyte. Other project-specific requirements may be used as well.

11.4.2 The MB must have acceptable surrogate recoveries. If surrogate recoveries are not acceptable, sample analysis should stop immediately. Corrective action should be taken. The MB should be reanalyzed if the analyst feels that the failure could be attributed to instrument problems. If the analyst feels that the failure is due to a poor extraction, the entire batch associated with the MB must be re-extracted.

11.4.2.1 If a MB recovers above the acceptance limits for a SUR/EIS compound and is ND for the associated target compound in the MB AND associated samples show acceptable recovery for the same SUR/EIS compound, the MB is acceptable and sample data may be reported as is. If a sample associated with a MB showing a high-failing result for a SUR/EIS compound also shows recovery above the acceptance range but is ND for associated target compound(s), the data may be reported for that sample.

11.5 Laboratory Control Sample (LCS) – An LCS is required with each extraction batch. The spiked concentration of the LCS will be at a low concentration of the calibration curve. See DoD acceptance criteria for LCS targets in Table 6. If the LCS results do not meet the criteria listed in Table 6 for method analytes, then all data for the problem analyte(s) must be considered invalid for all samples in the extraction batch. For target analytes not included in the DoD Limits for batch control table (Appendix C of QSM 5.3), in-house limits of 70-150% recovery will be used as acceptance criteria.

11.5.1 The LCS for ID-AQ is prepared by spiking 250 mL of reagent water with 200 µL of the 100X PDS mix (20 ppb) for a concentration of 16 ppt (GenX at 32 ppt). The LCS is also spiked with 100 µL of Full List 100 ppb SUR mix and extracted as normal alongside client samples.

11.5.2 For Wisconsin compliance and other non-DoD compliance samples, acceptance limits will be 50-150% recovery for all target compounds.

11.6 Surrogates (SUR/EIS/IDS) – The surrogate standard (SUR, also referred to as extracted internal standard [EIS] or isotope dilution standard [IDS]) is fortified into all samples, MBs, LCSs, MSs, MSDs prior to extraction. It is also included in the ICAL standards. SUR/EIS indicate extraction efficiency in sample prep and are used to quantitate target analytes in all samples.

11.6.1 The analyst must monitor the peak areas of the SUR in all injections during each analysis day. The SUR responses (peak areas) in any chromatographic run must not deviate by more than 50% from the area measured in the ICAL midpoint (L5) standard during initial calibration or in the daily opening CCV on days a calibration is not performed. When the SUR/EIS/IDS recovery from a sample, blank, or CCV is not within this range check the following: calculations to locate possible errors, standard solutions for degradation or contamination, and instrument performance. Correct the problem and inject a second preparation of that sample extract (or blank or CCV) prepared in a new capped autosampler vial. Loss due to evaporation has been observed when using polypropylene caps which can cause high SUR response.

11.6.2 For Wisconsin and other non-DoD compliance analysis, all SUR/EIS/IDS compounds must recover within the range 25-150% in extracted samples, except 13C8-PFOSA, d3-MeFOSA, d5-EtFOSA, d7-MeFOSE, and d9-EtFOSE, which must recover within the range 10-150% in extracted samples. Recovery will be based on area counts as described above. For all instrument QC (CCV, ICV, ICB, CCB, IBLK) used for Wisconsin compliance, SUR/EIS/IDS compounds must recover within the range 50-150% in each injection.

11.6.3 If extract reanalysis meets the surrogate recovery acceptance criteria, report only the data for the reanalyzed extract.

11.6.4 If the extract reanalysis fails the 50-150% acceptance criteria (or 10/25-150% for non-DoD compliance), the analyst should check the calibration by injecting the last ICAL standard that passed. If the ICAL standard fails the criteria of 9.2.6, maintenance and/or recalibration is in order. If the ICAL standard is acceptable, extraction of the sample should be repeated provided the sample is still within the holding time. If the re-extracted sample also fails the recovery acceptance criteria, an NCM will be generated describing that the results are suspect due to surrogate recovery. Alternatively, a new sample can be collected and re-analyzed.

11.7 Ion Ratios – In detections of analytes for which two ion transitions (quantitation and confirmation) are measured, the area ratio between the confirmation and quantitation transitions shall be monitored and documented. The ion ratio for all detected analytes in each injection should be within 50-150% of the average ion ratio for the same analyte in the ICAL. On days ICAL is not performed, the ion ratio should be within 50-150% of the initial CCV standard. Targets detected and identified with ion ratios that fail these acceptance criteria will be flagged in the quantitation report, but not disqualified.

11.8 Matrix Spike (MS) – Analysis of an MS is required in each extraction batch. Assessment of method precision can be accomplished by analysis of a duplicate collected in the field; however, infrequent occurrence of method analytes might hinder this assessment. If the occurrence of method analytes in the samples is infrequent, or if historical trends are unavailable, a matrix spike duplicate (MSD) must be prepared, extracted, and analyzed. Extraction batches that contain MSD will not require the extraction of an FD.

11.8.1 Within each extraction batch, a minimum of one sample is spiked as an MS for every 20 samples analyzed. Client samples are spiked in the same manner as the LCS. 250mL of sample is spiked with 200 µL of 100X PDS mix (20 ppb) plus 100 µL of Full List 100 ppb SUR mix and extracted as normal alongside other client samples.

11.8.1.1 Analyte recoveries may exhibit matrix effect. For matrix spike samples, recoveries should range between 70-150%. If the % recovery falls outside of the acceptable range, corrective action must occur. The initial corrective action will be to check all calculations. If the calculations are correct, check the recovery of that analyte in the LCS. If the recovery of the analyte in the LCS is within limits, then matrix interference has been demonstrated and the laboratory operation may proceed. Analytical reports will show qualifier flags in such cases.

11.8.1.2 If the recovery for any analyte is outside the acceptance criteria for the matrix spike and the LCS, the laboratory is out of control and corrective action will be taken. Corrective action may include re-preparation and reanalysis of the batch. An NCM will be generated to document the corrective action taken.

11.9 Field Duplicate (FD) or Matrix Spike Duplicate (MSD) – Within each extraction batch (not to exceed 20 Field Samples), a minimum of one FD or MSD must be analyzed. If method analytes are not routinely observed in field samples, an MSD should be analyzed rather than an FD. See Appendix G for MS/MSD, MS/FD sample selection guidance.

11.9.1 Relative Percent Differences (RPDs) – FDs should have RPDs that are ≤30% between the original sample and the FD. If the RPD of any analyte falls outside the acceptance criteria, and the laboratory performance for that analyte is shown to be in control in the LCS, the recovery is judged to be matrix biased.

11.9.2 RPDs for MS/MSDs should be ≤30%. If the RPD falls outside of the acceptable range, corrective action must occur. The initial corrective action will be to check all calculations. If the calculations are correct, check the recovery of that analyte in the LCS. If the recovery of the analyte in the LCS is within limits, then matrix interference has been demonstrated and the laboratory operation may proceed. Analytical reports will show qualifier flags in such cases.

11.9.3 Every effort is made to ensure that an MS/MSD or an FD is included in every batch. In the event that there is insufficient sample to analyze an MS/MSD pair or if no FD is available, a duplicate LCS (laboratory control sample duplicate (LCSD)) is included in the batch. The MS/MSD must be analyzed at the same dilution as the most concentrated reportable analysis of the parent sample (the un-spiked sample See Appendix G for MS/MSD, MS/FD sample selection guidance.

11.10 Trip Blank (TB) – The purpose of the TB is to ensure that PFAS measured in the samples were not inadvertently introduced into the sample during sample collection/handling. Analysis of the TB is required only if a sample contains a method analyte or analytes at or above the LOQ; by lab protocol, TB samples are prepared and analyzed when received, prior to any knowledge of associated sample contamination. The TB is processed, extracted and analyzed in exactly the same manner as the samples. If an analyte found in the sample is present in the TB at a concentration greater than 1/2 the LOQ, then all samples collected with that TB are invalid and must be recollected and reanalyzed.

11.11 Reagent Water Contamination Testing – in-house generated reagent water demonstrated to be reasonably free of PFAS compounds, will be used for QC samples (MB/LCS/LCSD) in extraction batches and also sent to clients for use as trip blanks (TB), field blanks (FB), and equipment blanks (EB). Tested reagent water may also be sent to client sampling sites for other uses. Reagent water used for these purposes will be tested by the lab to confirm the absence of PFAS compounds prior to shipping to clients or being used in the lab. Carboys routinely will be filled with reagent water from the in-house Milli-Q water filtration system in order to create in-house “lots” of water; a sample bottle will be prepared each time carboys are filled and tested as a MB (contamination check) and LCS (spike recovery check) using the ID-AQ method. The test samples will be logged into the LIMS system by the PFAS supervisor or a member of QA when a set of carboys are filled to create a new in-house lot. The physical test samples shall be created by sampling approximately equal amounts of water from each filled carboy, which together constitute the “lot” of water. These test samples will be treated exactly the same as all other client and QC samples, taken through the entire extraction and analysis process. Should there be any recovery issues or any PFAS contamination detected in the reagent water collected in a particular lot, the water in that lot will not be used further for PFAS QC or field use. The lot may be tested again to confirm the recovery issue and/or the presence of contamination. If long-term outage of the in-house reagent water system occurs, reagent water may be purchased from an approved vendor; when new lots

of reagent water are received from the vendor, one sample from one of the bottles of the new lot will be tested in the same manner as described above. Reagent water lots and testing results will be recorded in document ME0047N-01: PFAS Free Reagent Water Milli Q System Water Testing; naming convention for in-house generated water lots will follow the convention of PFAS-YY-###, in which "YY" is the last two digits of the current year and "###" is a three digit number indicating the sequential lot number (ex: PFAS-21-005 is the 5th lot generated in 2021).

11.12 Method Performance

11.12.1 Method Validation

11.12.1.1 Detection Limits

Detection limits (DL) and limits of quantitation (LOQ) are established at initial method setup and verified on an on-going basis thereafter. Refer to Pace ENV corporate SOP ENV-SOP-CORQ-0011 Method Validation and Instrument Verification and to the *Method Validation* SOP [QA Policy ME003BF] for these procedures.

11.12.1.2 The MDL spike samples were prepared by spiking 250 mL of reagent water with 50 µL of 1000X PDS mix (2ppb), for a concentration of 0.4 ng/L (ppt; 50 ppt on column), plus 100 µL of Full List 100ppb SUR mix and extracted as normal. Final extract was concentrated/reconstituted to a final volume of 2 mL. An equal number of MB (see section 11.4) were extracted and analyzed with MDL samples.

11.12.1.3 MRL samples for Wisconsin compliance analysis will be spiked at twice the target analyte concentration of the MDL spiked samples.

11.12.1.4 Routine, on-going MDLv samples will be prepared by spiking 250 mL of reagent water with 25 µL of 100X PDS mix (20ppb), for a concentration of 2 ng/L (ppt; 100 ppt on column), plus 100 uL of Full List 100ppb SUR mix and extracted as normal. Final extract will be concentrated/reconstituted to a final volume of 5 mL. These samples will be prepared and analyzed at least twice per quarter.

11.12.1.5 For non-standard, non-regulatory analytes, an MDL study should be performed, and calibration curve generated before analyzing any samples, unless lesser requirements are previously agreed to with the client.

11.13 Analyst Qualifications and Training

Employees that perform any step of this procedure must have a completed Read and Acknowledgment Statement for this version of the SOP in their training record. In addition, prior to unsupervised (independent) work on any client sample, analysts that prepare or analyze samples must have successful initial demonstration of capability (IDOC) and must successfully demonstrate on-going proficiency on an annual basis. Successful means the initial and on-going DOC met criteria, documentation of the DOC is complete, and the DOC record is in the employee's training file. Refer to the *Demonstration of Capability* SOP [QA SOP ME001F2] for more information.

12.0 Data Review and Corrective Action

12.1 Data Review

Pace's data review process includes a series of checks performed at different stages of the analytical process by different people to ensure that SOPs were followed, the analytical record is complete and

properly documented, proper corrective actions were taken for QC failure and other nonconformance(s), and that test results are reported with proper qualification.

The review steps and checks that occur as employees complete tasks and review their own work is called primary review.

All data and results are also reviewed by an experienced peer or supervisor. Secondary review is performed to verify SOPs were followed, that calibration, instrument performance, and QC criteria were met and/or proper corrective actions were taken, qualitative ID and quantitative measurement is accurate, all manual integrations are justified and documented in accordance with the Pace ENV's SOP for manual integration, calculations are correct, the analytical record is complete and traceable, and that results are properly qualified.

A third-level review, called a completeness check, is performed by reporting or project management staff to verify the data report is not missing information and project specifications were met.

Refer to the *Data Review* SOP [QA SOP ME003LP] for specific instructions and requirements for each step of the data review process.

12.2 Corrective Action

Corrective action is expected any time QC or sample results are not within acceptance criteria. If corrective action is not taken or was not successful, the decision/outcome must be documented in the analytical record. The primary analyst has primary responsibility for taking corrective action when QA/QC criteria are not met. Secondary data reviewers must verify that appropriate action was taken and/or that results reported with QC failure are properly qualified.

Corrective action is also required when carryover is suspected and when results are over range. Samples analyzed after a high concentration sample must be checked for carryover and reanalyzed if carryover is suspected. Carryover is usually indicated by low concentration detections of the analyte in successive samples analyzed after the high concentration sample.

Sample results at concentrations above the upper limit of quantitation must be diluted and reanalyzed. The result in the diluted samples should be within the upper half of the calibration range. Results less than the mid-range of the calibration (L5) indicate the sample was over diluted and analysis should be repeated with a lower level of dilution. If dilution is not performed, any result reported above the upper range is considered a qualitative measurement and must be qualified as an estimated value.

13.0 Pollution Prevention And Waste Management

Pace proactively seeks ways to minimize waste generated during our work processes. Some examples of pollution prevention include but are not limited to: reduced solvent extraction, solvent capture, use of reusable cycletainers for solvent management, and real-time purchasing.

The EPA requires that laboratory waste management practice to be conducted consistent with all applicable federal and state laws and regulations. Excess reagents, samples and method process wastes must be characterized and disposed of in an acceptable manner in accordance with Pace's Chemical Hygiene Plan / Safety Manual.

14.0 Modifications

14.1 A modification is a change to a reference test method made by the laboratory. For example, changes in stoichiometry, technology, quantitation ions, reagent or solvent volumes, reducing digestion or extraction times, instrument runtimes, etc. are all examples of modifications. Refer to Pace ENV corporate SOP

ENV-SOP-CORQ-0011 *Method Validation and Instrument Verification* for the conditions under which the procedures in test method SOPs may be modified and for the procedure and document requirements.

14.1.1 The analyst is permitted to modify LC columns, LC conditions, internal standards or surrogate standards, and MS and MS/MS conditions. Each time such method modifications are made, the analyst must repeat the procedures of the IDOC. **Modifications to LC conditions should still produce conditions such that co-elution of the method analytes is minimized to reduce the probability of suppression/enhancement effects.**

15.0 Responsibilities

Pace ENV employees that perform any part this procedure in their work activities must have a signed Read and Acknowledgement Statement in their training file for this version of the SOP. The employee is responsible for following the procedures in this SOP and handling temporary departures from this SOP in accordance with Pace's policy for temporary departure.

Pace supervisors/managers are responsible for training employees on the procedures in this SOP and monitoring the implementation of this SOP in their work area.

16.0 Attachments

16.1 Appendix A: Tables

16.1.1 Table 1 – Target Analyte List

16.1.2 Table 2 – Reporting Limits (LOQ)

16.1.3 Table 3 – Labeled Standard Associations

16.1.4 Table 4 – Instrument Conditions

16.1.5 Table 5 – Calibration Levels

16.1.6 Table 6 – DoD Batch Control Limits

16.2 Appendix B – PFAS ID – Solid Matrix

16.3 Appendix C – Aqueous Sample Centrifugation Protocol

16.4 Appendix D – PFAS by TCLP/SPLP

16.5 Appendix E - Aqueous Serial Dilution

16.6 Appendix F – Extract Dilution Preparations

16.7 Appendix G – MS/MSD, MS/FD Sample Selection Guide

16.8 Appendix H – Chemical Derivation of Ion Transitions

16.9 Appendix I – DoD/DOE QSM Requirements

17.0 References

NOTE: Where references exclude a date or edition, the latest edition of the referenced document adopted/recognized by the laboratory's accreditation bodies applies. Refer to the Quality Assurance Management Plan [QAMP ME0012K] for details.

17.1 *Determination of Selected Per- and Polyfluorinated Alkyl Substances in Drinking Water by Solid Phase Extraction and Liquid Chromatography* / Tandem Mass Spectrometry (LC/MS/MS), USEPA, Method 537.1, Version 1.0, November 2018.

17.2 *Department of Defense Department of Energy Consolidated Quality Systems Manual (QSM)* for Environmental Laboratories

17.3 Water Quality – Determination of Perfluorooctanesulfonate (PFOS) and Perfluorooctanoate (PFOA) – Method for Unfiltered Samples Using Solid Phase Extraction and Liquid Chromatography/Mass Spectrometry, ISO 25101:2009 €.

17.4 Solvent-Extractable Nonvolatile Compounds by High-Performance Liquid Chromatography/Thermospray/Mass Spectrometry (HPLC/TS/MS) or Ultraviolet (UV) detection, USEPA, SW846, Method 9321B, Revision 2, February 2007.

17.5 Knepper, T.P. (2003) Analysis and Fate of Surfactants in the Aquatic Environment. Amsterdam, The Netherlands; Elsevier Science B.V.

17.6 Knepper, T.P. (2012) Polyfluorinated Chemicals and Transformation Products. Berlin, Germany: Springer-Verlag Berlin Heidelberg.

17.7 Rapid Commun Mass Spectrom 2007;21 (23): 3803-14.

17.8 *Wisconsin Department of Natural Resources Notice of Final Guidance and Certification, Wisonsin PFAS Aqueous (Non-Potable Water) and Non-Aqueous Matrices Method Expectations*. Wisconsin DNR. Version 12.16.2019.

18.0 Revision History

Revision #	Section Modified	Modification	Reason for Modification
v04	Appendix C	Removed Chip Method	Created separate SWI
	Appendix D	Removed Bottle Rinsate Method	Created separate SWI

APPENDIX A: TABLES

TABLE 1 – TARGET ANALYTE LIST

Analyte Name	Analyte Acronym	CAS Number	Method 537.1	ID (Aqueous)	DAI	ID (Solid)
1H,1H,2H,2H-perfluorohexane sulfonic acid	4:2 FTS	757124-72-4*	No	Yes	No	Yes
1H,1H,2H,2H-perfluorooctane sulfonic acid	6:2 FTS	27619-97-2	No	Yes	No	Yes
1H,1H,2H,2H-perfluorodecane sulfonic acid	8:2 FTS	39108-34-4	No	Yes	No	Yes
1H,1H,2H,2H-perfluorododecane sulfonic acid	10:2FTS	120226-60-0*	No	Yes	No	Yes
N-ethylperfluoro-1-octanesulfonamidoacetic acid	EtFOSAA	2991-50-6	Yes	Yes	No	Yes
N-methylperfluoro-1-octanesulfonamidoacetic acid	MeFOSAA	2355-31-9	Yes	Yes	No	Yes
Perfluoro-1-butanesulfonic acid	PFBS	375-73-5*	Yes	Yes	Yes	Yes
Perfluoro-n-butanoic acid	PFBA	375-22-4	No	Yes	Yes	Yes
Perfluoro-1-decanesulfonic acid	PFDS	335-77-3*	No	Yes	No	Yes
Perfluoro-n-decanoic acid	PFDA	335-76-2	Yes	Yes	Yes	Yes
Perfluoro-n-dodecanoic acid	PFDoA	307-55-1	Yes	Yes	No	Yes
Perfluoro-1-heptanesulfonic acid	PFHpS	375-92-8*	Yes	Yes	No	Yes
Perfluoro-n-heptanoic acid	PFHpA	375-85-9	Yes	Yes	Yes	Yes
Perfluoro-1-hexanesulfonic acid	PFHxS	355-46-4*	Yes	Yes	Yes	Yes
Perfluoro-n-hexanoic acid	PFHxA	307-24-4	Yes	Yes	Yes	Yes
Perfluoro-1-nonanesulfonic acid	PFNS	68259-12-1*	Yes	Yes	No	Yes
Perfluoro-n-nonanoic acid	PFNA	375-95-1	Yes	Yes	Yes	Yes
Perfluorooctanesulfonic acid	PFOS	1763-23-1*	Yes	Yes	Yes	Yes
Perfluoro-1-octanesulfonamide	PFOSA	754-91-6	No	Yes	No	Yes
Perfluoro-n-octanoic acid	PFOA	335-67-1	No	Yes	Yes	Yes
Perfluoro-n-pentanoic acid	PFPeA	2706-90-3	Yes	Yes	Yes	Yes
Perfluoro-1-pentansulfonic acid	PFPeS	2706-91-4*	Yes	Yes	No	Yes
Perfluoro-n-tetradecanoic acid	PFTeDA	376-06-7	Yes	Yes	No	Yes

TABLE 1 – TARGET ANALYTE LIST (CONT'D)

Analyte Name	Analyte Acronym	CAS Number	Method 537.1	ID (Aqueous)	DAI	ID (Solid)
Perfluoro-n-tridecanoic acid	PFTrDA	72629-94-8	Yes	Yes	No	Yes
Perfluoro-n-undecanoic acid	PFUdA	2058-94-8	Yes	Yes	No	Yes
N-methylperfluoro-1-octanesulfonamide	MeFOSA	31506-32-8	No	Yes	No	Yes
N-ethylperfluoro-1-octanesulfonamide	EtFOSA	4151-50-2	No	Yes	No	Yes
Hexafluoropropylene oxide dimer acid	GenX	13252-13-6	Yes	Yes	No	Yes
4,8-dioxa-3H-perfluorononanoic acid	ADONA	919005-14-4	Yes	Yes	No	Yes
9-chlorohexadecafluoro-3-oxanone-1-sulfonic acid	9Cl-PF3ONS	756426-58-1*	Yes	Yes	No	Yes
11-chloroeicosafluoro-3-oxaundecane-1-sulfonic acid	11Cl-PF3OUDS	763051-92-9*	Yes	Yes	No	Yes
2-(N-methylperfluoro-1-octanesulfonamido)-ethanol	MeFOSE	24448-09-7	No	Yes	No	Yes
2-(N-ethylperfluoro-1-octanesulfonamido)-ethanol	EtFOSE	1691-99-2	No	Yes	No	Yes
Perfluoro-1-dodecanesulfonic acid	PFDOS	79780-39-5*	No	Yes^	No	Yes^
Perfluoro-n-hexadecanoic acid	PFHxDA	67905-19-5	No	Yes^	No	Yes^
Perfluoro-n-octadecanoic acid	PFODA	16517-11-6	No	Yes^	No	Yes^

* CAS Numbers are for the acid and not the salt.
^ Compounds for Wisconsin compliance analysis
NOTE: Methods 537.1 and DAI are addressed in SOPs ME002I6 and ME002I7 respectively.

TABLE 2A – REPORTING LIMITS (LOQ) – PFAS ISOTOPE DILUTION – AQUEOUS MATRIX

NOTE: Reporting Limits are subject to change. Current limits are available in LIMs

Analyte Acronym	Analyte Name	CAS Number	Spiked Conc[1] (ng/L)	DL (ng/L)	LOD (ng/L)	LOQ (ng/L)
EtFOSAA	N-ethylperfluoro-1-octanesulfonamidoacetic acid	2991-50-6	0.4	1	4	8
8:2 FTS	1H,1H,2H,2H-perfluorodecane sulfonic acid	39108-34-4	0.383	1	4	8
4:2 FTS	1H,1H,2H,2H-perfluorohexane sulfonic acid	757124-72-4[2]	0.374	1	4	8
6:2 FTS	1H,1H,2H,2H-perfluorooctane sulfonic acid	27619-97-2	0.379	1	4	8
MeFOSAA	N-methylperfluoro-1-octanesulfonamidoacetic acid	2355-31-9	0.4	1	4	8
PFBS	Perfluoro-1-butanesulfonic acid	375-73-5[2]	0.354	0.5	2	4
PFBA	Perfluoro-n-butanoic acid	375-22-4	0.4	0.5	2	4
PFDS	Perfluoro-1-decanesulfonic acid	335-77-3[2]	0.386	0.5	2	4
PFDA	Perfluoro-n-decanoic acid	335-76-2	0.4	0.5	2	4
PFDoA	Perfluoro-n-dodecanoic acid	307-55-1	0.4	0.5	2	4
PFHpS	Perfluoro-1-heptanesulfonic acid	375-92-8[2]	0.381	0.5	2	4
PFHpA	Perfluoro-n-heptanoic acid	375-85-9	0.4	0.5	2	4
PFHxS	Perfluoro-1-hexanesulfonic acid	355-46-4[2]	0.364	0.5	2	4
PFHxA	Perfluoro-n-hexanoic acid	307-24-4	0.4	0.5	2	4
PFNS	Perfluoro-1-nonanesulfonic acid	68259-12-1[2]	0.384	0.75	2	4
PFNA	Perfluoro-n-nonanoic acid	375-95-1	0.4	0.5	2	4
PFOS	Perfluorooctanesulfonic acid	1763-23-1[2]	0.371	0.5	2	4
PFOSA	Perfluoro-1-octanesulfonamide	754-91-6	0.4	0.75	2	4

TABLE 2A – REPORTING LIMITS (LOQ) – PFAS ISOTOPE DILUTION – AQUEOUS MATRIX CONT'D
NOTE: Reporting Limits are subject to change. Current limits are available in LIMs

Analyte Acronym	Analyte Name	CAS Number	Spiked Conc[1] (ng/L)	DL (ng/L)	LOD (ng/L)	LOQ (ng/L)
PFOA	Perfluoro-n-octanoic acid	335-67-1	0.4	0.5	2	4
PFPeA	Perfluoro-n-pentanoic acid	2706-90-3	0.4	0.5	2	4
PFPeS	Perfluoro-1-pentansulfonic acid	2706-91-4[2]	0.375	0.5	2	4
PFTeDA	Perfluoro-n-tetradecanoic acid	376-06-7	0.4	0.5	2	4
PFTrDA	Perfluoro-n-tridecanoic acid	72629-94-8	0.4	0.5	2	4
PFUdA	Perfluoro-n-undecanoic acid	2058-94-8	0.4	0.5	2	4
MeFOSA	N-methylperfluoro-1-octanesulfonamide	31506-32-8	0.4	2	8	16
EtFOSA	N-ethylperfluoro-1-octanesulfonamide	4151-50-2	0.4	1.5	4	8
10:2FTS	1H,1H,2H,2H-perfluorododecane sulfonic acid	120226-60-0[2]	0.386	1	4	8
GenX	Hexafluoropropylene oxide dimer acid	13252-13-6	0.8	1	4	8
ADONA	4,8-dioxa-3H-perfluorononanoic acid	919005-14-4	0.377	1	4	8
9Cl-PF3ONS	9-chlorohexadecafluoro-3-oxanone-1-sulfonic acid	756426-58-1[2]	0.373	1	4	8
11Cl-PF3OUDS	11-chloroeicosafluoro-3-oxaundecane-1-sulfonic acid	763051-92-9[2]	0.377	1	4	8
MeFOSE	2-(N-methylperfluoro-1-octanesulfonamido)-ethanol	24448-09-7	0.4	1	4	8
EtFOSE	2-(N-ethylperfluoro-1-octanesulfonamido)-ethanol	1691-99-2	0.4	1	4	8
PFDOS	Perfluoro-1-dodecanesulfonic acid	79780-39-5[2]	0.387	1	4	8
PFHxDA	Perfluoro-n-hexadecanoic acid	67905-19-5	0.4	1	4	8
PFODA	Perfluoro-n-octadecanoic acid	16517-11-6	0.4	1	4	8

[1]Spiking concentration used to determine DL.
[2]CAS Numbers are for the acid and not the salt.

TABLE 2B – REPORTING LIMITS (LOQ) – PFAS ISOTOPE DILUTION – SOLID MATRIX
NOTE: Reporting Limits are subject to change. Current limits are available in LIMs

Analyte Acronym	Analyte Name	CAS Number	Spiked Conc[1] (µg/kg)	DL (µg/kg)	LOD (µg/kg)	LOQ (µg/kg)
EtFOSAA	N-ethylperfluoro-1-octanesulfonamidoacetic acid	2991-50-6	0.1	0.25	1	2
8:2 FTS	Fluorotelomer sulfonate 8:2 [1H,1H,2H,2H-perfluorodecane sulfonate]	39108-34-4	0.096	0.25	1	2
4:2 FTS	Fluorotelomer sulfonate 4:2 [1H,1H,2H,2H-perfluorohexane sulfonate]	757124-72-4[2]	0.093	0.4	1	2
6:2 FTS	Fluorotelomer sulfonate 6:2 [1H,1H,2H,2H-perfluorooctane sulfonate]	27619-97-2	0.095	0.25	1	2
MeFOSAA	N-methylperfluoro-1-octanesulfonamidoacetic acid	2355-31-9	0.1	0.25	1	2
PFBS	Perfluoro-1-butanesulfonic acid	375-73-5	0.088	0.13	0.5	1
PFBA	Perfluoro-n-butanoic acid	375-22-4	0.1	0.13	0.5	1
PFDS	Perfluoro-1-decanesulfonic acid	335-77-3	0.096	0.13	0.5	1
PFDA	Perfluoro-n-decanoic acid	335-76-2	0.1	0.13	0.5	1
PFDoA	Perfluoro-n-dodecanoic acid	307-55-1	0.1	0.13	0.5	1
PFHpS	Perfluoro-1-heptanesulfonic acid	375-92-8	0.095	0.13	0.5	1
PFHpA	Perfluoro-n-heptanoic acid	375-85-9	0.1	0.13	0.5	1
PFHxS	Perfluoro-1-hexanesulfonic acid	355-46-4	0.091	0.13	0.5	1
PFHxA	Perfluoro-n-hexanoic acid	307-24-4	0.1	0.13	0.5	1
PFNS	Perfluoro-1-nonanesulfonic acid	68259-12-1	0.096	0.2	0.5	1
PFNA	Perfluoro-n-nonanoic acid	375-95-1	0.1	0.13	0.5	1
PFOS	Perfluorooctanesulfonic acid	1763-23-1	0.093	0.13	0.5	1
PFOSA	Perfluoro-1-octanesulfonamide	754-91-6	0.1	0.13	0.5	1

TABLE 2B – REPORTING LIMITS (LOQ) – PFAS ISOTOPE DILUTION – SOLID MATRIX CONT'D
NOTE: Reporting Limits are subject to change. Current limits are available in LIMs

Analyte Acronym	Analyte Name	CAS Number	Spiked Conc[1] (µg/kg)	DL (µg/kg)	LOD (µg/kg)	LOQ (µg/kg)
PFOA	Perfluoro-n-octanoic acid	335-67-1	0.1	0.13	0.5	1
PFPeA	Perfluoro-n-pentanoic acid	2706-90-3	0.1	0.13	0.5	1
PFPeS	Perfluoro-1-pentanesulfonic acid	2706-91-4	0.094	0.13	0.5	1
PFTeDA	Perfluoro-n-tetradecanoic acid	376-06-7	0.1	0.13	0.5	1
PFTrDA	Perfluoro-n-tridecanoic acid	72629-94-8	0.1	0.13	0.5	1
PFUdA	Perfluoro-n-undecanoic acid	2058-94-8	0.1	0.13	0.5	1
MeFOSA	N-methylperfluoro-1-octanesulfonamide	31506-32-8	0.1	0.25	1	2
EtFOSA	N-ethylperfluoro-1-octanesulfonamide	4151-50-2	0.1	0.4	1	2
10:2FTS	1H,1H,2H,2H-perfluorododecane sulfonate	120226-60-0[2]	0.096	0.25	1	2
GenX	Tetrafluoro-2-(heptafluoropropoxy) propanoic acid	13252-13-6	0.2	0.5	2	4
ADONA	4,8-dioxa-3H-perfluorononanoic acid	919005-14-4	0.094	0.25	1	2
9Cl-PF3ONS	9-chlorohexadecafluoro-3-oxanone-1-sulfonic acid	756426-58-1	0.093	0.25	1	2
11Cl-PF3OUDS	11-chloroeicosafluoro-3-oxaundecane-1-sulfonic acid	763051-92-9	0.094	0.25	1	2
MeFOSE	2-(N-methylperfluoro-1-octanesulfonamido)-ethanol	24448-09-7	0.1	0.25	1	2
EtFOSE	2-(N-ethylperfluoro-1-octanesulfonamido)-ethanol	1691-99-2	0.1	0.25	1	2
PFDOS	Perfluoro-1-dodecanesulfonic acid	79780-39-5[2]	0.097	0.13	0.5	1
PFHxDA	Perfluoro-n-hexadecanoic acid	67905-19-5	0.1	0.25	1	2
PFODA	Perfluoro-n-octadecanoic acid	16517-11-6	0.1	0.13	0.5	1

[1]Spiking concentration used to determine DL.
[2]CAS Numbers are for the acid and not the salt.

TABLE 3 – LABELED STANDARD ASSOCIATIONS – PFAS ISOTOPE DILUTION – AQUEOUS AND SOLID MATRIX

Target Analyte	Associated Labeled Standard
4:2 FTS	13C2_4:2FTS_2
6:2 FTS	13C2_6:2FTS_2
8:2 FTS	13C2_8:2FTS_2
10:2FTS	13C2_8:2 FTS_2
EtFOSAA	d5-EtFOSAA
MeFOSAA	d3-MeFoSAA
PFBS	13C3_PFBS
PFBA	13C4_PFBA
PFDS	13C8_PFOS
PFDA	13C6_PFDA
PFDoA	13C2_PFDoA
PFHpS	13C3_PFHxS
PFHpA	13C4_PFHpA
PFHxS	13C3_PFHxS
PFHxA	13C5_PFHxA
PFNS	13C8_PFOS
PFNA	13C9_PFNA
PFOS	13C8_PFOS
PFOSA	13C8_PFOSA
PFOA	13C8_PFOA
PFPeA	13C5_PFPeA
PFPeS	13C3_PFBS
PFTeDA	13C2_PFTeDA
PFTrDA	13C2_PFDoA
PFUdA	13C7_PFUdA
MeFOSA	d3-MeFOSA
EtFOSA	d5-EtFOSA
GenX	13C3-GenX
ADONA	13C3_PFHxS
9Cl-PF3ONS	13C8_PFOS
11Cl-PF3OUDS	13C8_PFOS
MeFOSE	d7-MeFOSE
EtFOSE	d9-EtFOSE
PFDOS	13C8_PFOS
PFHxDA	13C2-PFHxDA
PFODA	13C2-PFHxDA

NOTE: For method ID-AQ and ID-Solid, the labeled quantitation standards are contained in the SUR solution.

TABLE 4: ID INSTRUMENT CONDITIONS – AQUEOUS AND SOLID MATRIX

LC Program

Step	Total Time (min)	Flow Rate (uL/min)	A: 20mM Ammonium Acetate (%)	B: Methanol (%)
0	0.00	1200	95.0	5.0
1	0.10	1200	45.0	55.0
2	4.50	1200	1.0	99.0
3	6.00	1200	1.0	99.0
4	6.10	1200	95.0	5.0
5	8.10	1200	95.0	5.0

Built-in Diverter Valve Program

Step	Total Time (min)	Position
1	0.0	Waste
2	1.0	MS
3	5.8	Waste

Instrument Parameters

Parameter	Setting or Value
Syringe Size	100 µL
Injection Volume	10 µL
Draw Speed	50.0 µL/min
Eject Speed	50.0 µL/min
Needle Level	3.0 mm
Column Oven Temperature	40°C
MRM Scan Window	30 sec
Curtain Gas (CUR)	30.0
Collision Gas (CAD)	9
Ion Spray Voltage (IS)	-4500.0 V
Temperature (TEM)	450.0°C
Ion Source Gas 1 (GS1)	40.0
Ion Source Gas 2 (GS2)	60.0

MS/MS Conditions*

ID	Q1 Mass (Da)	Q3 Mass (Da)	Time (min)	DP (volts)	EP (volts)	CE (volts)	CXP (volts)
4:2 FTS	327	307	2.42	-20	-4	-28	-8
4:2 FTS_2	327	81	2.42	-20	-4	-50	-8
6:2 FTS	427	407	3.23	-20	-4	-32	-8
6:2 FTS_2	427	81	3.23	-20	-4	-72	-8
8:2 FTS	527	507	4.02	-20	-4	-40	-8
8:2 FTS_2	527	81	4.02	-20	-4	-82	-8
9Cl-PF3ONS	531	351	3.88	-75	-10	-38	-10
10:2 FTS	627	607	4.66	-20	-8	-45	-8
10:2 FTS_2	627	80	4.66	-20	-8	-92	-8
11Cl-PF3OUDS	631	451	4.52	-90	-10	-41	-13
ADONA	377	251	2.95	-47	-8	-18	-8
ADONA_2	377	85	2.95	-47	-8	-68	-8
EtFOSA	526	169	4.71	-50	-10	-37	-8
EtFOSA_2	526	219	4.71	-50	-10	-37	-8
EtFOSE	630	59	4.65	-39	-4	-58	-8
GenX	285	119	2.58	-51	-10	-38	-8
GenX_2	285	185	2.58	-51	-10	-28	-8
MeFOSA	512	169	4.52	-50	-10	-37	-8
MeFOSA_2	512	219	4.52	-50	-10	-37	-8
MeFOSE	616	59	4.49	-50	-10	-58	-8
N-EtFOSAA	584	419	4.36	-50	-10	-28	-8
N-EtFOSAA_2	584	526	4.36	-50	-10	-28	-8
N-MeFOSAA	570	419	4.20	-50	-10	-28	-8
N-MeFOSAA_2	570	483	4.20	-50	-10	-22	-8
PFBA	212.9	168.9	1.71	-10	-8	-12	-8
PFBS	298.9	80	2.15	-20	-4	-56	-5.5
PFBS_2	298.9	99	2.15	-20	-4	-46	-9
PFDA	513	469	4.03	-10	-8	-17	-8
PFDA_2	513	169	4.03	-10	-8	-27	-8
PFDoA	613	569	4.66	-10	-8	-18	-8
PFDoA_2	613	169	4.66	-10	-8	-30	-8
PFDOS	699	80	4.65	-150	-10	-125	-7
PFDOS_2	699	99	4.65	-150	-10	-120	-10
PFDS	599	80	4.34	-20	-7	-118	-5.5
PFDS_2	599	99	4.34	-20	-7	-95	-9
PFHpA	363	319	2.85	-10	-8	-14	-8
PFHpA_2	363	169	2.85	-10	-8	-25	-8
PFHpS	449	80	3.27	-20	-4	-80	-5.5
PFHpS_2	449	99	3.27	-20	-4	-70	-9
PFHxA	313	269	2.46	-10	-8	-14	-8
PFHxA_2	313	119	2.46	-10	-8	-25	-8
PFHxDA	813	769	5.31	-123	-13	-22	-19

*MS/MS Conditions**
Continued

ID	Q1 Mass (Da)	Q3 Mass (Da)	Time (min)	DP (volts)	EP (volts)	CE (volts)	CXP (volts)
PFHxDA_2	813	269	5.31	-123	-6.5	-37	-22
PFHxS	399	80	2.87	-20	-4	-74	-5.5
PFHxS_2	399	99	2.87	-20	-4	-60	-9
PFNA	463	419	3.66	-10	-8	-16	-8
PFNA_2	463	169	3.66	-10	-8	-26	-8
PFNS	549	80	4.02	-20	-5.5	-115	-5.5
PFNS_2	549	99	4.02	-20	-5.5	-92	-5.5
PFOA	413	369	3.26	-10	-8	-14	-8
PFOA_2	413	169	3.26	-10	-8	-26	-8
PFODA	913	869	5.70	-120	-9	-25	-15
PFODA_2	913	319	5.70	-120	-9	-42	-15
PFOS	499	80	3.66	-20	-4	-95	-5.5
PFOS_2	499	99	3.66	-20	-4	-87	-9
PFOSA	498	78	4.02	-20	-4	-85	-8
PFPeA	262.9	218.9	2.09	-10	-8	-13	-8
PFPeS	349	80	2.50	-20	-4	-70	-5.5
PFPeS_2	349	99	2.50	-20	-4	-60	-9
PFTeDA	713	669	5.15	-10	-4	-22	-8
PFTeDA_2	713	169	5.15	-10	-4	-38	-8
PFTrDA	663	619	4.92	-10	-4	-20	-8
PFTrDA_2	663	169	4.92	-10	-4	-36	-8
PFUdA	563	519	4.36	-10	-8	-18	-8
PFUdA_2	563	169	4.36	-10	-8	-28	-8
13C2-PFDA	515	470	4.03	-10	-8	-17	-8
13C2-PFDoA	615	570	4.66	-10	-4	-18	-8
13C2-PFHxA	315	270	2.46	-10	-8	-14	-8
13C2-PFHxDA	815	770	5.31	-107	-10	-24	-16
13C2-PFOA	415	370	3.26	-10	-8	-14	-8
13C2-PFTeDA	715	670	5.15	-10	-4	-22	-8
13C3-GenX	287	185	2.58	-55	-10	-24	-10
13C3-PFBA	216	172	1.71	-10	-8	-12	-8
13C3_PFBS	302	80	2.15	-20	-4	-56	-5.5
13C3_PFHxS	402	80	2.87	-20	-4	-74	-5.5
13C4_PFBA	217	172	1.71	-10	-8	-12	-8
13C4_PFHpA	367	322	2.85	-10	-8	-14	-8
13C4_PFOS	503	80	3.66	-20	-4	-95	-5.5
13C5_PFHxA	318	273	2.46	-10	-8	-14	-8
13C5_PFPeA	267.9	223	2.09	-10	-8	-13	-8
13C6_PFDA	519	474	4.03	-10	-8	-16	-8
13C7_PFUdA	570	525	4.36	-10	-8	-18	-8

MS/MS Conditions* Continued

ID	Q1 Mass (Da)	Q3 Mass (Da)	Time (min)	DP (volts)	EP (volts)	CE (volts)	CXP (volts)
13C8_PFOA	421	376	3.26	-10	-8	-14	-8
13C8_PFOS	507	80	3.66	-20	-4	-95	-5.5
13C8_PFOSA	506	78	4.02	-20	-4	-85	-8
13C9_PFNA	472	427	3.66	-10	-8	-16	-8
d3-MeFOSA	515	169	4.52	-50	-10	-37	-8
d3-MeFOSAA	573	419	4.20	-50	-10	-28	-8
d5-EtFOSA	531	169	4.71	-50	-10	-37	-8
d5-EtFOSAA	589	419	4.36	-50	-10	-28	-8
d7-MeFOSE	623	59	4.49	-50	-5.5	-58	-5.5
d9-EtFOSE	639	59	4.65	-60	-4	-60	-8
M2-4:2 FTS	329	309	2.42	-20	-4	-28	-8
13C2-4:2 FTS_2	329	81	2.42	-20	-4	-28	-8
M2-6:2FTS	429	409	3.23	-20	-4	-32	-8
13C2-6:2FTS_2	429	81	3.23	-20	-4	-32	-8
M2-8:2FTS	529	509	4.02	-20	-4	-40	-8
13C2-8:2FTS_2	529	81	4.02	-20	-4	-82	-8

*Some MS/MS conditions may need to be re-optimized for individual instruments

NOTE: See Appendix I for the chemical derivation of the ion transitions.

TABLE 5: CALIBRATION LEVELS (ng/L) – ID ICAL – AQUEOUS AND SOLID MATRIX

Analyte	Level 1	Level 2	Level 3	Level 4	Level 5	Level 6	Level 7	Level 8	Level 9	Level 10
	PFAS Full List Native PDS Mix, 1000X			PFAS Full List Native PDS Mix, 100X			PFAS Full List Native PDS Mix, 10X			
PFBA	50	100	200	500	1000	2000	5000	10000	15000	20000
PFPeA	50	100	200	500	1000	2000	5000	10000	15000	20000
PFBS	44	88	177	442	884	1768	4420	8840	13260	17680
PFHxA	50	100	200	500	1000	2000	5000	10000	15000	20000
PFPeS	47	94	188	469	938	1876	4690	9380	14070	18760
PFHpA	50	100	200	500	1000	2000	5000	10000	15000	20000
PFHxS	46	91	182	455	910	1820	4550	9100	13650	18200
PFOA	50	100	200	500	1000	2000	5000	10000	15000	20000
PFHpS	48	95	190	476	952	1904	4760	9520	14280	19040
PFNA	50	100	200	500	1000	2000	5000	10000	15000	20000
PFOS	46	93	186	464	928	1856	4640	9280	13920	18560
PFDA	50	100	200	500	1000	2000	5000	10000	15000	20000
PFNS	48	96	192	480	960	1920	4800	9600	14400	19200
4:2FTS	47	93	187	467	934	1868	4670	9340	14010	18680
6:2FTS	47	95	190	474	948	1896	4740	9480	14220	18960
8:2 FTS	48	96	192	479	958	1916	4790	9580	14370	19160
PFOSA	50	100	200	500	1000	2000	5000	10000	15000	20000

TABLE 5: CALIBRATION LEVELS (ng/L) – ID ICAL – AQUEOUS AND SOLID MATRIX CONT'D										
Analyte	**Level 1**	**Level 2**	**Level 3**	**Level 4**	**Level 5**	**Level 6**	**Level 7**	**Level 8**	**Level 9**	**Level 10**
	PFAS Full List Native PDS Mix, 1000X			**PFAS Full List Native PDS Mix, 100X**			**PFAS Full List Native PDS Mix, 10X**			
MeFOSA	50	100	200	500	1000	2000	5000	10000	15000	20000
EtFOSA	50	100	200	500	1000	2000	5000	10000	15000	20000
PFUDA	50	100	200	500	1000	2000	5000	10000	15000	20000
MeFOSAA	50	100	200	500	1000	2000	5000	10000	15000	20000
EtFOSAA	50	100	200	500	1000	2000	5000	10000	15000	20000
PFDS	48	96	193	482	964	1928	4820	9640	14460	19280
PFDoA	50	100	200	500	1000	2000	5000	10000	15000	20000
10:2FTS	48	96	193	482	964	1928	4820	9640	14460	19280
PFTrDA	50	100	200	500	1000	2000	5000	10000	15000	20000
PFTeDA	50	100	200	500	1000	2000	5000	10000	15000	20000
GenX	100	200	400	1000	2000	4000	10000	20000	30000	40000
ADONA	47	94	188	471	942	1884	4710	9420	14130	18840
9Cl-PF3ONS	47	93	186	466	932	1864	4660	9320	13980	18640
11Cl-PF3OUDS	47	94	188	471	942	1884	4710	9420	14130	18840
MeFOSE	50	100	200	500	1000	2000	5000	10000	15000	20000
EtFOSE	50	100	200	500	1000	2000	5000	10000	15000	20000
PFDOS	48	97	194	484	968	1936	4840	9680	14520	19360
PFHxDA	50	100	200	500	1000	2000	5000	10000	15000	20000
PFODA	50	100	200	500	1000	2000	5000	10000	15000	20000
Surrogates (SUR)	2000	2000	2000	2000	2000	2000	2000	2000	2000	2000

NOTE: See Table 1 for method specific target analytes.

NOTE: *The ID (Aqueous and Solid) SUR includes the following compounds:*

- Sodium 1H, 1H, 2H, 2H-perfluoro-[1,2-13C2] hexane sulfonate (M2-4:2FTS or 13C2-4:2FTS)
- Sodium 1H, 1H, 2H, 2H-perfluoro-[1,2-13C2] octane sulfonate (M2-6:2FTS or 13C2-6:2FTS)
- Sodium 1H, 1H, 2H, 2H-perfluoro-[1,2-13C2] decane sulfonate (M2-8:2FTS or 13C2-8:2FTS)
- Perfluoro-1-[13C8] octanesulfonamide (M8FOSA-I or 13C8FOSA)
- N-ethyl-d5-perfluoro-1-octanesulfonamide (d-N-EtFOSA-M)

- N-methyl-d3-perfluoro-1-octanesulfonamide (d-N-MeFOSA-M)
- N-ethyl-d5-perfluoro-1-octanesulfonamidoacetic acid (d5-N-EtFOSAA)
- N-methyl-d3-perfluoro-1-octanesulfonamidoacetic acid (d3-N-MeFOSAA)
- Perfluoro-n-[13C4]butanoic acid (MPFBA or 13C4PFBA)
- Perfluoro-n-[13C5]pentanoic acid (M5PFPeA or 13C5PFPeA)
- Perfluoro-n-[1,2,3,4,6-13C5]hexanoic acid (M5PFHxA or 13C5PFHxA)
- Perfluoro-n-[1,2,3,4-13C4]heptanoic acid (M4PFHpA or 13C4PFHpA)
- Perfluoro-n-[13C8]octanoic acid (M8PFOA or 13C8PFOA)
- Perfluoro-n-[13C9]nonanoic acid (M9PFNA or 13C9PFNA)
- Perfluoro-n-[1,2,3,4,5,6-13C5]decanoicanoic acid (M6PFDA or 13C6PFDA)
- Sodium perfluoro-1-[2,3,4-13C3]butanesulfonate (M3PFBS or 13C3PFBS)
- Sodium perfluoro-1-[1,2,3-13C3]hexanesulfonate (M3PFHxS or 13C3PFHxS)
- Sodium perfluoro-1-[13C8]octanesulfonate (M8PFOS or 13C8PFOS)
- Perfluoro-n-[1,2,3,4,5,6,7-13C7]undecanoic acid (M7PFUdA or 13C7PFUdA)
- Perfluoro-n-[1,2-13C2]dodecanoic acid (MPFDoA or 13C2PFDoA)
- Perfluoro-n-[1,2-13C2]tetradecanoic acid (M2PFTeDA or 13C2PFTeDA)
- Tetrafluoro-2-(heptafluoropropoxy)-13C3 propanoic acid (13C3-GenX)
- 2-(N-methyl-d3-perfluoro-1-octanesulfonamido) ethan-4-ol (d7-MeFOSE)
- 2-(N-ethyl-d5-perfluoro-1-octanesulfonamido) ethan-4-ol (d9-EtFOSE)
- Perfluoro-n-[1,2-$^{13}C_2$] hexadecanoic acid (13C2-PFHxDA)

TABLE 6A: DOD BATCH CONTROL LIMITS – AQUEOUS MATRIX*

The limits outlined in this table shall be used when reporting data for DoD/DOE projects

CAS	Analyte Acronym	Lower Control Limit (%REC)	Upper Control Limit (%REC)
2991-50-6	EtFOSAA	61	135
39108-34-4	8:2 FTS	67	138
757124-72-4	4:2 FTS	63	143
27619-97-2	6:2 FTS	64	140
2355-31-9	MeFOSAA	65	136
375-73-5	PFBS	72	130
375-22-4	PFBA	73	129
335-77-3	PFDS	53	142
335-76-2	PFDA	71	129
307-55-1	PFDoA	72	134
375-92-8	PFHpS	69	134
375-85-9	PFHpA	72	130
355-46-4	PFHxS	68	131
307-24-4	PFHxA	72	129
68259-12-1	PFNS	69	127
375-95-1	PFNA	69	130
1763-23-1	PFOS	65	140
754-91-6	PFOSA	67	137
335-67-1	PFOA	71	133
2706-90-3	PFPeA	72	129
2706-91-4	PFPeS	71	127
376-06-7	PFTeDA	71	132
72629-94-8	PFTrDA	65	144
2058-94-8	PFUdA	69	133
31506-32-8	MeFOSA	68	141
4151-50-2	EtFOSA	70	150
120226-60-0	10:2FTS	70	150
13252-13-6	GenX	70	150
919005-14-4	ADONA	70	150
756426-58-1	9Cl-PF3ONS	70	150
763051-92-9	11Cl-PF3OUDS	70	150
24448-09-7	MeFOSE	70	150
1691-99-2	EtFOSE	70	150

***For Wisconsin compliance analysis, LCS recovery limits for all compounds are 60-135% when spiked at mid-range or high-range concentrations; 50-150% when spiked at low-range concentration.**

TABLE 6B: DOD BATCH CONTROL LIMITS – SOLID MATRIX*

The limits outlined in this table shall be used when reporting data for DoD/DOE projects

CAS	Analyte Acronym	Lower Control Limit (%REC)	Upper Control Limit (%REC)
2991-50-6	EtFOSAA	61	139
39108-34-4	8:2 FTS	65	137
757124-72-4	4:2 FTS	62	145
27619-97-2	6:2 FTS	64	140
2355-31-9	MeFOSAA	63	144
375-73-5	PFBS	72	128
375-22-4	PFBA	71	135
335-77-3	PFDS	59	134
335-76-2	PFDA	69	133
307-55-1	PFDoA	69	135
375-92-8	PFHpS	70	132
375-85-9	PFHpA	71	131
355-46-4	PFHxS	67	130
307-24-4	PFHxA	70	132
68259-12-1	PFNS	69	125
375-95-1	PFNA	72	129
1763-23-1	PFOS	68	136
754-91-6	PFOSA	67	137
335-67-1	PFOA	69	133
2706-90-3	PFPeA	69	132
2706-91-4	PFPeS	73	123
376-06-7	PFTeDA	69	133
72629-94-8	PFTrDA	66	139
2058-94-8	PFUdA	64	136
31506-32-8	MeFOSA	70	150
4151-50-2	EtFOSA	70	150
120226-60-0	10:2FTS	70	150
13252-13-6	GenX	70	150
919005-14-4	ADONA	70	150
756426-58-1	9Cl-PF3ONS	70	150
763051-92-9	11Cl-PF3OUDS	70	150
24448-09-7	MeFOSE	70	150
1691-99-2	EtFOSE	70	150

***For Wisconsin compliance analysis, LCS recovery limits for all compounds are 60-135% when spiked at mid-range or high-range concentrations; 50-150% when spiked at low-range concentration.**

APPENDIX B. PFAS ID – SOLID MATRIX

1. Standard Preparation

NOTE: Refer to the main body of this SOP for information regarding reagents and standards not listed here, specifically section 8.2 through 8.3

1.1 Solid Spiking Standard (SSS) – For ID-Solid, a separate solution of target analytes will be prepared and used to spike all QC samples (LCS, MS/MSD) used for 3M-TSM regulated analyses prior to extraction. The nominal concentration of all target analytes will be 500 ng/mL, except GenX which will be 1000 ng/mL. The SSS is stable for 12 months when stored at 2-6°C and contains 96% MeOH:4% Water. Prepare according to the table below:

ID Solid Spiking Standard (SSS)

Component	Conc. of Stock Std.	Aliquot volume	Dilution Volume	Final Conc.
	ng/mL	µL	mL	ng/mL
PFAC-30PAR	1000	2000	4	500
MeFOSA	50000	40	4	500
EtFOSA	50000	40	4	500
10:2 FTS	48200	40	4	482
GenX	50000	40	4	500
MeFOSE	50000	40	4	500
EtFOSE	50000	40	4	500
PFDOS	50000	40	4	484
PFHxDA	50000	40	4	500
PFODA	50000	40	4	500

1.2 Method Blank (MB) – Weigh 1.0g of Ottawa sand into a pre-tared 15mL Falcon tube and spike with 100µL of 100ppb SUR mix. Extract as normal alongside client samples.

1.3 Continuing Calibration Verification/Instrument Sensitivity Check (CCV/ISC) – See Section 9.2.10 in the main body of this SOP.

1.4 Laboratory Control Sample (LCS) – The LCS is prepared by spiking approximately 1g of Ottawa sand with 100 µL of 100X PDS (20 ng/mL) for a concentration of 2 µg/kg (2000 pg/g; 2000 ng/kg; 2 ng/g). The LCS is also spiked with 100 µL of Full List SUR mix (100 ppb) and extracted as normal alongside client samples.

1.5 Matrix Spike/Matrix Spike Duplicate (MS/MSD) – Client samples are spiked in the same manner as an LCS. 1g of sample is spiked with 100 µL of 100X PDS (20 ng/mL) for a concentration of 2 µg/kg, plus 100µL of Full List SUR mix (100ppb) and extracted as normal alongside other client samples.

1.6 Method Detection Limit (MDL) – MDL sample preparation and analysis will be performed over three separate days. Each MDL sample will be extracted with an equal number of MB samples. The MDL is prepared by spiking approximately 1g of Ottawa sand with 50 µL of 100X PDS mix for a concentration of 1000 pg/g (1000 ng/kg; 1 µg/kg), plus 100µL of Full List SUR mix (100ppb) and extracted as normal. An equal number of MB (see section 1.16 above) will be extracted and analyzed with MDL samples.

1.7 Initial (and Continuing) Demonstration of Capability (IDOC/CDOC) – The IDOC/CDOC is prepared by spiking approximately 1g of Ottawa sand with 100 µL 100X PDS plus 100µL of Full List SUR mix (100ppb) and extracted as normal. IDOC/CDOC sample final concentration equals 2µg/kg. Four replicates should be prepared and analyzed.

1.8 Ammonia-Methanol (Amm-MeOH, 0.6%) – In a 1000 mL graduated cylinder, add 20 mL NH4OH (Ammonium Hydroxide) and fill to volume with methanol (980 mL reagent MeOH). Invert to mix.

2. Sample Preparation

2.1 Allow samples time to come to room temperature.

2.2 Homogenize sample with a tongue depressor and/or vigorously shake sample container to ensure sample homogeneity.

2.3 Weigh approximately 1.0 g of sample into a pre-labeled, pre-tared 15 mL Falcon tube, record sample weight.

2.4 Spike sample aliquot with 100 µL 100ppb SUR mix; spike QC samples appropriately with PDS

2.5 Add 4 mL MeOH and 4 mL 0.6% Amm-MeOH to sample tube and cap tightly.

2.6 Place sample tubes on orbital shaker table for 30-35mins, on level 9.

2.7 Place samples in a tray and place the tray in a sonic bath at room temperature, sonicate for 30-35mins.

2.8 Remove rack from sonic bath and dry individual sample tubes before placing in a centrifuge and centrifuge at 3000RPM for 5 mins.

2.9 If centrifugation of sample does not fully separate solids from the extraction fluids, the resultant supernatant can be decanted from original sample tube into a clean centrifuge tube by pouring or using a plastic pipette. Decanting the supernatant from poorly separated extracts may help speed up the filtration process.

2.10 Place 25mg GCB pass-through cartridges, with pre-labeled reservoirs attached, into individual active luer ports in the vacuum manifold top.

2.11 Wet rim of manifold body and place manifold top on manifold body. Start the vacuum pump and ensure that a proper seal is formed between the manifold top and body, and vacuum is at a proper level (approximately 5-10 in. Hg).

2.12 Condition the GCB cartridges by passing 3mL MeOH in a slow drop-wise fashion through the tube, allowing the conditioning solvent to fully soak the sorbent for 2 mins before passing through the cartridge. Discard eluent. Do not dry GCB cartridges; if a cartridge goes dry, restart the conditioning step.

2.13 Release vacuum and remove manifold top. Place a rack containing clean, labelled 15mL Falcon tubes in the manifold body and replace the top. Ensure that the correct luer is inserted into the corresponding falcon tube in the manifold body.

2.14 Start vacuum and ensure proper seal and vacuum are achieved.

2.15 Load decanted extracts into corresponding labelled reservoirs and begin passing the extracts through the GCB cartridges in a drop-wise fashion; collect in the previously positioned clean, labelled 15mL Falcon tubes.

2.16 When the entire extract has eluted through the tube, close the stopcock to keep the tube from drying before/during the following step.

2.17 Rinse each tube with 2mL of clean MeOH, allowing the rinse solvent to fully soak the sorbent for 2 mins before passing through the cartridge (as in 2.12 above), and collect the rinsate in a slow drop-wise fashion.

2.18 Release vacuum, remove manifold top from body, and remove collection tubes. Cap tubes and invert to mix.

2.19 Concentrate extracts to an approximate volume of 4.0 mL (1.5mL if targeted final volume is 2 mL) using the TurboVap LV under a gentle stream of nitrogen in a heated water bath (55–60 °C). Set Nitrogen flow at a level which creates a vortex in the extract tube, but does not cause splash-out; suggested starting flow rate is 1.5L/min

2.20 Create a final volume (FV) reference tube: using a verified pipette, place a 5 mL or 2 mL aliquot of 96% MeOH into a clean extract tube – reference aliquot volume will depend on the targeted FV for the particular analysis selected

2.21 Once the sample extract has been concentrated to approximately 4.0 mL (1.5mL if targeted final volume is 2 mL), remove elution tube from the TurboVap and allow to cool to room temperature.

2.22 Once cooled, reconstitute the extract following the appropriate row in the table below. After adding the water aliquot, use a transfer pipet and the reference tube created in 2.20 to bring the extract to the appropriate FV with clean reagent MeOH. Vortex reconstituted extract to ensure homogeneity. Final reconstituted extract solvent composition is 96% MeOH: 4% water.

Extract targeted FV (mL)	Water (µL)
5	200
2	80

2.23 Transfer the reconstituted extracts to either 2 mL cryovials or 8mL HDPE Nalgene bottles, depending on extract FV, for storage at room temperature until instrumental analysis. Avoid transferring any remaining settled solids in the reconstituted extracts. Ensure caps are fully sealed on all extract storage bottles.

2.24 Manifold cleanup – see section 9.3.29 in main body of SOP

2.25 For samples that show analyte detections above the range of the ICAL, sample dilutions will need to be prepared. See Appendix G for dilution preparation scheme

2.25.1 Samples requiring analyses prepared at post-extraction dilutions of 50X or greater will be refortified with EIS to enable proper quantitation. Samples diluted in this manner are no longer technically quantitated using isotope dilution quantitation. All analyses prepared at post-extraction dilutions of 20X, 10X, or 5X will not be refortified with EIS and will thus maintain isotope dilution quantitation

APPENDIX C: AQUEOUS SAMPLE CENTRIFUGATION PROTOCOL

Preliminary considerations – The DoD QSM5.3, Table B-15, states that "[aqueous] samples with >1% solids may require centrifugation prior to SPE extraction." Additionally, the Wisconsin Department of Natural Resources (WDNR) guidance document, titled "Wisconsin PFAS Aqueous (Non-Potable Water) and Non-Aqueous Matrices Method Expectations," states "add the EIS [Extracted Internal Standard] before any extraction, centrifuging, filtering or phase separation takes place…Samples should only be centrifuged when the suspended solids content appears visually high enough, by chemist inspection, that it would cause the SPE cartridge to clog…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 removing the 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…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…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. Bring to a quantitative final volume with the final injection solvent and vortex well." Whether or not an individual sample will require centrifugation for proper preparation will be determined and documented by the preparation analyst.

Procedure:

1.1 Inspect the sample and consider the necessity of centrifuging. Consider any visible indications of particulate matter including settled solids collected on the bottom of the container, cloudiness and/or dark color of the sample, suspended solids within the sample, increased viscosity, etc. If uncertain, seek a second opinion from another analyst, supervisor, or operations director.

1.2 If, in the judgement of the preparation analyst, a sample requires centrifugation the analyst will contemporaneously make a note on the prep batch log indicating this fact.

1.3 Spike samples requiring centrifugation in the same manner and with the same standard volume as samples which will not be centrifuged.

1.4 Label a 500mL conical centrifuge bottle with the sample ID for each sample that will be centrifuged. Set them in an appropriate rack with the caps removed.

1.5 Vigorously shake the spiked sample and then quickly pour into the labeled centrifuge bottle. Try to ensure that the original sample bottle is devoid of any solid material. Be careful to avoid spilling sample during the transfer process. Tightly cap each centrifuge bottle after transfers are complete.

1.6 Transfer capped centrifuge bottles to centrifuge, ensuring that the centrifuge carousel is symmetrically balanced. Close top and centrifuge at 3000 RPM for 6 minutes.

1.7 Remove centrifuge bottles and decant the centrifuged liquid off of the condensed solids, back into the original sample bottle. Try to avoid transferring any of the condensed solids from the centrifuge

bottle back to the original sample bottle, while maximizing the amount of liquid decanted off of the solid portion.

1.8 Weigh the full, decanted original sample bottle and document in the LIMS prep batch.

1.9 Extract the decanted sample as normal alongside un-centrifuged samples, up to the bottle rinse and elution steps.

1.10 When the SPE cartridges have been dried, rinse the original sample bottle as normal. Additionally, add 4mL of Methanol (MeOH) to each centrifuge bottle to rinse the inside of the centrifuge bottles as well as the cap. If the condensed solids become re-suspended while rinsing the centrifuge bottles, re-centrifugation may be required. Using a transfer pipet or mechanical pipet, transfer the MeOH rinse from the centrifuge bottle into the SPE cartridge and elute with the original sample bottle rinse into a 15mL conical centrifuge tube.

Note: If <u>any</u> samples in a prep batch have been centrifuged, all sample extracts in the batch should be eluted into 15mL conical centrifuge tubes, as the standard centrifuge tubes typically used to collect the eluent are shorter than the 15mL conical tubes. This may cause loss of extract during elution due to the tips of the male luers on the underside of the manifold not actually being located within the top of the shorter (standard) centrifuge tubes during elution.

1.11 Add an additional volume of MeOH to the elution of all batch QC samples (MB/LCS/LCSD) to match the volume used for elution for any centrifuged sample in the prep batch. Typically, this will mean that 4mL of clean MeOH will be added directly to the SPE reservoir and eluted with the normal bottle rinses.

Batch QC and client samples with additional container rinse volume should be filtered as normal.

1.12 After elution, all sample extracts (client and QC) shall be concentrated and reconstituted following the protocols in sections 9.3.22 through 9.3.27 in the main body of this SOP. Determine initial sample volume using the weights measured in 2.8 and the protocols in sections 9.3.20 and 9.3.21 in the main body of this SOP.

1.13 Generate a Non-Conformance Memo (NCM) noting which samples in the prep batch included centrifugation in the extraction process and any additional observations and/or deficiencies that were noted during the centrifugation process.

APPENDIX D: PFAS by TCLP/SPLP

SUMMARY

Clients may submit samples (solid or aqueous) for PFAS by TCLP or SPLP analyses. For solid samples, the TCLP and SPLP procedures are used to simulate the leaching of environmental contaminants over extended periods of time from a solid material into the environment. A subsample of the client's solid sample is weighed out and combined with a leaching solution and mechanically tumbled for a set period of time. Each leachate prep method (TCLP or SPLP) employs a unique leaching solution dictated by the TCLP and SPLP parent methods. After the sample has been tumbled/leached by the Extractions department, the leachate is filtered by the Inorganic Metals department and delivered to the PFAS sample holding area. The PFAS department is notified by email when the leachate solutions are ready for PFAS prep. Aqueous samples are not tumbled in the way that solid samples are prepared, but are simply filtered by the same method in the Inorganic Metals department. The filtered leachate solutions are prepared by the PFAS prep analysts using the ID-AQ SPE prep method, at a 1:10 dilution (1 part leachate solution, 9 parts reagent water).

PROCEDURE

Prep:

1. Samples requested for PFAS by SPLP/TCLP analysis will batched and leached by the normal SPLP/TCLP procedures used by the Extractions department (EXT). EXT will be the initial responsible party for samples analyzed for PFAS by SPLP/TCLP.
2. When the leaching process is complete, EXT will collect approximately 250mL (at minimum 100mL) of the leachate solutions in clean HDPE containers provided by the PFAS department.
3. After collecting the leachate solution, EXT will deliver the collected leachates to the Inorganic Metals department (IM) and verbally notify an IM prep team member. EXT will typically also send an email to the PFAS group to notify that the leaching process is complete.
4. An IM analyst will filter at least 100mL of each leachate solution using a Flipmate apparatus, using normal protocols for Flipmate filtration.
5. After filtering the leachates, the IM analyst will deliver the filtrates to the PFAS sample holding area (INM walk-in cooler) and send an email to the PFAS group to notify that the filtrates are ready for PFAS SPE prep.
6. Samples to be analyzed for PFAS by TCLP/SPLP will appear on a separate PFAS prep worklist (widget), the title of which will contain "SPLP" or "TCLP" (three separate lists so far, depending on leaching method and program area). PFAS analysts will select from these lists the samples to be extracted.
7. Using a verified variable pipet, transfer 25mL of filtrate solution to a pre-labeled HDPE PFAS sample bottle. Using pre-tested reagent water, fill the sample bottle to approximately 250mL. Each TCLP/SPLP filtrate sample will be prepared at a 10X dilution, using 25mL of the leachate filtrate, brought to a final volume of ~250mL using reagent water. Initial volume will be recorded as 25mL for all samples. As a result, LOQs for PFAS by TCLP/SPLP will be 10X higher than normal ID-AQ LOQs.
8. Following the instructions in step 7, use the leachate blank solution (typically has sample ID XX00000-038) to prepare two bottles for use as batch QC. Volume for the leachate blank and LCS will be recorded as 25mL, matching all samples.
9. Label and fill a clean 250mL HDPE bottle with ~250mL of pre-tested reagent water for use as a typical PFAS MB sample. Volume for the PFAS MB will be recorded as 250mL.

10. After preparing the diluted filtrate, filtrate batch QC, and PFAS MB bottles, follow the normal extraction steps for ID-AQ analysis. Each sample will be spiked with EIS standard as normal. The filtrate LCS will be spiked with target analytes according to the ID-AQ protocol for LCS target spiking.
11. Leachate batch QC (MB/LCS) should be documented in LIMS3 as a leachate blank (LEB) and as an LCS; the reagent water blank should be documented as the MB.

Analysis:

12. After PFAS SPE prep has been completed, the instrumental analyst will analyze the extracts by the full list ID-AQ method, as normal.
13. Before processing ***solid*** SPLP/TCLP samples in the AIM data processing software, the “Matrix” field in the Sample Editor app must be changed to “Aqueous”.
14. After processing, reviewing, and generating reports for the data, import the data into LIMS4. Before performing final calculations on the imported sample data in LIMS4, the values in the “InitialVolume” and “InitialWeight” columns must be made to match. For all but the PFAS MB, this will mean copying the 25 from “InitialWeight” to “InitialVolume;” for the PFAS MB, this will mean copying the 250 from “InitialVolume” to “InitialWeight.”
15. Once the changes in step 14 have been affected, calculate final results, then L1 and upload.

APPENDIX E. AQUEOUS SERIAL DILUTION

1 Standard Preparation

1.1 IS, SUR, and ICV standard solutions prepared for ID-AQ are used for samples analyzed by serial dilution instead of SPE. See Section 8 in the main body of the SOP for more information on preparation and contents of these solutions.

1.2 Dilutions of individual analyte stock standards are used for fortifying post-spike samples. Typically, these diluted stocks are prepared by a two-step serial dilution for a nominal concentration of 5ppb (some analytes have different concentrations due to differing stock concentrations). These diluted stocks are prepared by diluting 10uL of stock solution with 950uL of MeOH and 40uL of reagent water (FV=1mL), then further diluting 10uL of this initial 100X solution with 990uL of 96% MeOH, for a final dilution of 10,000X. The 10,000X DIL stock solution will typically be used for fortifying post-spike samples.

1.3 ICALs, ICAL standards, and instrument QC (CCVs, IBLKs) are the same as for ID-AQ and all acceptance criteria used for ID-AQ applies.

1.4 Samples analyzed by serial dilution do not require an LCS or MB to be prepared alongside the samples, as no extraction is performed. Daily IBLKs take the place of MBs.

2 Sample Preparation – Samples of known high PFAS concentrations can be prepared by serial dilution instead of SPE, with documented project approval.

2.1 All solutions prepared for instrumental analysis in this section and Section 3 shall have a solvent composition of 96:4% MeOH:water.

2.2 An initial dilution of the sample is made up with no IS or SUR added, to be used as the base dilution for successive serial dilutions. This initial dilution is typically prepared at 100X.

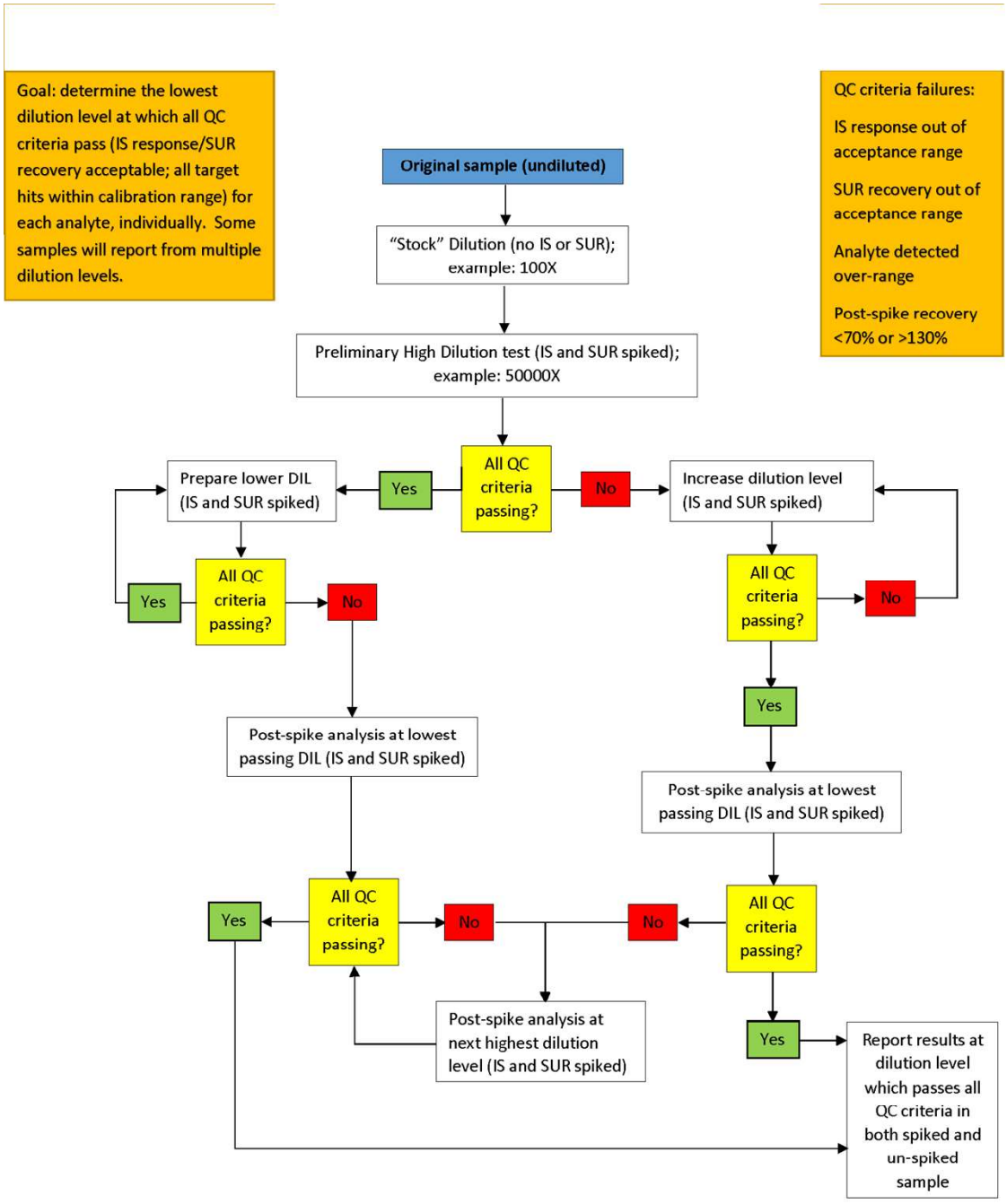
2.3 Using the initial sample dilution, prepare a high dilution (e.g. 50,000X) and analyze it to determine the approximate concentration of target analytes in the samples. Use the information obtained from this analysis to determine the next serial dilution to be prepared. Be sure to include IS and SUR standards at the appropriate concentration in each analyzed serial dilution. IS/SUR compounds should typically be present at a concentration of 1000pg/mL (1ppb).

2.4 Prepare successively lower dilutions of each serial dilution sample until all target analytes fail for over-range detection, IS response being out of acceptance, and/or SUR recovery being out of acceptance. Use the Non-Extracted Method PFAS Serial Dilution Prep Log and Post-spike Log (ME002DR) to record dilution and post-spike preparations. Be sure to include IS and SUR standards at the appropriate concentration in each analyzed serial dilution. No serial dilution samples will be analyzed at a dilution below 25X, in order to maintain proper solvent composition in the analyzed sample.

NOTE: Each target analyte should be evaluated individually in each serial dilution preparation. Associated IS/SUR compounds must pass acceptance criteria for an individual analyte to be reported. If the associated SUR and/or IS for one compound fails in a dilution sample, but *any* others pass, further dilution analysis will be necessary. Once a dilution level is reached in which all targets fail for one of the above-stated reasons, analysis will begin on the post-spiked samples.

2.5 For each target analyte, determine the dilution level at which the sample fails for one of the reasons stated in Section 2.4. The corresponding post-spike sample should be prepared at the next highest dilution level; in other words, determine the lowest dilution level at which a target analyte and its corresponding IS/SUR pass and prepare post-spike samples beginning at that dilution level.

Serial Dilution Decision Tree



3 **Post-spike sample preparation –** Post-spike samples must be prepared for all serial dilution samples which are ND for any target analyte at the reported dilution level. Non-detected target analytes will be individually spiked into post-spike dilution preparations at an expected on-column concentration equal to the stated LOQ in order to validate the stated LOQ in the sample matrix. If an analyte is detected in

a reportable dilution, no post-spiking of that analyte is required; the LOQ will equal the stated LOQ times the dilution factor of the reported analysis.

3.1 Post-spike samples must be prepared at the same dilution level as the reported sample results, and spiked at a concentration equivalent to the LOQ in the diluted sample. Post-spike analysis shall be prepared and evaluated for EACH non-detected analyte in EACH sample.

3.2 Calculate the appropriate amount of 10000X DIL stock solution necessary for the post-spike preparation by using the following equation:

$$\text{Spike Volume (mL)} = \frac{\text{LOQ(pg/mL)} * \text{final volume(mL)}}{\text{DIL stock(pg/mL)}}$$

3.3 Calculate the appropriate amount of 20ppb SUR and 20ppb IS necessary for the post-spike preparation by using the following equation:

$$\text{Spike Volume (mL)} = \frac{\text{1000(pg/mL)} * \text{final volume(mL)}}{\text{20000(pg/mL)}}$$

3.4 Prepare post-spikes at the reported dilution level for all ND analytes and record all post-spike preparation information using ME002DR. Use this logbook to ensure final volumes are correct and that all post-spike samples have solvent concentrations of 96% MeOH.

3.4.1 The analyte post-spiked into the dilution preparation must recover within 70-130% in order to be acceptable/reportable. All other QC criteria must be met as well (IS, SUR passing; opening/closing CCVs passing; acceptable IBLK).

3.4.2 Only the target analyte(s) being spiked and its corresponding IS/SUR must pass for each individual post-spike sample to be acceptable.

3.4.3 If a spiked analyte does not meet the 70-130% recovery limit, re-prepare the post-spike sample at successively higher dilutions using the steps above until recovery is within acceptance limits and corresponding IS/SUR compounds pass.

3.5 When a post-spike sample passes recovery and other QC criteria for the specific analyte(s) spiked, post-spiking analysis is complete for that sample/analyte combination.

3.6 The dilution reported for any individual analyte shall be the same dilution at which the post-spike sample passes for that analyte. If the initial post-spike sample fails when prepared at the expected reportable sample dilution, the LOQ has not been validated for this dilution level. Therefore, the reported dilution for that analyte/sample will be elevated to match the lowest passing dilution level of the post-spike analysis.

Report analyte results from the lowest dilution level which passes for all sample and post-spike QC criteria. The LOQ for ND analytes will equal the stated LOQ times the reported dilution factor.

APPENDIX F. EXTRACT DILUTION PREPARATIONS

Pace Analytical	Document Name: Extraction Dilution Preparations	Document Revised: 3/21/2022 Page 1 of 1
	Document No.: ME003.IZ-04	Issuing Authority: Pace ENV – Local Quality - WCOL

Extract Dilution Preparations

DILUTION	1X	5X	10X	20X	50X	100X	200X
537.1 DILUTION PREP							
EXTRACT (µL)	ALIQUOT	200	100	50	20	10	5
IS (µL)	0	40	45	47.5	49	49.5	49.75
96% MeOH (µL)	0	760	855	902.5	931	940.5	945.25
TOTAL (µL)	75	1000	1000	1000	1000	1000	1000
REFORTIFIED ID-AQ/ID-SOLID DILUTION PREP							
EXTRACT (µL)	ALIQUOT	200	100	50	20	10	5
ES-100ppb (µL)	0	16	18	19	19.6	19.8	19.9
MeOH (µL)	0	753	847	894	922	931	936
WATER (µL)	0	31	35	37	38.4	38.8	39
TOTAL (µL)	75	1000	1000	1000	1000	999.6	999.9
UNFORTIFIED ID-AQ/ID-SOLID DILUTION PREP							
EXTRACT (µL)	ALIQUOT	200	100	50	20	10	5
ES-100ppb (µL)	0	0	0	0	0	0	0
MeOH (µL)	0	768	864	912	941	950	955
WATER (µL)	0	32	36	38	39	40	40
TOTAL (µL)	75	1000	1000	1000	1000	1000	1000
In-vial 50X ID Screen							
In-vial 50X ID Screen		240µL 96%MeOH	+	5µL SUR 100ppb	+	5µL sample extract	
DAI DILUTION PREP							
SAMPLE (µL)	500	100	50	25	10	5	
ES (µL)	25	25	25	25	25	25	
MeOH (µL)	475	475	475	475	475	475	
Water (µL)	0	400	450	475	490	495	
TOTAL (µL)	1000	1000	1000	1000	1000	1000	
533 DILUTION PREP							
EXTRACT (µL)	950	200	100	50	20	10	5
IS (µL)	50	40	45	47.5	49	49.5	49.75
ES (µL)	0	40	45	47.5	49	49.5	49.75
80% MeOH (µL)	0	720	810	855	882	891	895.5
TOTAL (µL)	1000	1000	1000	1000	1000	1000	1000

NOTE: Serial dilution will be performed for dilutions higher than 200X.

APPENDIX G. MS/MSD, MS/FD SAMPLE SELECTION PROTOCOL

Background: EPA 537.1 and DOD QSM 5.3, Table B-15 both require that a matrix spike (MS) sample and a matrix spike duplicate (MSD) or field duplicate (FD) be prepped with every prep batch. Further, this SOP states that "every effort is made to ensure that an MS/MSD or an FD is included in every batch." Therefore, all aqueous prep batches must include an MS/MSD or MS/FD pair, if possible. Prep analysts will select samples to be used for this purpose following a hierarchy of preference. See below:

*****Any kind of blank (FB,TB,EB,RB,etc.) or samples designated as "DUP" by the client will not be used for MS/MSD/FD analysis.*****

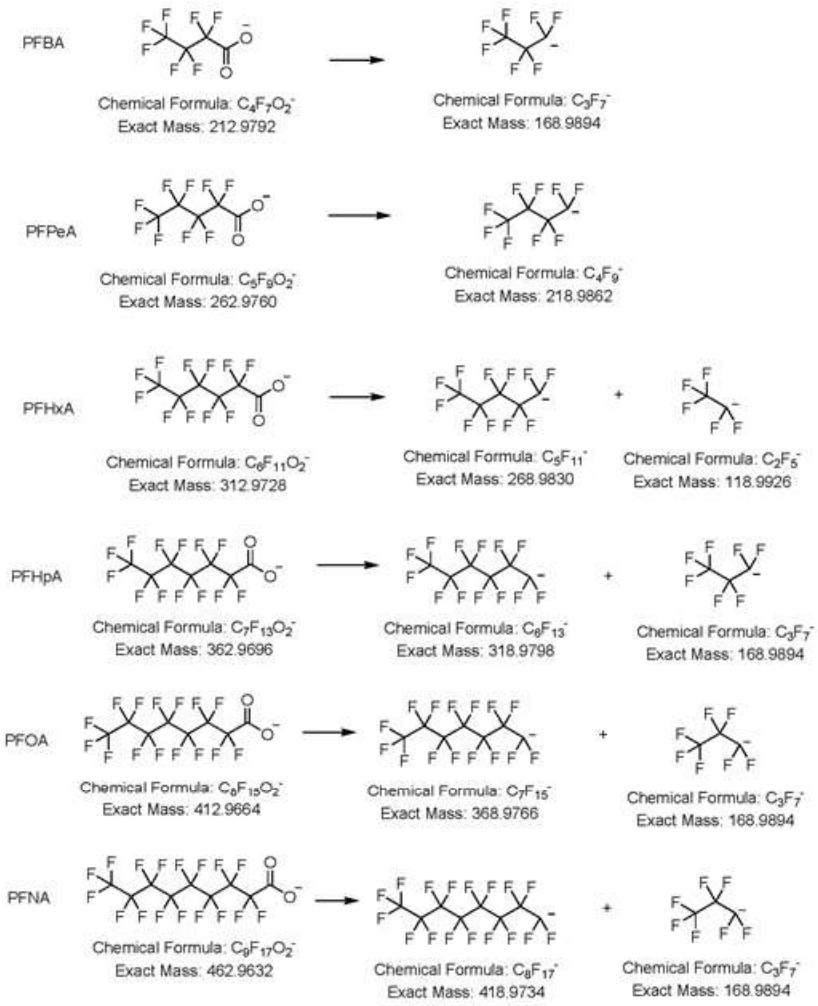
1. First preference is to use client-designated samples as MS/MSD samples. This designation should show up on the prep widget, under comments. It is possible that SR will miss adding this comment to the sample, but this designation will be present in the COC from the client, on the right side of the COC under "Remarks/Cooler ID." When a client designates a sample to be used for MS/MSD analysis, they will typically provide us with more than 2 bottles (often 4, sometimes as many as 6).

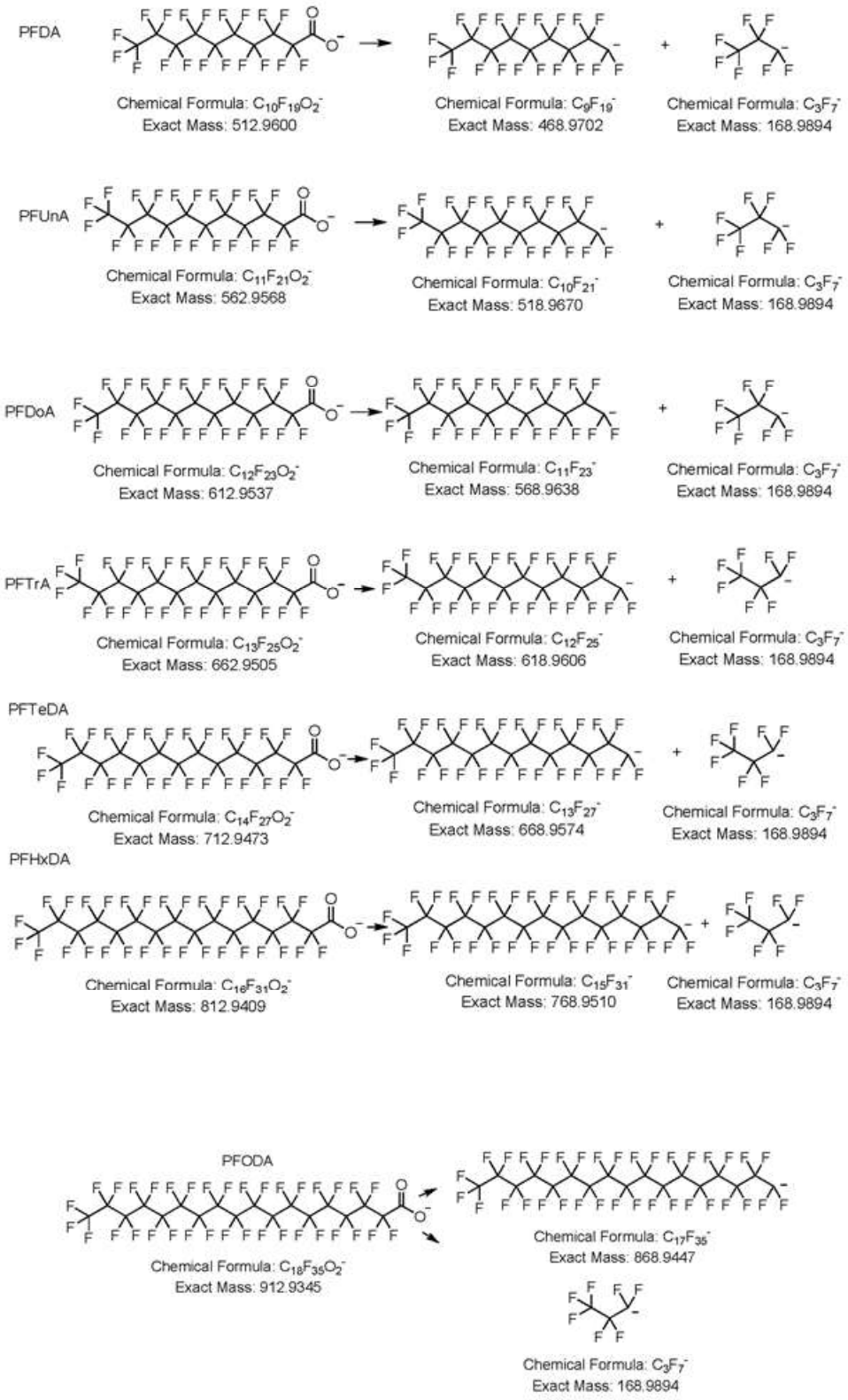
2. Lacking a client-designated MS/MSD sample, the next preference is to use any sample received with more than 2 bottles provided. If an analyst selects a set of samples for prep in which none of the samples are client-designated for MS/MSD, the analyst should check for any samples in the set that were received with 3 or more bottles. If there is a sample with 3 or more bottles, pull 3 of them and use one for the parent sample and spike the other two for analysis as MS/MSD samples.

3. Lacking any samples received with 3 or more bottles, the prep analyst must use two different samples to fulfill the MS/FD pair requirement. Find two samples out of the set of samples selected for prep which were received with 2 bottles, and pull both bottles for each sample. Pick one sample (pair of bottles) to be used for parent/MS prep and the other sample (pair of bottles) to be used for parent/FD. The sample selected for parent/MS will have one bottle spiked with targets and one prepped as normal, with no added spiking. The bottle which is spiked should be identified in the LIMS3 PB as MS (select parent sample in PB, click the MS/MSD button, then select the MSD sample and click the minus sign button to remove the MSD, leaving just the parent and MS). The sample selected for parent/FD will have both bottles prepped following normal procedures, but will have one of the two designated as DUP in the PB in LIMS3 (select parent sample in PB then click the "DUP" button to generate a DUP instance of the sample).

4. If all samples in a particular prep batch were all received in just one bottle, analysis of an MS/MSD or MS/FD pair will not be possible. In this case, the prep analyst will prep an LCS/LCSD pair and NCM all the samples in the PB for "MS/MSD – Insufficient volume – Ran LCS/LCSD". This should be a rare occurrence, as prep analysts will attempt to adjust batching to ensure that every PB contains an MS/MSD or MS/FD.

APPENDIX H. CHEMICAL DERIVATION OF ION TRANSITIONS

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Chemical Formula: $C_9F_{19}^-$
Exact Mass: 468.9702
Chemical Formula: $C_3F_7^-$
Exact Mass: 168.9894
PFUnA
Chemical Formula: $C_{11}F_{21}O_2^-$
Exact Mass: 562.9568
Chemical Formula: $C_{10}F_{21}^-$
Exact Mass: 518.9670
Chemical Formula: $C_3F_7^-$
Exact Mass: 168.9894
PFDoA
Chemical Formula: $C_{12}F_{23}O_2^-$
Exact Mass: 612.9537
Chemical Formula: $C_{11}F_{23}^-$
Exact Mass: 568.9638
Chemical Formula: $C_3F_7^-$
Exact Mass: 168.9894
PFTrA
Chemical Formula: $C_{13}F_{25}O_2^-$
Exact Mass: 662.9505
Chemical Formula: $C_{12}F_{25}^-$
Exact Mass: 618.9606
Chemical Formula: $C_3F_7^-$
Exact Mass: 168.9894
PFTeDA
Chemical Formula: $C_{14}F_{27}O_2^-$
Exact Mass: 712.9473
Chemical Formula: $C_{13}F_{27}^-$
Exact Mass: 668.9574
Chemical Formula: $C_3F_7^-$
Exact Mass: 168.9894
PFHxDA
Chemical Formula: $C_{16}F_{31}O_2^-$
Exact Mass: 812.9409
Chemical Formula: $C_{15}F_{31}^-$
Exact Mass: 768.9510
Chemical Formula: $C_3F_7^-$
Exact Mass: 168.9894
PFODA
Chemical Formula: $C_{18}F_{35}O_2^-$
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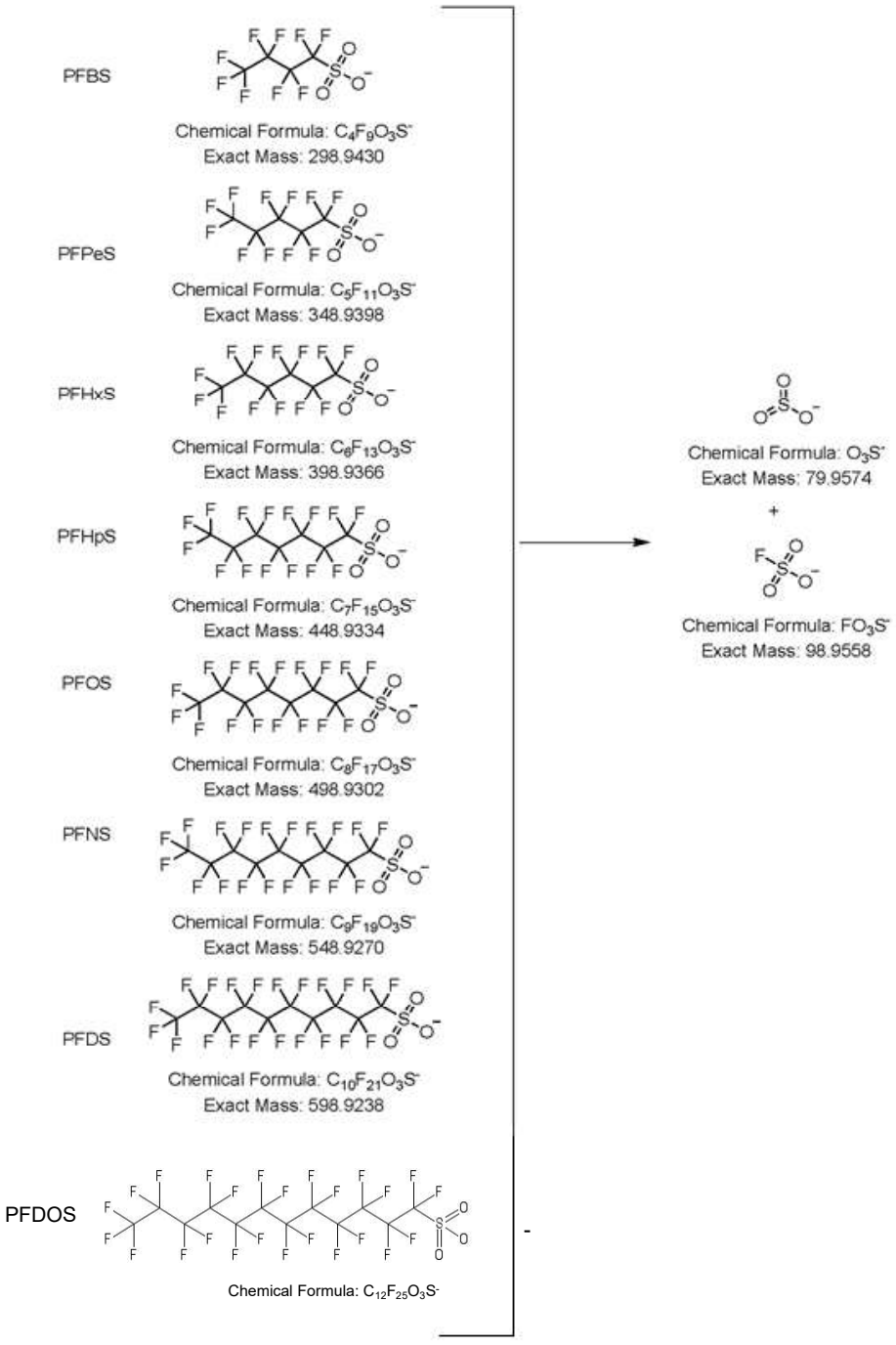
Exact Mass: 868.9447
Chemical Formula: $C_3F_7^-$
Exact Mass: 168.9894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Exact Mass: 298.9430
PFPeS
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Exact Mass: 348.9398
PFHxS
Chemical Formula: $C_6F_{13}O_3S^-$
Exact Mass: 398.9366
PFHpS
Chemical Formula: $C_7F_{15}O_3S^-$
Exact Mass: 448.9334
PFOS
Chemical Formula: $C_8F_{17}O_3S^-$
Exact Mass: 498.9302
PFNS
Chemical Formula: $C_9F_{19}O_3S^-$
Exact Mass: 548.9270
PFDS
Chemical Formula: $C_{10}F_{21}O_3S^-$
Exact Mass: 598.9238
PFDOS
Chemical Formula: $C_{12}F_{25}O_3S^-$
Chemical Formula: O_3S^-
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+
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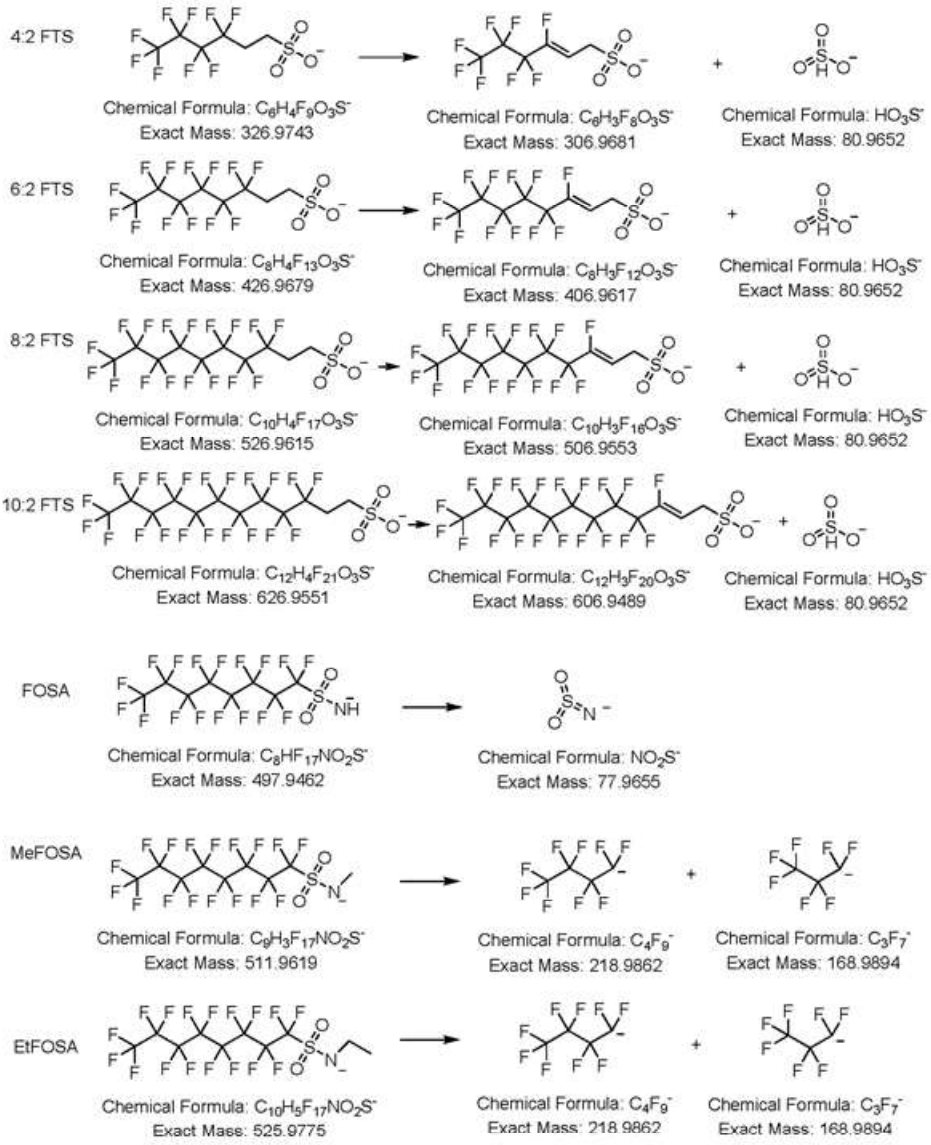
Exact Mass: 98.9558


4:2 FTS
Chemical Formula: $C_6H_4F_9O_3S^-$
Exact Mass: 326.9743
Chemical Formula: $C_6H_3F_8O_3S^-$
Exact Mass: 306.9681
Chemical Formula: HO_3S^-
Exact Mass: 80.9652
6:2 FTS
Chemical Formula: $C_8H_4F_{13}O_3S^-$
Exact Mass: 426.9679
Chemical Formula: $C_8H_3F_{12}O_3S^-$
Exact Mass: 406.9617
Chemical Formula: HO_3S^-
Exact Mass: 80.9652
8:2 FTS
Chemical Formula: $C_{10}H_4F_{17}O_3S^-$
Exact Mass: 526.9615
Chemical Formula: $C_{10}H_3F_{16}O_3S^-$
Exact Mass: 506.9553
Chemical Formula: HO_3S^-
Exact Mass: 80.9652
10:2 FTS
Chemical Formula: $C_{12}H_4F_{21}O_3S^-$
Exact Mass: 626.9551
Chemical Formula: $C_{12}H_3F_{20}O_3S^-$
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Chemical Formula: HO_3S^-
Exact Mass: 80.9652
FOSA
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Exact Mass: 497.9462
Chemical Formula: NO_2S^-
Exact Mass: 77.9655
MeFOSA
Chemical Formula: $C_9H_3F_{17}NO_2S^-$
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Chemical Formula: $C_4F_9^-$
Exact Mass: 218.9862
Chemical Formula: $C_3F_7^-$
Exact Mass: 168.9894
EtFOSA
Chemical Formula: $C_{10}H_5F_{17}NO_2S^-$
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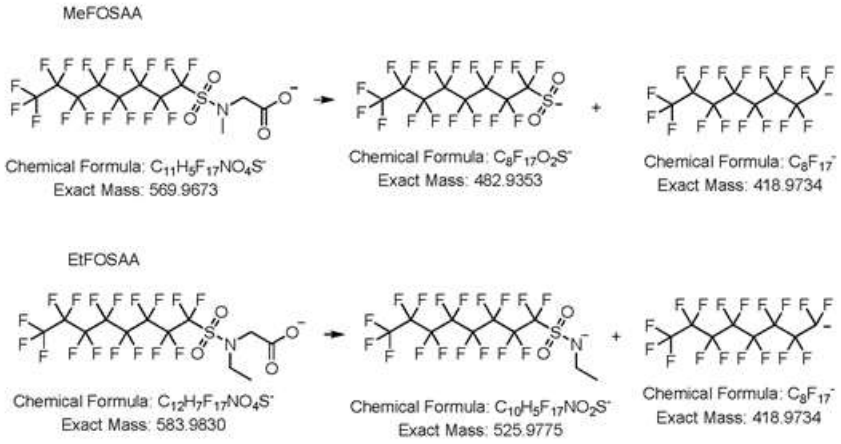
Chemical Formula: $C_3F_7^-$
Exact Mass: 168.9894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Chemical Formula: $C_8F_{17}O_2S^-$
Exact Mass: 482.9353
Chemical Formula: $C_8F_{17}^-$
Exact Mass: 418.9734
EtFOSAA
Chemical Formula: $C_{12}H_7F_{17}NO_4S^-$
Exact Mass: 583.9830
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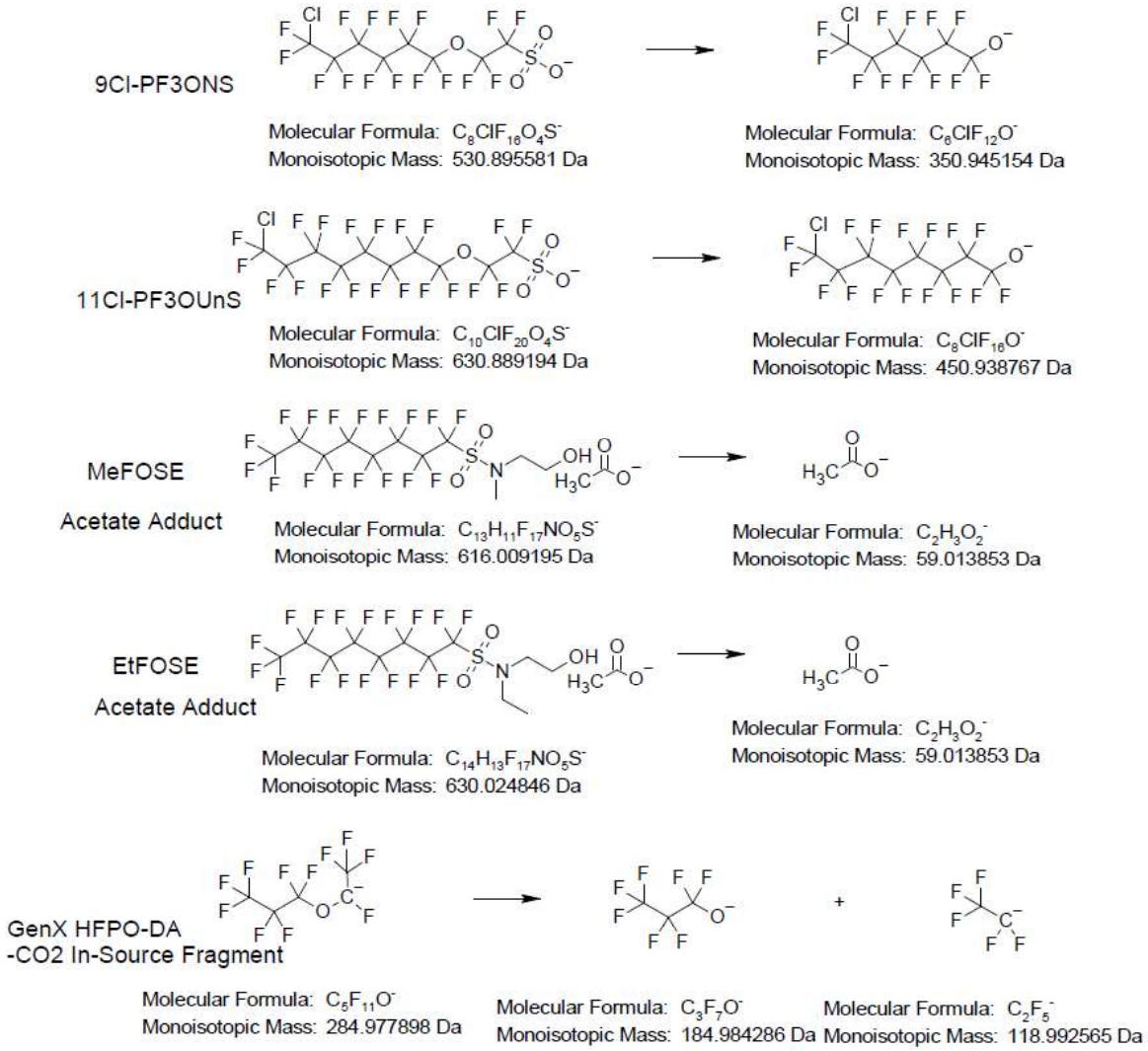
Exact Mass: 525.9775
Chemical Formula: $C_8F_{17}^-$
Exact Mass: 418.9734


9Cl-PF3ONS
Molecular Formula: C8ClF16O4S-
Monoisotopic Mass: 530.895581 Da
Molecular Formula: C8ClF12O-
Monoisotopic Mass: 350.945154 Da
11Cl-PF3OUnS
Molecular Formula: C10ClF20O4S-
Monoisotopic Mass: 630.889194 Da
Molecular Formula: C8ClF16O-
Monoisotopic Mass: 450.938767 Da
MeFOSE
Acetate Adduct
Molecular Formula: C13H11F17NO5S-
Monoisotopic Mass: 616.009195 Da
Molecular Formula: C2H3O2-
Monoisotopic Mass: 59.013853 Da
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Acetate Adduct
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Molecular Formula: C2H3O2-
Monoisotopic Mass: 59.013853 Da
GenX HFPO-DA
-CO2 In-Source Fragment
Molecular Formula: C5F11O-
Monoisotopic Mass: 284.977898 Da
Molecular Formula: C3F7O-
Monoisotopic Mass: 184.984286 Da
Molecular Formula: C2F5-
Monoisotopic Mass: 118.992565 Da

APPENDIX I: DOD/DOE QSM REQUIREMENTS

Sections found in this appendix replace and/or supplement the existing sections of the SOP. These requirements must be met when analyzing samples for the Department of Defense, as stipulated in the DOD Quality System Manual.

Table B-15. Per- and Polyfluoroalkyl Substances (PFAS) Using Liquid Chromatography Tandem Mass Spectrometry (LC/MS/MS) With Isotope Dilution or Internal Standard Quantification in Matrices Other Than Drinking Water

QC Check	Minimum Frequency	Acceptance Criteria	Corrective Action	Flagging Criteria	Comments
Aqueous Sample Preparation	Each sample and associated batch QC samples.	Solid Phase Extraction (SPE) must be used unless samples are known to contain high PFAS concentrations (e.g., Aqueous Film Forming Foam (AFFF) formulations). Inline SPE is acceptable. Entire sample plus bottle rinsate must be extracted using SPE. Known high PFAS concentration samples require serial dilution be performed in duplicate. Documented project approval is needed for samples prepared by serial dilution as opposed to SPE.	NA.	NA.	Samples with > 1% solids may require centrifugation prior to SPE extraction. Pre-screening of separate aliquots of aqueous samples is recommended.
Solid Sample Preparation	Each sample and associated batch QC samples.	Entire sample received by the laboratory must be homogenized prior to subsampling.	NA.	NA.	NA.
Biota Sample Preparation	Each sample and associated batch QC samples.	Sample prepared as defined by the project (e.g., whole fish versus filleted fish).	NA.	NA.	NA.

Table B-15. Per- and Polyfluoroalkyl Substances (PFAS) Using Liquid Chromatography Tandem Mass Spectrometry (LC/MS/MS) With Isotope Dilution or Internal Standard Quantification in Matrices Other Than Drinking Water

QC Check	Minimum Frequency	Acceptance Criteria	Corrective Action	Flagging Criteria	Comments
AFFF and AFFF Mixture Samples Preparation	Each sample and associated batch QC samples.	Each field sample must be prepared in duplicate (equivalent to matrix duplicate). Serial dilutions must be performed to achieve the lowest LOQ possible for each analyte.	NA.	NA.	Adsorption onto bottle is negligible compared to sample concentration so subsampling is allowed. Multiple dilutions will most likely have to be reported in order to achieve the lowest LOQ possible for each analyte.
Sample Cleanup Procedure	Each sample and associated batch QC samples. Not applicable to AFFF and AFFF Mixture Samples.	ENVI-Carb™ or equivalent must be used on each sample and batch QC sample.	NA.	Flagging is not appropriate.	Cleanup should reduce bias from matrix interferences.
Mass Calibration	Instrument must have a valid mass calibration prior to any sample analysis. Mass calibration is verified after each mass calibration, prior to initial calibration (ICAL).	Calibrate the mass scale of the MS with calibration compounds and procedures described by the manufacturer. Mass calibration range must bracket the ion masses of interest. The most recent mass calibration must be used for every acquisition in an analytical run. Mass calibration must be verified to be ±0.5 amu of the true value, by acquiring a full scan continuum mass spectrum of a PFAS stock standard.	If the mass calibration fails, then recalibrate. If it fails again, consult manufacturer instructions on corrective maintenance.	Flagging is not appropriate.	Problem must be corrected. No samples may be analyzed under a failing mass calibration. The mass calibration is updated on an as-needed basis (e.g., QC failures, ion masses fall outside of the ±0.5 amu of the true value, major instrument maintenance is performed, or the instrument is moved).

Table B-15. Per- and Polyfluoroalkyl Substances (PFAS) Using Liquid Chromatography Tandem Mass Spectrometry (LC/MS/MS) With Isotope Dilution or Internal Standard Quantification in Matrices Other Than Drinking Water

QC Check	Minimum Frequency	Acceptance Criteria	Corrective Action	Flagging Criteria	Comments
Mass Spectral Acquisition Rate	Each analyte, Extracted Internal Standard (EIS) Analyte.	A minimum of 10 spectra scans are acquired across each chromatographic peak.	NA.	Flagging is not appropriate.	NA.
Calibration, Calibration Verification, and Spiking Standards	All analytes.	Standards containing both branched and linear isomers must be used when commercially available. PFAS method analytes may consist of both branched and linear isomers, but quantitative standards that contain the linear and branched isomers do not exist for all method analytes. For PFAS that do not have a quantitative branched and linear standard, identify the branched isomers by analyzing a qualitative standard that includes both linear and branched isomers and determine retention times, transitions and transition ion ratios. Quantitate samples by integrating the total response (i.e., accounting for peaks that are identified as linear and branched isomers) and relying on the initial calibration that uses the linear isomer quantitative standard.	NA.	Flagging is not appropriate.	Standards containing both branched and linear isomers are to be used during method validation and when reestablishing retention times, to ensure the total response is quantitated for that analyte. Technical grade standards cannot be used for quantitative analysis.

Table B-15. Per- and Polyfluoroalkyl Substances (PFAS) Using Liquid Chromatography Tandem Mass Spectrometry (LC/MS/MS) With Isotope Dilution or Internal Standard Quantification in Matrices Other Than Drinking Water

QC Check	Minimum Frequency	Acceptance Criteria	Corrective Action	Flagging Criteria	Comments
Sample PFAS Identification	All analytes detected in a sample.	The chemical derivation of the ion transitions must be documented. A minimum of two ion transitions (Precursor → quant ion and precursor → confirmation ion) and the ion transitions ratio per analyte are required for confirmation. Exception is made for analytes where two transitions do not exist (PFBA and PFPeA). Documentation of the primary and confirmation transitions and the ion ratio is required. In-house acceptance criteria for evaluation of ion ratios must be used and must not exceed 50-150%. Signal to Noise Ratio (S/N) must be ≥ 10 for all ions used for quantification and must be ≥ 3 for all ions used for confirmation. Quant ion and confirmation ion must be present and must maximize simultaneously (±2 seconds).	NA.	PFAS identified with ion ratios that fail acceptance criteria must be flagged. Any quantitation ion peak that does not meet the maximization criteria shall be included in the summed integration and the resulting data flagged as "estimated, biased high".	For example: Ion Ratio = (quant ion abundance/ confirm ion abundance) Calculate the average ratio (A) and standard deviation (SD) using the ICAL standards. An acceptance range of ratio could be within A ±3SD for confirmation of detection.

Table B-15. Per- and Polyfluoroalkyl Substances (PFAS) Using Liquid Chromatography Tandem Mass Spectrometry (LC/MS/MS) With Isotope Dilution or Internal Standard Quantification in Matrices Other Than Drinking Water

QC Check	Minimum Frequency	Acceptance Criteria	Corrective Action	Flagging Criteria	Comments
Ion Transitions (Precursor-> Product)	Every field sample, standard, blank, and QC sample.	In order to avoid biasing results high due to known interferences for some transitions, the following transitions must be used for the quantification of the following analytes: PFOA: 413 → 369 PFOS: 499 → 80 PFHxS: 399 → 80 PFBS: 299 → 80 4:2 FTS: 327 → 307 6:2 FTS: 427 → 407 8:2 FTS: 527 → 507 NEtFOSAA: 584 → 419 NMeFOSAA: 570 → 419 If these transitions are not used, the reason must be technically justified and documented (e.g., alternate transition was used due to observed interferences).	NA.	Flagging is not appropriate	NA.

Table B-15. Per- and Polyfluoroalkyl Substances (PFAS) Using Liquid Chromatography Tandem Mass Spectrometry (LC/MS/MS) With Isotope Dilution or Internal Standard Quantification in Matrices Other Than Drinking Water

QC Check	Minimum Frequency	Acceptance Criteria	Corrective Action	Flagging Criteria	Comments
Initial Calibration (ICAL)	At instrument set-up and after ICV or CCV failure, prior to sample analysis.	The isotopically labeled analog of an analyte (Extracted Internal Standard Analyte) must be used for quantitation if commercially available (Isotope Dilution Quantitation). Commercial PFAS standards available as salts are acceptable providing the measured mass is corrected to the neutral acid concentration. Results shall be reported as the neutral acid with appropriate CAS number. If a labeled analog is not commercially available, the Extracted Internal Standard Analyte with the closest retention time or chemical similarity to the analyte must be used for quantitation. (Internal Standard Quantitation) Analytes must be within 70-130% of their true value for each calibration standard. *(continued next page)*	Correct problem, then repeat ICAL.	Flagging is not appropriate.	No samples shall be analyzed until ICAL has passed. External Calibration is not allowed for any analyte. Calibration can be linear (minimum of 5 standards) or quadratic (minimum of 6 standards); weighting is allowed.

Table B-15. Per- and Polyfluoroalkyl Substances (PFAS) Using Liquid Chromatography Tandem Mass Spectrometry (LC/MS/MS) With Isotope Dilution or Internal Standard Quantification in Matrices Other Than Drinking Water

QC Check	Minimum Frequency	Acceptance Criteria	Corrective Action	Flagging Criteria	Comments
Initial Calibration (ICAL) *(Continued)*		ICAL must meet one of the two options below: Option 1: The RSD of the RFs for all analytes must be ≤ 20%. Option 2: Linear or non-linear calibrations must have $r^2 \geq 0.99$ for each analyte.			
Retention Time window position establishment	Once per ICAL and at the beginning of the analytical sequence.	Position shall be set using the midpoint standard of the ICAL curve when ICAL is performed. On days when ICAL is not performed, the initial CCV is used.	NA.	NA.	Calculated for each analyte and EIS.
Retention Time (RT) window width	Every field sample, standard, blank, and QC sample.	RT of each analyte and EIS analyte must fall within 0.4 minutes of the predicted retention times from the daily calibration verification or, on days when ICAL is performed, from the midpoint standard of the ICAL. Analytes must elute within 0.1 minutes of the associated EIS. This criterion applies only to analyte and labeled analog pairs.	Correct problem and reanalyze samples.	NA.	Calculated for each analyte and EIS.

Table B-15. Per- and Polyfluoroalkyl Substances (PFAS) Using Liquid Chromatography Tandem Mass Spectrometry (LC/MS/MS) With Isotope Dilution or Internal Standard Quantification in Matrices Other Than Drinking Water

QC Check	Minimum Frequency	Acceptance Criteria	Corrective Action	Flagging Criteria	Comments
Instrument Sensitivity Check (ISC)	Prior to analysis and at least once every 12 hours.	Analyte concentrations must be at LOQ; concentrations must be within ±30% of their true values.	Correct problem, rerun ISC. If problem persists, repeat ICAL.	Flagging is not appropriate.	No samples shall be analyzed until ISC has met acceptance criteria. ISC can serve as the initial daily CCV.
Initial Calibration Verification (ICV)	Once after each ICAL, analysis of a second source standard prior to sample analysis.	Analyte concentrations must be within ±30% of their true value.	Correct problem, rerun ICV. If problem persists, repeat ICAL.	Flagging is not appropriate.	No samples shall be analyzed until calibration has been verified.
Continuing Calibration Verification (CCV)	Prior to sample analysis, after every 10 field samples, and at the end of the analytical sequence.	Concentration of analytes must range from the LOQ to the mid-level calibration concentration. Analyte concentrations must be within ±30% of their true value.	Immediately analyze two additional consecutive CCVs. If both pass, samples may be reported without reanalysis. If either fails, or if two consecutive CCVs cannot be run, perform corrective action(s) and repeat CCV and all associated samples since last successful CCV. Alternately, recalibrate if necessary; then reanalyze all associated samples since the last acceptable CCV.	If reanalysis cannot be performed, data must be qualified and explained in the Case Narrative. Apply Q-flag to all results for the specific analyte(s) in all samples since the last acceptable calibration verification.	Results may not be reported without valid CCVs. Instrument Sensitivity Check (ISC) can serve as a bracketing CCV.

Table B-15. Per- and Polyfluoroalkyl Substances (PFAS) Using Liquid Chromatography Tandem Mass Spectrometry (LC/MS/MS) With Isotope Dilution or Internal Standard Quantification in Matrices Other Than Drinking Water

QC Check	Minimum Frequency	Acceptance Criteria	Corrective Action	Flagging Criteria	Comments
Instrument Blanks	Immediately following the highest standard analyzed and daily prior to sample analysis.	Concentration of each analyte must be ≤ ½ the LOQ. Instrument Blank must contain EIS to enable quantitation of contamination.	If acceptance criteria are not met after the highest calibration standard, calibration must be performed using a lower concentration for the highest standard until acceptance criteria is met. If sample concentrations exceed the highest allowed standard and the sample(s) following exceed this acceptance criteria (>1/2 LOQ), they must be reanalyzed.	Flagging is only appropriate in cases when the sample cannot be reanalyzed and when there is no more sample left.	No samples shall be analyzed until instrument blank has met acceptance criteria. Note: Successful analysis following the highest standard analyzed determines the highest concentration that carryover does not occur. When the highest standard analyzed is not part of the calibration curve, it cannot be used to extend out the calibration range, it is used only to document a higher concentration at which carryover still does not occur.

Table B-15. Per- and Polyfluoroalkyl Substances (PFAS) Using Liquid Chromatography Tandem Mass Spectrometry (LC/MS/MS) With Isotope Dilution or Internal Standard Quantification in Matrices Other Than Drinking Water

QC Check	Minimum Frequency	Acceptance Criteria	Corrective Action	Flagging Criteria	Comments
Extracted Internal Standard (EIS) Analytes	Every field sample, standard, blank, and QC sample.	Added to solid sample prior to extraction. Added to aqueous samples, into the original container, prior to extraction. For aqueous samples prepared by serial dilution instead of SPE, added to final dilution of samples prior to analysis. Extracted Internal Standard Analyte recoveries must be within 50% to 150% of ICAL midpoint standard area or area measured in the initial CCV on days when an ICAL is not performed.	Correct problem. If required, re-extract and reanalyze associated field and QC samples. If recoveries are acceptable for QC samples, but not field samples, the field samples must be re-extracted and analyzed (greater dilution may be needed). Samples may be re-extracted and analyzed outside of hold times, as necessary for corrective action associated with QC failure.	Apply Q-flag and discuss in the Case Narrative only if reanalysis confirms failures in exactly the same manner.	Failing analytes shall be thoroughly documented in the Case Narrative. EIS should be 96% (or greater) purity. When the impurity consists of the unlabeled analyte, the EIS can result in a background artifact in every sample, standard and blank, if the EIS is fortified at excessive concentrations.
Method Blank (MB)	One per preparatory batch.	No analytes detected >½ LOQ or > 1/10th the amount measured in any sample or 1/10th the regulatory limit, whichever is greater.	Correct problem. If required, re-extract and reanalyze MB and all QC samples and field samples processed with the contaminated blank. Samples may be re-extracted and analyzed outside of hold times, as necessary for corrective action associated with QC failure. Examine the project-specific requirements. Contact the client as to additional measures to be taken.	If reanalysis cannot be performed, data must be qualified and explained in the Case Narrative. Apply B-flag to all results for the specific analyte(s) in all samples in the associated preparatory batch.	Results may not be reported without a valid MB. Flagging is only appropriate in cases where the samples cannot be reanalyzed.

Table B-15. Per- and Polyfluoroalkyl Substances (PFAS) Using Liquid Chromatography Tandem Mass Spectrometry (LC/MS/MS) With Isotope Dilution or Internal Standard Quantification in Matrices Other Than Drinking Water

QC Check	Minimum Frequency	Acceptance Criteria	Corrective Action	Flagging Criteria	Comments
Laboratory Control Sample (LCS)	One per preparatory batch.	Blank spiked with all analytes at a concentration ≥ LOQ and ≤ the mid-level calibration concentration. A laboratory must use the DoD/DOE QSM Appendix C Limits for batch control if project limits are not specified. If the analyte(s) are not listed, use in-house LCS limits if project limits are not specified.	Correct problem, then re-extract and reanalyze the LCS and all samples in the associated preparatory batch for failed analytes if sufficient sample material is available. Samples may be re-extracted and analyzed outside of hold times, as necessary for corrective action associated with QC failure. Examine the project-specific requirements. Contact the client as to additional measures to be taken.	If reanalysis cannot be performed, data must be qualified and explained in the Case Narrative. Apply Q-flag to specific analyte(s) in all samples in the associated preparatory batch.	Results may not be reported without a valid LCS. Flagging is only appropriate in cases where the samples cannot be reanalyzed.
Matrix Spike (MS)	One per preparatory batch. Not required for aqueous samples prepared by serial dilution instead of SPE.	Sample spiked with all analytes at a concentration ≥ LOQ and ≤ the mid-level calibration concentration. A laboratory must use the DoD/DOE QSM Appendix C Limits for batch control if project limits are not specified. If the analyte(s) are not listed, use in-house LCS limits if project limits are not specified.	Examine the project-specific requirements. Contact the client as to additional measures to be taken.	For the specific analyte(s) in the parent sample, apply J-flag if acceptance criteria are not met and explain in the Case Narrative.	For matrix evaluation only. If MS results are outside the limits, the data shall be evaluated to determine the source(s) or difference (i.e., matrix effect or analytical error).

Table B-15. Per- and Polyfluoroalkyl Substances (PFAS) Using Liquid Chromatography Tandem Mass Spectrometry (LC/MS/MS) With Isotope Dilution or Internal Standard Quantification in Matrices Other Than Drinking Water

QC Check	Minimum Frequency	Acceptance Criteria	Corrective Action	Flagging Criteria	Comments
Matrix Spike Duplicate (MSD) or Matrix Duplicate (MD)	For MSD: One per preparatory batch. For MD: Each aqueous sample prepared by serial dilution instead of SPE.	For MSD: Sample spiked with all analytes at a concentration ≥ LOQ and ≤ the mid-level calibration concentration. A laboratory must use the DoD/DOE QSM Appendix C Limits for batch control if project limits are not specified. If the analyte(s) are not listed, use in-house LCS limits if project limits are not specified. RPD ≤ 30% (between MS and MSD or sample and MD).	Examine the project-specific requirements. Contact the client as to additional measures to be taken.	For the specific analyte(s) in the parent sample, apply J-flag if acceptance criteria are not met and explain in the Case Narrative.	The data shall be evaluated to determine the source of difference. For Sample/MD: RPD criteria only apply to analytes whose concentration in the sample is ≥ LOQ. The MD is a second aliquot of the field sample that has been prepared by serial dilution.
Post Spike Sample	Only applies to aqueous samples prepared by serial dilution instead of SPE that have reported value of < LOQ for analyte(s).	Spike all analytes reported as < LOQ into the dilution that the result for that analyte is reported from. The spike must be at the LOQ concentration to be reported for this sample as < LOQ. When analyte concentrations are calculated as < LOQ, the post spike for that analyte must recover within 70-130% of its true value.	When analyte concentrations are calculated as < LOQ, and the spike recovery does not meet the acceptance criteria, the sample, sample duplicate, and post spike sample must be reanalyzed at consecutively higher dilutions until the criteria is met.	Flagging is not appropriate.	When analyte concentrations are calculated as < LOQ, results may not be reported without acceptable post spike recoveries.